



2<sup>me</sup> CONGRÈS INTERNATIONAL DE LA CORROSION MARINE ET DES SALISSURES  
2<sup>nd</sup> INTERNATIONAL CONGRESS ON MARINE CORROSION AND FOULING  
2. INTERNATIONALEN KONGRESS FÜR MEERWASSERKORROSION UND BEWUCHS  
2<sup>ο</sup> ΔΙΕΘΝΕΣ ΣΥΝΕΔΡΙΟΝ ΘΑΛΑΣΣΙΑΣ ΔΙΑΒΡΩΣΕΩΣ ΚΑΙ ΡΥΠΑΝΣΕΩΣ



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Du 20 au 24 Septembre 1968 à Athènes (GRÈCE)

Από 20 έως 24 Σεπτεμβρίου 1968 εις Ἀθήνας (ΕΛΛΑΣ)

20th to 24th September 1968 in Athens (GREECE)

Vom 20. bis 24. September 1968 Athen (GRIECHENLAND)

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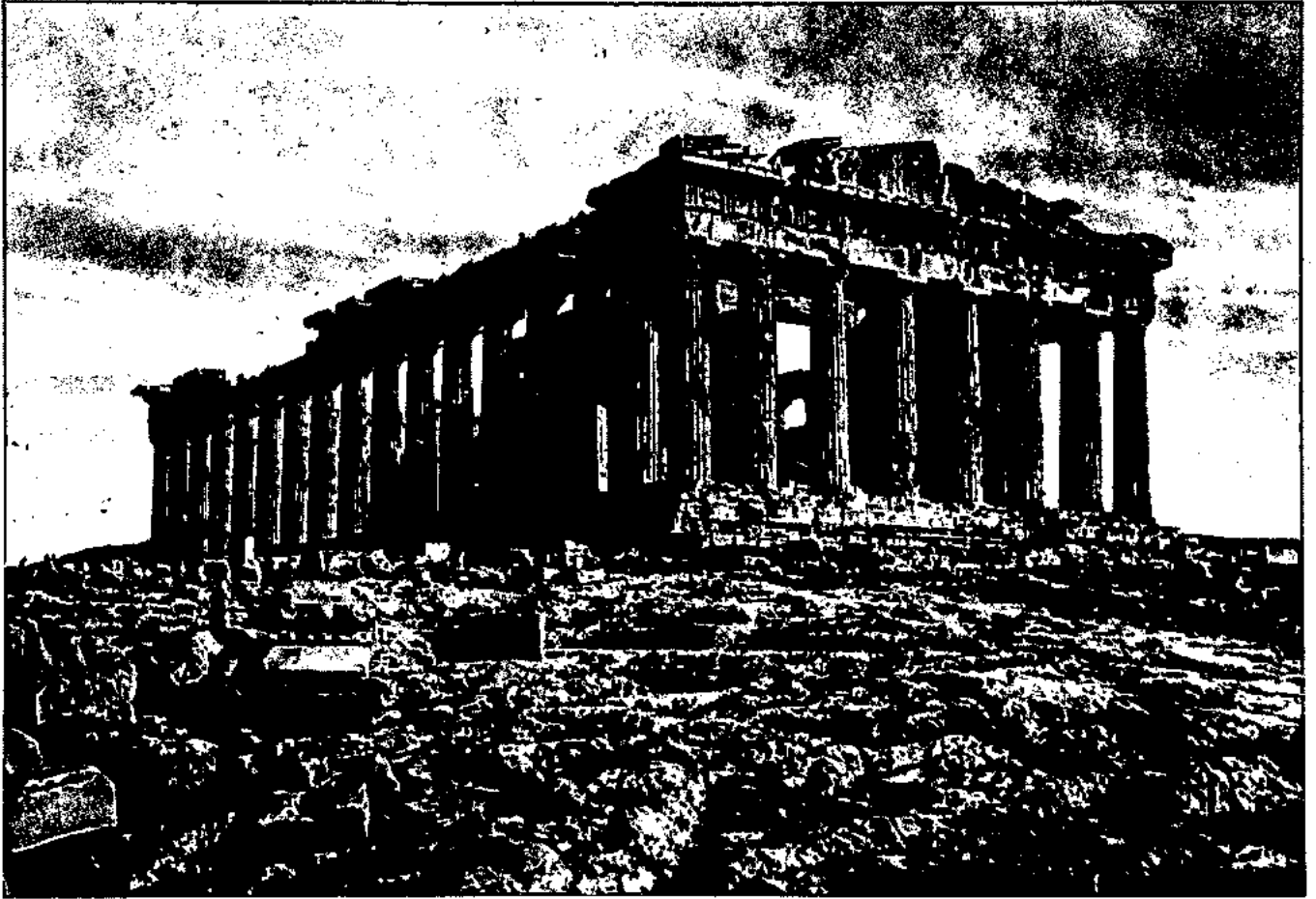
*V. PHILOPOULOS, Dipl. Ing. D.I.C., M.Sc.*

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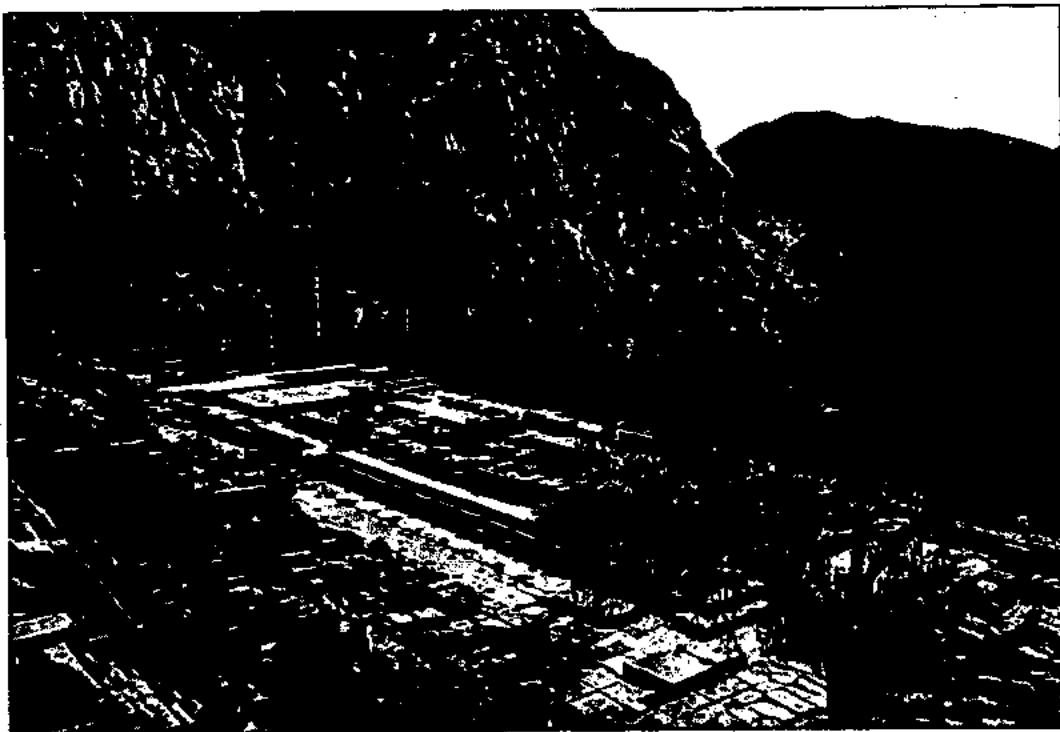
*Le Parthénon.*

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*L'île Delos que les congressistes ont visité.*



*Delphi. que les congressistes ont visité.*

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20 septembre 1968



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*Vue de la salle du Congrès.*



*Le président du congrès s'adressant aux congressistes.*

ALLOCUTION DU PRÉSIDENT DU CONGRÈS ET DU COMITÉ EXÉCUTIF  
ADDRESS OF THE PRESIDENT OF THE CONGRESS AND OF THE EXECUTIVE COMMITTEE  
ANSPRACHE VOM PRÄSIDENTEN DES KONGRESSES UND DES EXEKUTIVKOMITEES  
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C'est un grand honneur pour moi en ma qualité de Président du Congrès et du Comité exécutif, de m'adresser aux participants éminents du 2<sup>e</sup> Congrès International de la Corrosion Mariné et des Salissures et de souhaiter la bienvenue, à Athènes à tous les délégués Etrangers.

Nous sommes particulièrement reconnaissants à tous ceux qui ont fait un si long voyage pour honorer notre Congrès de leur présence.

Nous désirons également exprimer notre reconnaissance à tous ceux qui ont contribué à la réalisation du Congrès.

Au Gouvernement Hellénique, à la Mairie d'Athènes, au Comité International pour la Recherche sur la Préservation des Matériaux en Milieu Marin, à la Fédération Européenne de la Corrosion, à la Chambre Technique de Grèce dont le



soutient financier a grandement facilité l'Organisation du Congrès, à l'Université Nationale Technique d'Athènes, à la Commission Hellénique de l'Energie Atomique, à l'Association Hellénique des Ingenieurs Chimistes à l'Union de Chimistes Hellènes, à mes Collaborateurs au Laboratoire de l'Université Nationale Technique d'Athènes et au Personnel du Secrétariat sans l'aide desquels le Congrès n'aurait pas pu se réaliser.

Dans cette salle, Six Cent Cinquante Congressistes provenant des trente pays sont réunis à ce moment. Un intérêt scientifique commun est à la base de cette réunion. Les Sujets du Congrès, les Communications de valeur qui seront présentées et les discussions intéressantes qui suivront. En ce qui vous concerne Chers Participants Etrangers, permettez-moi de croire que ce n'est pas seulement l'intérêt scientifique qui vous a attiré ici, mais aussi, l'amour et l'admiration que vous nourrissez pour la Grèce Antique. Dans ce cas ne cherchez pas à découvrir cette Grèce Antique uniquement dans les ruines sacrées de l'Acropole ou des autres Temples éparpillés dans tout le pays. Vous la trouverez certainement dans l'âme et dans l'esprit du plus humble des Grecs contemporains. Nietzsche a dit: «Je hais les anciens Grecs car ils ne nous ont laissé rien de nouveau à dire». Je pense que c'est aussi le cas pour la corrosion. Lorsque j'ai proposé au Comité International pour la Corrosion Matine et les Salissures, de convoquer le 2<sup>e</sup> Congrès à Athènes c'était naturellement parce que la Grèce est baignée toute entière par la mer. C'était aussi parce que la plupart de ses usines sont situées au bord de la mer et utilisent l'eau de mer à des fins de chauffage et de refroidissement, par ce qu'elle possède la deuxième flotte marchande du monde. Mais c'était aussi dans le but d'honorer un de nos grands ancêtres Plutarch qui décrivant le mecanisme de la corrosion des statues en bronze à Delphes disait:

«Ο χαλκός ἀποπνέει καὶ μεθίσκει τὸν ἰόν»

de Cuivre s'émane et produit les fleurs, les oxydes.

C'est le mecanisme de la corrosion des métaux que l'éminent Prof. allemand Wagner a expliqué et prouvé, il y a quelques années, c'est-à-dire la migration des ions des métaux

à travers des places des desordres reversibles vers le milieu corrosive sous la force du pontentiel de corrosion qui s'exerce entre le métal et le milieu corrosif.

Pendant le Congrès soixante trois Communications seront présentées, dont trente trois sur la corrosion et trente sur les salissures.

Quelques conférenciers ou Présidents des Sessions mentionnés au Cinquième communiqué, n'ont malheureusement pas pu venir à notre Congrès pour des raisons ne dépendants pas de leur volonté. Tous nous ont écrit des lettres exprimant leur vœux pour le succès du Congrès. Nous avons dû les remplacer par d'autres spécialistes selon leur autorisation.

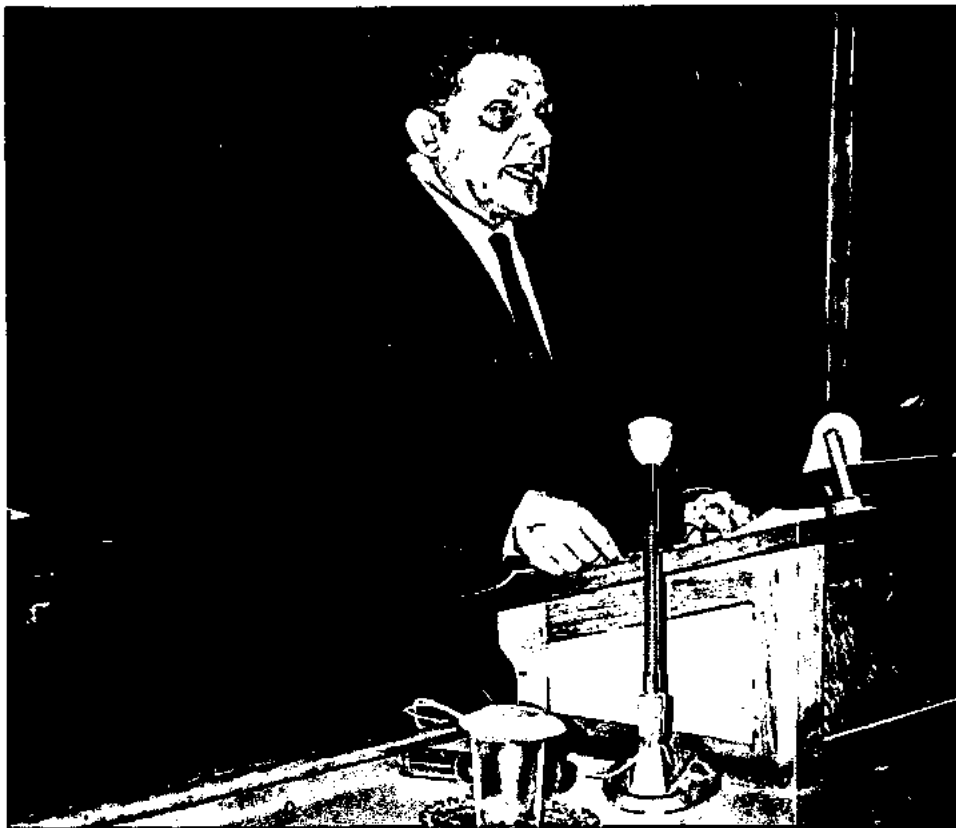
De la part du Comité Exécutif, je m'en excuse auprès des Congressistes.

De même cinq nouvelles communications nous ont parvenues depuis l'apparition du Cinquième Communiqué, vu la personnalité des auteurs nous les avons accepté.

Par les communications, vous aurez l'occasion de constater le grand progrès réalisé entre 1964 date du 1<sup>er</sup> Congrès à Cannes et ce 2<sup>ème</sup> Congrès, concernant l'étude et les moyens de la lutte contre la corrosion marine et les salissures.

Ces résultats ne sont pas dû seulement, aux efforts déployés par des hommes de Science travaillant individuellement, mais surtout à la collaboration étroite entre Organismes, Instituts et Laboratoires Nationaux et à la Coopération entre les divers nations. A cet égard nous nous devons rendre hommage à la Fédération Européenne de la Corrosion qui assure la collaboration entre les Nations Européennes, à l'O.C.D.E. et à la Commission Internationale Permanente pour la Recherche sur la Préservation des Matériaux en Milieu Marin, à la personne de son Président Dr. Romanovsky, qui assure la collaboration entre les Nations du Monde entier.

Ensuite je voudrais exprimer les vœux que tous ceux qui detiennent entre leurs mains le sort des Nations et de l'Humanité s'inspirent de cette noble collaboration entre hommes de Science, de couleur, de langue, de régime, de religion et des mœurs différents et trouvent les moyens nécessaires afin qu'à l'avenir tous les hommes de la terre puissent vivre en Paix et en Liberté.



*Le président du comité d'organisation s'adressant aux congressistes.*

ALLOCUTION DU PRÉSIDENT DU COMITÉ D'ORGANISATION  
ADDRESS OF THE PRESIDENT OF THE ORGANIZATION  
ANSPRACHE VON PRASIDENTEN DES ORGANISATIONSKOMITEES  
ΠΡΟΣΦΩΝΗΣΙΣ ΤΟΥ ΠΡΟΕΔΡΟΥ ΤΗΣ ΟΡΓΑΝΩΤΙΚΗΣ ΕΠΙΤΡΟΠΗΣ

Prof. Dr. D. KORONAIOS

Président de la Chambre Technique de Grèce.  
President of the Technical Chamber of Greece.  
Präsident der Griechischen Technischen Kammer.  
Πρόεδρος του Τεχνικού Έπιμελητηρίου της Ελλάδος.

*Votre Excellence, Messieurs les Congressistes, Mesdames et Messieurs,*

De la part du Comité d'Organisation du Congrès, de la Chambre Technique de Grèce, et du monde scientifique de notre pays, je désire exprimer nos vifs remerciements au Comité International Permanent pour la Recherche sur la Préservation des Matériaux en Milieu Marin, et au Comité Permanent pour l'Organisation des Congrès de Corrosion Marine et les Salissures, qui ont bien voulu accepter notre invita-

tion de convoquer le 2ème Congrès International de la Corrosion Marine et des Salissures à Athènes, et aussi aux Congressistes qui sont venus participer aux travaux du Congrès. Je désire vous souhaiter la bienvenue et le meilleur succès à vos travaux.

Je voudrais aussi exprimer nos remerciements à Son Excellence le Vice-Président du Gouvernement et à M.M. les Ministres, qui ont accepté de se mettre en tête du Comité d'Honneur du Congrès, et en particulier à son Excellence le Ministre

ici présent de la Marine Marchande, qui quoique si lourdement occupé a bien voulu trouver quelque temps pour nous honorer de Sa présence.

Je souhaite — et j'espère bien — que le ciel et le climat de la Grèce vous soient aussi hospitaliers que nous-mêmes afin que votre séjour soit le plus agréable possible et que vous ayez l'occasion, dans la marge de vos sérieuses occupations de visiter et de mieux connaître notre pays et d'emporter en nous quittant, en sus des bénéfices scientifiques du Congrès, un bon souvenir de la Grèce et ses habitants, dont l'esprit accueillant est le fruit d'une très longue tradition de laquelle nous sommes fiers.

J'espère aussi, pour tous ceux qui participeront à la croisière de demain, que même la mer, sera magnanime et ne voudra pas se montrer hostile, quoique le but de vos travaux est de l'empêcher dans l'exercice de son éternel travail de corrosion, et de restreindre ce privilège séculaire.

La Chambre Technique de Grèce, qui comprend l'ensemble des Ingénieurs de ce pays, de toute spécialité, et que j'ai l'honneur de représenter, a comme but, d'après ses Statuts, la promotion de la Technique de ce pays. Elle considère ainsi comme un de ses objectifs principaux, l'encouragement et le soutien de la recherche scientifique. Pour cette raison, c'est avec une grande joie qu'elle a accepté le patronage et s'est chargée de l'organisation du Congrès, en collaboration avec l'Université Technique National d'Athènes, et l'Association Hellenique des Ingénieurs Chimistes.

Le sujet de votre Congrès — Corrosion Marine et Salissures — est susceptible de provoquer l'intérêt purement scientifique des chimistes, des physiciens et des biologistes. Il y a quelques dizaines d'années, la mer constituait une barrière prohibitive pour le plus grand nombre des constructions, permettant tout au plus la construction des quais et jetées par des blocs de pierre naturelle. D'autre part, la vitesse des bateaux étant relativement petite, sa diminution à cause des salissures était

négligeable. Or, l'étude des phénomènes de la corrosion et des salissures, faisait l'objet d'un intérêt purement scientifique.

Depuis que les nouvelles techniques ont conquis ou tâchent de conquérir une plus vaste étendue de la région marine et depuis que la vitesse des bateaux a augmenté, les phénomènes de la corrosion marine et des salissures, de simple phénomène, sont devenus un problème. Problème vital tant pour la technologie que pour l'économie. Je changerais nos rôles mutuels si je tâchais de vous énumérer les pertes financières que cause la corrosion. En tout cas, je crois que le problème devient de jour en jour plus aigu. Et si vos travaux de recherche sont aujourd'hui très utiles, dans le proche avenir ils deviendront indispensables.

Pour notre pays, qui est entouré de toutes parts de la mer et qui est le deuxième en rang dans le monde pour sa flotte commerciale, le sujet de votre congrès présente un intérêt tout particulier.

Il est vrai que nous sommes entrés un peu tard dans la recherche du sujet. Il y a deux ans que l'Université Technique Nationale d'Athènes a installé un radeau de recherche au port du Pirée, en collaboration et à l'aide financière de l'Organisme Autonome du Port du Pirée. On aura les résultats des observations qui sont faites sur ce radeau dans une intervalle d'un ou deux ans. Un autre radeau est en train d'être installé par le Centre des Recherches de la Défense Nationale et un troisième est en projet par l'Université de Salonique.

En parcourant le programme des travaux de votre Congrès, et la liste des conférenciers et des sujets de leurs contributions, je m'aperçois que nombreux problèmes scientifiques et technologiques existent déjà ou se posent et attendent leur solution. Mais je crois que votre dévouement à la cause et la coordination de vos recherches parviendront dans peu de temps de résoudre un grand nombre de ces problèmes.

En terminant, je vous souhaite un succès absolu à votre oeuvre et un séjour agréable en notre pays.



*Le président du comité international pour la préservation des matériaux au milieu marin s'adressant aux congressistes.*

ALLOCATION DU PRÉSIDENT DU COMITÉ INTERNATIONAL PERMANENT POUR LA RECHERCHE SUR LA PRÉSERVATION DES MATÉRIAUX EN MILIEU MARIN.  
 ADRESSE OF THE PRESIDENT OF THE PERMANENT INTERNATIONAL COMMITTEE FOR RESEARCH ON THE PRESERVATION OF MATERIALS IN MARINE ENVIRONMENT.  
 ANSPRACHE DES PRÄSIDENTEN DES STÄNDIGEN INTERNATIONALEN KOMITEES DER MATERIALSCHUTZ-FORSCHUNG IN MARITIMER UMGEBUNG  
 ΠΡΟΣΦΩΝΗΣΙΣ ΤΟΥ ΠΡΟΕΔΡΟΥ ΤΗΣ ΜΟΝΙΜΟΥ ΔΙΕΘΝΟΥΣ ΕΠΙΤΡΟΠΗΣ ΔΙΑ ΤΗΝ ΕΡΕΥΝΑΝ ΕΠΙ ΤΗΣ ΠΡΟΣΤΑΣΙΑΣ ΤΩΝ ΥΛΙΚΩΝ ΕΙΣ ΘΑΛΑΣΣΙΟΝ ΠΕΡΙΒΑΛΛΟΝ

Dr. V. ROMANOVSKY

Monsieur le Ministre, Mesdames, Mesdemoiselles, Messieurs.  
 Je suis très honoré, mais également très gêné de prendre la parole devant vous après tout ce que les deux précédents orateurs ont pu vous dire.

Je n'ai absolument aucun don d'orateur, je serai très bref.

Je voudrais simplement vous retracer rapidement l'histoire de l'Organisation de ce Congrès. Mais avant, je voudrais rendre hommage à l'enthousiasme avec lequel mon très cher ami, le Docteur Skoulikidis, aidé par le Comité et le

Président des divers Comités, a pu résoudre de très graves problèmes.

Il me disait encore, il y a quelques jours, qu'il avait cent et quelques questions à régler et qu'il lui en restait à peu près les trois quart. Or, vous verrez, au cours de ce Congrès, qu'il les avait certainement déjà résolues depuis longtemps et qu'il était bien trop modeste.

Ce Congrès a une petite histoire. En 1964, nous avons eu, en France, l'idée d'organiser le 1<sup>er</sup> Congrès de Corrosion Marine et des Salissures. Nous n'avions pas, à cette époque,

beaucoup de moyens, mais nous avons, comme le Dr. Skoulikidis, beaucoup d'enthousiasme. Nous avons pourrnt obtenu certains appuis financiers, tout particulièrement celui qui nous est venu de la part de l'Organisation de Coopération et de Développement Economique (O.C.D.E.).

Ce Congrès a eu un certain succès, certainement pas un succès aussi important que celui qu'aura ce Congrès-ci. Nous avons réuni à peu près trois cent cinquante personnes. Vous voyez, à peu près la moitié de ce que vous serez ici.

A la fin de ce Congrès, la question s'était posée de savoir si l'on pouvait poursuivre une série de congrès et si un autre pays pouvait accepter une charge aussi lourde, peut-être pas uniquement du point de vue financier, car on dépense beaucoup d'argent dans nos pays respectifs et cet argent n'est peut-être pas toujours aussi utile.

Pour un congrès, je crois qu'il est difficile de trouver des hommes capables de l'organiser, ayant l'enthousiasme suffisant pour le faire avec le maximum d'atouts. J'ai une grande reconnaissance envers le Docteur Skoulikidis qui, dès 1965, en juin 1965 très exactement, avait officiellement accepté d'organiser le 2<sup>e</sup> Congrès de Corrosion.

A cette occasion, nous avons créé un petit Organisme International, dont j'avais l'honneur d'être le Président, qui s'appelait, si je ne me trompe pas «Comité Permanent pour l'Organisation des Congrès de Corrosion Marine et des Salissures».

Ce petit Comité n'avait absolument rien d'officiel, comme d'ailleurs les trois quart des Comités internationaux, il faut bien le dire, et il s'est réuni trois fois pour aider le Dr. Skoulikidis, à la suite de quoi le Comité Exécutif, strictement Grec, a pris tout à sa charge et, par conséquent, nous n'avions plus à intervenir.

Il faut que je vous dise également un petit mot, puisque je suis là à ce titre, sur le Comité International Permanent pour la Recherche sur la Préservation des Matériaux en Milieu Marin. Ce Comité est un enfant de l'O.C.D.E. Entre 1956 et 1965, l'O.C.D.E. avait un groupe d'experts qui s'occupait des problèmes de Corrosion et des Salissures, et dont le Président était un Hollandais, le Dr. Talen.

L'O.C.D.E. ne pouvant pas garder dans son organisation des groupes plus d'un certain temps, il a décidé, en 1965, de rendre sa liberté à ce groupe, de se séparer de son enfant, de l'abandonner. Avec l'aide de l'O.C.D.E., nous avons créé ce Comité International pour la Recherche sur la Préservation des Matériaux en Milieu Marin. Ainsi mes Collègues de l'ancien groupe sont-ils devenus mes Collègues de Comité. Je ne devrais d'ailleurs pas dire mes collègues, je devrais dire mes amis, car nous nous connaissons depuis de très nombreuses années. Ils m'ont fait l'honneur de me choisir comme Président de ce Comité. Ce Comité, dans ses statuts, a pris en charge la désignation des pays qui acceptaient d'organiser les futurs Congrès de Corrosion Marine et des Salissures.

Au cours de notre réunion d'hier, je ne sais pas si mon ami Mr. Guillen va m'en vouloir car ce que je dis là n'est pas absolument officiel, le Dr. Guillen (Espagne) nous a fait la proposition d'organiser le prochain Congrès, en 1972, à

Madrid.

Nous avons accueilli sa proposition avec évidemment beaucoup de joie, mais il n'est pas évident que d'autres pays ne se proposent pour organiser ce 3<sup>e</sup> Congrès.

Vous voyez, par conséquent, que, dans cette affaire, nous avons maintenant une sorte de continuité.

Le Congrès de Cannes a montré le chemin et je suis persuadé que le Congrès d'Athènes réaffirmera ce chemin. Celui-ci ne sera plus une petite route, se sera une grande route, une chaussée dans laquelle s'engageront les futurs Congrès.

Je crois que, à l'heure actuelle, ce Congrès de Corrosion Marine, et j'insiste sur le mot marine, et Salissures a une importance, il a une importance à deux titres, d'abord parce que vous savez très bien que les questions maritimes prennent de plus en plus d'importance, que l'on construit de plus en plus de structures dans la mer.

Je ne parle pas des bateaux, des bateaux il y en a toujours eu, mais, en plus des bateaux il y a les pétroliers qui s'intéressent de plus en plus au problème marin.

La corrosion des structures des installations «off shore» est un grave problème que je connais bien personnellement, et qui est un problème extrêmement important.

Il y aura également un jour, qui n'est pas si lointain, où l'on procédera à des extractions de minéraux sous-marins; par conséquent, on aura besoin de faire des installations, fixes ou mobiles.

L'homme devra certainement pénétrer de plus en plus profondément dans l'eau, y pénétrer lui-même personnellement, en tant qu'homme, emportant avec lui divers équipements; ceci pose également, en plus des problèmes de physiologie, des problèmes de Corrosion et de Salissures.

D'autre part, l'intérêt de ce congrès est de mettre en contact des gens qui, jusqu'il y a quelques années, s'ignoraient presque totalement. C'est-à-dire, d'un côté les Ingénieurs et les Physico-Chimistes et, de l'autre côté, les Biologistes qui s'intéressent aux salissures. Le fouling a une importance considérable sur la Corrosion et j'ai l'impression que, il y a quelques années, il était assez ignoré.

L'homme de la Corrosion était un peu trop l'homme du laboratoire, il a maintenant tendance à sortir de plus en plus de son laboratoire car on utilise de plus en plus des radeaux et des installations en mer. On collabore avec les biologistes, et je crois que l'intérêt de ce Congrès est justement cette co-existence entre les biologistes et les ingénieurs.

Je vois que je vous avais promis d'être bref et que je me suis laissé entraîner, peut-être un peu par mon enthousiasme dans ce domaine que je commence à connaître un peu. Je ne veux pas vous importuner plus longtemps.

Je tiens, avant de terminer, à vous dire que je suis persuadé que ce Congrès aura un très grand succès.

Je suis ici depuis déjà plusieurs jours, j'ai beaucoup discuté avec le Dr. Skoulikidis, j'ai vu toutes ses installations, toute son organisation, c'est absolument parfait. Je suis persuadé que tout marchera extrêmement bien et que ce Congrès dépassera très largement celui que nous avons fait à Cannes.

Je vous remercie.

ALLOCUTION DU REPRESENTANT DU MAIRE D'ATHÈNES  
ADDRESS OF THE REPRESENTING THE MAYOR OF ATHENS  
ANSPRACHE DES VERTRETERERS DES BÜRGERMEISTERS VON ATHEN  
ΠΡΟΣΦΩΝΗΣΕΙΣ ΤΟΥ ΕΚΠΡΟΣΩΠΟΥ ΤΟΥ ΔΗΜΑΡΧΟΥ ΑΘΗΝΑΙΩΝ

Mr. K. NIKOLOPOULOS

Monsieur le Ministre, Monsieur le Président du Congrès, Messieurs les Congressistes, Mesdames, Messieurs.

Le Maire d'Athènes Monsieur Ritsos, occupé au Congrès des Maires à Salonique, exprime ses regrets, parce qu'il ne peut pas participer aujourd'hui à Votre Congrès.

Comme Représentant du Maire d'Athènes je voudrais vous remercier de la part du peuple d'Athènes pour l'honneur que vous avez fait à notre ville et à notre pays, la Grèce, en le choisissant comme lieu du 2<sup>e</sup> Congrès International de la Corrosion Marine et des Salissures.

Votre Congrès intéresse beaucoup un pays marin avec d'histoire nautique comme la Grèce.

Je suis sûr que votre merveilleuse œuvre, votre effort scientifique sera reconnu de la part de tous ceux qui admettent le progrès dans ce domaine.

De la part de la ville d'Athènes et du Maire je vous souhaite la «Bienvenu».

Nous espérons que vous emporterez les impressions les plus belles de notre pays et je vous prie de les transmettre partout.



*Le Ministre de la Marine Marchande s'adressant aux congressistes.*

ALLOCUTION DU MINISTRE DE LA MARINE MARCHANDE DE GRÈCE  
 ADDRESS OF THE MINISTER OF MERCHANT MARINE OF GREECE  
 ANSPRACHE DES HANDELSMARINEMINISTER GRIECHENLANDS  
 ΠΡΟΣΦΩΝΗΣΙΣ ΤΟΥ ΥΠΟΥΡΓΟΥ ΕΜΠΟΡΙΚΗΣ ΝΑΥΤΙΑΙΑΣ

Prof. Dr. J. CHOLEVAS

Bien Honorables Messieurs les Présidents, Mesdames et Messieurs, Membres de ce Conseil, Mesdames et Messieurs.

J'éprouve un honneur exceptionnel, car, comme représentant du Gouvernement National Révolutionnaire, je me trouve parmi Vous, gens de science, d'élite et distingués pour annoncer le commencement du Second Congrès International de la Corrosion Marine et des Salissures.

Je désire tout d'abord Vous passer les remerciements cordiaux du Président de notre Gouvernement M. Georges Papa-

dopoulos, qui vraiment est bien chagriné de n'avoir pas pu honorer cette Séance inaugurale.

Je désire encore exprimer de la part du Gouvernement National, à la Fédération Européenne de Corrosion, le Comité International de la Corrosion Marine et des Salissures, ainsi qu'au Comité Permanent International Pour les Recherches sur la Préservation des Matériaux au milieu marin, des cordiaux remerciements pour leur décision que ce Conseil prenne place à Athènes, la capitale de notre pays — La Grèce. Je

désire également féliciter l'honorable Président ainsi que les Honorables Membres tant du Comité Exécutif que du Comité Scientifique. Aussi ceux qui ont organisé le Comité aujourd'hui inauguré, c'est-à-dire l'Université Technique Nationale d'Athènes, La Chambre Technique de Grèce, l'Association Hellénique des Ingénieurs Chimistes, pour leurs efforts et la parfaite organisation du Congrès.

Malgré le fait que comme une personne de Science, je me trouve bien loin des questions à être examinées par ce Congrès, pourtant l'étude du programme de ses Séances circulé, dans lequel sont mentionnées les futures communications, nous donne la conviction que de très importants problèmes d'une technique scientifique seront débattus entre vous.

Ces questions en dehors de leur importance théorique et leur valeur, elles contiennent aussi une importance pratique particulière surtout en ce qui concerne le secteur de la Marine Marchande, duquel Secteur, j'ai l'honneur de me trouver le Ministre, comme membre du Gouvernement National Révolutionnaire. Le fait que la Grèce est la seconde force Maritime dans le monde entier, donne la mesure de notre intérêt pour les résultats attendus de votre Conseil.

Vraiment, Messieurs Les Membres, elles ne sont que trop belles les rencontres internationales, l'objet desquelles n'est que la discussion des sujets scientifiques.

Egalement très beau est l'effort des gens de sciences — des doctes — lequel effort guide l'esprit humain sans cesse à plusieurs et plus grandes acquisitions. Aujourd'hui plus que jamais la science et la recherche sont en voie d'envisager n'importe quel problème, et par conséquent les seules à suivre. Et c'est bien juste que notre époque s'est titrée «l'époque de la technocratie et les gens de sciences technocrates».

Soyez sûrs que «Pallas Athina» étant le Symbole de la Sagesse de l'ancienneté Grecque, et l'esprit du père de la Science «Aristotle» ainsi que l'esprit des premiers pionniers de la Technique de «Archimèdes» et «Démocrite» et de nos savants ancêtres suivront avec affection la marche de vos travaux.

Messieurs, les Membres de ce Congrès, permettez-moi, sans croire que j'ai l'intention de devier votre Congrès de la science, de vous soumettre une bien chaleureuse prière:

Durant votre séjour en Grèce, vous êtes absolument libres de vivre l'actuelle réalité Grecque.

Comme vous tous vous êtes des gens de science et par conséquent vous appartenez à la classe supérieure, veuillez bien et tâchez, s'il vous plaît, de connaître bien et sans dissimulation la vie Grecque d'aujourd'hui et tout ce que vous verrez et en serez certains, communiquez le à vos compatriotes et amis n'importe où ils se trouvent. Nous nous intéressons à ce que la vérité, laquelle vérité est si grossièrement altérée de la part des facteurs qui ont des raisons de la haïr, soit connue partout.

Dites la vérité pour la Grèce d'aujourd'hui, laquelle après avoir été sauvée du gouffre de l'anarchie, se dirige en galopant vers le progrès dans tous les secteurs.

Terminant, je souhaite à Vous tous la bien-venu à notre pays et la ville d'Athènes.

Je vous souhaite de plus que les travaux de Votre Congrès soient couronnés d'un plein succès.

Je vous souhaite encore un excessivement agréable séjour à notre patrie qui aspire à maintenir pour toujours comme sien «l'hospitalier Jupiter».

Merci Bien.



# SECTION SEKTION - ΤΟΜΕΥΣ

## I

Corrosion et protection des ouvrages immergés dans l'eau de mer et émergés en atmosphère marine. Protection cathodique. Electrochimie de l'eau de mer. Influence des climats maritimes.

Corrosion and protection of structure immersed in sea water or subjected to marine environments. Cathodic protection. Electrochemistry of sea water.

Korrosion und Korrosionsschutz von Bauwerken in Meerwasser oder Küstenklima. Kathodischer Korrosionsschutz. Elektrochemie von Meerwasser. Einfluss von See - Atmosphäre.

Διάβρωση και προστασία κατασκευών εντός θαλασσίου ύδατος και εις θαλασσίαν ατμόσφαιραν. Ήλεκτροχημεία τοῦ θαλασσίου ὕδατος. Ἐπίδρασις θαλασσίων κλιμάτων.

Séance - Meeting - Sitzung - Συνεδρίασις

20.9.1968

Présidence - Presidency

Präsidium - Προεδρείον

Prof. G. CHAUDRON (Membre de l'Institut), France.

Prof. P. THEOHARIS (Grèce),

G. DECHAUX (France).

Prof. Dr SKOULIKIDIS : C'est un grand honneur pour moi, d'avoir à donner la parole, en premier, à Mr le Prof. CHAUDRON, Membre de l'Institut, spécialiste mondialement connu par ses travaux en Metallurgie et dans le domaine de la Corrosion, je ne donnerai pas la liste filante des autres distinctions internationales dont il est titulaire.

Il peut nous servir d'exemple à tous, par son activité scientifique, et j'en veux pour seule preuve le dernier livre qu'il vient de faire paraître, le tome relatif au Fer, du «Nouveau traité de Chimie Minérale», de Pascal.

Monsieur le Professeur CHAUDRON, je vous prie de prendre la parole sur le sujet :

## LES RECHERCHES FONDAMENTALES SUR LA CORROSION DES METAUX PAR L'EAU DE MER. CONSEQUENCES THEORIQUES ET PRATIQUES

Par Prof. Dr. G. CHAUDRON

Membre de l'Institut,  
Paris, FRANCE

Mes Chers Collègues, Mesdames, Messieurs,

J'ai l'honneur de remercier très sincèrement les organisateurs de ce Congrès International de la Corrosion Marine de m'avoir proposé la présidence des séances de cet après midi.

Cette réunion rappelle d'abord à beaucoup d'entre nous un Congrès qui avait été organisé à Cannes en 1964. Un magnifique volume a été publié à cette occasion et nous félicitons les auteurs des communications qui ont paru dans ce livre.

Mais je ne voudrais pas non plus oublier l'une des premières réunions sur la corrosion marine qui s'est tenue en 1937 à Monaco. Bien des noms d'auteurs seront rappelés dans les communications de ce Congrès, et plusieurs d'entre eux sont également parmi nous aujourd'hui. Qu'on me permette de signaler les noms de ces pionniers : le Dr. U.R. Evans, universellement connu par ses travaux d'électrochimie, le Dr. Hudson, l'un des premiers qui a étudié les essais de corrosion dans l'eau de mer, le Dr. La Que, le regretté Professeur Portevin, qui présidait cette réunion de Monaco, le Dr. Herzog, spécialiste de la corrosion du fer et beaucoup d'autres trop tôt disparus. Sans nul doute, le Congrès de 1968 pourra être considéré comme la suite logique de nos précédentes réunions de 1937, puis de 1964.

Il est important de remarquer que le programme des communications, au cours des journées actuelles, est beaucoup plus général que ceux qui avaient été envisagés à Cannes, et à Monaco. La biologie, les sciences naturelles ont apporté leur concours à l'étude des phénomènes de corrosion et des salissures dans l'eau de mer.

Les recherches sur la corrosion marine ont joué un rôle important dans les principaux pays qui se sont intéressés à la corrosion. C'est en 1924 qu'elles ont débuté en France grâce à l'initiative de nos Services techniques de l'Aéronautique. Il s'agissait de trouver les processus d'attaque de l'aluminium et de ses alliages par l'eau de mer et de mettre au point des procédés de protection par des revêtements protecteurs, en particulier pour éviter la corrosion des coques d'hydravions qui étaient réalisées en duralumin, mais ces recherches conduisirent à la découverte de nouveaux alliages résistants à l'eau de mer : les alliages Al-Mg préparés à partir de métaux d'une pureté relativement grande.

### L'EAU DE MER.

On considérait l'eau de mer avant 1930 comme une simple solution de chlorure de sodium à 3%. On avait déjà eu l'idée d'étudier la corrosion de l'aluminium et de ses alliages par une telle solution saline plus ou moins concentrée, mais on se souciait fort peu du rôle des additions qui pouvaient modifier, même à faible teneur, les propriétés de ces solutions de chlorure de sodium aux diverses concentrations.

Vers 1930, on imagine même dans divers laboratoires française et étrangers, l'eau de mer dite «synthétique». Ce sujet de recherche embarrassa beaucoup les chercheurs et conduisit à des erreurs mémorables. N'avait-on pas envisagé de remplacer dans la solution d'attaque l'oxygène dissous par de l'eau oxygénée?

Bien entendu, il n'était pas question de l'évolution, dans ces solutions, des composés organiques, ni du rôle et de l'existence des réactions photochimiques qui modifient complètement la concentration en oxygène. On sait que la photosynthèse est la réaction qui introduit le carbone dans le cycle vital en libérant de l'oxygène. L'énergie de la lumière permet à la réaction du gaz carbonique et de l'eau d'effectuer la synthèse des glucides. Ces eaux de mer synthétiques ont fait dire avec justesse à plusieurs auteurs que l'eau de mer réelle est vivante et que l'on doit tenir compte de ce fait capital dans l'étude de la corrosion.

### LA COMPOSITION DE L'EAU DE MER. LES INHIBITEURS DE CORROSION.

L'attaque des métaux et alliages dans l'eau de mer est due à un phénomène électrochimique qui est maintenant bien connu. A la surface des métaux il se forme des piles locales, et c'est la dépolarisation de ces piles par l'oxygène qui entraîne l'attaque anodique du métal. L'attaque dépend donc essentiellement de la combustion de l'hydrogène sur les cathodes. Dans le cas de l'eau de mer, les phénomènes électrochimiques sont sensiblement ralentis grâce à la présence d'inhibiteurs. C'est bien, je le pense, au Congrès de Monaco de 1937 que l'on a parlé pour la première fois de ces inhibiteurs et de leur importance théorique et pratique. En effet, dans l'eau de mer il y a des ions  $Mg^{++}$  et  $Ca^{++}$  qui se déchargent sur les cathodes, d'où il résulte un dépôt de magnésium et de chaux qui gêne notablement la dépolarisation cathodique et par suite il y a une diminution sensible du débit des piles locales.

### LE pH DE L'EAU DE MER.

Mais l'eau de mer présente une autre caractéristique d'un grand intérêt, due à la présence de carbonates et de phosphates qui maintiennent le pH dans des limites très étroites. Autrement dit, l'eau de mer renferme des corps tampons qui participent dans une proportion non négligeable à la protection du métal.

Le corps tampon gêne l'établissement d'une différence de pH entre la solution anodique acide et la solution cathodique basique. D'après le diagramme de R. Reiller (figure 1), l'effet pile ne pourra se produire d'une manière efficace que s'il s'établit une différence de pH notable et stable. On pourra

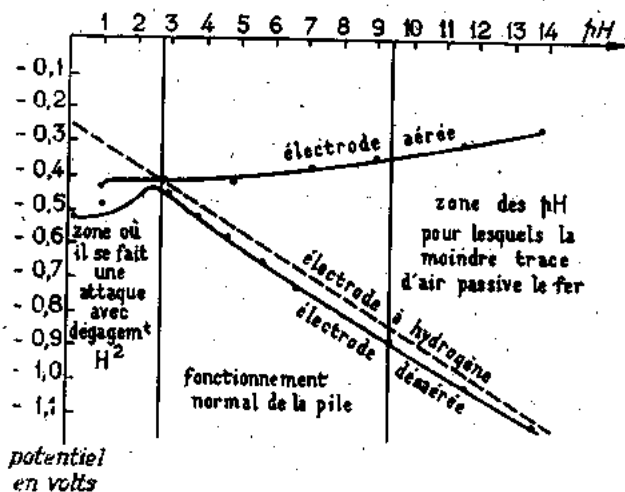


Figure 1

donc réaliser une protection avec des corps inhibiteurs, mais également avec des corps jouant le rôle de tampons.

Dans l'effet Evans, il se crée en surface des microdomaines cathodiques et anodiques sur lesquels se forment des solutions qui possèdent des pH très différents : acides à l'anode et basiques à la cathode. L'attaque sera d'autant plus efficace que la différence de pH entre deux domaines sera plus importante, et se maintiendra constante.

En conclusion, tous ces modérateurs de l'attaque électrochimique (dépôts cathodiques, corps tampons) permettront de protéger les métaux et alliages et ces mécanismes expliquent pourquoi l'eau de mer est moins corrosive qu'une solution saline pure.

Ces recherches ont pu diriger les travaux qui ont été effectués pour la préparation d'alliages moins corrodables, en particulier des alliages aluminium-magnésium pour lesquels il n'y avait pas lieu de redouter des effets de pile importants entre les zones anodique et cathodique. On sait que ces alliages, connus à l'origine sous le nom d'alumags, sont utilisés pour la construction des superstructures dans les bateaux modernes, et au cours des dix et quinze dernières années leurs applications se sont multipliées dans les domaines les plus variés.

### ATTAQUE BIOLOGIQUE.

Dans la plupart des cas de corrosion que nous venons de citer les métaux se trouvaient soumis à l'action de l'oxygène nécessaire pour la dépolarisation cathodique.

Mais on a pu constater que des corrosions importantes pouvaient se produire, en absence d'oxygène, par exemple à l'intérieur de certaines canalisations, dans le cas de tuyauteries enterrées : on a rendu responsable de ce phénomène la présence, dans la solution, d'une bactérie, qui se comporte comme un accepteur d'hydrogène; elle agit donc comme un dépolarisant de l'hydrogène cathodique. Mais on observe également des cas de corrosion biologique dans des canalisations à l'intérieur desquelles circule une eau aérée, le processus est alors très différent.

Nous aurons également l'occasion de suivre des communications sur l'emploi de substances qui jouent sans doute le rôle d'antiseptiques, et qui gênent le développement de l'attaque biologique. D'une part, on peut détruire la bactérie en introduisant du chlore dans l'eau. On peut également envisager des peintures qui renferment de véritables antiseptiques. Là encore il conviendra d'étudier les propriétés particulières de ces inhibiteurs.

### CORROSION EN MILIEU TROPICAL.

L'Institut de Recherches de la Sidérurgie a réalisé des essais dans l'eau de mer dans différentes stations, en particulier à Abidjan (Côte d'Ivoire). Au cours de ces essais, on a mis en évidence l'influence des «microclimats» (voir figure 2).

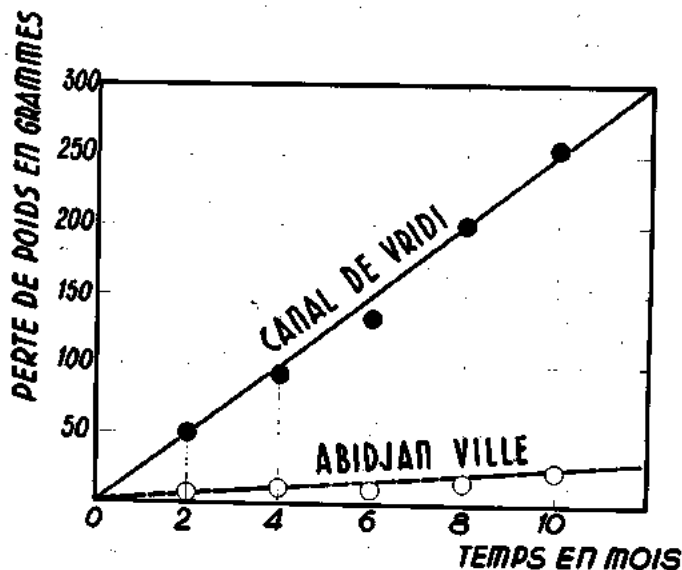


Figure 2

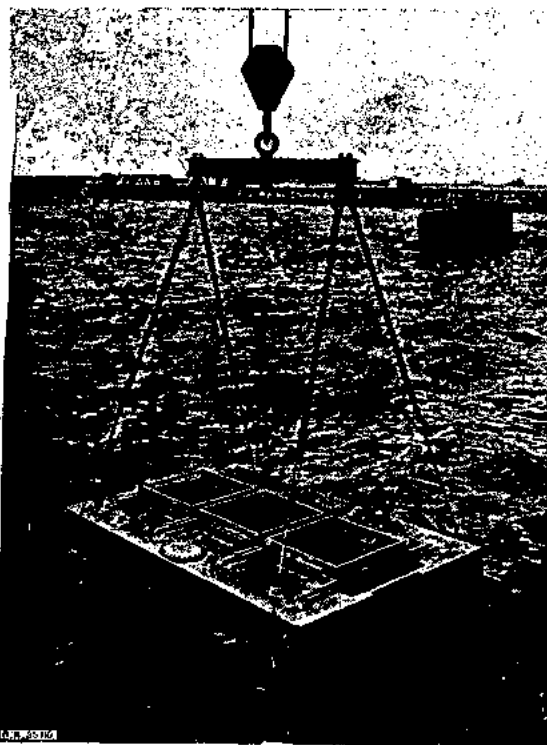


Figure 3

## LES ESSAIS DE L'O.T.U.A.

L'Office Technique pour l'Utilisation de l'Acier (O.T.U.A., Paris) a commencé des essais naturels en 1935.

Les figures 3 et 4 représentent la mise à l'eau d'un radeau portant les plaques-échantillons dans la rade de Boulogne

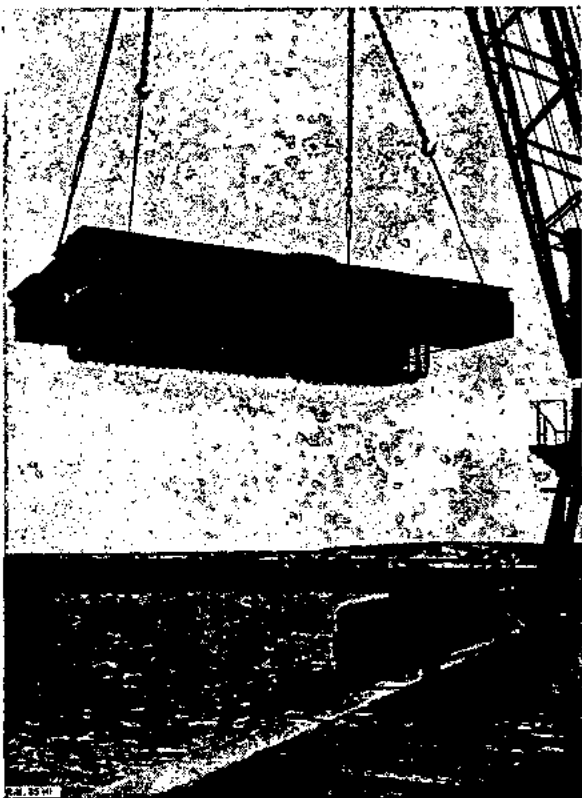


Figure 4

sur mer. Les figures 5 et 6 montrent la mise en place de radeaux portant des échantillons immergés dans de l'eau de rivière quasiment pure : eau de la Truyère (Massif Central), pour la figure 5, eau du Doubs (Jura), pour la figure 6.

Ces essais ont permis d'établir la différence importante qui existe entre divers milieux d'attaque, par exemple entre l'eau de mer et l'eau douce.

Je ne voudrais pas terminer ce préambule sans attirer l'attention des participants sur l'importance des travaux effectués dans différents centres d'essais. Les milieux d'attaques sont définis non seulement par les différents facteurs de la composition de l'eau de mer mais également par la température de l'eau et par celle de l'atmosphère, par l'influence des tensions mécaniques. Je voudrais citer tout particulièrement le laboratoire de Kure-Beach de l'International Nickel Company, dont le directeur est le Dr. T.P. May. Je pense qu'il sera très intéressant dans une réunion comme celle-ci, d'insister sur le rôle de ces centres qui fort heureusement, tendent à se développer dans les différents pays qui s'intéressent aux problèmes de la corrosion. Nous reconnaissons parmi nous aujourd'hui les organisateurs de différents centres d'essais importants.

La Grèce peut être fière de collaborer activement à la création de ces laboratoires pratiques qui doivent nécessaire-



Figure 5

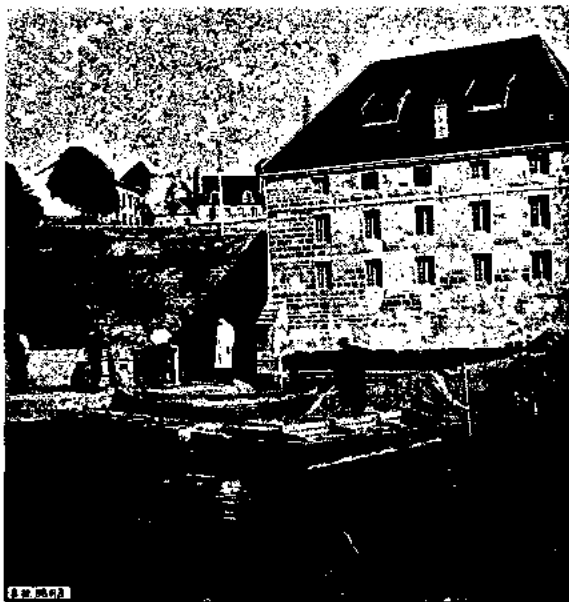


Figure 6

ment apporter bien des résultats nouveaux dans la lutte contre la corrosion dans l'eau de mer.

## BIBLIOGRAPHIE

On trouvera une bibliographie détaillée des questions abordées dans cet exposé dans l'article de G. Chaudron et collaborateurs du «Nouveau traité de chimie minérale», publié sous la direction de P. Pascal, tome 17, premier fascicule, page 567.

# THE SEA WATER CORROSION CONTROL OF CARBON STEEL BY MEANS OF INHIBITORS

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## SUMMARY

The use of sea water as a cooling medium in refineries etc. demands the study of carbon steel corrosion by such water in the temperature range of 45-70° C. Accordingly the corrosion action of different sea water salts was investigated

within the temperature limits of 20-100°. It was also studied the inhibiting action of mixtures of sodium nitrite and sodium benzoate and found the most effective ratio of the two substances in the mixture.

Sea water is a typical electrolyte and therefore all processes of corrosive-destruction in it are of electro-chemical nature. The aggressive action of sea water is accounted for by its high electric conductivity resulting from its high salinity and a high degree of the dissociation of salts.

Specific electric conductivity of sea water depends upon its general salinity which is 2-3 per cent and is equal to  $2.5 - 3.0 \times 10^{-2} \text{ Ohm} \times \text{cm}^{-1}$  (1).

Sea water is almost homogenous in its qualitative composition and therefore the rate of corrosion of metals in any sea water is almost the same, particularly in deeper layers. There would be no difference in the destruction of certain types of steel in different seas if the process of corrosion were not affected directly or indirectly by such factors as the temperature of the water, the degree of air circulation, biological factors and external impurities which are not characteristic of sea water.

Unlike some other electrolytes sea water causes non-uniform corrosion of metals and the formation of local affected spots which are very dangerous, particularly for pipe-lines (2).

The processes of corrosion occurring under the effect of sea water are complex in nature. These depend on the chemical composition and physico-chemical properties of the water, the maintenance regime, the nature of the construction, the nature of the metals etc. The combination of all these factors and their relationship determine the peculiarities of a corrosion process.

As is known, the main components of sea water are chlorides, sulphates, carbonates and bromide, alkaline — and alkaline-earth metals. Sea water contains almost all the elements of the Mendeleev periodic system which to this or that extent affects the corrosion process.

The most dangerous corrosive anions are  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Br}^-$ ,  $\text{J}^-$ .

According to the nature of the corrosion effect of the substances contained in sea water can be divided, conventionally, into four groups:

(a) those actively affecting the course of the anodic and cathodic processes and which are the most important for the characteristics of the aggressiveness of sea water (oxygen, ions of chlorine);

(b) strong cathodic depolarisers (free bromine, iodine, ozone and others) which enhance corrosion of metals thus being stimulators of corrosion;

(c) substances inhibiting corrosion processes (compounds of silica acid);

(d) substances not affecting corrosion of metals (inert gases) (3).

Among the gases dissolved in sea water, the most common and corrosion important is oxygen which finds its way into sea water from atmospheric air as well as a result of the processes of photo-synthesis of fitoplankton. The change in the percentage of the dissolved oxygen depends on the activities of algae which in the process of photo-synthesis absorbs carbon dioxide from water and release oxygen (4).

The degree of solubility of oxygen depends on the temperature and the salinity of water: the higher the temperature and the salinity of water, the lower the dissolution of oxygen (Table 1).

TABLE 1

SOLUBILITY OF OXYGEN IN SEA WATER (ml/m)  
AT DIFFERENT TEMPERATURES AND SALINITIES

Temperature °C	Salinity					
	0.0	1.0	2.0	3.0	3.5	4.0
0	10.3	9.65	9.00	8.36	8.04	7.72
10	8.02	7.56	7.06	6.63	6.41	6.18
20	6.57	6.22	5.88	5.52	5.35	5.17
30	5.57	5.27	4.95	4.65	4.50	4.35

The hydrogen indicator pH for sea water is 7.2-8.3. Fluctuations in pH depend on the season. It has been found that from Spring to Autumn oxygen is released entirely owing to photo-synthesis; during this process concentration of carbon dioxide diminishes while the numeric value of pH increases.

The biological factor plays an important part in the process of marine corrosion. Micro organisms contained in sea water contribute to the process of corrosion because their living functions require absorption of oxygen. Besides, these organisms are deposited on the metal which leads to a non-uniform access of air to the surface of the metallic parts and equipment. The living activities of the micro organisms increase the aggressiveness of the environment as they produce hydrogen sulphide, ammonium, carbon dioxide etc.

Micro-organisms can depolarise corrosion processes owing for instance to a shift in oxi-red equilibrium. Ferrous bacteria oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  at the expense of the oxygen dissol-

ved in the water.

Accumulation of micro-organisms on the surface of the metal largely affects the nature and development of corrosion processes through the effect of such accumulation is not confined to the above mentioned effect.

The aim of this research has been an investigation of the corrosion resistance of carbon steel in natural sea water depending on the temperature and speed of the motion of the liquid and the selection of inhibitors for these conditions.

In our research we used samples made of steel 10 prepared for testing in line with the accepted methodology. The investigation was carried out at temperatures from 20 to 100° C, both in natural sea water and in distilled water.

#### Results of Investigation

With increasing temperatures, the loss of metals varies both in distilled and sea water. As is seen in fig. 1, up to 60-70° C the rate of dissolution of iron in sea water increases

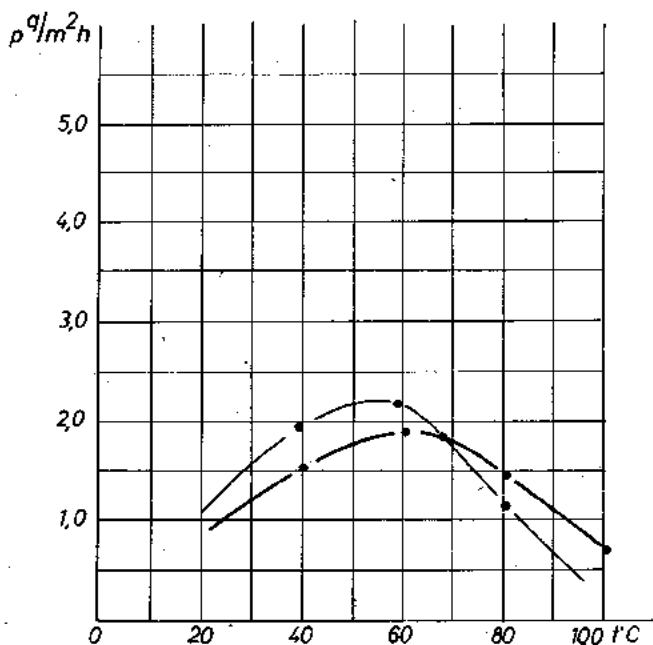


Fig. 1. — Corrosion in steel in sea (1) and distilled water (2) depending on temperature.

and then decreases. The rate of corrosion at 100° C almost coincides with the rate of corrosion at 20° C. A like phenomenon was registered for distilled water. Here the rate of corrosion reaches maximum at 80° C and then decreases (Fig. 1). This is explained by the fact that with increasing temperatures the solubility of oxygen diminishes (see Table 1). Corrosion in a current of sea water (the speed of the current is .5 M-Sec) shows the same regularity though, against stationary conditions, it increases sharply — at 60° C corrosion increases 5 times (fig. 2).

The influence of individual salts contained in sea water on the process of corrosion depending on the temperature was found to be the same as in sea water, that is at 60° C. The degree of dissolution of the metal is the highest (Fig. 3,4). The only exception was magnesium sulphate which at a high temperature undergoes hydrolysis with formation of sulphuric acid which results in intensified corrosion at higher temperatures.

A number of compounds have been tested as inhibitors of corrosion in sea water: salts of benzoic acid, chromates (organic and inorganic), sodium nitrate and their mixtures.

The results of the research are given in table 2.

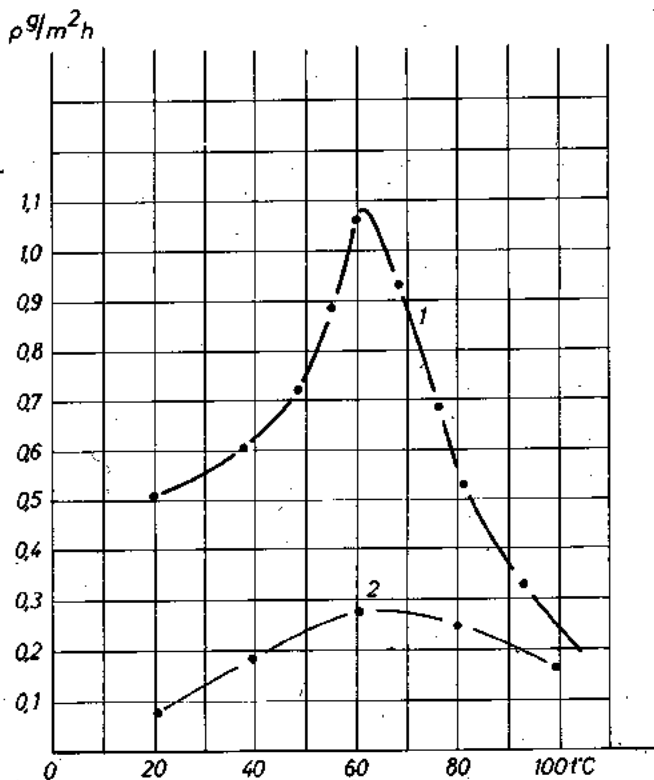


Fig. 2. — Corrosion of steel 10 in current 0.5 msec (1), in the stationary liquid (2) depending on the temperature.

TABLE 2  
PROTECTIVE EFFECT OF INHIBITORS OF  
CORROSION AND THEIR MIXTURES  
IN SEA WATER

Inhibitors	Concentration m Mole/l	corrosion rate $g/m^2$		
		(1)	(2)	(3) (ii)
Control (Natural sea water)			0.82	1.62
NaNO <sub>2</sub>	25		0.12	0.18 (spot corrosion)
Mixture of NaNO <sub>2</sub> + C <sub>6</sub> H <sub>5</sub> COONa	75 25		no corrosion	no corrosion
K <sub>2</sub> CrO <sub>4</sub>	50		0.23	0.41
Mixture of K <sub>2</sub> CrO <sub>4</sub> + NaNO <sub>2</sub>	50 50		no corrosion	no corrosion
Mixture of K <sub>2</sub> CrO <sub>4</sub> + NaNO <sub>2</sub>	25 75		no corrosion	no corrosion
MgCrO <sub>4</sub>	50		0.36	0.89

As is seen from the above data the metal is fully protected only in case of the application of a mixture of inhibitors.

To study the behaviour of these corrosion inhibitors in

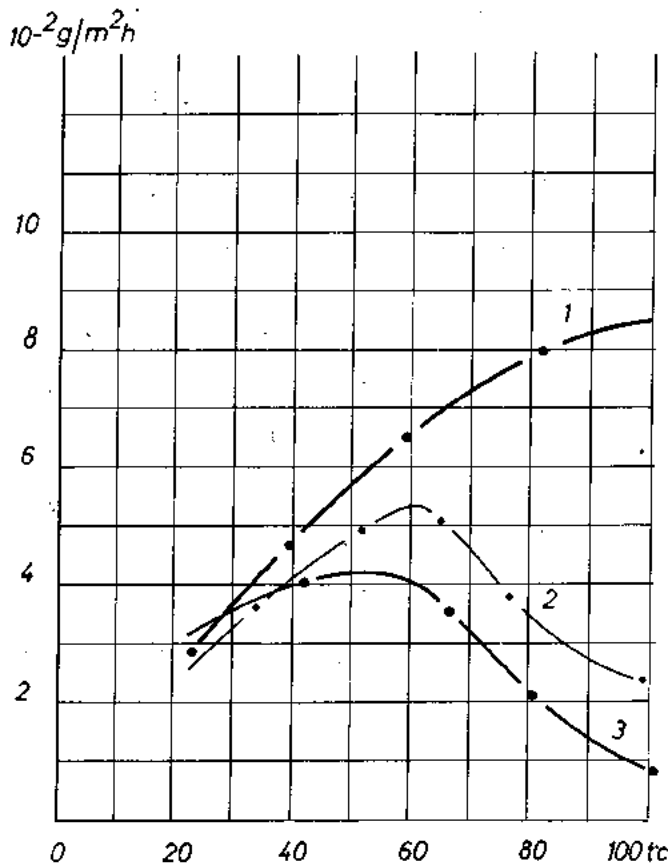


Fig. 3. — Effect of salts dissolved in sea water.  $MgSO_4$ , 3,305 g/l (c.1). M.A.B.R., 0,83 g/l (c.2),  $NaHCO_3$ , 0,202 g/l (c.3) on corrosion of steel 10 at different temperatures.

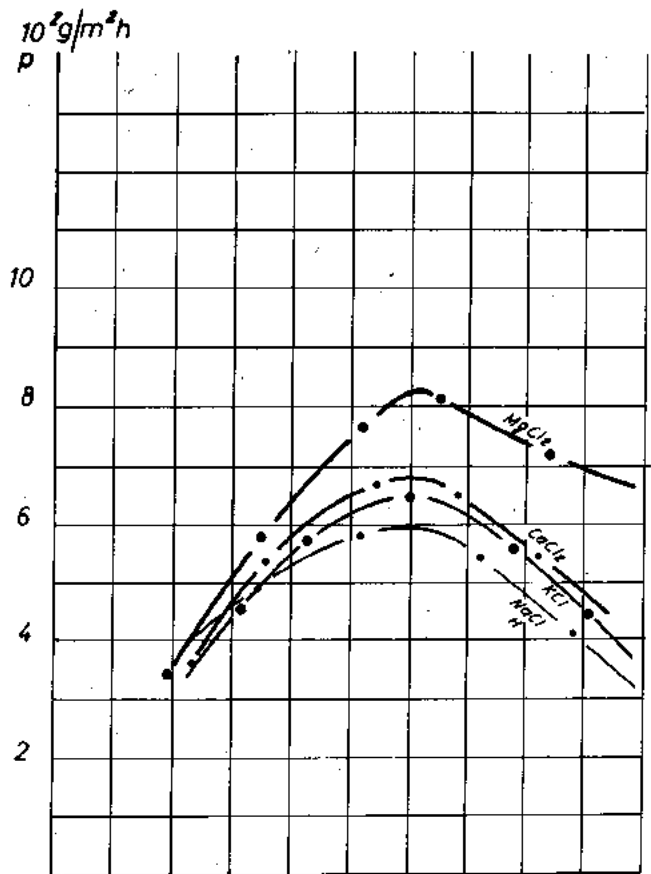


Fig. 4. — Effect of salts dissolved in sea water  $CaCl_2$ , 1,14 g/l (c.1),  $MgCl_2$ , 2,347 g/l (c.2),  $KCl$ , 0,725 g/l (c.3) and  $NaCl$ , 22,518 g/l (c.4) on corrosion of steel 10 at different temperatures.

sea water electric chemical methods have been used. These came down to measurement of electrode potentials, taking polarization curves and taking potentiodynamics curves on A.C.

The analysis of the obtained curves (fig. 5) shows that in sea water the initial value of the electrode potential of carbon steel at 20°C is equal to minus 193 mV versus the normal hydrogen electrode. During the initial stage of the experiment (from 30 seconds to 20 minutes) the potential is shifted to the negative region, the potential change being 150 mV. No substantial change in the potential was observed at later stages. In the presence of nitrites in sea water the change in the potential differs largely from the previous. The initial value of the potentials is -34 mV. During 20 minutes the potential shift was by 78 mV and it remains constant further. On the curve corresponding to the change in the electrode potential in a solution containing 100 m mole/l of sodium benzoate in sea water the initial value of the potential equals 114 mV. In the first 20 minutes the potential shift is 120 mV; in the subsequent 20-30 minutes the potential sharply shifts by -415 mV to the negative region; no further change in the potential occurs. The change in the potential of carbon steel in the mixture of solutions of sodium nitrite and sodium benzoate inhibitors occurs as follows:

The initial potential of carbon steel in this solution equals -94 mV. In the first five minutes as shift of about 80 mV is observed in potentials to the negative region; after 15 minutes, a 50 mV shift to the positive region, while after that the potential remained constant.

It follows from the above data that the more positive potential of carbon steel predominates in sodium nitrites solution whereas the most negative initial potential (-187 mV)

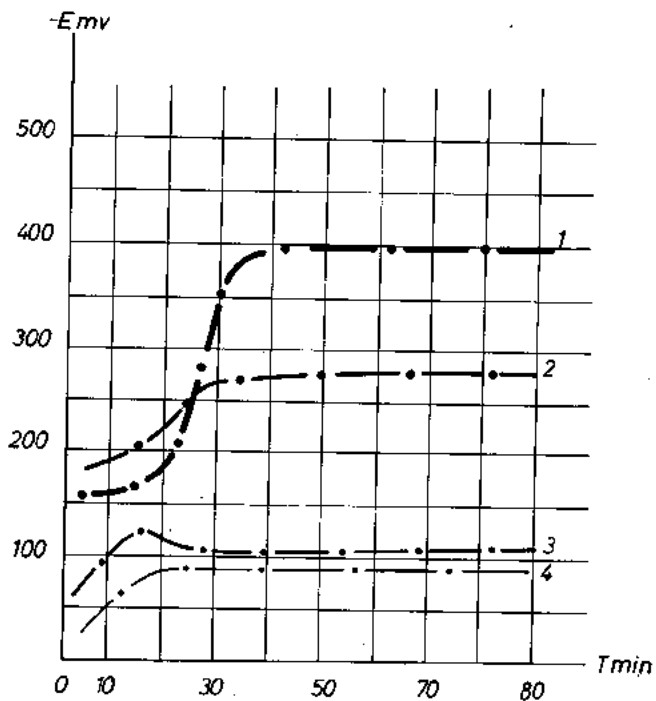


Fig. 5. — Polarization and potentiodynamic curves on A.C.



is characteristic of the electrode in sea water without inhibitors.

In sodium benzoate solution the electrode potential, after 30 minutes, equals  $-530$  mV. The most positive initial potential ( $-155$  mV) is characteristic of the electrode in solutions of sodium and benzoate and sodium nitrite and in solution of sodium nitrite.

The data on the change in the potentials are in agreement with the data of a weight analysis.

The largest loss of metal is observed in sea water with sodium benzoate which means that in such conditions sodium benzoate is a stimulator.

Further we took polarization curves prior to the establishment of the potential in solutions of the above-mentioned inhibitors. (Table 3).

TABLE 3  
POTENTIAL CHANGES OF STEEL ANODE FOR DIFFERENT DENSITIES OF CURRENT.

Concentration of inhibitors	current density $\mu\text{a} / \text{sqcm}$			
	40		800	
	cathod	anode	cathod	anode
Sea water (control)	-593	+115	-920	-93
Sodium nitrate (100 m mole/l)	-500	+60	-789	+209
Sodium Nitrate (75 mole and sodium benzoate 25 m-mole)	-593	+85	-813	+242
Sodium benzoate (100 m mole)	-830	+147	-965	+142

The largest effect on the cathodic process is produced by sodium benzoate solution of 100 m mole concentration. A mixture of sodium nitrate with sodium benzoate does not substantially effect the cathodic process. Considerable differences are observed on the curves of an anionic polarization. A slight inhibition of the oxidation process under the given conditions is observed in a solution of inhibitors mixture.

#### OBTAINING POTENTIAL DYNAMIC CURVES ON A.C.

The polarization cell is an ordinary polarographic cell with an auxiliary saturated calomel electrode. The electrode which is polarised is a length of steel wire insulated by BF-2 glue. The cut end of .225 sq. millimeter was used as the working part of the electrode. The time in all experiments was 10 minutes. The range of the variable constituent was roughly 15 mV at a frequency of 50 cycles per second.

The results of the experimental data are given in figure 6. From the curve of anionic polarisation by iron electrode in sea water (fig. 6, curve 1) it follows that first a well represented maximum is observed. This maximum is due to the process of formation of  $\text{Fe}^{2+}$  in the solution while the adding of inhibitors causes a shift in the iron potential to more positive values and the decrease in the height of the potential dynamic maximum. This may be due to the inhibiting action of the given inhibitors in respect of the process of the formation of iron ions in the solution.

The observed sharp fluctuation of the electric current shown in fig. 6 (curve 2) are due to the periodic process of formation and destruction of the protective oxide-film which appears on the surface of the electrode under the impact of

the action of sodium nitrate oxidiser. When sodium benzoate is added to this environment (fig. 6) (curve 3) the anodic-curve changes substantially — the sharp fluctuation of anodic current disappear. This is due to the formation of more firm and uniform protective film as a result of the inter-action of 2 inhibitors.

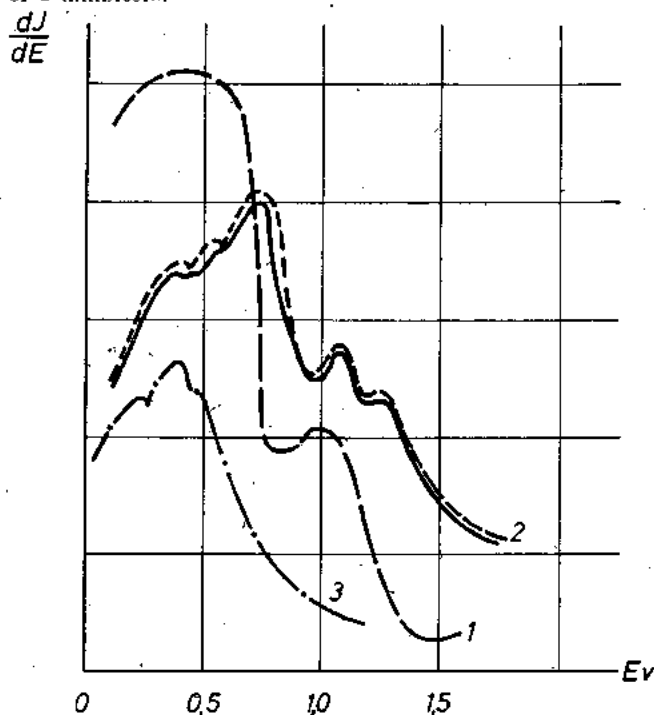


Fig. 6. — Anodic potential dynamic curves for carbon steel in sea water with inhibitor. 1. Control (sea water). — 2.  $\text{NaNO}_3$ , 100 mmoles.; 3-75 m.moles  $\text{NaNO}_3$ , + 25 m.mole  $\text{C}_6\text{H}_5\text{COONa}$ .

Potential dynamic curves make it possible to observe the formation of the oxide film in cathodic areas depending on time.

In the first 3-5 minutes the maximum appears which is due to the action of oxygen dissolved in water; then the maximum gradually disappears. This process can be explained by the formation of an oxide film on the iron electrode with participation of the oxygen dissolved in the solution. After 32-34 minutes the maximum disappears completely (Fig. 7, b) that is the process of reduction of the oxide film takes place.

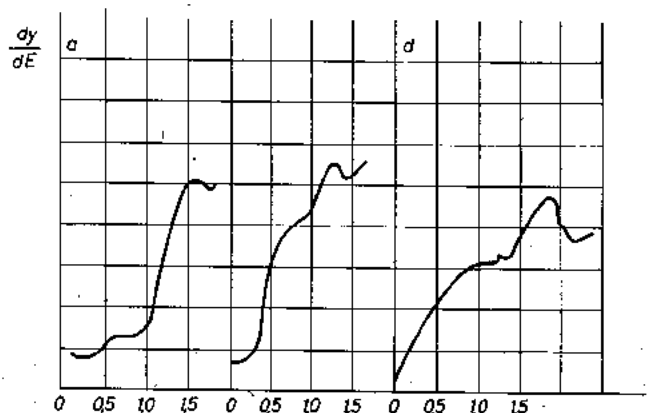


Fig. 7. — Cathodic potential dynamic curves for carbon steel in sea water a) samples were tested for 12 min. b) 24 minutes. c) 36 minutes.

Thus with the help of the potential dynamic method it is possible to investigate more accurately the occurrence of the anodic and cathodic processes and to determine, in 10-12 minutes, the protective action of the applied inhibitor being used in solutions of salts or acids.

### CONCLUSIONS

1. Between 20-100° C the rate of corrosion achieved maximum at 60-70° C.
2. A study of the new salts contained in sea water within the temperature range of 20-100° C helped to establish that for all salts with the exception of magnesium sulphate the temperature maximum is observed at 60-70° C while at higher temperatures the intensity of the corrosion process diminishes owing to the decrease of oxygen in the solution.
3. During the study of the motion of sea water at .5 m. per second during six hours it was established that the loss of metal increases within the range of temperatures of 20-60° C while further increase in the temperature leads to a decrease in the loss of the metal.
4. It was found that the best protection of metal is achieved by using a mixture of inhibitors (equally at 20 and 60° C): sodium nitrate with sodium benzoate, chromates with sodium nitrate. Chromates used separately (organic or inorganic) have less protective effect.
5. The use of the potential dynamic method enabled to establish finer differences in the occurrence of the cathode and anode processes. Analyses of anodic potential dynamic curves have shown that anodic process in the presence of sodium nitrate consists in a periodic formation and destruction of the

protective film which well agrees with the data of corrosion research (when sodium nitrate is used as inhibitor in sea water spot corrosion is observed).

6. This research has shown that to protect carbon steel exposed to sea water in a closed system, inhibiting mixtures can be recommended for large scale production tests, these inhibitors consisting of mixtures of chromates and sodium benzoate with sodium nitrate of above mentioned concentrations.

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# TENUE DES ALLIAGES D'ALUMINIUM ET DES ASSEMBLAGES ACIER - ALLIAGE D'ALUMINIUM EN EAU DE MER

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## RÉSUMÉ

L'emploi croissant des alliages d'aluminium en Construction Navale a conduit à entreprendre des recherches sur le comportement des alliages aluminium-magnésium en atmosphère marine. De tels essais étant toutefois très longs eu égard à l'excellente tenue de ces alliages, il a été aussi procédé

à des essais en immersion qui ont fourni d'intéressantes informations sur le comportement en eau de mer de ces alliages et celui d'assemblages rivés ou boulonnés comportant une tôle d'acier et une tôle en alliage aluminium-magnésium. La présente communication rend compte de ces essais.

## INTRODUCTION

Les alliages d'aluminium sont couramment utilisés pour la réalisation de superstructures de paquebots et pour de nombreux autres usages navals.

Ils sont alors soumis en permanence à l'action corrosive de l'atmosphère saline et souvent à celle des embruns.

Dans de nombreux cas enfin, ces alliages peuvent être en contact avec des eaux salées stagnantes.

On doit aussi noter que les superstructures en alliages d'aluminium sont en général fixées par rivetage sur des structures en acier. De tels assemblages, comportant deux matériaux de potentiels électrochimiques différents, doivent évidemment être réalisés avec grand soin.

Eu égard à ces circonstances d'emploi particulières, l'Institut de Recherches de la Construction Navale, l'Aluminium Français et le Centre de Recherches Métallurgiques de Pechiney ont entrepris une campagne d'essais pratiques inspirés par les constatations faites à bord.

La présente communication rend plus particulièrement compte des essais en immersion et en semi-immersion effectués sur des alliages nus ou anodisés et sur des assemblages acier-alliage d'aluminium.

Des essais ont aussi été effectués en atmosphère saline ou aux embruns.

D'autres essais ont porté sur des assemblages par soudage sous gaz inertes. Ils sortent du cadre de la présente communication et n'y sont mentionnés que pour mémoire.

Du fait de leur faible masse spécifique, les alliages d'aluminium présentent un très grand intérêt pour les Constructeurs de navires, en particulier lorsque ces alliages sont utilisés pour la réalisation des superstructures. Dans un tel cas, ils permettent en effet d'accroître la stabilité du navire ou de tracer des carènes plus fines permettant une plus grande vitesse à puissance égale ou une puissance plus faible à vitesse égale. L'emploi des alliages d'aluminium ne s'est d'ailleurs pas limité aux superstructures et on peut mentionner un certain nombre de réalisations ou de projets de navires dont la coque elle-même est en alliage d'aluminium (voir en particulier référence 2 à 6).

L'une des caractéristiques essentielles des alliages ainsi utilisés est leur résistance à l'atmosphère marine ou aux embruns. Il faut toutefois aussi tenir compte de leur résistance à l'eau de mer elle-même, car très souvent, les alliages des

superstructures sont immergés dans de l'eau de mer stagnante du fait par exemple de l'insuffisance des évacuations d'eau.

L'aptitude des alliages légers à être employés pour la réalisation de coques entraîne aussi l'obligation de procéder à la vérification de leur résistance en immersion.

Par ailleurs, les essais à l'atmosphère marine ou aux embruns sont, du fait de la bonne résistance à la corrosion des alliages d'aluminium, de très longue durée et il importe en conséquence, si l'on veut obtenir des informations relativement rapides, de compléter ces essais par des essais en immersion, même si ceux-ci, trop sévères, doivent être interprétés.

Depuis 1952 l'Institut de Recherches de la Construction Navale a procédé à de nombreux essais, non seulement en atmosphère saline et aux embruns, mais aussi en immersion et en immersion-émersion alternées.

Ces essais effectués en collaboration étroite avec l'Aluminium Français et le Centre de Recherches Métallurgiques de Pechiney, ont été faits à la Station de la Rochelle du Centre de Recherches et d'Etudes Océanographiques, aux Stations de Salin-de-Giraud (Méditerranée) et de Biarritz (Atlantique), de la Compagnie Pechiney et enfin à l'Arsenal de Toulon (Méditerranée).

Ces essais sont essentiellement pratiques et ont surtout pour but d'améliorer la mise en œuvre des alliages d'aluminium.

## 1. - ESSAIS SUR ALLIAGES NUS EN IMMERSION

Les premiers essais entrepris ont eu lieu à la Rochelle et ont porté sur des alliages A-G3 et A-G5 (composition 3 et 5% de Magnésium avec 0,40% de Manganèse).

Ces essais avaient fait apparaître des détériorations assez importantes consistant :

- En piqures profondes, en particulier sur l'A-G5 (fig. 1).
- En zones de forme circulaire à aspect décapé faisant penser à une action des balanes fixées.
- En ouvertures des tranches des éprouvettes (fig. 2).

A l'issue de ces essais, il a toutefois été admis que les résultats obtenus n'étaient pas à l'abri de toute critique et ne pouvaient être considérés comme définitifs car,

a) Les échantillons utilisés avaient été prélevés par le Chantier chargé de la préparation sur des stocks dont il disposait. Il en résultait que ces échantillons n'étaient pas dans des états métallurgiques identiques : certains pré-

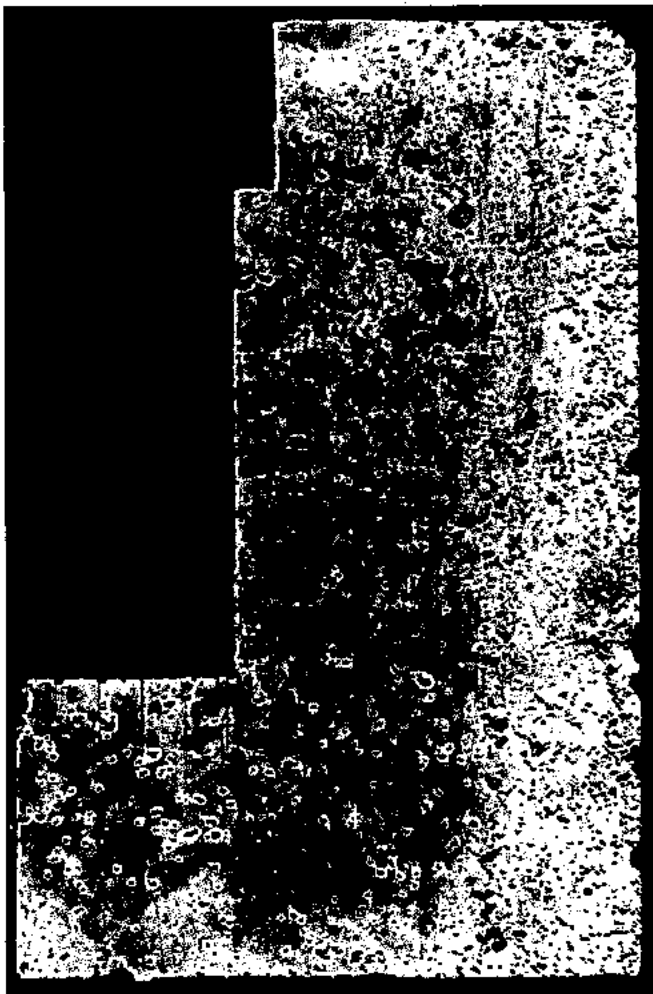


Fig. 1. — Tôle en A-G5 immergée pendant 2 ans et 6 mois à La Rochelle  
— Pallice — vue d'une face.

sentaient une structure de métal recuit, d'autres une structure de métal écroui, d'autres enfin étaient dans un état peu homogène (Précipitations d'Al<sub>3</sub>Mg<sub>2</sub> aux joints des grains).

b) Les tôles utilisées étaient des tôles assez anciennes (antérieures à 1952). Or, depuis cette époque, les fournisseurs de demi-produits avaient amélioré leurs procédés de fabrication et leurs contrôles.

Ces différents aspects de la question étaient apparus dès 1954 et il avait alors été décidé de procéder à une nouvelle série d'essais en utilisant un A-G5, anodisé ou non, de fabrication suivie et de composition et d'état (recuit 2 heures à 400° C) bien définis.

Ces essais ont été effectués en immersion à la Rochelle et Salin-de-Giraud et en immersion-émersion alternées à Biarritz.

Les éprouvettes mises en place au cours du premier trimestre 1954 ont été examinées régulièrement sur place avec des prélèvements périodiques pour examens au laboratoire.

Quelques éprouvettes de cette série d'essais sont encore en place. Elles étaient intactes lors du dernier examen (Février 1966) correspondant à 12 ans d'immersion. Un certain nombre d'entre elles seront présentées à Athènes. La figure 3 montre une tôle en A-G5 non anodisé immergée pendant 7 ans à a Rochelle.

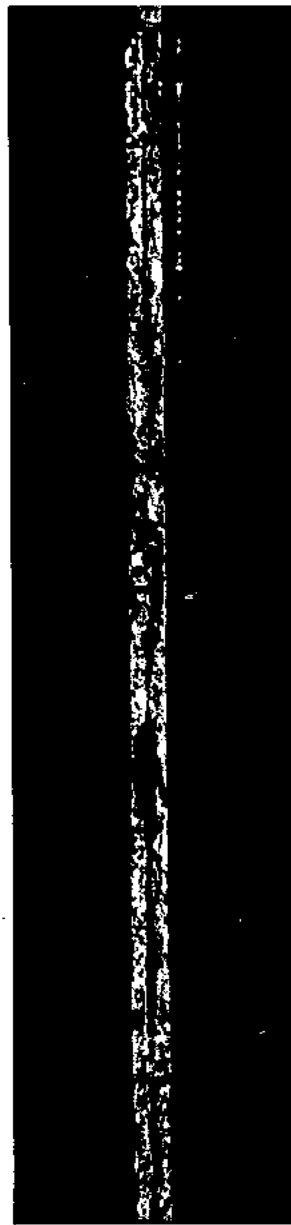


Fig. 2. — Tôle en A-G5 immergée pendant 2 ans et 6 mois à La Rochelle  
— Pallice — vue d'une tranche.

Les résultats obtenus étaient donc incontestablement très supérieurs à ceux de la première campagne d'essais et la différence de comportement constatée nous a conduits à nous demander si l'on n'avait pas été trop loin dans la recherche de l'homogénéité et de la qualité des échantillons.

Ce scrupule a conduit à mettre en route une troisième campagne d'essais comportant simultanément des alliages d'aluminium de fabrication courante et des alliages spécialement élaborés.

Pendant le long intervalle de temps écoulé depuis les premiers essais, de nouvelles catégories d'alliages avaient par ailleurs été introduites en Marine (A-G4 au manganèse et A-G4 au manganèse-chrome) et il fut décidé d'incorporer ces nuances dans le nouveau programme qui porta donc sur les nuances A-G4 M - A-G4 MC - A-G5 M et A-G5 MC.

Ce programme est en cours d'exécution depuis 1962 à

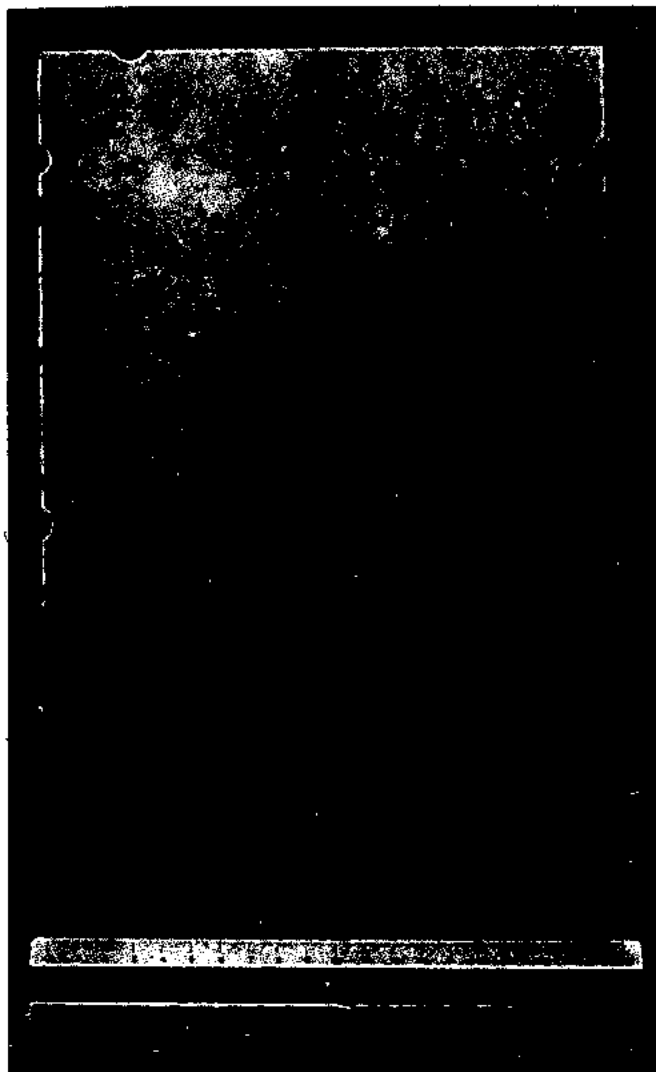


Fig. 3. — Tôle en A-G5 immergée pendant 7 ans à La Rochelle — Pallice.

la Rochelle (en immersion) et à Biarritz (en immersion-émersion alternées).

Un examen fait en 1966 a montré que ces éprouvettes étaient toujours en parfait état. On constate tout au plus des variations de teintes provoquées par les salissures qui se dessinent en clair sur fond légèrement plus foncé. Ces zones ont toutefois conservé un poli parfait.

Ces divers essais ont donc mis en évidence un très bon comportement des alliages d'aluminium magnésium en immersion à condition toutefois que l'état structural de ceux-ci soit bon et que leur homogénéité n'ait pas été altérée, ni par des incidents de laminage, ni par une maturation à chaud.

L'un de nous a d'ailleurs déjà publié une étude sur ce dernier sujet (réf. 1).

Des essais en atmosphère saline ou aux embruns avaient aussi révélé un excellent comportement des alliages aluminium-magnésium, le ternissement des éprouvettes étant toutefois plus accentué que pour l'immersion.

Certaines détériorations constatées dans divers essais, soit aux zones d'appui des supports d'éprouvettes en bakélite, soit sous les rondelles de fixation de ces éprouvettes ont conduit à considérer que les phénomènes d'aération différentielle étaient peut-être les plus importants en pratique

dans le cas des réalisations homogènes et à mettre sur pied un programme de laboratoire que nous allons résumer et commenter.

## 2. - ESSAIS SUR ALLIAGES NUS EN SEMI-IMMERSION

Des visites faites à bord de navires ont mis en évidence des cas de corrosions provoqués par des stagnations d'eau, entraînant des phénomènes d'aération différentielle.

Il a donc paru intéressant de procéder à quelques essais à ce sujet.

Pour ces essais, une méthode de laboratoire a été préférée car il est très difficile de réaliser au radeau une position fixe de la ligne de séparation de deux milieux sur l'éprouvette, le tirant d'eau et l'assiette du radeau variant avec son chargement et la mer malmenant les éprouvettes.

Les essais ont porté sur quatre séries d'éprouvettes réalisées en A-G4 au chrome manganèse (état recuit 2 heures à 400°C), nu ou plaqué A-Z1 et en A-U4G trempé nu ou plaqué A-5. L'A-U4G qui n'est pas un alliage d'usage naval, a été utilisé à titre de comparaison. Les éprouvettes étaient à demi-immergées dans une solution de chlorure de sodium à 3%.

Ces essais ont mis en évidence le rôle très important que joue la surface de séparation eau-air. Des corrosions très considérables apparaissent en effet au voisinage de cette surface dès le début des essais. Par ailleurs des dépôts de sels hygroscopiques restent au-dessus du niveau de l'eau lorsque celui-ci baisse. Ces sels constituent en pratique un danger permanent dans les atmosphères humides (figures 4, 5 et 6).

Du point de vue technique ces essais confirment les observations faites à bord et montrent qu'il est indispensable de prévoir des dispositions constructives évitant toute stagnation d'eau. Il est de même important d'éviter de placer des matériaux hygroscopiques au contact de l'aluminium si ces matériaux se trouvent dans un local très humide ou s'ils descendent assez bas pour permettre l'ascension de l'eau.

## 3. - ESSAIS SUR ALLIAGE PARTIELLEMENT RECOUVERT DE PEINTURE TOXIQUE

Comme vous le savez, la nécessité d'empêcher la fixation des organismes marins sur les carènes conduit à recouvrir celles-ci de peintures contenant en général des poisons minéraux (cuivre ou plus rarement mercure).

Quoiqu'il ne soit pas encore de pratique courante de réaliser des coques de grands navires en alliage d'aluminium, il a été jugé utile d'étudier le comportement de ces alliages en présence de telles peintures.

Il est précisé que les peintures toxiques utilisés ont été à dessein choisis parmi celles qui comportent des ions cuivre ou mercure a priori dangereux pour les alliages d'aluminium.

Les essais ont mis en évidence les corrosions sévères que de telles peintures peuvent provoquer.

Ces corrosions se manifestent surtout lorsqu'une surface dénudée de peinture est voisine d'une surface revêtue de peinture toxique et qu'à l'emplacement où baignent les éprouvettes l'eau de mer n'est pas agitée (fig. 7).

Si des structures immergées en alliage d'aluminium devaient être protégées contre la salissure, il faudrait faire usage de peintures à base de toxiques organiques.

## 4. - ESSAIS D'ASSEMBLAGES ACIER - ALLIAGE D'ALUMINIUM

Comme nous l'avons dit au début de cet exposé, les alliages d'aluminium sont surtout utilisés sur les grands navires pour la réalisations des superstructures, le reste de la coque étant en acier. Il y a donc entre acier et alliage d'aluminium une liaison qui est forcément réalisée par rivetage ou boulonnage.

Ces assemblages ne sont en principe pas immergés, mais il peut se produire, par exemple, dans le cas déjà cité d'un surbau trop bas et de la stagnation dans une gouttière due à une évacuation insuffisante, qu'ils soient plus ou moins

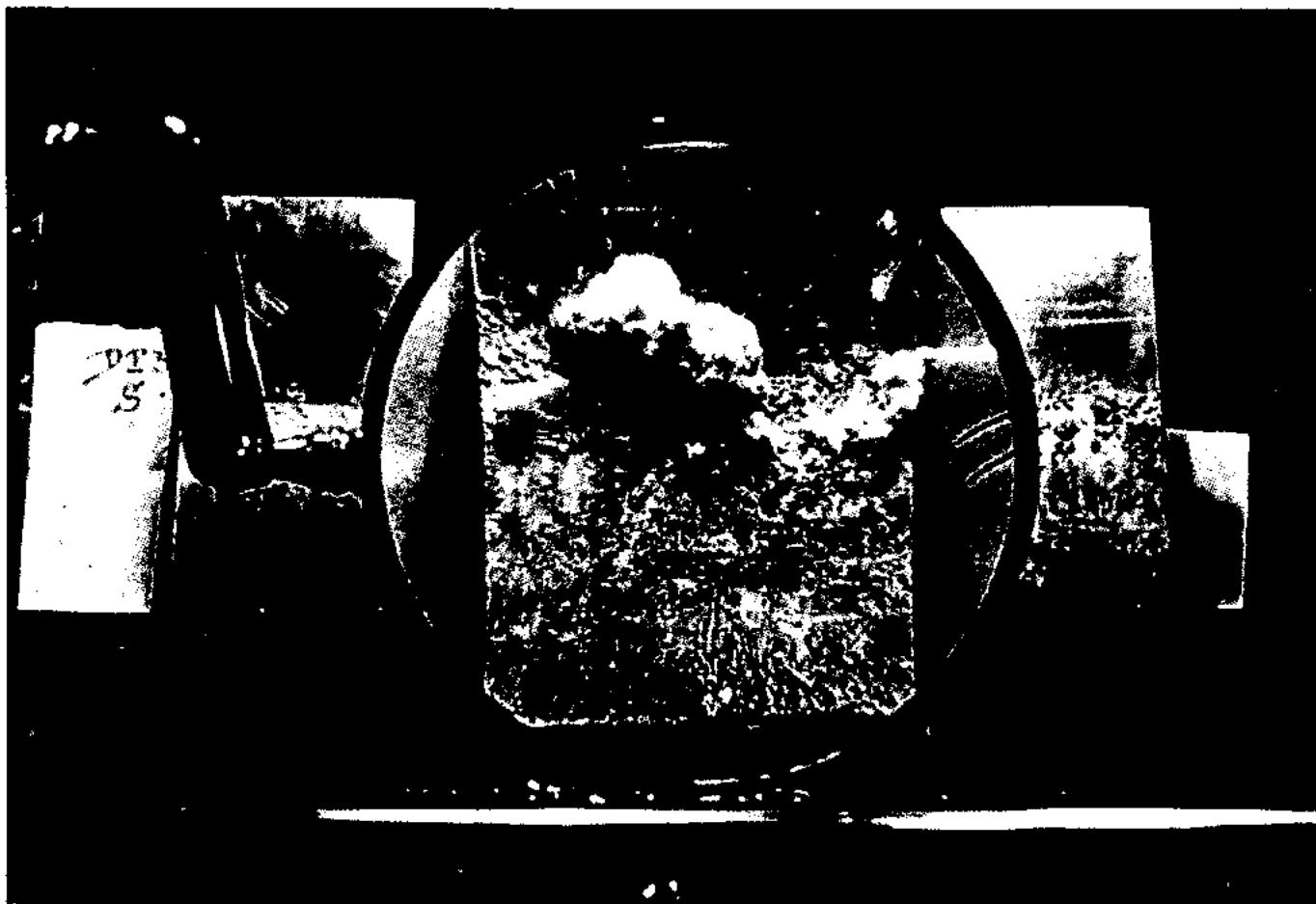


Fig. 4. — Tôle en alliage A-U4G semi-immersée pendant 3 mois dans une solution de chlorure de sodium à 30 g/l.

longtemps au contact de l'eau de mer stagnante et largement aérée. Ils présentent donc un risque de corrosion du fait que les potentiels des deux matériaux à assembler sont très différents.

En pratique, la plupart des incidents constatés sur les navires sont dus à des assemblages aluminium-acier, en particulier lorsque la conception des structures a exposé ces assemblages à des immersions prolongées.

En tout état de cause, il est indispensable de prévoir une isolation entre l'acier et l'aluminium.

Les principes de cette isolation ont été étudiés par l'Aluminium Français et le Comité TC.8 - Construction Navale de l'ISO.

Les potentiels électrochimiques des deux matériaux à assembler étant très différents, il est indispensable de prévoir entre eux une isolation. Sous sa forme la plus simple cette isolation est constituée par un ruban, voire par une couche de chromate de zinc; elle comporte, dans les solutions les plus élaborées, un zingage de l'acier et l'emploi d'enduits ou de gaines inertes autour des fûts des rivets et des boulons. Il va sans dire que les écrous et les têtes de boulons en acier doivent être séparés de la tôle d'aluminium par des rondelles isolantes.

Il a été jugé utile de procéder à des essais en vue de vérifier les prescriptions mentionnées ci-dessus, de les améliorer le cas échéant et d'étudier les divers paramètres dont dépend la bonne résistance à la corrosion des assemblages.

Ces essais ont été effectués, non seulement à l'air salin et aux embruns, mais encore en immersion.

De nombreux essais ont été faits à la Rochelle en partant, non de considérations théoriques, mais d'un point de vue utilitaire, c'est-à-dire en soumettant à l'épreuve des types d'assemblages utilisés en pratique ou des assemblages systématiquement mal conçus et en s'efforçant de déterminer les raisons du bon ou du mauvais comportement des uns et des autres.

Les essais ont porté en particulier sur,

- des tôles d'alliage d'aluminium-magnésium (300 × 200 mm) assemblées à des plaquettes d'acier (200 × 42 mm) par des rivets en alliage d'aluminium-magnésium,
- des tôles en acier et en alliage d'aluminium-magnésium de même surface assemblées, soit par rivetage en acier ou en alliage d'aluminium-magnésium soit par boulonnage-acier.

Dans ces derniers essais on a prévu :

- Des écartements variables entre rivets ou entre boulons.
- Des distances variables entre lignes de rivets ou de boulons et les bords des tôles.
- L'isolation entre tôles par divers procédés (rubans, plastique dur, couche épaisse de peinture au chromate de zinc).
- Le gainage des fûts, ou l'immersion préalable de ces fûts dans un enduit ou encore d'absence de toute protection.
- Des rondelles isolantes sous les têtes des boulons et sous les rondelles des écrous.

Des essais, dont nous ne pouvons donner ici le détail eu égard au peu de temps qui nous est imparti, ont permis de

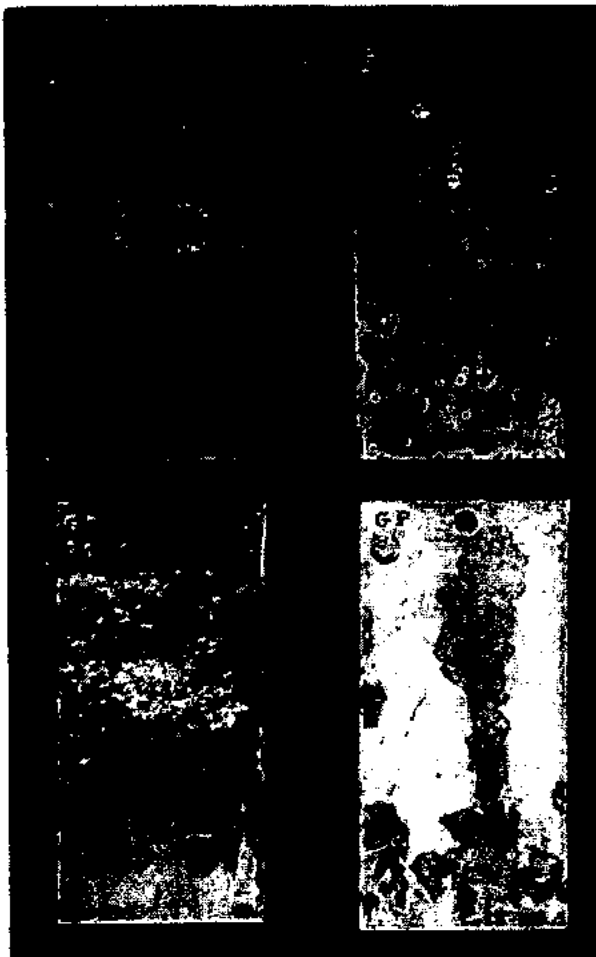


Fig. 5. — En haut A-G4 non plaqué, en bas A-G4 plaqué A-Zn, à gauche en semi-immersion — à droite en immersion permanente. Exposition pendant 10 mois en eau de mer artificielle.

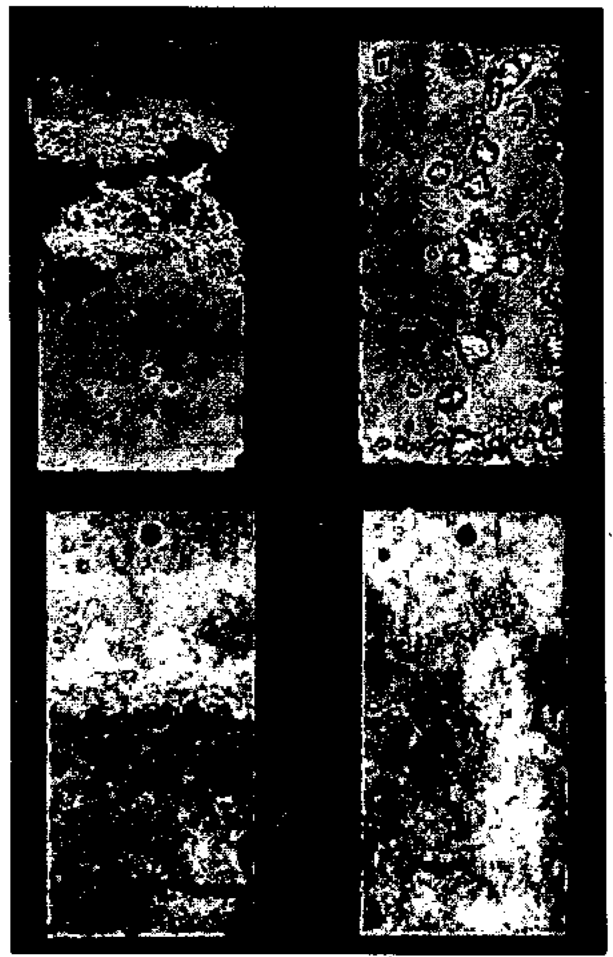


Fig. 6. — En haut A-U4G non plaqué, en bas A-U4G plaqué A5 — à gauche en semi-immersion, à droite en immersion totale. Exposition pendant 10 mois en eau de mer artificielle.

tirer les conclusions qualitatives pratiques ci-après:

— En atmosphère saline ou aux embruns, les assemblages rivés acier-alliage d'aluminium essayés se sont tous bien comportés lorsque la jonction était exécutée conformément aux règles de l'art, c'est-à-dire avec interposition entre les deux métaux d'un ruban ou d'une couche de peinture au chromate de zinc (fig. 8 et 9).

Par contre, des assemblages incorrects sans ruban, ni peinture, exposés aux embruns conduisent à des corrosions extrêmement sévères de la face de la tôle d'alliage d'aluminium en contact avec l'acier. Ces corrosions entraînent des gonflements susceptibles de détruire l'assemblage (fig. 10 et 11).

— Dans le cas de l'immersion (beaucoup plus sévère que la plupart des cas rencontrés dans les superstructures de navires) des corrosions importantes de l'alliage d'aluminium en contact avec le ruban isolant se produisent lorsque la tôle d'aluminium n'est pas peinte et lorsque le serrage assuré par les boulons ou les rivets est insuffisant pour obtenir l'étanchéité absolue du joint (fig. 12 et 13). Pour éviter ces corrosions, dues à des phénomènes d'aération différentielle, il y a lieu de prévoir des pas de rivetage ou de boulonnage et des distances entre car et lignes de rivetage ou de boulonnage aussi petites que possible; il faut, bien entendu, peindre au chromate de zinc avant montage.

Certains essais ont montré que les joints d'isolation ne pouvaient être considérés comme absolument permanents pendant de longues durées. Les rubans classiques se rongent localement et les joints en plastique dur deviennent fragiles. Ces destructions ou fissurations peuvent engendrer des phénomènes d'aération différentielle même sur des assemblages d'une excellente qualité initiale.

On peut par ailleurs se demander si l'élasticité des joints plastiques ne nuit pas à l'exécution correcte du rivetage et corrélativement à son étanchéité. S'il en était ainsi, un joint constitué seulement d'une peinture ou d'un enduit passé en couche épaisse peu avant l'assemblage, serait à préférer pour un assemblage prévu pour un service de longue durée.

Les assemblages acier-alliage d'aluminium souffrent en outre de corrosions galvaniques.

Les mesures faites sur divers types d'assemblages ont montré que les meilleurs systèmes d'assemblages ne permettent pas de garantir une isolation électrique entre l'alliage léger et l'acier lorsque le joint est humide. On constate de ce fait des corrosions en pleine tôle et des piqûres ou des sillons de corrosions sur l'alliage d'aluminium au voisinage immédiat des cans de l'acier.

Ces phénomènes, souvent graves en immersion, peuvent être atténués par l'emploi de peintures.

Pour les superstructures, la solution consiste évidemment

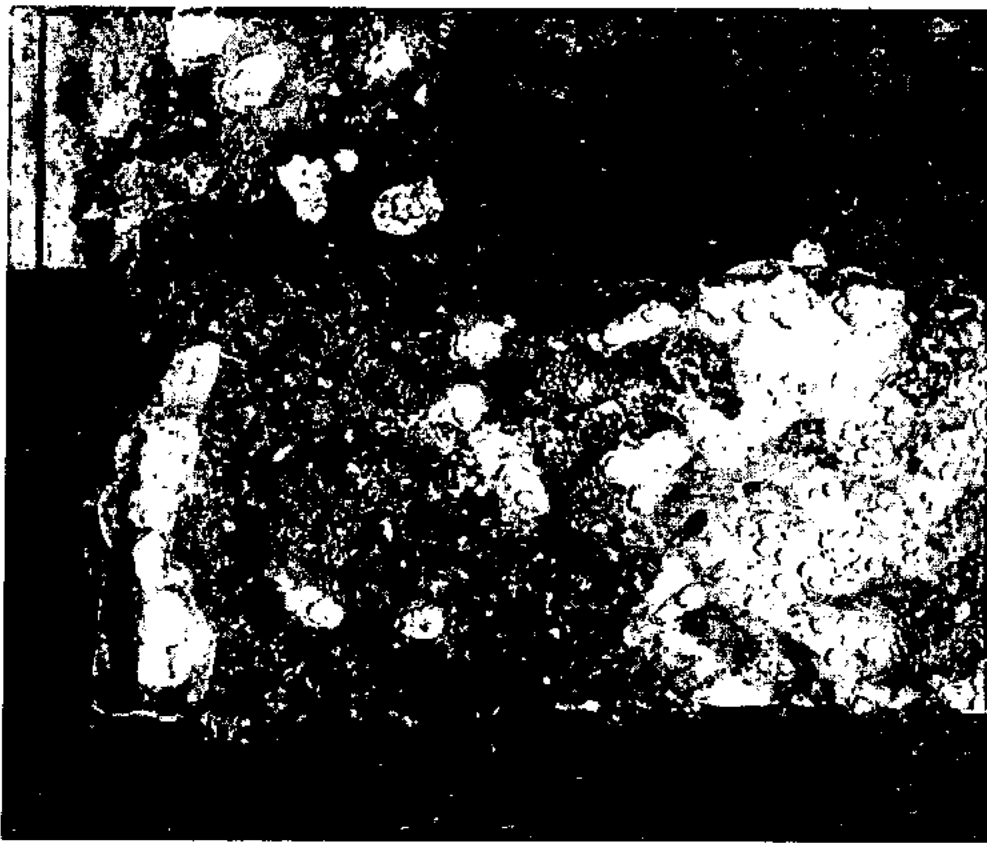


Fig. 7. — A-G5. Les zones non corrodées sont recouvertes de peinture antifouling sur couche primaire + couche isolante. La zone corrodée du milieu et celle du haut à gauche, n'étaient pas protégées. Immersion à La Rochelle pendant 1 an.

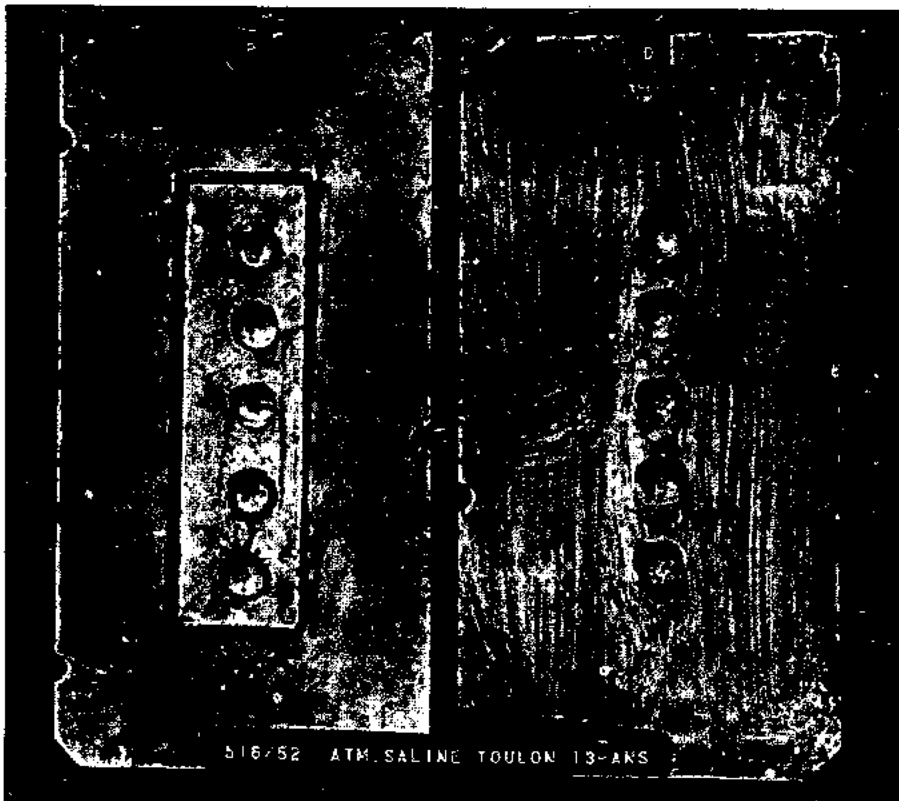


Fig. 8. — Tôles en A-G5 portant sur une face une bande en acier fixée par rivets en A-U4G. Protection du contact par ruban isolant et de l'ensemble par une peinture au chromate de zinc. Exposition à l'atmosphère saline à Toulon pendant 13 ans.



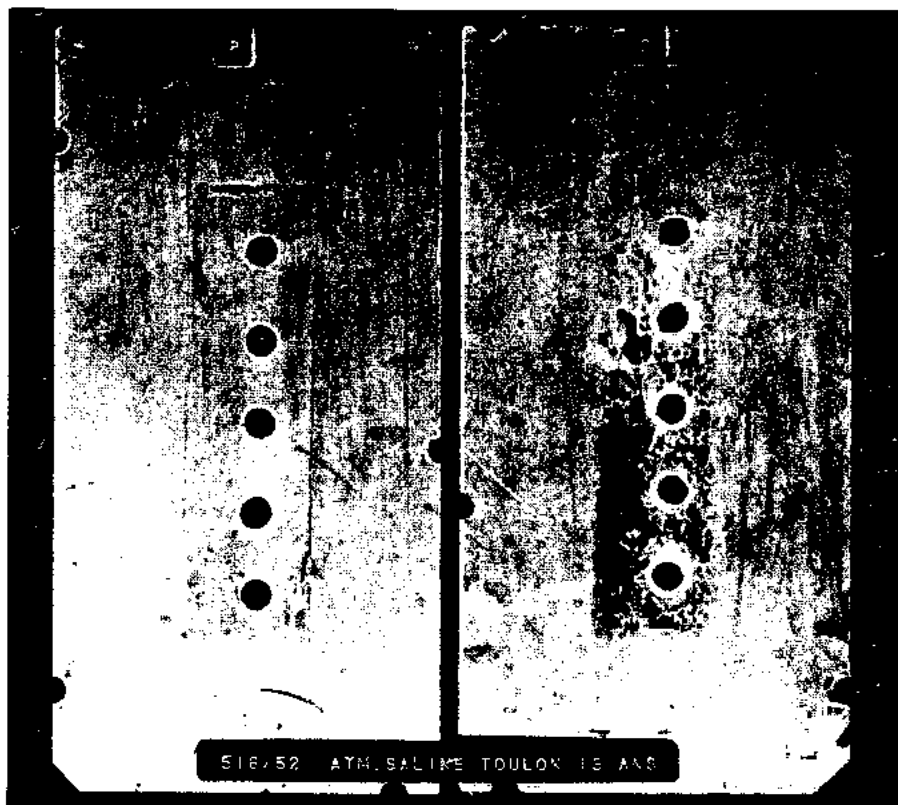


Fig. 9. — Mêmes tôles que sur la figure.8 photographées toutes les deux sur la face ayant porté la bande en acier et après enlèvement des rubans et de la peinture. Exposition à l'atmosphère saline de Toulon pendant 13 ans.

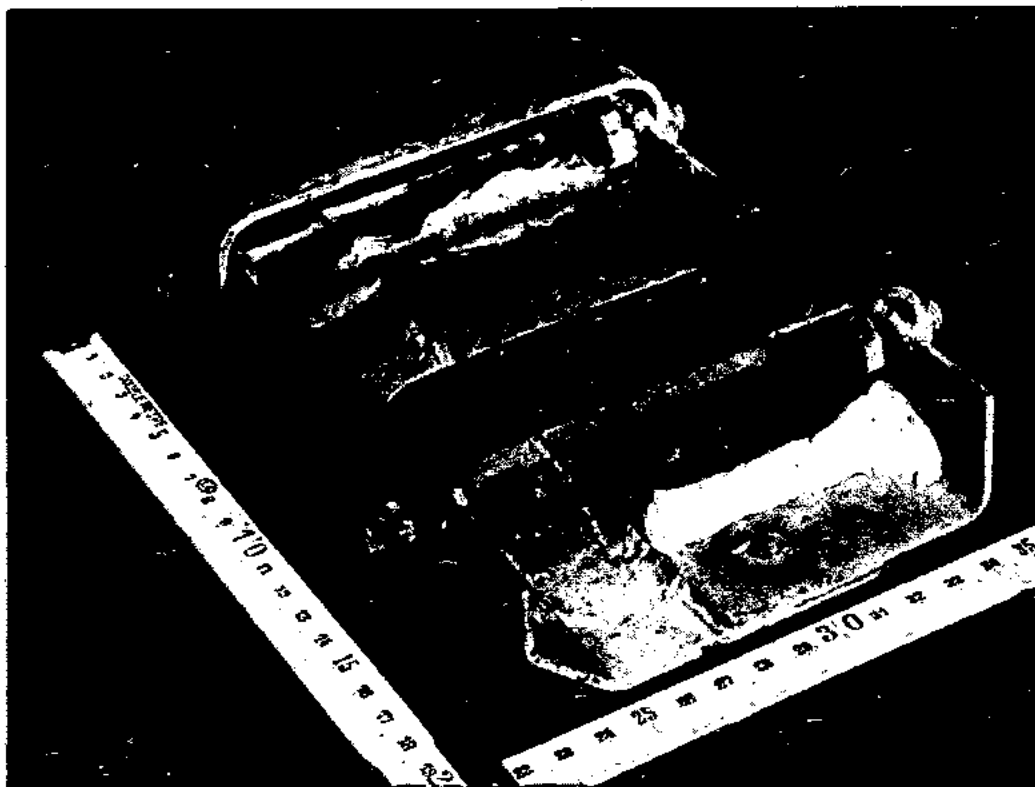


Fig. 10. — Montage comportant deux tôles, l'une en A-G5, l'autre en acier ordinaire assemblées par rivetage. Deux étriers en A-G5 fixés chacun par deux boulons permettent la fermeture électrique du circuit par l'extérieur.

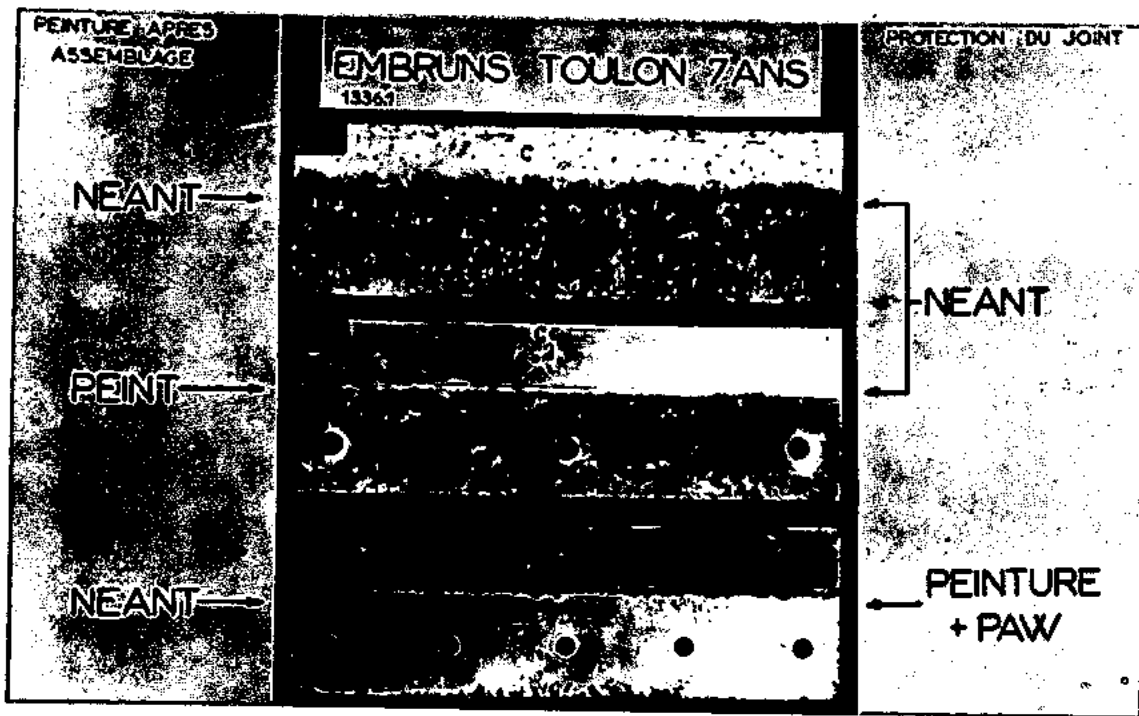


Fig. 11. — Etat de l'A-G5 dans les zones de contact avec l'acier sur des éprouvettes du même type que pour la figure 10 en fonction de la protection du joint.

à maintenir l'assemblage hors d'eau (surbaux assez hauts et bonne évacuation des eaux).

L'attention doit enfin être attirée sur le fait que l'on constate souvent des accentuations de la corrosion sur les tranches des tôles et autour des trous.

Jusqu'ici les essais n'ont pas fait apparaître de relation nette entre le mode de protection et d'isolation des boulons ou rivets et la résistance à la corrosion, dans leurs parties en contact, des tôles assemblées.

La tenue des rivets en alliage d'aluminium a conduit aux conclusions ci-après :

Les fûts de ces rivets sont bien protégés par les gaines, mais les portages des parties coniques n'assurent aucune étanchéité effective. La gaine autour de la partie cylindrique a peut-être même pour effet d'accentuer le jeu.

Lorsque la peinture tient sur les têtes, elle empêche la pénétration de l'eau, mais lorsqu'elle disparaît, les infiltrations conduisent à une situation critique. La combinaison des couples galvaniques et de l'aération différentielle engendre des corrosions très graves, tant des rivets, que de l'AG4.

On peut se demander s'il n'y aurait pas intérêt à prévoir au haut des têtes fraisées une petite fraisure en sens inverse réalisant une espèce de gouttière qui pourrait être remplie de peinture ou d'une matière plastique.

## 5. - ALLIAGES D'ALUMINIUM SOUDES

Le soudage sous atmosphère inerte étant d'un emploi sans cesse croissant pour l'assemblage des alliages d'aluminium, nous avons, bien entendu, été amenés à faire des essais sur assemblages soudés.

Ceux-ci ont eu lieu en immersion à Abidjan (Station du CREO très sévère pour la corrosion) et à la Rochelle.

Nous ne pouvons entrer dans le détail de ces essais eu égard aux limitations de texte qui nous sont imposées.

Indiquons cependant que les alliages du type A-G4 se sont bien comportés.

D'autres alliages et notamment les alliages A-SG se sont avérés moins satisfaisants.

Il faut dire toutefois que ces essais sont relativement anciens et que, de façon générale, les alliages ont été améliorés depuis.

## 6. - CONCLUSIONS

Les essais en immersion ou en immersion-émersion alternées entrepris sur alliages aluminium-magnésium ont mis en évidence un très bon comportement de ces alliages même nus, à condition que leur état structural soit bon et que leur homogénéité n'ait été altérée, ni par des incidents de laminage, ni par une maturation à chaud.

Il y a cependant lieu de réaliser les structures en évitant de placer certaines parties de celles-ci en semi-immersion. Il faut de même s'efforcer d'éviter les recoins susceptibles de retenir des eaux stagnantes, le plus souvent salées sur un navire. Dans de tels recoins, on peut en effet craindre des phénomènes d'aération différentielle provoquant des corrosions.

L'application de peintures anticorrosives est toutefois de nature à minimiser ces risques dans d'importantes proportions.

Les assemblages soudés sous gaz inerte se comportent bien en immersion lorsque l'on fait usage d'alliage du type A-G4. D'autres alliages et notamment les alliages A-SG se sont avérés moins satisfaisants aux essais.

Il faut toutefois dire que ces essais sont relativement anciens et que ces alliages ont pu être améliorés depuis.

La liaison entre alliage d'aluminium et acier constitue le point le plus délicat.

On ne peut considérer pour le moment que la réalisation des assemblages alliage d'aluminium-acier, destinés à être immergés en permanence, en est arrivé au stade de la perfection. Cependant on peut obtenir de bons résultats en appliquant les règles ci-après :

- Peindre au chromate de zinc la face de l'alliage léger appuyant sur le joint.
- Appliquer un revêtement de zinc sur la partie en acier concernée par le joint et prévoir sur ce revêtement des peintures compatibles avec lui.



Fig. 12. — Assemblage A-G4 acier véritable par des boulons en acier donnant un serrage variable. Protection du joint par ruban isolant. Rondelles isolantes en plastique sous les écrous. Peinture au chromate de zinc après assemblage. Immersion pendant 54 mois à Toulon.



Fig. 13. — Même assemblage que sur figure 12 montrant la déformation, résultant de la formation d'alumine, qui se produit sur la partie la moins serrée de l'assemblage.

- Réaliser un assemblage rigide empêchant toute pénétration d'eau, ce qui conduit à prévoir des tôles assez épaisses, un pas de boulonnage ou de rivetage assez serré (mais cependant pas trop dans le cas des boulons) et une distance aussi faible que possible entre la ligne de boulonnage ou de rivetage et le bord de la tôle.
- Prévoir un joint plastique permanent ou passer une couche épaisse de chromate juste avant l'assemblage.
- Enduire intégralement les rivets ou boulons et leurs trous d'une peinture au zinc ou d'un enduit ad-hoc.

Les rivets en alliage d'aluminium semblent devoir être rejetés dans le cas de l'immersion. Si leur emploi était indispensable, il faudrait étudier des têtes telles qu'elles forment, avec le trou conique, une petite gorge que l'on pourrait remplir de peinture ou d'une matière plastique.

Dans la plupart des cas pratiques que pose actuellement la réalisation des superstructures de navires, de tels assemblages ne sont pas immergés à condition que l'on ait prévu des surbaux suffisamment hauts et, de façon plus générale, évité de placer ces assemblages en un point où l'eau

peut stagner. Les assemblages réalisés suivant les règles de l'art ci-dessus décrites se comportent alors très bien.

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## DISCUSSION

Prof. H. ENGELL (Allemagne): J'ai entendu que la corrosion des alliages d'aluminium dans l'eau de mer est extrêmement influencée par traitement thermique. Je voudrais bien savoir quel est ce traitement thermique que vous mentionnez et comment peut-on s'imaginer la cause de l'influence du traitement thermique sur la corrosion.

A. GUILHAUDIS: Les alliages d'aluminium-magnésium utilisés pour la plupart de ces essais étaient à l'état recuit : 400° C pendant 2 heures avec un refroidissement à l'air. L'épaisseur des tôles était de l'ordre de 5 mm.

On a également d'excellents résultats avec les alliages d'aluminium-magnésium à l'état restauré. Ainsi un traitement de quelques minutes à 280° C sur un état dur donne un état demi-dur qui résiste fort bien à la corrosion marine.

Dr. GUILLEN (Espagne): J'aimerais bien savoir les résultats trouvés par Mr. Guilhaudis avec les éprouvettes anodisées exposées à l'atmosphère marine, et aussi si dans ces expériences il a été essayé la stabilité des colorants.

A. GUILHAUDIS. Une partie des essais relatés dans notre communication concerne des expositions dans la mer de pièces anodisées à 15 microns, en bain sulfurique classique avec colorant par une solution de bichromate de potassium.

Des échantillons non anodisés étaient soumis aux mêmes essais. Dans le cas particulier de l'aluminium-magnésium à 5% de magnésium et pour les expositions

- en immersion à La Rochelle
- en immersion-émersion alternées à Biarritz,

l'anodisation n'a apporté aucune amélioration, le métal non protégé résistant lui-même fort bien.

Nous avons constaté qu'en particulier à Biarritz, la couche d'oxyde se décolore.

Ce qui précède concerne la corrosion par immersion dans la mer mais la question de M. GUILLEN concerne, plus certainement, les applications décoratives de l'aluminium dans le bâtiment par exemple. Dans ce cas il s'agit de la tenue à l'atmosphère marine.

On sait que l'anodisation confère aux alliages d'aluminium une excellente protection contre l'action des embruns à condition que les couches d'oxyde soient formées dans de bonnes conditions et avec une épaisseur suffisante.

Cette protection est excellente sur les Al-Mg 5% et Al-Mg 0,5% Si 0,5%. On a actuellement une expérience de plus de dix ans pour des expositions au bord de la mer du Nord, à Ostende en Belgique, soit pour des couches incolores, soit pour des couches grises obtenues na-

tuellement sur les alliages Al-Si 4,5%.

Pour ces alliages, l'intensité de la couleur grise varie suivant l'épaisseur de la couche et le traitement thermique du métal.

Les couches d'oxyde incolores peuvent être colorées par des colorants organiques ou minéraux, comme cela se fait sur un tissu. La tenue des colorants à la lumière solaire se pose comme pour tous les objets colorés: peintures, tissus.

C. CABRILLAC (France): Je voulais vous poser deux questions: la première est semblable à celle posée par M. GUILLEN. L'oxydation anodique est elle aussi efficace du point de vue de l'anticorrosion sur les alliages autres que les Aluminium-Magnésium. Ne pourrait-on même dans des atmosphères agressives (bord de mer) avec immersion, se dispenser de réaliser une oxydation anodique?

La deuxième question concerne les plaques que vous nous avez montré tout à l'heure après 13 ans d'exposition à Toulon.

J'ai été frappé, effectivement, par l'excellente conservation de ces échantillons. Vous nous aviez dit que les couples galvaniques n'étaient pas dangereux parce qu'il y avait des rubans et des vernis.

Pouvez-vous nous dire quelle était la nature de ces vernis et des rubans et si vous avez pris des précautions particulières pour leur bonne application et surtout pour leur bonne adhérence?

A. GUILHAUDIS: Pour la première question, la protection par anodisation est intéressante, principalement pour l'aspect décoratif. Lorsqu'on expose des alliages d'aluminium non anodisés au bord de la mer, on observe une oxydation naturelle qui se traduit par un ternissement du métal. L'aspect des pièces, brillant au départ, devient terne.

Cependant l'altération des pièces reste superficielle et n'affecte en fait que l'aspect. La couche d'oxyde se produit au début de l'exposition et se développe ensuite très peu dans le temps. Cela se retrouve d'ailleurs dans l'évolution des caractéristiques mécaniques.

Pour les alliages aluminium-magnésium et aluminium-magnésium silicium, l'oxydation affecte surtout l'aspect mais très peu les caractéristiques mécaniques.

D'ailleurs notre politique pour le matériel utilisé dans nos stations d'essais de corrosion tels que les cadres ou pupitres supports d'échantillons, est de prendre des alliages non protégés. Nous savons très bien qu'ils se terniront mais que leurs caractéristiques mécaniques resteront excellentes dans le temps.

En ce qui concerne la seconde question je puis vous dire qu'une des peintures essayées était à base de chromate de zinc. Je pourrai vous communiquer ultérieurement les références des rubans.

# THE COMPARISON BETWEEN OUTDOOR AND INDOOR CORROSION RATE OF SOME COPPER AND ALUMINIUM ALLOYS IN NATURAL TROPICAL - SEA ENVIRONMENTS

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## SUMMARY

The tests were carried out at Julin, the place on the Hainan Isle in the Chinese Peoples Republic. The period of testing lasted three and a half years.

Ten sorts of copper alloys and five sorts of aluminium alloys were tested. The specimens of each individual sort of metal were prepared in form of round bar-sections of 15 mm diameter and round tensile test samples.

In Julin the specimens were laid out on stands situated in about 400 m. distance from the shore, in two places: outdoor and under the roof of the wooden shed protecting exposed specimens against the action of sun radiation, dusts and precipitations.

Every three months periodic visual examination of specimens was made and the increase in weight values were measured. When the time of specimens exposure at the station elapsed, the loss of weight of the specimens was determined, after corrosion products removal by pickling.

The largest loss in weight was noticed on copper alloys that had been exposed outdoors and among them especially on: silicon bronze — 0,34 mdd (mg on sq. decm per day), red bronze — 0,26 mdd and refined copper — 0,24 mdd. Corresponding values for the same alloys laid out under the roof were accordingly about 5, 15 and 10 times lower.

The decrease in weight values for aluminium alloys exposed in the open air were approximately double the values obtained for the same sorts of metals exposed under the roof.

After completion the exposure time and removing the specimens from the stands, strength test pieces made of the same sorts of metals were tested and changes in tensile strength and elongation values compared with those obtained for the same metals prior to corrosion testing were determined.

Amongst the copper alloys tested, the greatest loss in tensile strength was that of red bronze — about 20 percent for both indoor and outdoor conditions, as well as that of aluminium bronze — about 12 percent. These metals showed at the same time above 30 percent increasing in elongation. Amongst the aluminium alloys the greatest loss in tensile strength was that of metallurgical aluminium — about 20 percent, whereas the increase in elongation was approximately 10 percent.

The differences between loss of tensile strength of the outdoor and under the roof tested specimens are very slight and do not exceed 3 percent for all sorts of metals.

The metals tested have shown the different types of corrosion as: general attack, pitting, intergranular and selective corrosion.

## INTRODUCTION

In 1960 have been started investigations on determination of corrosion resistance of copper and aluminium alloys in tropical-sea climate conditions. The investigations were carried out in the Chinese Peoples Republic — Hainan, Kanton, Shanghai — and in Poland, but in moderate climate conditions. The subject of this work comprises the results of first series of investigations on 15 sorts of copper and aluminium alloys, carried out in the period of time beginning from november 1960 and lasting up to june 1964 in moist, tropical-sea climate of Hainan Isle.

The main agents of moist, tropical climate deciding about aggressiveness of atmosphere are: high temperature and humidity as well as great fluctuations of these agents during the day, causing the precipitation of the moisture on metal surface. On those areas appear also mould fungi and in wood regions there is considerable contents of CO<sub>2</sub> in the air, but in maritime environs, even in quite a distance from the sea (50 km), there is considerable contents of salt. Therefore, the moist tropical climate comprises all agents effecting in great degree on atmospheric corrosion of metals.

## SAMPLE PREPARATION FOR TESTING

Ten sorts of copper alloys and 5 sorts of aluminium alloys were submitted to testing. Chemical composition of chosen alloys is given in the table 1.

All metal samples were received from the smelting plant in the form of round bars 15 mm diameter, drawn to semi-hard, state. Samples for testing were prepared in the form of lengths about 70 mm long. These samples were grinded and polished by means of abrasive papers up to high lustre.

After degreasing and drying the initial weight of samples was determined with accuracy down to 0,1 mg.

To determine the corrosive action effect of the atmosphere on the changes of mechanical properties, the strength test pieces were made from the same metals. Three strength test pieces as well as three cylindrical samples were made from each sort of metal for each exposing place.

After preliminary visual inspections and measurements, prepared in this way samples were carefully packed to protect them against corrosion in the time of transport to China. The samples were transported to China by railway.

TABLE 1  
CHEMICAL PERCENT COMPOSITION OF TESTED METALS

Copper alloys													
Sample marking	Sort of alloy	Cu	Zn	Al	Pb	Mn	Fe	Si	Ni	Sn	Sb	Bi	As
A	Copper	99,96	0,001	—	0,002	—	—	—	0,001	0,001	0,002	0,001	0,001
B	58-40 Pb brass	57,80	remainder	0,10	1,61	—	0,10	0,002	0,05	0,006	0,003	0,001	—
C	Al brass	57,32	remainder	2,05	0,38	1,88	0,71	0,05	0,25	0,30	0,02	0,005	—
D	63-36 Pb brass	63,48	remainder	—	1,04	—	0,04	—	0,01	0,01	0,005	0,002	—
E	63-37 brass	63,15	remainder	—	0,04	—	0,03	—	0,10	0,02	0,002	0,002	—
F	Zn-Sn bronze	remainder	3,00	—	0,02	—	0,01	—	0,01	3,93	0,002	0,001	0,002
G	Si-Mn bronze	remainder	0,15	0,13	0,02	1,24	0,09	2,94	0,04	0,15	0,002	—	0,002
H	Al bronze	remainder	0,05	10,46	0,02	1,62	2,86	0,10	0,05	0,01	0,002	—	0,002
I	Cu-Zn nickel alloy	remainder	20,04	0,03	0,02	0,26	0,35	0,10	Ni+Co 15,56	—	0,001	0,001	0,002
J	Cu-Zn nickel alloy	remainder	15,81	0,002	0,004	0,25	0,12	0,002	Ni+Co 20,94	—	0,001	—	0,001
Aluminium alloys													
Sample marking	Sort	Al	Mg	Cu	Zn	Fe	Si	Mn	Ni				
K	aluminium	99,77	—	0,01	—	0,08	0,10	—	—				
L	hydronalium	remainder	2,74	0,08	—	0,15	0,22	0,22	—				
M	anticorodal	remainder	0,85	0,08	0,18	0,22	0,94	0,74	—				
N	duralumin	remainder	1,50	4,58	0,12	0,34	0,39	0,69	traces				
O	duralumin RR 59	remainder	1,46	2,36	0,30	1,26	0,77	0,02	1,45				

**EXPOSING PLACE AND THE COURSE OF INVESTIGATIONS**

The samples were exposed at Julin, the place on the Hainan Isle, on the grounds of the station situated about 400 meters from the seashore. This station is the most to the south put forward centre among Chinese research stations and characterizes with its typical tropical-sea climate. The average temperatures per day in this place just from the beginning of April exceed 25°C and remain higher of this temperature to the end of October. Under the influence of the sea, temperature fluctuations are considerably lower in comparison with other regions of China. The average maximum temperature per annum does not reach 35°C, while average minimum temperature per annum does not fall down below 15°C.

The air humidity fluctuations are also low, but absolute maximum values do not reach the values of moist tropical climate (Kanton).

In the specification below are given average results of meteorologic measurements of many years for Hainan Isle:

Average temperature per annum	25,5°C
Average maximum temperature per month	28,9°C (July)
Average minimum temperature per month	17,5°C (January)
Average relative humidity per annum	84%
Average maximum humidity per month	87% (February, March)
Average minimum humidity per month	82% (November)
Average quantity of precipitations per annum	1518 mm
Average maximum quantity of precipitations per month	257 mm (September)
Average minimum quantity of precipitations per month	24 mm (January)
Number of raining days per annum	111 days
Number of sunny hours per annum	2900 hours
Number of days per annum with dew appearance	237 days
Quantity of salt in the air	0,07 mg/litre.

Samples of the same sorts of metal in the same quantities were exposed on the grounds of station at Julin in two places: on the open air and under the roof. Samples remaining outdoors were fixed by means of nylon threads fastened to wooden stands directed with the angle of 45° to the south. The other identical set of samples was placed on the stand under the roof in wooden shed protecting samples against rain, dust and insolation.

Before exposing the samples on the stands, they were submitted to visual inspection for purpose of assertion of eventual changes which occurred on their surfaces during the transport. These inspections did not prove almost any changes, except the appearance of single spots on some copper alloys.

After exposition of samples on the stands, the samples were submitted to periodical inspections and measurements which determined changes on surface appearance of samples, loss of lustre and changes in the mass of samples.

The results of these measurements were recorded by the man servicing this research station on specially prepared for this purpose inspection cards accordingly to forwarded schedule of investigations. Periodical inspections were performed 10, 20 and 30 days after the day of exposure of samples and afterwards every 3 months. During the whole period when the samples remained on the station at the same time also were performed meteorological measurements of the temperature, humidity, precipitation etc.

The stay of samples on this station, similarly as in other places in China (Kanton and Shanghai), was planned for 5 years, but owing to winding up of this station by Chinese authorities the period of investigations was shortened to 3 and half years. After that period the samples were removed from the station, packed and sent back to Wroclaw, for performing the final testings and measurements.

#### CHANGES IN TENSILE STRENGTH

To determine influence of tropical-sea climate agents on change of strength and plasticity properties of metals being investigated, strength test pieces exposed for a period of 3 and half years on the Hainan Isle were ruptured on tensile testing machine and received results were compared with strength properties of these metals before investigations.

Tensile strength of samples after corrosion ( $R_r$ ) was calculated on the basis of rupture force (in kg) and of cross sectional area (in square mm) measured before investigation. Initial tensile strength ( $R_{r0}$ ) of tested alloys was determined by rupturing 10 samples of each sort of metal, just after they were delivered from smelting plant, and then the average value was calculated.

In the table 2 is given specification of average strength properties of the alloys measured before and after investigations (after rupture of three strength test pieces of each sort of metal).

TABLE 2.

THE AVERAGE STRENGTH PROPERTIES OF METAL SAMPLES BEFORE INVESTIGATION AND AFTER CORROSION ON THE PLACE OF JULIN (HAINAN) UNDER THE ROOF AND OUTDOORS

Marking	Sort of alloy	Properties before investigation		After corrosion under the roof		After corrosion outdoors	
		$R_r$ kg/mm <sup>2</sup>	$A_4$ %	$R_r$ kg/mm <sup>2</sup>	$A_4$ %	$R_r$ kg/mm <sup>2</sup>	$A_4$ %
A	Copper	28,5	29,0	29,1	29,2	27,8	29,0
B	58-40 Pb brass	52,2	31,9	50,4	29,8	50,3	29,5
C	Al brass	74,8	21,2	71,4	18,5	71,2	18,2
D	63-36 Pb brass	40,3	38,8	39,2	32,8	38,9	33,0
E	63-37 brass	40,2	40,0	39,9	39,0	38,9	39,7
F	Zn-Sn bronze	51,9	28,4	38,9	37,0	38,4	39,5
G	Si-Mn bronze	58,8	37,0	59,3	33,5	58,6	36,6
H	Al bronze	69,3	28,0	60,9	45,0	60,3	42,5
I	Cu-Zn nickel alloy	65,2	14,5	64,2	13,5	63,5	14,0
J	Cu-Zn nickel alloy	59,5	19,5	59,1	17,0	58,2	19,0
K	aluminium	12,6	21,6	10,4	23,8	10,6	23,6
L	hydronalium	19,1	23,5	19,5	21,8	19,5	21,5
M	anticorodal	32,5	21,4	35,3	16,3	35,7	15,3
N	duralumin	55,2	16,6	54,3	11,5	56,2	11,5
O	duralumin RR 59	41,8	21,5	40,2	20,3	40,5	20,2

Moreover on Fig. 1 are given proportional changes in tensile strength of samples after out-doors and under the roof investigations.

The changes of these values depending of sort of metal are influenced by: general reduction of sample diameters, caused by uniform surface corrosion, pitting corrosion and intercrystalline corrosion as well as structural changes caused by natural ageing of alloys in the time, or combination of these agents.

*Changes of sample mass*

At the time of periodical inspections and after conclusion the exposure time the changes of sample weight were measured. The changes of weight were measured after cleaning the surfaces of sand and dust by means of soft brush. The weight measurements has been made with the same analytical balance with accuracy of 0,0001 g.

On the Fig. 2 and 3 are shown average weight changes of some copper and aluminium alloys tested outdoors. In the table 3 are given weight losses of samples after removing by means of pickling the products of corrosion from their surfaces. Pickling process was performed in suitably matched solutions for each sort of metal which would etch only corrosion products and would not act with metals.

The whole loss of sample mass was determined from the difference of sample weights before investigation and after its conclusion when the products of corrosion have been removed.

*Changes in outer appearance*

Observations and description of changes occurring on the surfaces of tested metals have been made during periodical inspections and as well as they were transported back to Wroclaw. During these visual inspections the attention was paid to changes in colour of sample surfaces, to formation of spots and tarnishes, to appearance of pitting, efflorescence etc.

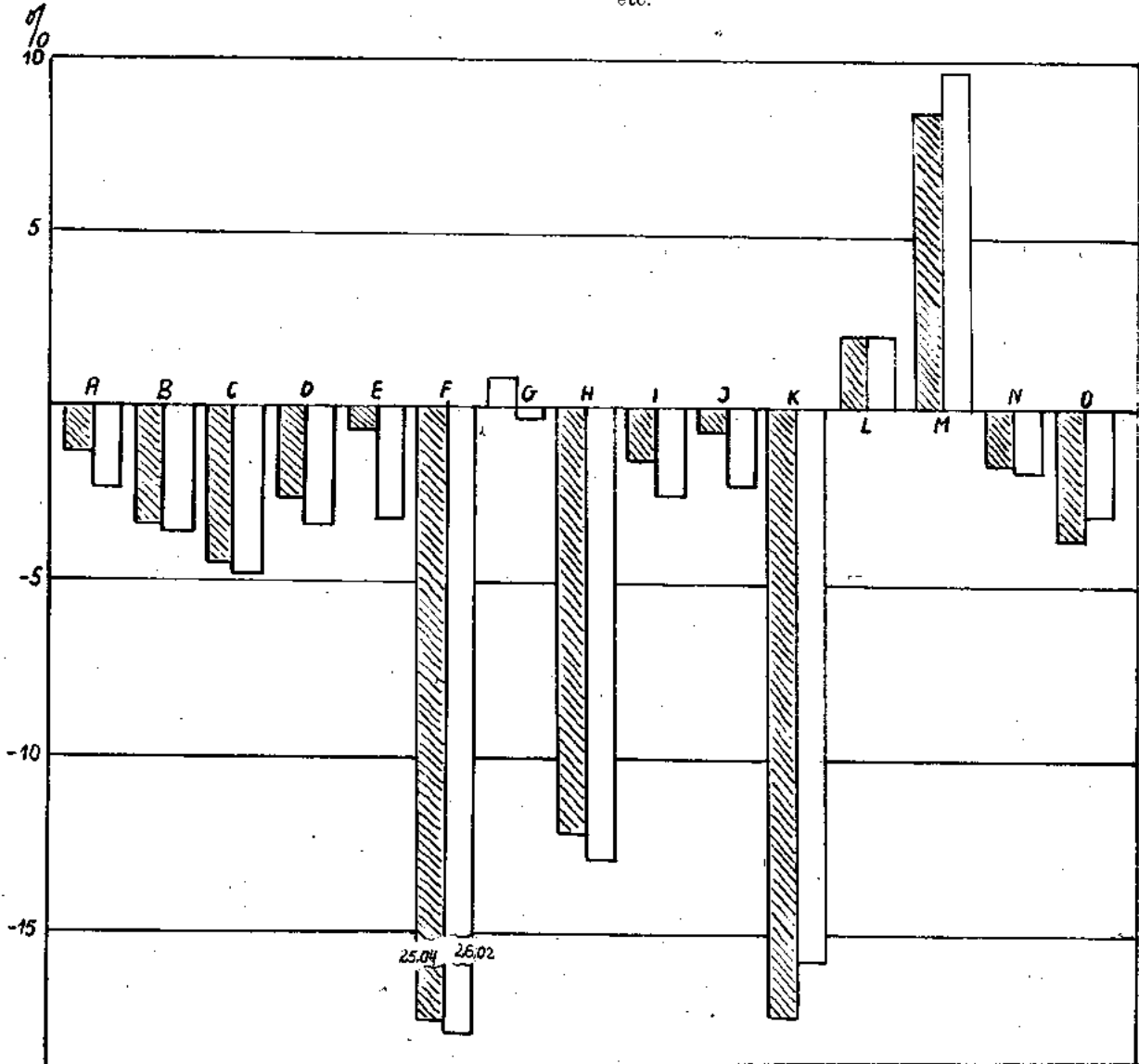


Fig. 1. — Proportional changes of strength properties ( $R_r$ ) of samples exposed on the open air (white pieces) in comparison with samples exposed under the roof (black pieces). Marking of individual alloys acc. to table 1.



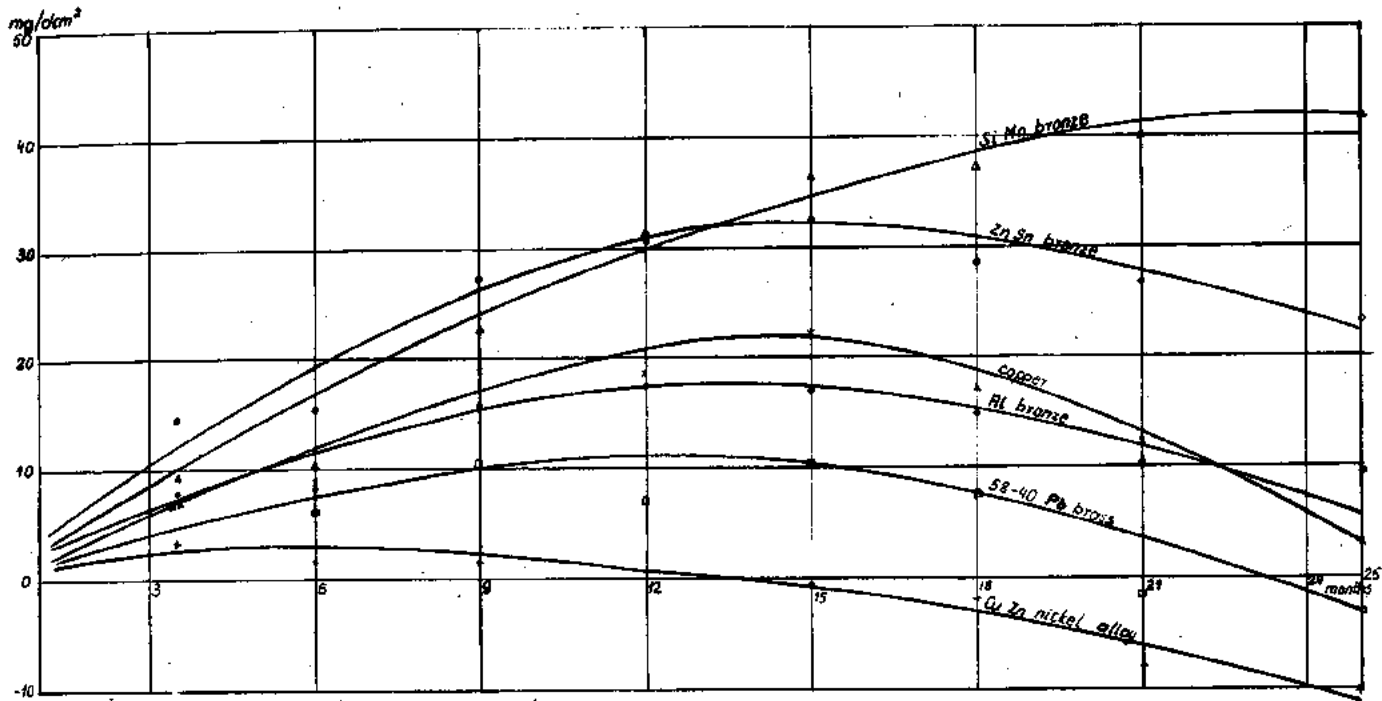


Fig. 2. — Weight changes versus time of some copper alloys investigated on the open air.

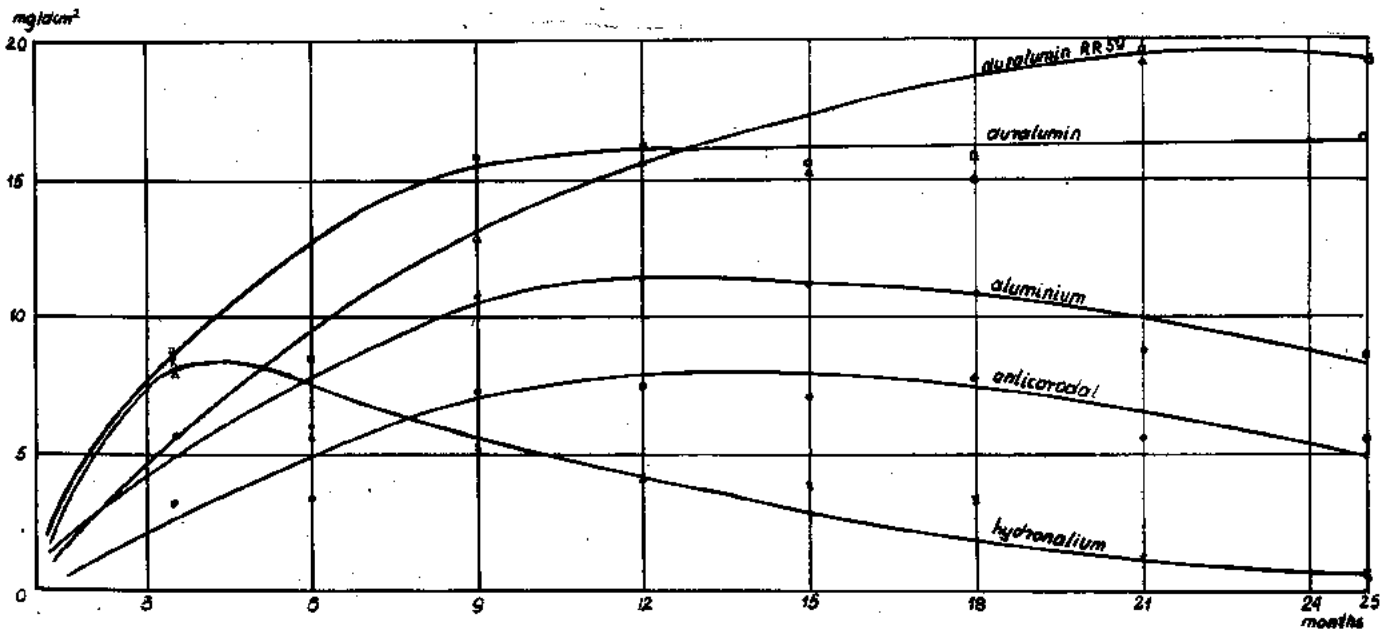


Fig. 3. — Weight changes versus time of aluminium alloys investigated on the open air.

TABLE 3.

CHANGE OF SAMPLE MASS AFTER THE WHOLE PERIOD OF INVESTIGATIONS in mg/dcm<sup>2</sup> per day.

Marking	Sort of metal	indoors	outdoors
		Loss of weight	loss of weight
A	Copper	0,026	0,239
B	58-40 Pb brass	0,026	0,064
C	Al-brass	0,020	0,056
D	63-36 Pb brass	0,016	0,080
E	63-37 brass	0,026	0,084
F	Zn-Sn bronze	0,016	0,265
G	Si-Mn bronze	0,074	0,344
H	Al bronze	0,026	0,075
I	Cu-Zn nickel alloy	0,027	0,098
J	Cu-Zn nickel alloy	0,025	0,057
K	aluminium	0,013	0,024
L	hydronalium	0,017	0,028
M	anticorodal	0,021	0,025
N	duralumin	0,022	0,044
O	duralumin RR 59	0,025	0,045

During periodical inspections has been stated similar course of changes on the sample surfaces exposed indoors as well as exposed outdoors. But changes on surfaces of samples exposed indoors took their course slower than of samples of the same metals investigated outdoors. It expressed itself with lower (in the same period of time) loss of lustre, as well as with appearance on samples investigated indoors similar changes of colouring, oxide coatings, pitting etc, with some delay (about 6-9 months) in relation to samples exposed outdoors.

The changes on surfaces of almost all copper alloys have been starting with appearance of single coloured points and spots which after some time (different for different sorts of alloys) joined themselves into more or less uniform oxide layer. After conclusion of investigations, copper, Sn-Zn bronze and Si bronze were covered with very smooth and closely adherent to the surface of metal, light bronze oxide layer.

But Al — bronze and Al brass in the same period of time become covered by spots and tiny pitting points, more intensive and more closely spread on samples exposed on the open air.

The surfaces of all aluminium alloys after the whole period of investigations were covered by pitting points and white oxide efflorescences, more distinctly and more densely appearing on samples investigated on the open air. The most large pittings and appearance of surface peeling off was stated on duralumin and duralumin RR 59.

#### MICROGRAPHY

After removing the corrosion products from sample surfaces by pickling, all sorts of metals were submitted to microscope investigation. During the structure inspection special attention was paid to the appearance of microsection in the nearness of side surfaces of samples, out of regard to location just on the surface or its nearness of characteristic changes in the shape of pittings, surface corrosion, intercrystalline corrosion etc. For this purpose transverse microsections of samples were made after previous their submersion in epoxy resin to avoid rounding the edges of samples when grinding.

Comparing the appearance of surfaces and structure of tested on the open air and under the roof samples, it was

stated that the corrosion was more intensive on the samples tested on the open air and that was expressed by slightly deeper pittings as well as by increased intercrystalline corrosion (duralumin), while maintaining similar character of corrosion changes.

Among tested copper alloys the largest changes were observed on Al brass, where on samples tested outdoors appeared local intercrystalline cracks (Fig. 1) in the nearness of drilled hole for purpose of hanging the sample on the stand, and at Al bronze on which appeared surface intercrystalline pitting (Fig. 2). These pittings have found their external effect in the shape of appearance on this alloy surface (what was stated during periodic inspections) of tiny but densely distributed efflorescence points, products of corrosion. At the remaining copper alloys the micrography has shown only the appearance of shallow surface losses and single pitting.

Among aluminium alloys the largest corrosion changes were stated on the samples of duralumin in the shape of far advanced intercrystalline corrosion (Fig. 3) and on the samples of duralumin RR 59 in the shape of deep pitting, appearing just on surface or under the surface (Fig. 4). The least changes occurred on hydronalium and anticorodal in the shape of tiny shallow surface pitting.



Fig. 4. — Intercrystalline crack of Al brass after 3 and half years exposing on the open air. Transverse microsection. Magnification 100X. Etched in FeCl<sub>3</sub>.

#### INVESTIGATION RESULTS DISCUSSION

Comparing corrosion resistance of tested on the open air and under the roof alloys, on the basis of investigation results of individual parameters, the largest differences were stated in changes of weight, especially in loss of mass of samples after removing products of corrosion by pickling (Table 3).

Among tested on the open air copper alloys, the alloys: Sn-Zn bronze, copper, Si bronze, and 57-62 Pb brass have shown about 15, 10 and 5 times greater loss of sample mass, in comparison with the same samples of metals tested under the roof.

Remaining copper alloys and aluminium alloys have shown about 2 to 3 times greater loss of mass (after pickling) at samples exposed on the open air in comparison with samples remaining during the whole investigation period under the roof.

Such large differences in loss of mass between samples exposed on the open air and under the roof is supposed to be caused by quicker and more intensive building up of corrosion product layer on some tested on the open air samples under direct influence of atmospheric agents acting upon them.

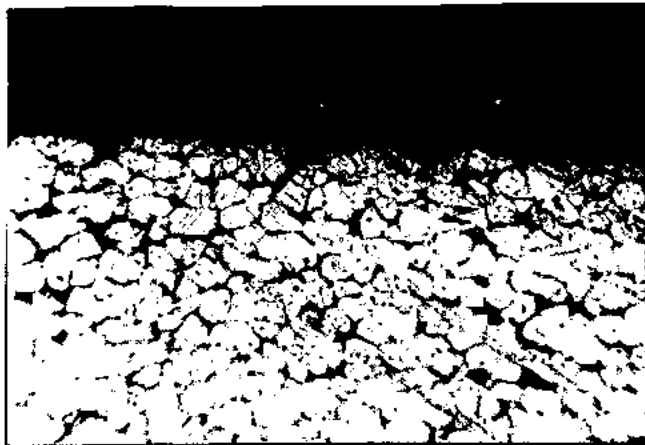


Fig. 5. — Surface pitting on Al bronze after 3 and half years exposing on the open air. Transverse microsection. Magnification 100X. Etched in  $\text{FeCl}_3$ .

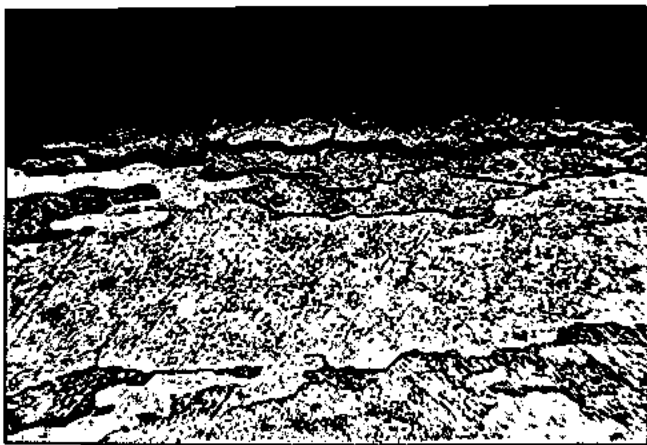


Fig. 6. — Advanced intercrystalline corrosion of duralumin after 3 and half years exposing on the open air. Transverse microsection. Magnification 100x. Etched in  $\text{HCl}$ .

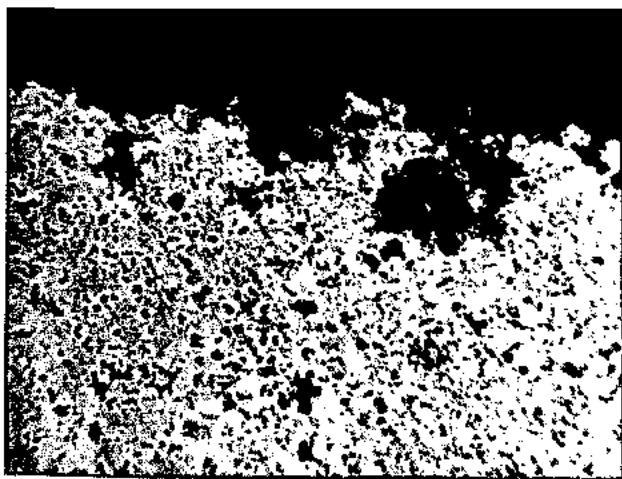


Fig. 7. — Surface pitting on duralumin RR-59 after 3 and half years exposing on the open air. Transverse microsection 100X. Etched in  $\text{HCl}$ .

Very great losses of mass occurred on tested on the open air samples, reach with copper alloys. Visual as well as microscope inspection have shown on these alloys the presence of uniform, smooth and well adherent to metal surface thick layer of corrosion products.

Performed X-ray analysis of these alloys corrosion products has shown  $\text{Cu}_2\text{O}$  as the main component. After the whole period of investigation these alloys exposed on the open air have shown still an increase of mass (without removal of corrosion products).

It proves about building up on the surfaces of these alloys of thick and not easily dissolving layer of corrosion products. These layers in spite of their great smoothness and apparent tightness allow for easy diffusion through them of oxygen and humidity, what causes building up of the corrosion product almost in steady manner.

However great solubility of corrosion-product layers due to action of humidity and precipitation have shown all brasses and nickel alloys tested on the open air, about what proves the loss of mass of these alloys after the whole period of investigation without removal of corrosion products (Fig. 2). X-ray analysis of corrosion products of these alloys has shown different from above discussed and yet unidentified component. It proves that about magnitude of mass losses caused by action of atmospheric agents in main measure decides the kind and durability of forming on metal surface layer of corrosion products.

Contrary to weight changes, the tensile strength changes of almost all tested on the open air samples in less considerable grade differ from strength property changes of samples tested under the roof. Proportional loss of strength ( $R_r$ ) of tested on the open air samples in average is about 20 % higher than of samples tested under the roof.

Among copper alloys the highest strength loss ( $R_r$ ) in relation to average values measured before investigation was stated at Zn-Sn bronze and Al bronze about 25% and 12% respectively by simultaneous considerable increase of elongation ( $a_1$ ) about 35% and 55%.

Among aluminium alloys the highest strength loss about 16% was noted at aluminium itself at simultaneous increase of its plasticity property about 10%. Unexpectedly small decrease of strength property about 1, 7% has shown the duralumin alloy at which during microscope investigation was stated far advanced intercrystalline corrosion (Fig. 3). Also duralumin RR-59 at which has been stated the appearance of deep subsurface pitting (Fig. 4) has shown not too large decrease of tensile strength about 3,5%. Simultaneously hydronalium and anticorodal have shown sufficiently large increase of strength properties with in the same time large decrease of plasticity (table 2).

These changes may be explained by joined action on strength property decrease due to presence of pitting, intercrystalline corrosion and general loss of sample mass and natural ageing of alloys causing at some alloys (especially at aluminium alloys) increase of strength property ( $R_r$ ) by simultaneous decrease of plasticity, often in the manner outweighing the loss of these properties due to corroding action of medium.

# CORROSION BEHAVIOUR OF METALS AND ALLOYS UNDER IMMERSED CONDITIONS IN INDIAN HARBOURS

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## SUMMARY

The results reported in literature on corrosion rate of metals and alloys in seawater are in relation to temperate climates. There is paucity of information on the corrosion behaviour of bare metals in tropical waters and more particularly, no work has been reported on such behaviour at the Indian harbours.

The corrosion behaviour of a number of common metals and alloys such as mild steel, stainless steel, copper, naval brass, zinc and aluminium have been determined under immersed conditions in seawater at Bombay and Cochin harbours covering a period of eight years' immersion.

Corrosion rate (mil/yr) of mild steel at Bombay and Cochin harbours are on the higher side of such values reported in the literature for temperate and tropical waters. Mild steel is susceptible to pitting attack under immersed conditions in seawater. Penetration due to pitting has been

observed to be about seven times more severe than the penetration indicated by corrosion rate. Accelerated pitting is more important to structures like dock-gates, wharf walls, buoys, ships' hulls etc. than average penetration based on weight loss measurements.

Corrosion rates of copper, naval brass and zinc at Bombay and Cochin harbours are comparable to values reported for temperate waters as well as for tropical Panama Canal Zone. Copper and stainless steel panels suffered perforation in both the harbours due to pitting.

Aluminium has been found to be extremely resistant to corrosion including pitting attack under immersed conditions at Cochin suggesting the use of (a) aluminium as sheathing material for wooden crafts, and (b) its alloys for fabrication of small crafts operating in the area.

## INTRODUCTION

The corrosion rates of metals and alloys under immersed conditions in seawater have been investigated by a number of workers<sup>1, 2</sup> at different localities throughout the world. Most of these investigations have, however, been carried out in temperate waters. Little quantitative information exists on these rates in the tropics except in the Panama Canal Zone<sup>3-5</sup>. Corrosion rates of mild steel, brass and aluminium have been determined in Lagos and Port Harcourt harbours, Nigeria by Ambler and Bain<sup>6</sup> by immersion of metal panels for very short duration of two months.

No work has been reported on corrosion behaviour of metals under immersed conditions in Indian harbours. The progressive expansion of ports, dockyards etc. in India called for a systematic study of the subject at the Indian harbours. Exposures were started in Bombay and Cochin in 1959 and the present paper reports the results of investigation on the corrosion rates of six common metals and alloys namely mild steel, 18:8 stainless steel, copper, naval brass, zinc and aluminium at Bombay and Cochin harbours covering a period of eight years.

A review of the literature<sup>1, 2, 5, 7</sup> on corrosion rates of unalloyed carbon steels shows that majority of the workers have expressed the corrosion characteristics of the metal under immersed condition as ipy (inches penetration per year) or g/dm<sup>2</sup>/month from loss in weight determinations. The nature of corrosion observed with unalloyed low carbon steel under immersed conditions comprises of general as well as pitting attack as against general corrosion observed normally under atmospheric conditions.

LaQue<sup>1</sup> has reported corrosion rates of mild steel between 1-7.7 mils/year in different harbours with an average of 4.5. This figure (4.5 mils/year) is comparable to the corrosion rates of mild steel under corrosive atmospheric conditions<sup>8</sup>.

In view of the localised attack corrodibility of steel in seawater environment is not reflected to the Users when the results are expressed in ipy or g/dm<sup>2</sup>/month. Pitting is more significant than the average weight loss for immersed structures. Pitting on vessels, buoys and hulls, if permitted to proceed to perforation, is obviously more critical than larger weight losses spread evenly over entire surface area. In the present paper, therefore, emphasis has been given on assessment of corrosion behaviour of steels as well as metals subjected to localised attack by studying the pitting behaviour in detail.

## METHODS

### Test sites

Metal panels were immersed at Bombay harbour (latitude 18°55'N) from a floating raft (Fig. 1) moored to a buoy.

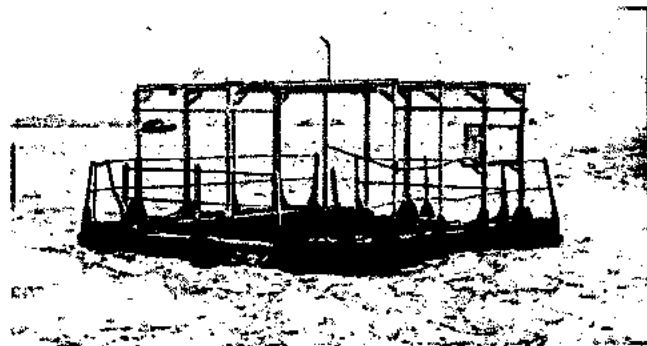


Fig. 1. — Exposure raft at Bombay harbour.

The raft was situated in the harbour about half a mile from the Naval Dockyard pier. At Cochin (latitude 9°43'N), the panels were fixed to frames and suspended from the Naval Boat Jetty in the Ernakulam Channel. The top of the frame was maintained one foot below the lowest tide level so as to keep the panels continuously immersed during the exposure period.

#### Materials

Six common metals and alloys namely unalloyed low carbon steel, mild steel, stainless steel, copper, naval brass, zinc and aluminium were exposed at both Bombay and Cochin harbours. The selection of materials was guided by their use on board ships as well as shore installations. Composition of the materials used are given in Table I.

TABLE I  
CHEMICAL COMPOSITION OF  
THE METALS AND ALLOYS USED

		Per cent
Mild steel	Carbon	0.13
	Manganese	0.30
	Silicon	0.13
	Sulphur	0.04
	Phosphorous	0.02
	Iron	Remainder
Stainless steel	Nickel	8.33
	Chromium	17.40
	Iron	Remainder
Copper	Copper	99.90
Naval brass	Copper	60.80
	Zinc	37.15
	Tin	1.27
Aluminium	Copper	0.13
	Iron	0.33
	Manganese	0.09
	Zinc	0.04
	Silicon	0.16
	Aluminium	Remainder

#### Specimens

The metal panels were cut to 6" × 4" in size. Thickness of the panels in respect of the different metals/alloys is given below:

Zinc	—	0.250"
Mild steel	—	0.125"
Copper	—	0.064"
Naval brass	—	0.064"
Stainless steel	—	0.072"
Aluminium	—	0.056"

The panels were rigidly fixed to exposure frame by mild steel bolts and nuts. The exposure frames were fabricated using  $\frac{3}{4}$ " ×  $\frac{3}{4}$ " angle iron. The panels were electrically insulated from the metal frame by using suitable bakelite washers and sleeves to prevent galvanic corrosion. The panels could be identified by  $\frac{1}{2}$ " deep slits cut perpendicular to the edge of the panel. The slits were situated at

$\frac{1}{2}$ " intervals from the left top corner which was chamfered. The panel could be identified by measuring the distance between the slit and chamfered corner.

#### Surface preparation

The mild steel panels were freed from millscale by pickling for 10 minutes at 80°C in 5 per cent sulphuric acid inhibited with a proprietary pickling inhibitor «Galvener». Immediately after pickling, the panels were washed with boiling water to remove the adhering acid and expel the adsorbed hydrogen. The panels were then degreased with acetone, dried and stored in a desiccator before final weighing and immersion.

Copper, naval brass and zinc panels were abraded with 1G Oakey emery paper, degreased with benzene and stored in desiccator before final weighing and immersion. The stainless steel and aluminium panels were exposed in «as received» condition after degreasing with benzene.

#### Immersion schedule

12 samples of each metal were immersed at each site so that duplicate panels could be removed for examination at the end of six months, one year, two years, four years and eight years. Two extra panels were provided to compensate for any loss during exposure or for any additional data required during the course of the investigation. The panels were immersed at Bombay and Cochin harbours during 1959. Panels have been withdrawn in both the harbours after 6 months, one year, two years, four years and eight years of immersion.

Stainless steel panels exposed for longer periods had to be removed after two years and four years of immersion at Bombay and Cochin respectively owing to severe crevice corrosion near the support. Aluminium panels exposed at Bombay were also removed after two years of exposure for similar reason. Mild steel panels exposed at Bombay for eight year periods were lost in 1966 owing to excessive corrosion of the panel.

#### Environment

The salinity and temperature of the seawater were determined weekly at Bombay and Cochin harbours during the exposure period. Temperature determinations were carried out at about 1200 hours. Data in respect of temperature and salinity at Bombay and Cochin harbours for a period of one year are given in Figs. 2 and 3 respectively. Temperature of the seawater at Bombay harbour varied between 25° and 32°C and at Cochin from 28° to 32°C.

The salinity decreased in both the places with the onset of monsoon. In Bombay the salinity remained low for 3-4 months (June to September) while in Cochin, it was low for over 6 months (June to December). In Cochin, at certain periods (July - August), the salinity became less than 1‰.

#### Cleaning of specimens after exposure

On the specimens, drawn at different intervals, assessment of fouling was carried out initially. The panels were photographed and then they were freed from fouling organisms carefully by a blunt metal scraper. The corrosion products on different metals were finally removed by the following chemical treatment.

Metal	Cleaning solution
Mild steel	5% Sulphuric acid (inhibited)
Copper	5% Sulphuric acid
Stainless steel	10% Nitric acid
Zinc	10% Chromic acid
Aluminium	5% Phosphoric acid and 2% Chromic acid
Naval brass	Saturated ammonium acetate solution.

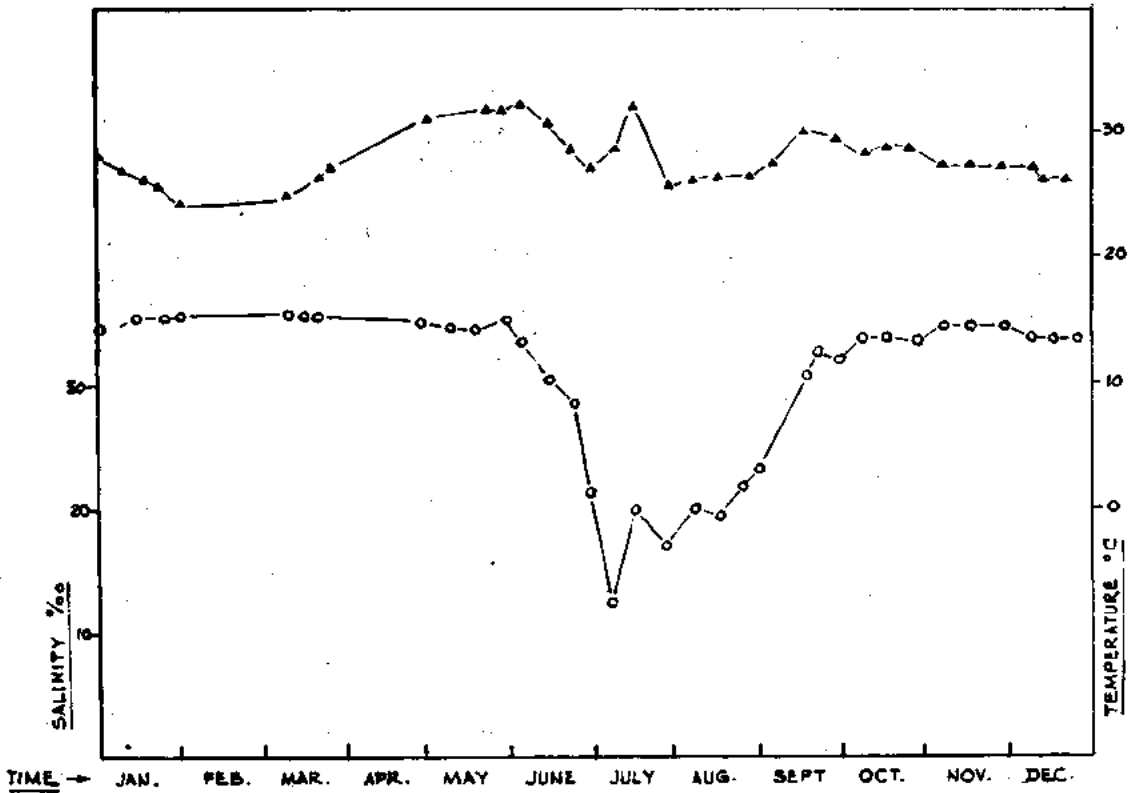


Fig. 2. — Salinity and temperature at Bombay harbour during 1960.

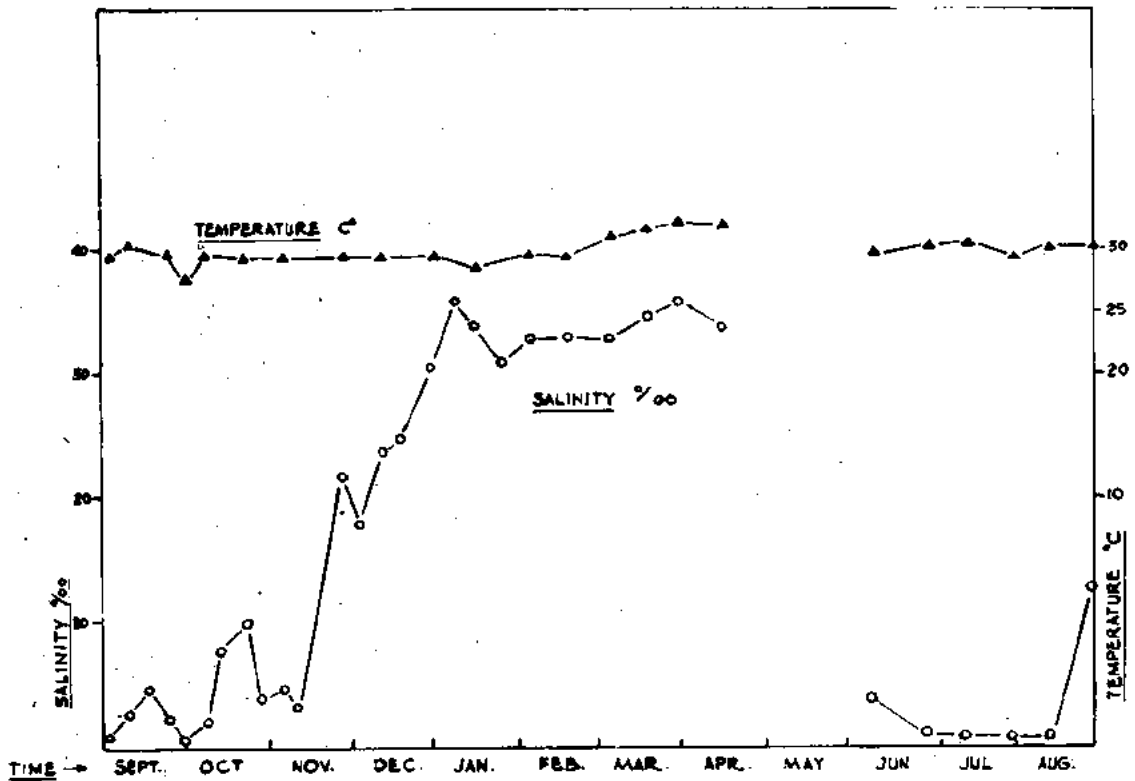


Fig. 3. — Salinity and temperature at Cochin harbour during Sept. 1959 to Aug. 1960.

### Corrosion evaluation of exposed panels

Throughout the programme of work, endeavour was made to study and evaluate as many types of corrosion damage as are considered significant. After cleaning, each surface was carefully inspected to determine the types of corrosion. The corrosion panels were also photographed, when necessary, as an additional aid in evaluating results.

The cleaned panels were weighed to determine the loss in weight. The average penetration (mils per year) was calculated from weight loss, specific gravity and period of exposure. In the case of metals like mild steel, copper and to a certain extent zinc, general corrosion as well as pitting were observed. Aluminium suffered pitting only at Bombay harbour. Extent of general corrosion was ascertained by determination of average calculated penetration from weight loss measurement.

The assessment of pitting characteristics has been difficult owing to lack of a suitable variable which can be measured quantitatively and treated mathematically<sup>9</sup>. One of the most commonly used method is to measure the maximum pit depth developed on samples exposed to a corrosive environment for a fixed time. Additional information can be obtained by carrying out such determination for different periods of immersion and then plotting rate curve. The pitting rate curve so obtained provides in principle a satisfactory means of determining the influence of changes in the environment and in the metal on pitting.

The major drawbacks to the above technique is the often excessive scatter precluding any precise quantitative evaluation of the results and permitting only qualitative comparison<sup>9</sup>. Pitting characteristics of metals like mild steel, copper, zinc and aluminium in Bombay harbour was ascertained initially by a method similar to that used by the previous workers like Forgeson et al<sup>9</sup> by determination of maximum pit depth as well as 5 deepest pits on each side of the duplicate panels and then averaging the 20 deepest pits. The pitting factor based on the ratio of the deepest measured penetration to the average calculated penetration was also determined.

In addition to above, for a more detailed study of the pitting characteristics, depth of all the pits were determined and from these, a pit depth distribution curve for different periods was obtained. The pit depths were determined with a dial micrometer depth gauge to an accuracy of 0.001 cm. To prevent higher reading due to indentation by the sharp probe, the contact between the probe and the bottom of the pit was ascertained by completion of an electrical circuit resulting in the illumination of an indicator lamp.

### Fouling

Settlement of marine fouling organisms is intense, both at Bombay and Cochin harbours. The Naval Chemical and Metallurgical Laboratory have studied the incidence of marine organisms in Bombay waters since 1953<sup>10-12</sup>. All the major fouling groups have been encountered in Bombay. Amongst these, however, Hydroids, Annelida, Cirripedia and Bryozoans and to a certain extent Molluscan are the important groups that settle in abundance on submerged structures. Settlement of fouling organism occurs throughout the year with the peak during the summer months and moderate fouling during the monsoon period. The metal panels immersed at Bombay and Cochin were assessed in respect of settlement of fouling organisms at the time of withdrawal of the panels. The types of settlements which occurred on different metals and alloys are described below.

#### Mild steel and aluminium

Mild steel and aluminium panels were found to be heavily fouled in both the harbours even on six month panels (Figs. 4 and 5). The types of fouling organisms settled on mild steel and aluminium at Bombay harbour, comprised of barnacles, hydroids, encrusting bryozoans and tubeworms. In Cochin,



Fig. 4. — Mild steel panels (left 3 rows) and stainless steel panels (right 3 rows) after six months immersion at Cochin. Mild steel panels show heavy settlement. Stainless steel panels are less fouled.



Fig. 5. — Aluminium (left 3 rows) and zinc (right 3 rows) panels after six months immersion at Cochin. Aluminium panels are heavily fouled while zinc panels are comparatively less fouled.

in addition to those organisms encountered in Bombay, *Mytilus* and *Oysters* were found to be predominant.

#### Stainless steel

Stainless steel panels were also fouled both at Bombay and Cochin harbours. Fouling organisms with calcareous shells like barnacles, *Mytilus* and *Oysters* were observed in Cochin while barnacles were predominant on panels at Bombay. The density of settlement on stainless steel was generally lower compared to mild steel and aluminium (Fig. 4).

#### Zinc

Zinc panels at both Bombay and Cochin harbours were

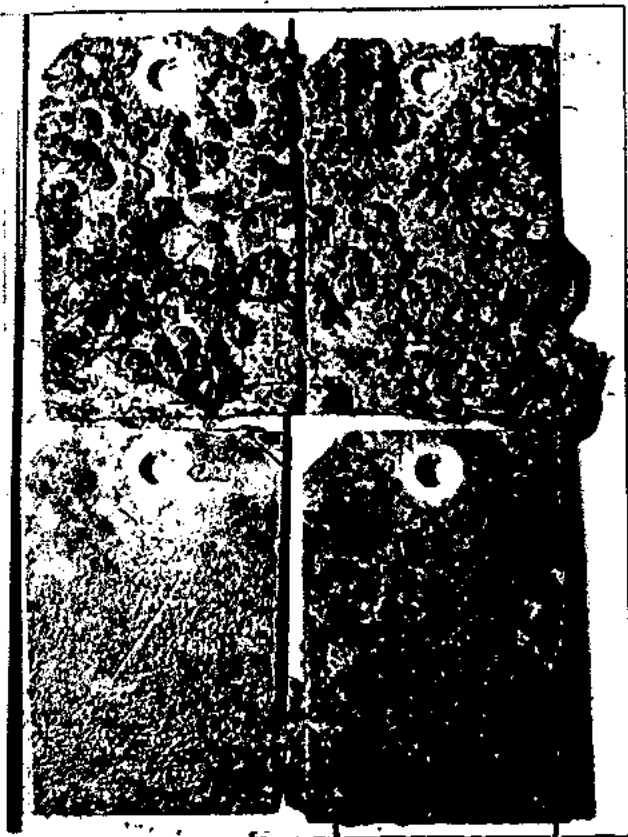


Fig. 6. — Close up view of aluminium (top row) and zinc (bottom row) panels after six months exposure at Cochin. Comparative freedom of zinc panels from settlement of fouling organisms can be seen.

less fouled (Fig. 5). There was slight settlement during the first six months of immersion in both the harbours. Panels in Cochin were fouled predominantly by Oysters and those in Bombay by barnacles and encrusting Bryozoans.

#### Copper and Naval Brass

Copper and naval brass were found to be free from persistent settlement of fouling organisms in both the harbours even after 8 years' immersion. The absence of fouling organisms on copper and naval brass panels is shown in Fig. 7. Encrusting Bryozoans were occasionally observed on these panels. The organisms, however, suffered detachment from the substrate owing to their short life cycle.

#### Corrosion

Comprehensive data on the corrosion behaviour of the six different metals and alloys at Bombay and Cochin harbours are given in Tables II to V. Type (s) of corrosion observed during inspection of cleaned panel as well as corrosion rate (mils/year) calculated from weight loss measurements have been shown in Tables II and III for Bombay and Cochin harbours respectively. Data in respect of pitting characteristics like deepest pit, pitting factor and average of 20 deepest pits are presented in Tables IV and V.

Weight loss of stainless steel panels and that of aluminium at Bombay was entirely due to pitting attack. Hence corrosion rate based on weight loss measurement has not been presented in Tables II and III. Naval brass in both the harbours as well as aluminium at Cochin did not suffer any pitting attack.

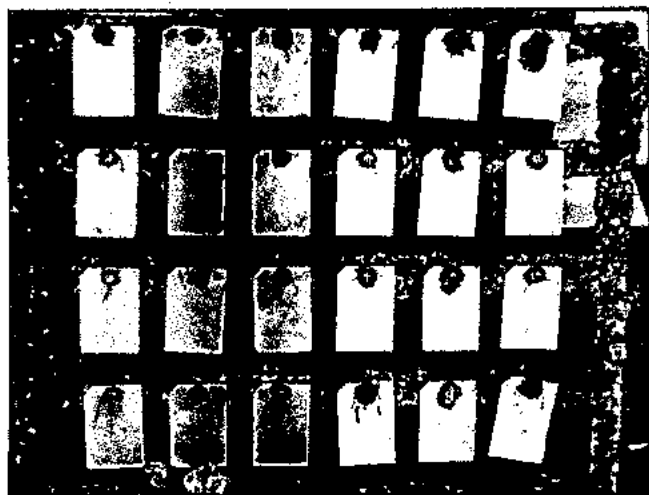


Fig. 7. — Copper (left 3 rows) and naval brass (right 3 rows) after six months immersed at Cochin. Panels free from fouling settlement. Heavy fouling settlement can be observed on the mild steel frame.

Corrosion rate (mil/yr) — time curves, deepest pit-time curves and pitting frequency of the various metals under immersed conditions at Bombay and Cochin are presented in Figures 8-19. Photographs of corroded panels are shown in Figs. 20 to 24 as an additional aid for appreciation of the results.

## DISCUSSION

### Mild steel

Corrosion rate of mild steel (Fig. 8) decreases with time owing possibly to accumulation of a layer of corrosion product and settlement of fouling organisms. Decrease in corrosion rate with time indicates the inadequacy of short time assessment of corrosion behaviour of ferrous materials in natural seawater. A minimum period covering exposure for four years is considered essential to ascertain the corrosion behaviour of unalloyed low carbon steels under immersed conditions in seawater.

Corrosion rates of mild steel at Bombay (7.8 mils/yr) and at Cochin (6.7 mils/yr) are slightly higher than the values reported by Forgeson and others<sup>1</sup> for tropical waters in Panama Canal Zone for comparable periods of immersion (4.6 mils/yr). LaQue<sup>2</sup> has given values of corrosion rates of mild steel and iron ranging from 1.0 to 7.7 mils/year exposed under conditions of continuous immersion at several places in the world. The figures for Bombay and Cochin thus fall on the high side of the values obtained by other workers. The comparatively higher values in Bombay and Cochin harbour may be due to local factors like current, wave action, sand and silt content, pollution etc. The higher corrosion rate at Bombay than at Cochin could be due to prevalence of lower salinity in Cochin for a longer period.

It will be observed from the Tables II to V and Figs. 8 and 14 that corrosion of mild steel under immersed conditions in seawater is more severe due to pitting than general wastage expressed by average penetration from loss in weight measurements. To illustrate, under immersed condition for a period of 2 years, mild steel suffers 7.8 and 6.2 times more penetration by pitting at Bombay and Cochin harbour than indicated by the corrosion rate (mil/yr) results. Pitting behaviour of mild steel, should therefore be taken into consideration during design and estimation of life of underwater structures rather than corrosion rate data. Pitting characteristics of mild steel in the 2 harbours is more severe than similar values reported for the Panama Canal Zone<sup>3, 4</sup>. Pitting rate of mild steel is



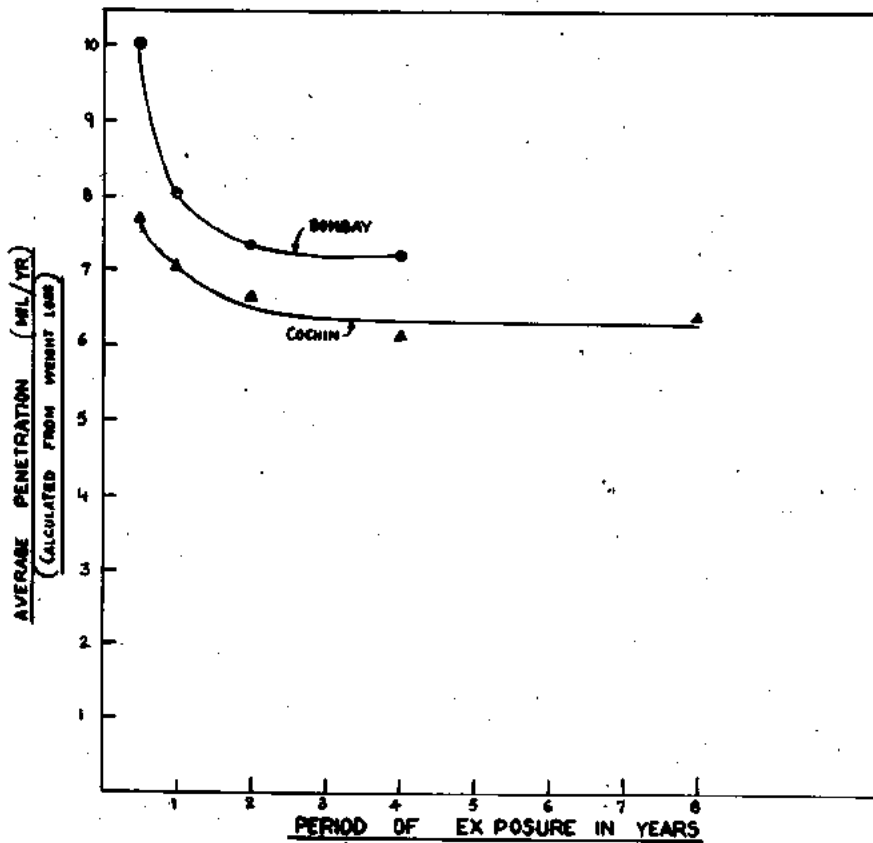


Fig. 8 CORROSION RATE (MILS/YR) OF MILD STEEL IN BOMBAY AND COCHIN HARBOURS

Fig. 8. --- Corrosion rate (mils/yr) of mild steel in Bombay and Cochin harbours.

T A B L E II

CORROSION EVALUATION OF METALS/ALLOYS UNDER IMMERSSED CONDITION AT BOMBAY HARBOUR

Material	Type of corrosion attack	Corrosion rate (mil/yr)				
		Six months	One year	Two years	Four years	Eight years
(1)	(2)	(3)	(4)	(5)	(6)	(7)
Mild steel	General and pitting corrosion	10.04	8.09	7.37	7.20	Panels lost
Copper	General and pitting corrosion	1.44	1.25	1.13	0.90	0.50
Naval brass	General corrosion; no pitting	0.95	0.84	0.76	0.78	0.74
Zinc	General corrosion; slight pitting	3.28	1.83	1.64	1.70	1.19
Stainless steel	pitting and crevice corrosion; elongated pits	—	—	—	—	—
Aluminium	Crevice attack and pitting corrosion	—	—	—	—	—

T A B L E III

## CORROSION EVALUATION OF METALS/ALLOYS UNDER IMMERSSED CONDITION AT COCHIN

Material	Type of corrosion attack	Corrosion rate (mil/yr)				
		Six months	One year	Two years	Four years	Eight years
(1)	(2)	(3)	(4)	(5)	(6)	(7)
Mild steel	General and pitting corrosion	7.73	7.02	6.69	6.10	6.40
Copper	General and pitting corrosion	1.85	0.97	1.04	1.02	0.64
Naval brass	Uniform corrosion; pitting absent	0.62	0.88	1.07	1.28	1.01
Zinc	General corrosion; slight pitting	4.39	1.89	1.77	1.40	0.76
Aluminium	Slight uniform attack but free from pitting and crevice corrosion	0.14	0.11	0.07	0.06	0.07
Stainless steel	Crevice attack near the supporting hole and pitting corrosion; elongated pits.	—	—	—	—	—

T A B L E IV

## PITTING CHARACTERISTICS OF METALS/ALLOYS UNDER IMMERSSED CONDITION AT BOMBAY

Material	Average 20 Deepest pit (Mils)					Deepest pit (Mils)					Pitting factor				
	6 Mon.	1 Yr.	2 Yr.	4 Yr.	8 Yr.	6 Mon.	1 Yr.	2 Yr.	4 Yr.	8 Yr.	6 Mon.	1 Yr.	2 Yr.	4 Yr.	8 Yr.
Mild steel	8.0	19.4	58.1	(P)	*	12.0	58.0	115.0	(P)	*	2.4	7.1	7.8	—	*
Copper	13.5	18.8	22.4	43.0	(P)	14.0	31.0	59.0	(P)	(P)	19.4	24.8	26.7	—	—
Zinc	3.6	2.5	5.4	19.0	61.0	4.0	4.0	9.0	19.0	61.0	3.0	2.2	2.7	2.8	6.4
Aluminium	14	25.5	—	—	—	15.75	(P)	(P)	—	—	—	—	—	—	—

(P) = Panel Perforated \* Panels lost

higher at Bombay than at Cochin possibly owing to prevalence of higher salinity in Bombay for a longer period.

Pit-depth distribution curves of mild steel at Bombay and Cochin (Figs. 16 and 17) are «J» shaped in nature with the curve bent to the right. When the panels were first immersed, a large number of pits initiate and start propagating. With progress of time, majority of the pits progressively stifle and only a small number continues to propagate giving the distribution of pits as «J» shaped curve.

*Copper*

Corrosion rates of copper at Bombay and Cochin harbours (Fig. 9) decrease with times owing to formation of a protective film of corrosion products. Dissolution of copper was, however, adequate to prevent settlement of fouling organisms during the entire exposure period. Corrosion rates of copper in both the harbours are comparable to the values reported for metals in temperate as well as in Panama Canal Zone<sup>8</sup>.

T A B L E V

PITTING CHARACTERISTICS OF METALS/ALLOYS UNDER IMMersed CONDITION AT COCHIN

Material	Average 20 deepest pit (Mils)					Deepest pit (Mils)					Pitting factor				
	6 Mon.	1 Yr.	2 Yr.	4 Yr.	8 Yr.	6 Mon.	1 Yr.	2 Yr.	4 Yr.	8 Yr.	6 Mon.	1 Yr.	2 Yr.	4 Yr.	8 Yr.
Mild steel	10.6	39.0	52.0	104.0	(P)	13.0	55.0	83.0	(P)	(P)	3.4	6.8	6.2	—	—
Copper	23.4	25.6	30.7	53.0	(P)	34.0	45.0	(P)	(P)	(P)	33.3	40.2	30.9	—	—
Zinc	6.3	7.8	11.8	21.6	32.0	6.3	7.8	11.8	21.6	32.0	2.6	3.6	3.3	3.9	5.3

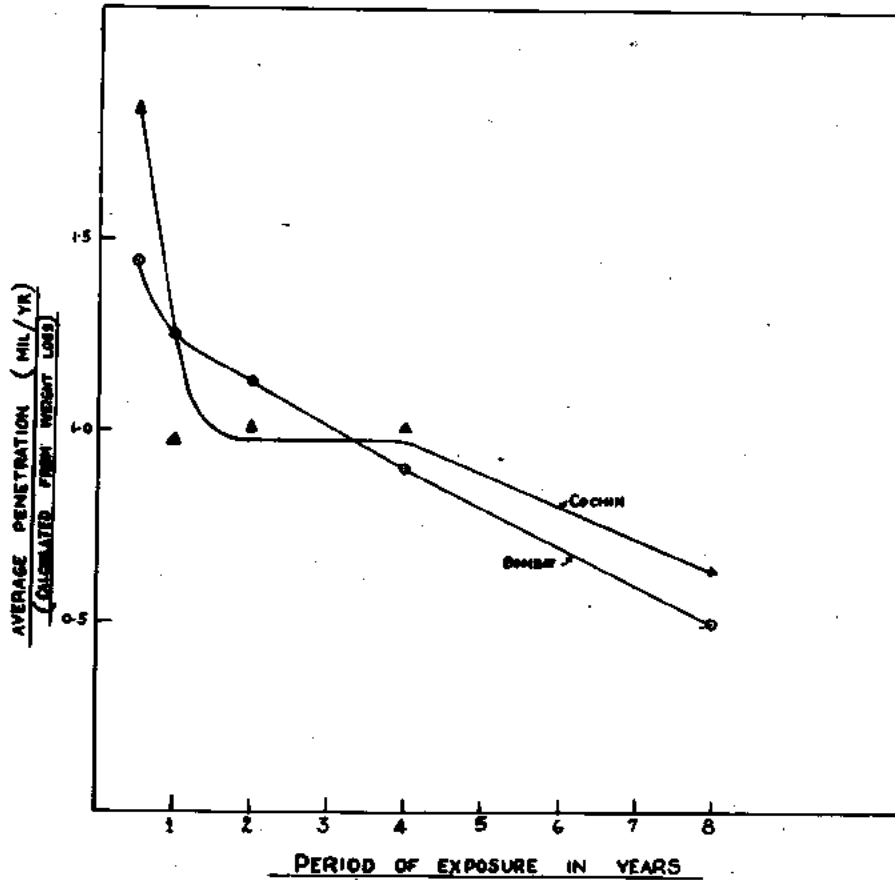


Fig. 9. — Corrosion rate (mil/yr) of copper in Bombay and Cochin harbours.

Copper panels (64 mils thick) suffered deep pitting leading to perforation in two year period at Cochin and in less than four years at Bombay. Copper was found to suffer in a period of 2 years, 26.7 and 30.9 times more penetration at Bombay and Cochin harbours than the calculated corrosion rate values. Excessive pitting of copper panels leading to perforation is considered to be due to impingement attack caused by tidal movement or wave action. Intensity of pitting of copper at Bombay and Cochin is higher than the values reported for the metal in the Panama Canal Zone<sup>2</sup> possibly owing to local factors like current, wave action, sand and silt content, pollution etc.

Naval brass

Naval brass has been found to be immune to pitting attack owing to its resistance to impingement attack towards slowly moving seawater. Corrosion of naval brass was uniform in contrast to pitting attack observed with copper. The corrosion rate at Bombay and Cochin harbours (Fig. 10) is comparable to the values reported for the metal in temperate waters<sup>2</sup>.

Zinc

Corrosion rate of zinc (Fig. 11) decreases with immersion

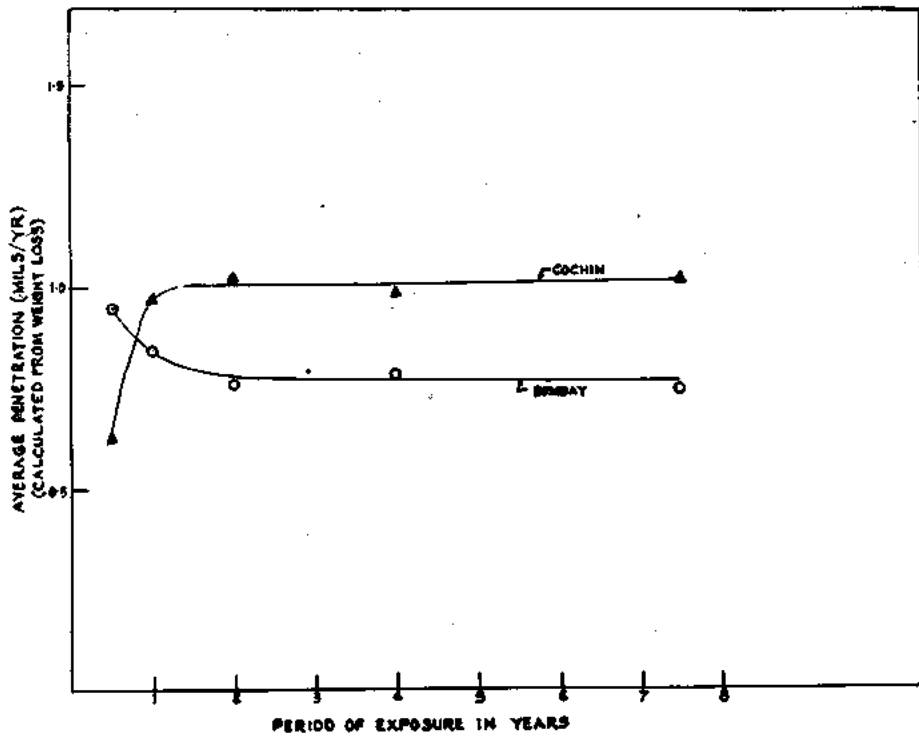


Fig. 10. — Corrosion rate (mils/yr) of naval brass in Bombay and Cochin harbours.

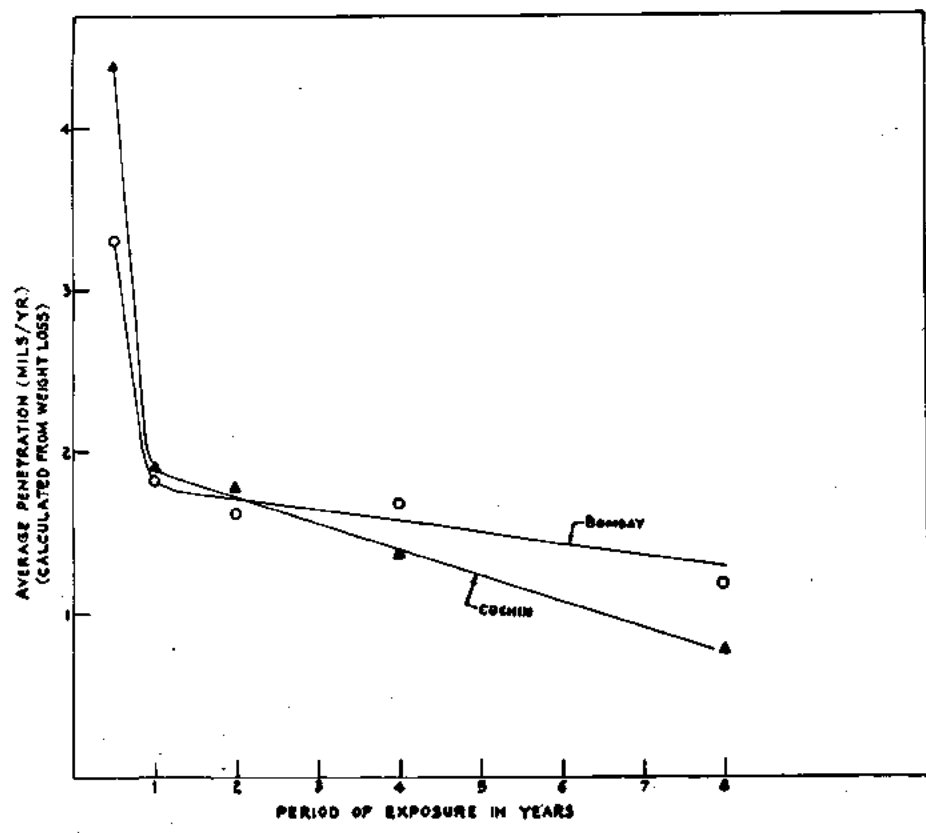


Fig. 11. — Corrosion rate (mils/yr) of zinc in Bombay and Cochin harbours.

period owing to formation of a protective film of corrosion products. The values for corrosion rate of zinc in both the harbours is comparable to those reported for the metal in temperate<sup>1</sup> and Panama Canal Zone<sup>2</sup>. Zinc has got mild antifouling property (Fig. 6) owing to toxic nature of the metal towards marine organisms<sup>13</sup> and also possibly due to gradual dissolution of the metal.

#### Aluminium

Aluminium was found to be fairly resistant to pitting attack as well as crevice corrosion at Cochin harbour. Though barnacles settled on aluminium, no corrosion was observed below the settlement. The corrosion resistance of aluminium in Cochin harbour commends the uses of aluminium and its alloys for construction of small crafts and as sheathing material for wooden boats operating in these areas.

Aluminium panels suffered pitting attack in Bombay harbour. The difference in behaviour between Bombay and Cochin may be due to local factors. Immersion of aluminium panels at Bombay just prior to monsoon could also have facilitated pitting owing to initial exposure of the metal to seawater environment with lower salinity. Forgeson et al<sup>14</sup> have reported pronounced local pitting with aluminium immersed in fresh water Gatun lake in the Panama Canal Zone. Pit distribution curves of aluminium at Bombay (Fig. 18) for various periods of immersion are «J» shaped in nature owing to initiation of a large number of pits at the time of immersion followed by stifling of most of the pits initially formed and subsequent propagation in depth of only a small number of pits.

#### Stainless steel

Stainless steel panel in both the harbours suffered pitting

below the settlement of barnacles as well as near the supporting holes owing to crevice corrosion (Fig. 22). The formation of pits below the fouling settlement as well as crevice corrosion near the support arise from destruction of passivity in chloride solution under the settlement or below the bakelite washer. The elongation of pit observed on stainless steel panels has been caused by formation of a high density acidic ferric chloride solution within the pit that breaks down the passivity of the metal directly below. The pitting then progresses in the direction of gravity. Because of its vulnerability to pitting attack in tropical seawater at low velocity, 18:8 stainless steel is not considered satisfactory for any structures that would be affected by deep and numerous pits. The material, however, can be protected by application of antifouling paint and/or coupling to mild steel.

#### CONCLUSIONS

The corrosion behaviour of a number of common metals and alloys such as mild steel, stainless steel, copper, naval brass, zinc and aluminium have been determined under immersed conditions in seawater at Bombay and Cochin harbours covering a period of 8 years of immersion.

Methods for preparation and exposure of specimens alongwith techniques employed for their cleaning after exposure as well as measuring the intensity of corrosion of corroded panels have been described in the paper.

Comprehensive data on corrosion evaluation giving figures for average penetration, deepest pit, average of 20 deepest pits, pitting factor and pit depth distribution of the corroded panels have been presented in the paper. These data will be of considerable value in (a) selecting materials, and (b) development of protective measures for use in these locations.

The main conclusions arrived at on the basis of the results obtained are given below:

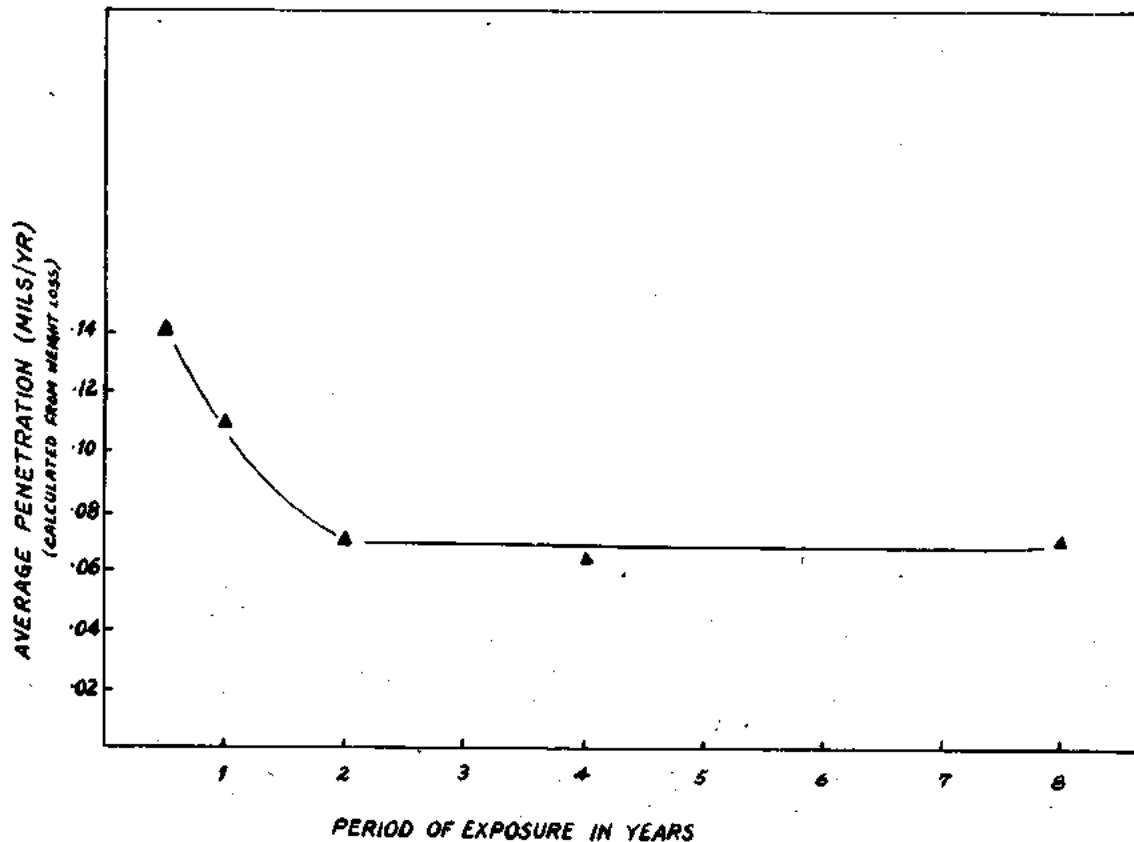


Fig. 12. — Corrosion rate (mils/yr) of aluminium in Cochin harbour.

- (a) The decrease in corrosion rate with increase in period of immersion caused by settlement of fouling organisms as well as presence of corrosion products shows the inadequacy of short term data for such investigations. Exposure should be carried out preferably covering a minimum period of four years for studying the corrosion behaviour of metals under immersed conditions in tropical waters.
- (b) Corrosion rates of mild steel at Bombay and Cochin harbours are on the high side of the values reported for the metal in the literature for temperate and tropical waters.
- (c) Mild steel is susceptible to pitting attack under immersed conditions in seawater. Penetration due to pitting is about seven times more deep than the average penetration based on weight loss measurements. In one year period, penetration of mild steel due to pitting is of the order of 60 mils under static immersed condition in the two harbours. Accelerated pitting is more important to structures like dock gates, wharf walls, buoys, ships' hulls than average penetration values based on weight losses measurements.
- (d) Corrosion rates of copper, naval brass and zinc in Bombay and Cochin harbours are comparable to those reported for temperate waters. Copper, however, suffers pitting and perforation owing to impingement

attack caused by tidal movement. Naval brass is immune to pitting attack and suffers only uniform general corrosion.

- (e) Aluminium is extremely resistant to corrosion including pitting attack under immersed conditions at Cochin suggesting the use of this material for construction of small crafts and for sheathing of wooden boats operating in the area.
- (f) Stainless steel is susceptible to pitting and perforation under immersed condition in slowly moving tropical water owing to settlement of fouling organisms. Remedial measures like application of antifouling paint or galvanic protection are considered necessary for stainless steel used in these areas.

#### ACKNOWLEDGEMENTS

The authors express their thank to Shri S.K. Ranganathan, Director of Scientific Research (Navy) for his kind interest in the work. Thanks are also due to Shri A. Balakrishnan of Indian Naval Physical Laboratory, Cochin for data on salinity and temperature at Cochin. The authors also record their sincere thanks to Dr. V. Ranganathan, Deputy Chief Scientist, Research and Development Organisation, Ministry of Defense, for his kind encouragement and sustained interest in the work.

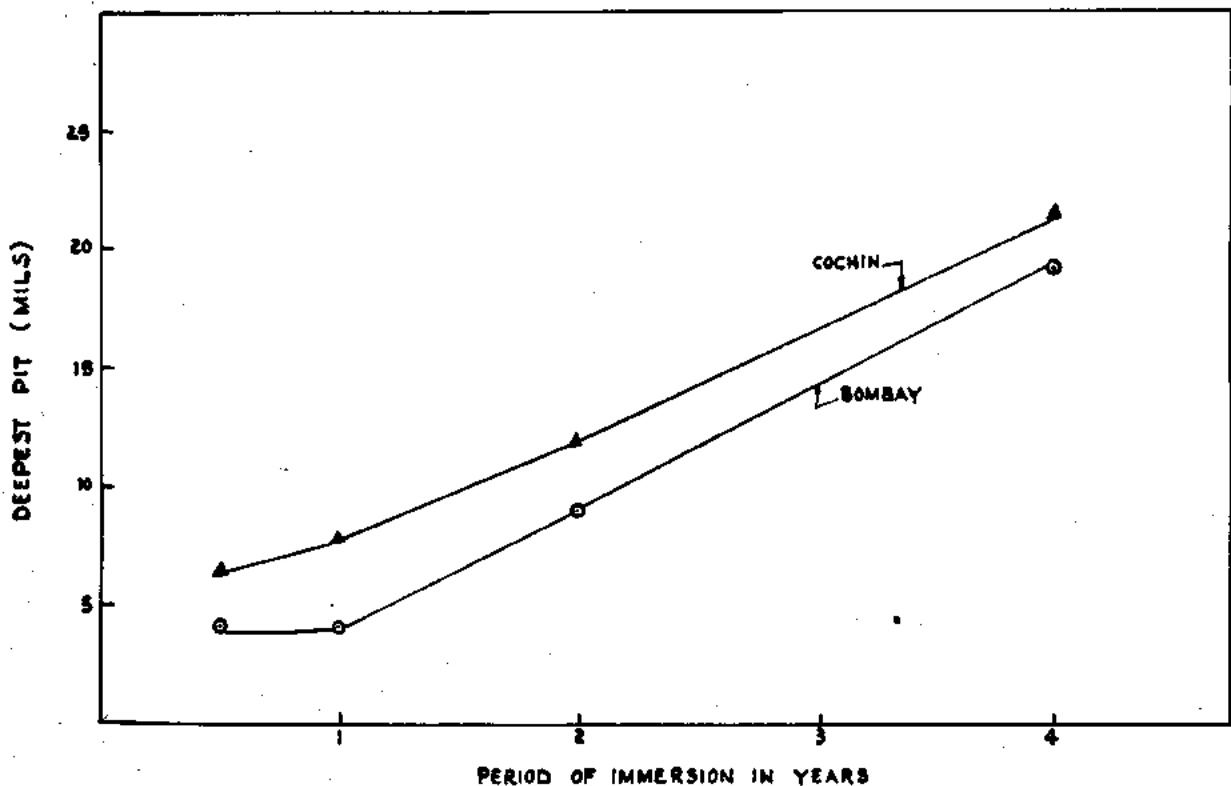


Fig. 13. — Maximum pit depth of zinc in Bombay and Cochin harbour.

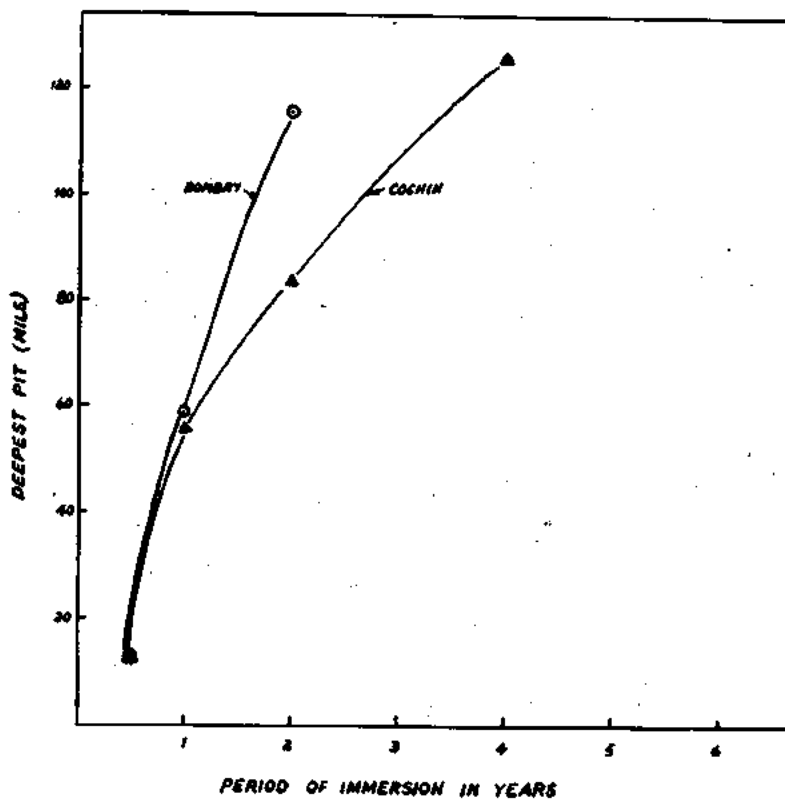


Fig. 14. — Maximum pit depth of mild steel in Bombay and Cochin harbours.

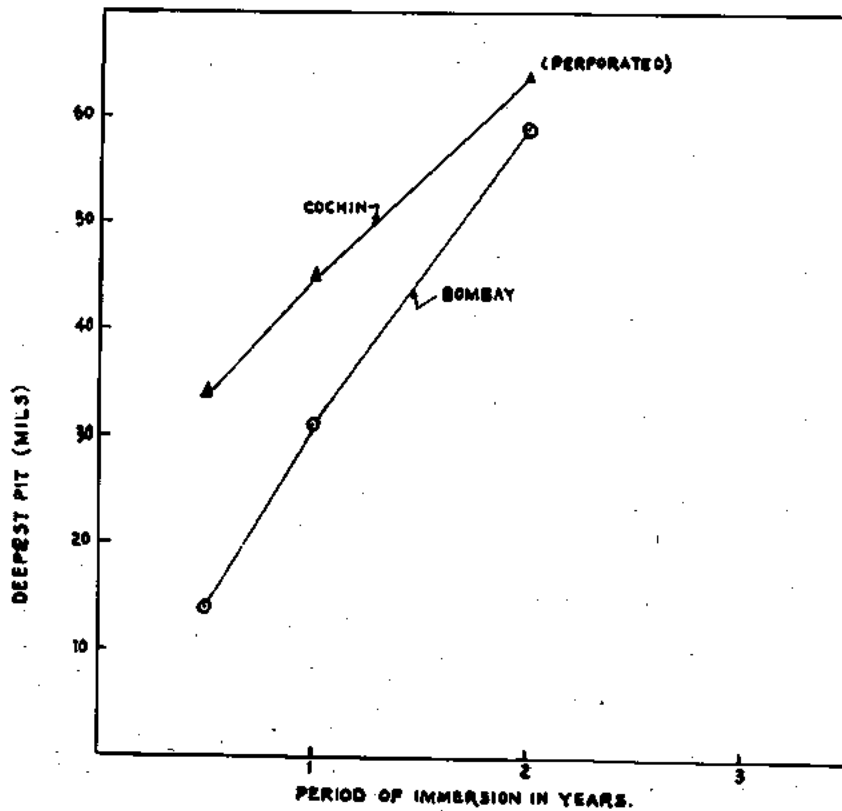


Fig. 15. — Maximum pit depth of copper in Bombay and Cochin harbour.

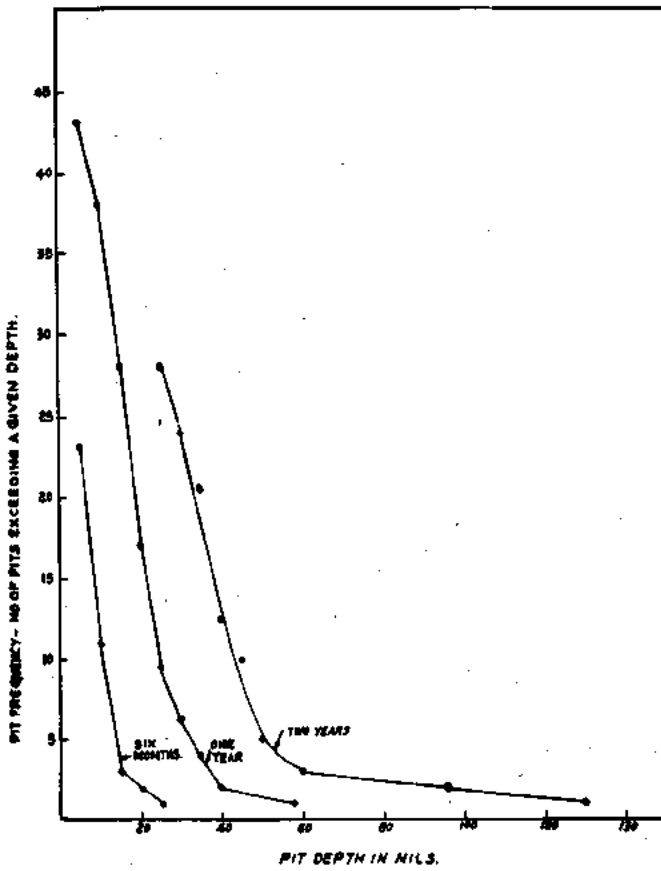


Fig. 16. — Pit depth distribution curves for mild steel immersed in Bombay harbour for six months, one year and two years.

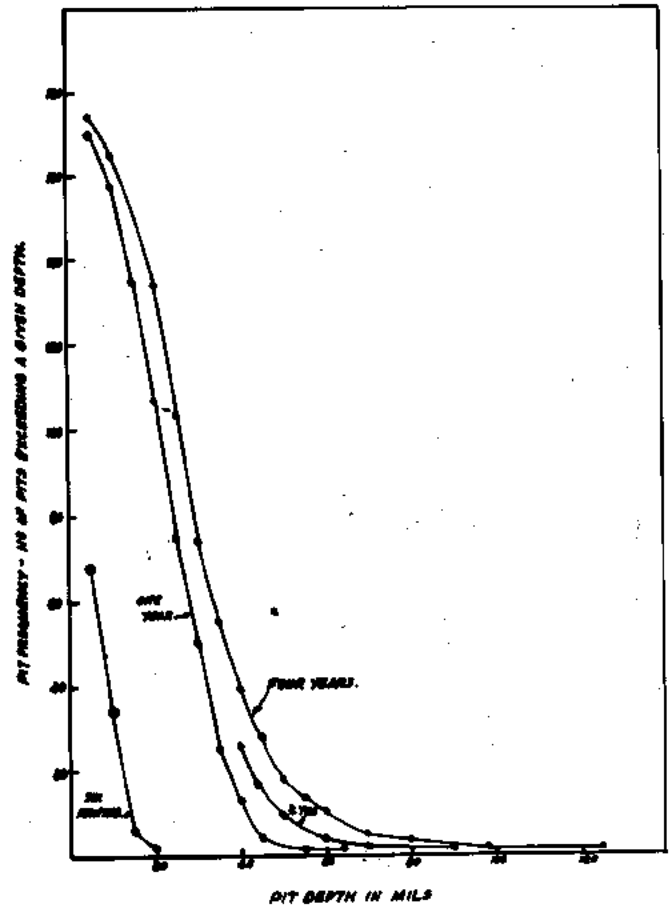


Fig. 17. — Pit depth distribution curves for mild steel immersed in Cochin harbour for six months, one year, two years and four years.



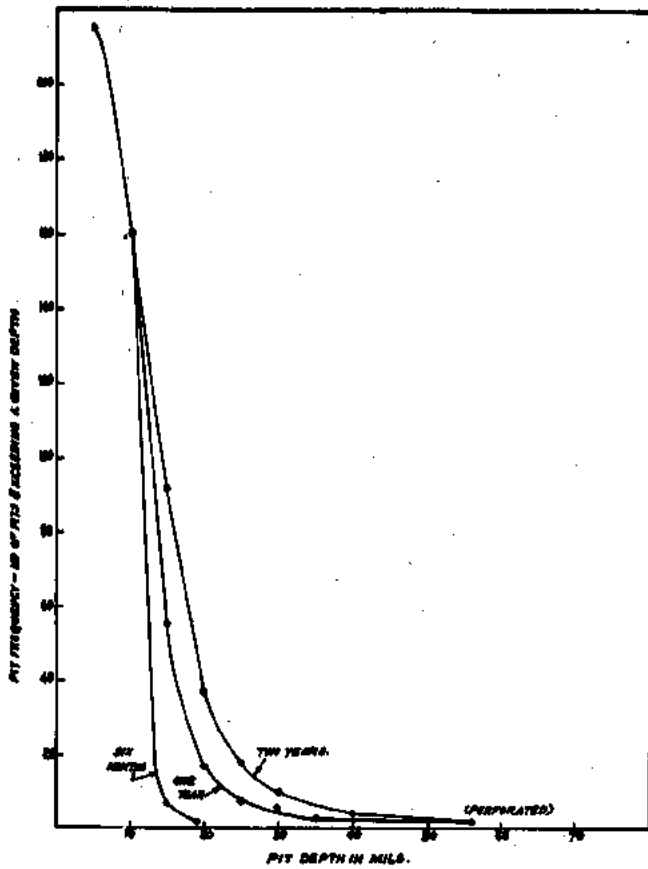


Fig. 18. — Pit depth distribution curves for aluminium in Bombay harbour for six months and two years.

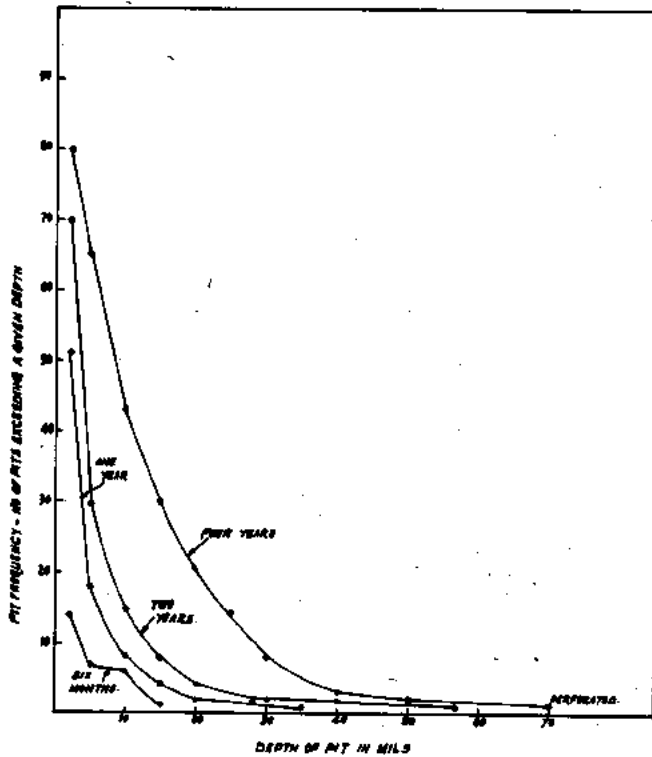


Fig. 19. — Distribution of pit depth on copper immersed in Bombay harbour for six months, one year, two years and four years.



Fig. 20. — Mild steel panels after one year (top left), two years (top right), four years (bottom left) eight years (bottom right) immersion at Cochin 4-year panel perforated at two places 8 year panels suffered heavy general wastage and perforations and thinning.

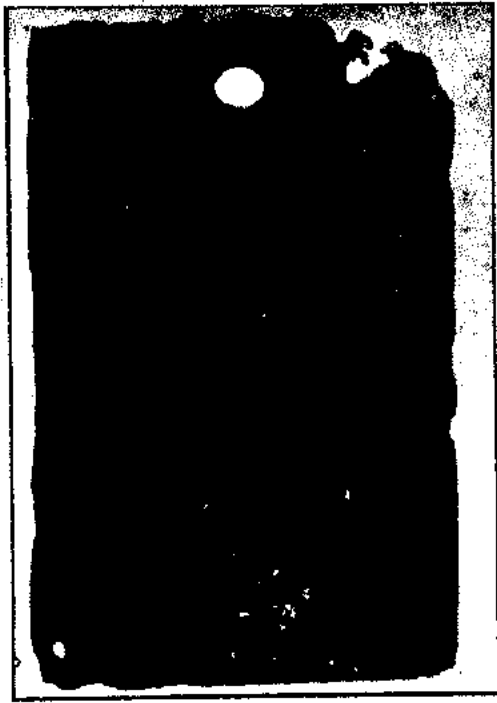


Fig. 21. — Mild steel panel at Bombay after 4 year immersion. Panel heavily pitted and perforated.

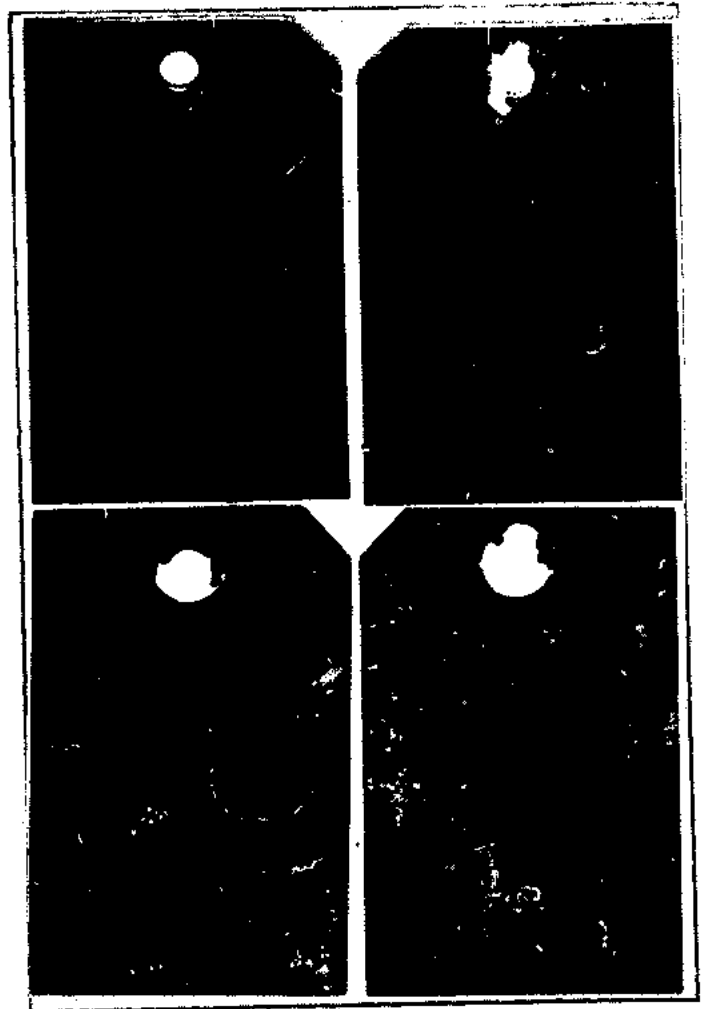


Fig. 22. — Stainless steel panels after six months (top left) one year (top right), two years (bottom left) and four years (bottom right) immersion at Cochin. Severe corrosion near the supporting holes. Panels heavily pitted and perforated under barnacle settlement.



Fig. 23. — Aluminium panel (left) after one year immersion at Bombay, extensive pitting and crevice corrosion near the supporting holes. Zinc panel (right), after 8 years immersion at Cochin. Pitting can be seen all over the surface.

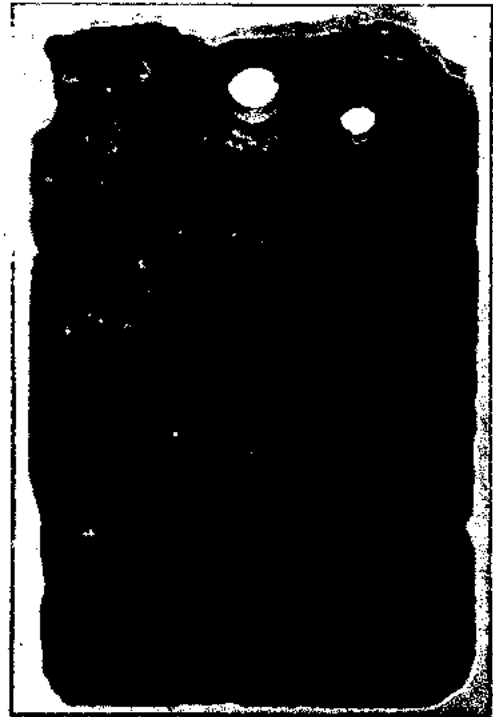


Fig. 24. — Copper (right) and naval brass (left) after 8 years, immersion at Cochin. Naval brass panels free from pitting. Copper panel perforated due to impingement attack.

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## DISCUSSION

T. HOAR (England): Could I ask Dr Dé if the pitting he observed on copper was the typical deep scoring pitting one sees in copper pipe when that is exposed in rapidly flowing water? Was it long trenching, or was it the pitting one observes when copper is exposed to still water, which is more or less hemispherical?

C.P. DE: The pits observed were deep and irregular in shape and they occurred mostly near the supporting bolt. In addition, edges of the panels were consistently eroded showing excessive dissolution of copper in areas of local turbulence. Hence the nature of corrosion is considered to be of the type of 'impingement attack' though the appearance was not typical 'deep scoring' observed in copper pipe under flowing conditions possibly due to difference in geometry of the flowing water over a panel and that in a tube.

A. GUILHAUDIS (France): I would like to ask two questions. First, what was the state of the aluminium used, and second have you found a relation between the formation of pitting and of fouling?

C.P. DE: Aluminium panel used was 36 V.P.N.  $\frac{1}{2}$  H. On the basis of present exposure, no correlation can be drawn between the formation of pitting and fouling. Panels exposed both in Bombay and Cochin were heavily fouled while pitting occurred only on the panels exposed in Bombay harbour.

Prof. Dr. YAHALOM (Israel): I would like to ask two general questions with regard to the general technic of such experiments: It is true that we should be able to give an accurate information to engineers.

As we know for these measurements of the pitting is very important, what size of specimen we should use, because, the unpitted area acts as a cathode. So it is difficult to tell, what must be the right size of the specimen to use, in order to measure actual pit, which will be similar to natural conditions.

Second question which I would like to ask is what does Dr. Dé mean about the real importance of determining the pitting factor; because I do not think that anybody would suggest that using well closed measurements multiplying by the pitting factor will give the reliable results. Can you comment on this please?

C.P. DE: The size of the panel is determined by experimental convenience and at the same time ensuring that the surface area is not too small for reproducible and useful results. The dependence on surface area has been minimised by determining the pit depth distribution instead of measurement of isolated single deepest pit or average of the few deepest pits. The size of the panel used is considered adequate for collection of such data.

The pit depth distribution curve is more representative than the 'pitting factor'. However, determination of pit depth distribution curve is more elaborate and time consuming. 'Pitting Factor' values are, however, more representative than the currently used corrosion rate (ipy) based on loss in weight measurements and provides the engineer a more realistic appraisal of the corrosivity of the environment and corrodibility of the metal.

# KORROSIONSVORHALTEN VON UNGESCHÜTZTEM STAHL IN HAFENWÄSSERN DES DEUTSCHEN KÜSTENGEBIETES

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## ZUSAMMENFASSUNG

Der zeitliche Verlauf der Korrosion von Stahl in natürlichen Hafenwässern von vier namhaften deutschen Häfen wurde in Abhängigkeit von der Lage der Stahloberfläche bezogen auf den Wasserspiegel, die Tidebedingungen und die örtlichen Bedingungen hinsichtlich der Wasserzusam-

ensetzung untersucht.

Initiator der Arbeit war der Ausschuss für Korrosionsfragen der Hafenbautechnischen Gesellschaft, der sich aus Vertretern der zuständigen Behörden, der Stahlbauunternehmen und der Stahllieferanten zusammensetzt.

## DURCHFÜHRUNG DER ARBEITEN

Von einem namhaften deutschen Stahlwalzwerk wurden aus dem Thomasstahl USt 37 aus der gleichen Stahlcharge gewalzte Profile durch Sandstrahlen gereinigt, genau gewogen und hinsichtlich ihrer Dicke vermessen. Die Messpunkte wurden dabei durch Rasterschablonen festgelegt, und es erfolgten an jedem einzelnen Profil, je nach Länge, 2700 bis 4200 Einzelmessungen.

Je sechs Profile wurden 1960 in den vier folgenden Häfen ausgesetzt:

1. in Bremerhaven im Fischereihafen II  
Es handelt sich hier um einen stark verschmutzten Dockhafen mit Brackwasser, in dem die Einsatzbedingungen insofern erschwert sind, als ein Abwassersiel direkt neben dem Prüfstand in das Hafenbecken mündet.
2. in Cuxhaven innerhalb der Brückenkonstruktion der «Alten Liebe», wo eine stark turbulente Brackwasserströmung an der Elbmündung herrscht. Das Wasser ist verschmutzt durch die Cuxhavener Hafenanlagen und das Cuxhavener Siel, das 300 m oberhalb des Prüfstandes mündet.
3. in Kiel im Hafen des Tonnenhofes Kiel-Holtenau in der Nähe der Mündung des Nord-Ostsee-Kanales mit einem sauber erscheinenden klaren Ostseewasser.
4. in Hamburg im Hansahafen mit stark verschmutztem Süßwasser jedoch im Tidegebiet.

Nach zwei Jahren wurden in jedem der Häfen zwei Profile gezogen, gereinigt, mit inhibierter Säure gebeizt, gewogen und an den durch die Schablonen genau festgelegten Messpunkten erneut vermessen. Die Messergebnisse wurden graphisch dargestellt wobei die Dicke der Profile und damit die Tiefe der Abrostung zehnfach vergrößert und die Länge der Profile 50fach verkleinert — also 500fach überhöht — dargestellt wurde.

Es zeigte sich dass die Abrostungskurven von zwei parallel eingesetzten Profilen sich fast völlig deckten.

Die auf diese Weise gewonnenen Abrostungskurven nach 2-, 4- und 6jähriger Einsatzzeit sind in den folgenden Diagrammen zusammengestellt.

Charakteristisch für die Abrostung in Bremerhaven (Diagramm 1) ist das zunächst relativ gleichmässige Fortschreiten

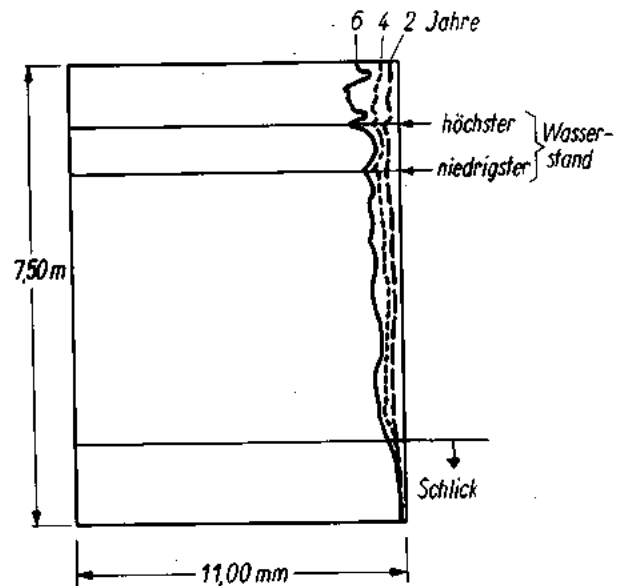


Diagramm 1: Abrostung von ungeschütztem Stahl im Fischereihafen Bremerhaven (Dockhafen) nach zwei-, vier- und sechsjährigem Einsatz (500fache Überhöhung der Darstellung).

der Korrosion, die in der Spritzwasserzone, also oberhalb des normalen Wasserspiegels ihre grösste Tiefe erreichte. In Höhe des normalen Wasserstandes blieb ein «Berg» mit deutlich verringertem Angriff zurück. Dieser örtlich deutlich geschwächte Angriff wird auf den im Hafenwasser vorhandenen Ölfilm zurückgeführt.

Wie nicht anders zu erwarten, war die Stahloberfläche in der Bewuchs- und in der Schlickzone nach Reinigung völlig blank, so dass das Bild einer «Säurekorrosion» vorlag. Es

herrsichten offensichtlich unter dem Bewuchs und im Schlack anaerobe Bedingungen.

In Cuxhaven zeigen die Abrostungskurven nach 2-, 4- und 6 jährigem Einsatz in vergleichbaren Bereichen eine gleichmässige Progression (Diagramm 2). Der stärkste Angriff

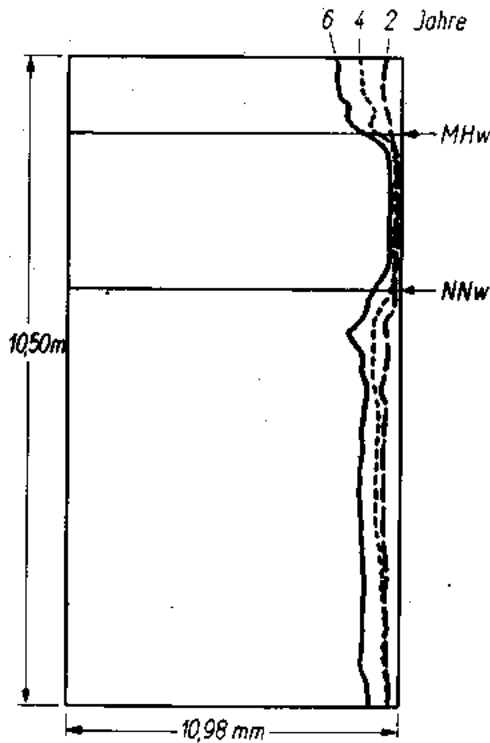


Diagramm 2: Abrostung von ungeschütztem Stahl in der Elbmündung bei Cuxhaven.

findet in der Spritzwasserzone über dem mittleren Tidenhochwasser und ein praktisch gleichmässiger Angriff findet unter dem Tidenniederwasser bis zum Ende des Profils statt, was bei der sehr turbulenten Strömung unter der Brücke der «Alten Liebe» nicht verwunderlich ist. Auffallend ist hier die erheblich schwächere Korrosion innerhalb des Tidengebietes, die wir auf starke Ölablagerungen zurückführen können. Ein verstärkter Angriff in der Belüftungszone unterhalb des Tidenniederwassers, wo eine starke Luftwirkung bei Fehlen des Schutzfilms auftritt, konnte beobachtet werden.

Bemerkenswert ist das Auftreten dicker Rostblasen von 20 bis 30 mm Durchmesser innerhalb der Spritzwasserzone. Beim Anschlagen dieser Blasen trat eine schwarz getrübe Flüssigkeit aus, die im wesentlichen aus Chloriden des Eisens bestand und stark sauer reagierte (pH-Wert bis 3,8). Hierunter befanden sich, wie nicht anders zu erwarten, tiefe Korrosionsnarben.

Die Belüftungszone mit der stärksten Korrosion der Profile trug einen erheblichen Seepockenbewuchs. Die Bewuchszone hingegen zeigte bevorzugt Muschelbewuchs und nur vereinzelt Seepocken. Unter dem schichtförmig aufgebauten Rost der Bewuchszone und in der Schlackzone zeigte sich nach Entfernen der Beläge metallisch blanker Stahl; es herrschten dort anaerobe Bedingungen vor.

Die in Kiel nach zwei, vier und sechs Jahren erhaltenen Abrostungskurven (Diagramm 3) vertiefen in den entsprechenden Beanspruchungszonen wiederum sehr gleichartig. Auffallend war, dass der Angriff in der Atmosphäre, in der Höhe des normalen Wasserspiegels und im Schlack praktisch gleich stark fortschritt. In der Spritzwasserzone und in der Bewuchszone war der Angriff wesentlich stärker und nahm

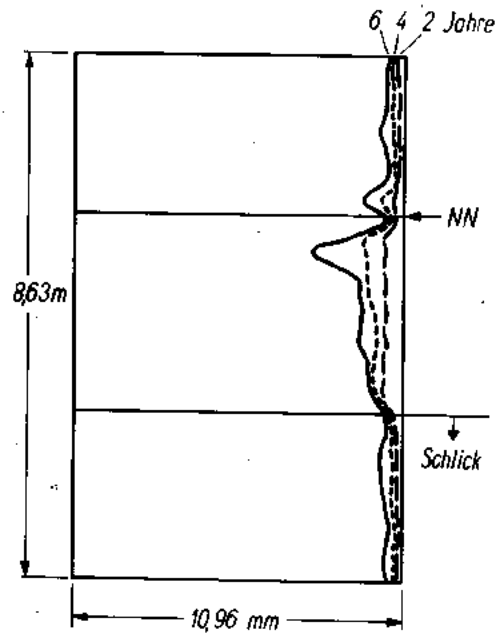


Diagramm 3: Abrostung von ungeschütztem Stahl in der Kieler Förde (Ostseewasser).

ein Vielfaches seiner Grösse in der Belüftungszone kurz unterhalb des Wasserspiegels an.

In der atmosphärischen Zone zeigte sich ein körniger Rostbelag, der mit Eintritt in die Spritzwasserzone dicker wurde, leicht abblätterte, und unter dem sich tiefe Narben fanden. In der schmalen Zone des normalen Wasserspiegels war nur ein geringer Angriff unter einem kaum erkennbaren Ölfilm feststellbar. Die anschliessende Belüftungszone zeigte unter unwesentlichem Bewuchs dicken bräunlichgrünlichen stark abblätternden Rost und darunter tiefe Narben. Der Bewuchs in der anschliessenden Zone bestand in erster Linie aus Muscheln und Seepocken. Unter dem Bewuchs war dicker schwarzbrauner, schichtförmig aufgebauter Rost, unter dem das Eisen blank vorlag. In der Schlackzone fand sich ebenfalls blanker Stahl.

Im Hamburger Hansahafen (Diagramm 4), der im Tidegebiet liegt, schritt der Angriff nach 2, 4 und 6 Jahren ausserordentlich gleichmässig fort. Im Bereich der Atmosphäre musste die stärkste Abtragung des Stahles, die über die ganze Länge gleichmässig verlief, beobachtet werden. Im Tidegebiet ging der Angriff auf einen Bruchteil zurück und erreichte im Abschnitt unterhalb des normalen Niederwassers wieder grösseren Umfang. In diesem ständig getauchten Bereich ging die Geschwindigkeit des Angriffs mit zunehmender Tiefe linear zurück.

In der atmosphärischen Zone trug der Stahl einen dunkelbraunen, feinschuppigen Rostbelag, unter dem sich zahllose kleine flache Rostnarben befanden. In der Tidenzone fand sich ein gleichmässig schwarzbraun-grünlicher, etwas ölig erscheinender Belag. Der Stahl darunter schien kaum angegriffen zu sein. Die nur schmale Belüftungszone hob sich aus dem Gesamtbild des Profils stark ab; sie wies einen blasenförmigen hellbraunen Rostbelag auf, unter dem sich Korrosionsnarben unterschiedlicher Grösse, jedoch beträchtlicher Tiefe befanden. In der Bewuchszone zeigte sich ein schleimiger bis algenförmiger Bewuchs auf bräunlichen bis schwärzlichen Rostschichten. Das darunterliegende Material zeigte nur relativ kleine Korrosionsnarben.

Der Stahl erschien in diesem Fall in der Bewuchszone bräunlich angerostet; Es herrschten keine anaerobe Bedingungen. In der Schlackzone zeigte sich nach Entfernung des Schlicks grossenteils metallisch blankes Eisen; Hier herrschten hingegen wieder anaerobe Bedingungen.

ZUSAMMENSTELLUNG DER DURCHSCHNITTLICHEN  
ABROSTUNGSWERTE IN DEN VERSCHIEDENEN ZONEN  
IN DEN EINZELNEN HAFENWÄSSERN.

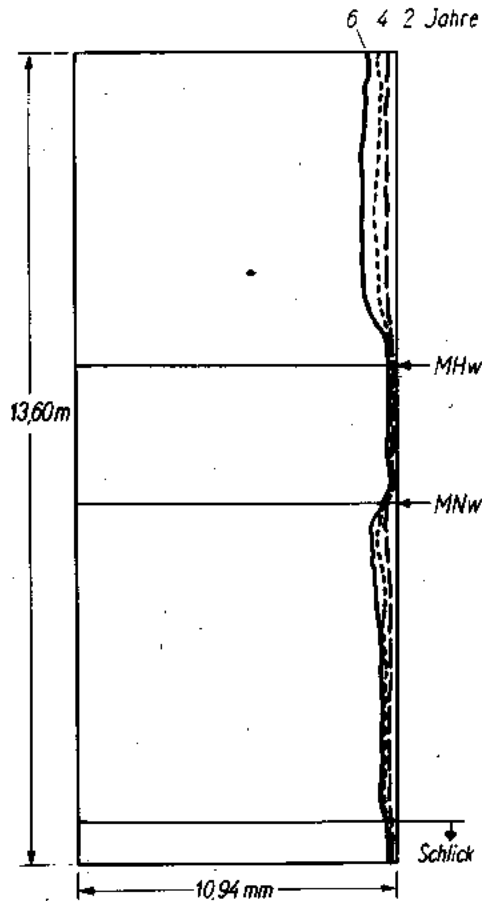


Diagramm 4: Abrostung von ungeschütztem Stahl im Hamburger Hafen.

Zur besseren Übersichtlichkeit wurden die nach 6jähriger Beanspruchung gewonnen Abrostungskurven schematisiert und für die vier Häfen derart gegenübergestellt, dass NN bzw. die Höhe des mittleren Wasserstandes im Diagramm 5 in gleicher Höhe liegen. In den Häfen Hamburg und Cuxhaven zeigten die Profile im Tidebereich den wenig angegriffenen einem Tafelberg ähnlichen Bezirk, der auf abgelagerte Öl- und inhibierende Schmutzstoffe zurückzuführen ist. In Cuxhaven fiel dabei gegenüber Hamburg noch ein etwas stärkerer Angriff in der Belüftungszone auf. Im tidefreien Ostseehafen Kiel machte sich ein starker Angriff im Spritzwasserbereich und ein ausserordentlich starker Angriff im Belüftungsbereich bemerkbar. Im tidefreien Fischereihafen von Bremerhaven, der schmutziges Brackwasser führt, verlief der Angriff über die ganze Länge relativ gleichmässig nach unten zu abnehmend mit einem etwas verzögerten Angriff im Bereich des normalen Wasserstandes.

Setzen wir den Angriff in der Atmosphäre jeweils = 100%, so betrug die Abrostung in der Tidezone in Hamburg und in Cuxhaven nur jeweils etwa 20%. In Kiel hingegen musste beobachtet werden, dass oberhalb des normalen Wasserstands in der Spritzwasserzone der Angriff dann 280% und in der Belüftungszone 600% betrug.

Die durchschnittlichen Angriffstiefen in den einzelnen Zonen der vier Häfen sind in der folgenden Tabelle wieder gegeben:

Abrostung in mm nach sechsjährigem Einsatz (abgerundete Werte)				
	Bremerhaven (Dockhafen)	Cuxhaven	Hamburg	Kiel
Atmosphärische Zone	1,1	2,1	0,9	0,6
Spritzwasserzone	1,6	2,1	1,1	1,4
Wasserpiegel bzw. Tidebereich	0,8	0,4	0,2	0,5
Belüftungszone	1,6	1,6	0,9	3,0
Bewuchszone	1,0	1,2	0,5	1,3
Schlickzone	0,3	—	0,2	0,6

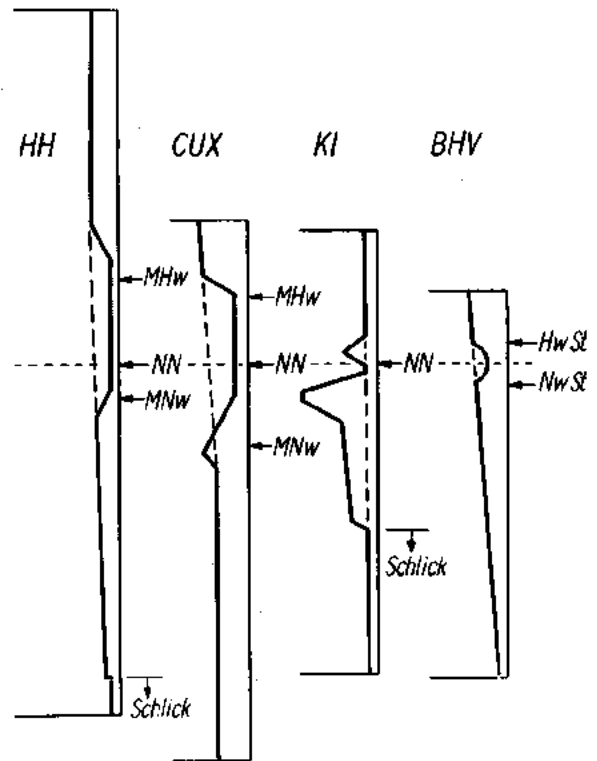


Diagramm 5: Gegenüberstellung der schematisierten Abrostungskurven von den Häfen Hamburg, Cuxhaven, Kiel und Bremerhaven (gleicher Massstab der Darstellung).

Gleichzeitig mit den Stahlprofilen wurden kleine Eisenbleche in verschiedenen Tiefen den gleichen Wasserbedingungen ausgesetzt. Ein Teil dieser Bleche wurden isoliert montiert, während die übrigen Bleche elektrischen Kontakt miteinander hatten. Aus diesen Versuchen konnte erkannt werden, dass der Angriff an den isolierten Blechen unter rein chemischen Gesichtspunkten ablief, während bei den Versuchsblechen mit metallischem Kontakt die Korrosions-

geschwindigkeit durch Bildung von Konzentrations-elementen beeinflusst wurde. Diese Konzentrationselemente bilden sich in erster Linie infolge unterschiedlicher Temperatur, Salzgehalte und Sauerstoffgehalte in verschiedenen Wassertiefen.

Weiterhin zeigten die Versuche deutlich den Einfluss des Bewuchses: Bleche, die zu Beginn der Bewuchsperiode getaucht wurden, zeigten einen erheblich stärkeren Angriff, als Bleche, die erst am Ende der Bewuchsperiode eingebracht wurden. Diese Ergebnisse scheinen sich auch nicht zu ändern, wenn die Proben weit über ein Jahr getaucht bleiben. Die Untersuchungen darüber sind noch nicht abgeschlossen.

Parallel zu den Korrosionsversuchen mit den Stahlprofilen wurden in den vier Häfen periodisch Wasserproben entnommen und chemisch eingehend untersucht.

Etwa viermal in jedem Jahr wurden Proben in Höhe des Wasserspiegels, in etwa  $\frac{1}{2}$  m Tiefe und 0,2 m über dem Grund genommen. Eine zunächst durchgeführte Probenahme in jeweils 2, 4, 6 und 8 m Wassertiefe wurde eingestellt, da die Analyseergebnisse der in größeren Tiefen genommenen Proben keine Unterschiede zeigten.

In den Tidehäfen wurden die Proben jeweils bei auflaufendem Wasser, bei Hochwasser, bei ablaufendem Wasser und bei Niederwasser genommen. Zunächst erfolgte die Probenahme durch Tauchlote, die in geeigneter Tiefe geöffnet wurden. Wegen der stark turbulenten Strömung an der «Alten Liebe» in Cuxhaven führte dieses Verfahren jedoch zu erheblich technischen Schwierigkeiten, so dass späterhin ein Schlauch an einem Lot abgelassen wurde und das Wasser mit einer Kreiselpumpe aus entsprechenden Tiefen abgepumpt werden konnte.

Es wurde dabei derart vorgegangen, dass der Sauerstoffgehalt elektrometrisch mit einer vom Wasser durchströmten Sonde während der Probenahme bestimmt wurde. Vergleichende Sauerstoffbestimmungen nach WINKLER ergaben die gleichen Werte. Der pH-Wert, die Leitfähigkeit, die freie Kohlensäure, der Gehalt an Schwefelwasserstoff, Nitrat, Nitrit, Ammonium, Phosphat, der Kaliumpermanganat-Verbrauch sowie das Säure-Bindungsvermögen wurden an Ort und Stelle feldmässig bestimmt. Weitere 20 Einzelbestimmungen von jeder einzelnen Wasserprobe wurden später in der BAM durchgeführt.

Auf die Einzelergebnisse einzugehen — es sind etwa 12 000 Analysendaten — verbietet leider der Rahmen dieses Referates. Die Auswertung dieser Ergebnisse erfolgte vornehmlich graphisch, da dies die einzige Möglichkeit ist, System in eine grosse Anzahl von Einzelergebnissen bringen zu können.

Es sei lediglich an Hand von den drei Diagrammen (6, 7 und 8) demonstriert, wie ausserordentlich stark die einzel-

Extrem- und Mittelwerte aller Proben der 4 Hafenswässer

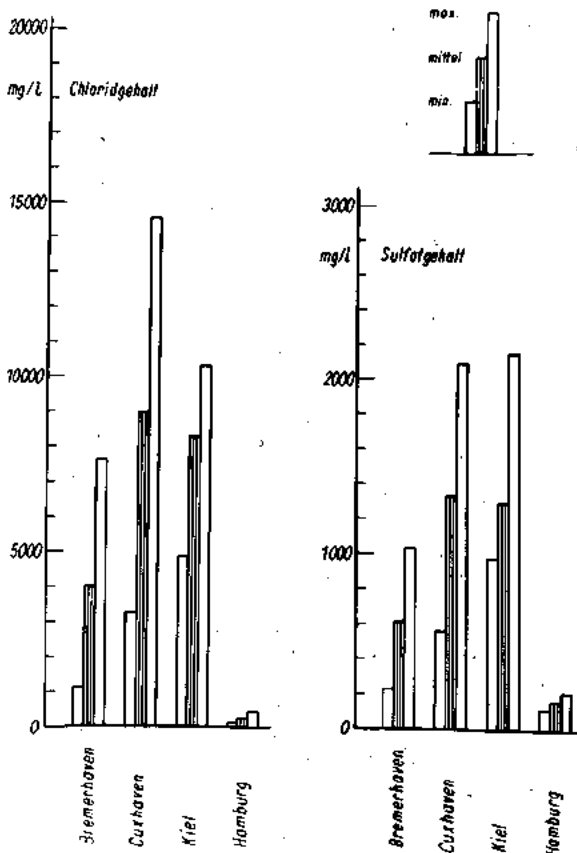


Diagramm 6: Stark schwankende Wasserzusammensetzung bei den einzelnen Probenahmen und in den verschiedenen Häfen.

Extrem- und Mittelwerte aller Proben der 4 Hafenswässer

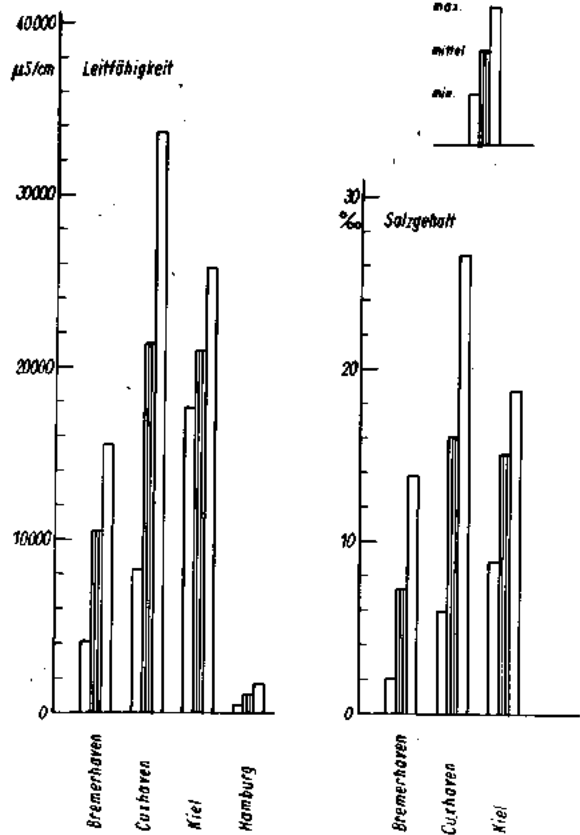


Diagramm 7: Stark schwankende Wasserzusammensetzung bei den einzelnen Probenahmen und in den Häfen.

nen Messwerte an jedem einzelnen Hafen streuen, so dass Streuungen im Verhältnis 1:4 bis 1:5 keine Seltenheit sind. Es ist deshalb unmöglich, auf Grund einer einzelnen Analyse eine Aussage über den Charakter des Wassers eines Hafens machen zu wollen.

Besonders beachtenswert erscheint die Tatsache, dass die Wasserzusammensetzung in Kiel und Cuxhaven sehr ähnlich ist, dass jedoch einerseits der Grad der Abrostung und andererseits die Verteilung der maximalen Korrosionsgebiete an den Profilen in den beiden Häfen ganz ausserordentlich dif-



Extrem- und Mittelwerte aller Proben der 4 Hafenwässer

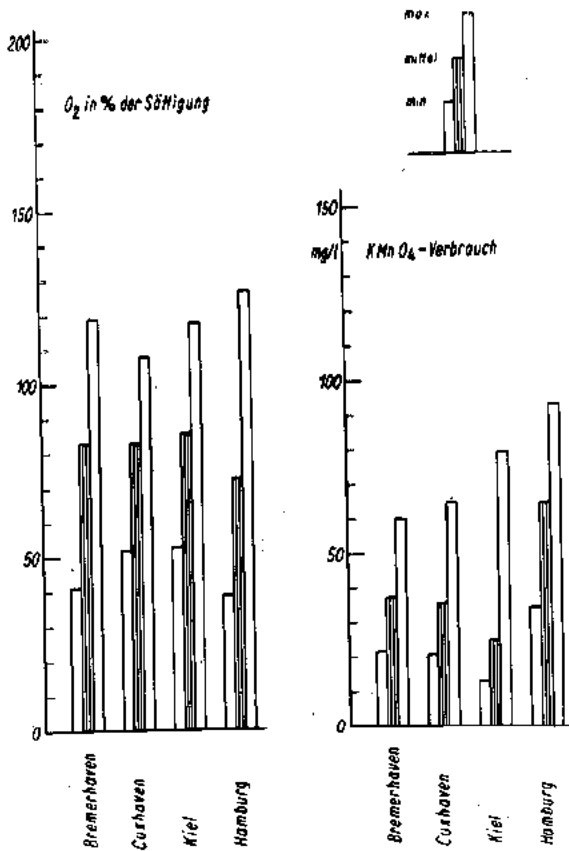


Diagramm 8: Stark schwankende Wasserzusammensetzung bei den einzelnen Probenahmen.

ferieren. Durch diese Versuche wurde die Vermutung bestätigt, dass allein an Hand von Wasseranalysen keine Aussagen über die mutmassliche Rostungsgeschwindigkeit von Stahl in natürlichen Wässern gemacht werden können.

Es sei in dem Zusammenhang noch erwähnt, dass zugleich mit den Versuchen mit kleinen Blechen bakteriologische Proben genommen und untersucht wurden. Ausser den seit langem bekannten sulfatreduzierenden Bakterien, die in geringerer Anzahl vorhanden waren, konnten vor allem säurebildende (Wasserstoff und CO<sub>2</sub> produzierende) Bakterien erkannt und isoliert werden. Die mit diesen Bakterien durchgeführten Korrosionsversuche zeigten eine vielfache Korrosionsgeschwindigkeit gegenüber Untersuchungen mit sulfatreduzierenden Bakterien. Über diese Ergebnisse, die teilweise schon veröffentlicht sind, wird an anderer Stelle publiziert.

Zusammenfassend können wir feststellen, dass allein an Hand chemischer Untersuchungen keine Rückschlüsse auf die Geschwindigkeit der Korrosion des Stahls in natürlichen Wässern gezogen werden können.

Die für die Erstellung und Erhaltung von Stahlwasserbauten verantwortlichen Stellen können aus den Untersuchungen die Konsequenz ziehen, dass die Korrosionsgeschwindigkeit des Stahls in verschiedenen Hafenwässern sehr unterschiedlich abläuft und dass die Verteilung der Korrosion mit maximalen Tiefen in zum Teil sehr eng begrenzten Zonen grösste Beachtung verdient.

Aussagen über die Verteilung der Korrosion — das etwaige Auftreten und die Lage von Maxima — können oft mühelos aus Untersuchungen von vorhandenen Stahlbauten (Spundwänden) gemacht werden.

Aufgabe des Bauingenieurs ist es dann, zu verhüten, dass maximale Biegemomente mit den Gebieten der maximalen Korrosion zusammenfallen (Diagramm 9) oder zu bewirken, dass die durch Korrosion am meisten gefährdeten Bereiche besonders geschützt oder verstärkt werden.

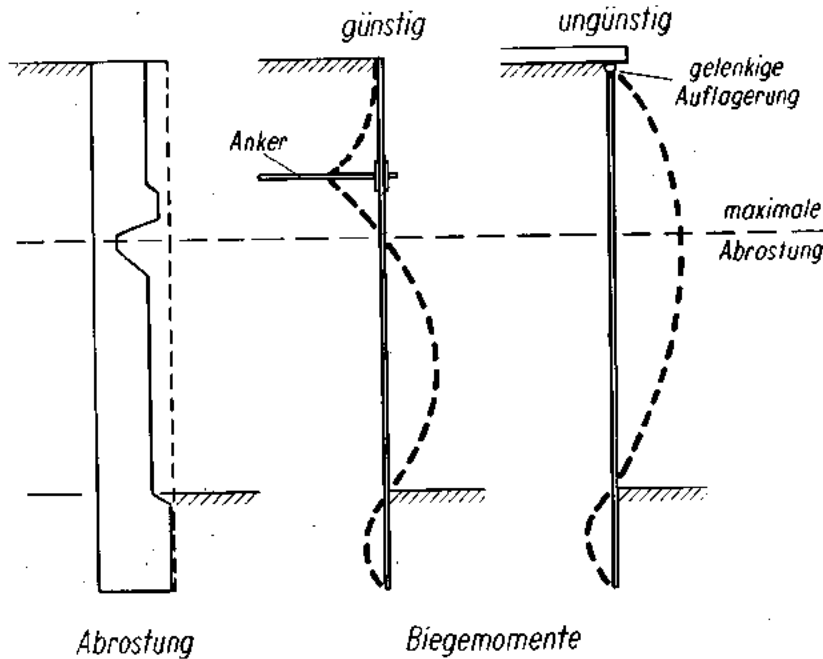


Diagramm 9: Lage der möglichen Biegemomente in Bezug auf den Bereich maximaler Korrosion.

Dr DETERMANN (Deutschland): Ich möchte zu dem Bericht, den Herr Dr. Ladeburg gegeben hat, noch einige Ergänzungen machen. Herr Ladeburg hat gezeigt, dass die Korrosion in der Wasserwechselzone, also zwischen Hoch- und Niedrigwasser an einer Spundwand besonders gering und unter der Niedrigwasserlinie gross ist. Die Ursache für diese Erscheinung ist meines Erachtens durch grossflächige Belüftungselemente, die sich an der Spundwand bilden, gegeben.

Abb 1 zeigt das Potential einer Spundwand in Abhängigkeit von dem Wasserstand. Die Vergleichselektrode schwimmt in ca 30 cm Abstand von der Spundwand an der Wasseroberfläche. Bei Niedrigwasser misst man ein niedriges, bei Hochwasser ein hohes Potential, weil die Tidenzone bei der jeweiligen Trocknung durch den Luftsauerstoff veredelt wird. Bild 1 ist über den Verlauf einer Tide gewonnen. Auf Bild 2 werden nun Messergebnisse bei konstantem ungewöhnlich hohem Wasserstand dargestellt. Die Elektrode schwamm nicht wie bei Bild 1 auf dem Wasser, sie wurde vielmehr an der Spundwand entlang in die Tiefe abgesenkt. Auch hier finden wir eine starke Veredlung von der Niedrigwasserlinie bis zur Hochwasserlinie hin. Bei dieser starken Veredlung in der Wasserwechselzone ergibt sich hier also eine grosse kathodische Fläche, die zwangsweise zu einer starken Korrosion unter der Niedrigwasserlinie führt.

Die Korrosionszone liegt dicht unter der Niedrigwasserlinie, wenn die Leitfähigkeit des Wassers gering ist. Das Wasser in Hamburg ist Süsswasser. Bild 3 zeigt Messergebnisse, die in Cuxhaven bei höherer

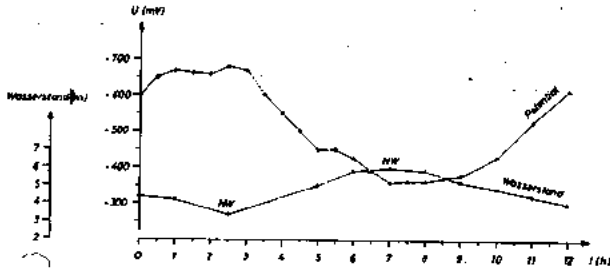


Abb. 1: Elektrochemisches Potential einer Spundwand im Hamburger Hafen in Abhängigkeit vom Wasserstand. Messung mit einer  $Cu/CuSO_4$ -Elektrode

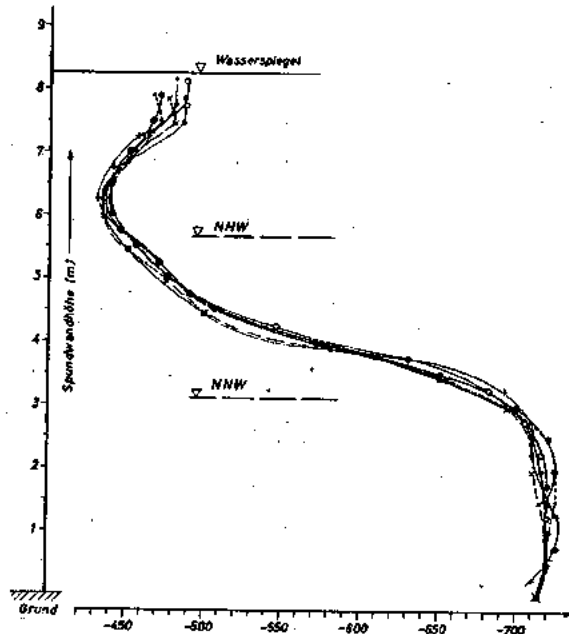


Abb. 2: Elektrochemisches Potential entlang einer Spundwand im Hamburger Hafen. Abstand zwischen der  $Cu/CuSO_4$ -Elektrode und der Wand: 30 cm.

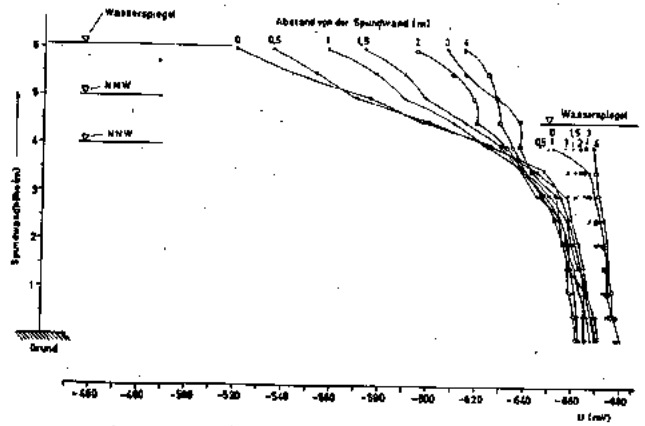


Abb. 3: Elektrochemisches Potential senkrecht entlang einer Spundwand im Amerika Hafen in Cuxhaven. Einfluss des Abstandes der Messzelle von der Spundwand (0-4 m).

Leitfähigkeit des Wassers gewonnen wurden. Hier sind mehrere Messreihen in verschiedenen Abständen von der Spundwand durchgeführt. In grösseren Abständen werden Mischpotentiale gemessen. Für die Stärke der Korrosion sind die Messwerte dicht an der Spundwand entscheidend. Wegen der höheren Leitfähigkeit des Wassers ist die Korrosion unter der Niedrigwasserlinie aber nicht auf eine so schmale Zone wie in Hamburg beschränkt. Die Ursache für die Korrosion ist aber auch hier die grosse kathodische Fläche in der Korrosion, denn die Veredlung durch den Luftsauerstoff vermindert. Ein Althellmittel ist allerdings durch diesen Anstrich nicht gegeben, denn das den Korrosionsstrom erzeugende Belüftungselement bildet sich auch an gestrichenen Stahlblechen aus.

Auf Bild 4 sind Messergebnisse an einem gestrichenen Schwimm-

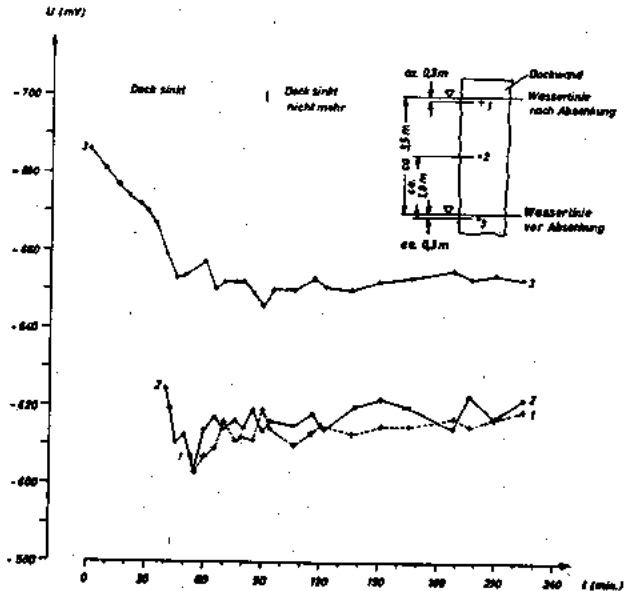


Abb. 4: Elektrochemisches Potential verschiedener Bereiche eines Schwimmdocks während des Absenkens.

dock gezeigt. An dem Schwimmdock sind an den Messstellen 1, 2 und 3 je eine Messzelle befestigt. Bei der Absenkung des Docks findet man an der Messstelle 1 laufend eine Veredlung, weil die Flächen über dieser Messstelle, die ursprünglich an der Luft gelegen hatten, also veredelt waren, mit gemessen werden. Nach etwa 40 Minuten taucht die Messstelle 2 ein, hier ergibt sich ein wesentlich edleres Potential und nach etwa 50 Minuten zeigt sich dasselbe bei der Messstelle 3.

Nach der Absenkung wurde das Potential noch mehrere Stunden gemessen. Man sieht, dass sich das Potential an allen Messpunkten langsam wieder veredelt. Nach etlichen Stunden liegen alle Werte auf der Höhe, die die Messstelle 3 zu Beginn des Versuchs hatte. Abb. 5 zeigt die Wirkung des Belüftungselementes an einem Schiff. Solange

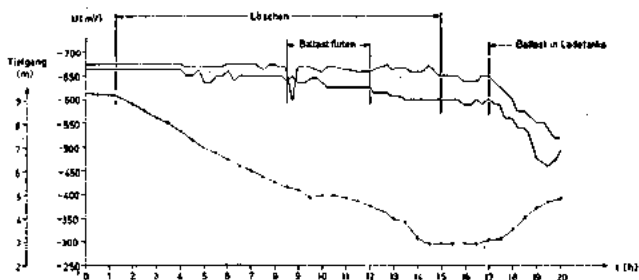


Abb. 5: Elektrochemisches Potential an der Aussenhaut eines Tank-schiffes 30 cm unter der Wasseroberfläche während des Löschens und Ballastwasser-Flutens im Hamburger Hafen. Abstand zwischen der  $Cu/CuSO_4$ -Elektrode und dem Schiff: 30 cm.

das Schiff im Hafen entladen wird, zeigt sich keine Veränderung des Potentials der Aussenhaut, da die aus dem Wasser austauchenden Flächen ja nicht mitgemessen werden. Nach ca 17 Stunden wurde Ballastwasser in die Tanks gelassen und sofort zeigt sich eine starke Verdünnung an den frisch eingetauchten Aussenhautflächen. Dies Ergebnis zeigt sich sowohl bei Süß- wie bei Seewasser. Durch das Ein- und Aus-tauchen ergibt sich also ein Belüftungselement, das die Korrosion fördert.

Dr LADEBURG (Deutschland): Ich habe weiter dazu nichts zu sagen, interessant war, dass die Versuche nicht rein theoretisch beschrieben wurden, und dass auch Versuche mit gestrichenen Stahlobjekten durchgeführt wurden.

B. HEUZE (Frankreich): Ich möchte wissen, ob der Unterschied zwischen den aufgenommenen Kurven bei Hoch- und Niedrigwasser betrachtet worden ist und in welcher Richtung sich dieser Unterschied auswirkte.

Dr DETERMANN: Bei Hochwasser ist das Potential edler, bei Niedrigwasser unedler, ich glaube, dass dies auf die Belüftung der grossen Flächen zwischen der Niedrig- und Hochwasserlinie zurückzuführen ist. Durch die Belüftung wird die Fläche kathodisch.

J. CARSON (Canada): Ich möchte fragen, ob diese erwähnte sehr kleine Korrosion in dem Tidengebiet, die besonders in zwei Häfen betrachtet wurde, auf Ölfilmen zurückzuführen ist, die als schützende Überzüge dienten.

Dr LADEBURG: Wir sind geneigt diese starke Änderungen in Höhe der Wasserwechselzone also in Höhe des Tidengebietes auch weitestgehend auf Ablagerungen von Ölfilmen und anderen inhibierenden Schmutzstoffen, zurückzuführen.

Vermutlich auch zum Teil durch diese Ablagerungen wird erreicht dass die Unterschiede in den Potentialen über die ganze Spundwandhöhe auftreten. Die Ausführungen über Dr. Determanns Messungen scheint das auch zu bestätigen.

Prof. CHAUDRON (Frankreich): Haben Sie die Gelegenheit gehabt, Platten in Schleusen zu untersuchen. Gab es keine entsprechenden Effekte bei Schleusenplatten?

Dr. LADEBURG: Wir wurden mit der Aufgabe der Untersuchung betraut, als die Korrosionsversuche bereits angesetzt worden waren. Es bestanden also bereits 4 Prüfstände als wir die Betreuung übernommen hatten. Wir hatten also keinen Einfluss auf die örtliche Erstellung der Stände und ich kann daher auch nur Auskünfte geben über die Stellen, die wir vorgefunden haben. Es wäre vernünftig gewesen in Bremerhafen in normalen Tidengebieten Untersuchungen durchzuführen direkt an Schleusentoren usw. Leider hatten wir keine Möglichkeit dazu.

Die Versuchen sind etwas ungeschickt angesetzt worden.

**Séance - Meeting - Sitzung - Συνεδρίαση**  
**21.9.1968**

**Présidence - Presidency**  
**Präsidium - Προεδρείον**

**Prof. R. COLLÉE (Belgique)**

**Prof. P. SAKELLARIDIS (Grèce)**

**Dr. Ing. L. KENWORTHY (Great Britain)**

# SUR LE COMPORTEMENT DE QUELQUES MATERIAUX DANS L'EAU DE MER

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## RÉSUMÉ

A l'aide d'une analyse électrochimique on a examiné le comportement de différents matériaux métalliques dans l'eau de mer artificielle pour mettre en évidence l'influence de paramètres tels que la température, l'aération et l'agitation de l'électrolyte sur la résistance à la corrosion.

On donnera les résultats obtenus sur les matériaux suivants:

aciers inoxydables AISI 316,  
alliage de nickel Hastelloy C;  
cuivre électrolytique, Cu90-Ni10, Cu70-Ni30.

Pour les aciers inoxydables et les alliages de nickel on a particulièrement cherché à mettre en évidence, des courbes de polarisation anodique, la résistance de ces matériaux à la

corrosion par piqûres dans les conditions expérimentales choisies, par la détermination de la valeur du potentiel critique de rupture de la passivité. Sur ce paramètre on a considéré l'influence de l'aération, de l'agitation de l'électrolyte, de la température et de la vitesse d'imposition de la tension.

La résistance à la corrosion du cuivre et de ses alliages a été examinée par une analyse des courbes de polarisation. En considérant que le mécanisme de l'attaque dans le milieu en examen s'explique par l'action dépolarisante de l'oxygène, on a enregistré aussi les courbes de polarisation cathodique.

Dans les conditions expérimentales choisies, les alliages cuivre-nickel offrent une résistance à la corrosion supérieure à celle du cuivre.

La résistance à la corrosion des matériaux dans l'eau de mer est le facteur qui principalement conditionne l'emploi de métaux et alliages dans la construction d'installations dans ce milieu (1-7).

L'importance de ce problème est témoignée par l'usage de l'eau de mer dans des échangeurs de température, pour la production d'énergie électrique dans les usines maremotrices et pour des installations produisant de l'eau douce de la mer.

Les caractéristiques d'agressivité de l'eau de mer, considérée comme une solution à une élevée conductibilité contenant des chlorures, peuvent résulter agrandies par des changements de composition par la présence d'oxygène dissous, de microorganismes et macroorganismes; on a le même effet à une température élevée et en condition d'agitation.

Plusieurs auteurs ont étudié les mécanismes de la corrosion des matériaux métalliques dans l'eau de mer (8) (9) et on a élaboré des techniques différentes pour l'étude, le contrôle et la prévention des phénomènes d'attaque. A côté des expériences faites sur des installations pilote (10) ou dans la production (11) on trouve des méthodes accélérées (12) (13) et un plus grand emploi des techniques électrochimiques pour l'étude du comportement soit d'aciers inoxydables (14, 15, 16, 17) soit d'alliages à base de nickel ou de cuivre (18).

Dans ce travail, à l'aide d'une analyse de paramètres électrochimiques, on examine le comportement de différents matériaux métalliques dans l'eau de mer artificielle pour mettre en évidence l'influence de paramètres tels que la température, l'aération et l'agitation de l'électrolyte sur la résistance à la corrosion.

## TECHNIQUES EXPÉRIMENTALES

On a examiné les matériaux suivants:

acier inoxydable 18 Cr, 8 Ni au Mo - type AISI 316;  
Hastelloy C;  
cuivre électrolytique non recuit, pureté 99,9;  
cupronickel - CuNi 10; CuNi 30.

Les échantillons en plaquettes de 35 × 15 mm. épaisseur de 1 à 3 mm., utilisés comme reçus par les producteurs, étaient enrobés dans une résine afin de permettre l'exposition d'une face au milieu d'attaque. Une baguette métallique à vis placée derrière assurait le contact électrique. La fermeture à un tuyau de verre était obtenue à l'aide d'épais anneaux en teflon. La surface des électrodes ainsi obtenues était traitée au papier émeri n. 240, tandis que pour le cuivre la préparation de la surface était accomplie par un décapage en HNO<sub>3</sub>-H<sub>2</sub>O 1 : 3 pendant 5 minutes à température ordinaire. Les traitements étaient effectués immédiatement avant les essais et complétés par un dégraissage soigné des électrodes au moment de l'immersion dans la solution. Cette solution était formée de l'eau de mer artificielle préparée, selon la normalisation ASTM D 1141-50 T, avec des substances pures et de l'eau déionisée (Tableau 1). La valeur du pH de la solution était

TABLEAU 1  
EAU DE MER ARTIFICIELLE SELON ASTM D 1141-50 T

Composants	Concentration g/l
NaCl	24,53
MgCl <sub>2</sub> · 6 H <sub>2</sub> O	11,11
Na <sub>2</sub> SO <sub>4</sub>	4,09
CaCl <sub>2</sub>	1,16
KCl	0,695
NaHCO <sub>3</sub>	0,201
KBr	0,101
SrCl <sub>2</sub> · 6 H <sub>2</sub> O	0,042
H <sub>3</sub> BO <sub>3</sub>	0,027
NaF	0,003

porté à 8,2 avec NaOH 0.1 N, sous contrôle potentiométrique. Les conditions de désaération étaient obtenues par un barbotage prolongé d'azote dans la solution. Dans d'autres mesures la solution était maintenue en équilibre avec le milieu ou saturé avec de l'air. L'agitation de l'électrolyte était obtenue avec un agitateur magnétique à une vitesse réglable. On a effectué des essais en repos, à 100 et 200 tours par minute. Les mêmes essais ont été effectués à des températures de 25, 50 et 70°C. La solution était maintenue à des températures fixées ( $\pm 0,1^\circ\text{C}$ ) à l'aide d'une circulation d'eau thermostatée dans le manteau de la cellule de mesure. La cellule était à compartiments séparés par des sections de verre fritté.

Les électrodes étaient laissées à contact avec la solution pendant une heure avant de commencer les mesures de polarisation. En partant de la valeur de potentiel acquis, on a enregistré les courbes de polarisation par points en changeant le potentiel de 30 mV toutes les deux minutes. Les valeurs du courant étaient enregistrées avant l'imposition d'une nouvelle valeur du potentiel. On a employé un potentiostat électronique AMEL mod. 555, tandis que l'enregistrement des potentiels par rapport à l'électrode à calomel saturé a été effectué avec un voltmètre électronique à une haute impédance.

### RÉSULTATS EXPÉRIMENTAUX

L'exposition des résultats expérimentaux est effectuée séparément pour l'acier inoxydable et l'Hastelloy C d'un côté et pour les matériaux à base de cuivre de l'autre côté. La raison de cette subdivision est justifiée soit à cause des différentes compositions des alliages soit à cause de la différence

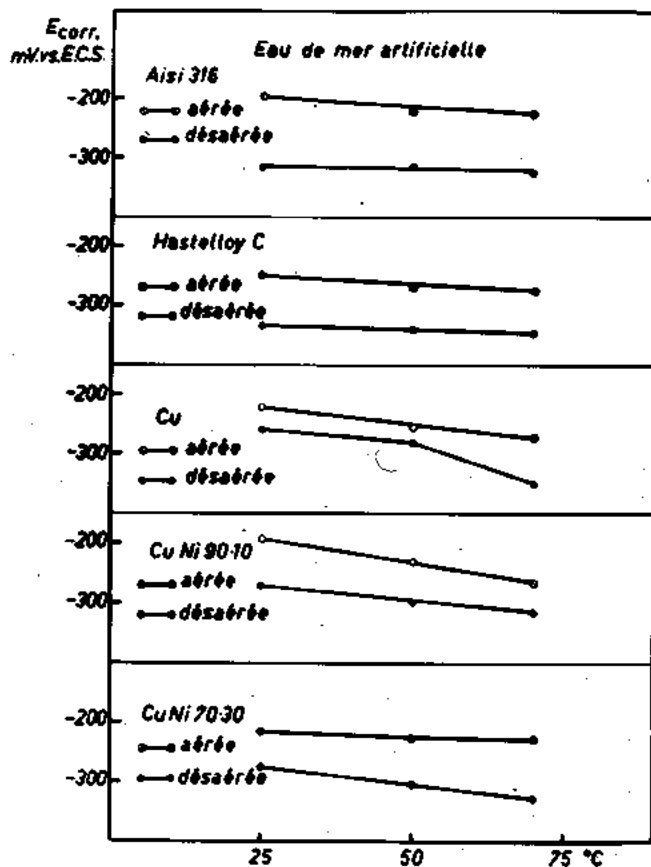


Fig. 1

des types d'attaque corrosive des alliages en examen dans l'eau de mer.

Pour l'AlSi 316 et l'Hastelloy C on a particulièrement cherché à mettre en relief des courbes de polarisation anodique la résistance de ces matériaux à la corrosion par piqûres dans les conditions expérimentales choisies, à l'aide de la détermination de la valeur du potentiel critique de rupture de la passivité. On a considéré l'influence de l'aération, de l'agitation de l'électrolyte et de la température sur ce paramètre et sur la valeur du potentiel de corrosion. A la Figure 1 on montre les valeurs de potentiels de corrosion en fonction de la température.

Pour les deux matériaux cités on peut observer que l'augmentation de la température portée à des valeurs moins nobles, tandis que l'effet de l'oxygène dissous, en donnant lieu à un déplacement des potentiels à des valeurs plus nobles, est très évident.

Une comparaison de la résistance à la corrosion par piqûres des deux matériaux cités peut être obtenue des courbes de polarisation, dont un exemple est montré à la figure 2. La

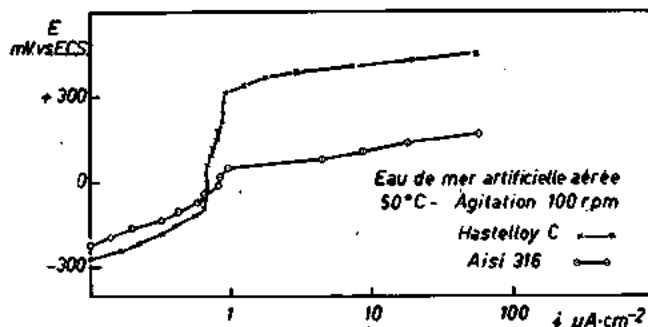


Fig. 2

valeur du potentiel critique de piqûres paraît plus noble à mesure que la probabilité de l'attaque par piqûres, en condition de corrosion libre, paraît plus faible. C'est-à-dire qu'on pourra employer d'une façon plus convenable les matériaux métalliques cités dans des milieux où ils atteignent une valeur de potentiel moins noble que le potentiel de rupture de la passivité. Les déplacements des potentiels critiques en fonction de la température, dans les différentes conditions expérimentales choisies, sont montrés à la figure 3. En augmentant la température les potentiels critiques se déplacent vers des valeurs moins nobles ce qui Leckie et Uhlig ont démontré en solution de NaCl 0.1 N sur acier AlSi 304 (19) et Defranoux sur des différents aciers dans l'eau de mer artificielle (14). Ce phénomène correspond à l'augmentation de la probabilité d'une attaque par piqûres et il est justifié par l'augmentation de la vitesse des réactions électrochimiques avec la température. On peut observer que la résistance de l'Hastelloy C à l'attaque par piqûres est plus grande de celle de l'AlSi 316 et elle n'est que faiblement influencée par l'augmentation de la température. Pour l'acier inoxydable la diminution des valeurs de potentiel critique par rapport à l'augmentation de la température est très évidente même si l'allure de la courbe fait penser que pour des températures supérieures à 70°C cette diminution s'affaiblit. De cette façon toutefois la valeur du potentiel critique de rupture se trouve à  $\Omega$  V/E.C.S. environ, ce qui diminue remarquablement le domaine du potentiel sans attaque par piqûres. L'emploi de l'Hastelloy C est par conséquent plus avantageux, en particulier à des hautes températures, en accord avec les résultats d'essais sur des installations (3).

L'aération de la solution qui peut jouer un rôle remarquable sur le déplacement des valeurs des potentiels critiques aux plus faibles températures, n'exerce pratiquement aucun effet à la température de 70°C à cause de la diminution de la

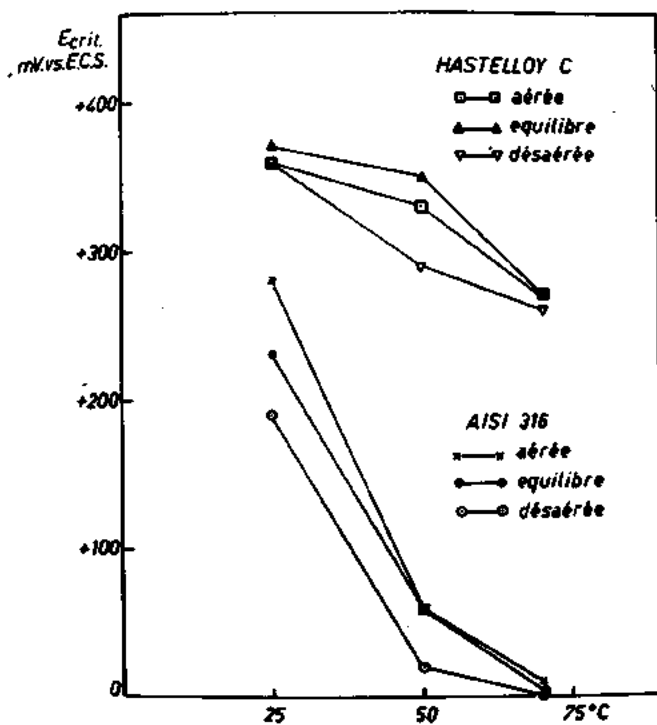


Fig. 3

solubilité de l'oxygène. On peut déduire d'une façon indirecte l'influence de l'oxygène sur la valeur de potentiel critique de rupture aux faibles températures des données à la figure 4. Dans cette figure on montre les variations de ce paramètre en fonction de la vitesse d'agitation de l'électrolyte en équilibre avec l'ambiant. L'annoblissement du potentiel de rupture de l'AISI 316 avec l'agitation, dans les conditions expérimentales fixées, peut trouver une explication à cause du grand apport d'oxygène à l'électrode aux plus grandes vitesses d'agitation. Les conditions d'agitation influencent faiblement l'Hastelloy C qui est plus noble que l'acier inoxydable en examen.

La résistance à la corrosion du cuivre et de ses alliages a été examinée à l'aide d'une analyse de paramètres électrochimiques. En considérant que le mécanisme de l'attaque dans le milieu en examen s'explique par l'action dépolarisante de

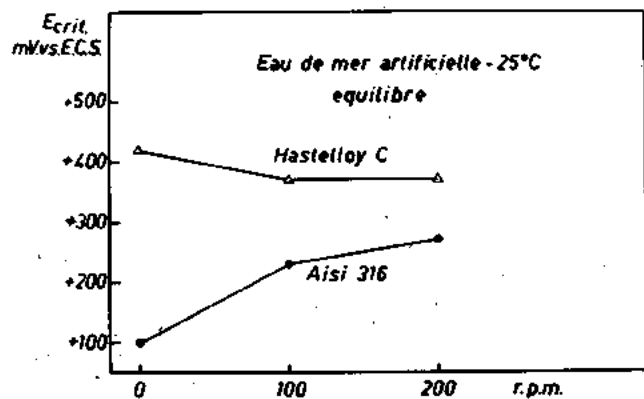


Fig. 4

l'oxygène, on a enregistré aussi les courbes de polarisation cathodique. En solution neutre, pour les matériaux du type en examen, Bianchi (20) admet que la réduction cathodique de l'oxygène suit une voie indirecte. En particulier pour le cuivre, à des faibles densités de courant, l'électrode se corrode initialement en se recouvrant d'un film de produits de corrosion qui sont réduits cathodiquement et de nouveau oxydés chimiquement par l'oxygène dissous dans la solution, à l'aide d'un mécanisme cyclique.

L'influence de l'oxygène sur les valeurs des potentiels de corrosion aux différentes températures est montrée à la figure 1. Les résultats des mesures électrochimiques effectuées sur le cuivre et sur les cupronickel sont consignés au Tableau 2. Les densités de courant cathodique de diffusion, clairement

TABLEAU 2

CUIVRE ET SES ALLIAGES DANS L'EAU DE MER ARTIFICIELLE

	T°C	Solution aérée		Solution désaérée	
		E <sub>corr</sub> (mV/ E.C.S.)	i <sub>corr</sub> (μA. cm <sup>-2</sup> )	E <sub>corr</sub> (mV/ E.C.S.)	i <sub>corr</sub> (μA. cm <sup>-2</sup> )
Cu	25°C	-217	34	-260	15
		-195	6,7	-269	1
		-213	(°)	-275	(°)
Cu 90/Ni 10	50°C	-253	65	-280	20
		-231	13,5	-297	1,4
		-224	(°)	-306	(°)
Cu 70/Ni 30	70°C	-268	41	-352	1,8
		-265	14,5	-342	3,7
		-230	(°)	-325	(°)

(°) La vitesse de corrosion de ces alliages est très faible; l'absence de zones linéaires dans les courbes de polarisation ne permet pas un calcul exact des valeurs i<sub>corr</sub> par extrapolation.

supérieures dans les solutions aérées (exemple figure 5), augmentent en fonction de la température. Cela se vérifie à cause de l'augmentation de la vitesse du processus et de la diffusion de l'oxygène. En suite, les densités de courant de diffusion s'affaiblissent à 70°C à cause de la diminution de la solubilité de l'oxygène (exemple figure 6).

L'effet de l'aération est moins évident sur les courbes de polarisation anodique du cuivre et cupronickel que sur les courbes cathodiques, en particulier pour des faibles valeurs de la surtension. Pour des valeurs de surtension anodique qui dépassent 200 mV l'allure de la courbe de dissolution n'est plus monotone et elle prend une forme de S. On peut croire que cela est dû comme conséquence de la formation d'un film de produits de réaction à l'électrode qui ralentit, dans un étroit domaine de potentiel, le processus de dissolution. Un déplacement ultérieur du potentiel imposé en direction noble donne lieu à une augmentation de la densité de courant de dissolution anodique.

Une modification de la vitesse d'agitation de l'électrolyte cause les effets visibles par exemple en figure 7. Avec l'augmentation de la vitesse d'agitation les densités de courant de diffusion pour la réaction cathodique se déplacent vers des valeurs plus élevées, tandis que la résistance du film de

produits superficiels de la réaction anodique est plus faible lorsqu'on travaille avec l'électrolyte en mouvement.

L'effet de la composition du matériel électrodeur sur l'allure des courbes de polarisation à 25°C est montré, par exemple, à la figure 8. En augmentant la teneur en nickel les

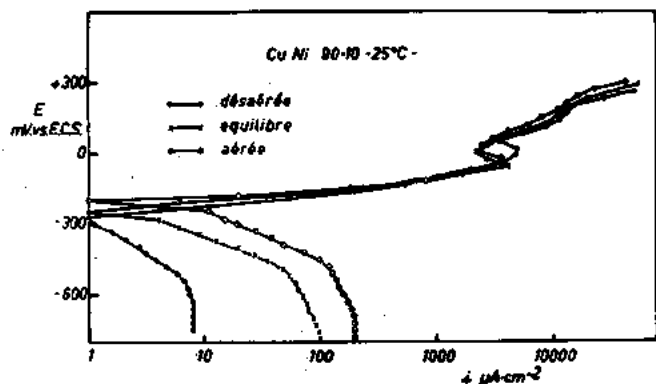


Fig. 5

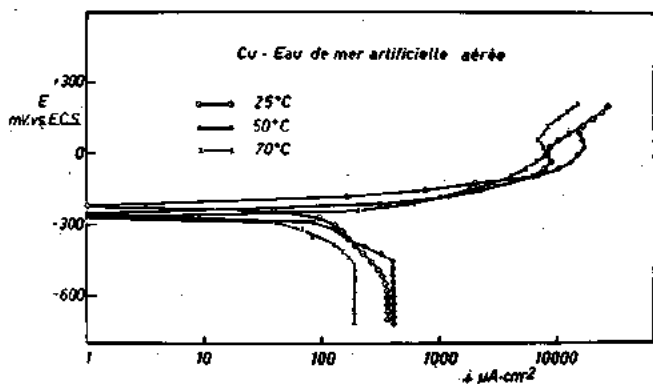


Fig. 6

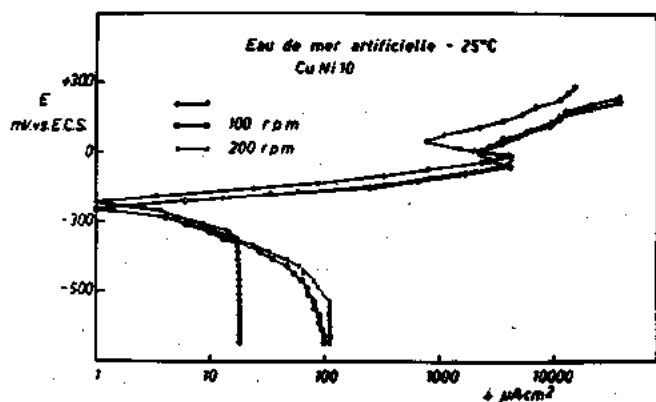


Fig. 7

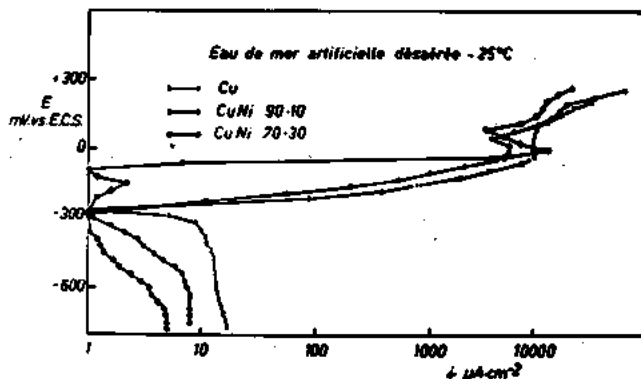


Fig. 8

courbes de polarisation anodique présentent la transition à S pour des valeurs plus faibles de densité de courant anodique, tandis que les valeurs des densités de courant cathodique limite, qui ne dépendent pas de la nature du métal, sont presque les mêmes (environ  $10 \mu\text{A}\cdot\text{cm}^{-2}$ ).

Les vitesses de corrosion du cuivre et des cupronickel ont été déduites des courbes de polarisation puisque on a démontré qu'il existe un accord entre les données ainsi calculées et celles qu'on a obtenues des pertes de poids (18). En tout cas l'effet de l'oxygène dissous sur l'entité du processus est évident. Les cupronickel offrent une résistance à la corrosion supérieure à celle du cuivre; pour ce dernier on a un ralentissement de l'attaque aux températures les plus élevées (70°C). Au contraire, pour les cupronickel l'attaque augmente jusqu'à la température de 70°C.

## CONCLUSIONS

L'enregistrement de paramètres électrochimiques permet d'obtenir rapidement une vision comparative du comportement de matériaux métalliques différents dans l'eau de mer artificielle. Ces techniques accélérées peuvent être employées pour choisir un matériel métallique pour l'emploi pratique dans l'eau de mer. Un jugement plus objectif peut être obtenu avec de l'eau de mer naturelle (13). En ce cas la présence de micro- et macroorganismes et la nature des pollutions urbaines et industrielles peut exercer une action importante.

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# THE BEHAVIOUR OF THREE HIGH-NICKEL ALLOYS IN MARINE ENVIRONMENTS

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## SUMMARY

Three alloys containing from 40 to 60 per cent nickel which have excellent resistance to corrosion in sea-water environments are available for marine engineering applications. The major alloying elements in all three alloys are chromium and molybdenum; one also contains a high proportion of iron.

Data are given for the corrosion behaviour of these three alloys in marine atmospheres, low velocity sea water, high velocity sea water and, in one case, hot sea water. Corrosion fatigue data are also presented. The mechanical properties of the alloys are summarized and a brief description is given of the ways in which the materials have already been used and of possible future applications.

Wrought nickel has generally good resistance to corrosion in many media, particularly caustic alkalis, but its overall resistance to dilute chloride solutions such as sea water is only moderate. In fast-flowing sea water its corrosion rate is very low, rates of attack being generally about 0.013 mm per year. However, in low velocity or stagnant conditions pure nickel is susceptible to pitting attack, particularly if crevice conditions are present. Even if crevices are not present in the original design, differential aeration effects can occur under deposits of solid material and under marine fouling. In this connection it should be noted that, unlike copper, nickel is not toxic to marine organisms and it is therefore readily fouled.

The resistance of pure nickel to attack by sea water can be considerably improved by the addition of alloying elements

and probably the best-known of the high nickel alloys in marine engineering is nickel-copper alloy 400 which is basically in nickel-30 per cent copper alloy. The characteristics of this material in sea water environments were discussed at the First International Congress on Marine Corrosion and Fouling (1). Other nickel-base alloys with excellent resistance to sea water have been developed and three of these, all containing substantial amounts of chromium and molybdenum, are the subject of this paper. The alloys in question are

1. Nickel-chromium-molybdenum-tungsten alloy C ('Hastelloy' \*alloy C). This is a well established material of moderately high strength which has an outstanding resistance to sea water.
2. Nickel-iron-chromium-molybdenum alloy 825. ('Incoloy' \*alloy 825). This alloy was developed originally for use in the chemical industry and it has proved to give a very useful service in marine engineering applications. It is now finding use for condenser tubes and other components which have to withstand particularly arduous conditions.
3. Nickel-chromium-molybdenum alloy 625 ('Inconel' \*alloy 625) Although first developed as an alloy for high temperature applications (a field in which it is currently used in the U.S.A.), this material also has excellent resistance to aqueous corrosion. Because of its resistance to sea water and its high strength, alloy 625 is beginning to find application in the marine engineering field.

\* Trade Mark

properties of wrought bar are:

Tensile Strength	85 kg/mm <sup>2</sup>
0.2 per cent Proof Stress	36 kg/mm <sup>2</sup>
Elongation (in 50 mm)	50 per cent
Izod V-notch impact strength	3 kg.-m.

### Corrosion in Marine Environments

(a) Marine Atmosphere. Eleven samples of alloy C were exposed for fifteen years on racks about 240 metres from the shore line at Kure Beach, North Carolina. During this time they were exposed to the continuous action of sun, rain and sea water spray. At the end of the fifteen-year period none of the specimens showed any measurable weight loss or pitting and all the surfaces were still highly reflecting (3).

(b) Immersion in Low-Velocity or Stagnant Sea Water. Test panels 10 cm × 30 cm of wrought material were exposed in duplicate in quiet sea water and in sea water moving at two feet per second. After exposure for 731 days without disturbance, they were completely free of any crevice corrosion or pitting, even though the specimens in quiet sea water were completely fouled with marine organisms. The

## NICKEL-CHROMIUM-MOLYBDENUM-TUNGSTEN ALLOY C

This is an established alloy with outstanding resistance to corrosion by a wide variety of media and it also has good strength and resistance to oxidation at temperatures approaching 1000°C. It is available in all normal wrought forms and as castings.

### Composition and Mechanical Properties (2)

Element	Nominal Composition, per cent
Chromium	15.5
Molybdenum	16
Tungsten	4
Iron	5
Nickel	balance.

The alloy also contains cobalt for which a 2.5 per cent maximum is normally specified. It is usually supplied in the solution heat-treated condition for maximum ductility and corrosion resistance and in this condition typical mechanical

corrosion rates under these two conditions were negligible, being less than 0,0025 mm per year. In another test both wrought and cast specimens of this alloy also corroded at less than 0,0025 mm per year while exposed to quiet sea water for as long as 3,645 days without any evidence of pitting or crevice corrosion. During this test, the specimens were temporarily removed from the sea water for cleaning and inspection on several occasions.

This alloy is also highly resistant to sea water that is polluted by raw sewage, as exemplified by a 412-day test in the harbour of Havana, Cuba. In spite of the severe pollution that existed there, the alloy was completely free of crevice corrosion and pitting, while its average corrosion rate was less than 0.0025 mm per year.

Another test involved immersion in the deep ocean — at a depth of 1700 metres — for 123 days. Alloy C was completely unattacked in this exposure and at the end of the test period still retained its metallic sheen (4).

The alloy has been in service in the form of a shell and tube heat exchanger with deaerated sea water at 121°C flowing through the tubes at about 2.5 to 3 metres per second and no corrosion has been experienced over extended periods of time.

Welds in the standard grades of alloy C should be heat-treated before exposure to the corrosive environment to avoid the possibility of preferential attack in the heat-affected zones. Provided that this precaution is taken, welded alloy C has the same immunity to sea-water corrosion as the unwelded material. The need for postweld heat treatment can be avoided however by the use of the more recently developed version of the alloy, C276.

(c) Exposure to High Velocity Sea Water. Specimens of alloy C were tested in the high velocity jet apparatus described by May and Weldon (1). In this test sea water at ambient temperatures flows at very high speeds over the surface of the specimen which is held in a specially designed nylon nozzle. After a 30-day test in sea water at 12°C flowing at 40 metres per second, the corrosion rate of this material was 0,005 mm per year.

(d) Exposure to High-Temperature Sea Water. Tests were carried out in flowing sea water at elevated temperatures. The apparatus used provided for rotation of the specimens in hot sea water in an autoclave, the specimens having a peripheral velocity of 3 metres per second. After 1080 hours (about 6½ weeks) in these conditions at a temperature of 177°C, there was a weight gain of 0.065 g. and the only visible sign of corrosion was a staining of the material at the contact with the fixture. A similar test was carried out at 288°C for 575 hours which resulted in a weight loss of 1.246 mg/cm<sup>2</sup>/month, representing an average penetration of less than 0.018 mm per year.

#### Applications

From the foregoing it is obvious that this material is virtually immune to corrosion in sea water in a wide variety of exposures. With its high nickel and molybdenum content it is however, a relatively expensive alloy and is therefore normally used only where conditions are particularly severe or where failure of a component could be costly or dangerous. Because alloy C has excellent resistance to corrosion by a wide range of organic and inorganic reagents it is also useful for components such as heat exchangers and coolers which have to withstand an industrial chemical on one side and cooling water on the other.

#### NICKEL-IRON-CHROMIUM-MOLYBDENUM ALLOY 825

This material, which is available as a wrought alloy in the usual mill forms, was developed more recently for use particularly in the chemical industry to provide resistance to a range of reagents, particularly oxidizing acids and their salts. It is highly resistant to stress-corrosion cracking. With a relatively high iron content, alloy 825 can be considered as intermediate in many ways between the austenitic stainless steels and the nickel-base alloys.

There has recently been an increasing interest in the use of this material in the marine engineering field and in a number of applications it has already proved satisfactory.

#### Composition and Mechanical Properties

Element	Nominal Composition, per cent
Nickel	42.5
Chromium	21.5
Molybdenum	3
Copper	2
Titanium	1.0
Iron	30

Alloy 825 is normally supplied in the annealed condition with typical mechanical properties as follows:

Tensile Strength	66 kg/mm <sup>2</sup>
0.2 per cent Proof Stress	28 kg/mm <sup>2</sup>
Elongation (in 50 mm)	52 per cent

#### Corrosion in Marine Environments

(a) Marine atmosphere. Two panels of alloy 825 were exposed for 3 years and 3 months on racks about 24 metres from the shore line at the Kure Beach, North Carolina, atmosphere exposure site of the International Nickel Co. where they were open to sun, rain and salt water spray. At the end of this period the entire surfaces were covered with a light stain. There were also some darker stains covering about 20 per cent of the surfaces and a few very small superficial rust spots, these covering a total of less than one per cent of the surfaces. All the stains and rust spots could be removed easily with a mild abrasive.

Similar results were obtained on two more panels which were exposed on racks at 240 metres from the shore line. Again, all the stains and light rust spots were removed easily with a mild abrasive.

After a total of ten years exposure these specimens in both locations had acquired a uniform, gray film but had not suffered any appreciable corrosion.

(b) Immersion in Low Velocity or Stagnant Sea Water. Four panels were fully immersed from a wharf at Harbor Island, N.C. for three years and three months. At the end of this time all the panels were covered with marine fouling — barnacles, filamentous and encrusting bryozoans, sponges and serpula tubules. Very slight crevice corrosion occurred under the barnacles; heavier crevice corrosion was encountered under the Bakelite washers used to secure the specimens. Fig. 1 shows the type of fouling encountered by immersion of alloy 825 in sea water flowing at 0.6 metres per second for 2½ years. The crevice attack suffered under this fouling is shown in Fig. 2.

Two identical specimens that were continued in test in quiet sea water for fourteen years suffered no pitting whatsoever, even though they were completely fouled with oysters, barnacles, tunicates and bryozoa. However, considerable crevice corrosion occurred where the specimens were insulated by Bakelite washers from their supports. This crevice corrosion ranged from 0.025 mm to 1.5 mm with an approximate average depth of about 0.75 mm.

Panels of alloy 825 were also immersed at a depth of 1700 metres for 123 days to evaluate the possible use of the material in deep ocean environments. At the end of this exposure no visible corrosion had taken place and the panels had retained their metallic sheen (4).

The long-term tests in quiet sea water have shown that whilst pitting of alloy 825 can occur, the alloy is more capable than the stainless steels of retaining passivity when shielded from aerated sea water by fouling organisms or by the Bakelite insulators at its supports. This passivity, due primarily to the high nickel, chromium and molybdenum contents, is illustrated in other tests involving exposure to aerated sea water moving at moderate to high velocities.

Alloy 825 has been tested in the BNFMR jet impingement



Fig. 1. Alloy 825 covered with marine fouling after 2½ years exposure to sea water flowing at 2 feet per second.

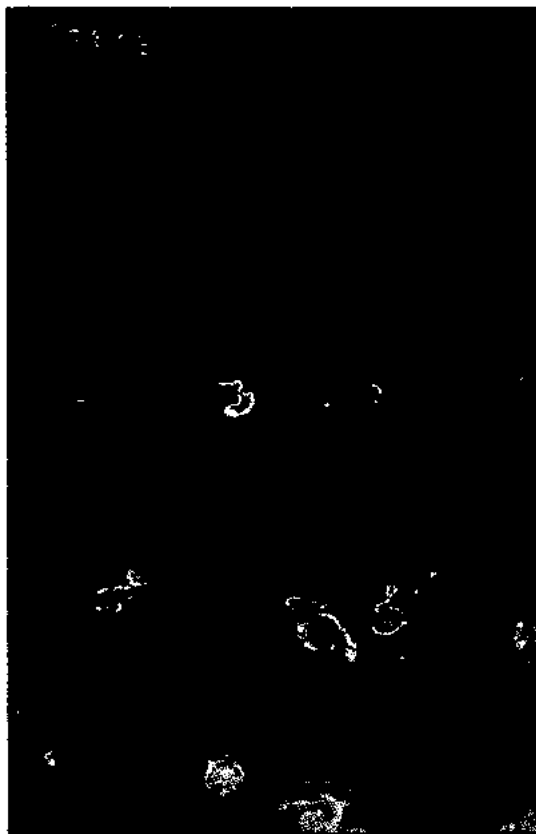


Fig. 2. Alloy 825 panels as in Fig. 1 after removal of marine fouling and showing crevice corrosion.

apparatus at the Harbour Island Corrosion Laboratory. In this test, a jet of sea water containing 2 to 4 per cent added air is directed at the surface of the specimen which is immersed in sea water. The jet velocity used in this instance was 4.5 metres per second and the specimen of alloy 825 suffered no attack in the jet area (the most resistant copper alloys used for condenser tubes are normally attacked to a depth of 0.025 mm to 0.1 mm in a similar 28-day test). This resistance to flowing sea water is common in alloys containing substantial amounts of chromium such as the stainless steels. However, the latter materials tend to suffer attack in the area removed from the jet impingement, particularly in the crevices caused by the method of holding the specimen. The better resistance of alloy 825 to crevice conditions was thus illustrated in this test by its weight loss which was 0.4 mg per day compared with 3 mg per day for Type 316 austenitic stainless steel and 30 mg per day for Type 430 ferritic stainless steel.

In a 60-day test in sea water at 8 metres per second, the weight loss on alloy 825 was negligible. In more severe velocity tests, the alloy was exposed for 30 days in the high-velocity jet tests at Harbor Island on two occasions. In the first case the water temperature was 11°C and the speed 40 metres per second; a corrosion rate of only 0.0075 mm per year resulted. In the second test the average water temperature was 13°C, and water velocity was 29 metres per second; the resultant corrosion rate was 0.0125 mm per year.

#### Applications

The behaviour of alloy 825 in sea water can be summarized as being excellent where the water flow or other conditions prevent the occurrence of fouling. Where fouling does occur, the alloy is liable to some pitting corrosion but this is much less severe than in the case of the stainless steels.

There is an important potential use for the alloy in condensers and heat exchangers using sea water where the water velocity is normally too high for the satisfactory use of copper alloys or where entrained sand and silt particles increase the erosive action of the water. It may also be used in certain highly polluted sea waters where the sulphide content causes excessive corrosion of copper alloys. However, it is recommended that crevices should be avoided in the design of such equipment and that care should be taken to prevent fouling or the deposition of solid matter during operation since some pitting may occur in the resulting shielded areas.

One example of the use of alloy 825 in such an environment has been in the Thames estuary. A plate-type heat exchanger using this water for cooling purposes has to withstand attack by heavily polluted brackish water (approximately 75 per cent sea water, 25 per cent fresh water) containing sulphonated detergents. Stainless steel failed after about 7 months service and was replaced with alloy 825. This has so far operated for over three years although the latest information indicates that some pitting has occurred in crevices and under deposits.

Service trials on the alloy are in progress at other sites where such aggressive conditions are encountered such as in power stations at La Spezia, Italy and Linden, New Jersey, U.S.A. There is also potential use in desalination plants handling sea water brines at temperatures up to about 150° or 175°C.

Another successful use of the alloy has been for the propeller shafts of fishing vessels in a harbour in the U.S.A. where the water was badly polluted by refuse which released hydrogen sulphide on decaying. The shafts were formerly made of nickel-copper alloy K-500, which normally gives good service

in sea water but in this instance suffered severe pitting corrosion due to the sulphide contamination. These shafts were replaced with alloy 825 shafts which have behaved satisfactorily (1).

More recently a case has occurred of the replacement of nickel-copper alloy 400 by alloy 825 for the demisters in a large desalination plant. Alloy 400 is used extensively for these components which consist essentially of a mesh of fine wire which separates droplets of sea water brine from the vapour in multi-stage flash distillation plants. In this case, however, corrosion occurred in a little over one year due to the high concentrations of  $H_2S$  and  $CO_2$ . The demisters were replaced using alloy 825 wire mesh and this material has now operated satisfactorily for about two years and is still in service.

#### NICKEL-CHROMIUM MOLYBDENUM ALLOY 625

Although this alloy was developed in the U.S.A. originally as a high temperature material, it has a very high resistance to corrosion by sea water. In addition, it can be drawn to very high levels of strength without any loss of this corrosion resistance.

The alloy is only recently becoming commercially available in Europe in the form of wire and strip; evaluation of wire rope produced in the U.S.A. is in progress in Europe to augment the data so far available.

#### Composition and Mechanical Properties

Element	Nominal Composition per cent
Chromium	22
Molybdenum	9
Niobium	4
Iron	3
Nickel	balance

The tensile properties of hot-rolled rod, 19 mm diameter, are as follows:

Tensile Strength	100 kg/mm <sup>2</sup>
0.2 per cent Proof Stress	63 kg/mm <sup>2</sup>
Elongation (in 50 mm)	45 per cent.

However, most applications call for a maximum tensile strength in cold-drawn wire for wire rope and cable and the tensile strength of 0.5 mm dia. hard-drawn wire as used to make wire rope is approximately 215 kg/mm<sup>2</sup>.

#### Corrosion in Marine Environments

Testing of alloy 625 in marine environments is still in a relatively early stage. However, data provided up to the present time by exposures at the Harbor Island Corrosion Laboratory indicate that this material has exceptional resistance to sea water corrosion.

In the first series of exposures, alloy 625 was immersed in quiet sea water for three years by hanging specimens from a wharf while other specimens were placed in a trough through which clean sea water flowed at 0.6 metres per second. In both cases an intentional crevice area was provided by fastening a plastic washer in contact with the surface. Extensive fouling occurred but after this had been removed it was determined that the corrosion rate was essentially zero; no evidence of local attack could be found under the fouling or under the plastic washers.

In another test, 50 mm diameter circular weld rings were deposited on 6 mm thick plates and the specimens immersed for one year in sea water. No evidence of stress-corrosion cracking was found.

Samples of wire rope in alloy 625 (6 mm dia. 7 × 19 rope) were also exposed to the following conditions at the Harbor Island Corrosion Laboratory:

- in quiet sea water (constant water line)
- in tidal zone sea water

(c) partially buried in the bottom mud.

At the end of one year these samples were examined and no visible corrosion had occurred; all the external wires were still bright. The tests are being continued.

Specimens of the same rope are also being exposed to coastal waters in the U.K. One metre lengths are being suspended from rafts with about 15 cm. in the splash zone and the remainder immersed; specimens taken off test after one year were heavily fouled below the water line but no signs of corrosion could be found on removal of this fouling.

Further tests are in progress on similar wire rope. These include immersion in sea water in a trough at Harbor Island (0.6 metres per second velocity) and deep water tests - at 1400 metres. Similar programmes are being carried out in the U.K. and corrosion fatigue tests and stress-corrosion tests are also scheduled.

The virtually complete resistance of alloy 625 to sea water corrosion is further indicated by results of corrosion fatigue tests and results to date on resistance to stress corrosion cracking. The corrosion fatigue strength as determined by rotating cantilever beam specimens in flowing sea water is about 35 kg/mm<sup>2</sup> at 100,000,000 cycles. This is in sharp contrast to carbon steel which has almost negligible corrosion fatigue strengths in sea water. When tested in the same manner as alloy 625, mild steel had a value of about 0.7 kg/mm<sup>2</sup> 100,000,000 cycles. High-strength steels are only slightly better than mild steel. Corrosion fatigue curves are shown in Fig. 3 for alloy 625 and mild steel in sea water.

In applications involving crevices and corrosion fatigue, as in the case of wire strand and wire rope, alloy 625 has most attractive properties that far overshadow its only disadvantage, namely cost.

#### Applications

Alloy 625 is being developed mainly as a high strength wire rope alloy and it is already being used for a yacht centre-board hauling pennant and for the taut line mooring of an electronic package approximately 15 metres above the ocean floor (at relatively shallow depths). If the promise of the early tests is fulfilled, alloy 625 should find extensive uses in the oceanographic field for ropes towing instruments and for deep instrument moorings. Other potential uses are sounding wires, the armouring of marine electrical cables and wire rope for marine engineering applications as in offshore drilling rigs and permanently moored mid-ocean weather stations.

#### Galvanic Considerations

The alloy content of these alloys is such that they exhibit very noble potentials when exposed to sea water. Under conditions of moderate velocity, these potentials are in the range of 0.0 to -0.150 volt vs. saturated calomel reference electrode. This range is similar to that of titanium and its alloys, of high alloy stainless steels and nickel-copper alloys 400 and K-500. It is distinctly more noble than the copper base alloys (by as much as 0.1 to 0.3 volt) and 0.4 to 0.7 volt more noble than cast irons and low-alloy or carbon steels. Hence, in most sea water applications they are unlikely to suffer galvanic corrosion when in contact with other metals or alloys. Furthermore, in view of their alloy content, they are likely to be compatible with more active metals and alloys because of their ease of cathodic polarization in such galvanic couples.

#### CONCLUSION

The three high-nickel alloys discussed have particularly high resistance to sea water corrosion. The first, is practically inert to sea water corrosion, even in crevices and under severe fouling. The second alloy is less expensive and shows excellent resistance to sea water under flow conditions. It offers an excellent alternative to copper-base alloys and stainless steels where conditions have proved too severe for these materials.

○ Tested at 725 r.p.m.

● Tested at 1400 r.p.m.

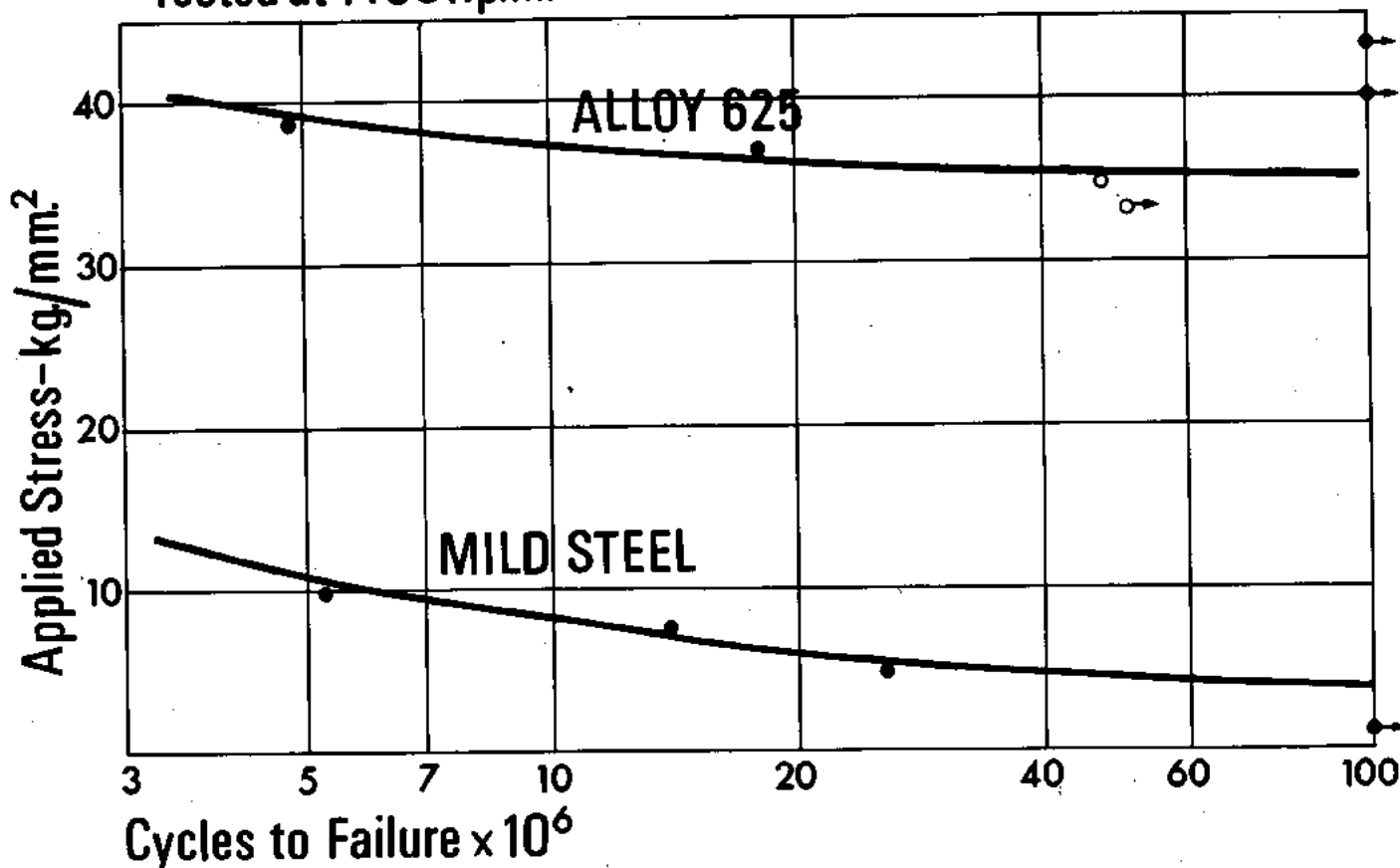


Fig 3 Corrosion-fatigue curves for Alloy 625 and Mild Steel in Sea Water

but some care must be exercised to prevent excessive fouling or other factors which might introduce crevice corrosion. The third alloy is being developed as a high-strength material for use in marine environments and shows great promise for marine wire rope and related applications. In the tests so far completed it has shown excellent resistance to sea water even where crevice corrosion conditions apply.

The galvanic characteristics of these alloys makes them particularly attractive for many marine applications where galvanic coupling with other metals and alloys cannot be avoided.

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#### DISCUSSION

Dr. POSCH (Holland): I should like to ask whether alloy 625 with its high strength has complete resistance towards Sulphide - Stress - Corrosion Cracking.

B. WELDON: I am sorry that I am unable to give a definite answer on this point as we haven't tested the alloy in this medium. From our knowledge of the alloy system we would expect Alloy 625 to be highly resistant but we would be interested to learn more of the particular environments.

Prof. Dr. YAHALOM (Israel): Considering the price of these alloys, have you any suggestion about practical applications for which

they can be used economically?

B. WELDON: In practical applications, Alloy C has been used for quite a long time but in rather small quantities because it is, as I have said, quite expensive material. It has been used in laboratory equipment where the quantity of material is very small and the price is perhaps rather of secondary importance compared with the behaviour of the material. It has been used occasionally for heat exchangers but the tonnage is again fairly small. This is partly the reason why the alloy 625 was developed, which includes about 30% iron.

This material, although it is rather more expensive than the stainless

steels, is considerably lower in cost than Hastelloy alloy C. It is being used in heat exchangers in chemical plants. It has been used for heat exchangers on the Thames Estuary which are handling fluid products on one side and polluted estuary water on the other and more recently it has been evaluated for coastal power stations, particularly in Italy. Tests have been in progress by the Italian electricity authorities for two years at la Spezia where the water is fairly heavily polluted. Copper alloys have been unsuccessful, so has steel which has suffered from pitting but so far the 325 has been quite satisfactory.

Alloy 625 was originally developed as a high temperature alloy and it is used in the U.S. for this purpose but the European interest seems to be more for the wire rope application. Again, I think because of the price it is not likely to be used for ordinary commercial installations to any large extent, but it has very considerable application for Naval use, where complete reliability and high strength are required.

Dr. KENWORTHY (England): In view of the relatively high cost of these materials, has any consideration been given to their application

as coatings in one form or another over mild steel?

B. WELDON: We have not metal-sprayed these particular alloys, but we have had some rather peculiar results when we tried some other nickel alloys as sprayed metal coatings. For some reason the corrosion behaviour does not seem to be at all related. For instance, in the case of Monel alloy 400, this has been used as sprayed metal coating for the repair of cavitation damage of propellers but the corrosion rate of the Monel in this form has been disappointing.

T. HOAR (England): In the later part of your paper you mention the noble potentials of these nickel alloys and you say that they are similar to that shown by titanium. I would take issue with you there: titanium can show very much more noble potentials in sea water than these that you quoted. I don't think this necessarily means that titanium is a better basis for an alloy than nickel. But it is certainly better passivated in sea water than even the high nickel alloys.

B. WELDON: I am sorry that I am not very well equipped to answer that without referring back to the original data from Harbor Island.

# FUNDAMENTAL AND TECHNICAL STUDIES ON THE CORROSION BEHAVIOUR OF CUNIFER 10 ALLOYS IN SEAWATER

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## SUMMARY

A joint program is performed by a group of dutch research laboratories on the evaluation of cunifer-10 as a seawater piping material. Fundamental studies were executed on the mechanism of segregation and precipitation, which will result in a classification of the conditions of the material to be expected in practice. The mechanism of oxidation was studied at conditions which occur during installation, like hot bending and welding.

The corrosion behaviour of the material in the mentioned

conditions, was investigated after exposure to harbour water and seawater.

The corrosion circuit for the testing of the different material conditions in running seawater is described.

Welding tests on actual tubes have shown that precipitation may occur in normal practice of welding.

Potential measurements on new tubes were performed on a ship sailing in different types of water.

## I. INTRODUCTION

The corrosion behaviour of materials in seawater piping systems of sea-going ships is of increasing importance. As automation of the engine room is becoming more and more important, the reliability has to be increased. Failure of seawater pipes can be a serious hinder in the operative conditions of ships in the Mercantile and Navy Marine. Earlier research in Holland into the corrosion resistance of materials was mainly carried out on the hull of the ship. It was therefore decided to form a special working group, with the aim to study the corrosion behaviour of materials in seawater piping systems and to encourage research into new materials. Representatives of the Mercantile and Navy Marine were invited to take part in this working group. The research program was set up in close co-operation with several research institutes. Financial support was supplied by the Netherlands Ship Research Centre (Delft). As cunifer-10 seemed to be the most promising material in seawater piping systems a research program was set up for this alloy. The research program was divided into two parts:

- a. fundamental research to examine the metallurgical aspects and the corrosion behaviour;
- b. technical research to examine the difficulties encountered in seawater systems.

## II. FUNDAMENTAL CORROSION STUDIES

Distinct from the usual approach of corrosion studies, the present work is based on a fundamental study of the base material. The project has shown that very short exposure times under service conditions may give substantial information if, however, the material is analysed before and after exposure with great detail.

Modern techniques like electron microscopy and electron microprobe analysis have been used to this purpose.

The present investigation have given further details on:

- 1) metallurgical aspects (impurities, segregation);
- 2) the precipitation process;
- 3) the information of oxide scales in air;
- 4) the influence of precipitation and oxidation on the corrosion process.

The present paper will deal with each of these topics with the restriction that only a part of the corrosion studies is reported.

### *Cunifer-10*

Among the well-known materials such as pure copper, admiralty brass and aluminium brass, the copper-nickel 30 alloy has an excellent resistance to erosion-corrosion (impingement attack). The copper-nickel 30 alloy, modified with iron, was developed further to cheaper material: the iron modified copper-nickel-5 alloy (cunifer-5) and the cunifer-10 (with iron and 10% nickel). From these two in particular the cunifer-10 seems to have the best possibilities to be used in practice.

The cunifer-10 alloy used in this study has the following composition: 10% Ni; 1,7% Fe; 0,7% Mn; balance Cu. The ASTM specification gives rather wide ranges: 9,0-11,0% Ni; 0,5-2,0% Fe; max. 1,0% Mn; min. 86,5% Cu and also max. 1,0% Zn and 0,05% Pb.

Together with the nickel content, the iron concentration is of great importance. Experimentally Bailey (1951) shows a minimum in corrosion rate at 2% iron content, expressed as depth of attack at a seawater velocity of 4,5 m/sec. (fig. 1). A similar curve is obtained for the cunifer-5 alloy. Here the optimum corrosion resistance is found at about 1,5% iron. Ageing at 600°C showed a severe increase of corrosion rate for cunifer-5, while cunifer-10 showed no differences in corrosion rate. It was noted, however, that the homogeneous material forms a transparent gold coloured oxide scale in seawater, the aged material forms a black scale.



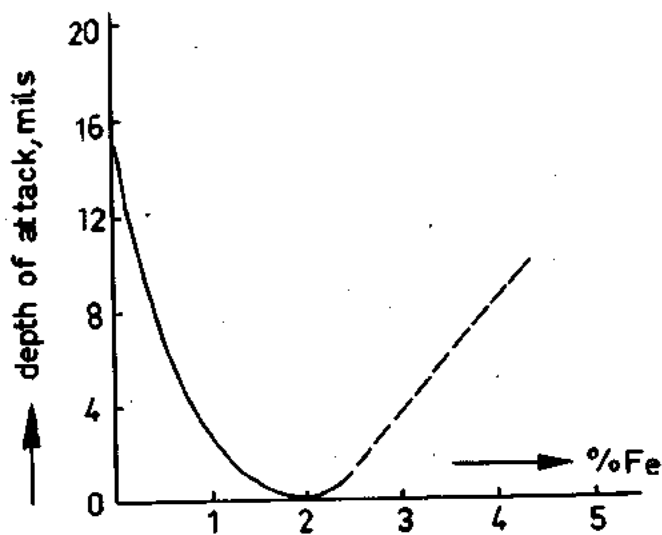


Fig. 1. Effect of iron content on the resistance to impingement attack of copper-nickel 10 alloys (after Bailey, 1951)

### Metallurgical aspects

The investigation of the metallurgical aspects of cunifer-10 were concentrated on two aspects, which may influence the service behaviour:

- The impurities in commercial grades in distinction from high purity melts made in the laboratory. As a reference for the corrosion studies a cunifer-10 alloy was made from pure components (composition: 9,84% Ni; 1,45% Fe, balance Cu). Special attention is given to the role of manganese, which is always present at about 1% as a de-oxidant in commercial alloys. Any influence of this element on segregation and precipitation could not be determined. During oxidation the manganese forms an internal oxide in the same zone as iron and nickel.
- The segregation in commercial tubes compared with the homogenised material.

In the as received condition the tubes show an inhomogeneous structure remaining from the macro-segregation in the original ingot. The concentration-variations across the layers, measured by means of electron microprobe analysis are plus and minus 25% for iron and nickel.

Although the homogenised condition is expected to be more ideal, it turns out that the heat treatment for full homogenization is economically unattractive. The experiments showed even after 7 hours at 1950°C variations in concentration of plus and minus 8% for iron and nickel.

### Precipitation

The equilibrium diagram by Palmer and Wilson (1952) shows that for a 10% Ni-alloy containing 1,7% Fe a second phase is formed below 735°C (fig. 2).

The mechanism of precipitation is partly explained by an electron microscopic study on thin foils. In the homogeneous condition cunifer has a face centered cubic structure with a lattice parameter of 3,60 Å. The second phase nucleates and grows coherently in this cunifer matrix. In this process stresses are built up around the precipitate (fig. 3). At a size of about 400 Å it loses coherency and boundaries of the cubic particles are observed. This great amount of coherency indicates that the structure of the second phase does not differ much from the matrix structure. Indeed electron diffraction showed that the lattice parameter of the face centered cubic precipitate is 3,58 Å. The other important factor concerning the precipitate is the composition. The analysis of the grain boundary pre-

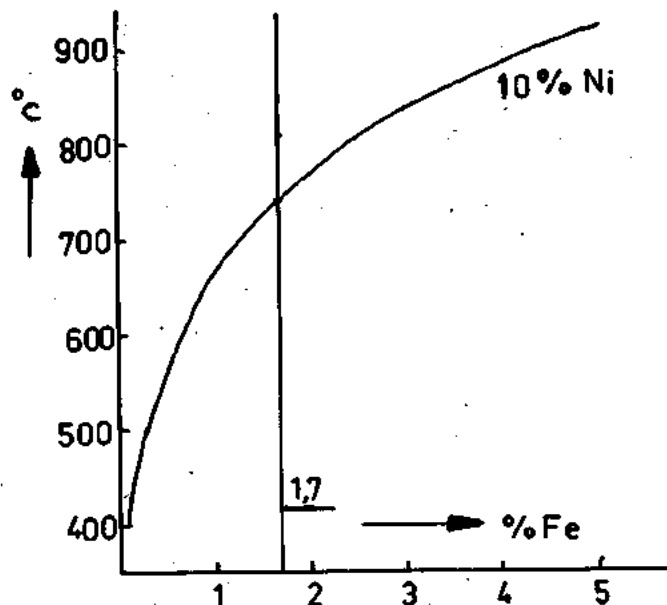


Fig. 2. Solubility of iron in copper-nickel 10 (after Palmer and Wilson, 1952).

cipitate, which in equilibrium has the same composition as the precipitate in the matrix, is determined by electron microprobe analysis as: 31% nickel, 17% iron, balance copper.

The conclusion is that although the crystal structures of precipitate and matrix are very similar, the composition shows marked differences.

It may be expected that the differences in composition, and the decrease of nickel and iron content in the matrix have consequences for the corrosion behaviour.

The precipitation process was studied in isothermal tests at different temperatures, starting from the homogeneous condition. The relation between hardness and ageing time is represented in fig. 4a for different temperatures. The onset of precipitation was defined as the first hardness value rising over the scatter band of the homogeneous material.

The heating times corresponding with these hardness values were used to constitute the isothermal time-temperature-transformation (T.T.T.) diagram, showed in fig. 4b. This diagram shows that precipitation starts after 30 seconds at 600°C already.

### Oxidation in air

It must be kept in mind that the interface between the cunifer and the seawater is usually formed by an oxide film. The oxide film will be different, depending on the mode of formation, for example on a clean pickled surface, or by heating during welding or bending.

The experiments show that the formation of the oxide can be divided into two stages. The first stage, a preferential oxidation of nickel to NiO takes only the first 30 seconds at about 600°C. At increasing oxidation times a layer of internal oxides of Fe, Ni and Mn is formed, covered at the outside with a layer of pure cuprous oxide Cu<sub>2</sub>O (fig. 5a-f).

The thickness of this layer is a function of the oxidation time.

As it is known from literature (Kubaschewski and Hopkins, 1962) the oxide on pure copper grows by diffusion of copper-ions towards the surface through the copper-oxide. On the other hand oxygen diffuses inwards and reacts with nickel, iron and manganese. In this way a layer of internal oxides of nickel, iron and manganese in a matrix of copper is formed, under the copper-oxide layer.

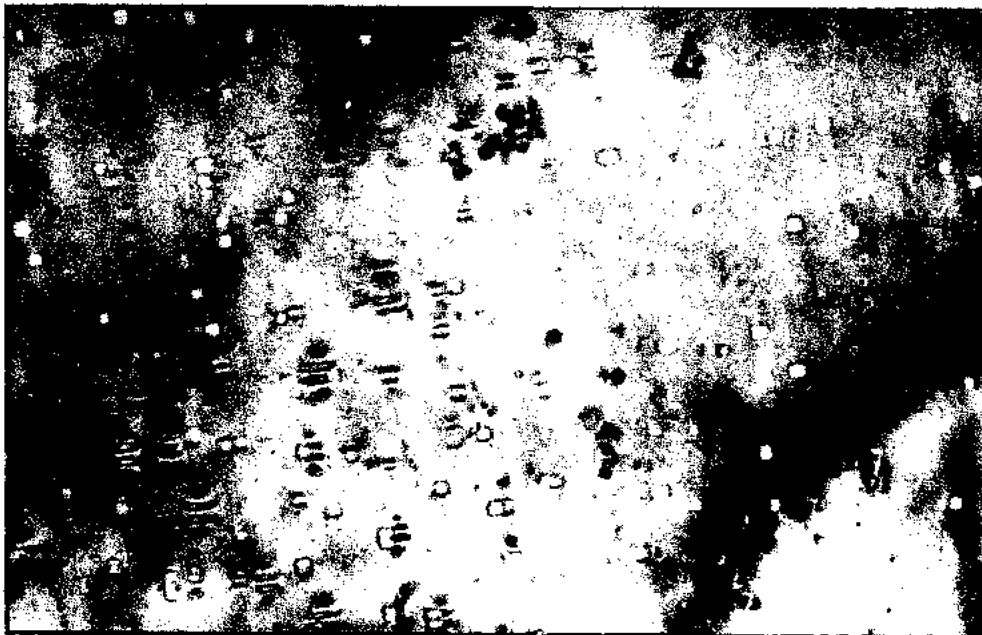


Fig. 3. Coherent precipitates with stress zones and incoherent precipitates (white rectangles), thin foil. 48,000 x

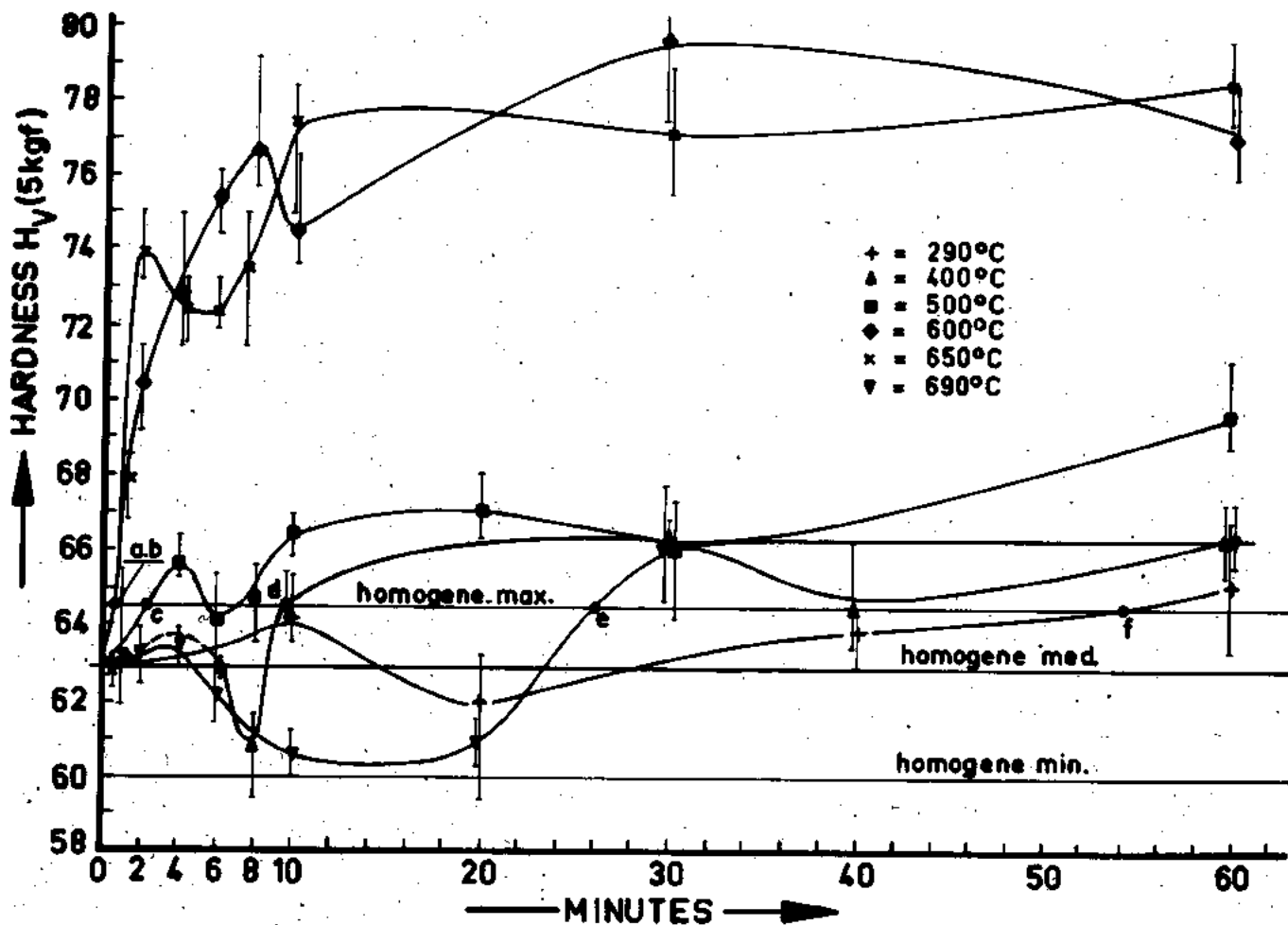


Fig. 4a. Hardness versus time of isothermal aging. Reference state: homogenised for 1 hour at 900°C.

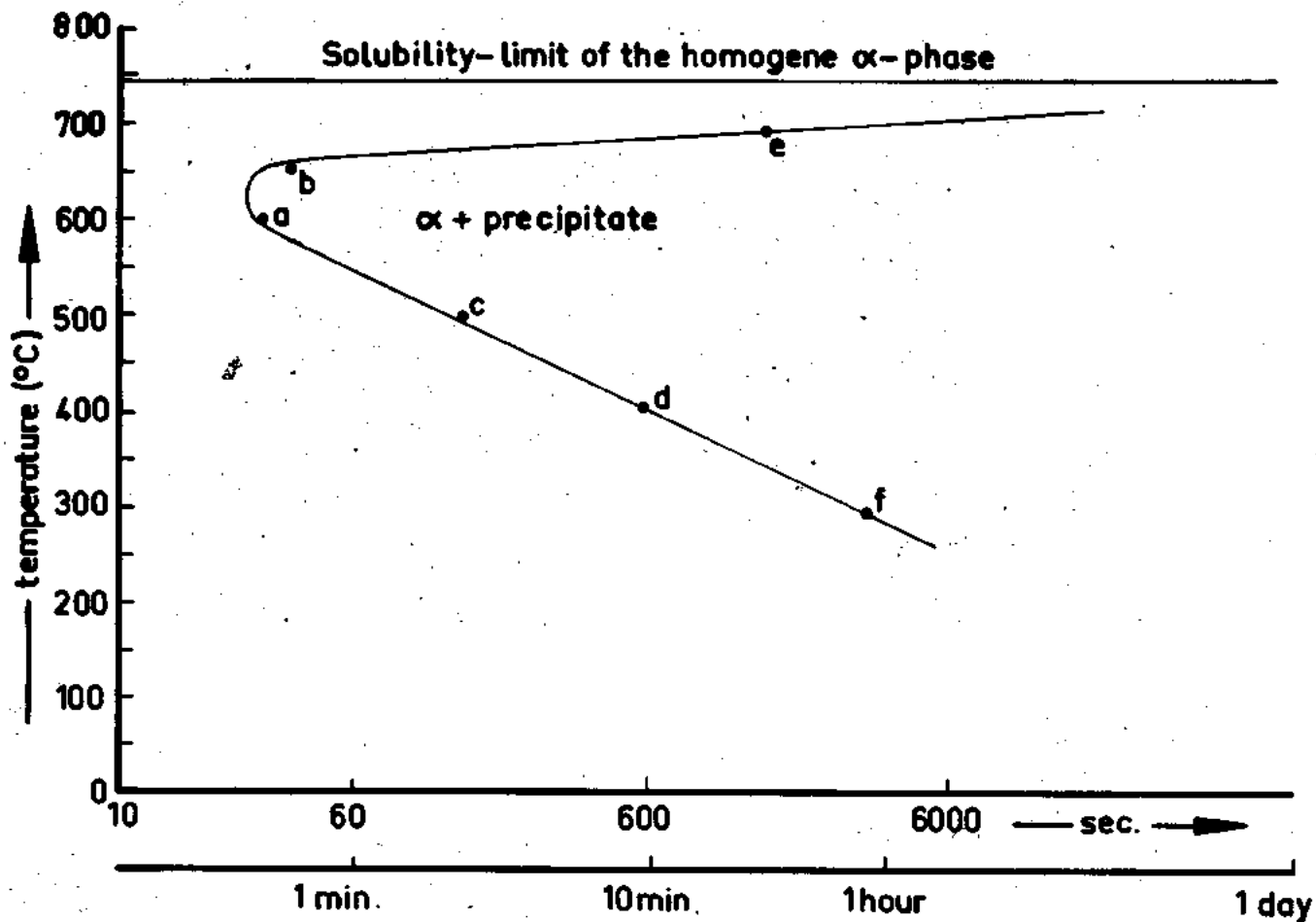


Fig. 4b. TTT-diagram, determined by points a-f of fig. 4a for specific temperatures.

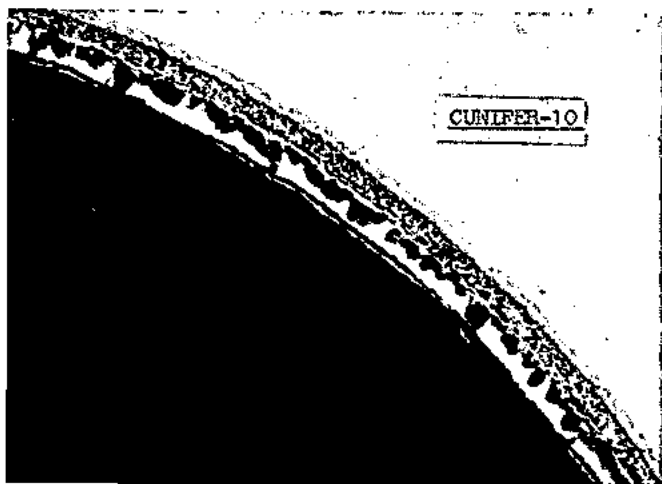


Fig. 5a. Oxide layers on cunifer 10. Material: Hom. 1050°C 2h, W.Q. Oxidation in air: 900°C, 5 min. 400 X

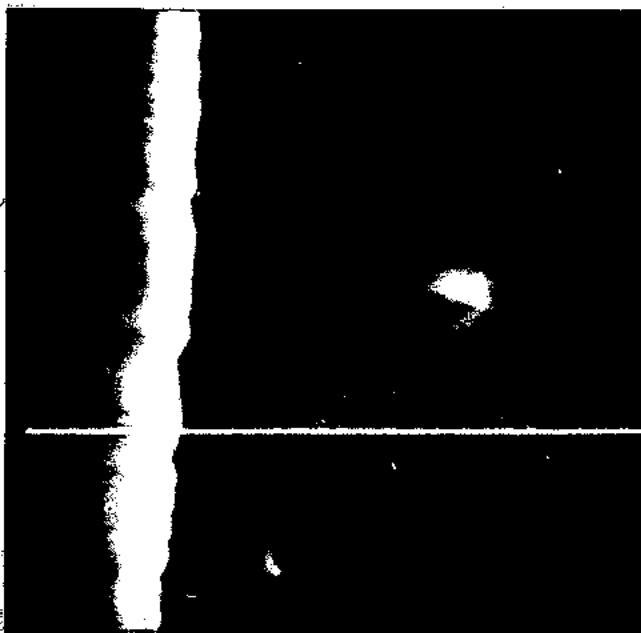


Fig. 5b. Electron image.

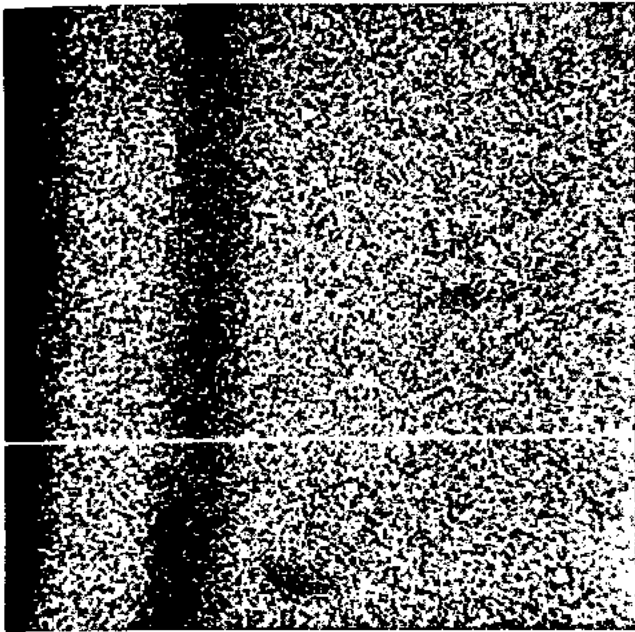


Fig. 5c. Copper image.

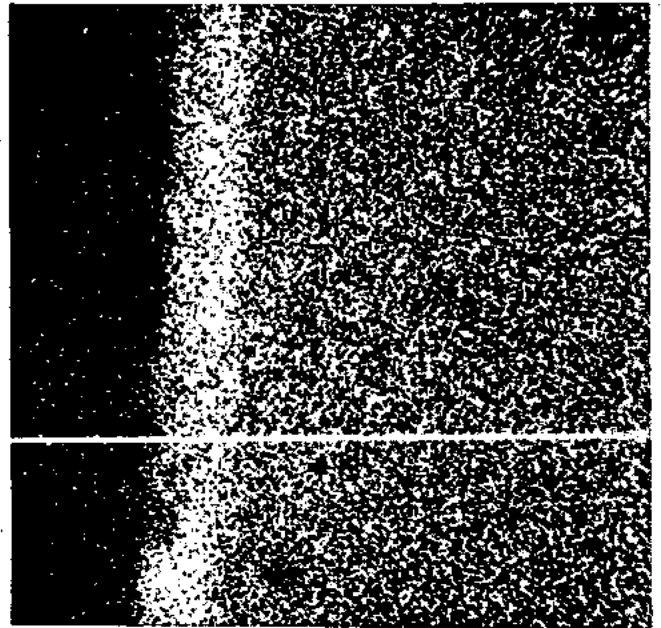


Fig. 5d. Nickel image.

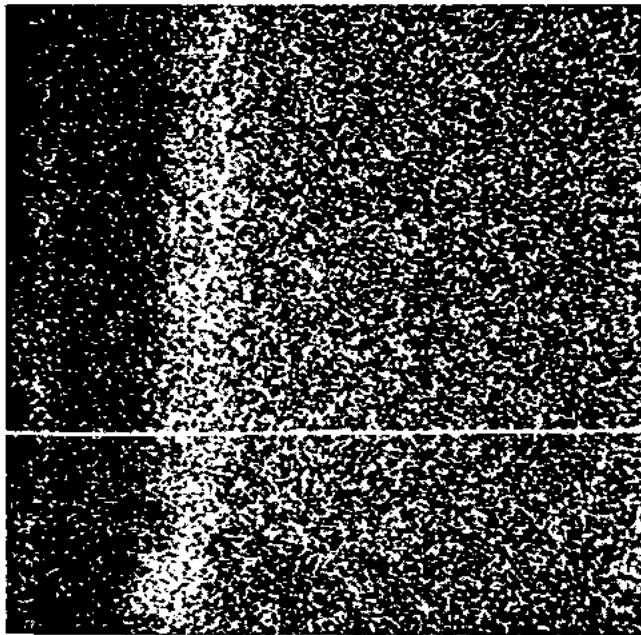


Fig. 5e. Iron image.

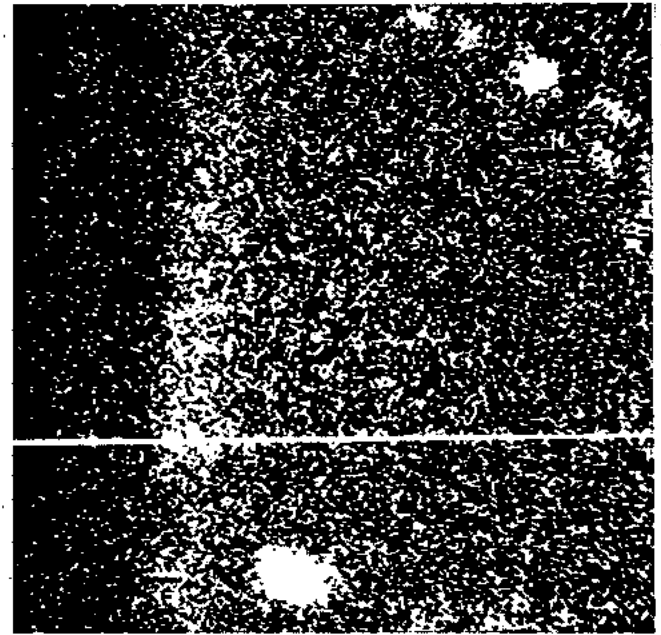


Fig. 5f. Manganese image.

Fig. 5b-f. Electron microprobe analysis of oxide layers on Cunifer-10.  
 Material: Hom., 1050°C, 7h W.Q. aged 780-590°C/92h. Oxidation in air:  
 700°C, 30 min. 1400 X

The mechanical properties of the two layers are different. The copper oxide scale is brittle and shows a tendency to blister. In the internal oxidelayer the copper metal gives a strong connection with the matrix.

This investigation by electron microprobe analysis leads to the important point that the scale in contact with the medium consists of internal oxides of iron, nickel and man-

gene with a reduced content of metallic copper and incidently some residues of the copper-oxide layer.

#### *Corrosion*

As mentioned before, Bailey (1951) observed a marked difference in appearance after exposition to seawater: the

homogeneous material showing a transparent gold coloured scale, the aged material showing a black scale. In the present corrosion studies this effect was brought in connection with differences in composition, in particular with the loss of iron and nickel in the matrix during precipitation. Further it should be expected that adhesion of the two types of oxide scale may be different. The initial water speed of 4.5 m/sec. (Stewart and Laque, 1952) for the homogeneous condition, might be decreased for the aged condition.

The phenomena mentioned so far apply to clean surfaces. In practice it must be expected that during hot bending or welding oxide scales are formed. It has been shown before in this paper that precipitation also will occur preferentially near the welds.

In the present investigation corrosion tests were performed on oxidised specimens, both for homogeneous and aged material. A thin oxide film was formed on the materials by oxidation in air during 30 seconds at 640°C.

After 40 hours exposure in stagnant water, a blistering of the oxide film is observed (fig. 6). This phenomenon is similar

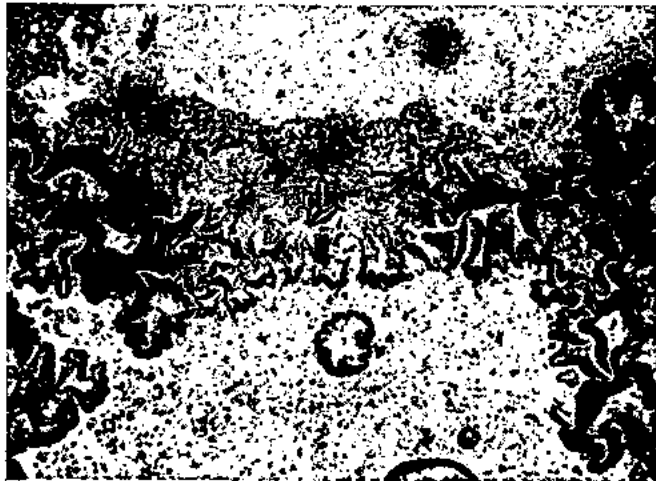


Fig. 6. Blistering of oxidised cuprifer-10 after 40 h in stagnant harbour water. 150 x

in seawater or harbour water, and also occurs in distilled water.

The blistering therefore seems to be connected with the water itself, and not with specific solutes in the water. Electron microprobe analysis was performed over the blistered surfaces after exposure to seawater and harbour water. The diagrams for Ni and Fe were similar for both types of specimens. Chlorine was detected, however, in high concentrations at the blistered areas after exposure to seawater. Sodium could not be detected at the areas of high chlorine content. Sulphur could not be detected after exposure to harbour water, although this element might be expected.

The blisters, as loose parts of the cuprous oxide layer, could be easily removed with plastic replica's. The specimen exposed to seawater showed pitting of the material under the blisters (fig. 7). The specimen exposed to harbour water showed instead of pitting a uniform corrosion of the oxide scale. The results indicate that during exposure chlorine ions penetrate preferentially in the voids between the blisters and the metal, causing a pitting of the metal. Sodium and sulphur seem not to play a part in this process. After 25 days exposure in seawater precipitates were detected in the oxide layer (fig. 8). The cuprous oxide of this layer showed diffuse rings in electron-diffraction, indicating that the oxide reacts with the seawater to an amorphous corrosion product.

The metal surface show etch-effects, while the precipitates remain unattacked (fig. 9).



Fig. 7. Pitting after 25 days in stagnant sea-water. 600 x

The results indicate that the precipitate themselves do not influence the corrosion process. The precipitation rather influences the corrosion of the matrix, due to the decrease in iron and nickel content.

### III. TECHNICAL RESEARCH

The technical research was divided into two parts.

1. Corrosion experiments by means of a seawater piping system.
2. Potential measurements on board of a sailing ship.

#### 1. Corrosion experiments

In the harbour of Den Helder a seawater piping system is built in the scope of this program.

The outlay of this systems is given in figure 10. By means of this circuit the next points will be studied:

- a. the influence of increasing velocity of the seawater on test pieces heat-treated in different conditions,
- b. the reliability of welded and brazed connections,
- c. the influence of different valves on the stream pattern.
- d. the corrosion behaviour of several materials in different conditions.

To simulate the technical conditions of hot bending some test pieces were subjected to different heat treatments. The data for these treatments were derived from the fundamental studies about precipitation and oxidation, mentioned in chapter II. The results of these technical corrosion experiments are brought into relation with the corrosion behaviour under laboratory conditions.

Prior to welding experiments and to the final T.T.T.-diagram (fig. 4b), the need was felt to have approximative information as to the position of the T.T.T. curve. To this purpose Brouwer and Platerink (1967) performed ageing experiments based on electrical resistivity.

These data were used for choosing the proper conditions for a program of welding experiments. In this program pipes were welded under controlled conditions of welding speed and welding current. Temperature-time diagrams (Fig. 11) were plotted for areas at different distances from the weld (Goetzee, 1967).

Comparing the cooling curves with the T.T.T.-diagram shows no intersection and from this it might be concluded that precipitation will not occur during welding. However, as welding in this experiment is done under controlled conditions, it is conceivable that precipitation will happen in practice, for example if incidentally very low welding speeds are applied.

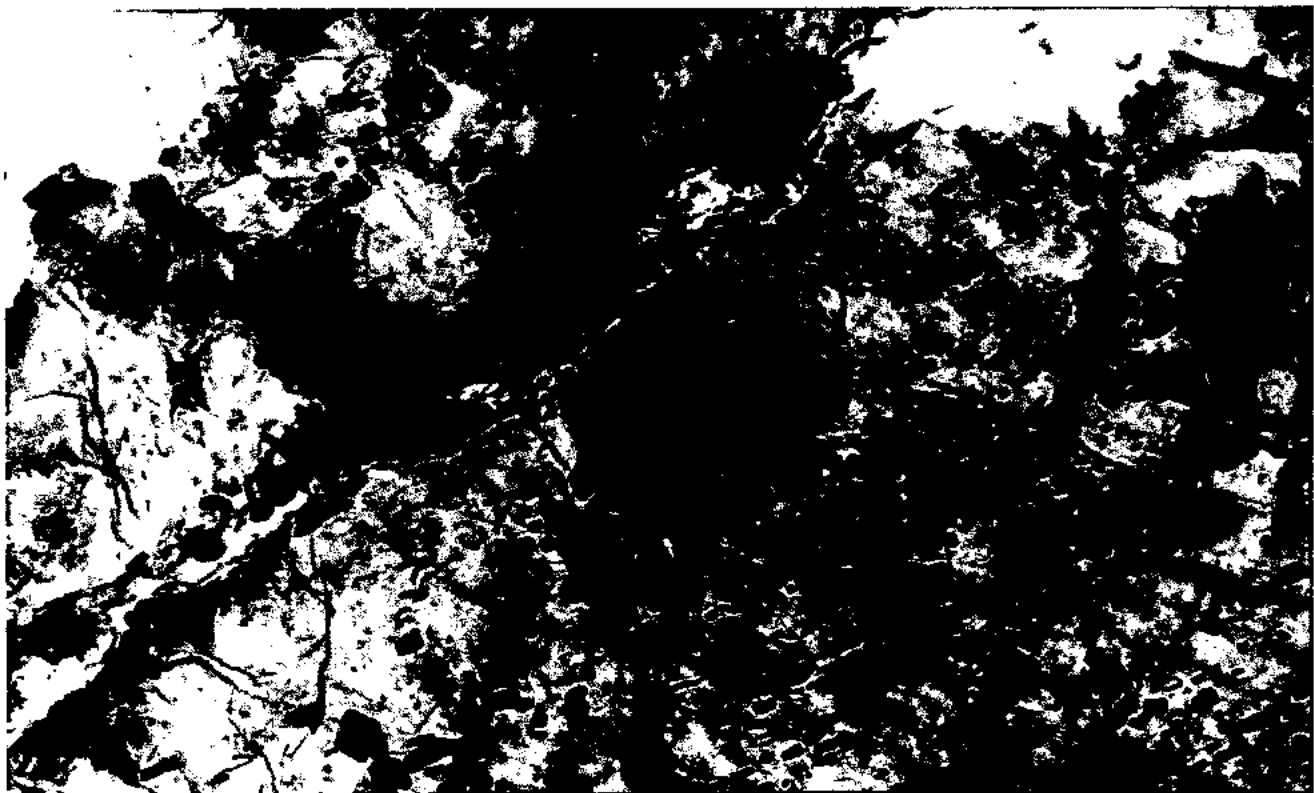
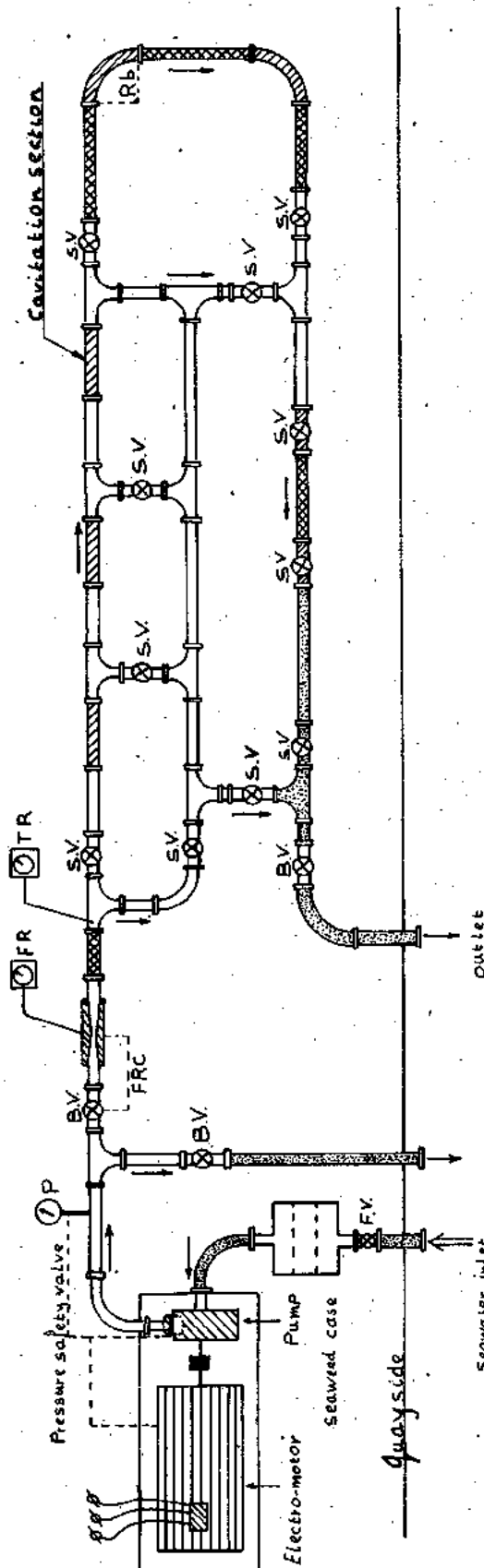


Fig. 8. Oxide layer with precipitates. Stripped by plastic replica after 25 days in stagnant sea-water. 23,000 ×



Fig. 9. Etch effects round a grain boundary after 25 days in stagnant sea-water of aged copper-10. 24,500 ×



Code

- S.V. = Slide Valve
- B.V. = Ball Valve
- F.V. = Foot Valve
- FR = Flow Recorder
- TR = Temp Recorder
- FRC = Flow Recorder Control
- P = Pressure measurement
- Rb = 30r4s  $\phi$  pipe = 123 cm.

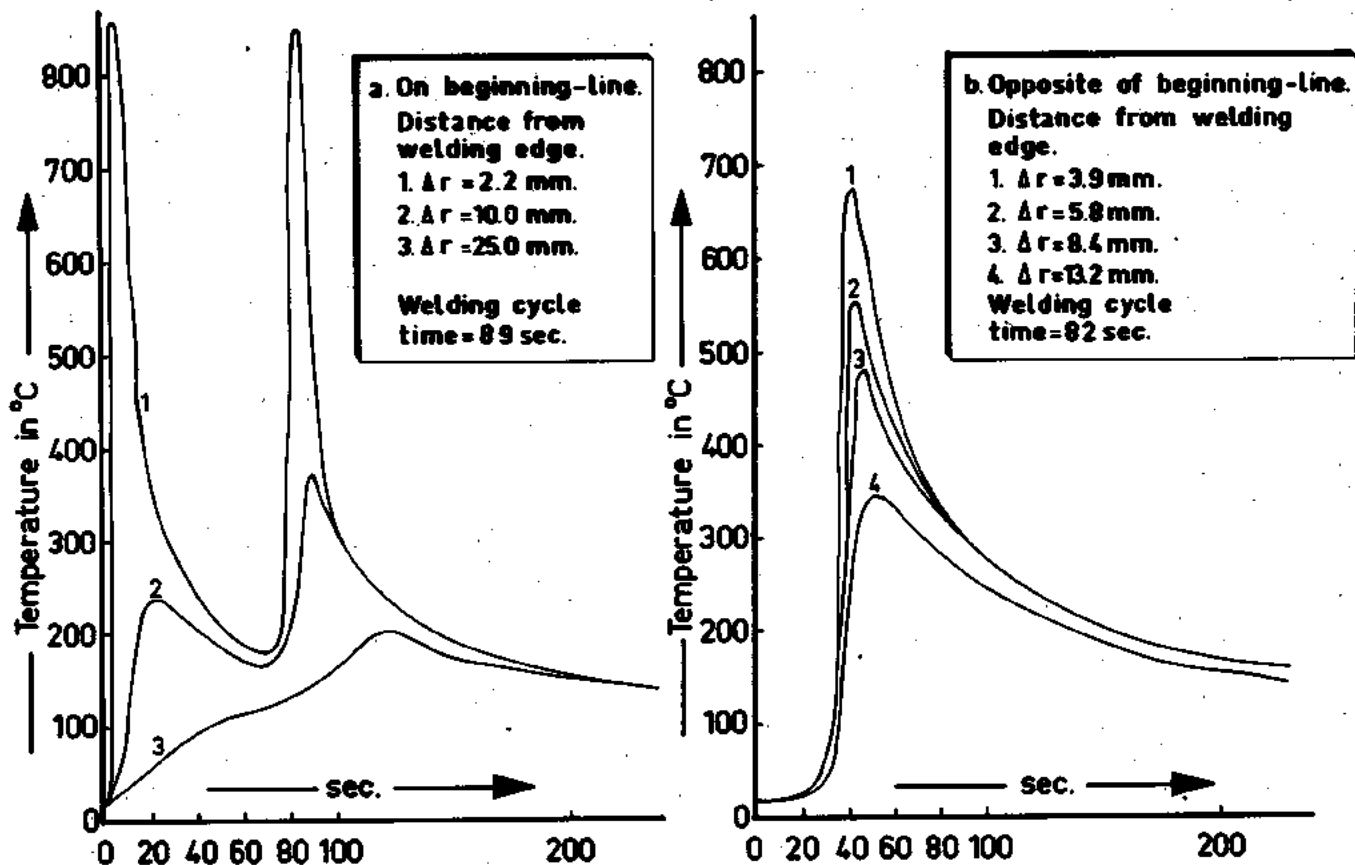
Data

- Electromotor : 5 hp
- Pump in serging point:
- $\dot{V} = 5 \cdot 10^{-3} \text{ m}^3/\text{sec} \rightarrow \Delta P = 625 \text{ atm.}$
- $\phi$  Pipe = 6,6 cm.

Materials

- Cunifer-10
- Test section
- fiberglass
- PVC.

Fig. 10. Outlay of the piping system in the harbour of Den Helder.



Temperature-time curves by welding of Cunifer-10 pipe.

Fig. 11

Welded test pieces are fitted in the seawater system to study the influence of welding-heat on the corrosion behaviour. As the influence of a bad weld is well known, the weld was made as smooth as possible. These experiments are still running.

#### 2. Potential measurements

To study the formation of an oxide layer, potential measurements of a new pipe in a seawater piping system of a sailing ship (motorship «Mercurius» K.N.S.M.) were carried out in the North sea. The potential was measured on the seawater side of the tube with an AgCl reference electrode (fig. 12). As can be seen from this figure the potential curve can be divided into two slopes. The steepest slope

( $\Delta \frac{\Delta v}{\Delta t} = 4,1 \frac{mv}{hr}$ ) is thought to be responsible for the

formation of an oxide layer. This slope will become less steep

( $\Delta \frac{\Delta v}{\Delta t} = 0,63 \frac{mv}{hr}$ ) and probably stabilisation of the o-

xide layer will take place. When the ship entered the waterway to Rotterdam (Nieuwe Waterweg) a potential decrease was measured. This phenomenon is not yet understood and can possibly be the effect of the polluted water in the waterway. New experiments on naval ships are planned to examine this.

#### IV. CONCLUSIONS

- 1) Commercial Cunifer-10 (as received) shows a strong segregation, which is not readily eliminated by heat treatment.
- 2) Ageing between 290°C and 735°C results in the formation of a precipitate. The crystal structure of matrix and precipitate are very similar (face centered cubic, lattice parameter 3,60 Å and 3,58 Å, resp.).
- 3) The oxidation of Cunifer-10 consists of an outer layer of brittle Cu<sub>2</sub>O and an inner zone of internal oxides of iron, nickel and manganese.
- 4) The corrosion in stagnant seawater is influenced in the beginning by the oxide-scale. At longer immersion times crystal orientation determines attack by pitting corrosion.
- 5) From welding experiments and a T.T.T.-diagram it is to be expected that precipitation can be avoided if proper measures are taken during welding.
- 6) Potential measurements of pipes in a seawater system in a ship may give information of the oxide layer.

#### V. ACKNOWLEDGMENT

The authors wish to thank the Netherlands Ship Research Centre, Delft for the permission to publish this paper. Among the staff of the Metal Research Institute the authors wish



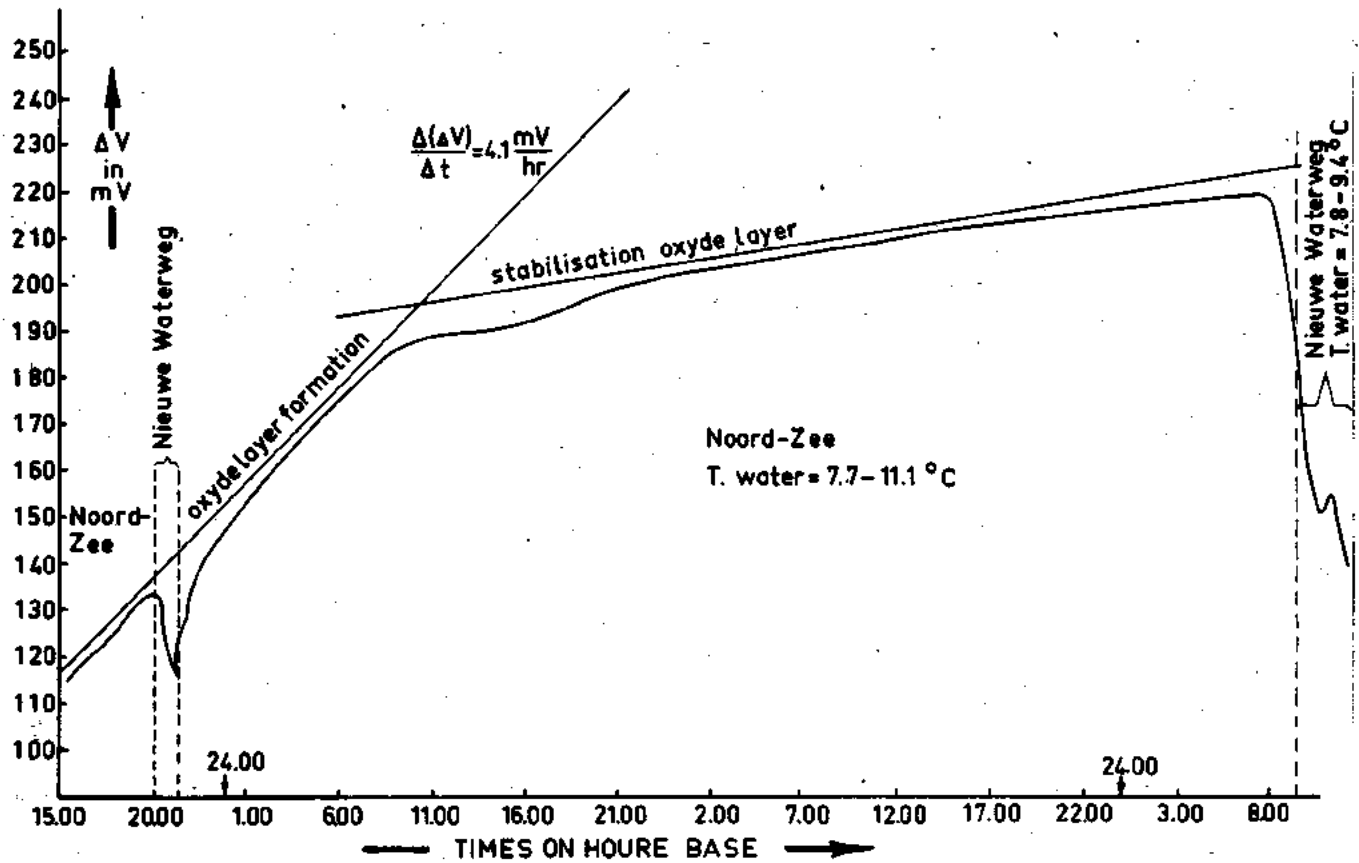


Fig. 12. Potential measurements of a new pipe in a sea-water system of a seagoing ship on the North sea. Potential measurements of cunifer-10 with respect to Ag/AgCl - reference - electrode A/B m.s. MERCURIUS (K.N.S.M.) from 28/11 till 2/12 1966.

to thank Dipl.-Ing. A.P. von Rosenstiel (electron microprobe analysis), Ir H.B. Zeedijk (electron microscopy) and Ing. P. Breedveld (microscopy) for their contributions to this program.

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## DISCUSSION

Prof. ENGELL (Germany): I congratulate first the speaker and second I have to ask a few questions.

The first concerns the application of isothermal T.T.T. diagram to precipitation during welding. I think it would be better to use the continuous T.T.T. diagram to see what may happen during welding.

The next question concerns the role of the precipitation on pitting corrosion. You have shown in your 1st diagram that at a certain content of iron, there is a minimum in corrosion. I would like to ask you whether the precipitation which was achieved under these special pretreatment conditions will decrease the iron content of the mixed crystal and thereby change the rate of corrosion.

The last of my question is: do you use the term pitting for what you have observed on the surface of your crystals? I would like to call this etching. If you have preferential attack in some crystallographic directions of the grain then I would call that an etch pit and not a pit or corrosion pit. Normally a corrosion pit I think is mostly like a shell of a ball and it shows no influence of the lattice orientation upon the corrosion rate. I think what you observed is mainly etching and not just pitting.

Dr. DE LANGE: As to the selection of the TTT diagram I think the isothermal diagram has a certain advantage in measuring it and I fully agree that in the conditions of the rising temperatures of welding or hot bending is not a very exact diagram, but I still feel it gives you a very good dead line if under certain conditions of wallthickness and method of welding or heating, precipitation is to be expected or not. So I think from the isothermal TTT diagram this can be used as an establishing matter. And for each conditional welding, which is new or when it deviates from a practice it will not be very difficult to establish the temperature recording such as we know them for one specificates of other pippings and yet to obtain an impression if precipitation will be there, if it will be there in a severe degree or if it may be expected to be avoided.

The first question also concerning the precipitation process is what we observed in corrosion pitting or not. I think it is very largely a method of definition and of course I should know that we used very short exposure times and that the surface affects which you can observe in the elektron microscope are rather limited, so we have the feeling to be in the very beginning of what should afterwards be

a normal pitting process and in fact if we continue our tests too long the surface roughening is too severe to be inspected in a proper manner by the electron-microscope. We feel that all we show on the surface is the beginning of the pitting and I think is discutable if we still call it etching or if you call it pitting already this is a rather arbitrary method. Well and the relation between the precipitates and the pitting is shown in the photographs.

Inside the grain we have very small precipitates and in the photographs made of the exposed specimens we could also observe many small pits inside grain, which is a very clear indication to connect the precipitation with local pitting of the surface.

Dr. HOAR (England): I would like to comment on the pitting process in iron modified cupronickel. I am sure Prof. ENGELL is correct in regarding this type of pitting as etch pitting, or I should call it low potential pitting, but I have seen high potential pitting of the hemispherical type in rather similar but more severe of cases of corrosion of the alloy. This in a heat exchanger that was evaporating brine at a salt works. Now this is a higher concentration of chloride and of course at much higher temperature than sea water; very bad pitting occurred at certain times but not at others, and it was traced to the absence when the pitting occurred of small amounts of calcium bicarbonate, and the presence, when the alloy was satisfactory, of sufficient calcium bicarbonate in the feed to give a scaly calcareous deposit. I believe that the resistance of these copper-nickel alloys to saline solutions may very often be greatly improved if some calcareous matter, is present as an overlying scale. Of course, this can happen under sea-water conditions especially if cathodic protection has been used. I would like to know if you have any experience of the formation of calcareous film on cupronickel in sea-water.

Dr. DE LANGE: I wish to point out Dr. HOAR that the conditions be mentioned are rather different from ours, firstly I do not see a real connection, but I just wish to mention that we found calcium under the cuprous oxide which may be linked to the results he mentioned. Secondly I wish to mention that the pitting which we observed and brought in connection with precipitates, was just in the beginning of the process and as I showed in the following slide, that is after 40 days of exposure, we feel that the attack is more of a crystalline nature and less influence by the precipitates, so perhaps the precipitates, play only an important role in some intermediate states of the process of attack.

Dr. POSCH (Holland): Has in your experiments the coupling in practical applications between copper-nickel alloy and steel shell been taken into account? For, if it has then you have much more chance to get the calcareous deposits as the copper-nickel alloys would be essentially cathodic.

Dr. DE LANGE: We did not investigate these aspects, so we only took the specimens not in connection with iron.

B. WELDON (England): I think it is been recognised in the past in the use of copper nickel piping and condenser tubes that very much better corrosion behaviour is obtained if the system in which the piping installed can have clean sea water put through at an early stage as is possible. This of course builds up the film which provides the corrosion resistance of the material. I wonder if the authors are considering going on to investigate the behaviour of material which has had this

exposure to clean sea water and then is put back into the stagnant condition in harbour waters to find the effect of this 'good' film?

Dr. DE LANGE: Yes, Mr. Chairman this is one of the problems and one of the purposes of this investigation. The potential measurements on board of the ship, which I showed you and we have just beginning a more serious investigations special started for the purpose to examine the matter you raised. The initial conditions of exposure may be of a great influence on the surface layer but this is still under execution, so I cannot mention here any results not the observations we are trying to make from the metal side in the very early beginning, so corrosion and oxidation are certainly the matter you raised.

Dr. KENWORTHY (England): Following up Mr. Weldon's last question could you tell us more about the loop installed at den Helder, of which you showed us a slide? In particular, could you state what water speeds you will be able to circulate and whether it will be re-circulated or 'once-through' sea water?

Dr. DE LANGE: Mr. Chairman, the corrosion loop is installed at this time in the harbour of Den Helder, and the water is used once through. The water speeds are going up to five meters per second in the circuit and the special purpose of this corrosion loop to test more samples as we are using them in fundamental studies and to study the influences of special construction parts. Actually the faulty circumstance that this loop is very close to the sea and can use fresh sea water, once through, is an advantage on one side but it has proved to be serious disadvantage on the other side as it was floated a few months ago and it was seriously damaged, which causes some delay on the execution of the tests.

Dr. KENWORTHY (England): I presume you will be able to install turbulence raisers in the loop so that you can study turbulent flow conditions.

I should also like to take this opportunity of congratulating you and your co-authors on the important contribution you have made to our knowledge of the metallurgy and corrosion behaviour of 90/10 copper nickel iron alloy.

Dr. HOAR (England): A very short remark following Mr. KENWORTHY'S question: as far as copper-nickel alloys are concerned, I think we should be worried more about low flow rates in copper-nickel systems because they have sufficiently established themselves for high rates. I think most of the corrosion cases nowadays in copper-nickel alloys, is at low flow rates for some reason.

Dr. DE LANGE: I can truly agree with the speaker in fact as I mentioned, the purpose of this investigation is to the material for applications in cold water tubings on ships for exemple in fire prevention systems. Here we may have either rather high water speed or very long periods of stagnancy of the water; so certainly the low rates of water velocity are at least in this purpose of investigation very important.

Dr. KENWORTHY (England): A final point: have you investigated the resistance of the alloy to hot spot corrosion?

Dr. DE LANGE: No.

# PASSIVIERUNGSVERHALTEN UND SPANNUNGRISSEKORROSION VON EISEN-MANGAN-CHROM-LEGIERUNGEN IN NATRIUMCHLORID-LÖSUNG

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## ZUSAMMENFASSUNG

In 3% NaCl-Lösung werden an MnCr-Stählen des Legierungsbereiches

C (%)	Mn (%)	Cr (%)	N (%)
< 0,03	20-28	0-12	0,01-0,2

Zusammenhänge zwischen der Passivierungsneigung und dem Auftreten selektiver Korrosionserscheinungen untersucht. Eine Bewertung des Passivierungsverhaltens der einzelnen Werkstoffe erfolgt anhand der charakteristischen Kenngrößen von Stromdichte-Potential-Kurven. Gefügebestandteile der metastabilen hexagonalen Phase  $\epsilon$ -Martensit haben einen passivitätsverringenden Einfluss gegenüber rein austenitischen Legierungen. Während hohe Mangangehalte die Neigung zur Passivierung herabsetzen, wird der Passivbereich mit steigenden Chromgehalten erweitert.

Die unterschiedliche Tendenz zur Deckschichtbildung bei  $T = 20^\circ\text{C}$  und  $T = 100^\circ\text{C}$  wird mit den Bildungsmechanismen von Primär- und Sekundärschichten erklärt.

In sauerstoffhaltiger Lösung findet eine ausgeprägte Korrosion im Lochfrassbereich statt.

Aussenstromlose und potentiostatische Untersuchungen

über das Standzeitverhalten der verschiedenen Stähle erfolgten an Zugproben mit der Anfangsspannung  $\sigma_a = 0,8 \sigma_B$  in Lösungen von  $T = 20^\circ\text{C}$  und  $T = 100^\circ\text{C}$ . Die Standzeiten zeigen in Beziehung zu den jeweils gültigen Lochfrassraten den prinzipiellen Zusammenhang mit den elektrochemischen Kenngrößen.

Standzeitergebnisse vergleichbarer Stähle werden mit variierendem C-Gehalt und der Gefügeverschiedenheit beeinflusst. Stähle ohne Chrom und mit 4% Chrom gehen durch transkristalline Spannungsrisskorrosion zu Bruch, während reizgeglühte Proben des Stahles X 40 MnCrN 19 durch Ausscheidungen von Chromkarbiden an den Korngrenzen einen interkristallinen Rissverlauf zeigen.

Das Vermeiden interkristalliner Rissbildung in C-armen MnCr-Stählen mit 4% Chrom verschiebt den Anfälligkeitsbereich gegen selektive Korrosionsschäden in positiver Potentialrichtung bis über das Lochfrasspotential.

In Stählen mit 8% und 12% Chrom treten lochfrassartige Schäden ohne Anhaltspunkt einer Spannungsrisskorrosion auf. Die Lebensdauer derartiger Zugproben wird durch die Querschnittsverminderung der wachsenden Löcher begrenzt.

## 1. EINLEITUNG

Nichtmagnetisierbare Stähle bewirken keine Störung und Abschirmung von magnetischen Feldern und finden daher auf einigen Gebieten der Elektrotechnik seit langem eine breite Anwendung. In letzter Zeit machten besondere Aufgaben im Schiffbau den Einsatz nichtmagnetisierbarer Stähle erforderlich. Die metallurgischen Möglichkeiten zur Erzielung eines ferritfreien, stabil austenitischen Gefüges wiesen unter Berücksichtigung wirtschaftlich günstiger Bedingungen zunächst auf die MnCr-Stähle des Typs X 40 MnCrN 19 (1).

Aus den langen Standzeiten in hochkonzentrierter siedender  $\text{MgCl}_2$ -Lösung schloss man ohne Kenntnis der elektrochemischen Zusammenhänge auf ein günstiges Verhalten der MnCr-Stähle in kaltem Meerwasser (2).

Bei dem Einsatz dieses Stahles in Seewasser traten aber in einer bestimmten Entfernung von der Schweissnaht interkristalline Risse im Grundwerkstoff auf (3).

Nach Arbeiten von H. Kohl (4) und von A. Bäumel und O. Tramposch (5) sollen nur angelassene MnCr-Stähle in Meerwasser anfällig gegen interkristalline Spannungsrisskorrosion sein. Als Hauptursache der Rissbildung wird die Ausscheidung von Chromkarbiden des Typs  $\text{M}_7\text{C}_3$  und die

damit verbundene Chromverarmung in Korngrenzennähe angesehen. Ein unterschiedliches elektrochemisches Verhalten von Korngrenzen und Kornflächen, und damit ein selektiver Angriff, ist nur in schwach angreifenden Medien festzustellen (5).

Nach der Chromverarmungstheorie (6) lässt sich die interkristalline Spannungsrisskorrosion legierungstechnisch durch Weglassen des Chroms vermeiden. Diese Möglichkeit ist von A. Bäumel anzuwenden versucht worden (7).

Bei Untersuchungen über das Auftreten von Spannungsrisskorrosion weisen viele Autoren darauf hin, dass Rissbildung nur dann eintritt, wenn der betreffende Werkstoff eine Neigung zur Deckschichtbildung im angreifenden Medium hat (8) bis (14). Passivierend wirkende Schutzschichten gelten auch bei Stählen als notwendige Voraussetzung für das Auftreten der Spannungsrisskorrosion.

Das überraschende Phänomen einer ausgeprägten interkristallinen Spannungsrisskorrosion bei dem üblicherweise als aktiv geltenden Stahl X 40 MnCrN 19 in Seewasser stellte die Aufgabe, Zusammenhänge zwischen der Passivierungsneigung und dem Auftreten selektiver Korrosionserscheinungen im System MnCr-Stahl/Meerwasser zu finden.

Unsere Untersuchung umfasst folgenden Legierungsbereich:

TAFEL 1

CHEM. ZUSAMMENSETZUNG, MECHANISCHE KENNWERTE UND GEFÜGE DER UNTERSUCHTEN STÄHLE

Stahl	Analysen				Mechan. Kennwerte /T=20 °C				Gefüge
	C(%)	Mn(%)	Cr(%)	N(%)	$\sigma_{0,2}$ (Kp·mm <sup>-2</sup> )	$\sigma_B$ (Kp·mm <sup>-2</sup> )	$\delta_5$ (%)	$\psi$ (%)	
765	0,01	20,0	—	0,09	46,6	80,8	29,3	32,0	$\gamma + \epsilon$ (3)
523	0,6	20,2	—	0,09	40,0	98,7	42,5	30,4	$\gamma$
354	0,01	19,6	4,2	0,01	41,4	76,2	28,8	46,8	$\gamma + \epsilon$ (3)
355	0,01	19,9	4,2	0,10	35,4	77,6	43,3	50,0	$\gamma + \epsilon$ (2)
767	0,10	20,5	4,3	0,09	27,9	87,5	41,3	37,5	$\gamma + \epsilon$ (1)
X 40 MnCrN 19	0,41	18,8	4,5	0,12	46,7	94,8	46,3	34,5	$\gamma$
361	0,02	24,0	4,6	0,01	44,5	80,2	30,2	38,0	$\gamma + \epsilon$ (2)
362	0,02	24,4	4,3	0,11	27,1	69,9	42,5	48,8	$\gamma + \epsilon$ (1)
388	0,01	27,8	4,1	0,14	28,8	61,9	48,8	56,4	$\gamma + \epsilon$ (1)
363	0,01	24,3	8,3	0,01	39,1	78,2	35,3	56,3	$\gamma + \epsilon$ (2)
364	0,01	24,3	8,4	0,11	28,7	67,2	48,4	58,2	$\gamma + \epsilon$ (1)
365	0,02	23,9	8,0	0,16	33,0	67,5	52,6	63,3	$\gamma$
366	0,01	24,2	11,6	0,02	31,2	67,0	43,1	53,9	$\gamma + \epsilon$ (1)
377	0,01	24,0	12,1	0,11	25,5	62,1	52,5	50,1	$\gamma$
378	0,01	24,3	12,4	0,21	31,0	62,2	56,3	54,4	$\gamma$

Wärmebehandlung:  
30 min 1100° C/Wasser  
+ 3 h 700° C/Luft  
 $\sigma_{0,2}$  — Dehngrenze mit Feindehn-  
messung bestimmt

$\gamma$ —Austenit  
 $\epsilon$ —Martensit  
(1) wenig  
(2) mittel  
(3) viel

C [%]	Mn [%]	Cr [%]	N [%]
< 0,03	20 - 28	0 - 12	0,01 - 0,2

Tafel 1 sind die Analysenwerte zu entnehmen.

Die Bezeichnung der Stähle erfolgte nach den Chargennummern.

Durch Absenken des Kohlenstoffgehalts unter 0,03% wurde erreicht, dass die Legierungen auch im angelassenen Zustand keine Ausscheidungen von Chromkarbiden an den Korngrenzen aufwiesen.

Die Stähle 523 und 767 mit erhöhtem Kohlenstoffgehalt wurden zu Vergleichszwecken untersucht. Sie sind als nahe Varianten des Stahles X 40 MnCrN 19 anzusehen.

## 2. KONSTITUTION UND MECHANISCHES VERHALTEN VON MANGANSTÄHLEN

Aus dem umfangreichen Schrifttum über niedriggekohte Fe-Mn-Legierungen ist bekannt, dass sich ein stabil austenitisches Gefüge nur mit Mangangehalten über 30% erreichen lässt. In Mn-Stählen mit 10 bis 30% Mn findet bei Temperaturen unter 200°C eine diffusionslose Umwandlung in die metastabile hexagonale Phase  $\epsilon$ -Martensit statt.

H. Schumann hat in mehreren Veröffentlichungen auf die physikalischen und technologischen Besonderheiten von Mn-Stählen mit einem Mischgefüge aus  $\gamma$ -Austenit +  $\epsilon$ -Martensit hingewiesen (16) bis (24). Eine austenitstabilisierende Wirkung hat neben dem Mangan auch ein Zusatz von Chrom. In der gleichen Richtung wirkt ein erhöhter Stickstoffgehalt.

Für die Durchführung von Spannungskorrosionsversuchen bei definierten Zugbelastungen ist die Kenntnis der mechanischen Kennwerte wichtig. Ein Vergleich der in Tafel 1 aufgeführten mechanischen Werte mit den qualitativen Gefügebefunden unterstreicht den verfestigenden Einfluss der

metastabilen Phase  $\epsilon$ -Martensit im  $\gamma$ -Austenit. Bild 1 zeigt eindeutig, dass die bekannte festigkeitssteigernde Wirkung

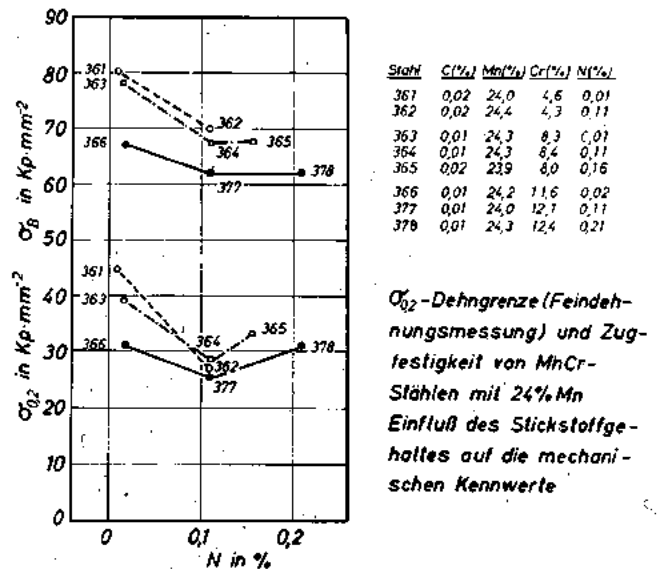
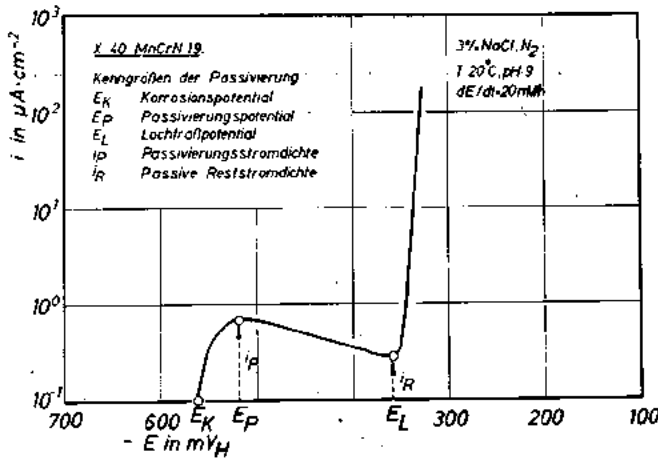


Bild 1

von Stickstoffzugaben in Legierungen mit Mischgefüge nicht eintritt. Legierungen ohne Stickstoff haben aufgrund ihrer hohen Anteile an  $\epsilon$ -Martensit bedeutend höhere Werte der  $\sigma_{0,2}$ -Dehngrenze und Zugfestigkeit als Legierungen mit einem Stickstoffgehalt von 0,1%. Eine Erhöhung der  $\sigma_{0,2}$ -Dehngrenze ist erst bei weiteren Stickstoffzugaben im stabilen  $\gamma$ -Austenit zu erreichen.

### 3. ELEKTROCHEMISCHES VERHALTEN UND DECKSCHICHTBILDUNG

Bei dem Begriff der Passivität von Metallen und Legierungen handelt es sich nicht um ein eindeutig abgrenzbares Phänomen (25). Im folgenden wird eine Metalloberfläche als passivierbar bezeichnet, wenn durch die Bildung einer Deckschicht eine deutliche Hemmung des anodischen Vorganges einsetzt. Eine Beurteilung und Bewertung der Passivierungsneigung der einzelnen Legierungen erfolgt anhand der charakteristischen Kenngrößen von Stromdichte-Potential-Kurven. In Bild 2 sind die für das Passivierungsverhalten massgebenden



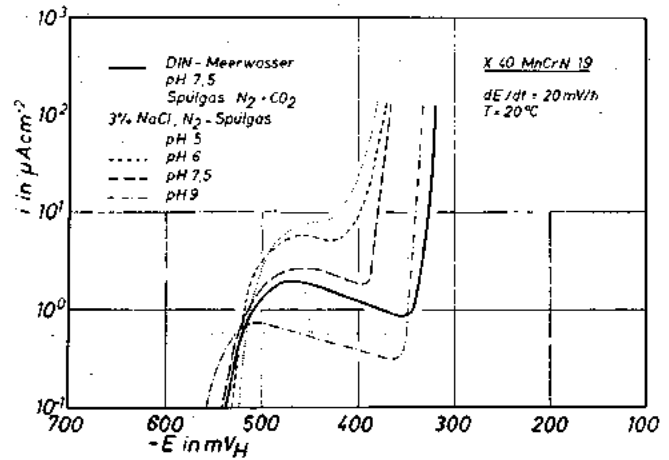
Potentiokinetic Stromdichte-Potential-Kurve des Stahles X 40 MnCrN 19 und Kennzeichnung der charakteristischen Passivierungsgrößen

Bild 2

den Grössen in eine Stromdichte-Potential-Kurve eingezeichnet. Ausgehend vom Ruhe- oder Korrosionspotential  $E_K$  des Stahles im nahezu sauerstofffreien Elektrolyten erfolgt bei dem Passivierungspotential  $E_P$  und der Passivierungsstromdichte  $i_P$  ein Abfallen des anodischen Stromes bis auf den kleineren Wert  $i_R$ , der passiven Reststromdichte. Der kleine Reststrom  $i_R$  im passiven Zustand wird für den stationären Zustand der Auflösung und Nachbildung des Passivfilms benötigt (26). Bei dem Potential  $E_L$  setzt unvermittelt ein steiler Anstieg der Stromwerte ein. Das Potential  $E_L$  ist als Grenze des passiven Bereiches aufzufassen. In Anlehnung an die Nomenklatur bei passiven CrNi-Stählen in chloridhaltigen Medien wird das Potential  $E_L$  auch hier als «Lochfrasspotential» bezeichnet, obwohl die Korrosionserscheinungen an Legierungen mit niedrigem Chromgehalt sich von dem bekannten Lochfrass der CrNi-Stähle unterscheiden.

Die elektrochemischen Untersuchungen über das Passivierungsverhalten der MnCr-Stähle erfolgten potentiostatisch in Glaszellen der früher beschriebenen (27) Bauart. Sämtliche Stahlproben wurden nach dem Homogenisieren 3 Stunden bei 700°C gegläht, um mit dieser Wärmebehandlung einen möglichen anfälligen Gefügezustand herbeizuführen. Die Proben von der Grösse 20 mm × 15 mm × 5 mm wurden nach dem Schleifen bis zur Körnung 600 ohne weitere Nachbehandlung in den Elektrolyten eingesetzt.

Beim Einleiten von Stickstoff in künstliches Meerwasser nach DIN 50900 entweicht CO<sub>2</sub>. Das führt zu allmählicher Alkalisierung und zu einer Abnahme des Carbonatgehaltes. Durch Zugabe von CO<sub>2</sub> zum Spülgas in einer geeigneten Mischvorrichtung lässt sich das Kohlensäuregleichgewicht aufrechterhalten (28). Die schlechte Reproduzierbarkeit der Ergebnisse in diesem komplexen System veranlassten uns, sämtliche Untersuchungen in 3% NaCl-Lösung durchzuführen. In Bild 3 ist die potentiokinetic aufgenommene Strom-

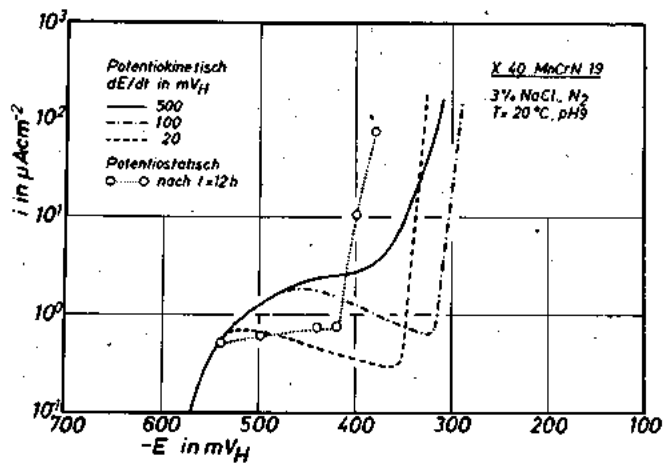


Potentiokinetic Stromdichte-Potential-Kurven von Stahl X 40 MnCrN 19 in Abhängigkeit vom pH-Wert der Lösung. Vergleich der Passivierungsneigung in 3% NaCl und Meerwasser nach DIN 50900

Bild 3

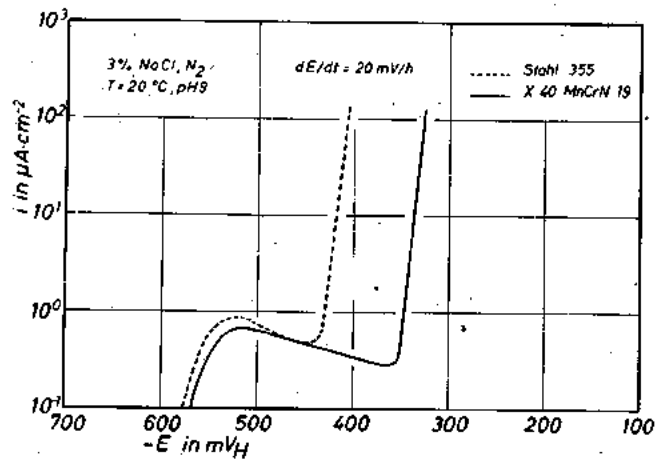
dichte-Potential-Kurve des Stahles X 40 MnCrN 19 in DIN-Meerwasser mit dem pH-Wert 7,5 dem Verhalten in 3% NaCl-Lösung unterschiedlicher Azidität gegenübergestellt. Die Kurven zeigen eindeutig, dass DIN-Meerwasser einen ausgedehnteren Passivbereich  $E_P/E_L$  bewirkt als 3% NaCl-Lösung. Die passivitätssteigernde Wirkung karbonathaltiger Lösungen im schwach alkalischen Bereich lässt sich mit einer Pufferwirkung der karbonathaltigen Lösung erklären. Veränderungen des pH-Wertes in der probennahen Schicht durch den anodischen Vorgang  $Me^{2+} + zOH^- \rightarrow Me(OH)_z$  treten in Pufferlösungen nicht in Erscheinung. Eine weitgehende Übereinstimmung des Passivbereiches besteht in 3% NaCl bei pH 9 und in DIN-Meerwasser (28). Für die folgenden Versuche bei Raumtemperatur galt der pH-Wert 9 als verbindliche Bedingung. Versuche bei T = 100°C wurden bei dem aufgrund der zunehmenden Dissoziation entsprechenden pH-Wert 7,5 durchgeführt. Alle pH-Angaben beziehen sich auf Messwerte bei Raumtemperatur.

Die Nachteile der potentiokinetic Methode für Messungen der wahren Lochfrasspotentiale sind in den Arbeiten von W. Schwenk (29) und G. Herbsleb (30) ausführlich diskutiert. In den Bildern 4 und 5 sind an zwei Stählen mit verschiedener Polarisationsgeschwindigkeit kinetisch aufgenommene Stromdichte-Potential-Kurven den potentiostatisch ermittelten Kurven gegenübergestellt. Es ist hier bemerkenswert, dass bei Werkstoffen mit geringer Passivierungsneigung die hohe Potentialänderungsgeschwindigkeit  $dE/dt = 500$  mV/h dem Vorgang der Deckschichtenbildung keine Zeit lässt. Eine Neigung zur Passivierung ist aber auch hier unverkennbar. Der Wendepunkt der Kurven fällt in den Bereich des potentiostatisch ermittelten «Lochfrasspotentials». Die langsameren Geschwindigkeiten von 100 mV/h und 20 mV/h geben der Oberfläche genügend Zeit, die für eine Deckschichtenbildung benötigte Ladung zu speichern.



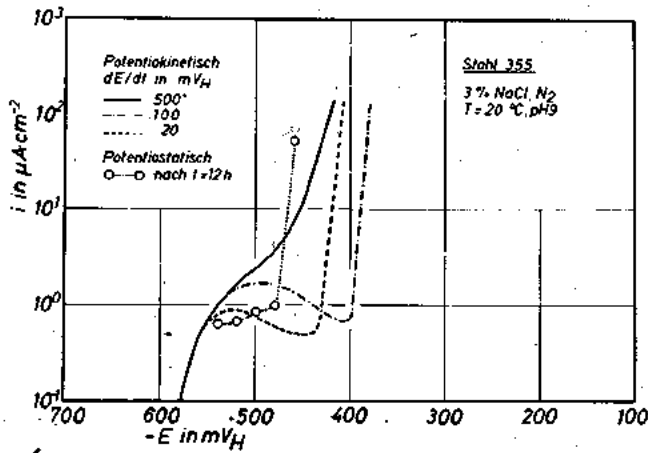
**Einfluss der Polarisationsgeschwindigkeit auf den Verlauf der Stromdichte-Potential-Kurven Vergleich zu potentiostatischen Werten**

Bild 4



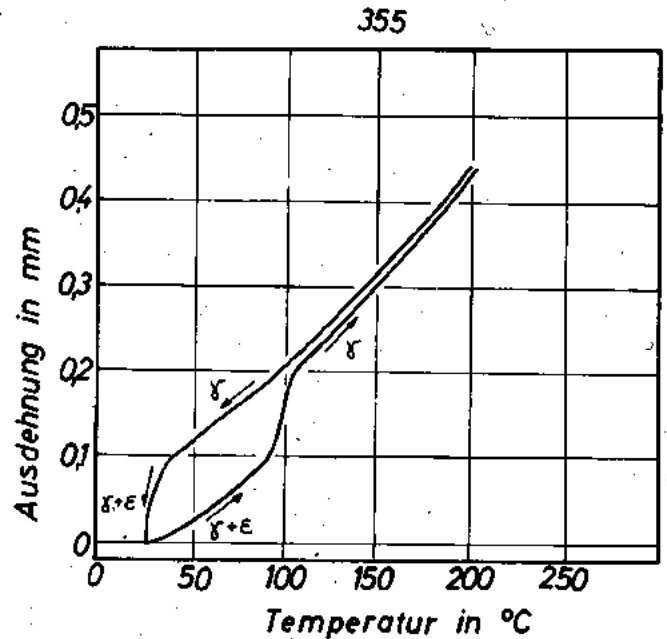
**Stromdichte-Potential-Kurven von zwei MnCr-Stählen mit verschieden hohem C-Gehalt**

Bild 6



**Einfluss der Polarisationsgeschwindigkeit auf den Verlauf der Stromdichte-Potential-Kurven Vergleich zu potentiostatischen Werten**

Bild 5



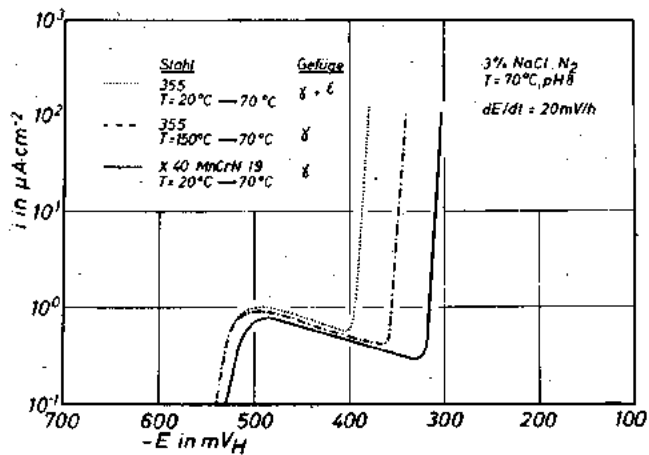
**Dilatometerkurve von Stahl 355**

Bild 7

Der Wiederanstieg des Stromes bei -300 bis -450 mV entspricht dem Beginn von Lochfrass, der hier allerdings nur zu einer narbigen Anfrassung führt. Das Lochfrasspotential verschiebt sich mit fallender Polarisationsgeschwindigkeit zunächst zu edleren Werten. Hier liegt der bekannte «Trainiereffekt» vor, der eine in Wahrheit nicht vorhandene Oberflächengüte vortäuscht (29). Bei weiterer Senkung der Polarisationsgeschwindigkeit fällt das Lochfrasspotential wieder ab. Es hat sich bei den vorliegenden Untersuchungen bewährt, die Polarisationsgeschwindigkeit  $dE/dt = 20 mV/h$  zu benutzen.

Ein sehr interessantes Ergebnis ist die verschieden ausgeprägte Passivierung der beiden Stähle 355 und X 40 MnCrN 19 (Bild 6). Bis auf den Kohlenstoffgehalt haben beide Werkstoffe die gleiche chemische Zusammensetzung. Die Unterschiede können auf einer passivitätsmindernden Wirkung des  $\epsilon$ -Martensits im Stahl 355 beruhen, oder es muss eine spezifische passivitätssteigernde Wirkung des Kohlenstoffs im Austenit angenommen werden. In Versuchen von H.E. Bühler und W. Schwenk (31) an einer 18/10Cr/Ni-Legierung mit zweiphasigem Gefüge aus Austenit +  $\alpha$ -Martensit

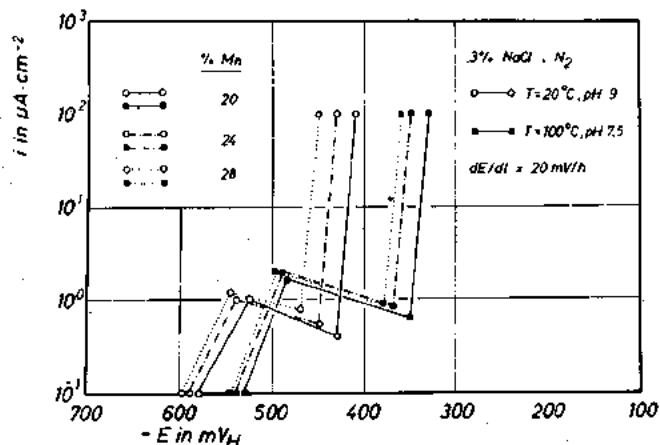
wurde eine Verschiebung des «aktiven Astes» der Stromdichte-Potential-Kurve zu negativeren Potentialen festgestellt. Eine bevorzugte selektive Martensitkorrosion wurde in 1n  $H_2SO_4$  im Aktivbereich nachgewiesen. In chloridhaltigen Lösungen traten Löcher bevorzugt im Martensit auf. Anhand der Umwandlungshysterese in der Dilatometerkurve für den Stahl 355 (Bild 7) (32) lassen sich bei  $T = 70^\circ C$  die Gefügestände  $\gamma + \epsilon$  beim Aufheizen und reiner  $\gamma$ -Austenit beim Abkühlen einstellen. Die Stromdichte-Potential-Kurve des Stahles 355 mit Austenitgefüge zeigt eine Annäherung an die Charakteristik des X 40 MnCrN 19 (Bild 8). Neben dem durch Bild 8 belegten Einfluss der Struktur auf die Stabilität von Deckschichten in chloridhaltigen Medien (33) besteht offenbar auch eine passivitätsfördernde Wirkung des Kohlenstoffs.



*Einfluss des C-Gehaltes und des Gefüges auf die Passivierung von MnCr-Stählen*

Bild 8

Der passivitätsverringere Einfluss steigender Mangangehalte ist in Bild 9 an Stählen mit 4% Chrom dargestellt. Die rein chemische Wirkung des Mangans wird hier allerdings

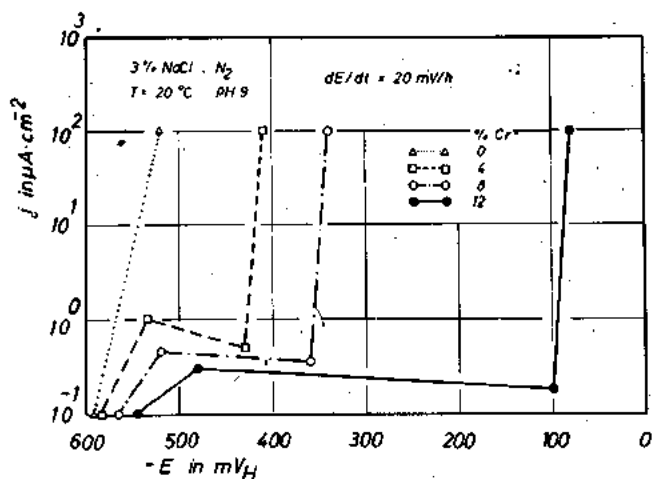


*Potentiokinetic Stromdichte - Potential - Kurven (halb - schematisch) von MnCr-Stählen mit 4% Cr Einfluss des Mangangehaltes auf die Passivierungsdaten*

Bild 9

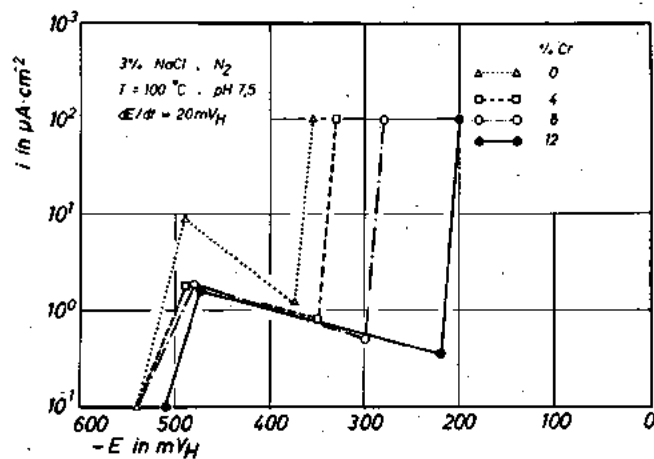
durch den gegenläufigen Struktureffekt überdeckt, da mit zunehmendem Mangangehalt der Anteil der  $\epsilon$ -Phase abnimmt. Der Einfluss von Chromzusätzen kommt in den Bildern 10 und 11 zum Ausdruck. Die halbschematisch gezeichneten Kurven repräsentieren die Mittelwerte von Chargen verschiedener Mangangehalte bei den angegebenen Chromgehalten. Stähle ohne Chrom zeigen bei 20°C überhaupt keine Passivierung. Mit zunehmendem Chromgehalt dehnt sich der Passivbereich aus. Bei 100°C tritt auch bei Stählen ohne Chrom eine ausgeprägte Passivierung auf. Die Passivbereiche von Stählen mit 4% und 8% Chrom werden durch die Temperaturerhöhung ausgedehnt, die der Stähle mit 12% Chrom eingeengt.

Beobachtungen an Metalloberflächen nach potentiostatischen und potentiokineticen Versuchen bei niedriger und hoher Temperatur lassen den Schluss zu, dass zwei Bildungsmechanismen von Deckschichten an Legierungen mit Chromgehalten von 0 bis 12% angenommen werden können: Die Bildung von Primär- und von Sekundärschichten. Primärschichten entstehen durch unmittelbare Reaktion des Metalls mit der Lösung. Sie bestehen aus Oxiden, Oxidhydraten oder



*Potentiokinetic Stromdichte - Potential - Kurven (halb - schematisch) von MnCr-Stählen Einfluss des Chromgehaltes auf die Passivierung*

Bild 10

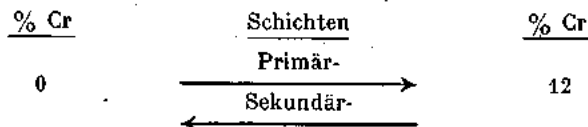


*Potentiokinetic Stromdichte - Potential - Kurven (halb - schematisch) von MnCr-Stählen Einfluss des Chromgehaltes auf die Passivierung*

Bild 11

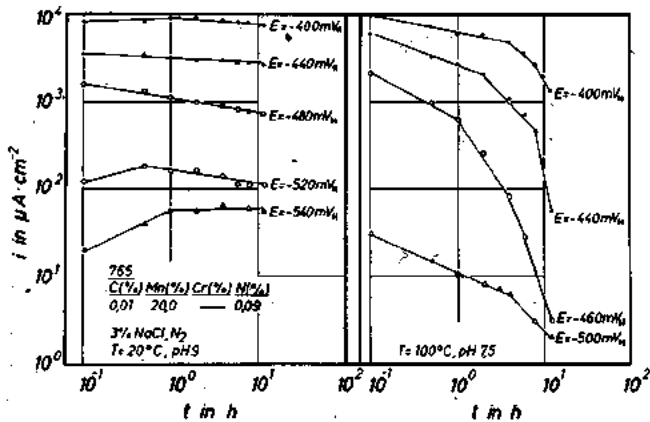
Hydroxiden, sind porenfrei und geben trotz geringer Dicke der Oberfläche einen hohen Korrosionsschutz (34). Sekundärschichten werden als Korrosionsprodukte aus der Lösung ausgefällt und auf dem Metall niedergeschlagen. Derartige Schichten sind porig und bieten einen weniger ausgeprägten Schutz vor weiterer Korrosion (35).

Häufig geht die Bildung der Sekundärschichten der Bildung einer Primärschicht voraus, da erst in den Poren der Sekundärschicht die zur Passivierung nötigen hohen Stromdichten erreicht werden. Mit steigendem Chromgehalt fallen die wahren Passivierungsstromdichten ab. Daher treten bei höheren Chromgehalten Primärschichten auf, ehe die zur Ausfällung der Sekundärschicht nötigen hohen Metallionen-Konzentrationen bzw. Auflösungsstromdichten erreicht werden. Dieser Zusammenhang lässt sich graphisch folgendermaßen darstellen:



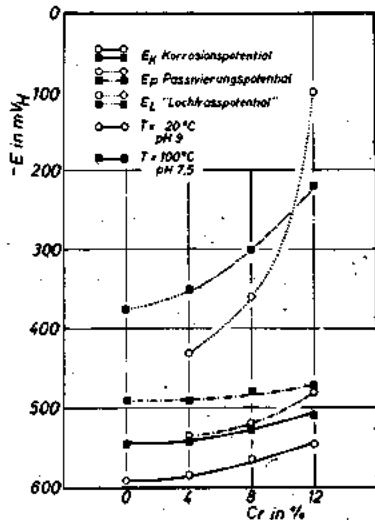
Legierungen mit 12% Chrom bilden nur Primärschichten. Das erklärt die oben genannte Abnahme des Lochfrasspotentials mit erhöhter Temperatur. Stähle mit Chromgehalten von 4 und 8% können wegen der erhöhten Lösungsgeschwindigkeit der Primärschichten bei 100°C Sekundärschichten bilden. Bei Werkstoffen ohne Chrom verstärkt die höhere Temperatur die Neigung zum Bilden von Sekundärschichten. Diese Schichten sind erheblich dichter als die lockeren Ablagerungen von Korrosionsprodukten bei Raumtemperatur, so dass die Stromspannungs-Charakteristik einen passiven Bereich anzeigt. Das kann auf der Wirkung der Sekundärschichten selbst oder auf ihrer Mithilfe bei der Bildung von Primärschichten beruhen. Der Stromdichte-Zeit-Verlauf bei potentiostatischen Halteversuchen in Lösungen von 20°C und 100°C zeigt die Unterschiede in der Tendenz zur Deckschichtbildung der chromfreien Stähle bei 20 und 100°C an (Bild 12).

In Bild 13 sind die kennzeichnenden Potentialgrößen des



Stromdichte-Zeit-Kurven eines Manganstahls ohne Chrom in 3% NaCl-Lösung  
Potentiostatische Halteversuche mit verschiedenen Potentialen bei T = 20°C und T = 100°C

Bild 12



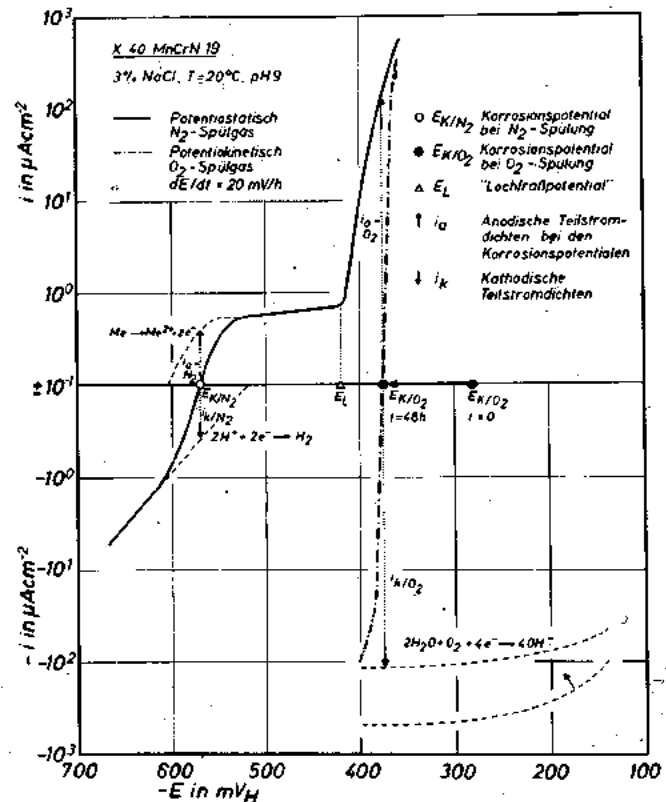
Einfluss des Chromgehaltes in MnCr-Stählen auf die charakteristischen Passivierungsgrößen in 3% NaCl-Lösung mit N<sub>2</sub>-Spülgas Potentiokinetisch mit dE/dt = 20 mV/h

Bild 13

Passivierungsverhaltens in Abhängigkeit vom Chromgehalt dargestellt. Hier kommt noch einmal die potenzialeinengende Wirkung erhöhter Temperatur auf die Lage der Lochfrasspotentiale bei Legierungen von 4 bis 12% Chrom zum Aus-

druck. Der Potentialbereich der Lochfrassäste von 330 mV bei T = 20°C wird auf 130 mV bei T = 100°C reduziert. Dieser Befund muss bei der Interpretation von Spannungsrisversuchen bei verschiedenen Temperaturen beachtet werden.

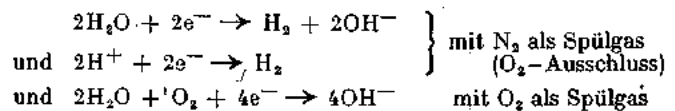
Die Bestimmung der Passivierungsneigung der untersuchten Werkstoffe ist in sauerstofffreien Lösungen leichter möglich, weil dort die Wasserstoffionenreduktion die einzige kathodische Reaktion darstellt. Die Korrosionsvorgänge in sauerstoffhaltigen Lösungen lassen sich nur mit Hilfe der im sauerstofffreien Medium erhaltenen Stromdichte-Potentialkurve verstehen. In Bild 14 wird das Korrosionsverhalten des X 40 MnCrN 19 in sauerstoffhaltiger 3% NaCl-Lösung erläutert.



Stromdichte-Potential-Kurven des Stahles X 40 MnCrN 19 in O<sub>2</sub>-freier und O<sub>2</sub>-haltiger Lösung

Bild 14

Die Korrosionspotentiale bei N<sub>2</sub>-Spülung und mit O<sub>2</sub>-Spülung liegen im stationären Zustand durch die unterschiedlichen kathodischen Teilreaktionen



um 200 mV auseinander. Das Korrosionspotential in sauerstoffhaltiger Lösung bewegt sich zwar nach dem Einsetzen der Proben in den Elektrolyten um etwa 100 mV in negativer Richtung, aber es muss grundsätzlich festgestellt werden, dass der stationäre Zustand sich stets positiver als das Lochfrasspotential einstellt. Daraus folgt, dass in sauerstoffhaltiger Lösung eine ausgeprägte Korrosion des Stahles im Lochfrassbereich stattfindet. Das Wandern des Korrosionspotentials in negativer Richtung wird nur verständlich unter der Annahme, dass der Diffusionsgrenzstrom durch entstehende Korrosionsschichten und damit verminderte Nachlieferung von Sauerstoff zur Metalloberfläche abnimmt (28).



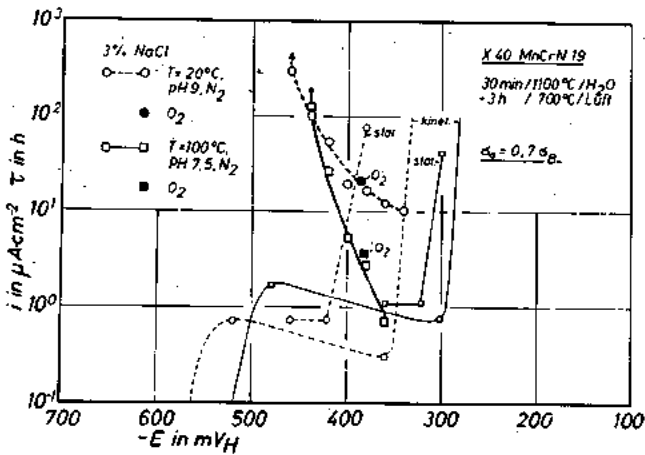
#### 4. DIE BESTÄNDIGKEIT GEGEN SPANNUNGSRISSKORROSION

Untersuchungen über das Spannungsrisssverhalten der Werkstoffe wurden an Rundstäben mit einer Prüflänge von  $L_0 = 40$  mm und einem Durchmesser der Prüflänge von  $d_0 = 5,0$  mm durchgeführt. Da trotz sorgfältiger mechanischer Bearbeitung in den äusseren Schichten Druckschwingungen und Verformungen entstehen (36) (37), erfolgte ein Abtragen der oberflächlich verformten Randschichten um 0,3 mm durch Elektropolieren in einem Gemisch aus Perchlorsäure, Äthylalkohol und Butylglycol. Die Probenschäfte wurden dann mit Schlauchstücken aus Silikonkautschuk überzogen und an den konischen Übergängen zum Prüfteil mit Araldit ausgegossen. Auf diese Weise konnten störende Effekte an der Phasengrenze Flüssigkeit/Dampf vermieden werden. Ausserdem wird durch diese Abdeckung die Berechnung der Stromdichten an der Prüfstrecke möglich. Die elektrochemischen Messzellen entsprachen im Prinzip der von R. Münster und H. Gräfen skizzierten Anordnung (38).

Die Zugspannungen wurden in den Prüfmaschinen durch Gewichtbelastung mit einer Hebelübersetzung 30:1 aufgebracht. Als Bezug für gleiche Anfangsspannungen verschiedener Stähle dienten die bei der betreffenden Prüf-

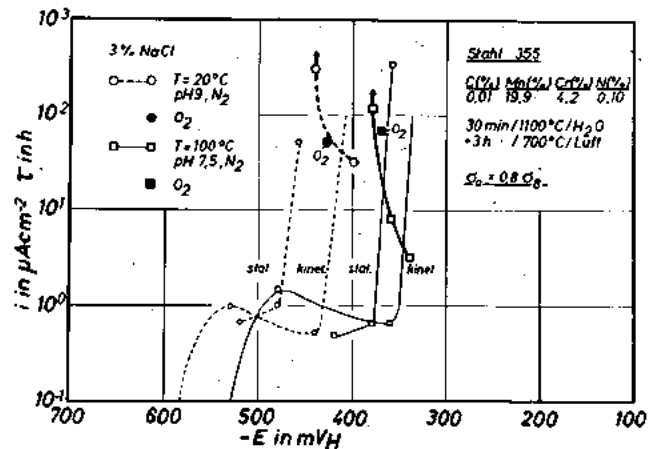
weniger prägnant auswirken. Die erreichten Standzeiten in siedender Lösung sind kürzer als in kaltem Elektrolyten. Bei -440 mV tritt ein Schnittpunkt der beiden Standzeitkurven auf. Bei sauerstoffhaltigen Lösungen stellen sich an den hier behandelten Stählen Korrosionspotentiale ein, die im Bereich des durch Lochfrass ausgelösten Steilanstiegs der Stromdichte-Potential-Kurve liegen. Aus diesem Grunde ist es für die praktische Verwendung sinnvoll, die Standzeiten jeweils auf gleiche Differenzen von Probenpotential und zugehörigem Lochfrasspotential  $E_L$  zu beziehen.

Die Untersuchungen der Standzeiten an den übrigen Legierungen mussten bei der noch höheren Anfangsspannung  $\sigma_a = 0,8 \sigma_B$  durchgeführt werden, da niedrigere Belastungen in aussenstromlosen Versuchen bei der Mehrzahl der Werkstoffe zu keinem Bruch führten. Die Standzeitergebnisse am Stahl 355 verdeutlichen den negativen Einfluss des Kohlenstoffgehaltes bei X 40 MnCrN 19. Der Stahl 355 entspricht bis auf den fehlenden C-Gehalt dem Stahl X 40 MnCrN 19 und bietet bei den vergleichbaren Potentialen erheblich längere Standzeiten. Bild 16 zeigt, dass bei diesem Stahl das «Lochfrasspotential» ein Grenzpotential bedeutet, dessen Überschreiten in negativer Richtung einen kathodischen Schutz gegen Spannungsrissskorrosion ermöglicht.



Standzeit-Potential-Diagramm des Stahles X 40 MnCrN 19 und Angabe der Stromdichte-Potential-Kurven (potentiokinetisch mit 20 mV/h und potentiostatisch)

Bild 15



Standzeit-Potential-Diagramm des Stahles 355 und Angabe der Stromdichte-Potential-Kurven (potentiokinetisch mit 20 mV/h und potentiostatisch)

Bild 16

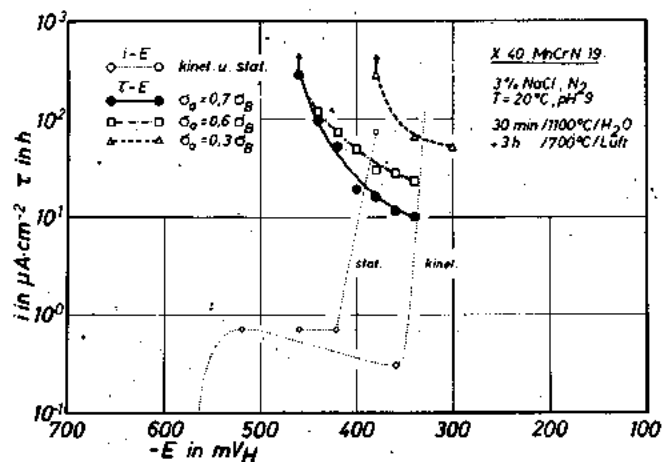
temperatur ermittelten wahren Zugfestigkeiten. Es wurden aussenstromlose Versuche in sauerstoffhaltigen Lösungen und potentiostatische Versuche in sauerstofffreien Lösungen bei den Temperaturen  $T = 20^\circ\text{C}$  und  $T = 100^\circ\text{C}$  durchgeführt. Eine zeitliche Begrenzung der Standzeitversuche erfolgte bei Raumtemperatur auf 300 Stunden und bei Siedetemperatur auf 120 Stunden. Die erzielten Standzeiten werden bei jeder bildlichen Darstellung auf die betreffende Stromdichte-Potential-Kurve ungespannter Proben bezogen. Die eingetragenen Messpunkte stammen zum Teil aus Einzelversuchen oder bedeuten die Mittelwerte von zwei Parallelversuchen.

Bild 15 zeigt die Standzeiten von 3 h bei  $700^\circ\text{C}$  reizgeglühten Zugproben des Stahles X 40 MnCrN 19 mit der Anfangsspannung  $\sigma_a = 0,7 \sigma_B$ . In die Kurvenverläufe der potentiostatischen Versuche wurden auch die Standzeiten der aussenstromlosen Versuche mit den über die Standzeit gemittelten Korrosionspotentialen eingetragen. Die Übereinstimmung mit den potentiostatischen Ergebnissen ist gut. Die Standzeitkurve bei hoher Temperatur verläuft steiler als die Raumtemperaturkurve. Die Reproduzierbarkeit der Ergebnisse ist daher in kalten Lösungen besser, da sich geringfügige Ungenauigkeiten in der Potentialeinstellung und -korrektur

Während bei dem Stahl 355 bei einem Potential  $E_L + 40$  mV eine Standzeit über 300 Stunden zu verzeichnen ist, tritt dieser Fall bei dem X 40 MnCrN 19 erst bei einem Potential  $E_L - 40$  mV ein. Das bedeutet, dass der Anfälligkeitsbereich des X 40 MnCrN 19 um 80 mV in negativer Potentialrichtung gegenüber dem des C-freien 355 verschoben ist.

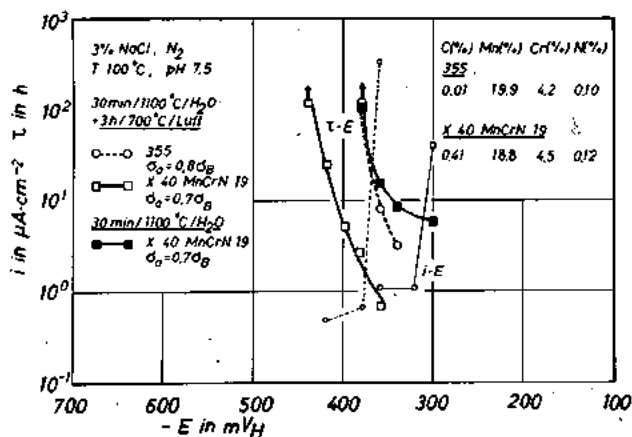
Die in Bild 17 dargestellte Abhängigkeit der Standzeiten von der gewählten Belastung ergibt die Aussage, dass am Stahl X 40 MnCrN 19 erst bei den niedrigen Anfangsspannungen  $\sigma_a = 0,3 \sigma_B$  die gleiche Standzeitcharakteristik wie bei dem Stahl 355 mit  $\sigma_a = 0,8 \sigma_B$  auftritt, wenn man die Potentiale jeweils auf  $E_L$  bezieht.

Eine Verbesserung der Standzeit bei dem Stahl X 40 MnCrN 19 sollte erzielt werden können, wenn durch eine geeignete Wärmebehandlung Ausscheidungen von Chromkarbiden auf den Korngrenzen vermieden werden. A. Bäumer konnte an abgeschreckten Bügelproben nach mehreren Wochen Prüfdauer keine Anrisse feststellen (5). Unsere Ergebnisse an Zugproben zeigen aber in Bild 18, dass auch an homogenisierten Proben Spannungsrissskorrosion eintritt. Eine Verbesserung gegenüber den angelassenen Proben ist unver-



Standzeit-Potential-Diagramm des Stahles X 40 MnCrN 19 bei verschiedenen Anfangsspannungen  $\sigma_0$  und Lage der Stromdichte-Potential-Kurven

Bild 17



Standzeit-Potential-Schaubild von zwei Manganstählen mit 4% Chrom und verschiedenem Kohlenstoffgehalt Lage der potentiostatischen Stromdichte-Potential-Kurven

Bild 18

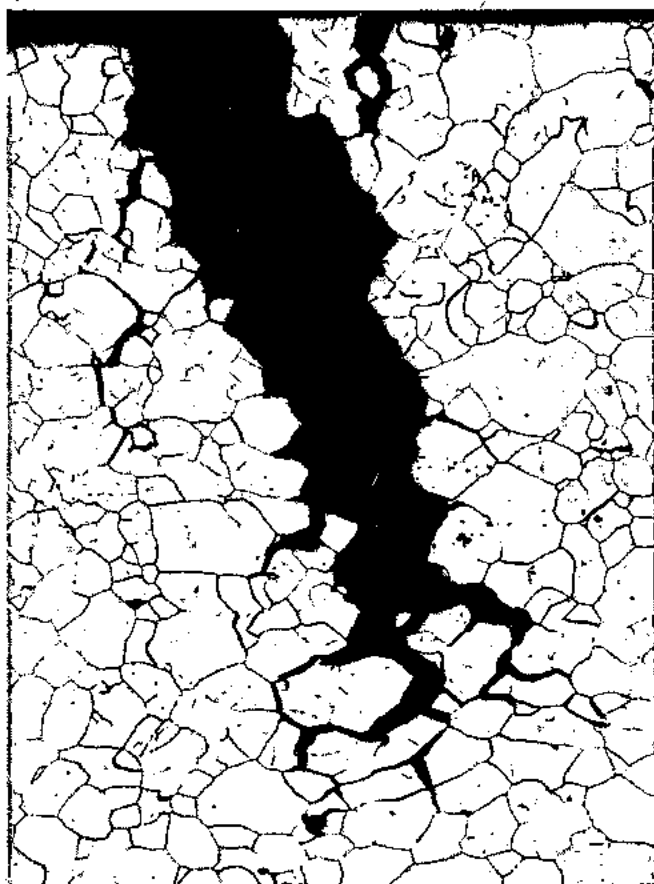


Bild 19. — Stahl X 40 MnCrN 19 C (%) Mn (%) Cr (%) N (%)  
30 min 1100°C/Wasser + 3 h 700°C/Luft  
Rissverlauf interkristallin  $V = 100$

zur Stromspannungskurve. Eine Besonderheit trat nur bei dem Stahl 767 mit einem C-Gehalt von 0,1% auf. Die nach dem mittleren C-Gehalt erwarteten Standzeiten zwischen denen des Stahles X 40 MnCrN 19 und des Stahles 355 wurden deutlich überschritten. Besonders bei Siedetemperatur ergab sich eine unerwartet hohe Beständigkeit. In ausstromlosen Versuchen liess sich bei 20 und 100°C auch bei höchster Belastung kein Bruch der Proben herbeiführen. Offensichtlich liegt die Schwelle des C-Gehaltes für eine Sensibilisierung von Korngrenzen bei Legierungen mit 4% Chrom bedeutend über der bei CrNi-Stählen mit 18% Cr angegebenen Grenzkonzentration von  $\sim 0,03\%$  C. Darüber hinaus liegt im erhöhten C-Gehalt von 0,1% eine Beständigkeitsverbesserung besonders bei erhöhter Prüftemperatur vor, die bei Raumtemperatur nicht in gleicher Weise zu verzeichnen ist. Es müssen anhand dieses Beispiels Bedenken erhoben werden, bei der Anwendung hoher Prüftemperaturen generell auf ein parallel gutes Verhalten in kalter Lösung Schlüsse zu ziehen.

Variierender Kohlenstoffgehalt und Gefügeverschiedenheit beeinflussen auch die Ergebnisse für die beiden Stähle 765 und 523 ohne Chrom. Bei Raumtemperatur verhält sich der austenitische Stahl 523 vorteilhafter als der Stahl 765 mit Mischgefüge (Bild 22), bei Siedetemperatur kehren sich die Verhältnisse um (Bild 23). Die Umwandlungstemperatur  $\gamma + \epsilon \rightarrow \gamma$  liegt hier bei  $T = 150^\circ\text{C}$ . Das ungünstigere Verhalten des Stahles 765 bei niedriger Temperatur kann mit



Bild 20. — Stahl x40 MnCrN 19 C (%) Mn (%) Cr (%) N (%)  
 0,41 18,8 4,5 0,12  
 30 min 1100°C/Wasser  
 Rissverlauf transkristallin V = 500

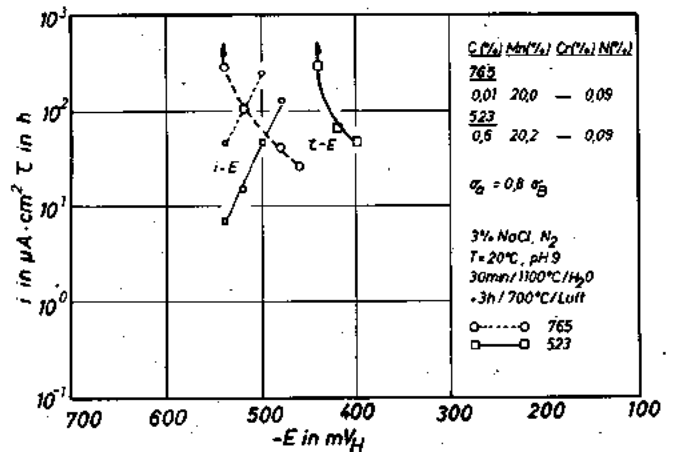


Bild 21. — Stahl 355 C (%) Mn (%) Cr (%) N (%)  
 0,01 19,9 4,2 0,10  
 30 min 1100°C/Wasser  
 + 3 h 700°C/Luft  
 Rissverlauf transkristallin, bezogen auf die Austenitkorn-  
 grenzen. V = 500

der starken Versprödungsneigung dieses Stahles erklärt werden. Die Proben sind durch den extrem hohen Gehalt an  $\epsilon$ -Martensit ausgesprochen kerbempfindlich und gehen beim Entstehen geringer Anrisse durch Korrosion spröde zu Bruch.

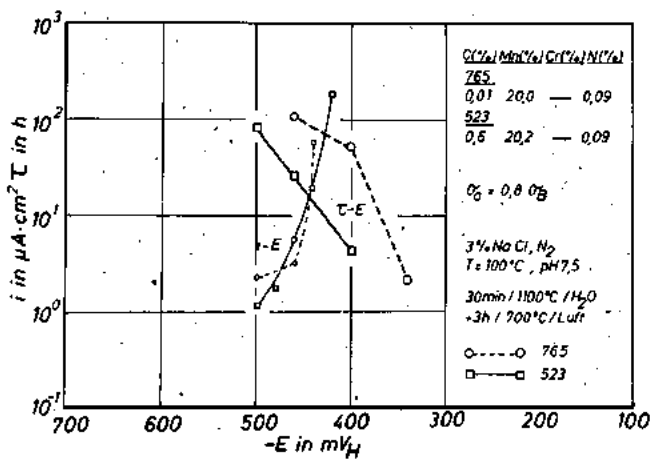
In Bild 24 und 25 veranschaulichen Proben der beiden Stähle mit etwa gleich grossen Standzeiten das sehr unterschiedliche Vermögen zum Ausbilden von Rissen. Während der Stahl 523 in der Bruchzone eine Vielzahl von Nebenrisen hat, führte bei dem Stahl 765 ein einziger Korrosionsschaden zum Bruch der Probe.

Das Vorhandensein und Aufbrechen von Deckschichten als Kriterium für das Einsetzen von Spannungsrisskorrosion ist auch bei den Stählen ohne Chrom bei  $T = 100^\circ\text{C}$  festzustellen, wie die Aufnahme der Stromdichte-Potential-Kurven aufgezeigt hatte. Ob diese Schichten notwendigerweise echte Passivschichten sein müssen, muss zunächst unbeantwortet bleiben. Eine örtlich gesteigerte Reaktionsgeschwindigkeit während plastischer Verformung ist jedenfalls auch bei verletzten Sekundärschichten zu erwarten (12). Das Auftreten von Spannungsrisskorrosion an Stählen ohne Chromgehalt in kalter Lösung bereitet dagegen bei der Interpretation erhebliche Schwierigkeiten, da sich elektrochemisch keine Deckschichten nachweisen liessen. In Korrosionsnarben, die auch ohne besonders wirksame Deckschichten zustande kommen können, liegen aber andere Verhältnisse vor. Hier kann eine Deckschichtbildung durch die Verlängerung der Diffusionswege und die damit erfolgende Anreicherung der Korrosionsprodukte eintreten, die den weiteren Angriff



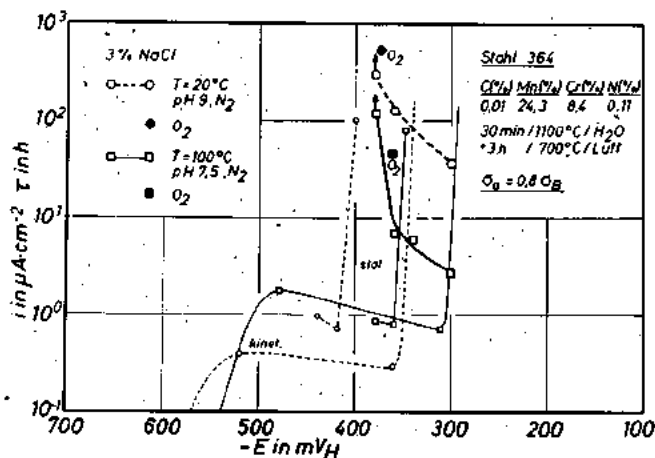
Standzeit-Potential-Schaubild von zwei Manganstählen mit verschieden hohem Kohlenstoffgehalt  
 Lage der potentiostatischen Stromdichte-Potential-Kurven

Bild 22



Standzeit-Potential-Schaubild von zwei Manganstählen mit verschiedenem Kohlenstoffgehalt  
Lage der potentiostatischen Stromdichte-Potential-Kurven

Bild 23



Standzeit-Potential-Diagramm des Stahles 364 und Angabe der Stromdichte-Potential-Kurven (potentiostatisch mit 20 mV/h und potentiostatisch)

Bild 26



Bild 24. — Spannungskorrosion von Manganstählen  
Stahl 765 C (%) Mn (%) Cr (%) N (%)  $\sigma = 0,8 \sigma_B$   
0,01 20,0 — 0,09 E = -340 mV\_H  
3% NaCl, N₂, T = 100°C, pH 7,5  $\tau = 2,1$  h

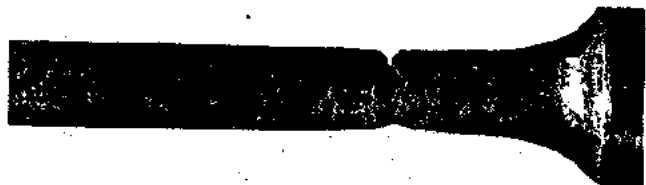


Bild 25. — Spannungskorrosion von Manganstählen, Stahl 523  
C (%) Mn (%) Cr (%) N (%)  $\sigma = 0,8 \sigma_B$   
0,6 20,2 — 0,09 E = -400 mV\_H  
3% NaCl, N₂, T = 100°C pH 7,5  $\tau = 4,2$  h

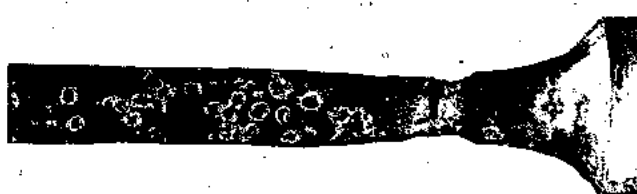


Bild 27. — Spannungskorrosion von Manganstählen, Stahl 364  
C (%) Mn (%) Cr (%) N (%)  $\sigma = 0,8 \sigma_B$   
0,01 24,3 8,4 0,11 E = -340 mV\_H  
3% NaCl, N₂, T = 100°C, pH 7,5  $\tau = 5,2$  h



Bild 28. — Spannungskorrosion von Manganstählen, Stahl 364  
C (%) Mn (%) Cr (%) N (%)  $\sigma = 0,8 \sigma_B$   
0,01 24,3 8,4 0,11 E = -300 mV\_H  
3% NaCl, N₂, T = 100°C, pH = 7,5  $\tau = 2,8$  h

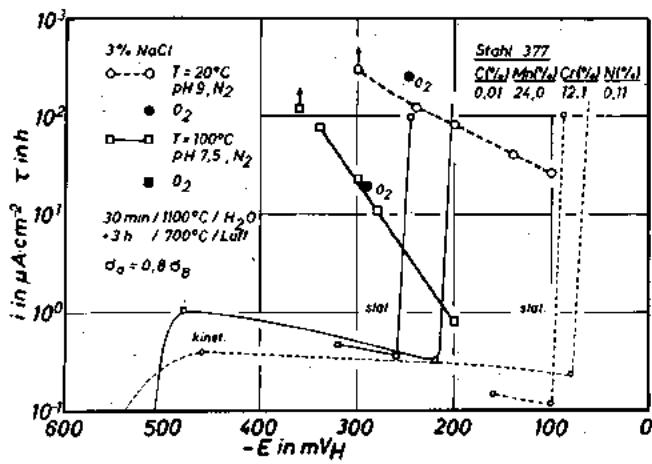
ausreichend auf den fließenden Rissgrund konzentriert.

Die Abhängigkeit der Standzeit vom Potential bei Zugproben mit einem Chromgehalt von 8% ist in Bild 26 dargestellt. Gegenüber dem steilen Abfall der Standzeiten bei dem Stahl 355 mit 4% Chrom ist der flachere Verlauf der Kurven auffällig. Eine Beurteilung der Proben nach dem Bruch ergibt einen muldenartigen Schadensverlauf in kalter Lösung und ein lochfrassartiges Erscheinungsbild in der heißen Lösung. Aus den Bildern 27 und 28 folgt eine zunehmende Lochzahl dichte mit positiverem Potential.

Legierungen mit 12% Chrom zeigen sehr flach geneigte Standzeit-Potential-Kurven (Bild 29), die weit in den passiven Bereich ungespannter Proben hineinreichen. Das Lochfrasspotential unbelasteter Proben kann hier nicht als Grenzpotential für den Beginn selektiver Schäden fungieren, da

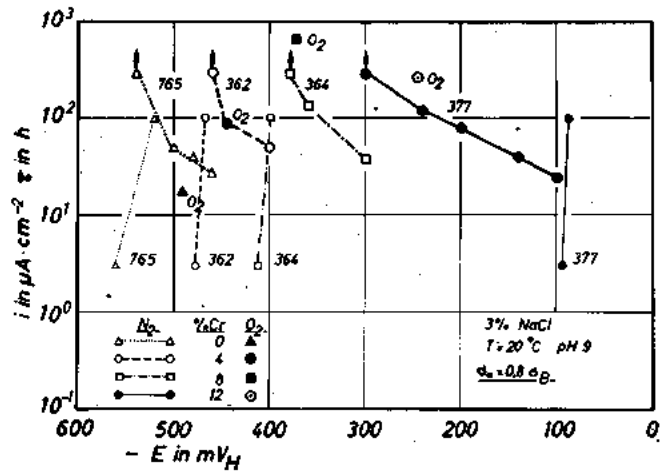
die mechanische Belastung eine hohe Kriechgeschwindigkeit der austenitischen Proben bewirkt. Durch das starke Kriechen werden ständig die Passivschichten verletzt, so dass das Lochfrasspotential belasteter Proben zu negativeren Werten verschoben wird. Die Schäden in den Proben sind in kalter und heisser Lösung lochfrassartig ohne den geringsten Anhaltspunkt einer Spannungsrissskorrosion. Auch hier ist der Einfluss des Potentials auf die Lochzahl dichte eindeutig zu erkennen (Bild 30 bis 32). Die Lebensdauer der Proben ist durch die Querschnittsverminderung begrenzt, die die wachsenden Löcher verursachen.

Eine Zusammenstellung von Standzeiten an Stählen mit Chromgehalten von 0 bis 12% in Beziehung zu den jeweils gültigen "Lochfrassästen" zeigt deutlich in Bild 33 den prinzipiellen Zusammenhang mit den elektrochemischen Kenn-



Standzeit-Potential-Diagramm des Stahles 377 und Angabe der Stromdichte-Potential-Kurven (potentiokinetisch mit 20mV/h und potentiostatisch)

Bild 29



Potentiostatische Standzeit-Potential-Kurven von MnCr-Stählen in Beziehung zur Lage des potentiostatisch ermittelten "Lochfraßastes" in 3% NaCl mit N<sub>2</sub> als Spülgas

Standzeiten außenstromloser Versuche in O<sub>2</sub>-haltiger Lösung

Wärmebehandlung: 30min/1100°C/H<sub>2</sub>O  
→ 3h/700°C/Luft

Bild 33



Bild 30. — Spannungskorrosion von Manganstählen, Stahl 377  
C (%) Mn (%) Cr (%) N (%)      σ = 0,8 σ<sub>B</sub>  
0,01 24,0 12,1 0,11      E = -300 mV<sub>H</sub>  
3% NaCl, N<sub>2</sub>, T = 100°C, pH = 7,5      τ = 22,5 h



Bild 31. — Spannungskorrosion von Manganstählen, Stahl 377  
C (%) Mn (%) Cr (%) N (%)      σ = 0,8 σ<sub>B</sub>  
0,01 24,0 12,1 0,11      E = -280 mV<sub>H</sub>  
3% NaCl, N<sub>2</sub>, T = 100°C, pH = 7,5      τ = 10,5 h



Bild 32. — Spannungskorrosion von Manganstählen, Stahl 377  
C (%) Mn (%) Cr (%) N (%)      σ = 0,8 σ<sub>B</sub>  
0,01 24,0 12,1 0,11      E = -200 mV<sub>H</sub>  
3% NaCl, N<sub>2</sub>, T = 100°C, pH = 7,5      τ = 0,8 h

größen. In dem Diagramm kommt die erläuterte Sonderselung der Legierung mit 12% Chrom zum Ausdruck.

In martensitischen Chromstählen mit 13% Chrom ist in 3% NaCl-Lösung das Auftreten von Spannungsrisskorrosion bekannt. Hier wird als beginnender Angriff eine Lochbildung festgestellt, die aufgrund des entstehenden dreiaxigen Spannungszustandes zu Spannungsrisskorrosion führt (40). Das Ausbleiben dieser Rissbildung bei MnCr-Stählen mit einem Chromgehalt über 8% muss auf metallphysikalischen Ursachen beruhen, die eine Rissbildung nicht zulassen.

In verschiedenen Arbeiten der letzten Zeit wurde ein Zusammenhang zwischen der Stapelfehlerenergie und Nahordnungsrate eines Werkstoffes, seiner Versetzungsanordnung und der Anfälligkeit gegen transkristalline Spannungsrisskorrosion gefunden und die Ursachen dieses Zusammenhangs erörtert (41 bis 44).

Die Stapelfehlerbildung in Eisen wird durch Zusatz von Mangan oder Chrom verstärkt (45). Bei gleichzeitiger Anwesenheit von Mangan und Chrom soll die Wirkung des Mangans auf die Erniedrigung der Stapelfehlerenergie den Ausschlag geben (46). Nach C.H. White und R.W.K. Honeycombe (47) tritt der hexagonale ε-Martensit dann auf, wenn die Stapelfehlerenergie des Austenitgitters auf hinreichend niedrige Werte abgesenkt wird. Ein Zusatz von Chrom stabilisiert das γ-Gitter gegen die Umwandlung in den hexagonalen ε-Martensit. Es ist daher anzunehmen, dass er in MnCr-Stählen die Stapelfehlerenergie erhöht und mit einem veränderten Versetzungstyp die Neigung zum Entstehen von Spannungsrisskorrosion vermindert.

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#### DISKUSSION

Dr. POSCH (Holland): Ich möchte gerne Herrn Prof. Engell fragen, ob das Passivierungsverhalten dieser Eisen-Mangan-Chromstähle in siedender Magnesiumchloridlösung prinzipiell anders ist als im Seewasser?

Prof. ENGELL: Das Passivierungsverhalten dieser Stähle in siedender Magnesiumchloridlösung von 42% Magnesiumchlorid ist grundsätzlich anders. Die Stähle sind in dieser Lösung voll aktiv, es ist keine Spur von Passivierung kennbar. Aus diesem Grunde ist es auch nicht erstaunlich, unserer Meinung nach, dass diese Stähle in 42%iger Magnesiumchloridlösung keinerlei Spannungsrisskorrosion mehr zeigt.

Dr. POSCH (Holland): Noch eine Frage bitte. Es ist bekannt, dass Zusätze von Iodiden die Spannungsrisskorrosion von austenitischen-Chromnickelstählen verzögern oder verhindern, was auch von der

Konzentration von Iodiden abhängt. Nun sind im Seewasser Iodide und Bromide anwesend. Ist hier diese Konzentration nicht genügend oder geht dieser bremsende Effekt von Iodidzusätzen der Spannungsrisskorrosion im Seewasser nicht entgegen?

Prof. ENGELL: Wir haben die Spannungsrisskorrosionsbeständigkeit dieser Legierungen nicht nur in 3% Natriumchlorid von pH Wert 9 sondern auch im synthetischen Meerwasser untersucht was ja auch Iodide enthält, und keinerlei Verzögerung der Spannungsrisskorrosion durch Iodide feststellen können. Unsere Erklärung dafür ist die, dass die Wirkung der Iodide vermutlich auf einer bevorzugten Adsorption beruht und diese Adsorption dürfte Potentialabhängig sein. Wir befinden uns hier in einem Potentialbereich der wesentlich unedler ist als der Potentialbereich, in dem Chromnickelstähle an Spannungsrisskorrosion erliden. Das könnte sehr wohl sein, dass bei diesen Potentialen keine bevorzugte Adsorption von Iodiden mehr stattfindet.

# SOME PRINCIPLES OF CORROSION AND PROTECTION OF METALS IN SEA - WATER

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## SUMMARY

The case of the failure of a polyvinyl paint due to replacement of unvaporized solvent by water is discussed. Owing to the excessive solvent retention a far from impermeable

film was produced.

Futhermore the case of corrosion resistant of metals and alloys is discussed.

## INTRODUCTION

Mr. Chairman, Ladies and Gentlemen, I am honoured to address this gathering. I would ask that you do not take the title too seriously, because such a subject requires a book, and I have less than half an hour. I shall first consider the two main principles of corrosion and protection of metals in sea-water and then give one example from practice of each, showing how the principle can be applied to the explanation and alleviation of the corrosion problem concerned. The two principles are:

A. We must try to keep water, oxygen and chloride ion away from the metal. With sea-water, this is easier said than done.

B. If we cannot exclude the corrosive reactants we must make the metal either sufficiently cathodic or suitably anodic, so that it is either under cathodic protection or is in the passivity range of electrode potential. I shall now consider a special practical case involving A and another involving B.

## TWO PRACTICAL PROBLEMS

A. The first case that I shall discuss [a paint failure on a ship's hull] is not an experiment but an observation, because partial failure had occurred long before I got to see this particular ship's bottom.

This was a new ship; the plates had been shop-primed, with a zinc-filled epoxy primer, a common practice in England to-day; the primer contained about 60% of zinc powder, so it was *not* a zinc-rich, electrically conducting primer. The plates were then welded in the usual way, so that along the welds there would be a somewhat destroyed zone of primer.

The paint system used was a polyvinyl composition. In the U.S.A. and to a less extent in the U.K., a multicoat system of polyvinyl paint (really lacquer, because it is completely polymerized before application and dries by evaporation of solvent) has given good service; it is included in our U.K. standard code of practice. It consists of the co-polymer of vinyl chloride and vinyl acetate, sometimes with the addition of a small percentage of maleic acid, dissolved in methyl-isobutyl ketone, and it dries by evaporation of this solvent (MIBK). Up to ten coats, each very thin and needing only a few minutes to dry by evaporation, are applied: the process in practice needs several operating gangs, following one another at appropriate intervals, since speed of operation is necessary in ship-painting practice.

The new ship had been treated with a polyvinyl system, but instead of the many thin coats, only two coats of a high-

build polyvinyl composition had been used, to obtain the same total thickness as that given by the normal ten thin coats. Each coat was thus about five times thick as the standard coat.

Now in paint coats generally, we rely upon total thickness as a major factor that determines the ability of the paint to exclude oxygen, water and sodium chloride, because according to the laws of diffusion, the rate of permeation of the film is proportional to the square of its thickness. Consequently, at first sight one would say two coats of high-build polyvinyl, each five times as thick as the ordinary thin coats, would give protection equal to that given by ten ordinary thin coats.

Unfortunately the same laws of diffusion govern the drying of the film by solvent evaporation and, in the present case it turned out that insufficient drying time, for the high-build coats, had been allowed.

The ship was launched and within three months in a river estuary in England, developed many blisters in the polyvinyl coats, of average size perhaps that of a thumb-nail, and some larger than a ten-drachma piece. At this stage I examined the hull in dry dock. Several explanations of the blistering had been put forward: some blamed the cathodic protection system, others the original shop primer. However, on examination of the fluid inside the blisters, I found it to be of pH 8.5 or so, to contain some sodium chloride and—significantly—a considerable amount of MIBK, easily detected by its characteristic odour.

Clearly, what had occurred was that the thick polyvinyl films had not sufficiently dried out, and on immersion in water the surplus MIBK had been partially replaced by water: this is a well-known way of making a porous plastic film. Thereafter water and some sodium chloride diffused in as far as the zinc-epoxy primer (which was unharmed), and slight hydrolysis of sodium chloride to give a little mild alkalinity within the blister was provided by the perm-selective action of the polymer films, which contain —COOH groups. This action in turn led to the failure of adhesion between primer and vinyl, and to the further development of the blisters.

The primer was practically untouched and there was no rusting of the ship, but it was not in a condition to receive further paints coats because the polyvinyl coating was substantially disintegrated in many parts. The coatings had to be removed by shot-blasting, and repainting was done with a different system.

It seems likely that, during the vinyl painting with the high-build composition, only about five times as long a period was allowed for solvent evaporation as would have been suit-

able for the thin films: diffusion principles indicate, of course, that about 25 times as long was in fact required. Owing to the excessive solvent retention, a far from impermeable film was produced, and water exclusion, such as would have been achieved with a solvent-free system built up in thin well-dried layers, was not produced.

B. Now let us consider a situation where no water-excluding paint films are possible and where a resistant alloy such as a stainless steel, a nickel-base alloy or a titanium alloy has to be used in direct contact with sea-water. Several such alloys are available and under many conditions they can remain completely passive. However, many are subject to attack at crevices. We will examine how this may occur.

The fundamental corrosion reaction is the anodic dissolution of the metal. Fortunately, in the case of resistant metals and alloys the anodic reaction changes from the production of soluble metal salts to the production of an insoluble and adherent oxide film over a considerable range of electrode potential. When an anode goes passive in this way, the anodic current density and dissolution rate fall to very small values, because of the blocking action of the oxide film. A schematic but typical diagram of the anodic current changes at different electrode potentials is shown in Fig. 1, OABCD. At potentials below O, the metal cannot corrode at all. This

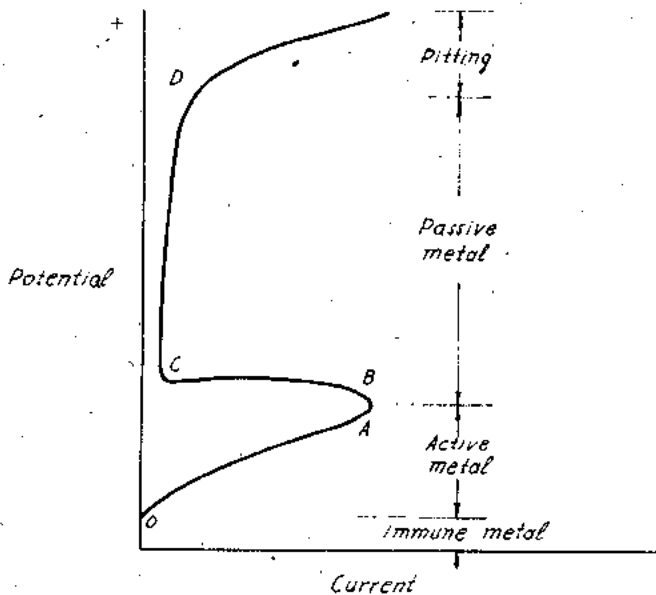
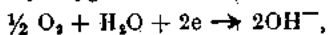


Fig. 1. Anode polarisation curve (schematic)

is cathodic protection or immunity, relatively well understood and much practised, and I do not discuss it here.

Between O and A, the anodic dissolution current increases and active corrosion occurs. If the potential is raised beyond B, either by an external cathode or by a cathodic reaction on the same metal surface, the current drops sharply (often by several orders of magnitude) and passivity sets in at C. If the potential is further raised, beyond D, pitting corrosion occurs. But between C and D, the metal is resistant to corrosion.

A good resistant alloy is one in which the natural cathodic reaction, ordinarily oxygen reduction,



polarizes so that the cathode polarization curve PE intersects the anode polarization curve between C and D, Fig. 2, and proceeds beyond B. The metal potential is then that corresponding to the intersection point a, and the anodic current, equivalent to the dissolution rate, is very small.

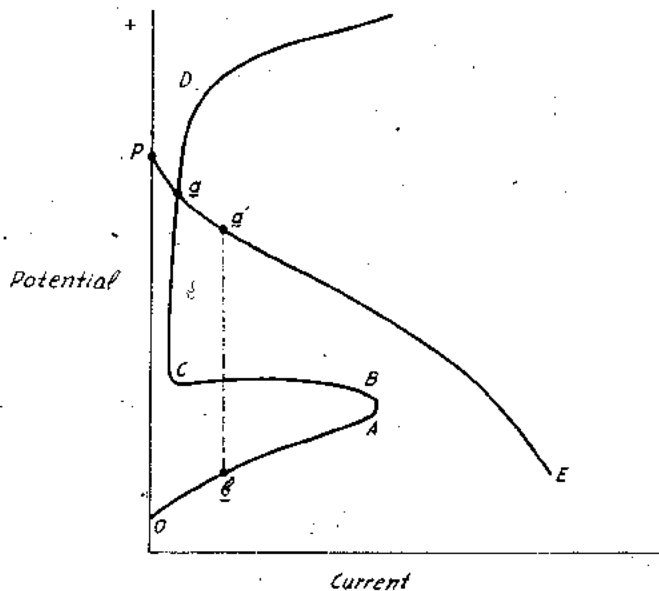


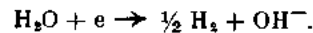
Fig. 2. Anode and cathode polarisation curves (schematic).

a. Freely exposed surface, negligible ohmic drop between cathode and anode, metal is passive.

b. Anode in crevice, ohmic drop ab, crevice corrodes.

However, if there is a crevice, oxygen scarcely penetrates it and any cathodic reaction must be outside the crevice. Such a cathode cannot raise the potential of any anode inside the crevice to the point a, because there may be a considerable ohmic drop caused by the solution resistance in the narrow crevice. It may, however, raise it to b, the cathode potential falling to say a, so that the ohmic drop is a'b. But under this condition the anode in the crevice is active at b, and crevice corrosion occurs.

The only real way to stop crevice corrosion of stainless steels in sea water is to eliminate crevices. This can sometimes be done in one of two ways (i) a very adherent non-conducting sealing compound can be used (ii) the surfaces forming the crevice can be coated with zinc and (for the crevice itself only) cathodic protection can be achieved. With nickel alloys, the rate of active dissolution in crevices is often small enough to be negligible. With titanium and its alloys, the cathodic reaction is the reduction of water, not oxygen (owing to the very negative potential of active titanium),



Not requiring oxygen, this reaction can take place within the crevice, so that the ohmic drop between anode and cathode is abolished and the reaction still operates at potentials within the passive range for titanium, where protective oxide is formed on the metal. Consequently titanium and its alloys are substantially immune to crevice corrosion.

It is not by any means always economically possible for alloys not subject to crevice corrosion to be used in sea-water environments, but for vital components containing crevices, a knowledge of the principles of crevice corrosion can assist design of more reliable articles.

In a special case I investigated, small stainless steel bolts were suffering violent crevice attack in a brackish water: replacement by titanium cured the trouble at small expense.



## CONCLUSION

I have always strongly held the view that all practical matter should be looked at from the scientific point of view both in the examination of failures and in the design of improved articles, be they screws or ships. One must hope that engineers will avail themselves of the enormous amount of scientific knowledge that we now have in the fields of physical chemistry and electrochemistry, and will allow us to help

them to the full in the solution of practical problems of corrosion and protection of metals. The two examples of the application of principles to practice that I have given can be multiplied a hundredfold. Of course, the details vary in every practical problem, and great care must be given to take them into account. The «scientist» has the principles, the «engineer» has the special case. Discussion between them based on mutual understanding and confidence can lead to nothing but progress in the solution of practical corrosion problems.

## DISCUSSION

Prof. Dr. YAHALOM (Israel): It is a very rare occasion, I think, to hear about principles, in a conference from an Authority like Doctor Hoar and I wonder if I can ask a simple question?

Usually, when we consider an anodic polarization curve, we have the transpassive range above the passive range. As far as standard steels are concerned this transpassive range is quite obvious from simple chemical consideration, when we assume that the trivalent chromium is oxidized into the soluble hexavalent chromium. But what about simple steel, ordinary steel? Of course, when we draw the curve we get an increase, due to reduction of oxygen, but does this correspond also in increased corrosion in the transpassive range too?

Dr. HOAR: With an ordinary steel not containing chromium in an alkaline solution not containing chlorides (which I haven't considered to day, because we are talking about the sea-water corrosion), if you take the potential high enough you will get, solution of iron as the soluble ferroate. In chloride containing environments, when we reach the breakdown potential due to the very complicated effects of chloride ion on the outside of the film, this is well below the transpassive line. As the potential is raised three things can happen: film break down, leading to pitting transpassivity giving general attack, oxygen evolution and even chlorine evolution.

S. BARTHA (Sweden): Are these blisters caused by a bad local polarization or by diffusion?

Dr. HOAR: It was diffusion entirely, I think, through a polymer film, that had become porous owing to the retention of solvent. Solvent had not diffused out sufficiently, therefore it became partly replaced by water and salt. The rise in pH would have come about, by some selective membrane of hydrolysis giving rise to hydroxide inside and acid outside.

B. WILSON (England): I should like to endorse what Dr. Hoar says about the problems of solvent retention in thick paint films. We have encountered this problem with marine paints; for example, with one chlorinate rubber paint it was possible to peel off sheets almost a square metre in area several months after the application of the paint. The undersides of these sheets had a very strong smell of solvent and were tacky.

Turning now to the permeability of paint films, we have carried out quite a lot of work on the water-permeability of paints using radioactive tracer techniques. More recently we have been using labelled sodium and chlorine and we have come to the conclusion that although all paints are to some extent permeable to water, good quality modern marine paints, properly applied, are almost impermeable to sodium and chloride ions. In these circumstances paint failures arise from what I can best describe as physical defects—pin holes, mechanical damage in service, pores due to the slow evaporation of solvent and paint film cracking due to hardening. Defects of this type, which are comparatively large on an atomic scale, appear to be the main cause of gross penetration of paint films by sodium and chloride ions.

Dr. PICOU LIS (Greece): In my opinion the whole problem is the solvents contained in the paints and my question is whether you have tested solvent-free paints, let us say, solvent-free epoxy formulations.

Dr. HOAR: There have been many tests, of epoxy paints and indeed the primer I referred to was epoxy based. The epoxy paints tend to be extremely good from the point of view of not retaining solvent, because there is no solvent in the true sense of the word in them, and I am very much in favour of them. We used them on the lower parts of the deck sections of the new severn bridge in England. Zinc-titled epoxy was used for the sections because they were pontoons in themselves, and were floated down in the river after being moored for some time and then raised into position to form the bridge. So this was a considerable corrosion problem. We did a number of tests with modern type of paints, such as these based on epoxy resins and polyurethanes, and compared them with the older type of polymerizing paints containing also solvents. The epoxies were found to be the best.

J. CARSON (Canada) I wonder if Dr. Hoar would elaborate a bit more on the cathodic process for the corrosion of Titanium? Did I understand him to say that the cathodic process was not oxygen reduction?

Dr. HOAR: No, it is reduction of water to hydrogen. The evolution from hydrogen from  $H_2O$  directly occurs because the potential of titanium is about  $-1V$  or even lower. Consequently water is readily reduced by titanium, the over all chemical reaction being:  $Ti + 2H_2O = TiO_2 + 2H_2$ .

# SUR UN CAS COMPLEXE DE CORROSION MARINE

Par Prof. Dr. Ing. Chim. TH. SKOULIKIDIS

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## RÉSUMÉ

A une presse d'une usine pour contre-plaqué, qui est chauffée avec de l'eau saumâtre, on constatait une corrosion des tuyaux en acier.

Nous avons pu constater qualitativement et quantitativement sur place et au laboratoire que la corrosion de ces tuyaux dépendait des facteurs suivants:

- a) température, composition du métal, conductibilité, pH de l'eau et oxygène dissous, qualité de métallisation et courant-électrique parcourant de métal.
- b) la déformation plastique et les désordres structuraux de l'acier.

c) la déformation élastique de l'acier.

Nous avons examiné surtout l'influence des facteurs b et c.

Nous avons pu vérifier sur place et au laboratoire que le désordre structural et les déformations plastiques et élastiques de l'acier le rendent plus anodiques.

Nous avons été conduit aux mesures nécessaires pour ralentir les faits de corrosion de la construction et à des mesures pour empêcher une accélération éventuelle de la corrosion sur toutes pièces où peuvent apparaître les déformations plastiques et élastiques.

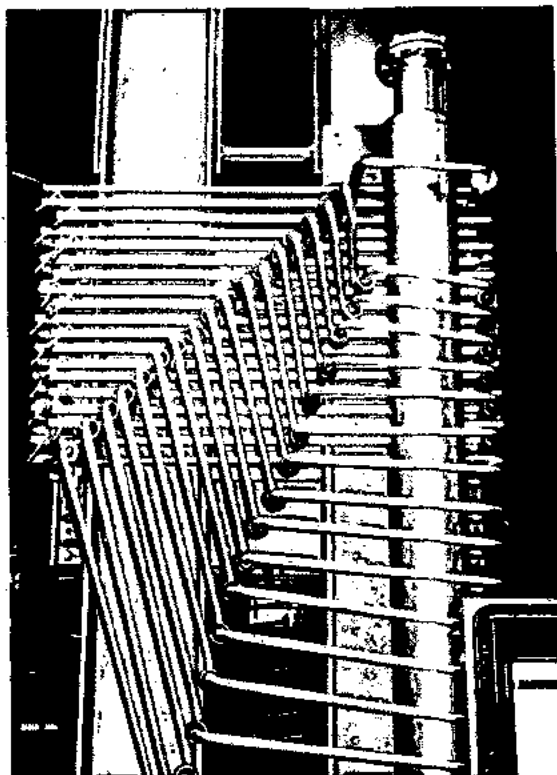
## INTRODUCTION

Dans une usine grecque de fabrication de contre-plaqué, on utilise des presses, chauffées par la circulation de l'eau saumâtre dans des tuyauteries en acier (ST. 35. 29), d'une

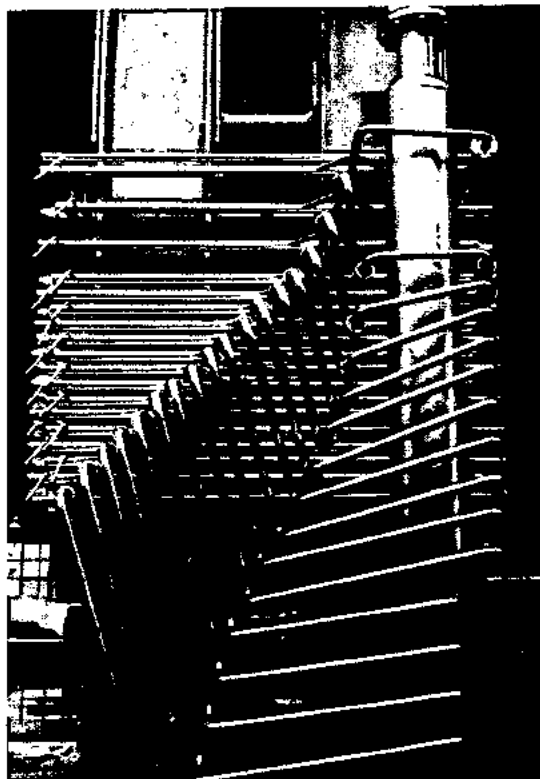
température de 140° à l'entrée et 35°C à la sortie.

Dans les figures ci-dessous (Fig. 1a, b, c, d, e) on voit la partie de la presse avec les tuyauteries.

Les différentes figures indiquent les positions successives des tuyaux pendant le fonctionnement de la presse.



a



b

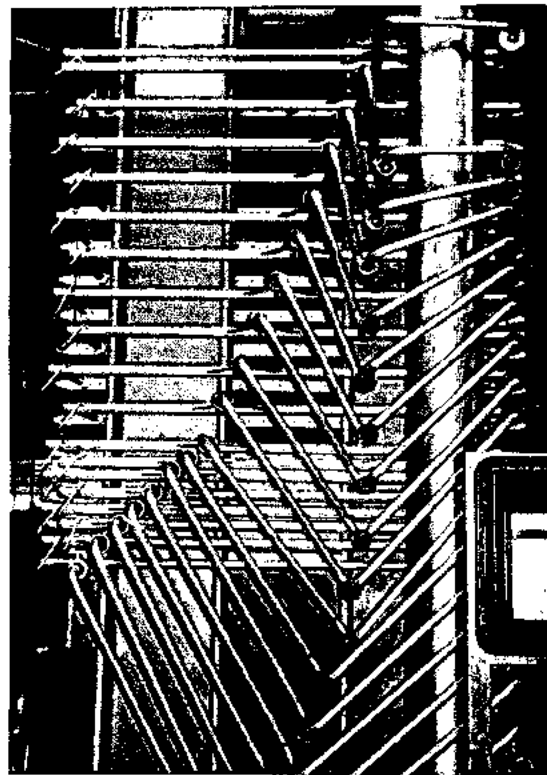
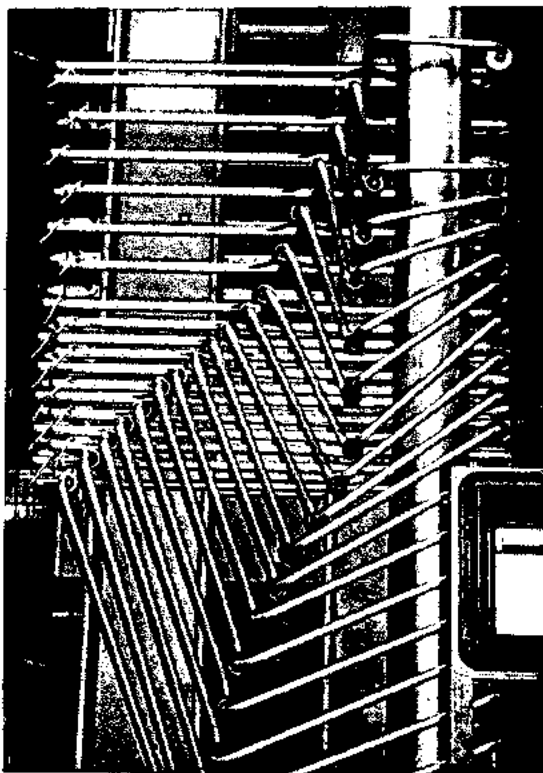


Fig. 1. — Positions successives des tuyaux pendant le fonctionnement de la presse.

Dans la figure ci-dessous (Fig. 2) on voit les tuyaux en acier. Chaque tuyau aboutit à un raccordement (Fig. 2, A, et 3) en acier de la composition ci-haut mentionnée (ST 35.29), qui est chromé par électrolyse (l'épaisseur du chrome est de 0,02 mm).

Quand la presse a été mise en œuvre pour la première fois, on a mis les raccords de la figure 3 à leur place sur la presse et on les a soudés ensemble avec les tuyaux aux points BB de la figure 2.

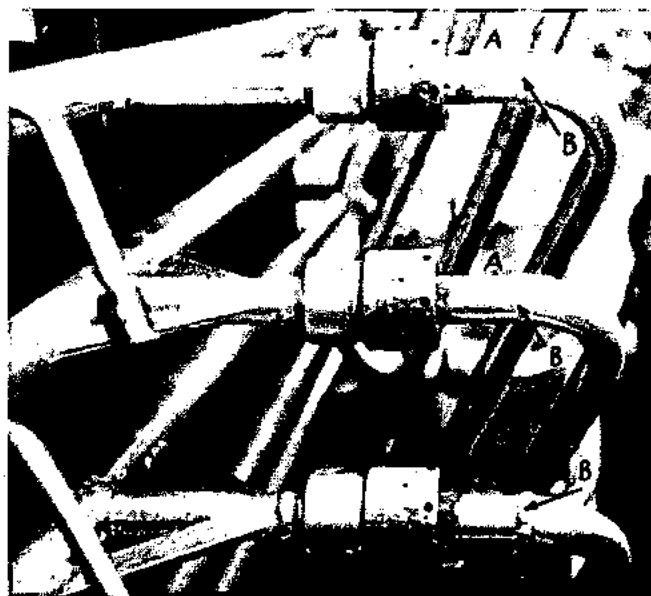
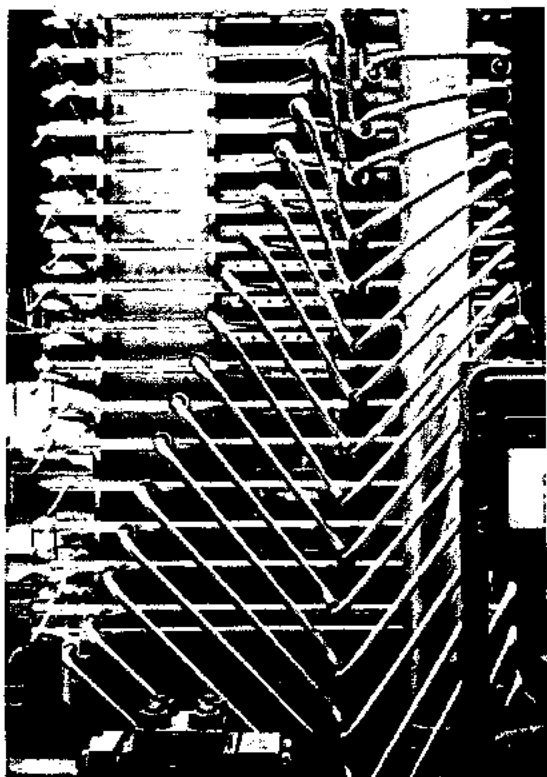


Fig. 2. — Tuyaux avec les traces des soudures avec les raccords.

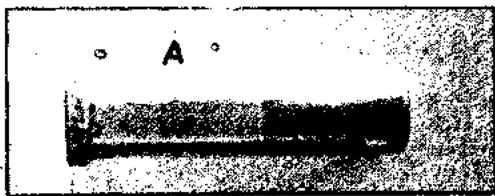
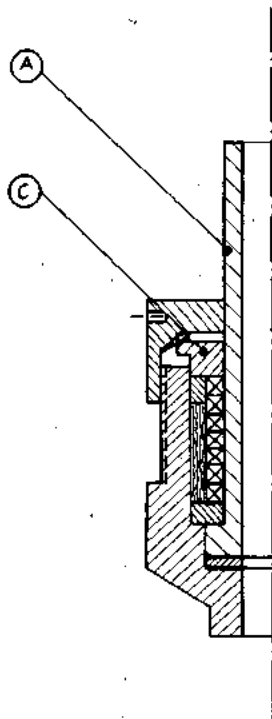


Fig. 3 — Raccordement.

Pour faciliter les ouvriers au soudage des autres raccords A, on refroidissait le tuyau déjà préparé par de l'eau à la température ambiante. On travaillait de la même sorte pour remplacer les raccords, quand ils étaient corrodés.

Dans la figure ci-dessous (Fig. 4) est indiqué un des liens étanches entre un raccordement et un tuyau de l'installation de chauffage de la presse.



A. Raccordement à être soudé avec le tuyau de l'installation de chauffage.  
C. Bague métallique.

Fig. 4. — Liens étanches. Est indiqué le raccordement et la bague.

Tous les 3 à 5 mois du fonctionnement de la presse, les raccords A d'une épaisseur de 3 mm étaient complètement corrodés et découpés (Fig. 5a, b, c, d), chacun à l'endroit sous les bagues (Fig. 4 et 6a, b) de la même (ST 35.29) composition, où s'échappaient parfois des gouttes d'eau saumâtre.

### MESURES

Pour déceler les causes d'une corrosion si intense les mesures suivantes ont été effectuées:

a) Composition du métal et qualité de la métallisation; composition, conductibilité et pH de l'eau.

1. La composition de l'acier était en effet celle de ST 35.29, comme prévue par les prescriptions.

2. Par des mesures électrographiques on a constaté que la couche du chrome était très poreuse, comme est toujours le chrome posé par électrolyse.

Le chrome était déposé directement sur la surface de l'acier et non suivant l'ordre: acier-cuivre-nickel-chrome-nickel-chrome, qui est indiqué pour obtenir une couche ad-

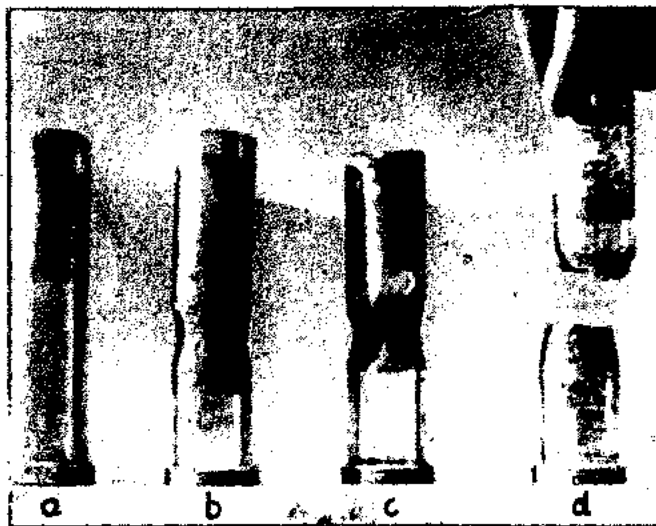


Fig. 5. — Corrosion des raccords par rapport au temps.

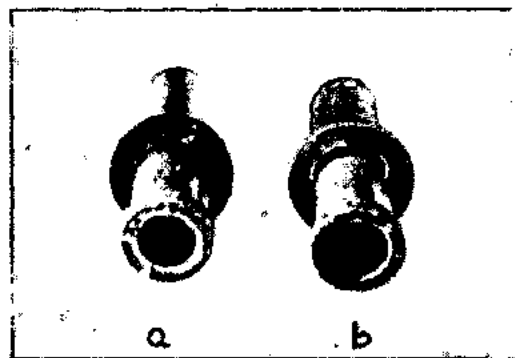


Fig. 6. — Corrosion des raccords sous la bague (a. Raccordement pas utilisé, b. Raccordement après 3 mois de fonctionnement de la presse, c. Après 4 mois, d. Après 5 mois).

hérente et sans pores.

3. La composition de l'eau circulante était à peu près celle de l'eau de mer; elle contenait de plus l'hydrazine pour régler son pH à 11,2.

4. On n'avait pris aucune précaution pour débarrasser l'eau de l'oxygène dissous (désaération).

5. La conductibilité spécifique de l'eau et son pH avait les valeurs correspondantes:  $5,6 \cdot 10^{-3}$  mhos.  $\text{cm}^{-1}$  et 11,2.

b) Observations et mesures de potentiel.

#### I. Sur place

##### A. Observations:

1. Les raccords A (Fig. 2), qui fonctionnaient depuis plus d'un mois n'avaient pas de couche de chrome.

2. La couche de chrome sur les raccords qui fonctionnaient depuis moins d'un mois avait des bulles, de nombreuses traces de corrosion par piqure et des fentes et elle pouvait être facilement écorchée.

##### B. Mesures de potentiel:

1. A l'aide d'un voltmètre électronique, on a constaté que le potentiel des tuyaux par rapport à la terre était 600mV (Pôle négatif: les tuyaux).

2. Le potentiel entre les raccords A (Fig. 2) et les bagues change périodiquement pendant le fonctionnement de la presse entre 0,9 et 1,3 V (Pôle négatif: les raccords). Les valeurs avaient les mêmes limites quand la presse ne fonctionnait pas et les mesures étaient effectuées pour des positions différentes des tuyaux.

## II. Au laboratoire:

Pour mesurer au laboratoire les potentiels ci-dessous nous avons utilisé l'eau qui circulait dans la presse à une température de 80°C (La moyenne entre les températures-limites et un voltmètre électronique).

1. Le potentiel entre la couche de chrome d'un raccordement (Fig. 3) pas utilisé et une bague pas utilisée étaient de 70mV. (Pôle négatif: la bague).

2. Le potentiel entre un raccordement sans couche de chrome pas utilisé et une bague pas utilisée était de 80mV (Pôle négatif: le raccordement).

3. Le potentiel entre un raccordement utilisé (sans couche de chrome) et la bague était de 500mV (Pôle négatif: le raccordement).

4. Le potentiel dans le cas (2) après chauffage du raccordement A jusqu'à une température de 800°C et refroidissement brusque (élaboration du type «trempé»), s'élevait jusqu'à 550mV (Pôle négatif: le raccordement).

5. Le potentiel dans le cas (2) variait entre 80mV et 300mV, quand le raccordement A subissait des déformations élastiques à l'aide du dispositif de la figure 7.

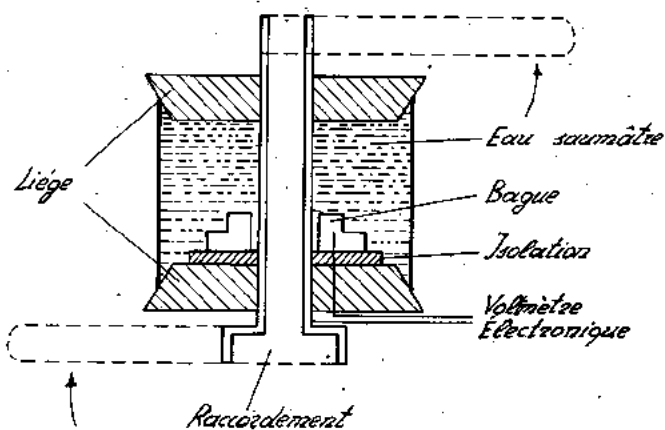


Fig. 7. — Dispositif pour effectuer en raccordement des déformations élastiques et pour mesurer le potentiel.

6. Si dans les cas (3) et (4) le raccordement subissait des déformations élastiques semblables à celles du cas (5), le potentiel augmentait dans les deux cas de 300mV, c.a.d. jusqu'à 800 mV (cas 3) et 850mV (cas 4).

Dans le tableau 1 on voit tous les résultats obtenus.

## CONCLUSIONS

Sur la base des mesures et des observations ci-haut mentionnées, on a abouti aux conclusions suivantes:

1. La corrosion intense des raccords A commençait après l'écorchement de la couche de chrome, qui avait lieu à cause d'une corrosion par piqûres de l'acier et d'une érosion de la couche.

TABLEAU 1

Cas	Potentiel (mV)	Poles	
		Raccordement	Bague
1. Entre la couche de chrome d'un raccordement pas utilisé et une bague pas utilisée	70	+	-
2. Entre un raccordement sans couche de chrome pas utilisé et une bague pas utilisée ...	80	-	+
3. Entre un raccordement utilisé (sans couche de chrome) et la bague .....	500	-	+
4. Le cas (2) après une élaboration du type «trempé» du raccordement .....	550	-	+
5. Le cas (2) quand le raccordement subissait des déformations élastiques .....	80 - 300	-	+
6. Les cas (3) et (4) quand le raccordement subissait des déformations élastiques ...	500 - 800 550 - 850	-	+
7. Entre les raccords sur la presse et la terre .....	600	-	+
8. Entre les raccords sur presse et les bagues, quand la presse fonctionnait .....	900 - 1300	-	+
9. Les cas 8 par calcul (cas 6 et 7) .....	1100 - 1400 1150 - 1450	-	+

2. Après l'éloignement de la couche de chrome, le potentiel de corrosion entre les raccords et les bagues changeait périodiquement entre 900 et 1.300 mV.

3. Ce potentiel provenait de la superposition des potentiels suivants:

a) Du potentiel entre les raccords et les bagues d'une valeur de 600mV, à cause d'une charge électrique des raccords par rapport à la terre (Tab. cas 7).

b) Du potentiel entre les raccords et les bagues, ayant subi différents traitements thermiques et mécaniques qui entraînent des défauts structurels cristallins différents pour les raccords et les bagues (Tab. cas 2) d'une valeur de 80mV.

c) Du potentiel subséquent du traitement du type «trempé» d'une valeur de 420mV. (Tabl. cas 3).

d) Du potentiel dû aux déformations élastiques des raccords (Tabl. cas 5 et 6).

e) La superposition de ces potentiels conduit à des valeurs (1100-1400mV, Tabl. cas 9) qui, en considérant les fautes des mesures, sont les mêmes avec les valeurs obtenues par mesures sur place (Tabl. cas 8).

f) Toutes ces données nous amènent à conclure qu'à l'exception des autres conditions qui influencent la corrosion marine, il faut considérer aussi:

1. Le type des traitements thermiques et mécaniques des métaux.
2. Les déformations plastiques du type «trempé».
3. Les défauts cristallins structurels.
4. Les déformations élastiques.

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## DISCUSSION

Prof. Dr. YAHALOM (Israël): J'étais très intéressé d'entendre que l'eau saumâtre est utilisée en Grèce pour refroidissement, car en Israël nous sommes intéressés en ce qui concerne l'eau de mer et l'eau saumâtre pour le refroidissement industriel dans des installations côtières. Nous affrontons des problèmes considérables surtout en ce qui concerne l'eau saumâtre et même dans des systèmes construits à l'aide de nickel cuivre nous avons des salissures dans les condensateurs et des problèmes de corrosion (par piqûres). Ainsi j'étais surpris d'entendre que cela est utilisée en Grèce.

Je voudrais poser deux questions: 1<sup>ère</sup> Quelle était la concentration de l'eau saumâtre et 2<sup>ème</sup> Y-a-t-il une expérience suffisante en Grèce dans l'utilisation de l'eau saumâtre et l'eau de mer pour le refroidissement industriel, puis si ces tuyauteries d'acier sont satisfaisantes.

Prof. Dr. SKOULIKIDIS: Cette eau saumâtre que j'ai mentionnée, c'était presque de l'eau de mer et de plus il ne s'agissait pas de refroidissement, mais de chauffage à 140° C. Je ne suis pas spécialiste aux salissures, mais je crois qu'à une telle température les salissures ne peuvent pas être abondantes. Ce n'est pas seulement l'eau saumâtre que nous utilisons ici, mais aussi l'eau de mer pour le chauffage et le refroidissement dans les industries qui sont situées au bord de la mer.

Nous sommes obligés d'utiliser ces eaux à cause du fait que souvent n'existe pas de l'eau douce en abondance à l'approximité des fabriques et naturellement nous subissons toutes les conséquences de la corrosion. Selon le cas nous essayons de la combattre et plusieurs fois avec succès.

Prof. Dr. YAHALOM (Israël): Pouvez-vous nous dire Mr. le Professeur quels sont les matériaux les plus utilisés pour ce système de refroidissement.

Prof. Dr. SKOULIKIDIS: Acier ST 33 29, 35 29, 37 29. Le deux premiers types sont fabriqués en Grèce. Dans le cas, que j'ai mentionné, nous avons essayé de prendre quelques mesures en plus contre la corrosion. D'abord nous avons chromé les tuyaux au cuivre, nickel, chrome, nickel, chrome, après nous avons fait une mise à la terre de la presse, nous avons défendu qu'on refroidit brusquement les tuyaux après les soudures, et nous avons centré les tuyaux pour éliminer les déformations élastiques. C'est alors que nous avons obtenu un potentiel de 300 millivolt, et de plus je crois que peut-être on pouvait employer une protection cathodique à la presse.

S. BARTHA (Suede): Je voudrais savoir s'il n'est pas possible de considérer le phénomène comme résultat d'oxydation et dans ce cas il serait peut-être meilleur de faire l'élaboration à l'aide de plastique, de matériaux plastique, de teflon par exemple, au lieu du fer, au lieu du chrome, je pense qu'il est meilleur d'avoir une couche de teflon.

Prof. Dr. SKOULIKIDIS: Ce n'était pas possible, car nous avons des déformations mécaniques. Vous avez vu comment les tuyaux, subissent des tensions mécaniques, pendant le mouvement des tuyaux, pendant le fonctionnement de la presse. On a centré les tuyaux, mais en tout cas il y en avait des déformations élastiques qu'ils seraient dangereuses pour l'adhésion entre la couche du plastique et de l'acier. De plus nous avions besoin d'un matériaux très dur à cause des fentes constatées sur la surface du chrome.

B. HEUZE (France): Mr. le Professeur avez vous envisagé de faire la protection intérieure des tubes avec un inhibiteur, par exemple du chromate de sodium; autrement dit, est-ce que les pertes du circuit sont importantes?

Prof. Dr. SKOULIKIDIS: Non, nous n'avons pas essayé. Nous avons ici une corrosion intérieure des tuyaux, mais elle n'était pas importante envers la corrosion extérieure sous la bague, où des gouttes d'eau échappaient, et c'était cette corrosion que nous voudrions combattre. La température des tuyaux était 140° C, alors nous aurions une évaporation de l'eau, des gouttes qui échappaient, et une augmentation de la concentration de l'inhibiteur et une cristallisation. Sous ces conditions son

action ne pourrait pas être prévue. Tandis que avec les mesures mentionnées nous avions des résultats satisfaisants. Naturellement il ne faut pas exclure a priori les inhibiteurs.

B. HEUZE (France): Oui je pense en effet que la méthode que vous avez employé est la seule valable, et je ne vois pas la possibilité d'une protection cathodique à moins qu'on entende par protection cathodique un dépôt de surface.

Prof. Dr. SKOULIKIDIS: Non je n'entendais pas formellement une protection cathodique, dans ce cas. J'ai parlé généralement. Mais je crois que quand on a un potentiel de 1,3 Volt et on peut restreindre le potentiel jusqu'à 300 millivolt, c'est assez pour une plus grande durée du tuyaux.

B. HEUZE (France): Je voudrais encore vous poser une question Les différences de potentiel que vous avez mesuré sont en valeur relative très importante par rapport aux potentiels naturels communs. Ces valeurs ont-elles été mesurées en état de marche à la température de fonctionnement?

Prof. Dr. SKOULIKIDIS: Oui et de plus au laboratoire avec une température de 80° au lieu de 140°.

B. HEUZE: Avez vous étudié l'influence de la température?

Prof. Dr. SKOULIKIDIS: Non

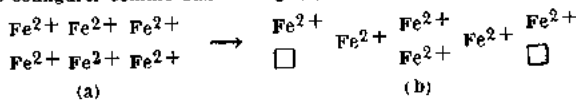
B. HEUZE: Je pense qu'il est très important.

Prof. Dr. SKOULIKIDIS: Naturellement, c'est connu généralement. Comment nous ne pourrions pas changer la température pendant le fonctionnement nous nous sommes concentrés seulement aux élaborations élastiques, aux déformations plastiques à la mise à la terre de la presse, à l'amélioration des qualités de la couche du chrome.

B. HEUZE: La température des différentes pièces était la même c'est à dire qu'il n'y avait pas de couples thermoélectriques?

Prof. Dr. SKOULIKIDIS: Non, la température des bagues et des tuyaux était la même. De plus je voudrais expliquer quelque chose. Quand j'ai parlé des déformations de type trempe, je n'entendais pas seulement une déformation allotropique, c'est à dire la congélation d'une autre forme cristalline à la température ambiante, mais j'entendais aussi la congélation de désordre réversible qui s'impose à cause du brusque refroidissement.

Les ions du fer dans le métal à la température ambiante peuvent être configurés comme dans la Fig. (a) (liaison métallique)



Quand le métal est chauffé à une température plus grande que le 1/3 de son point de fusion en échelle de Kelvin, c'est-à-dire d'une température plus grande que 330° C un nombre d'ions migre à des places, qui ne sont pas prévues par le système cristallin, alors à des places de désordre, en laissant ses places vides (Fig. b). Si on refroidit lentement, les ions reviennent à leurs places naturelles, si on refroidit brusquement les ions restent aux places de désordre. On peut ainsi expliquer le voltage mesuré car l'acier devient plus anodique à cause de désordres mentionnés.

B. HEUZE: Une dernière question. Vous avez mesuré une différence importante par rapport à la terre. Comment était prise la référence «terre»? était-ce le sol mesuré avec une électrode de référence ou un circuit de terre ou bien des masses?

Prof. Dr. SKOULIKIDIS: C'était par rapport à la mise à la terre de la fabrique.

B. HEUZE: En cuivre?

Prof. Dr. SKOULIKIDIS: En cuivre et en charbon aussi.

**Séance - Meeting - Sitzung - Συνεδρίασις**

**23.9.1968**

**Présidence - Presidency**

**Präsidium - Προεδρείον**

**Prof. B. FRANGOULIS (Grèce).**

**Prof. P. MOLLOTIS (Grèce).**

**Dr. H. DETERMANN (Deutschland).**

# THE SURFACE PREPARATION OF SHIP-PLATE FOR PAINTING

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## SUMMARY

After briefly reviewing recent developments in surface preparation techniques, this paper discusses the blast cleaning of ship-plate. There is a real need for field tests to show whether surfaces have been cleaned to the required standard, and tests evolved for this purpose are described. These include tests to assess freedom from rust and millscale, and peak heights, and ways to detect soluble contaminants, such as chlorides and sulphates.

The cleaning of new steelwork presents different problems from those with old steelwork. Almost all new steelwork is cleaned by impeller machines using steel shot or chopped steel wire. Peak heights are not excessive, but many shipyards process the steel too quickly and make no allowance for the different types of millscale. A greater range of steels is now used in shipbuilding and millscale can vary greatly in thickness and adherence.

Old steelwork on ships' hulls is cleaned with expendable, non-metallic abrasives. Where sand is not permitted, coarse grits made from copper or iron slags are frequently used. These grits can give rise to excessively high peaks, but the roughness due to corrosion is even greater. The deep rust pockets on these surfaces are very difficult to clean out and generally contain deliquescent iron chlorides. A surface which appears clean immediately after blasting can soon become covered with droplets of water which gives a strongly acid reaction (pH 1), in conditions where normal condensation would be impossible. Even if paint is applied when the surfaces are still dry, the droplets form on top of the paint film. It is probable that these chloride pockets are responsible for the poor paint performance on blast-cleaned surfaces on old ships. Ways of overcoming this problem are discussed.

## INTRODUCTION

The amount of research effort devoted to improving techniques of surface preparation of ship-plate is only a small proportion of that devoted to the development of new and improved marine paints. This is unfortunate, for no paint, however good, can be expected to give satisfaction when applied to a badly prepared surface. It has always been accepted that a scrupulously clean surface is required when metallic coatings are applied. Non-metallic coatings also warrant the same standard of surface preparation: unfortunately, they rarely get it. Paint is still applied to rusty surfaces and, provided the rust is covered, the job is judged satisfactory. This fallacious approach is encouraged by some paint manufacturers who market paints they say are suitable for application on top of rust. Some paints may perform quite well when applied on top of rust; they would be even better if applied to a properly prepared surface.

In the ship-building industry enormous progress has been made in the techniques of surface preparation and protection in the last ten years. For example, not long ago tankers were built from millscaled and rusted plates which were wire-brushed and painted on the outside, and left to rust on the inside. The advent of coating materials able to withstand the solvent action of crude oil and oil products provided an opportunity for attempting to overcome the corrosion problem in cargo compartments in tankers. If these new coating materials were to have any chance of success it was essential that surface preparation be improved. It soon became apparent that the only satisfactory way to achieve the requisite standard of surface preparation economically is to use impact cleaning<sup>1</sup>. For new ships the most satisfactory solution is to install large shot-blasting machines in the shipyards to clean the steelwork before it is built into the ship. Immediately following shot-blasting the steel should be primed with a good quality

primer which will protect the steelwork for up to one year in the shipyard. With expert supervision this method can give a very high standard of surface cleanliness and a surface that is very suitable for painting. The performance of paints applied to surfaces prepared in this way is very satisfactory and it seemed logical to see whether improved techniques of surface preparation might be applied to arresting the corrosion on old ships. The only efficient way to clean rusted surfaces on old ships is by blast-cleaning which was once rather expensive, but can now be carried out at a reasonable cost. On old ships it is rarely possible to recover the abrasive and so a cheap expendable material must be employed. In practice, this means the use of a non-metallic abrasive. In some parts of the world sand can be used and this is probably the best and cheapest material for this purpose. However, in many places the use of sand is not permitted for health reasons, and alternative materials must be used. Whatever techniques have been used on old steel work the results obtained have been rather disappointing and it must be conceded that the problem of surface preparation on old steel work is quite different from that on new steel work.

This paper is divided into three sections. The first describes field tests which the authors have evolved in order to ensure that adequate standards of surface preparation are attained and maintained in shipyards. The second discusses the preparation of new steelwork and the third describes some problems encountered on old steelwork and suggests ways in which these might be solved.

## THE EVALUATION OF IMPACT-CLEANED SURFACES

### *Surface cleanliness*

#### (a) *Freedom from rust and millscale*

For surfaces intended for normal painting a 90% rust-



free surface is considered acceptable, provided any oxides remaining are present in small, widely scattered, adherent fragments. For surfaces intended for coating with zinc silicates a 100% clean surface, a so-called «white-metal» finish, is required. In practice it has proved difficult to decide unambiguously when these standards have been achieved. The most widely used specifications covering the cleanliness of impact-cleaned surfaces are that issued by the Steel Structures Painting Council (SSPC) in the U.S.A. and the Swedish Standard MEDDELANDE No. 16. The U.S. specification is based on a description of the surfaces, whereas the Swedish specification relies on pictorial standards. The proposed British standard will follow the U.S. lead. Unfortunately, no-one has yet succeeded in laying down acceptable inspection methods for deciding when the required standards of cleanliness have been achieved. A major difficulty is that the appearance and colour of impact-cleaned surfaces depend not only on the degree of cleanliness but on other factors, such as the type of abrasive used (which alters the surface texture and reflectivity) and on the nature of the steel. Clean shot-blasted surfaces on higher tensile steels and hardened and tempered steels, which are being increasingly used in ship construction, can appear very different from clean surfaces on ordinary mild steel. These differences in tone and surface texture make it difficult to use pictorial standards, and impossible to use reflectivity devices for assessing surface cleanliness. In order to solve this problem we introduced the copper sulphate test six years ago<sup>2</sup>. In this test an aqueous solution containing copper sulphate (4%w) and sulphuric acid (1%v) is applied by pressing a pad impregnated with it onto the test surface. The copper is deposited preferentially on the bare steel and areas of millscale and rust become visible as dark areas against a background of copper. The test works best on freshly cleaned surfaces and is particularly useful in badly lighted areas. Judging by the number of requests (over 1,000) received for details of this test it is gaining in popularity. It has been found useful to prepare colour photographs of surfaces of varying degrees of cleanliness which have been tested by the copper sulphate test. These colour photographs can be used as standards by inspectors.

(b) *Residual dust*

Most blast-cleaned surfaces are covered with fine dust and debris. In some installations attempts, which are usually inadequate, are made to remove these contaminants by rotating brushes. The amount of debris on a surface can be determined by pressing strips of adhesive cellulose tape onto the surface and then peeling them off. Figure 1 shows some strips taken from typical commercial installations.

(c) *Detection of soluble iron, sulphates and chlorides*

The rust which forms on steel surfaces exposed to either industrial or marine atmospheres may contain significant quantities of sulphates and chlorides. If these compounds are not removed they can give rise to premature paint failure. Spot tests have been developed to detect the presence of soluble iron, sulphates and chlorides on blast-cleaned ship-plate. In these spot tests colour reactions are used to indicate the sites of contaminated rust. Each method employs pieces of chemically treated filter paper (Whatman Grade 541 is very suitable since it is hardened to withstand water) which can be dried after use to provide permanent records. The papers are pressed against the steel surfaces with a pad which is made from a ball of soft plasticine contained in a polythene bag. This has proved to be the most satisfactory method for ensuring good contact between the papers and the very rough blast-cleaned surfaces. After a short time in contact with the steel the papers are removed and treated to fix the colours that have formed.

Test for soluble iron:

This is a modification of a test described by Mayne<sup>3</sup>. A dry filter paper is pressed against the steel for about 20 seconds, a second filter paper, soaked in potassium ferrocyanide (5%w) solution being interposed between the pad and the dry filter paper. The «dry» paper is then peeled off and, after a further 60 seconds during which the colour develops, excess solution is washed away, leaving blue areas where soluble iron compounds have contacted the paper. In many instances it has proved possible to work with a single sheet of wet filter

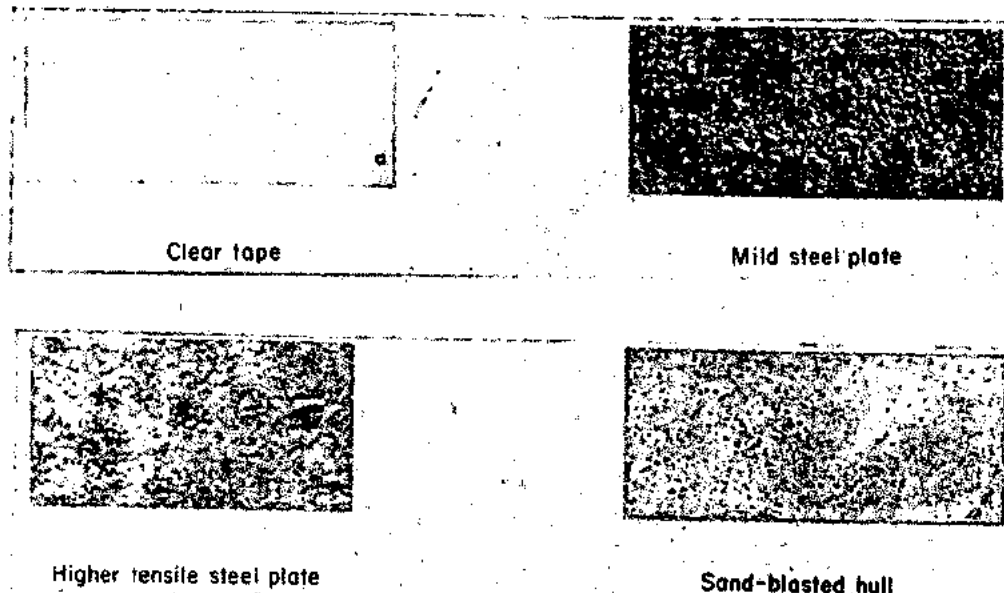


Fig. 1. — Tests for residual dust on blast-cleaned surfaces using adhesive cellulose tape

paper, when the blue spots develop not only on the filter paper but also on the steel surface.

#### Test for soluble sulphates:

For this test, papers are prepared by being soaked in a barium chloride dihydrate (6%w) solution and dried. The dry paper is then pressed against the test surface, backed by a second paper soaked in saturated potassium permanganate solution. Any soluble sulphates on the steel react with the barium chloride to form insoluble barium sulphate. Potassium permanganate is absorbed and held in the barium sulphate lattice, imparting a pink colour to those parts of the paper which contacted sulphates.

Excess permanganate can be washed away with sulphate-free water and any general yellow stains on the paper removed by a rinse in oxalic acid (4%w) solution. After a final wash in distilled water the paper is dried.

#### Test for soluble chlorides:

In this test a filter paper is wetted with silver nitrate (2%w) solution and then pressed against the steel surface for about 20 seconds. It is then peeled off and thoroughly washed with chloride-free water. Any silver chlorides formed remain in the paper and can be detected by immersion in photographic developer. Chloride sites show as brown-black areas. The paper can be washed and dried for record purposes.

The tests for sulphates and chlorides are extremely sensitive (for example, the test for chlorides will detect tap water splashes on rough steel plate), so it is most important to ensure that the water and reagents employed are free from chlorides and sulphates.

If there is no necessity to locate the sites of chloride and sulphate contaminants, the surfaces may be washed with distilled water, and the washings collected and tested for sulphate and chlorides by standard techniques.

#### Surface texture

The most important aspect of the texture of surfaces intended for painting is the height of the roughness peaks. The height of a peak may be defined as the greatest vertical distance between the summit of the peak and the bottom of an immediately adjacent trough. (The word «peak» implies a feature with steep sides rather than a rounded hill). Peak heights may be measured directly on steel surfaces or on plastic replicas taken from these surfaces. A number of replica techniques have been described in the literature: not all these techniques approach 100% fidelity and any proposed replica method must be checked by comparing an original surface with its replica. Replica methods which have proved satisfactory on ship-plate are the «Triafol» method<sup>1</sup>, the «Replic» lacquer method<sup>1</sup> and the use of certain silicone rubber formulations. The Triafol and the Replic lacquer method give replicas sufficiently hard for use with stylus-type instruments. On the other hand they cannot be used to replicate surfaces with re-entrant angles without suffering damage on removal. Silicone rubbers can replicate re-entrant angles but are too soft for use with surface profile instruments.

It is the authors' view that the measurement of peak height on impact-cleaned surfaces cannot be made satisfactorily with any currently available stylus-type instruments, or with any instrument that merely provides a two-dimensional representation of the surface. The basis for this statement is that it is desirable to locate and measure the tallest peaks on surfaces intended for painting. These peaks are usually distributed rather sparsely over the surface and it may be necessary to make a very large number of traverses with a stylus-type instrument before any one of these peaks passes under the stylus. The chance that the stylus of the measuring instrument passes over the tip of the peak is very remote indeed. An extreme example of an isolated peak is shown in Figure 2 and a typical gritblasted steel surface is shown in Figure 3. Evidence is accumulating which indicates that many premature paint failures are due to isolated peaks on surfaces and so it is most important that these peaks should be located and measured. When measuring peak heights on ship-plate



Fig. 2. — Isolated peak on grit-blasted surface caused by oversize particle  $\times 15$ .

we prefer to use the direct microscope method in which a short focus objective is focused first on a peak and then on the lowest adjacent valley and the distance the focus has to be altered noted. The fine focus knob can be calibrated directly in microns. In order to obtain representative values at least ten peaks in any particular area of plate or on any particular replica are measured and the maximum value recorded. At least ten different areas are assessed in this way. A comparison of average values of peak-heights with the maxima measured gives some indication of the frequency of the highest peaks. When transparent replicas are used, it is a great help if a thin film of metal can be evaporated onto them to increase reflectivity. Also, when a transparent replica with a film of evaporated metal is viewed through the plastic, the replica behaves as a positive replica, that is, the peaks are seen as peaks and not as valleys as would be the case with most single stage replicas.

Surface profile traces may be used to give an indication of overall surface texture but the horizontal magnification should always be the same as the vertical magnification otherwise the impression may be very misleading. Profiles obtained on shot- and grit-blasted surfaces are shown in Figure 4. The differences which are immediately obvious between these two surfaces with equal horizontal and vertical magnifications would not be so apparent if the horizontal scale had been less than the vertical scale by a factor of, say, 50. It should be noted that although average roughness values on shot-blasted surfaces can sometimes be related to peak heights, there is no correlation whatsoever on grit-blasted surfaces.

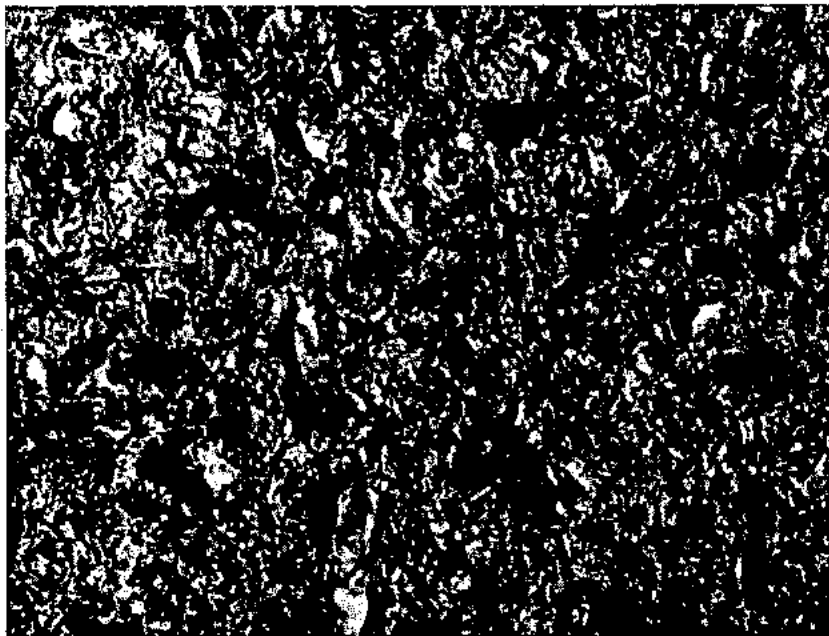


Fig. 3. — Typical grit-blasted surface: 1-2 mm grit × 15

### NEW STEELWORK

In this section it is assumed that new steelwork is mainly covered by millscale. As was indicated in the introduction impeller machines are used to clean new steelwork prior to fabrication. For best results, these machines should be under cover, and the plates should be heated to dry them before being blasted. Shot or chopped wire is preferred to grit; the use of grit greatly increases the wear and tear on the machines, and offers no benefits in increased cleaning rates. In 1962, of 12 European shipyards, two were using grit in impeller machines<sup>1</sup>; in 1964, of 23 shipyards worldwide, none were using grit; in 1966, no grit was being used in any impeller machines in 13 European shipyards building ships for the Shell Group of Companies.

On shot-blasted surfaces intended for painting, a 90% clean surface, with peaks not more than 75 microns high, is regarded as a reasonable standard. In 1962, very few shipyards were producing plate to this standard and the situation today is not much better. Results obtained in European shipyards building supertankers are given in Table 1.

If the peak height measurements show a few very tall peaks this generally indicates that one or two oversized angular particles are present in the shot. Shot-blasted surfaces cleaned with properly graded shot should have a very uniform appearance, essentially consisting of shallow overlapping, saucer shaped depressions, as is shown in Figure 5. The ridges between these depressions are the peaks but, as can be seen from Figure 4, these peaks do not have steep sides. Regardless of size of shot, peaks should not be a problem on shot-blasted surfaces unless the shot contains angular foreign particles. Even if tall peaks are present the normal handling which the steel receives during fabrication will blunt many of them. In many yards the plates pass through straightening rolls after shot blasting and priming, and this provides an excellent way of eliminating tall peaks.

Shipyards wish to achieve maximum cleaning rates and the most common cause of inadequately cleaned plate is too high a speed through the machine (pass speed). However, this is by no means the only cause. Some machines have too high a proportion of «fines»; in some yards all the dust and debris

round the machine are swept up and put in with the shot. Sometimes the grade of shot used is too fine to crack and disrupt thick, hard millscale quickly. A grade of shot which successfully cleans a mild-steel plate covered by thick flaking millscale may not be suitable for alloy steel plate with a thin layer of hard adherent millscale. On some plates atmospheric rust may be present, particularly near the edges, and this is very difficult to remove. It is not practicable to change the shot in a machine to match the variety of surfaces which are presented; the only alternative is to vary the pass speed and use a general purpose charge of shot. If the pass speed is sufficiently slow, clean surfaces can be obtained with almost any grade of shot. However, if the machines are to operate at maximum efficiency, a certain amount of experimentation «on site» is called for, and this is where the copper sulphate test has proved its worth.

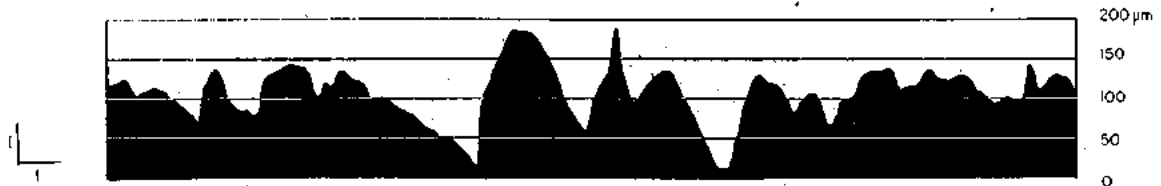
Probably the best general purpose shot is a mixture containing a significant amount (say 10%w) of about 2 mm diameter material and a somewhat larger proportion of fines down to about 0.2 mm diameter, the balance being medium-grade material of about 0.5-mm diameter. The large particles serve to crack and loosen the millscale and the small ones clean out the bottoms of rust pits. There should be no dust. Our observations show that with shot the amount of embedded material in surfaces is very low but the amount of loose dust and debris is usually shockingly high. There is no excuse for this; effective dust-removing devices could easily be fitted.

### OLD STEELWORK

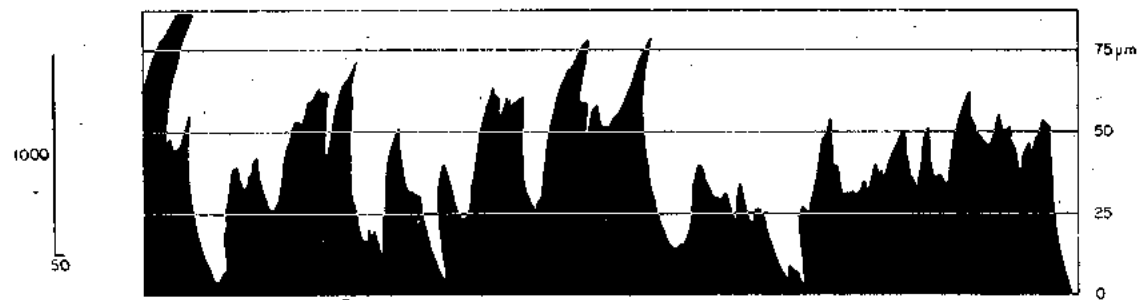
In view of the success which attended use of blast-cleaning on new steelwork, it was logical to apply similar techniques to old steelwork. Thus, there was the possibility of arresting the corrosion in the cargo compartments of tankers, particularly on the bottom and the underdeck surfaces. The corrosion could also be halted, on the outer hull where, in addition, there was an opportunity to reduce the «drag» on the hull, thereby improving the propulsive efficiency. Since the impact-cleaning on old ships has to be carried out «in situ» in dry docks, it is not possible to use expensive metallic abrasives; cheap, expendable, non-metallic abrasives are used. The



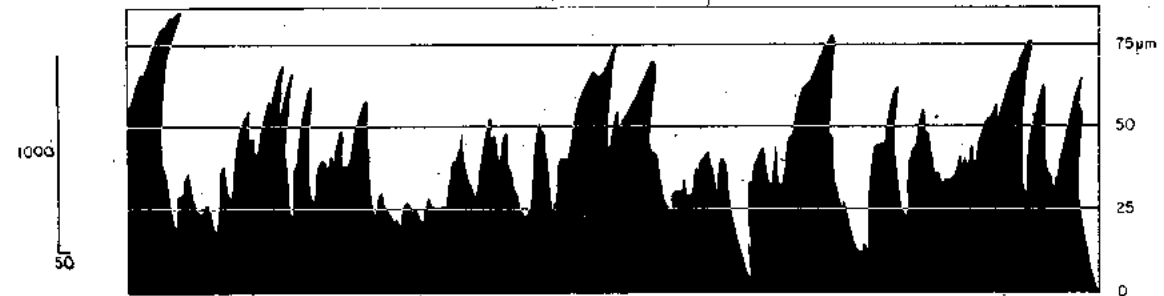
Shot-blasted surface 1:1  
(0.8mm shot)



Grit-blasted surface 1:1  
(0.8mm chilled iron grit)



Shot-blasted surface 20:1



Grit-blasted surface 20:1

Fig. 4. — Profile traces, grit- and shot-blasted surfaces. Effect of different magnification ratios

Table 1  
Performance of shot-blasting machines in European shipyards building superintanters.

Shipyard	Machine type	Site	Preheating	Nature of plates entering machining	Pass speed, m/min	Abrasive		Peak height, $\mu\text{m}$		Cleanliness		Residual dust
						Initial charge	Used material below 0.3 mm, %	Righest peak	Average maximum from 10 different areas	Millicaled areas, % clean	Rusted areas, % clean	
A	Vertical plate	Under cover	Yes	Mild steel; millcaled, with isolated rust patches.	1.6	1.2 mm shot	3	360 <sup>K</sup>	106	95 - 95	50	Excessive
	Horizontal plate	Under cover	No	Mild steel; entirely millscale	2	0.8 mm shot	10	123	107	75 - 95	-	Excessive
B	Vertical plate	Open	No	Mild steel; entirely millscale	1.3	0.8 mm shot	11	174	124	85 - 90	-	Excessive
	Section and bar	Open	No	Mild steel; 50:50 millscale; rust.	-	0.8 mm shot	0.2	117	106	100	80	Considerable
	Horizontal plate	Under cover	No	Higher tensile steel; millscale, some rust at edges.	1	0.8 mm shot	8	117	101	85 - 90	85	Excessive
	Horizontal plate	Under cover	Yes	Higher tensile steel; millscale, some rust at edges.	2	0.8 mm shot	14	122	92	85 - 100	85 - 100	Excessive
C	Section and bar	Under cover	Yes	Mild steel; millscale with isolated rust patches.	2	0.8 mm shot	3.3	117	109	100	100	Very bad
	Horizontal plate	Under cover	Yes	Mild steel; entirely millscale.	5	50% 1.2 mm 50% 1.0 mm shot	4.2	173	126	30 - 60	-	Excessive
E	Horizontal plate	Under cover	No	Mild steel; millscale, some rust at edges.	4.5	1.0 mm shot	0.06	119	102	60 - 90	-	Excessive
	Section and bar	Under cover	No	Mild steel; mostly millscale	4	1.0 mm shot	7.8	120	104	40 - 50	-	Very bad
F	Horizontal plate	Under cover	Yes	Mild steel; millscale with some rust patches.	1.20	0.8 dia. x 1.0 mm chopped wire	1.5	132	119	85	40	Excessive
	Horizontal plate	Under cover	No	Higher tensile steel; millscale, with rust at edges.	2.5	0.8 dia. x 1.0 mm chopped wire	1.0	137	99	95	50	Excessive
G	Horizontal plate	Under cover	No	Mild steel; millscale with rust patches.	2.5	0.8 dia. x 1.0 mm chopped wire	1.0	132	112	85	50	Very bad
	Horizontal plate	Under cover	No	Mild steel; millscale, rust at edges.	1.8	1/3 1.2 mm 1/3 1.0 mm shot 1/3 0.8 mm shot	0.2	129	122	100	50	Excessive
I	Vertical plate	Open	Yes	Mild steel; millscale, rust at edges.	1.4	0.8 mm shot	29	137	99	100	70	Considerable
	Section and bar	Under cover	Yes	Mild steel; 50:50 millscale; rust.	1.4	0.8 mm shot	3.8	91	88	95	95	Considerable
J	Vertical plate	Under cover	No	Mild steel; mainly millscale but some general rusting.	1.0	0.65 to 0.75 mm shot	0.7	137	112	85	50	Considerable
	Vertical plate	Under cover	No	Mild steel; millscale, rust patches.	1.2	0.8 to 1.8 mm shot	1.2	126	114	60	30	Excessive
K	Section and bar	Under cover	No	Mild steel; mostly rust, very little millscale.	3	0.9 mm dia. chopped wire	-	132	124	-	30	Excessive
	Vertical plate	Under cover	Yes	-	-	0.9 mm dia. chopped wire	0.5	91	-	-	-	-
L	Vertical plate	Under cover	Yes	Mild steel; one side mainly millscale, other mainly rust	2	0.7 mm shot	1.4	101	-	85	60 - 70	-
	Vertical plate	Under cover	Yes	Mild steel; one side mainly millscale, other mainly rust	1.4	1 to 1.2 mm shot	traces	106	-	90	85	-

\* Angular particles greater than 2.0 mm diameter present in unused shot

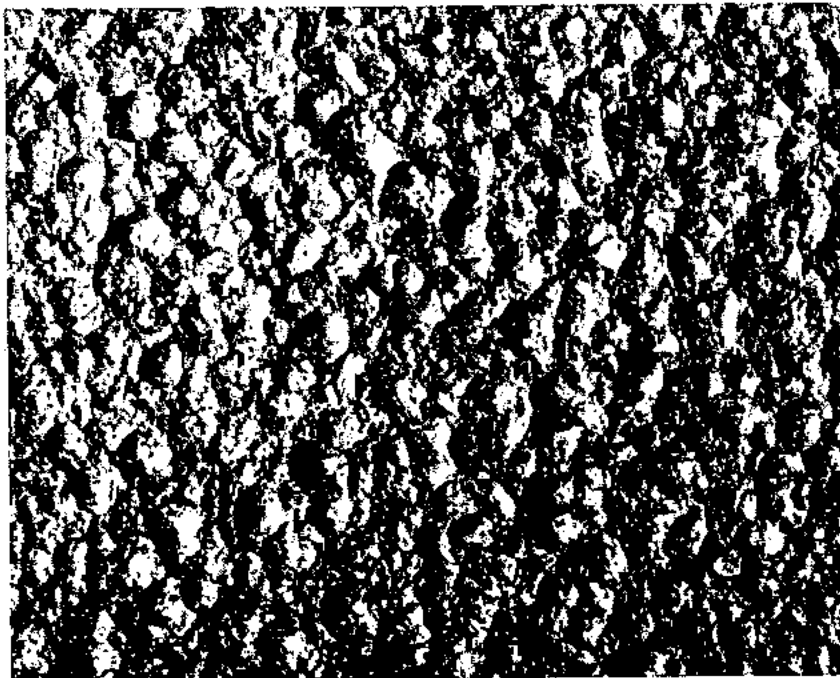


Fig. 5. — Surface blast - cleaned with 0,8 mm shot.  $\times 16$

abrasive is propelled by air or water. In some countries the uses of sand is still permitted, but in many parts of the world sand is not allowed and abrasives with low silicon contents must be employed. The most widely used alternatives to sand are iron and copper slags, which are available as grits in various size ranges. The finer grades are more expensive.

In general, the results show blast-cleaning to be better than other methods of surface preparation and economically justifiable but a number of unexpected difficulties have been encountered. Firstly, the improvements in ships' performance have been marginal. The reason for this is fairly obvious. Surfaces which have been exposed to marine atmospheres

for long periods are extremely rough (Figure 6). Deep rust pits form, and when the rust is removed, for example, with inhibited acid, so that the true surface texture is exposed, steep-sided pits up to 1 mm deep are frequently encountered (Figure 7). In fact, the peak heights on weathered surfaces are far greater than those resulting from grit blasting (Figure 8), and it is impossible to counteract the effect of roughness of this magnitude by applying paint films of normal thickness.

A second problem is that even on smooth surfaces the abrasives used can introduce sharp peaks which are difficult to cover with an adequate thickness of paint. The most commonly used grit size range is 1 to 3 mm diameter and this



Fig. 6. — Ship's hull before cleaning



Fig. 7. — Deep corrosion pits on ship's hull

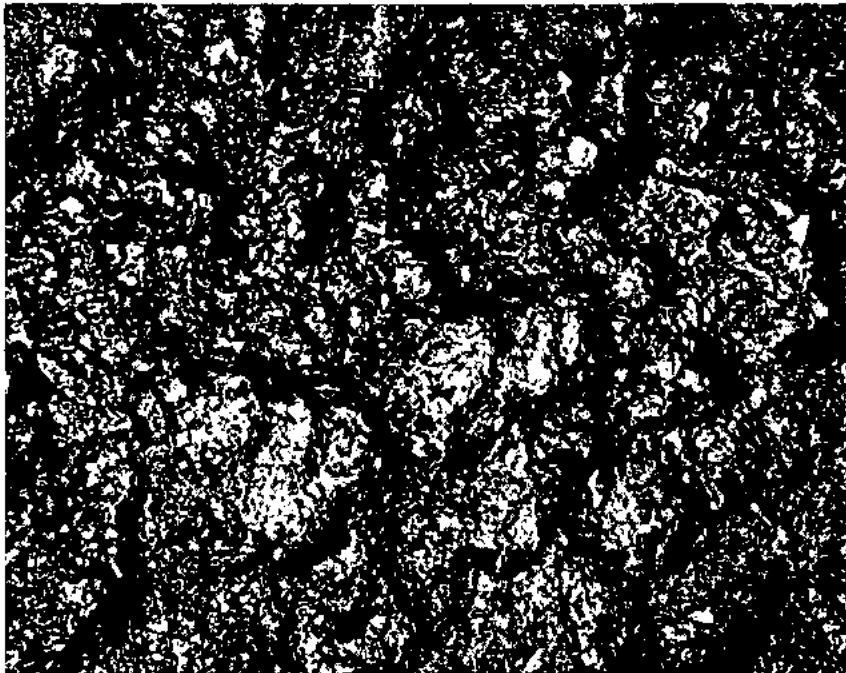


Fig. 8. — Corrosion pattern on ship's hull, with superimposed fine roughness due to grit blasting  $\times 5$

size gives rise to peaks as high as 250 microns. Coarse grits are favoured by the contractors because they are cheap and because they are thought to give a high rate of cleaning. This is not the case with sand; fine sand cleans faster than medium or coarse sand<sup>4</sup>, but how fine an abrasive can be used before this trend reverses has not been established. In any case, very fine materials are not practicable because they spread dust everywhere. Fine (0.3 mm) crushed iron abrasives are reported to have three times the cleaning rate of 1 mm iron

grit<sup>4</sup>. Thus it appears that there are strong arguments for using fine abrasives; not only will the peak heights be reduced but the cleaning rates should be increased. The increased cleaning rate should counteract the increased cost of fine abrasive. When fine abrasives are used it is essential that they should be free from dust; preferably, they should not contain particles below 0.2 mm.

Perhaps the greatest disadvantage of using coarse abrasives on old steelwork is that they cannot penetrate and

clean the deep, steep-sided, rust pockets. It might be thought this deep seated rust could be safely painted over but this is not the case. The rust next to the steel contains most of the soluble impurities. On ships' hulls the principal contaminant is chloride, on land-based structures it is sulphate. Evans<sup>6</sup> suggested that under humid conditions sulphate ions are driven towards the anodic portions of the corroding surface (i.e. the rust/metal interface) by the potential gradient. The potential is sufficient to counteract the tendency for sulphate to diffuse outwards under the concentration gradient. Schwarz<sup>4</sup> used spot tests, and Ross and Callaghan<sup>7</sup> the electron probe, to examine the distribution of sulphate pockets and generally confirmed Evan's hypothesis. It appears that the same reasoning can be applied to chlorides.

The presence of the chloride on surfaces exposed to marine atmospheres can readily be demonstrated by the spot tests described earlier. However, on the blast-cleaned surfaces of ships' hulls the chloride reveals its presence in a devastating fashion. Immediately following blasting the surface appears clean, but within an hour or two it is covered by droplets of highly acid water. (The pH of this water is often as low as 1). The droplets soon develop a skin of hydrated iron oxide and, within this skin, they grow to a considerable size. They are due to the deliquescence of the residual iron chlorides, and consequently they form even when the humidity is comparatively low. This is the reason for the widespread reports of damp surfaces on ships when atmospheric conditions and surface temperatures are such that normal condensation would not take place. Even if good quality priming paints are applied to chloride-containing surfaces before deliquescence can occur, the droplet formation can proceed through the paint layer as is shown in Figure 9.

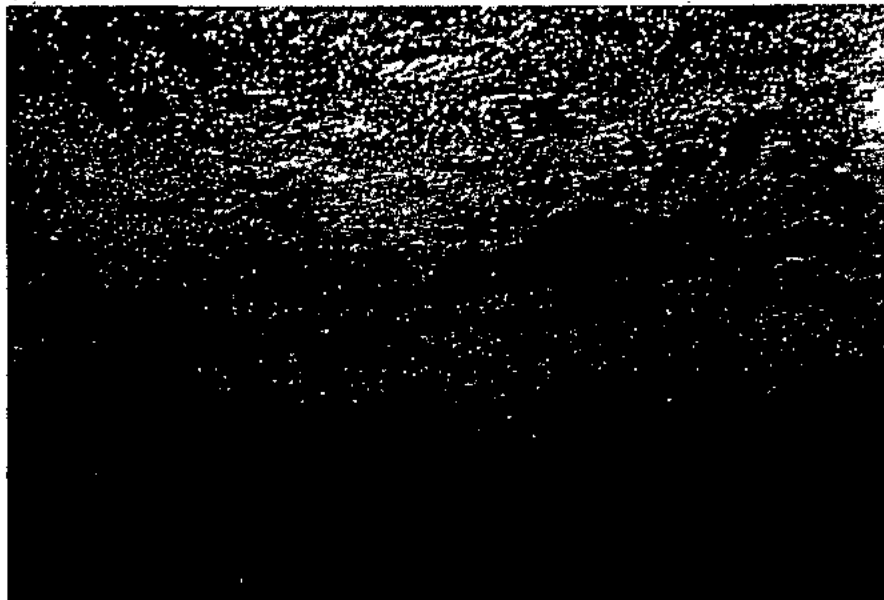


Fig. 9. — Droplets forming on the freshly blasted and primed surface of a ship's hull

Investigations into ways of overcoming this problem of surface contamination are still proceeding. Obviously, there is every incentive to use fine abrasives; these will penetrate and clean the deep chloride-containing rust pits. Mayne<sup>8</sup> has proposed washing as a means of removing soluble contaminants. On surfaces as rough as ships' hulls the washing would have to be continued for some time to be effective and one is then faced with the problem of drying the surface before painting.

Paints which can be applied to wet surfaces are under development and it is possible that the final solution to the problem will be to wet-blast with a fine abrasive and follow this with one of the new paints. Wet-blasting also minimizes the dust problem and the use of finer abrasives would also reduce peak heights.

## CONCLUSIONS

The problems associated with the cleaning of newsteelwork are very different from those with old steelwork. Shot blasting can be used on new steelwork and, provided that the components are not passed through the machines too rapidly and the shot is kept clean and free from extraneous particles, the surfaces will be satisfactorily cleaned and the peak heights will not be excessive. Spot tests are available to help the operators of the machines assess the quality of the surface finish. There is still a real need to remove residual dust from freshly blasted surfaces.

On old steelwork, particularly on ships' hulls, there are deepseated rust pockets that are difficult to clean. Expendable abrasives have to be used and, in areas where sand is not permitted, coarse grits made from iron or copper slags are frequently employed. These coarse grits can give rise to excessive peak heights. However, the surfaces are generally roughened by corrosion to a greater degree than by the abrasives. The rust pockets on ships' hulls contain iron chlorides, which, if not completely removed, deliquesce, giving rise to droplets of acid water even in comparatively dry atmospheres. Provided they are dust-free, fine abrasives will produce a cleaner surface than coarse ones will and their extra cost might be compensated by a higher cleaning rate. Alternatively,

wet-blasting might be used in conjunction with a paint which can be applied to wet surfaces.

### Acknowledgements

The authors wish to thank Mr. J. Jackson of Shell International Petroleum Ltd. and all others who helped in the work described in this paper.



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## DISCUSSION

G. DECHAUX (France): In order to examine the conditions of the shiplates which are covered with rust you use a solution of copper sulphate. The advantage is that you have a permanent photograph of the regions, which have been cleaned properly.

Afterwards you are obliged to remove small copper particles, which are deposited on the iron.

I would like to give you the method, which I use for a long time, perhaps the word method is too much, it is only a rule of thumb. Wetting the horizontal plate with white spirit i.e. a solvent and at the moment of total evaporation of the solvent, until you reach the dissipated zone, the rust appears dark and the surface of steel appears bright, because steel is reflective, that is, you haven't to remove the deposited copper afterwards.

Only the time of the appearance of the effect is relatively short and it does not last at all afterwards.

That was my first point. The second one, is on the subject of ferric chloride, which is concerned with all plates. Since 1920, I believe, the following method has been used by the National Navy of France to avoid what is called acidity from chlorides.

A solution of zinc oxide in water, having one part by weight zinc oxide and two parts of fresh water, is forming a composition of oxychloride of zinc, which is insoluble in water after exposure in air.

I believe that all who are working in the Navy know well this.

That was what I wanted to say. Thank you for your paper, which was extremely practical and very interesting. Thank you.

Dr. WILSON: I should like to thank M. Dechaux for his most interesting comments. The particular advantage of the copper sulphate test, in our case, is that it provides a more permanent record of the presence and distribution of residual rust. We are carrying out regular inspections in the ship yards and this test provides visible evidence which people can see and argue about. Also, the fact that we are seen to be carrying out these inspections has a great psychological effect on the personnel in the ship yards.

Turning now to the use of zinc to neutralize the acidity I am not certain at what stage you would apply the zinc compounds, or whether there would be any adhesion problems when painting on top of these materials. I have heard of some trials in which zinc particles have been used as a blast-cleaning material, but in this case I understand that the zinc was expected to provide local galvanic protection and was not intended to neutralize the acid.

G. DECHAUX (France): This is for after shot-blasting for the elimination of these droplets which are made of hydrolized iron chloride, which is very acidic (pH. 4). The droplets are neutralized entirely.

Dr. CAMERON (Great Britain): I would like to ask Mr. Wilson whether he considers that the first coat (the shop primer) is the most important one in a ship's life and whether he would agree that more time and effort should be given to developing better shop primers even at much greater cost than at present, also whether it might be possible to develop new techniques for welding so as to allow thicker shop primers to be applied instead of at present the paint manufacturer having always to formulate for existing welding practice.

Dr. WILSON: I think it is clear from the paper that I have a lot of sympathy for the paint manufacturers. The first coat of primer is certainly the most important, and there are some excellent modern shop primers. In general the problems with welding become greater as the primer coats get thicker. Some of these problems are technical and some are human. Thick primers can have an adverse effect on weld quality and fumes from some primers can be harmful. However, the welders do tend to complain excessively in order to justify extra payments. If the primer is not more than 25 microns thick these welding problems are minimal.

Dr. CAMERON: I would agree with Mr. Wilson if he said that some of the primers are good, but would it not be much better if they could be much thicker?

Dr. WILSON: Most paints are better when they are applied in greater thicknesses. However thick primer coats do present considerable problems. As I have already indicated, thick primer coats, if not cleaned away locally, can effect the quality of welds. They can also give rise to excessive amounts of harmful fumes. Another consideration is that they have to be overcoated at some stage, and it may be more difficult to guarantee good adhesion when over-coating thicker films than thin ones.

A promising alternative to the use of thick primer coats is fully to paint the large pre-fabricated sections of ships' hulls whilst these are still under cover, before they are finally welded in position. Sections prepared and assembled in this state have suffered remarkably little damage subsequently.

M. BARRILLON (France): In their very interesting paper Mr. Singleton and Mr. Wilson are indicating that the only effectively practical adjustment on a grit blasting during operation, was that of the speed of passage of the plate or profile.

This adjustment is by itself difficult due to the fact that the plates pass through the machine with a rapid rate.

It must be born in mind the fact that all these plates may be different (thickness, composition of scale). Apart of this, the time of storage in the yard and the place in the pile of the different plates, have an influence on the state of the scale.

How the operator of the machine will decide about the speed which has to use for a comming plate?

The solution which is consisted of establishing a priori a tag for each

plate is expensive in time of control and in manipulations. The solution which is consisted of passing the plate again from the grit blasting, if the cleaning was insufficient, it seems by itself neither practical nor economical, because brings an interruption in the normal flow of the plates. On the other hand, it must not be forgotten, that the plates are in general painted with a primer and the time available for the detection of insufficiencies in grit blasting is small.

Dr. WILSON: This is a very difficult, practical problem to which we have given a great deal of thought, and in the section of our paper which deals with new steel work we have briefly outlined this problem and suggested one possible solution. This is to use a mixed wide-range shot. The fine shot particles will penetrate and clean the pockets of atmospheric rust which form as the steel "weathers". These fine particles should be present in any case. On the other hand, some of the new higher-strength steels are covered by a very adherent millscale; very large shot particles are needed to break-up this tenacious scale.

Ideally, one would like several machines with different shot blends, or a quick method of switching charges in one machine. In practice, one has to accept that all types of plate will pass through one machine and that charges cannot be changed frequently. We think that the best solution is to use a very wide-range shot. It is also important to have skilled machine operators who can judge from the initial appearance of plates what pass speeds should be employed. One could set a low safe speed limit; this is not acceptable and if we are to work the shot-blasting machines at maximum capacity then the people who operate them must have the necessary expertise. They should not be up-graded floor sweepers.

QUESTION (speaker unknown): I would like to comment on this lecture, that few months ago, we have confronted the formation of droplets on surfaces. We were not able to apply any of the existing knowledge in this field and we got exactly 55 hours from the sponsor to solve it. We examined the iron plates by the microanalysis and we gave a few advices, which I should like to discuss here.

I think iron chloride, could be removed just by rinsing with water after of course a coarse blasting and perhaps followed by fine blasting. If this is not possible for practical reasons, coarse blasting and fine blasting would do it. But we also found that it is very dangerous and in practice, part of the coarse grit, which is broken at the surface, is recirculated in the coarse grit in order to have a lower average grit size. So we concluded that the iron chlorides were removed they will take the water from the air and if you blow them again to the surface they have a high probability to stick at the surface and to start oxidation there. So I think this recirculation, should be avoided in practice. Finally I should like to ask a question about the formation of chlorides which is really not a clear matter to me. Thank you.

Dr. WILSON: The main point is that new plates that are cleaned by recirculated shot do not suffer from chloride contamination. Droplet formation due to residual chlorides occurs on old steelwork, particularly the underwater surfaces of ships' hulls. The normal cleaning method for old steel is to use a cheap expendable grit or sand which is not recirculated. This avoids the danger of introducing additional contamination.

On old steel it is possible to use coarse grit and follow this up by a fine grit and by water washing. However, all this takes valuable time and we prefer to use a wide range grit or sand with a size range from 0.2 to 1.0 mm. This gives a high rate of cleaning and removes practically all the deep-seated chloride contamination.

The other question about the chemical reactions which takes place in the rust pockets is rather difficult to answer. These chloride-containing compounds exist in the bottom of deep rust pits, generally shielded from the marine environment by thick rust or paint film. They are probably not very active until they are exposed to air. Unfortunately, they are very unstable when exposed to air and in order to collect them for investigation we have had to sample immediately after dry-docking and to store the samples in air-tight containers under a nitrogen atmosphere. It appears that they are very complex oxy-chlorides and hydroxy-chlorides often with unrecorded X-ray diffraction patterns. We have succeeded in producing some of these compounds in the laboratory and have established their chemical formulae. At the same time we are studying the corrosion reactions which take place when these unstable compounds are exposed to the atmosphere.

C.P. DE (India): We are much interested in blast cleaning of hulls of old ships as we would like to change over to synthetic resin paints. I shall very much like to hear from Mr. Wilson about the most suitable method of cleaning of such hulls particularly about the choice of abrasives, use of dry or wet blasting and prevention of chloride contamination.

Dr. WILSON: Sand is a very good abrasive if you are allowed to use it. In many countries it is not permitted for health reasons and crushed metallic slags are substituted. Most of our experiments with blast cleaning have been carried out on ships in dry docks, not in laboratories, so we are fully aware of the practical problems.

It is possible to reduce the residual chloride contamination after blasting, by washing with clean water to which corrosion inhibitors may be added. We tried one experiment in which a hull which exhibited severe chloride contamination after grit-blasting was water-washed prior to painting. The subsequent performance of the paint system was compared with that of a vessel of similar age grit-blast cleaned to about the same standard but not water-washed. The paint on the water-washed vessel was in much better condition after one year's service.

The amount of rust after water-washing with uninhbited water is not excessive and it may not be worthwhile to use inhibitors.

# CORROSION OF SHIPYARD UNDERWATER STEEL STRUCTURES

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## SUMMARY

The purpose of this paper is to bring out the experience of a Shipyard regarding corrosion of its underwater steel structures under the particular conditions of sea water temperature, relative humidity etc. prevailing at the area.

A subdivision of the structures is made according to the prevailing position of the structure with respect to the water level and the corrosive conditions in the area such as chemical composition of sea water, extent of fouling, relative humidity, etc. are examined in order to correlate the corrosion results to the environment.

The results of the corrosion on a number of shipyard under water structures such as floating docks, mooring dolphins, steel piles, supporting piers over a number of 7 to 8 years

are established by a large number of ultrasonoscope measurements of the thickness of such steel elements and the extent of corrosion is derived by comparison to the original thickness of the structure.

The type of treatment of the steel surface in each case is given and the influence of the treatment on corrosion is shown as well as the advantages of certain preservatives on maintenance.

A great number of pictures are attached to illustrate the extent of fouling, the corrosion of internal dock areas, the significance of the proper paint application, the effect of floating oil on bituminous paints etc.

## 1. INTRODUCTION

The purpose of the present paper is to bring out our experience with the corrosion effects of sea water on the shipyard underwater steel structures under the particular conditions prevailing in a shipyard area.

Factors playing an important role on the progress of the corrosion phenomena on protection of steel such as sea water composition, temperature variations, air moisture content and steel surface treatment have been investigated to elucidate the corrosion effects observed on the underwater steel structures during a 7-8 year period of service.

It is admitted that the period of the observations is not large enough to provide for definitive conclusions. It is however thought that the trend of the phenomena is indicative of the behaviour of the structure on a long term basis.

### 2. *The Shipyard underwater steel structures*

Shipyard underwater steel structures will normally fall into one of the following groups:

1. Floating Docks
2. Dock gates and Graving Dock main inlet valves
3. Mooring Dolphins and guides
4. Steel piles supporting piers
5. Sheet piling of quay walls, piers etc.
6. Mooring buoys
7. Other auxiliary steel structures permanently or temporarily operating under water such as gratings, underwater pipes etc.

All the above structures have something in common, the fact that they operate continuously in sea water and that once installed, protection treatment against corrosion — apart from the original one — is extremely difficult if at all possible.

### 3. *The problem of corrosion in Floating Docks*

The corrosion of Floating Docks is one of the most important problems a shipyard has got to face.

Due to their large size these structures unless of special construction (self docking type) can be very rarely docked within the Yard's own facilities. Even in a case of a self docking sectional type dock, or when a larger dock is available within the Yard, the taking out of commissioning of a dock is a very costly affair and one which has a direct influence on all Yard's activities.

Therefore the requirements for corrosion protection of a dock before its commissioning are usually very severe and every attempt is made to protect the dock with the most effective protection scheme.

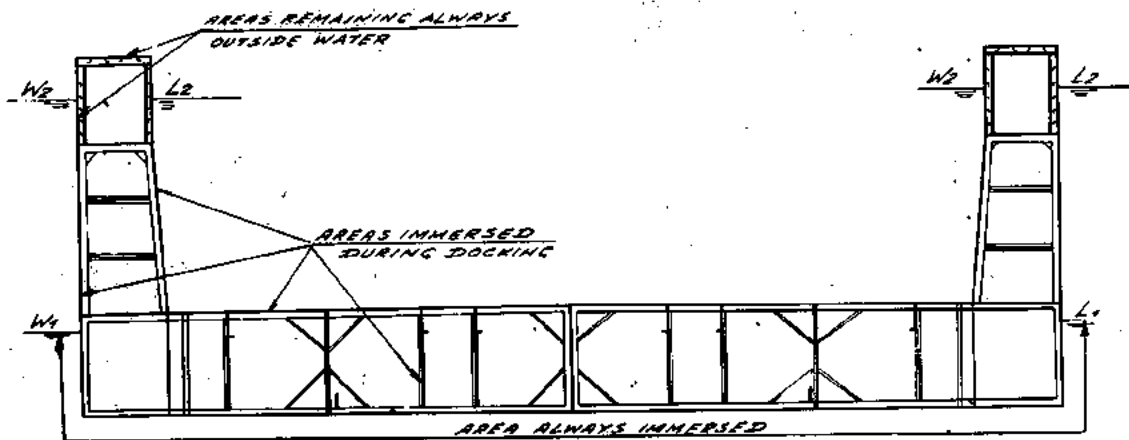
### 4. *The particular corrosive conditions prevailing in Floating Docks*

Floating docks compared to other sea under water structures are subject to a very peculiar sequence of conditions. The steel areas of floating docks can be divided in three main groups.

a) External underwater parts which are always immersed during the normal operating life of the dock such as external areas below the dock light water line W1, L1 (see sketch No. 1).

These surfaces are subject to the electrolytic action of sea water and also some stray currents due to welding machines working ashore for ships under repairs. They are also subject to the adhesion of barnacles, marine growth and mechanical damage from ships moored alongside the dock or tugs during towage, inadvertent grounding of the dock due to small clearances under the bottom or heavy silting etc.

b) Internal and external areas of tanks which are alternately immersed and emmersed during the docking opera-



GROUPING OF AREAS IN A DOCK

SKETCH NO 1

tion. Under this group one should include the external area between the dock light water line and deep immersion line W2L2 including the pontoon deck as well as all internal areas and stiffeners inside the tanks.

These areas remain under water for about 2-3 hours time every 3 or 4 days during the docking operation. Subsequently they remain exposed to air and humidity, large temperature variations etc. In practice the lower part of the tanks remains always covered with an amount of water which cannot be pumped out completely or which is necessary for trim and ballast purposes. From corrosion point of view this part should normally be dealt with the first group.

Theoretically the areas of the second group are accessible during most of the time and should be treated as such.

Unfortunately experience has shown that maintenance of these areas, although accessible, is not an easy job.

The humidity inside the tanks is so high that practically no paint can be applied effectively on the wet steel surface unless the dock is taken out of operation and the tanks are completely emptied and dried out through intense ventilation and/or heating.

c) External and internal areas which remain always above water.

This group comprises all areas which are above the deep submersion line and consequently remain always above water.

These areas are subject to the corrosive action of the atmosphere and also mechanical damage from works executed in the dock (handling of weights, repair work on ships, grit blasting operations, dragging of steel wires).

Maintenance of these areas is relatively easy.

##### 5. The corrosive conditions in the area

To analyse the factors affecting corrosion of each group of surfaces an investigation has been carried out with the purpose of determining the particular conditions prevailing in the surrounding area.

###### a) Chemical composition of sea water

It has been argued that at least for unprotected bare steel the speed of corrosion depends primarily on the oxygen content of the sea water and that salt content and small temperature differences of sea water do not have a substantial influence on corrosion progress.

On protected steel areas however which are not fully active, the seawater conditions play definitively an important role on the corrosion phenomena so that corrosion effects in one place can be hardly considered as representative of the results one may expect in another.

In order to relate the observations to the particular conditions of sea water in the surrounding area — possibly influenced by the proximity of industries such as cement factories, oil distilleries etc. — a chemical analysis of a sample has been made which has shown the following results.

###### Examination of sea water sample

Impurities: .....	0,190 ‰
Chlorides (as Cl) : .....	21,983 ‰
Sulphates (as SO <sub>4</sub> ): .....	3,007 ‰
Alkalinity (HCO <sub>3</sub> ): .....	0,195 ‰
Phosphate reaction: .....	slightly positive
Nitrates " : .....	" "
Nitrides " : .....	negative

###### Hardness in french degrees:

a) Calcium.....	388,17
b) Magnesium .....	81,86
c) Total .....	470,03
d) Temporary .....	16,00
Free CO <sub>2</sub> .....	0,026 ‰
H <sub>2</sub> S .....	0,025 ‰
Potassium Permanganate used for oxidising organic matter in one litre of water. .	0,0028 gr.

Sampling was done from various depths in the area and within a distance of 150-400 meters from the shore.

It should be noted that at the time of the sampling, excavation work was in progress at the sampling area and thus the figure of impurities given above must be somewhat higher than the normal of the area under review.

Some seasonal change in the composition of water, might be expected, and it is possible that the above results are subject to a slight alteration.

###### b) Barnacles and marine growth

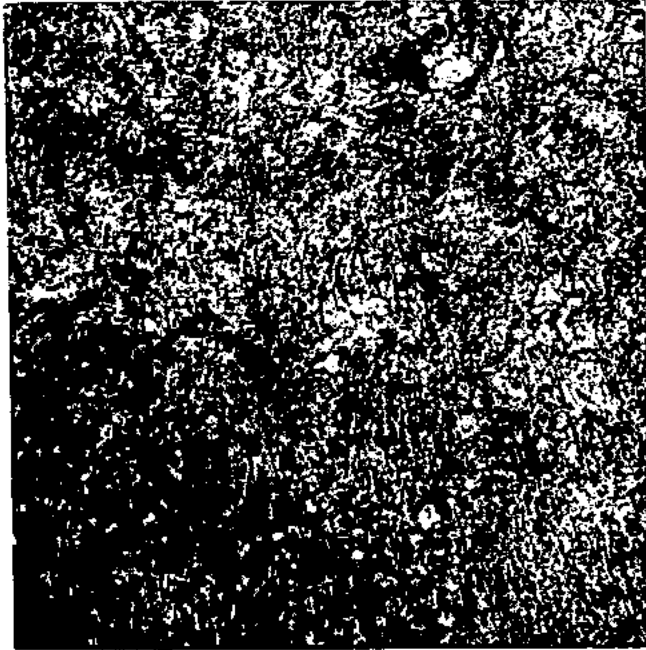
Barnacles and marine growth play an important role on the endurance of the paint. In docks and other shipyard structures such as dolphins, dock gates, piles, etc. the bar-

nacles and marine growth are primarily responsible for the destruction of the paint film.

Barnacles are attached to the external surface where they start forming their shell. The sides of the shell penetrate the soft layer of paint composition until they meet the hard steel surface. When barnacles die out the shell is dropped and a hole is formed exposing the steel surface to corrosion. It is well known that barnacles are mainly formed in stationary or slow moving structures such as Shipyard underwater installations.

The formation of barnacles in the area under consideration has been repeatedly noticed on ships docked after long period of laying up or on dock sides, piles etc. and although there are no absolute methods of determining the extent of growth it could be termed as heavy.

Picture 1, 2 give a good idea of the marine growth encountered in greek waters on the bottom and sides of a floating dock which was immersed for a number of years. Dark spots are spots where the paint was blistered due to a barnacle drop, leaving a deep pit.



Pict. 1

Marine growth on the bottom of a Floating Dock in Greek Waters after 4 years of immersion.

- e) No copper traced
- f) Qualitatively observed small traces of FeO.

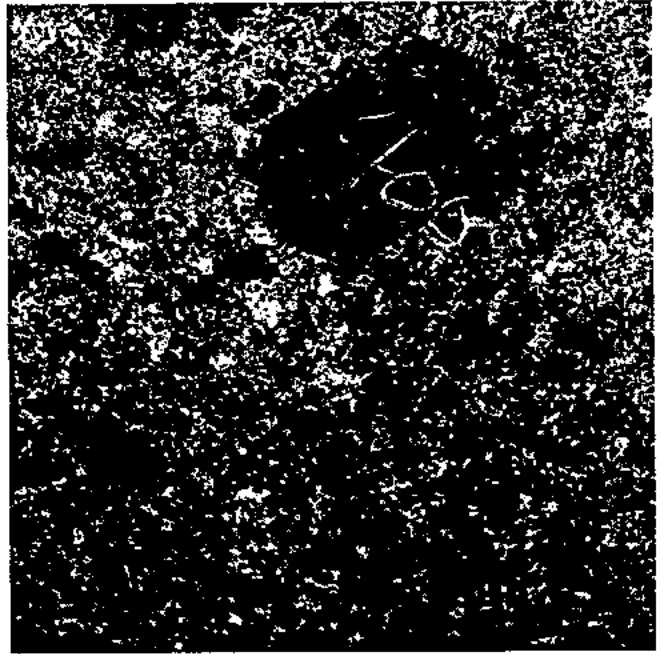
Sample No. 2:

- a) In this case also concentrated acid Treatment leaves traces of Silica and Organic Matter.
- b) Tracing of Carbonates: Negative
- c) Loss through incandescence (mainly carbonised matter): ..... 22,60%
- d) Iron as Fe<sub>2</sub>O<sub>3</sub> ..... 71,20%
- e) No copper traced
- f) Qualitatively observed slight traces of FeO.

From the above analysis it can be concluded that the corrosion products do not reveal any abnormal conditions such as presence of copper etc.

d) *The atmospheric conditions inside a dock*

As previously stated the corrosion progress inside a dock



Pict. 2

c) *The Chemical analysis of the corrosion products*

To determine the sort of corrosion which takes place inside a Dock, samples have been taken from the tenaceous film formation on the side shell and stiffeners inside the dock structure. The chemical analysis of the corrosion products gave the following results:

*Analysis of rust deposits from the internal compartments of a floating dock:*

Sample No. 1:

- a) Sample No. 1 treated with concentrated acid leaves a small trace of Silica and Organic matter.
- b) Tracing of carbonates: Negative
- c) Loss through incandescence (mainly carbonised matter): 15,20%
- d) Iron as Fe<sub>2</sub>O<sub>3</sub> ..... 81,20%

depends largely on the atmospheric conditions prevailing there.

These conditions are of a peculiar nature in the sense that the large water surface inside the tanks, under the external high temperatures which heat up the steel walls and deck of the dock, results in a high degree of evaporation.

The vapours condense on the inner steel walls of the dock forming droplets. The condensation is extremely heavy during the coolest hours of the night. A large number of temperature and relative humidity measurements were taken (see appendix I) from which one can see that the relative humidity inside the tanks is very high and that almost under all outside temperatures, this humidity is between 80% ÷ 95%.

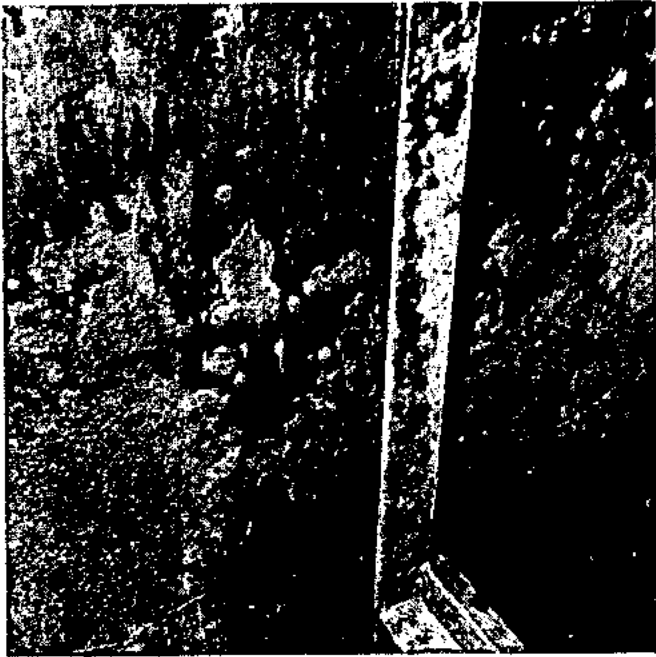
Although however the ambient temperature within a tank is practically constant over the tank, there are distinct temperature differences between the steel walls exposed to the sun and the sheltered dock areas. This in turn causes on some surfaces a faster condensation and evaporation rate which

promotes corrosion.

In fact it was noticed that the corrosion on the sun exposed sides of a dock is considerably heavier than on the others. Pict. 3 and 4 taken on the sheltered side compared with 5 and 6 on the sun exposee side indicate this difference.

We have examined the ph of the droplet formation to determine the degree of acidity due to possible content of substances in solution and found its reaction to be slightly alkaline with a ph value of 6.2.

In way of the lower parts of the tanks which are sub-



Pict. 3



Pict. 4

Corrosion on the sun sheltered sides of a dock.



Pict. 5



Pict. 6

Corrosion on the sun exposed sides of a dock is considerably heavier compared to sun sheltered areas.

sequently immersed, the droplets are washed away by the sea water. In the upper parts, where the sea water can not reach due to the air belows, the droplets evaporate again due the warming of the steel plates exposed to sun, leaving a corrosion spot.

Pict. 7, 8 indicate the spots on the safety deck and upper members of a dock structure from which one may conclude that local corrosion cells are formed due to factors such as differences in metal structure, millscale etc.



Pict. 7  
Local spot corrosion of deck and upper sides. Droplet formations are easily distinguished.

and its elasticity have prevented blistering.

The areas adjacent to the water level showed some signs of spot corrosion and melting down of the bitumen through the high summer temperatures.

No serious mechanical damage has been noticed and this is mostly due to the protection which is offered to the docks by the mooring dolphins.

Pict. 9 and 10 show the internal area of the dock «Y» near the bottom. The lower parts are in very good condition.



Pict. 8

#### 6. The treatment of the steel surfaces

Having examined the corrosive and fouling conditions prevailing in the area, it is necessary to mention the sort of treatment which the steel surfaces of the docks have undergone before entering in service. The docks were all constructed of ST-42-2R steel. Dock «X» was sandblasted and treated with one coat of «Tenax» solution black and one coat of «Hot Ferroid» enamel blue of the Firma C. Dunker of Hamburg.

Dock «Y» has received a similar treatment outside and inside but without internal sandblasting above the 1.0 meter level.

For experimental purposes a few internal areas were treated only with two coats of «Tenax» solution. Dock «Z» was treated during repairs with bitumen enamel placed cold over a steel area which was previously scraped.

#### 7. The results of corrosion and fouling on the dock structures

A careful visual inspection of the underwater parts of dock X and Y revealed that during a service period of 8 and 7 years respectively, the accumulation of barnacles and marine growth was heavy. The condition however of the outside surfaces remaining constantly below water (1st group) could be considered as very good. There were no signs of loose paint areas and the elastic nature of the bitumen had resulted in the avoidance of cracks in spite of the repeated deflections of the docks in sagging or hogging. Barnacles have created local pits but again the good adherence of the protective coating

The upper parts (above 1.0 m.) show signs of blistering where the paint was applied on non-blasted surface.

Pict. 11, 12, 13, 14, 15, 16, 17 show heavily rusted internal areas near the top of the tank where the water level reaches during immersion.

Pict. 18 and 19 show the separation zone between areas laying above water level and those below it inside a tank.

Pict. 20 shows a heavy rusting about 4 m/m thick on a valve rod which was left without treatment.

Pict. 7 and 8 previously mentioned show the under side of the safety deck where condensation of the vapours occur. The evaporation of the droplets is followed by local spot corrosion.

Pict. 21 and 22 indicate heavy corrosion on the internal horizontal stiffeners which should be expected as the sea water accumulates on the surface of the top flanges.

Pict. 23 in dock «X» is a good example of a perfect protection. The paint is almost intact showing a flat smooth surface without any signs of corrosion.

Pict. 24 and 25 belong also to dock «X» and one can see a remarkable difference when comparing them to the corresponding areas of dock Y.

Pict. 26, 27, 28 belong to dock «Z» and they indicate that the paint was not properly bonded to the steel surface as a result of which it has blistered or peeled off in many places resulting in heavy corrosion.

Rivet heads are the first to corrode as it is anyhow difficult to scrape and apply properly a new paint coat over them.



Pict. 9



Pict. 10

Near bottom side of a floating dock. Lower strake treated with bitumen solution followed by hot Enamel is in good condition. Upper parts, 1,0 m. above bottom indicate signs of blistering where the paint was applied on non blasted surface.



Pict. 11

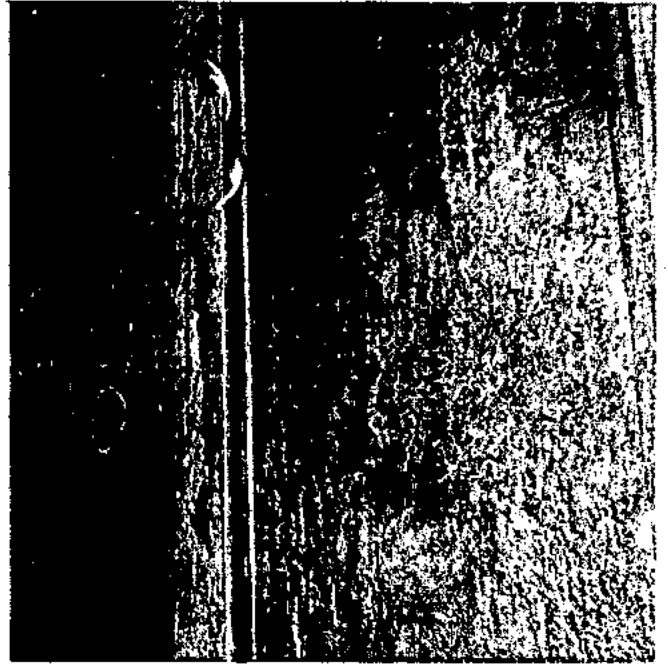


Pict. 12

Heavily rusted upper internal areas near the top of a tank.

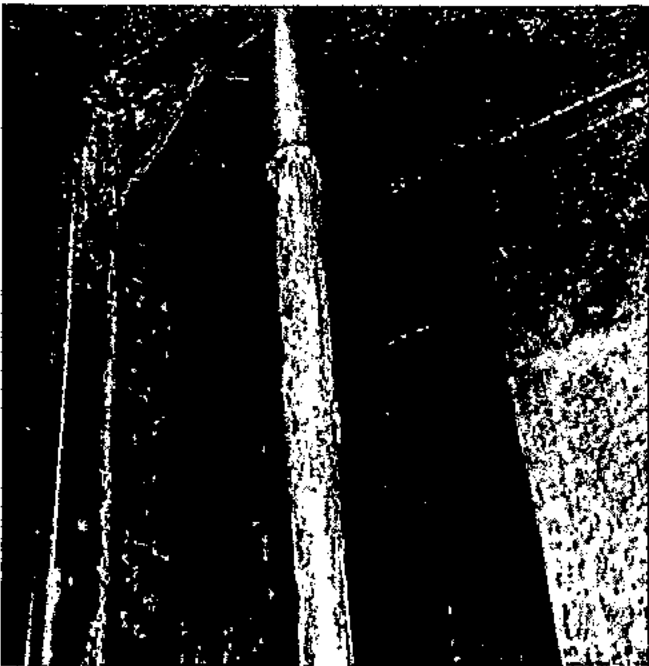


Pict. 13



Pict. 14

Heavily rusted upper internal areas near the top of a tank.



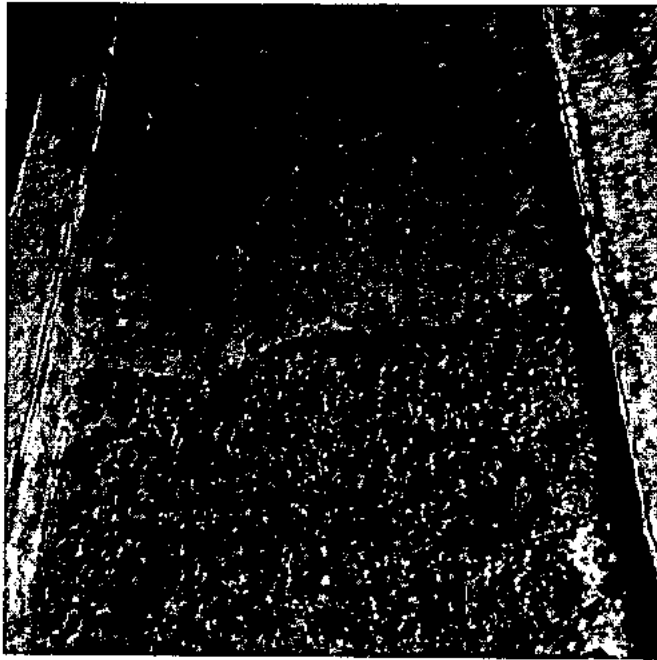
Pict. 15



Pict. 16

Rusted areas near the top of a tank.

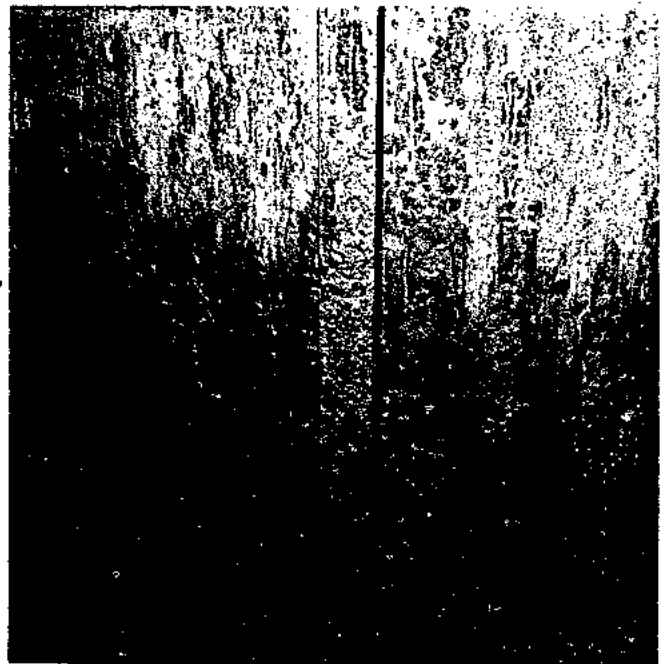




Pict. 17  
Heavily rusted area in way of an access tank.



Pict. 18



Pict. 19

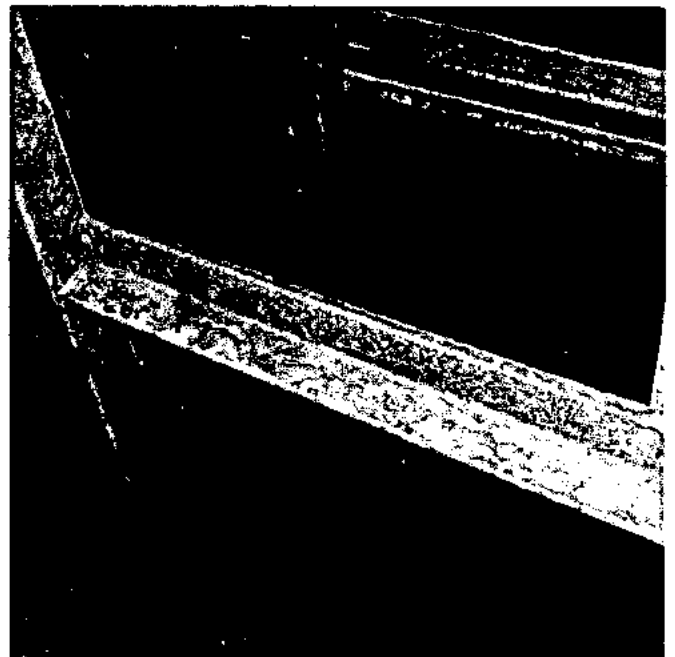
The rust separation zone inside a tank (near water level during immersion).



Pict. 20  
Heavily rusted valve rod rust layer about 4 mm thick left without treatment.

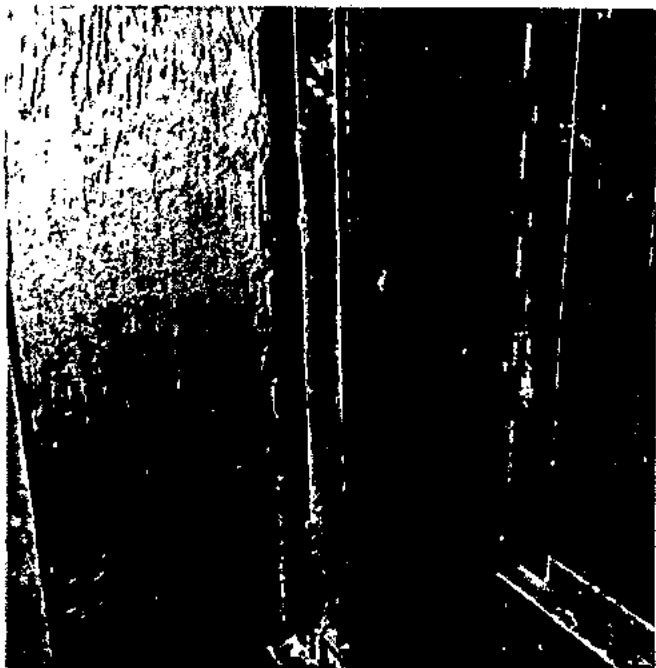


Pict. 21



Pict. 22

Heavy corrosion on internal horizontal stiffeners. Accumulation of water on flanges creates more adverse corrosive conditions compared to vertical members.



Pict. 23



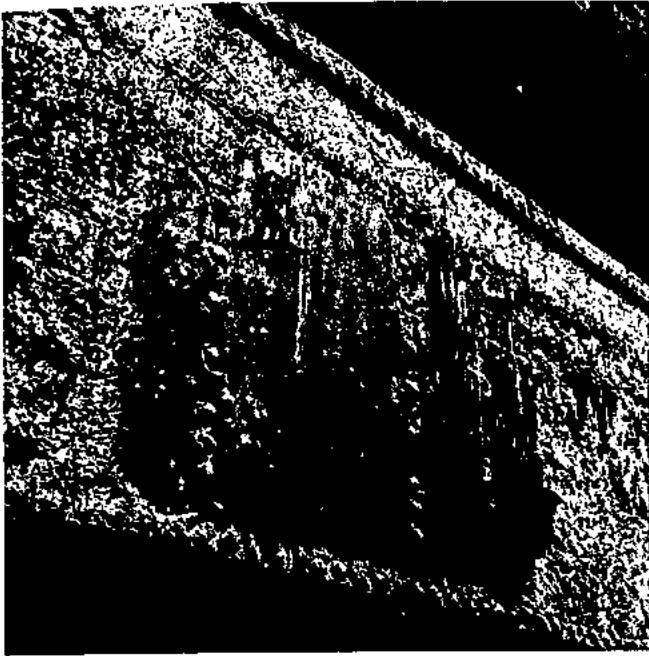
Pict. 24

An example of perfectly protected internal side of a dock after 8 years of service. Dock was treated with Bituminous Solution followed by Hot Enamel.



Pict. 25

Good protection as above. Only local spots of calcerous formations are noticed.



Pict. 26

Examples of paint on outside surfaces not properly bonded to steel due to wrong application.



Pict. 27



Pict. 28

Easy removal of paint by scraper indicates wrong application.

#### 8. The extent of corrosion

The life expectancy of a dock depends entirely on the extent of corrosion. In order to investigate the extent of

material wear due to corrosion we have carried out a considerable number of thickness measurements on the plates and profiles of the docks «X» and «Y». Measurements were taken by the ultrasonoscope and it should be made clear at this stage that their accuracy should be considered as being within the limits of field practice for the purpose intended i.e. with a tolerance of  $\mp 0.15$  mm.

Sketch No. 2 indicates the thickness measurements on the inside and outside shell plating of the Dock X after 8 years of service.

From these one may deduce that the average wastage of the shell over the above period has been of the order of  $0.5 \div 0.6$  mm for the upper end of the outside plating and  $0.7 \div 0.9$  mm for the lower side.

Inside shell plating shows a slightly minor wastage varying from  $0.3 \div 0.6$  mm.

Sketch No. 3 shows the reduction in thickness of the internal members. Vertical members indicate a wastage of  $0.3 \div 0.7$  mm whilst the horizontal a wastage of  $0.4 \div 0.7$  mm, with a slightly higher average value. Assuming that the speed of corrosion can be evaluated in accordance with the following table:

0.075	mm per year	light
0.100	» » »	medium
0.125	» » »	heavy
0.150	» » »	very heavy
0.175	» » »	extremely heavy

the corrosion occurring under the aforementioned conditions in dock X could be termed as light to medium.

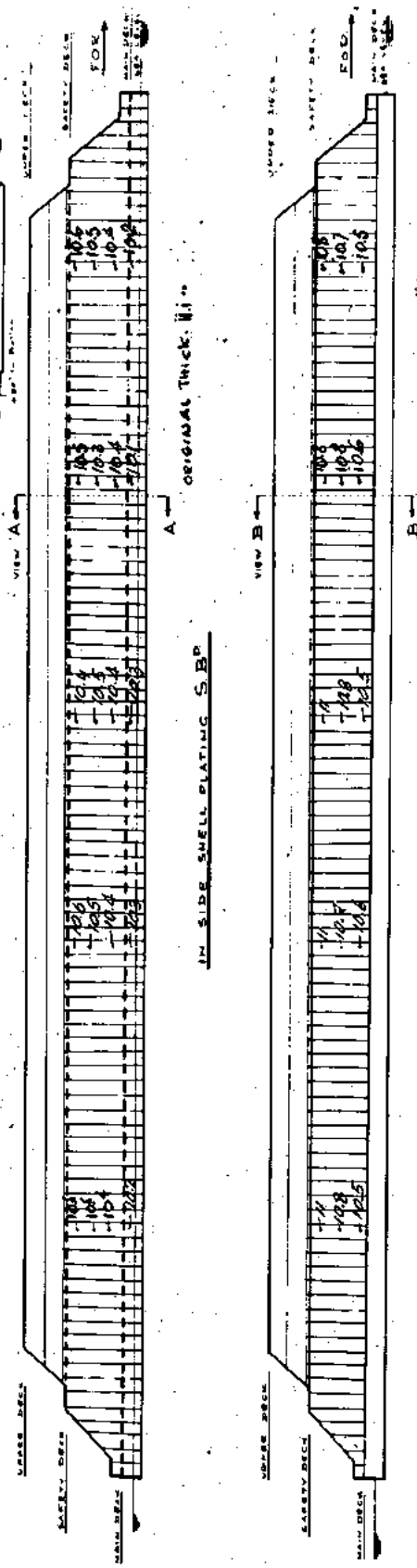
The overall performance of the painting scheme of the dock is considered as entirely satisfactory.

Sketch No. 4A and 4B indicate the reduction in thickness of the shell plating of Dock «Y» after 7 years of service. The average wastage of material is  $0.5 \div 0.7$  mm for the upper zone and  $0.7 \div 1.00$  mm for the area near the water level.

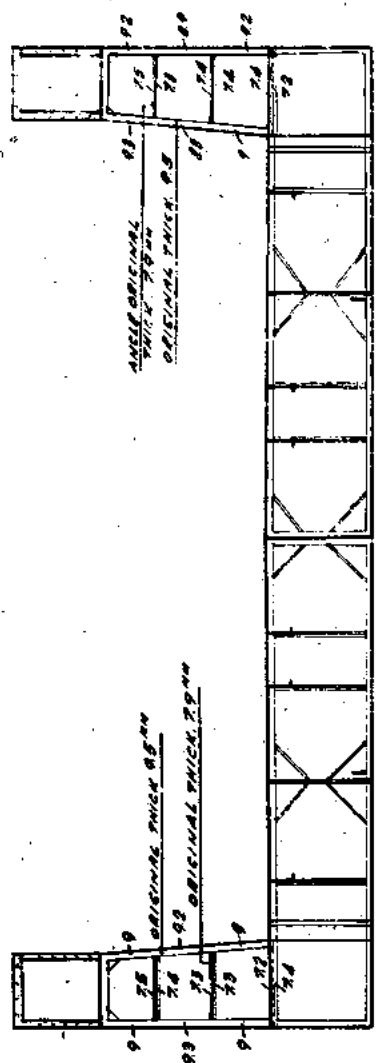
Sketch-No. 5 shows the reduction in thickness of internal members non coated with Bitumen but treated for experi-

# FLOATING DOCK 'X'

OUT SIDE SHELL PLATING S.B.P.



# CROSS - SECTION DOCK 'X'

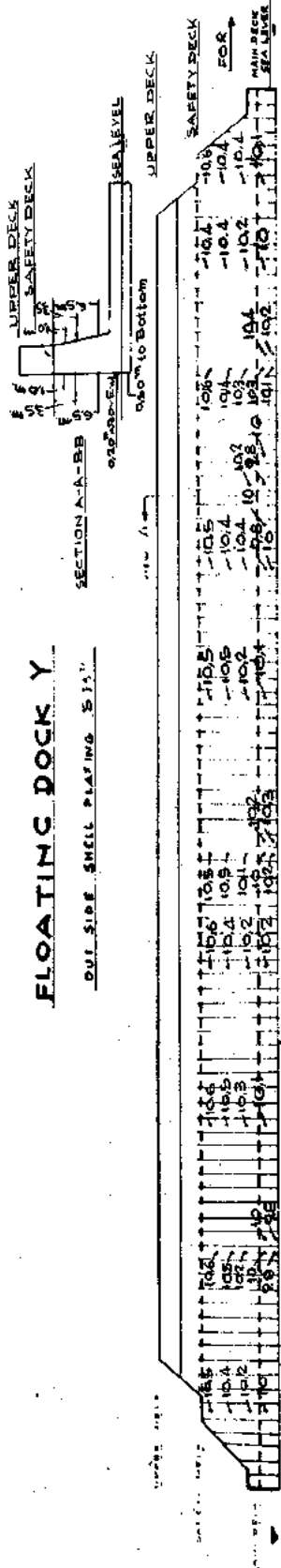


REDUCTION IN THICKNESS OF INTERNAL MEMBERS AFTER EIGHT YEARS OF SERVICE

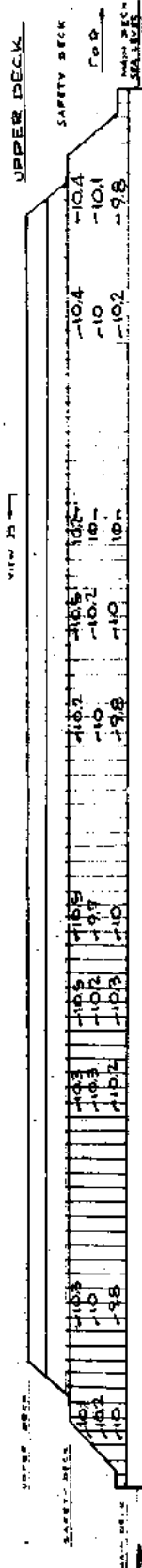
SKETCH NO. 3  
NOT TO SCALE

# FLOATING DOCK Y

OUTSIDE SHELL PLATING S.P.



IN SIDE SHELL PLATING S.P.



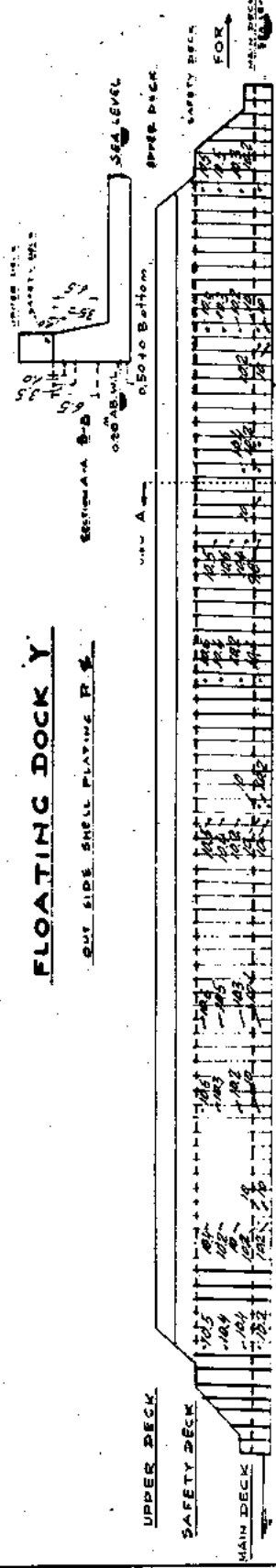
REDUCTION IN THICKNESS OF SHELL PLATING AFTER 7 YEARS OF SERVICE

SKETCH NO. 48

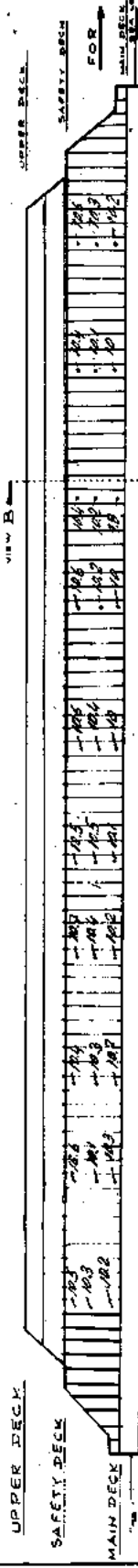
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# FLOATING DOCK Y

OUTSIDE SHELL PLATING P.S.



IN SIDE SHELL PLATING P.S.

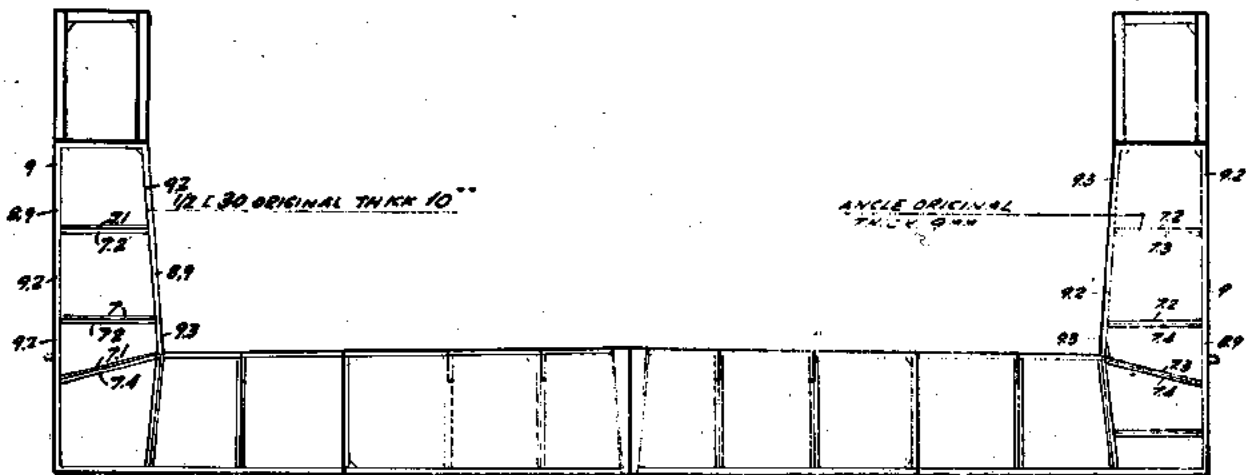


REDUCTION IN THICKNESS OF SHELL PLATING AFTER 7 YEARS OF SERVICE

SKETCH NO. 49

NOT TO SCALE

GROSS SECTION DOCK Y



REDUCTION IN THICKNESS OF INTERNAL MEMBERS (NON COATED WITH BITUMEN ENAMEL)  
AFTER 7 YEARS OF SERVICE

SKETCH NO 5  
NOT TO SCALE

mental purposes with two coats of primer only. The wastage, as expected, is very high indicating a heavy corrosion especially in the horizontal members.

9. General remarks on Dock preservation.

The life expectancy of a dock depends entirely on the protection scheme and on the quality and grade of preparation.

A long lasting durability of preservation can only be achieved by application of the preservative on surface free of mill scale, moisture, oil grease and dirt.

The minimum grade of steel surface preparation for application of Hot Enamel coatings is the sand blasting of steel surfaces to B Sa2 standards followed up immediately by a suitable shop primer. Normally a coat of tar pitch solution followed by a hot asphalt product based on bitumen and coal tar pitch are considered as the minimum requirements for a good preservation.

Picture No. 29 indicates the finished surface of a Hot Enamel preservation.

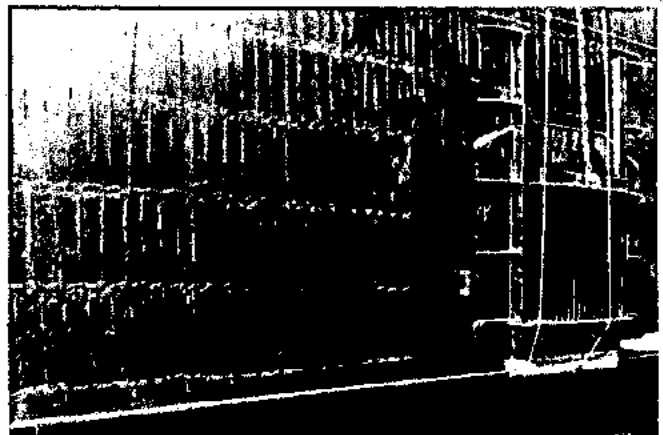
Picture No. 30 of a ballast tank coated with Hot Enamel shows clearly the influence of mill scale in the duration of the preservation.

The top plates indicate serious blistering of the paint due to peeling off of the mill scale. The plates underneath have been derusted and hardly show any damages.

A serious danger in applying protective potential of wrong rating is illustrated in Pict. 31 where local blistering of the paint is attributed to cathodic hydrogen formation on mill scale caused by aluminium anodes.

Pict. No. 32,33 indicate damages of paint caused by mechanical stresses such as tug towing alongside.

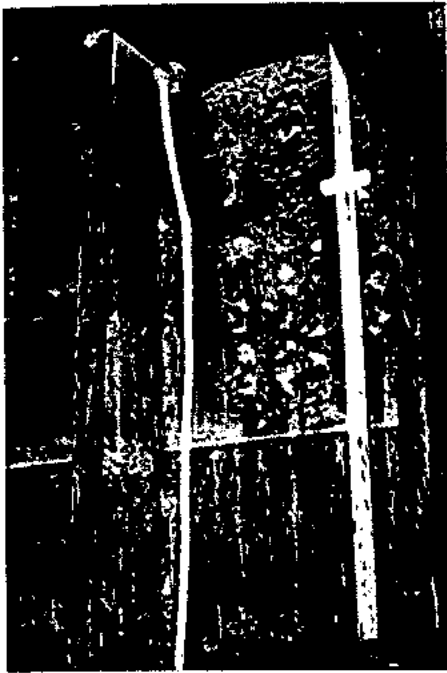
Pict. Nos. 34, 35 show another common cause of damage



Pict. 29  
Finished Hot Enamel preservation.

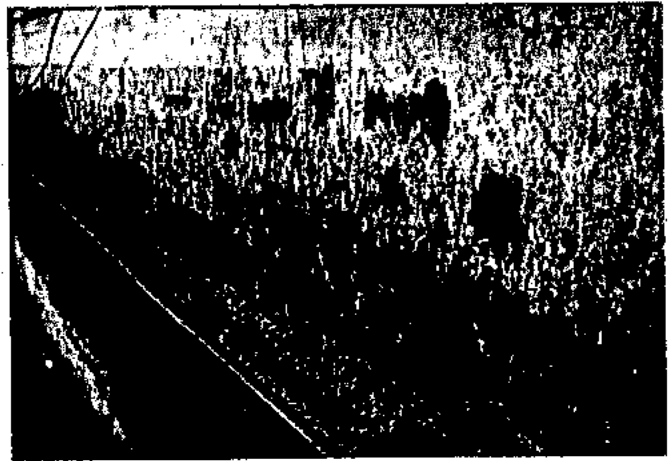
which is the oil floating around the area of ships under repair. Unfortunately in spite of all measures taken to avoid pollution of sea, the inadverted oily film formation around the areas where the docks operate can not be avoided. As a result in the area where coating has been in touch with oil, the softening point of the Hot Enamel has been decreased. Subsequent solar radiation leads to breaks up of the coating and flaking off.

Note: Pict 29 to 35 are due to the courtesy of the Firma C. Fr. DUNKER of Hamburg.



Pict. 30

Ballast water tank. Top plates indicate signs of blistering due to mill scale. Plates below were derusted prior to painting.



Pict. 32

Damages or paint caused by mechanical stress such as tugs going along side.



Pict. 33

Damages on paint caused by mechanical stresses.



Pict. 31

Blistering of paint attributed to cathodic hydrogen formation caused by aluminium anodes.

#### 10. Dolphins and steel piles

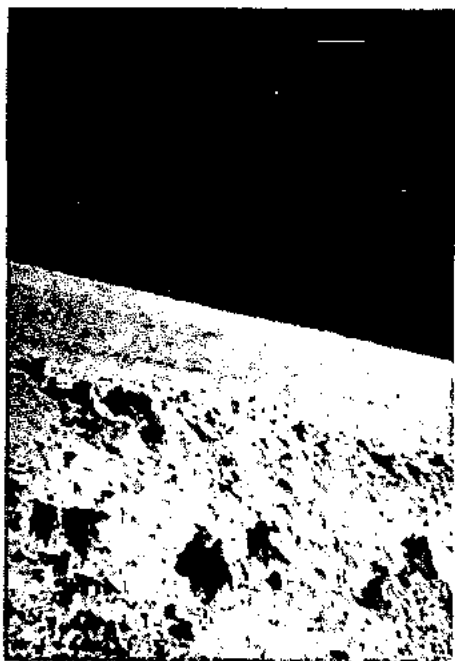
Dolphins are circular columns made out of steel sheet piles driven well below the bottom of the sea (12.00 ÷ 20.0 meters) which serve as anchoring posts for the Docks.

Dolphins are usually made of LARSEN, Manessman or other type of tubular individual sections of high tensile steel, in thicknesses of 8 ÷ 26 mm. The life expectancy of the dolphins is theoretically the same as that of the dock. Dolphins are designed to withstand the wind loads exerted on the dock and ship and also side thrusts from ships moored alongside the docks. These forces, depending on the size of dock, may be of the order of 50 ÷ 200 T. per dolphin.

At the early stages of their use, these underwater structures were designed with ample provision for a reduction of the thickness of the steel piles due to corrosion.

It has however been argued that the corrosive conditions of the water near the bottom of the sea or slightly below that, at the position where the maximum bending moment occurs, are considerably better than those at the sea surface where steel is periodically exposed to the alternate action of water





Pict. 34

In the area of coating which has been in contact with oil the softening point of the Hot Enamel has been decreased. Solar radiation has led to break up of the paint film and the coating flaked off.



Pict. 35

The Hot Enamel coating has been loosened in the area of the oil zone.

and air and the modern practice is to allow for a good painting scheme of the piles after surface preparation with sand blasting without allowance for corrosion.

The area exposed to the alternate action of water and air is receiving a highly sophisticated treatment through special paints, bituminous paints, galvanising paints like «Amercoat» etc. or at the best a protective sleeve of stainless steel welded around the tubular structure.

Similar piles driven about seven years ago and having received a simple bituminous composition treatment indicate an extensive fouling below water line.

In the exposed area the paint has deteriorated and ultra-sonic tests have indicated (sketch No. 6A, 6B) that the thickness of the piles due to corrosion has been diminished by  $0.4 \div 1.1$  mm within 8 years of service.

The influence of this reduction in thickness in the strength of the pile should be considered in conjunction with the structural function of the pile. In the case of the dock mooring dolphins which do not carry vertical loads but are only subject to bending with the highly stressed area at the fixation point near the bottom of the sea, the influence of this reduction in way of the sea surface, an area normally very lightly stressed, is very limited and one is really entitled to disregard it in the design.

If however the pile is required to support a concrete structure quaywall or pier i.e. to carry primarily vertical loads, than the reduction of thickness in any part of the length is equally important and should be carefully considered during the initial calculation. Sketch No. 7 indicates the results of thickness measurements on steel piles supporting a pier. The pier has been constructed eight years ago and the reduction of thickness over these years is of the order of  $0.6 \div 1.2$  mm.

The small difference in the thickness reduction at the upper and lower level is due to the fact that all the pile area is very close to the water surface and subject practically to the same conditions. If one takes into consideration that in most cases replacement of the corroded pipes is not possible nor are they any other improvements possible, one can readily access the significance of corrosion control in these structures.

#### 11. Other underwater structures - Dock Gates etc.

What has been said above for the dolphins piles, etc. is also valid for dock gates. Dock gates are large structures, flat, completely removable or hinging at the lower side, which close up watertightly the entrance of building berths or graving docks. Although theoretically these structures could be lifted off the sea for maintenance purposes, experience has shown that the lifting of the gate is very seldomly done, if ever, during its life time and therefore sandblasting and painting scheme are extremely important.

Dock inlet valves and gratings differ from other shipyard underwater structures in that they are subject to the action of the sea water flow.

The speed of corrosion is greatly increased and to our experience all gratings of docks have been replaced at least once in their life due to excessive wear irrespective of the treatment received prior to the installation.

The only remedy in this case is to provide originally a structure with ample margin for corrosion combined with some special corrosion resistant material such as Spheroidal cast iron.

#### 12. CONCLUSIONS

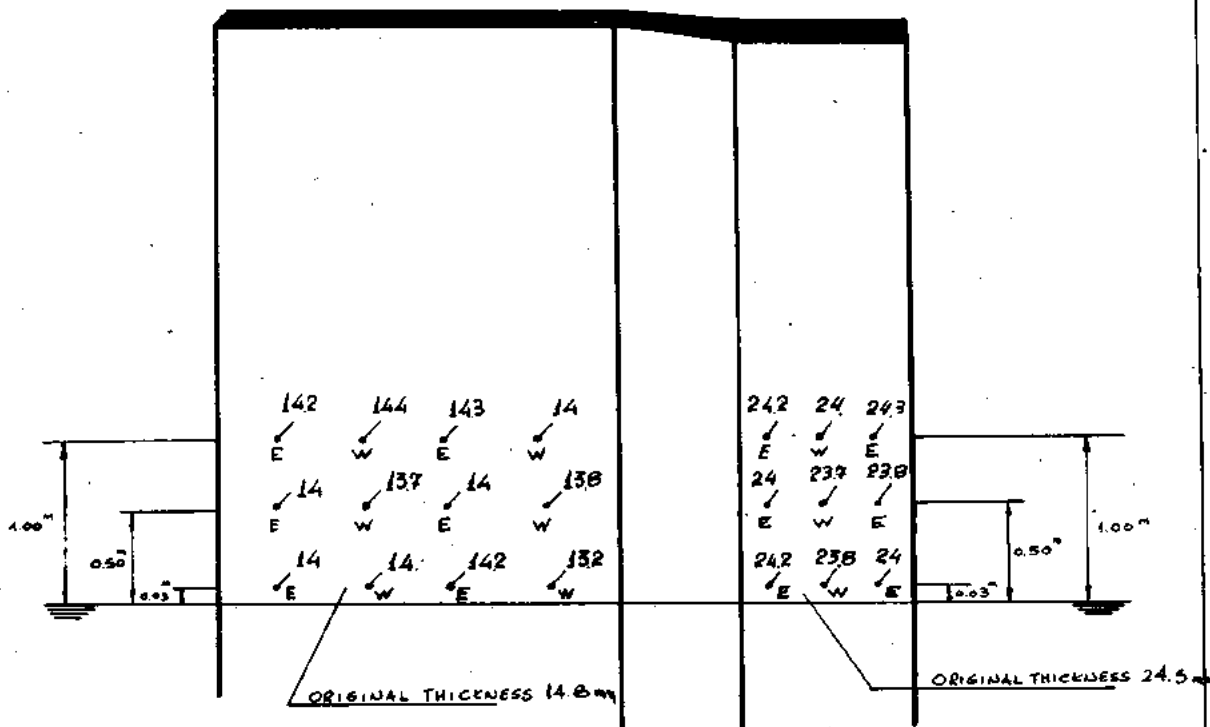
The general conclusions drawn from the above are the following:

a) In floating docks the internal members are the most suffering from corrosion due to the highly corrosive conditions prevailing inside the tanks.

b) Horizontal internal members are more heavily rusted than vertical ones. This should be expected as the sea water remains on these members longer, forming pools where corrosion in the presence of air continues for longer periods.

c) Corrosion of members sandblasted and painted properly with bituminous coatings or other efficient protectives is practically negligible over long periods of time.

d) Bituminous coatings if properly selected and applied offer an excellent protection even under the high temperature conditions encountered in warm areas whilst at the same time the access of the painted areas for maintenance of equipment inside the tanks is very easy as the bitumen is hard and does not stick. Other non drying type of coatings offer also excellent protection but dock crews indicate a reluctance to get into these spaces as the paint is always soft and sticky. Bituminous coatings for the outside underwater areas should be preferably of the two component plastic compound type



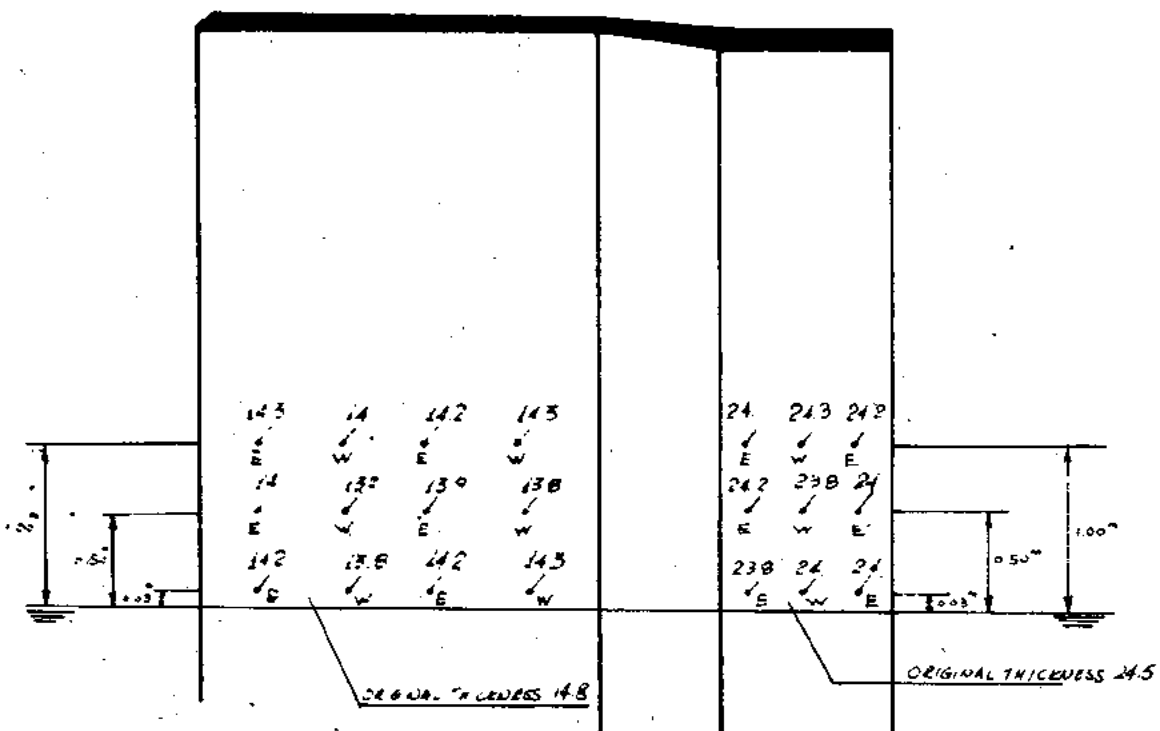
W = WEST SIDE  
 E = EAST SIDE

SKETCH N° 6 A

NOT TO SCALE

DOLPHIN DOCK 'X' (FORE END)

REDUCTION IN THICKNESS AFTER 6 YEARS



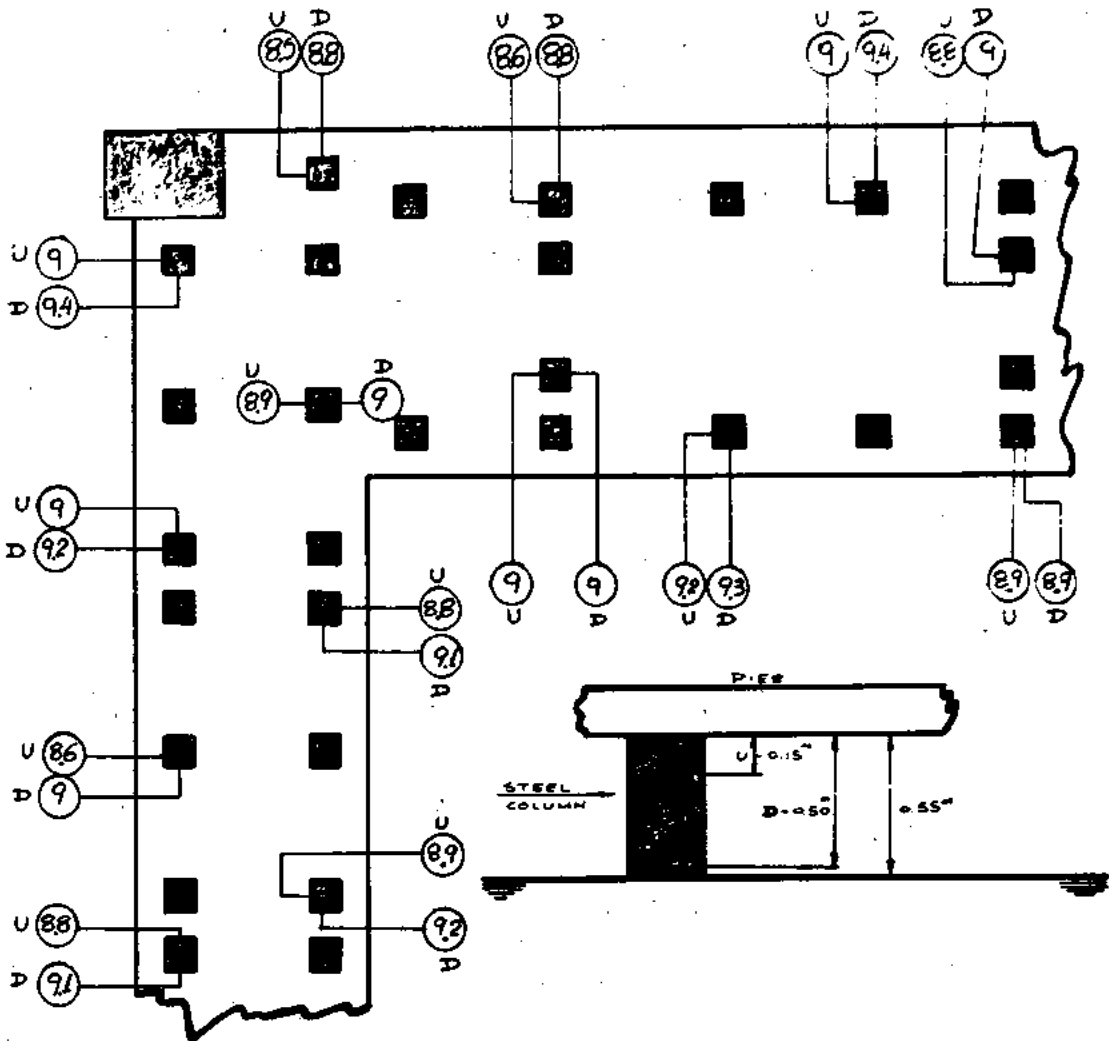
W = WEST SIDE  
 E = EAST SIDE

SKETCH N° 6 B

NOT TO SCALE

DOLPHIN DOCK X° (AFTER END)

REDUCTION IN THICKNESS AFTER 6 YEARS



NOTES

- O: MEASURED THICKNESS
- U: UPPER END
- D: LOWER END
- : STEEL COLUMNS KP24

ORIGINAL THICKNESS 10%

SKETCH N° 7

NOT TO SCALE

PIER STEEL COLUMNS

REDUCTION IN THICKNESS AFTER 6 YEARS OF SERVICE

with coal tar pitch and epoxy resins which due to their hardness can not be damaged by settlements of seashells or barnacles and are more resistant to oily water and mechanical stress.

e) Experience shows that the repair of the protective coatings inside a dock whilst the dock is in operation is practically not feasible as the humidity inside the tank is so high that no paint can be applied on the steel surface. The only possibility to repair a coating is to dry out the tank and the surface by compressed air or flame but this is not as easy as it may appear and therefore the proper treatment of steel surface during construction is absolutely essential.

f) The extent of corrosion in properly treated areas can be termed as light to medium with an average reduction in plate thickness of the order of  $0.056 \div 0.100$  mm per year. The

corrosion in areas covered only with bituminous solution not followed by bituminous enamel is heavy ranging from  $0.10 \div 0.16$  mm per year for the vertical internal members and a great deal more for the horizontal.

g) Dolphins and steel piles supporting piers are mostly suffering from corrosion in the near water level area. The resulting reduction in thickness is more serious in the case the piles are subject to compression.

h) Dock gratings, dock inlet valves and other underwater shipyard structures indicate corrosion the extent of which depends primarily on the water velocity through them.

i) Due to the continuous operation of the structures under water and the difficulties encountered in renewing the protective coatings, shipyard structures must receive the best possible treatment.

#### APPENDIX I

Tank No. Port	Outside Temperature	Hygrometer Reading		Relative Humidity %	Tank No. Stbd.	Hygrometer Reading		Relative Humidity %
		Dry Bulb	Wett bulb			Dry Bulb	Wett Bulb	
No.1	20.6°C	25 ½°C	22 ½°C	80	No.1	21 ½°C	20 ½°C	92
No.3	12.2°C	12 ½°C	12	94	No.3	12 ½°C	12°C	94
No.2	15.0°C	16°C	14	82	No.2	15 ½	14	86
No.3	11.1°C	13	12 ½	94	No.3	12	11 ½	94
No.5	10.6°C	13 ½	12	85	No.5	13	12 ½	94
No.4	15.6°C	16 ½	15	86	No.4	16	15	90
No.3	13.3°C	15	13 ½	86	No.3	15	14	90
No.6	13.3°C	14 ½	13	86	No.6	15	13 ½	86
No.4	17.2°C	21	20	90	No.4	20	19	92
No.1	18.9°C	27 ½	26	90	No.1	25	24	94
No.3	21.1°C	28	27	93	No.3	27 ½	26	90
No.5	11.1°C	12 ½	12	94	No.5	13	12 ½	94
No.4	18.3°C	17	15	82	No.4	16	15	90
No.1	22.2°C	24 ½	33 ½	94	No.1	33	29	77
No.5	21.1°C	23	22 ½	96	No.5	23	20 ½	80
No.1	21.7°C	29 ½	25 ½	75	No.1	26	23	80
No.3	25.6°C	29	27 ½	90	No.3	27	25	86
No.2	21.1°C	29 ½	28	90	28	25	25	80
No.3	22.2°C	25	24 ½	96	No.3	25 ½	24	82
No.4	15.6°C	20	19	92	No.4	20 ½	21	95
No.6	15.6°C	20 ½	19 ½	92	No.6	20	19	92
No.5	18.3°C	22	21	92	No.5	23	21 ½	88
No.3	14.4°C	20	19	92	No.3	19	18	92
No.5	15.6°C	18	16.5	87	No.5	18 ½	17 ½	90
No.2	14.4°C	15°C	14 ½	95	No.2	14	13 ½	96
No.4	15.6°C	18	17	90	No.4	19	17	82
No.6	16.7°C	23	22	92	No.6	21	20 ½	95
No.3	22.2°C	25	24	92	No.3	26	25	92
No.2	21.1°C	28	25	90	No.2	26	24	86
No.1	21.1°C	27	25	86	No.1	26	23	80
No.4	23.9°C	32	28	76	No.4	31	28	80
No.3	22.2°C	30	28	87	No.3	30	27	90
No.6	22.2°C	29	26	80	No.6	28	25	80
No.1	25.6°C	31	27 ½	78	No.1	31 ½	26 ½	70
No.4	26.1°C	32	28	76	No.4	32	28	76
No.5	24.4°C	31	29	87	No.5	32	29	82
No.2	25.6°C	32	30	87	No.2	31	28	82
No.3	24.4°C	30	28	87	No.3	30	27	80
No.4	24.4°C	31	29	87	No.4	31	28	82
No.6	25.0°C	28	26	86	No.6	29	26	80
No.1	25.6°C	27	26	94	No.1	26	24.5	90
No.2	25.6°C	25	24	93	No.2	26	24	86
No.3	25.6°C	29	27	87	No.3	27	26	92
No.1	23.3°C	26	25	93	No.1	25	24	93

## DISCUSSION

Dr. KENWORTHY (England): Mr. Chairman, I am wondering whether cathodic protection would not have overcome the corrosion of floating docks, and also whether the fouling problem could not have been reduced by the use of a good antifouling paint.

Dr. ANTONIOU: Unfortunately the case is not as simple as that, the floating docks, remain under water for a period of as much as twenty years. In this period of twenty years, I do not think that any paint Manufacturer could maintain that an antifouling paint would stand and this is the reason why antifouling paints have not been used on the floating docks.

As a matter of fact it has been tried to use antifouling paints on floating docks. But their effect after one or two years has been continuously diminishing. It is almost sure for this long period of twenty years, that we expect the dock to last, these antifouling paints would not have been effective. As far as the second part of the question whether we could apply current to preserve the docks, theoretically it is possible, but practically it is not.

The reason is this: along the floating docks, we have always ships under repair, these ships are having various protective coatings, and the potential differences which exist on the hull of a ship even within a period of a day, vary to such extent that no system of impressed current could cope up with the changes in the potential between the various ships.

We carry out welding on the ships, other ships are under repairs, some others are under outfitting and needless to say not all the ships are properly earthed.

The differences which have been noticed in the electrochemical potential on the ships even if we are not welding on them, ranges from something like - 350 millivolts to - 1800 millivolts and some time they go to the plus sign, when some of the ships become anodic and some become cathodic.

So no system could be applied which could take into consideration these variations. If we did apply a system like this, it is very probable that we would destroy the paints of the nearby ships and this would be disastrous for the shipyard.

E. ARTEMIS (Greece): Can it be made clear if oxides paints, called anticorrosive, have any way in providing an anticorrosive effect by keeping the water under the paint film?

Dr. ANTONIOU: The normal paints we know, are protecting the steel from coming in contact with the water and when the water comes into contact with the steel surface it means that already has passed under the paint film. In this case the life of the paint is not very long. Within a short time from the time water will penetrate under the paint film the paint will blister off and the area will be exposed. Whether a paint could be developed such that the water entering under the film could be maintained there without blistering the paint film is a question that we could not answer.

# PEINTURES POUR LA PROTECTION ANTICORROSION DE COQUES DE NAVIRES RESULTATS DES ESSAIS EN RADEAU EFFECTUES EN ARGENTINE

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La Plata, ARGENTINA

## RÉSUMÉ

On a étudié les caractéristiques des peintures anticorrosion pour la protection des carènes de navires. Les dites peintures ont été préparées en employant des pigments de plomb (sulfate basique, carbonate basique et minium de plomb), de zinc (chromate basique, tetroxychromate et oxyde de zinc) et de la poudre d'aluminium. Comparativement on a essayé des formules du BISRA (sulfate basique de plomb-aluminium-oxyde de fer rouge) et américaines (MIL Spécifications). On utilise des liants avec des vernis de résines formophénoliques pures ou modifiées, caoutchoucs chlorés, esters de résines époxydes, et des résines vinyliques. Toutes les peintures ont été broyées au laboratoire.

Les essais en radeau pendant six mois comportent des systèmes pour ligne de flottaison (plaques en immersion partielle) et pour carène (immersion totale). On utilise des peintures de finition, et dans le cas des systèmes de carène la peinture employée a des propriétés antisalissures.

Tenant compte spécialement le point de vue anticorrosion, les résultats obtenus nous indiquent le meilleur pouvoir protecteur des peintures aux chromates. Les formules à base de sulfate basique de plomb-aluminium (BISRA) ont aussi un bon comportement anticorrosion.

Le liant semble ne pas avoir un rôle si important que le pigment, mais il doit être choisi parmi des matériaux ayant une bonne résistance électrochimique à l'eau de mer. De ce point de vue les résines vinyliques semblent avoir les meilleures caractéristiques de protection.

On fait quelques considérations sur l'importance de l'utilisation du wash-primer vinylique comme prétraitement pour les systèmes classiques, et sur le degré de passivation qui proportionne.

Les essais continuent pour établir le comportement des peintures dans un délai d'un an.

Tenant compte de l'état actuel de notre connaissance sur la nature des phénomènes de corrosion de l'acier dans l'eau de mer (milieu marin) et aussi des principaux travaux publiés en rapport avec les caractéristiques des peintures anticorrosion pour la protection des coques de navires (1 à 9) et sur la base de notre expérience personnelle à ce sujet (10), on a préparé un plan de recherches comprenant les points suivants :

### I) *Etudes programmées pour 1966/67, en exécution:*

- Influence des prétraitements type «wash-primers» vinyliques sur le comportement des systèmes classiques.
- Influence des caractéristiques physiques et chimiques des pigments (de plomb et de zinc) et des liants (à base de résines formophénoliques pures ou modifiées, caoutchoucs chlorés, esters de résines époxydes avec des acides gras d'huiles siccatives, résines vinyliques, etc.).

Cette partie se complète avec l'étude des conditions biologiques et hydrologiques du port de Mar del Plata (11), ou on a placé le radeau d'essais, à 150 m de la côte.

### II) *Etudes prévues pour 1967/68:*

- Etude de l'influence des caractéristiques chimiques et métallographiques de l'acier.
- Influence de l'état des surfaces à protéger.
- Influence des méthodes de préparation de l'acier, chimiques et physiques (décapage, sablage, etc.).

d) Influence de l'action des soudures ou des boulons.

e) Influence de l'épaisseur du film.

f) Compatibilité des systèmes de peinture avec la protection cathodique.

On espère obtenir dans un délai de deux ans une connaissance précise sur la possibilité de formulation de peintures sous-marines, avec les matières premières qui sont d'utilisation normale dans l'industrie de notre pays. En plus, on espère compléter aussi une troisième étape, avec des essais sur la coque de navires, les seuls valables, à notre avis, pour en obtenir des conclusions définitives sur ce sujet. Il n'est pas nécessaire de remarquer que pendant la marche du bateau, il se produit sur la carène un régime hydrodynamique (laminaire ou tourbillonnant) qui peut faire varier le comportement du système (1). En plus, il faut considérer les autres conditions qui existent sur les carènes (vibrations, tensions, frottements, etc.), et qui n'existent pas sur les plaques dans l'essai en radeau.

## RADEAU D'ESSAIS

Pour l'exécution de nos expériences, on a fait construire un radeau entièrement en acier. Toutes les surfaces métalliques ont été sablées et protégées par l'application d'une couche de «wash-primer» vinylique et par une peinture «coal-tar epoxy» (250 microns d'épaisseur). Avant sa mise en service, on a appliqué deux couches de peinture antisalissure.

Ce radeau est une structure de 5 sur 4 mètres, avec deux flotteurs (fig. 1, 2, 3), qui ont été remplis avec des blocs de

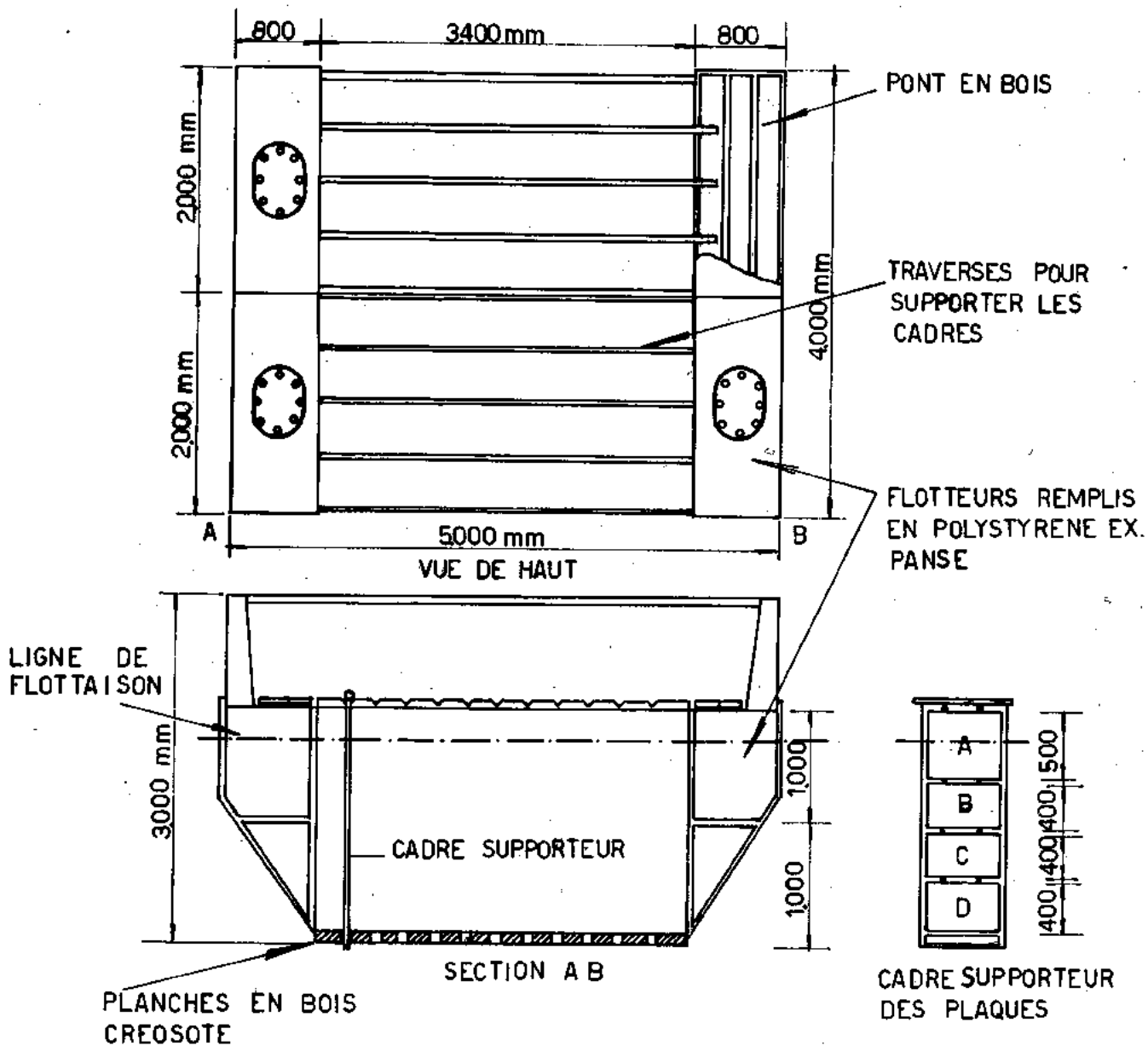


FIG. 1- SCHEMA DU RADEAU D'ESSAI

polystyrène expansé (du type utilisé dans le radeau du CREO à La Rochelle). Ces flotteurs sont soutenus par des traverses, supérieures et inférieures. Ces traverses permettent de fixer les cadres supportant les plaques. La partie inférieure est renforcée par des planches en bois créosoté, ayant des espaces pour l'emplacement des cadres. Un pont, construit aussi en bois, nous permet le déplacement sans problèmes pendant les observations.

On a 88 cadres porte-épreuves, en acier, qui permettent de placer, chacun, 4 plaques: la supérieure (50 × 30 cm, 1,6 mm épaisseur, en acier doux, immergée partiellement),

qui permet l'essai des systèmes pour ligne de flottaison; les autres trois (40 × 30 cm), en immersion totale, à profondeurs variables entre 0,35 et 2 m, sont pour les systèmes de carène. On a au total 352 plaques, dont 88 à demi-immersion. On peut étudier dans chaque cadre une peinture anticorrosion sur quatre plaques; les trois de carène sont protégées aussi par une peinture antisalissure qui nous assurerait l'empêchement de la fixation des organismes marins pendant toute la période de l'essai (1 an). De cette façon on considère seulement l'action de l'électrolyte, c'est-à-dire de l'eau de mer, sur les peintures anticorrosion et sur l'acier.



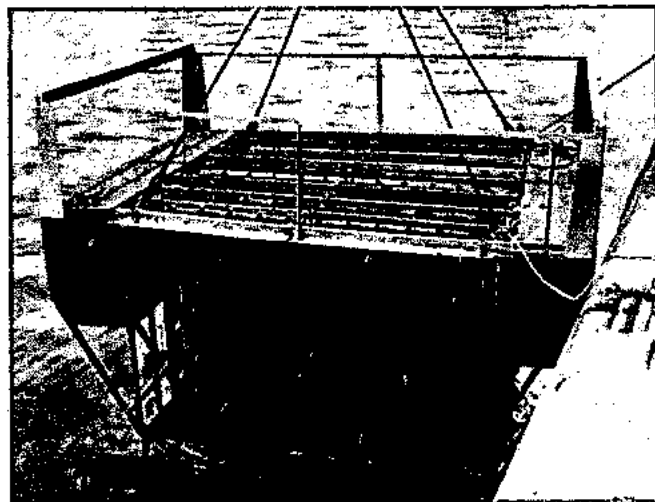
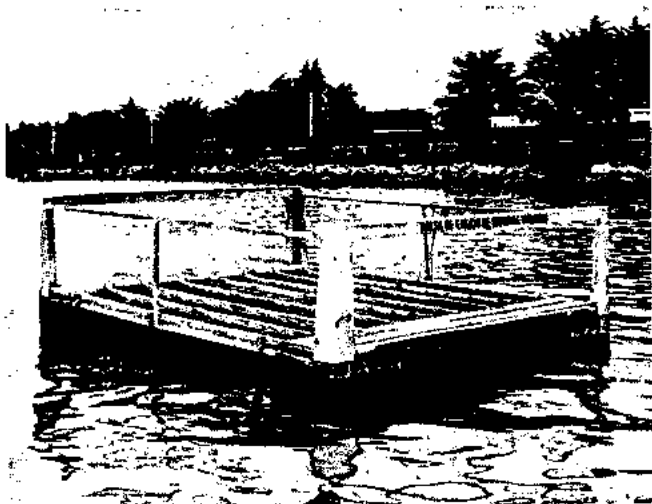


Fig. 2 et 3. Photos du radeau d'essais prises pendant sa mise en service dans le port de Mar del Plata.

## PEINTURES ÉTUDIÉES. PROCÉDÉS D'APPLICATION SUR LES PLAQUES

Notre programme actuel comporte une première série d'essais (durée d'environ 4 mois) dans le radeau; et une deuxième partie, déjà commencée, restreinte celle-ci aux matériaux qui ont donné le meilleur comportement, et dont on présente les résultats des premiers six mois d'immersion. A l'époque du Congrès on en pourra faire une communication plus complète, tenant compte que la fin de l'essai est prévue pour septembre 1967.

### PIGMENTS

On a employé dans les formules des peintures anticorrosion des pigments de plomb et de zinc, et aussi de la poudre d'aluminium (type «no leafings»).

Notre première série d'expériences a été programmée sur la base des différents mélanges indiqués dans le tableau I, colonne de gauche. La peinture identifiée avec le N° 1, pour chaque liant, correspond à la peinture de couche de surface (ligne de flottaison) sans pigments inhibiteurs; les N° 2 à 9 sont des formules à base de sels basiques ou oxydes de plomb, en rapport avec les nombreuses expériences réalisées par les chercheurs anglais du BISRA (2, 3, 4, 5, 9) tandis que les N° 11, 12 et 14 sont d'accord avec les tendances actuelles aux États-Unis (12, 13) et en Argentine (Norma IRAM 1110) (15).

Dans la deuxième série, on s'est borné aux trois compositions anticorrosion indiquées à droite dans le tableau I, (N° 5, 11, 12).

Pour le cas particulier des peintures vinyliques (tableau III), les formules anticorrosion ont été préparées en utilisant le minium de plomb, le tetroxychromate de zinc et la poudre d'aluminium (type «haut leafings»). Les peintures pour les couches de finition et les antisalissures figurent dans le même tableau.

### Liants (milieux de suspension)

En rapport avec les liants, le tableau II nous indique ceux qui ont été utilisés dans les deux séries d'expériences. Ils furent préparés dans le laboratoire avec les huiles siccatives et les résines suivantes :

Huile de lin raffinée  
Huile de lin polymérisée (standolie 60 poise)

Huile de ricin deshydratée et polymérisée (30 poise)  
Huile de Bois de Chine  
Résines formophénoliques pures ou modifiées  
Caoutchoucs chlorés (Parlon 20 et 50 cP)  
Résine vinylique VAGH et VYHH, Union Carbide (tableau III)

et dans la deuxième série, en plus, des esters des résines époxydes (Epikote 1001 et 1004) avec des acides gras de l'huile de lin.

Dans tous les cas la préparation a été faite au laboratoire, par chauffage des huiles à la température nécessaire pour obtenir la solubilisation de la résine (environ 200-220°C pour les huiles de lin et de ricin, et 180°C pour l'huile de Bois de Chine), en agitant et avec un courant de CO<sub>2</sub>; après on a augmenté la température jusqu'à 240-250°C, pour polymériser; on a refroidi et on y a ajouté les diluents.

La dispersion des pigments dans les liants et les solvants est faite au moyen d'une broyeuse à boulets, pendant 24 heures dans tous les cas.

Les rapports pigment/liant utilisées sont les indiqués au pied du tableau I.

Il faut citer très spécialement les formules du BISRA que nous avons essayées (5):

BISRA 622 A - 3	I - 3	BISRA 658D	- 6	IV - 6
BISRA 652 B - 6	I - 6	BISRA 177N I	- 5	
BISRA 656 C - 6	III - 6	BISRA 189N I	- 6	

### PRÉPARATION DES PLAQUES

Elle a été faite à la brosse, sur des plaques d'acier doux, sablées (toutes de la même origine) sous les conditions de température et d'humidité normales de la saison (printemps).

Les conditions d'application fixées par les normes argentines sont les suivantes :

a) Norme IRAM 1110 (14) pour les peintures conventionnelles, avec des systèmes à 3 couches (2 anticorrosion et une couche de surface — plaques à immersion partielle — ou 2 anticorrosion et 1 antisalissure — plaques de carène à immersion totale —); temps de séchage 18 à 24 heures pour tous les cas. Celui-ci, c'est le système appliqué sur le recto des éprouvettes. Sur le verso on a fait, sur l'acier sablé, un pré-traitement au «wash-primer» vinylique avant peinture.

La peinture antisalissure utilisée pour les systèmes conventionnels est identifiée AF-100 (16) dans notre communica-

**TABLEAU I**  
Composition des pigments

1ere. série d'essais		2eme. série d'essais		
1	Oxyde de fer rouge Baryte	4 p 1 p	1 Oxyde de fer rouge Baryte	2 p 1 p
2	Sulfate basique plomb Minium de plomb	2 p 1 p		
3	Sulfate basique plomb Aluminium (poudre)	2 p 1 p		
4	Sulfate basique plomb Minium de plomb Aluminium (poudre)	1 p 1 p 1 p		
5	Sulfate basique plomb Minium de plomb Oxyde de fer rouge Baryte	2 p 1 p 1 p 1 p	5 Sulfate basique plomb Minium de plomb Oxyde de fer rouge	2 p 1 p 2 p
6	Sulfate basique plomb Aluminium (poudre) Oxyde de fer rouge Baryte	2 p 1 p 1 p 1 p		
7	Sulfate basique plomb Minium de plomb Aluminium (poudre) Oxyde de fer rouge Baryte	2 p 1 p 1 p 1 p 1 p		
9	Sulfate basique plomb Carbonate basique Pb Aluminium (poudre) Baryte	3 p 1 p 1 p 3 p		
11	Chromate basique de zinc Oxyde de zinc Oxyde de fer rouge Baryte	3 p 1 p 3 p 3 p	11 Chromate basique de zinc Oxyde de zinc Oxyde de fer rouge Baryte	2 p 0,5 p 2 p 1 p
12	Tetroxychromate de zinc Oxyde de zinc Oxyde de fer rouge Baryte	3 p 1 p 3 p 3 p	12 Tetroxychromate de zinc Oxyde de zinc Oxyde de fer rouge Baryte	2 p 0,5 p 2 p 1 p
14	Chromate basique de zinc Oxyde de zinc Minium de plomb Oxyde de fer rouge Baryte	1 p 1 p 1 p 2 p 1 p		

Nota. Les peintures pour les couches de surface ont été formulées avec un minimum de 35% de pigment; celles anticorrosion avec 50% environ. Les rapports pigment/liant (en poids) sont 1/1 pour le premier cas; et entre 1/0,35 à 1/0,55 pour la plupart des peintures anticorrosion.

tion sur ce sujet présentée au Congrès. Elle est pigmentée avec  $Cu_2O$ ,  $HgO$  et  $AsO_2.Hg_2$  comme substances toxiques.

b) Pour les peintures vinyliques d'accord avec la Norme IRAM 1145 (15):

Recto	Verso
1 couche «wash-primer»	1 couche «wash-primer»
2 couches de fond anti-corrosion	3 couches de fond anti-corrosion
2 couches de surface	3 couches de surface

La peinture antisalissure vinylique pour les plaques de carène est à base d'oxyde cuivreux.

Le contrôle de l'épaisseur avec un appareil électromagnétique nous a permis d'arriver à la fin de la préparation des plaques avec les épaisseurs moyennes indiquées ci-dessous en microns :

**TABEAU II**  
**COMPOSITION DES MILIEUX DE-SUSPENSION (LIANTS)**

1ere. série d'essais			2eme. série d'essais		
Identif.	Matières solides	Solvants et diluants	Identif.	Matières solides	Solvants et diluants
A	Vernis de résine formophénolique modifiée <sup>1</sup> Standolie de lin 60 Poise (50% résine)	White spirit toluène	I	Vernis de résine formophénolique modifiée <sup>1</sup> Standolie de lin 60 Poise (50% résine)	White spirit toluène
B	Vernis de résine formophénolique modifiée <sup>1</sup> Standolie de lin 60 Poise et ricin deshydratée 30 Poise (50% résine, rapport des huiles 2:1)	White spirit toluène	II	Vernis de résine formophénolique modifiée <sup>1</sup> Standolie de lin 60 Poise - Huile ricin deshydratée 30 Poise (50% résine, rapport des huiles 2:1)	White spirit toluène
C	Vernis de résine formophénolique modifiée <sup>1</sup> Standolie de lin 60 Poise - Huile bois de Chine (50% résine, rapport des huiles 1:1)	White spirit toluène	IV	Vernis de résine formophénolique modifiée <sup>1</sup> Standolie lin 60 Poise - Huile Bois de Chine (50% résine, rapport des huiles 1:1)	White spirit toluène
D	Vernis de résine formophénolique modifiée <sup>1</sup> Standolie lin 60 Poise - Huile Bois de Chine (50% résine, rapport des huiles 2:1)	White spirit toluène	III	Vernis de résine formophénolique modifiée <sup>1</sup> Standolie lin 60 Poise - Huile Bois de Chine (50% résine, rapport des huiles 2:1)	White spirit toluène
E	Vernis de résine formophénolique modifiée <sup>2</sup> Huile Bois de Chine (33% de résine)	White spirit toluène	V	Vernis de résine formophénolique pure <sup>3</sup> - Huile de lin raffinée (50% résine)	White spirit toluène
			VI	Vernis de résine formophénolique pure <sup>3</sup> - Standolie lin 60 Poise (40% résine)	White spirit toluène
			VII	Vernis de résine formophénolique pure <sup>3</sup> - Huile de lin raffinée - Huile Bois de Chine (33% résine, rapport des huiles 1:1)	White spirit toluène
			VIII	Vernis de résine formophénolique pure <sup>3</sup> - Huile de lin raffinée Huile Bois de Chine (33% résine, rapport des huiles 1:1)	White spirit toluène
F	Vernis de résine formophénolique pure <sup>4</sup> - Huile Bois de Chine (40% résine)	White spirit toluène	IX	Vernis de résine formophénolique pure <sup>4</sup> - Huile Bois de Chine (50% résine)	White spirit toluène
G	Vernis F-Caoutchouc chloré (20 cp) <sup>4</sup> (3:1), plastifiant paraffine chlorée	Toluène	X	Vernis IX-Caoutchouc chloré 20 cP (3:1), plastifiant diphenyle chloré	Toluène
H	Vernis F-Caoutchouc chloré 20 cP (2:1) - Plastifiant paraffine chlorée	Toluène	XI	Vernis IX-Caoutchouc chloré 20 cP (2:1) plastifiant diphenyle chloré	Toluène Xylène Ac. amyle
J	Caoutchouc chloré 20 cP, plastifiant paraffine chlorée (2:1)	Xylène Ac. amyle	XII	Vernis IX-Caoutchouc chloré 20 cP (1:1)	Toluène Xylène
K	Caoutchouc chloré 20 cP, plastifiant diphenyle chloré (2:1)	Xylène Ac. amyle	XIII	Caoutchouc chloré 20 cP, plastifiant diphenyle chloré (3:1)	Xylène Ac. amyle
I	Caoutchouc chloré 50 cP, plastifiant paraffine chlorée (1:1)	Xylène Ac. amyle	XIV	Ester de résine epoxyde 1001 <sup>5</sup> avec 30% acides gras d'huile de lin	White spirit Toluène MEK
			XV	Ester de résine epoxyde 1004 <sup>5</sup> avec 30% acides gras d'huile de lin	White spirit Toluène Acet. oxitol

Noté: Dénomination commerciale des résines utilisées:

- (1) Superbeckacite 1100 (210 C)
- (2) Superbeckacite 1123
- (3) Superbeckacite 1001 (5209)
- (4) Parton et Pergut
- (5) Epikote 1001
- (6) Epikote 1004

Siccatis Naphthenates de Pb, Co, Mn.

**TABEAU III**  
**COMPOSITION DES SYSTHÈMES À BASE DE RÉSINES VINyliQUES**

Type de peinture	Pigment	Liant (solides)	Solvants
Ligne de flottaison (couche de surface)	Noir fumée Asbestine 3X	Résine VYHH (1) Phosphate de tricrésile	MIBK Toluène
	Oxyde de fer	Résine VYHH Phosphate tricrésile	MIBK Xylène Cyclohexanone
	Aluminium haut «leafing»	Résine VYHH Phosphate tricrésile	MIBK Toluène
Anticorrosion	Minium 97 %	Résine VAGH (2) Phosphate tricrésile	MIBK Toluène
	Aluminium haut «leafing»	Résine VAGH Phosphate tricrésile	MIBK Toluène
	Tetroxychromate de zinc Asbestine 3X	Résine VAGH Phosphate tricrésile	MIBK Toluène
Antisalissure ou antifouling	Oxyde de cuivre (Cu <sub>2</sub> O)	Résine VYHH Rosin (colophane) Phosphate tricrésile	MIBK Toluène
	Oxyde de cuivre (Cu <sub>2</sub> O)	Résine VAGH Rosin (colophane) Phosphate tricrésile	MIBK Toluène
Wash-primer	A Tetroxychromate de zinc Noir fumée Asbestine 3X	Résine Mowital B-60-H(3), contratype XYHL (4)	Isopropanol 99% Butanol
	B		Acide phosphorique 85% Isopropanol 99% Eau

- Notas. (1) Résine VYHH Union Carbide, 87% chlorure de vinyle et 13% acetate de vinyle.  
 (2) Résine VAGH Union Carbide, copolymère chlorure - acetate de vinyle, avec un contenu de chlorure légèrement supérieur à celui de la résine VYHH.  
 (3) Résine Mowital B-60-H, Farbwerke Hoechst A.G., Germany, à 76-78% polyacetal de vinyle, 1% de polyacetate de vinyle et 18-21% de alcool polyvinylique.  
 (4) Résine de polyvinyl butiral de la Union Carbide (USA).

	Peintures conventionnelles	Peintures vinyliques
Peinture anti-corrosion	100 (2 couches)	60 (3 couches)
Peinture de surface (ligne)	35 (1 couche)	40 (2-3 couches)
Total	135 (3 couches)	100 (5-6 couches)
Peinture anti-corrosion	100-110 (2 couches)	50 (3 couches)
Peinture anti-salissure	35 (1 couche)	60 (2-3 couches)
Total	135-145 (3 couches)	110 (5 couches)

#### CONSIDÉRATIONS SUR LES RÉSULTATS

a) Première série d'essais (préliminaire) :

D'accord avec la Norme IRAM 1185 (17), il faut tenir

compte des différentes conditions du film pour qualifier les peintures sous-marines anticorrosion après l'essai en radeau: formation d'ampoules, craquelage, écaillage ou décollement, et on doit établir aussi l'état d'oxydation ou de corrosion de la plaque. Maintenant, en considérant que cet essai préliminaire avait été programmé seulement dans le but d'écartier rapidement les peintures n'ayant ni résistance électrochimique à l'eau de mer ni pouvoir inhibiteur approprié, on a considéré seulement le point de vue anticorrosion.

Un jugement exact des résultats est évidemment difficile, vue l'impossibilité de les exprimer au moyen d'un chiffre. En conséquence on a appliqué le même criterium établi dans le British Standards Code of Practice (CP 2008 : 1966), c'est-à-dire on a fait un classement basé sur des photos témoin, qui ont été choisies parmi les mêmes plaques examinées. De cette façon on établit cinq types de protection, correspondant à :

- Type I (fig. 4): Plaque sans oxydation dans les bords ou dans le centre. Les peintures de ce type accomplissent la Norme IRAM.
- Type II (fig. 5): Plaque avec un peu d'oxydation dans les bords, sans progrès vers le centre; pour celles présentant de l'oxydation dans la partie centrale, le maximum accepté est de cinq petits points de 2 mm de diamètre. Ces peintures accomplissent aussi la Norme IRAM.
- Type III (fig. 6): Plaque avec oxydation moyenne; oxydation dans les bords, avec progrès, et dans le centre.
- Type IV (fig. 7): Trop d'oxydation dans les bords et dans le centre.
- Type V (fig. 8): Attaque général de la plaque.

On ne considère pas dans ce jugement la zone autour des boulons et un centimètre dans tout le rebord des plaques (marqué sur les fig. 4 et 5).

Le but d'élucider entre la *convoenance d'utiliser des pigments de plomb ou de zinc a été accompli*: comme peintures du type I (maximum de protection), on a trouvé quatre échantillons, pigmentés au chromate basique de zinc-oxyde de zinc (C-11, D-11, F-11, H-11), trois utilisant le tetroxychromate de zinc (C-12, D-12, F-12), deux au minimum-sulphate basique de plomb (G-5, H-5) et les trois peintures vinyliques. Dans le type II, avec une légère oxydation, on a quatre peintures (E-6, F-5, G-14, J-12).

Les plaques correspondantes aux formules du BISRA, dans cet essai préliminaire, ont été perdues au cours d'un orage.

Dans le cas des peintures avec les liants J, K, I, caoutchouc

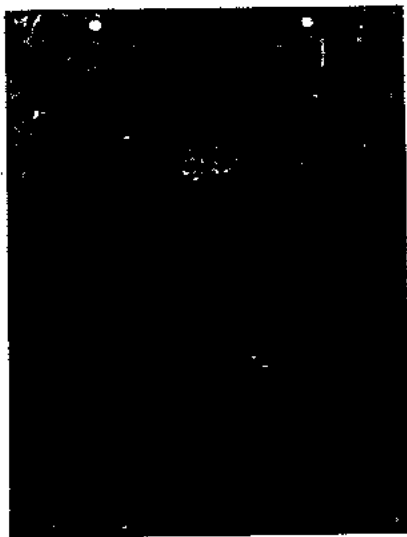


Fig. 4. Type I: Plaque sans oxydation dans les bords ou dans le centre.



Fig. 6. Type III: Plaque avec oxydation moyenne.

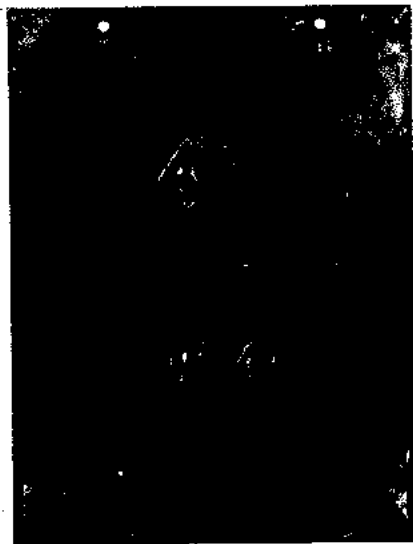


Fig. 5. Type II: Plaques avec peu d'oxydation dans les bords ou dans le centre.



Fig. 7. Type IV: Trop d'oxydation dans les bords ou dans le centre.

b) Deuxième série.

Comme on l'a déjà établi, elle a été restreinte aux compositions 11 et 12, (pigments de zinc), à la N° 5 (pigments de plomb) et aux formules du BISRA déjà indiquées.

Les résultats au bout de six mois dans le radeau à Mar del Plata (on juge seulement des plaques de carène), sont présentés dans le tableau IV. Cet essai nous confirme le meilleur pouvoir protecteur des peintures aux chromates de zinc (15 formules) sur les produits qui utilisent sulfate basique de plomb-minium de plomb. D'ailleurs on voit que les formules BISRA 652 (II-6), 656 (III-6) et 658 (IV-5), pigmentées au sulfate basique de plomb-poudre d'aluminium ont une bonne tenue face au milieu marin et aussi un bon comportement anticorrosion.

Le liant semble ne pas avoir un rôle si important que le pigment. On trouve dans les types I et II, des peintures contenant des liants aux résines formophénoliques pures ou modifiées (on utilise aussi des différents types d'huiles), un liant de résine formophénolique pure avec du caoutchouc chloré (X) et les deux liants à base de résines époxydes esterifiées avec des acides gras de l'huile de lin (XIV, XV) (18)II. Il faudra attendre les prochains six mois, c'est-à-dire le délai d'une année d'immersion, pour établir des conclusions définitives sur le comportement en service des peintures. On trouvera, peut-être, au bout de l'an, un nombre plus réduit de peintures appartenant à ces deux groupes.

Les plaques correspondant aux peintures XII et XIII ont été immergées, par erreur, sans la protection antisalissure. Elles ne sont pas considérées parce que la fixation très grande d'organismes a été le facteur le plus important de leur échec.

Le liant XIII, caoutchouc chloré plastifié, reproduit les résultats obtenus dans la première série: la dégradation considérable du film, par formation de grosses ampoules caractéristiques (peut-être dues au détachement de chlore).



Fig. 8. Type V : Attaque général de la plaque.

chloré plastifié, il est nécessaire de faire noter l'échec total des films essayés, attribué à l'excès de plastifiant.

En général, on trouve une supériorité des peintures aux chromates, raison par laquelle on a écarté la plupart des compositions à base de pigments de plomb dans la deuxième série.

TABLEAU IV

COMPORTEMENT DES PEINTURES ANTICORROSION DE CARÈNE AU BOUT DE SIX MOIS À MAR DEL PLATA (DEUXIÈME SÉRIE)

Type I	Type II	Type III	Type IV	Type V
Pas d'oxydation	Très peu d'oxydation sur les bords ou dans le centre	Oxydation moyenne	Beaucoup d'oxydation	Attaque général
III - 6 III - 11 IV - 6 IV - 11 VI - 11 IX - 12 V - 1 V - 2 V - 3	II - 6 II - 11 V - 11 VII - 11 VII - 12 VIII - 12 IX - 11 X - 11 XIV - 11 XIV - 12 XV - 11 XV - 12	I - 3 I - 11 V - 12 VI - 12 VIII - 5 VIII - 11 X - 12 XI - 11 (x)	I - 12 II - 5 II - 12 III - 12 IV - 5 IV - 12 V - 5 VI - 5 IX - 5 X - 5 XI - 5 (x) XI - 12 (x) XII - 5 (x) XII - 11 (x) XII - 12 (x) XIII - 11 XIII - 12 XIV - 5 XV - 5	I - 5 III - 5 VII - 5 XIII - 5

Note. Les plaques correspondant aux peintures marquées (x) ont été immergées sans protection antisalissure.

Les peintures vinyliques nous donnent de nouveau un excellent résultat: les trois compositions essayées protègent complètement contre la corrosion. Des expériences de laboratoire, spécialement le comportement envers le brouillard salin et l'exposition aux intempéries au bord de la mer, nous indiquent un meilleur pouvoir inhibiteur pour le tetroxychromate dans les zones détériorées mécaniquement. On fera référence à ce problème dans un autre travail, actuellement en exécution (19).

Il nous reste à faire une considération finale: l'examen du verso des plaques, dans lequel on a utilisé un prétraitement (wash-primer vinylique) pour toutes les peintures étudiées, nous montre l'importance décisive de cette application. Toutes les plaques, sauf celles correspondant au liant XIII, ont été protégées d'une manière totale (fig. 9). En conséquence on tire une conclusion très importante pour les applicateurs et pour les travaux à réaliser dans la cale sèche: la préparation de la surface à protéger est plus importante, peut-être, que la peinture qu'on utilise. En tout cas, on recommence de ne pas sous-estimer l'importance de cette étape.



Fig. 9. Verso de la plaque correspondant à la peinture 1-5 (avec prétraitement avec wash-primer vinylique). Le recto de cette plaque est présenté dans la fig. 8.

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E. ARTEMIS (Grèce): Je voudrais demander s'il y a une peinture qui peut protéger les métaux dans l'eau de mer.

Dr. RASCIO: Oui. Dans le cas de nos expériences une protection totale a été obtenue avec des peintures vinyliques à base de tetroxychromate de zinc. En plus, une bonne protection est obtenue avec des peintures oléoresineuses (verniss formophénolique avec caoutchouc chloré) ou avec des esters de résines époxydiques (Epikote 1001 avec des acides gras de l'huile de lin), pigmentées avec chromate basique de zinc, oxyde de zinc et oxyde de fer rouge.

E. ARTEMIS: Vous considérez que les peintures donnent une couche isolatrice, sur le métal?

Dr. RASCIO: Toutes ces peintures protègent sur la base de l'action inhibitrice du pigment (le tetroxychromate de zinc ou le chromate basique de zinc). Dans les peintures vinyliques, avec un liant qui est très résistant à l'action de l'eau de mer (un copolymère de chlorure-acétate de polyvinyle), on obtient des meilleurs résultats avec le pigment de zinc déjà nommé que avec le minium de plomb ou la poudre

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## DISCUSSION

d'aluminium. Les résultats obtenus sur le radeau ont été confirmés par les essais de laboratoire (chambre de brouillard salin): les plaques essayées, avec des coupures pour établir le comportement des pigments du point de vue inhibiteur, nous indiquent que les peintures aux chromates de zinc protègent mieux. Deux conditions sont accomplies dans le cas des peintures vinyliques: bonne résistance du liant et bonne passivation de l'acier au moyen des pigments.

E. ARTEMIS: Si l'eau de mer traverse le film et arrive à la surface du métal, celui-ci se corrode-t-il?

Dr. RASCIO: Premièrement la peinture doit isoler la surface du métal de l'eau de mer. Cette possibilité dépend des caractéristiques chimiques du liant et de l'épaisseur du film. C'est presque impossible, avec des épaisseurs de l'ordre de 150/250 microns obtenir une protection complète. C'est-à-dire, pour les peintures les plus résistantes, il y a toujours une certaine quantité d'eau qui se met en contact avec le métal; l'action du pigment, en modifiant le pH ou en donnant des ions chromate, solubles, passivants, complètent l'action des liants. Un prétraitement protecteur, avec une couche de wash-primer appliquée sur l'acier sablé complète cet schéma.

# NEW METHODS OF CORROSION PREVENTION IN THE MARINE FIELD

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## SUMMARY

This paper briefly explains the electrochemical nature of corrosion and then describes the organic coatings, which are used for its prevention: red lead in oil, zinc chromate primer and zinc-rich paints. All these paints require careful preparation of the steel surface. Zinc-rich paints, which function by sacrificial action of zinc dust, are particularly susceptible and should not be used on rusty substrates.

Great efforts have been made to develop rustinhibitive primers which can be applied without previous sandblasting or power-tool cleaning of steel. Groundcoats, working as acidic rust converters or merely by penetration are only partly successful.

However, very good results have been achieved by rust stabilization. In principle, this type of primer works by transforming rust (ferric oxide hydrate) into magnetite, a very

stable iron oxide, during a period of 8-12 months.

The layer of magnetite which develops under the paint film prevents further subcorrosion. The technical and economical aspects of rust stabilization are fully discussed and several examples of its application in marine environment are cited.

Rust stabilization is being used on ocean going ships, on river barges and on harbour installations. The complete rustpreventive coating system consists of two coats of primer and one adequate top finish. Important savings can be achieved by using this rustinhibitive system because surface preparation is at a minimum and its durability reduces maintenance costs. Future aspects of rust stabilization are quite promising.

Corrosion is one of the oldest enemies of mankind. It has been a serious problem in the marine field since the day that iron became a shipbuilding material. In our own age it has grown to tremendous dimensions due to the increased use of steel in ship yards and harbour installations.

We shall only briefly touch on the electrochemical aspects of corrosion. Basically, marine corrosion is just a variation on a familiar theme. Its mechanism is similar to the principle of the electrical battery. In atmospheric corrosion moisture represents the always present electrolyte. In marine environment sea water takes its place. Conditions vary greatly according to climate and circumstances. Salt deposition and high tropical humidity are aggravating factors. In principle, corrosion on land as on sea follows the well known tendencies of iron to revert to its natural state namely iron oxide, its original native form. The basic task of the corrosion engineer is to prevent iron and steel from rusting.

His struggle never ends and rising costs of painting and derusting render his plight an economic factor of importance. The enormous damage caused by corrosion has become a heavy drain on the world economy. Industrial countries are particularly hard hit because of growing air and water pollution. The latter is a serious threat to shipping traffic on contaminated water ways.

Organic protective coatings are still the most common remedy against corrosion. Their original aim was simply to prevent the access of moisture to steel. This can be achieved by creating a film barrier for example by a heavy bituminous coating. Of course, such coatings cannot prevent rust by any chemical action.

Red lead is still the most commonly used pigment in rustinhibitive paints. Its virtues are undisputed but so are its shortcomings. Among the latter are slow dry, limited chemical resistance, toxicity and poor durability if left without a top coat. Red lead in oil or alkyd resins forms waterrepellent lead soaps which strengthen the paint film against disintegration.

Zinc chromate, also widely used in rustinhibitive primers, acts in a different manner. As it is a slightly watersoluble pigment it emits chromate ions, that exert a passivating action on iron. It is often combined with red iron oxide for better coverage. Basic lead silico chromate, whose action is similar, is often used for the so-called «defense in depth» system. Here the rustinhibitive pigment is incorporated in primer, intermediate coat and top finish.

As rusting is an electrochemical process, theoretically any metal, less noble than iron, should function as a corrosion inhibitor. In practice only zinc provides protection by sacrificial action. This is the principle of galvanizing steel. If the content of zinc dust is high enough, a zinc coat can also be deposited on steel by applying a «zinc-rich» paint. Such paint films contain up to 95% zinc dust, thoroughly dispersed in a neutral binder. In such a system zinc pigment will become the anode, the iron substrate the cathode and moisture will function as the electrolyte.

Zinc-rich paints have gained a considerable market in marine construction, especially as so-called shop primers for tankers. They can be welded without difficulty, as the electrically conductive zinc metal will fuse to the iron substrate. As the effectiveness of zinc-rich paints depends on the contact between zinc and iron, they cannot function on contaminated surfaces. No proper results can be obtained on corroded areas; therefore, careful surface preparation is of the essence. The steel surface must be sandblasted or at least very thoroughly freed from rust by cleaning with powerdriven tools or by flame-derusting.

All rustpreventive paints mentioned require removal of rust prior to painting. Today, this represents high additional expenses, mainly because of the increased costs of sandblasting. Therefore, efforts to develop rustinhibitive primers, which do not require such costly surface preparation, were made by many paint technologists. Not all formulations for use on rusty steel have been successful. In theory, rust can be



turned into iron phosphate or other iron salts by primers, containing acid.

But in practice the stoichiometric proportions for such chemical reactions rarely exist. Attempts have also been made to render rust harmless by penetration with certain vehicles or additives. This is a constructive idea but penetration alone will not prevent further subcorrosion.

A far more promising approach is stabilization of rust, a method that has found growing acceptance since 1956. The basic idea is to transform iron oxide hydrate (rust) into a more stable oxide. Such a form of iron is magnetite,  $Fe_3O_4$ , long known to engineers for its stability and used as a raw material for electrodes. That iron converts into magnetite at high temperatures, for example in blast furnaces, is a long established fact. The problem was to find a method to stabilize rust into magnetite at normal temperature. The chemical reactions which lead to such a conversion are complicated and not yet fully understood. However, the fact that epitactic magnetite layers of high corrosion resistance can be formed by means of adequate primers, is firmly established.

Such a continuous layer will develop slowly and gradually if the proper primer is applied on firmly adhering rust.

Naturally, loose rust crusts and scale must be removed prior to paint application. To achieve thorough penetration, the primer is applied by brush, later to be followed up by a second coat. It is always necessary to apply two coats for adequate film thickness. The importance of that highly significant factor should not be neglected. A prime coat of low film thickness carries the seeds of destruction in itself. This is easily understood if microphotographs of corroded steel are studied. They are remindful of moon craters. Their profile shows tops and valleys and if the pinnacles are not fully covered by paint, they shall soon turn into new centers of corrosion.

Examination of epitactic magnetite layers has been carried out by a number of chemical research laboratories in Switzerland, Germany, Norway, Sweden, France and the USA. The results were always the same: during a period of 8-12 months a continuous magnetite layer develops until the rust has been converted.

Asides from magnetite which forms up to 95% of the new surface, there is generally a small amount of hematite but no ferri oxide hydrate. This unstable, spongy substance, the true source of subcorrosion has disappeared.

Some researchers have pointed out that sea rust itself generally contains 20-40%, sometimes up to 60% magnetite. Why then does this considerable percentage provide no protection? Unfortunately, the magnetite particles are deeply imbedded in loose rust. They never form a homogeneous film and therefore they cannot act as inhibitor. They can only turn rust-preventive when transformed into a strongly adhering, continuous, epitactic layer. Porous, spongy oxides can never inhibit rust, in the contrary they are the best feeding ground for further corrosion.

Our knowledge of the crystalline structure of iron oxides is still limited. We will probably learn more about its rust-inhibitive aspects during the next decade.

What possibilities does this new type of primer open for application on ships and harbour installations? Perhaps, the most interesting application is its use on the boottop area which is exposed constantly to the alternating influence of water, atmosphere and sun radiation. Maintenance becomes easier when firmly adhering rust can remain undisturbed, especially when elaborate surface preparation is not feasible for lack of time.

Rust stabilizing primer can be topcoated with about any type of organic finish. The system can be adapted to almost any condition as the primer can be overpainted with alkyd, phenolic, epoxy and vinyl finish. Polyurethane finishes have also been used with good success for example on the dry docks of the harbour of Marseille. Another interesting application are buoys, which have also been ruststabilized in France in the port of St. Nazaire.

Since 1962 two coats of ruststabilizing primer have been used as the only rust protection on the hull of numerous tug-boats and passengerboats, built in Austria for the Soviet Union. These ships maintain constant traffic on the river Danube. It is interesting to note that the ship bottom was not painted with antifouling or any other top coat. In Japan a new method of shipbuilding has been adapted by many shipyards. By welding finished sections together, the construction period is considerably shortened. However, this speedy process makes sandblasting impracticable. The steel primer has to be applied on partly rusty surfaces. Here the ruststabilizing system has greatly contributed to the success of the new procedure.

There was a time when the economical aspects of structural painting could be largely ignored.

Today those who neglect them pay a heavy penalty. One of the primary duties of corrosion engineers is to save labor costs. It must always be understood that labor presents a multiple of the price of paint itself. In some industrial countries the paint represents only 15% of the total expense. Therefore, a manager who uses poor quality paint on large harbour installations would be very illadvised indeed. He will soon incur increased costs for repair and maintenance. By the ruststabilizing system the heavy costs of surface preparation are decreased from the start. Furthermore, two coats of ruststabilizer plus one durable topcoat will produce a weather-resistant system of about 125 micron (= 5 mils) film thickness. In most cases this will provide sufficient durability for many years to come. Some shipyards use two topcoats like for example the large Stülcken shipyard at Hamburg where 10,000 square meters (107,640 Square Feet) of crane installation were painted with two coats of rust stabilizer and two coats of a micaceous topcoat with excellent results.

Let us say in conclusion, that the ruststabilizing system offers significant advantages in maritime construction. No anticorrosive method is a panacea and undoubtedly paint formulators and maintenance engineers have still a great deal to learn about its working and potential. A universal rustinhibitive system remains the goal of all, involved in corrosion research. Certainly, it presents a thrilling challenge for the new generation of coatings chemists.

## DISCUSSION

Dr. BOUTH (England): The prospect of producing modified corrosion products with protective properties offers considerable possibilities. There have been found, in archeological investigations in England, iron objects dating from the Roman occupation of 2000 years ago, still in perfect condition in soil that would be expected to be corrosive. Examination of the coating on these objects shows it to be a mixture of basic iron phosphates closely resembling vivianite, but obviously of a peculiar quality and protective nature that we have not been able to reproduce artificially. I think that there are possibilities for the development of a protective coating of this nature, if it can be done without having to bury the object for 2000 years first!

Dr. MAASS: Sir, I am familiar with this phenomenon. I have read a paper, which described iron plate, dating from the time of Edward the Confessor (1002-1066), found during construction of a British airfield. In that case, I believe the soil was saturated with tannine, an organic acid. The organic iron salts formed were the cause of this long protection. There is no doubt that iron salts are very often very good, active protective agents. The great difficulty remains to apply them correctly.

B. HEUZÉ (France): Are these products compatible with cathodic protection on immersed surfaces?

Dr. MAASS: Yes, they are.

# COMPARATIVE ASSESMENT OF GALVANIC ANODES BASED ON MAGNESIUM, ZINC AND ALUMINIUM ALLOYS FOR CATHODIC PROTECTION OF SHIPS

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## SUMMARY

The paper describes the results of Service trials carried out with magnesium, zinc and aluminium alloy anodes on cathodic protection of ships of the Navy operating in tropical waters and using oleoresinous anticorrosive paint.

The trials have shown that all the three galvanic anodes have adequate dissolution characteristics suitable for cathodic protection of ships in tropical waters. Consumption of aluminium anodes, however, has been found to be the lowest. Cathodic protection with aluminium alloy anode also works

out to be lower than that with zinc and magnesium alloy anodes. In addition, aluminium is available in the country indigenously.

Aluminium and zinc have got additional advantage that in view of the low driving potential, the anodes can be fitted directly to the hull. In the case of magnesium anodes, control of anodic current by external resistance is necessary making the system more costly.

## INTRODUCTION

Anticorrosive paints have proved to be the main defence against corrosion of the underwater hulls of ships. The protection offered by anticorrosive paints, however, is not complete in view of (a) *holidays* left under the keel block during the painting, (b) physical damage caused to the paint film during Service, and (c) susceptibility of paint film getting detached in the stern area owing to proximity of the noble bronze propeller as well as additional turbulence.

During the last fifteen years, protection offered by anticorrosive paints has been supplemented by cathodic protection either by galvanic anodes or from externally generated currents. Alloys of magnesium, zinc and aluminium have been used as galvanic anodes for cathodic protection of steel in seawater.

The choice of the most satisfactory galvanic anode system for cathodic protection of underwater hulls of ships will depend upon (a) driving potential, (b) current output per pound of anode consumed, (c) cost, and (d) indigenous availability of the material. The design of cathodic protection system, particularly in respect of anode requirement is dependent upon underwater paint system, seawater temperature and other local variations.

With a view to ascertaining the most satisfactory galvanic anode for cathodic protection of the underwater hull of ships of the Indian Navy, Service trials are in progress on five ships using (a) magnesium anode on one ship, and (b) zinc and aluminium alloy anodes separately on two ships each. Trial with magnesium anode has been completed.

The paper describes the performance, anode consumption and relative advantages and disadvantages of the three galvanic anode materials based on the Service trial results available to-date.

## TRIAL ON WATER BOAT VARIDA USING MAGNESIUM ALLOY ANODE

The water boat VARIDA (144' long  $\times$  26' beam  $\times$  10'8" draught having an underwater area of 5350 sq.ft. under fully loaded condition, was fitted with magnesium anodes.

The cathodic protection system fitted was based on the design worked out by the Laboratory in respect of (a) number, dimensions, composition and distribution of anodes, (b) painting schedule including the paint system near the anode, (c) method of installation of the anode and connecting cables as well as (d) control panel. During preparation of the design, assistance was taken of the information available on the subject in the published literature<sup>1</sup>.

### Dimension and composition of anode.

The anodes used were 5' long, 5" wide and 3" thick and provided with a 5/16" diameter steel conductor rod cast longitudinally. Composition of the anode is given below. Each anode weighed about 25 kg.

Aluminium	—	7.4 p.c.
Zinc	—	3.2 p.c.
Manganese	—	0.14 p.c.
Iron	—	0.013 p.c.
Nickel	—	Absent
Silicon	—	Trace
Magnesium	—	Remainder

### Number of anodes

The number of anodes required for cathodic protection is dependent on (a) underwater area of the ship, (b) performance characteristics of the anticorrosive paint, (c) seawater temperature, (d) interval between dry-docking, (e) period for which the ship is expected in motion as well as the maximum speed, and (f) painted areas bared during Service. In the absence of any previous data on anode requirements in Indian waters, data published by the Canadian Navy<sup>1</sup> were taken into consideration. It was found that twelve anodes would be required for a life of one year but it was thought prudent to increase the number to sixteen to suit the Indian conditions with higher prevailing temperature of seawater and use of oleoresinous anticorrosive paint. Thus eight anodes were fitted to VARIDA on each *bilge keel* (Fig. 1).

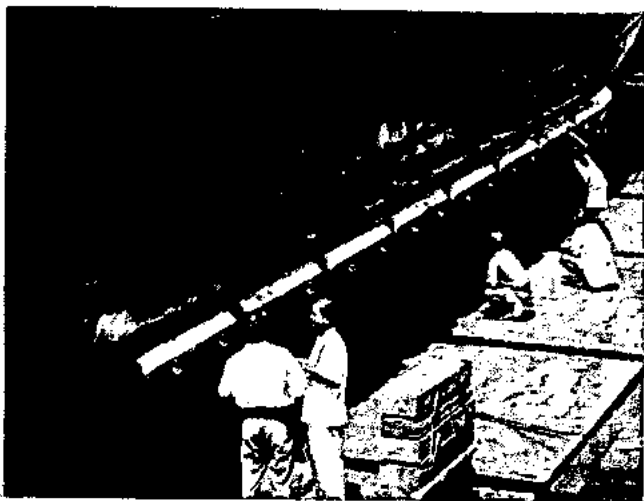


Fig. 1. — Array of eight magnesium anodes fitted on the bilge keel of Varida.

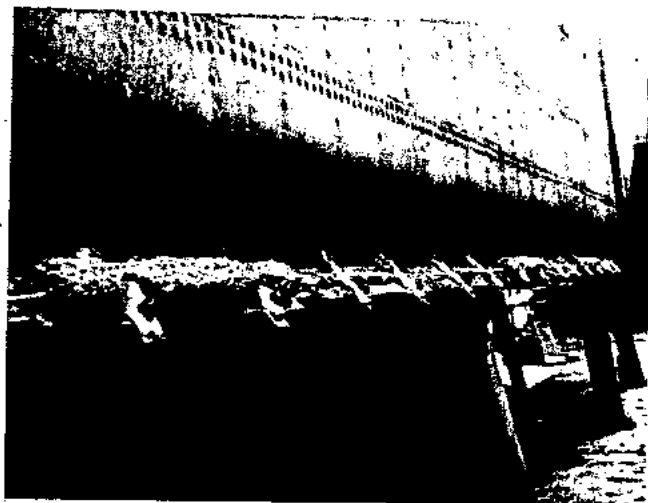


Fig. 2. — View of underwater hull of Varida showing remarkable freedom from corrosion.

### Painting Schedule

The area round the bilge keel on which the anodes were mounted was sand blasted extending to five ft. on either side and coated with one coat of neoprene primer followed by three coats of neoprene paint. The rest of the hull was coated with two coats of anticorrosive and one coat of antifouling composition.

### Fitting of the anodes

The anodes were fitted by means of mild steel studs ( $2 \frac{1}{2}$ " long x  $\frac{3}{4}$ " dia) welded to the bilge keel. A rubber sheet (1/8" thick) was inserted between the anode and the bilge keel to insulate the anode from the hull. Bakelite ferrules were also provided between the stud and the mild steel panel to ensure electrical insulation. After securing the anodes, the insulation was tested for each anode separately and found to be more than 1 megohm. The anodes on each bilge keel were connected electrically by welding the adjoining conductor rods forming two anode arrays.

### Connecting cable

The mild steel conductor rod of one of the terminal anodes on either side was connected by silver brazing to the copper conductor of a low resistance cable. The conductor cable on either side was laid along the ship side secured by clamps. The entire length of the cable was encased in a half round mild steel casing to prevent damage to the cable.

### Control panel

The two cables were connected to the control panel consisting of an ammeter, variable resistance and a switch for each anode array. The control panel was mounted in the wheel house.

### Trial results

After undocking of the water boat, current output from each anode array was adjusted to maintain the hull potential between 800 to 850 mV (measured against saturated calomel electrode).

### Assessment of underwater hull after trial

VARIDA was dry-docked after 280 days Service. The entire underwater hull below the minimum low water line, which remains fully immersed, was found to be completely free from corrosion. The rudder, water inlets as well as the rivet heads which are very susceptible to paint failure and corrosion were also found to be remarkably free from rust (Fig. 2). The total consumption of magnesium anode was about 300 kg. during a period of ten months' Service. Requirement of magnesium anode on the basis of this result works out to be 66 kg./1000 sq.ft./year.

### CATHODIC PROTECTION USING ZINC ALLOY ANODES

Cathodic protection system using commercially available zinc alloy anodes was installed on two frigates using commercially available zinc anodes prepared from high purity zinc and having the following composition.

Iron	—	0.0025 per cent
Aluminium	—	0.25 per cent
Silicon	—	0.06 per cent
Zinc	—	Remainder.

### Dimension of anode

Each anode, 32" long, 4" wide and  $1 \frac{1}{2}$ " thick, weighed 20 kg and was provided with galvanised steel inserts for fitting the anode to the hull by welding.

### Number of anodes

Since no data on requirements of zinc anodes for satisfactory protection of ships in Indian waters was available, published information on zinc anodes used in the U.K.<sup>2</sup>, USA<sup>3</sup> and Canada<sup>4</sup> was considered for working out the anode requirement. It was also observed that the Canadian Navy had fitted three times more anodes in comparison to those in the U.K. and the U.S.A. The number of anodes were varied in the two trials using 90 and 60 anodes for the two ships having underwater area of 10,200 and 13,500 sq.ft. respectively.

### Fitting of anodes

The anodes were fitted directly to the hull by welding the mild steel inserts. In view of the lower potential difference between zinc anode and painted hull, no external control of the current was considered necessary as in the case of magnesium anodes.

### Hull potential measurements.

Hull potential measurement taken from the two ships have shown the underwater hull to be adequately protected. The potential reading on the two ships fitted with 90 and 60 anodes was of the order of 900 and 850 mV respectively:

### Trial results

The two ships fitted with zinc alloy anodes have been dry-docked a few times since installation of the cathodic protection system. The trials have been in progress till March 1967 for periods of 23 & 22 months. Underwater hull of both the ships has been found to be completely free from any corrosion since installation of the anodes (Fig. 3). Condition of the underwater paint film was also satisfactory without showing any blistering or flaking. On the basis of anode consumption observed during dry-docking, the anodes are expected to have lives of 4 years (90 anodes) and 3 years (60 anodes) on the two ships. Consumption of anodes works out to be 45 and 30 kg/1000 sq.ft./yr.

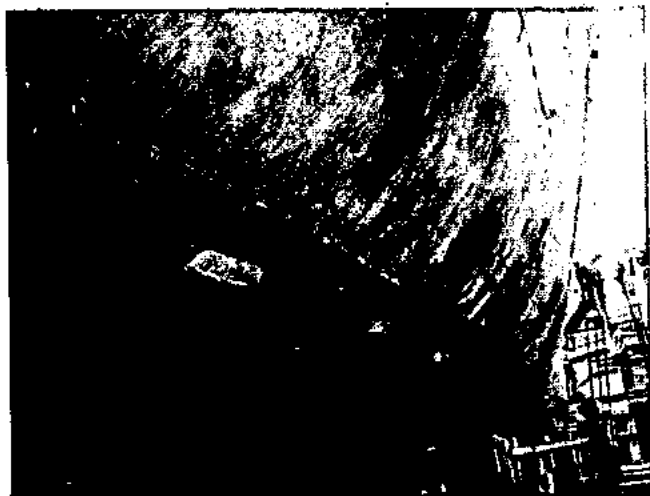


Fig. 3. — View of underwater hull of a frigate, showing complete freedom from corrosion since fitting of the zinc alloy anodes.

### CATHODIC PROTECTION USING ALUMINIUM ANODES

Owing to the presence of protective oxide film on the surface, aluminium does not suffer free dissolution when coupled to iron in seawater. With a view to improve the dissolution characteristics of aluminium, over twenty binary and ternary anode compositions were cast in the Laboratory incorporating small quantities of metals such as lead, antimony, zinc, cadmium and tin. The experimental anode compositions were then evaluated in the Laboratory in running seawater using a technique similar to that used by Carson<sup>6</sup> and Grennell<sup>7</sup>.

### Service trial

Aluminium alloy anodes weighing about 8 kg. each have been fitted on two frigates having underwater area of 10,200 (52 anodes) & 13,500 sq.ft. (64 anodes) in May 1966 and

September 1966 respectively. The anodes were similar to zinc anodes in respect of dimensions and the steel inserts were welded directly to the hull.

The hull potential readings have been regularly recorded & found to vary between 800-850 mV (52 anodes) and 850-900 mV (64 anodes) against saturated calomel electrode. One of the frigates has been dry-docked after about eleven months' Service when all the anodes were found to be active and to be dissolving uniformly (Fig. 4).

Estimate on consumption of aluminium anode during the trial period indicates the rate of consumption to be about 20 kg/1000 sq.ft./yr.

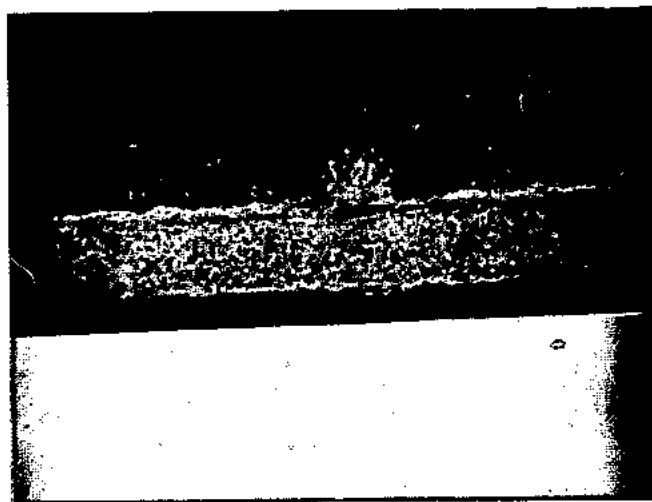


Fig. 4. — Close view of an aluminium alloy anode, developed in this laboratory, showing uniform dissolution

### DISCUSSION

The three galvanic anode materials have shown dissolution characteristics adequate for cathodic protection of ships in tropical seawater using oleoresinous based anticorrosive paint. In the case of cathodic protection using magnesium anodes a dielectric shield based on one coat of neoprene primer followed by three coats of neoprene paint is necessary for an area about five feet around the anodes to improve the cathodic current distribution and prevent loss of adhesion of the paint film.

In view of the high nominal solution potential of magnesium anode (-1.50V against Ag/AgCl electrode)<sup>7</sup> in seawater compared to that of zinc (-1.05V) and of aluminium (-1.00V) the current output from magnesium anodes requires control by an external resistance as in the case of VARIDA. This makes installation of cathodic protection with magnesium anodes more costly. In addition, the system requires constant supervision by the ships' staff. In contrast, zinc and aluminium anodes, having low driving potentials, can be fitted directly to the hull electrically and do not require external control and supervision during Service.

The consumption of aluminium anodes (20 kg/1000 sq. ft./yr) has been found to be lower than that of zinc (30 and 45 kg/1000 sq.ft./yr) and of magnesium (65 kg/1000 sq. ft./yr). On the basis of the existing price of zinc, aluminium and magnesium being about four, five and six rupees per kg. respectively, the material cost for protection using aluminium alloy anode also works out to be the lowest amongst the three galvanic anode materials.

The higher consumption of zinc (45 kg/1000 sq.ft./yr) in one ship is considered to be due to the number of anodes

Table 1  
Performance of shot-blasting machines in European shipyards building super tankers

Shipyards	Machine type	Site	Preheating	Nature of plates entering machining	Pass speed, m/min	Abrasive		Peak height, $\mu\text{m}$	Cleanliness		Residual dust	
						Initial charge	Used material below 0.3 mm, %		Milliscaled areas, % clean	Rusted areas % clean		
A	Vertical plate	Under cover	Yes	Mild steel; milliscaled, with isolated rust patches.	1.5	1.2 mm shot	3	380*	109	65 - 95	50	Excessive
B	Horizontal plate	Under cover	No	Mild steel; entirely milliscale	2	0.8 mm shot	10	123	107	75 - 95	-	Excessive
	Vertical plate	Open	No	Mild steel; entirely milliscale	1.3	0.8 mm shot	11	174	124	85 - 90	-	Excessive
	Section and bar	Open	No	Mild steel; 50:50 milliscale; rust.	-	0.8 mm shot	0.2	117	106	100	80	Considerable
	Horizontal plate	Under cover	No	Higher tensile steel; milliscale, some rust at edges.	1	0.8 mm shot	8	117	101	85 - 90	85	Excessive
C	Horizontal plate	Under cover	Yes	Higher tensile steel; milliscale, some rust at edges.	2	0.6 mm shot	14	122	92	85 - 100	85 - 100	Excessive
	Section and bar	Under cover	Yes	Mild steel; milliscale with isolated rust patches.	2	0.6 mm shot	3.3	117	108	100	100	Very bad
D	Horizontal plate	Under cover	Yes	Mild steel; entirely milliscale	3	50% 1.2 mm 50% 1.0 mm shot	4.2	173	128	20 - 60	-	Excessive
	Horizontal plate	Under cover	No	Mild steel; milliscale, some rust at edges.	4.5	1.0 mm shot	0.06	119	102	60 - 90	-	Excessive
E	Section and bar	Under cover	No	Mild steel; mostly milliscale	4	1.0 mm shot	7.6	120	104	40 - 90	-	Very bad
	Horizontal plate	Under cover	Yes	Mild steel; milliscale with some rust patches.	1.25	0.8 dia. x 1.0 mm chopped wire	1.5	102	119	65	40	Excessive
G	Horizontal plate	Under cover	No	Higher tensile steel; milliscale, with rust at edges.	2.5	0.8 dia. x 1.0 mm chopped wire	1.0	127	99	95	50	Excessive
	Horizontal plate	Under cover	No	Mild steel; milliscale with rust patches.	2.5	0.8 dia. x 1.0 mm chopped wire	1.0	132	112	85	50	Very bad
H	Horizontal plate	Under cover	No	Mild steel; milliscale, rust at edges.	1.8	1/3 1.2 mm 1/3 1.0 mm 1/3 0.8 mm shot	0.2	129	122	100	50	Excessive
	Vertical plate	Open	Yes	Mild steel; milliscale, rust at edges.	1.4	0.8 mm shot	29	127	99	100	70	Considerable
I	Section and bar	Under cover	Yes	Mild steel; 50:50 milliscale; rust.	1.4	0.8 mm shot	3.8	91	86	85	95	Considerable
	Vertical plate	Under cover	No	Mild steel; mainly milliscale but some general rusting.	1.0	0.65 to 0.75 mm shot	0.7	137	112	85	50	Considerable
J	Vertical plate	Under cover	No	Mild steel; milliscale, rust patches.	1.2	0.8 to 1.8 mm shot	1.2	128	114	50	30	Excessive
	Section and bar	Under cover	No	Mild steel; mostly rust, very little milliscale.	3	0.9 mm dia. chopped wire	-	132	124	30	30	Excessive
K	Vertical plate	Under cover	Yes	-	-	0.9 mm dia. chopped wire	0.5	91	-	-	-	-
L	Vertical plate	Under cover	Yes	Mild steel; one side mainly milliscale, other mainly rust	2	0.7 mm shot	1.4	101	-	85	60 - 70	-
	Vertical plate	Under cover	Yes	Mild steel; one side mainly milliscale, other mainly rust	1.4	1 to 1.2 mm shot	trace	106	-	90	85	-

\* Angular particles greater than 2.0 mm diameter present in unused shot

being larger than in the other ship. This is also corroborated by the higher potential readings.

Of the three galvanic anode materials, aluminium is at present available in the country from indigenous sources. Casting of aluminium anodes also requires less stringent control than that of magnesium and zinc.

#### CONCLUSIONS

Service trials have been carried out on cathodic protection of ships using magnesium, zinc and aluminium alloy anodes. Design of the cathodic protection systems fitted has been described in the paper. The performance and consumption of anodes in tropical waters with oleoresinous anticorrosive paint have been determined.

Magnesium, zinc and aluminium alloy anodes have shown dissolution characteristics adequate for cathodic protection of ships and submerged steel structures in tropical waters. Aluminium and zinc anodes can be fitted directly to the hull while control of anodic current by external resistance is necessary with magnesium anodes.

Consumption of aluminium anodes is lower than that

of zinc and magnesium. On the basis of the existing price of anode materials, cost of cathodic protection with aluminium anodes is also the lowest.

In view of the above, it is concluded that aluminium alloy anode works out to be the most suitable material for cathodic protection of ships using galvanic anodes.

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# CORROSION AFTER SHOTBLASTING

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## SUMMARY

It is known that previous corrosion has an influence on the later performance of steel. This has now been more systematically followed. Panels, which had been used for earlier immersion trials on a raft, were shotblasted. After a few days

the old corrosion pattern(s) return(s). Some examples are discussed, and an explanation is offered. It is proved that a correlation exists between the corrosion patterns before and after shotblasting. It is stressed that such steel is too sensitive for an effective protection by normal paints.

## 1. INTRODUCTION

As a matter of experience, it has been expressed that steel, once it has corroded, will be very difficult to preserve. A typical example is the difference in performance in the protection given by paints on ships constructed in summer time, and in winter time. Except from these rather general statements, we could not find much more pertinent information, either theoretical or experimental. We considered the question whether steel, once it has corroded, can be properly prepared for a new coating, or whether the corrosion pattern is already indelibly impressed on the steel surface.

In the present paper are described some observations we have made of the sensitivity and subsequent corrosion of shotblasted steel panels, previously used in trials for ships' hull panels. For the investigation there were available a large number of panels with a complete record of all phases during exposure: notes, colourslides, formulations of the paints, etc. In this way we were able to investigate either whether there is correlation between corrosion of the panel before and after blasting, or whether the corrosion after shotblasting develops at random.

## 2. THE PANELS

All panels investigated measured 40 x 40 cm, and varied from 2 to 6 mm. Steel no. 37 had been ordered, but they were not taken from one lot. The panels were coated in our workshop, and as soon as possible immersed on our North sea raft and attached to a chain by locks, coated with Rilsan; in this way they were electrically isolated from each other, to avoid electro-chemical effects. The panels were cut to size (an important point for further consideration). A complete record was available, including pre-treatment, exposure (notes and slides), paints used, etc. Only a few examples from the extensive material at our disposal are discussed.

## 3. EXPERIMENTAL PART

A number of panels were selected at random from our stocks. These were obtained in different years, and the steel of the panels cannot be considered uniform (from one delivery), though always the same graded steel was ordered. The panels were impact cleaned, and kept in our laboratory, without protection. Rusting did not proceed evenly over the surface, as expected, but we observed a distinct pattern. From the panels examined, only three examples will be dis-

ussed. We include also a fourth of blistering returning, re-touched after washing (without blasting).

- a. A bituminous system was applied on panel V 5706, and immersed. Corrosion was found on the edges,

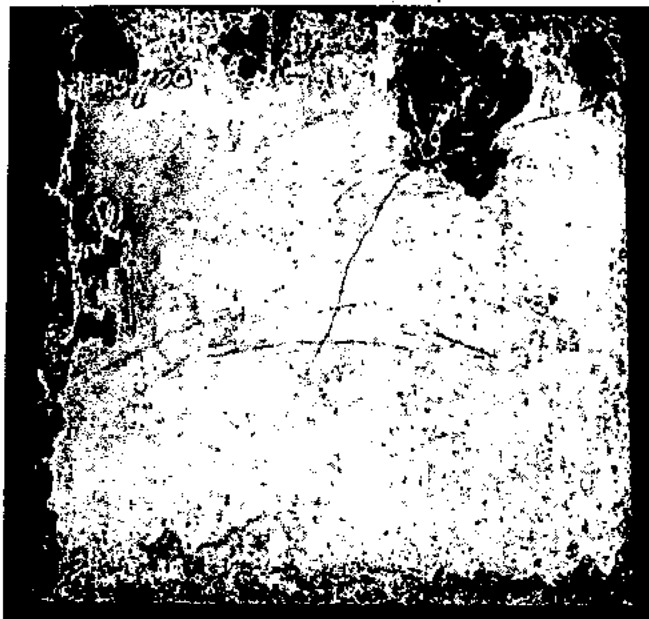
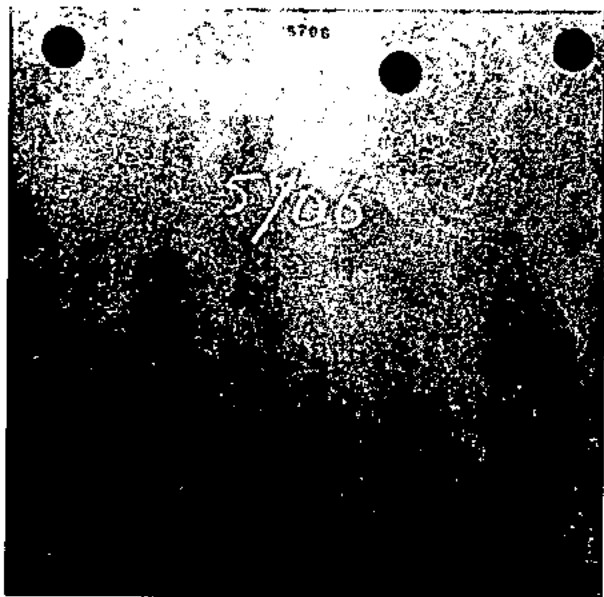


Fig. 1. Panel V 5706.

1.1 Panel with bituminous coating after immersion during 6 months.

and some other places (fig. 1.1). After shotblasting to SA 3, the panel appeared perfectly clean (fig. 1.2), but after a few days it had rusted exactly on those places where before shotblasting, corrosion had been visible (fig. 1.3). Also some pitting-due to anodic corrosion- was observed.

- b. A vinyl copolymer coating was applied to the whole panel 5950, but the half with one hole was formed with a washprimer, applied on the bare steel (fig. 2.1 and



1.2 Panel after shotblasting.



1.3 Panel some days after shotblasting; Note return of corrosion pattern in figure 1.1 (compare § 3. a).

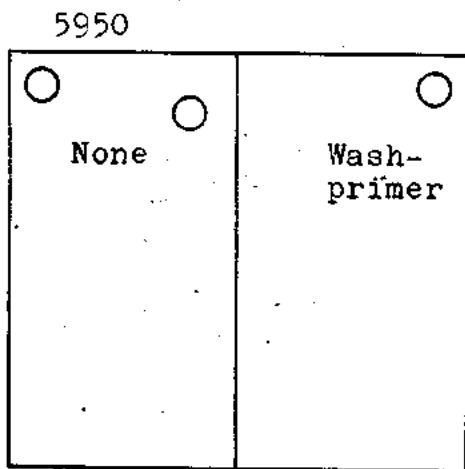
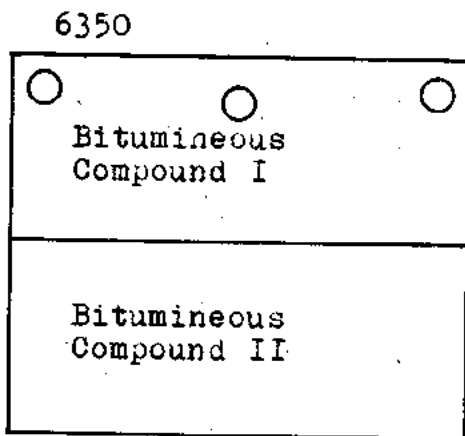


Fig. 2. Panel A 5950/6350.

2.1 Division of the panel in trial A 5950: right side with washprimer, left side no washprimer applied. Over the whole surface a vinyl-copolymer coating.



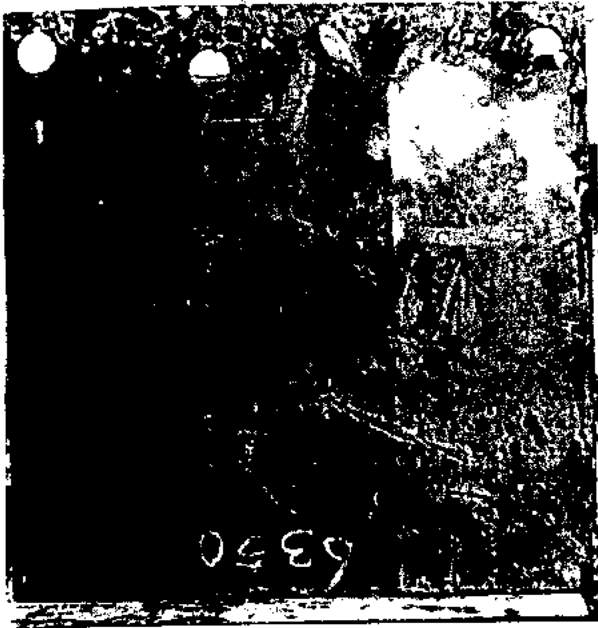
2.3 Division of the panel in trial A 6350: two modifications of a bituminous paint on upper and lower part.



2.2 Panel 5950 after six months immersion. Note some blistering on the edges.

2.2). After immersion and subsequently shotblasting two different bituminous systems were applied to the lower and upper halves (two modifications of the same formula), and the panel immersed under number 6350 (fig. 2.3). Once again it was shotblasted and again the pattern of the original trial 5950 was found (division left-right). But there was also a pattern which corresponded to the damaged places in trial 6350 (fig. 2.4). The edges should also be noticed. Evidence of the correlation of the corrosion from both trials is found (fig. 2.5 and 2.6).

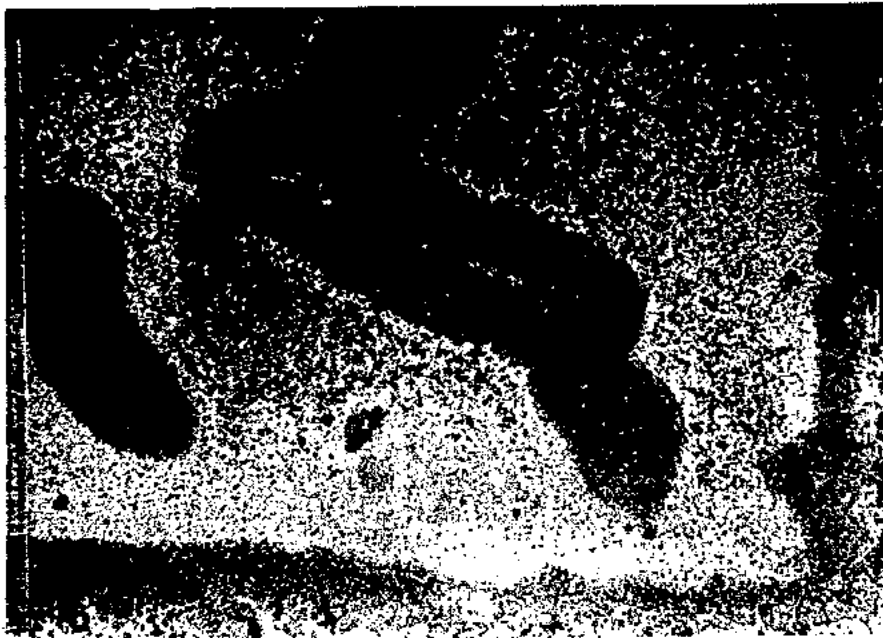




2.4 Panel A 6350 after five months immersion. Note scratches in the surface of the coating.



2.5 Panel A 6350 some days after shotblasting. Note corrosion on the right side due to the use of washprimer from the first trial and the corrosion corresponding to the scratches shown in fig. 2.4 from the second trial. Compare 2.7.

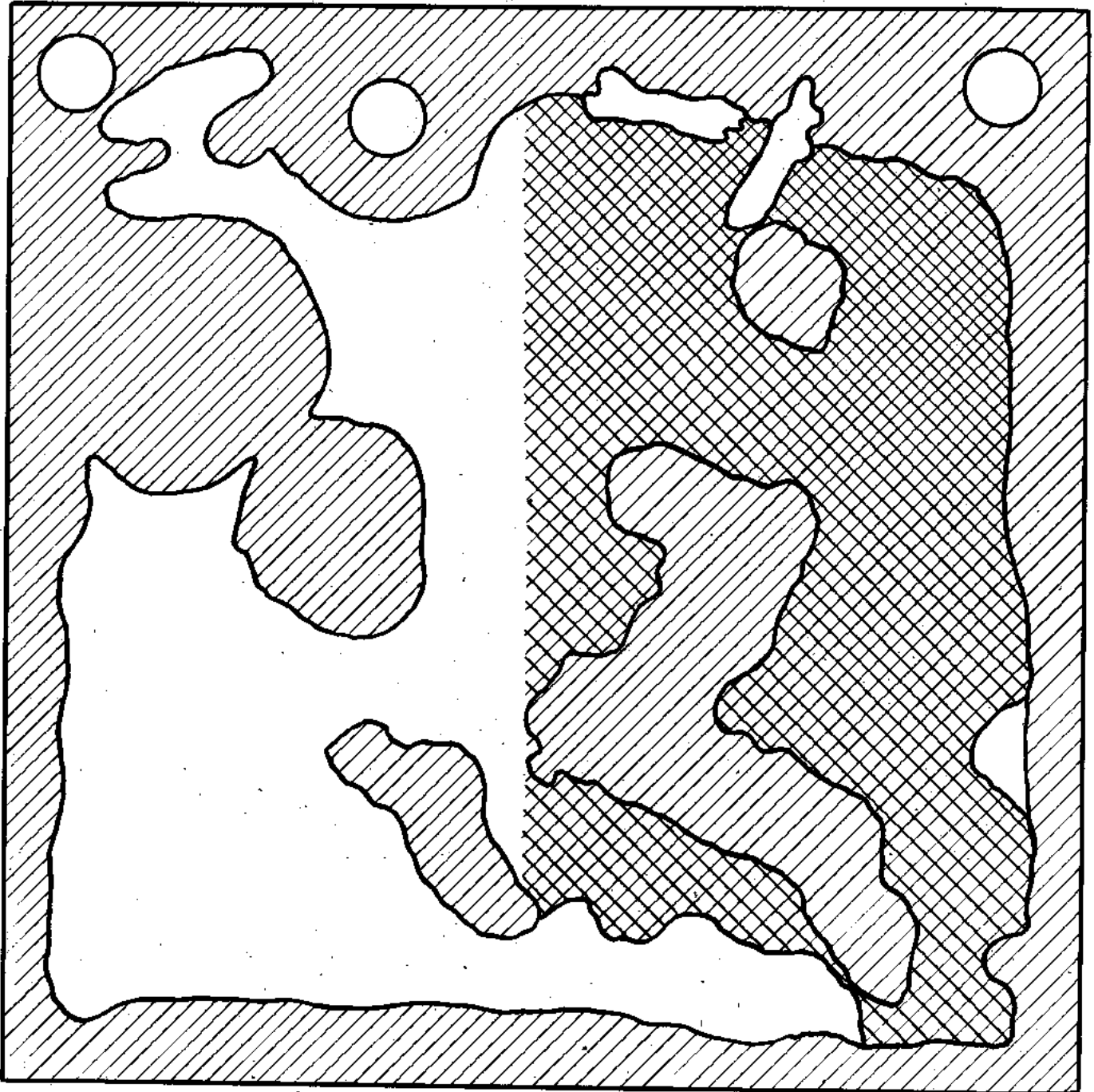


2.6 Detail of fig. 2.5. Note spreading of the corrosion from the scratch (compare § 3 b).

c. A red lead chlorinated rubber coating was applied to the shotblasted panel 6137 (fig. 3.1), and after immersion no corrosion was found, though there was marine growth. After shotblasting again a thin coaltar epoxy system was applied with four antifouling trials, and immersed under the codenumber 6410 (fig. 3.2). In this case correlation was found, as expected, between the corrosion after shotblasting and the marine-growth in the earlier trial (fig. 3.3). After application

of a low grade system, some months later the cathodic areas were marked (fig. 3.5).

d. On our panels 6418 (fig. 4.1) and 6419, the coating was severely blistered. After cleaning and patching with an anti-corrosive paint, one coat anti-corrosive and one coat of anti-fouling paint was applied, and the panel immersed. After two months blistering started at the same places as previously (fig. 4.2).



second trial 6350



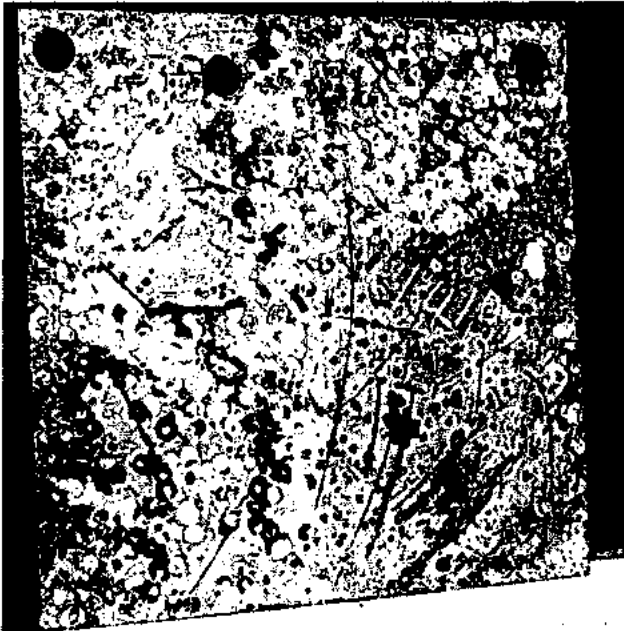
first trial 5950

2.7 Scheme, indicating the sources of the corrosion.

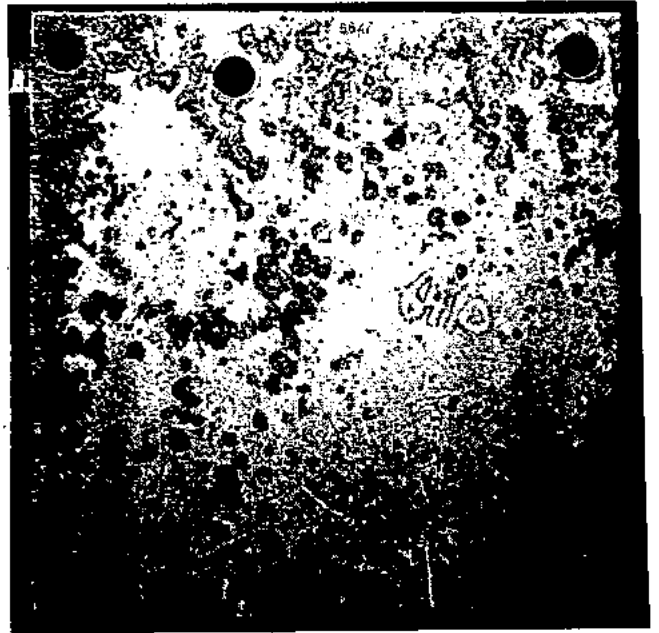


Fig. 3. Panel 6137/6410/6647.

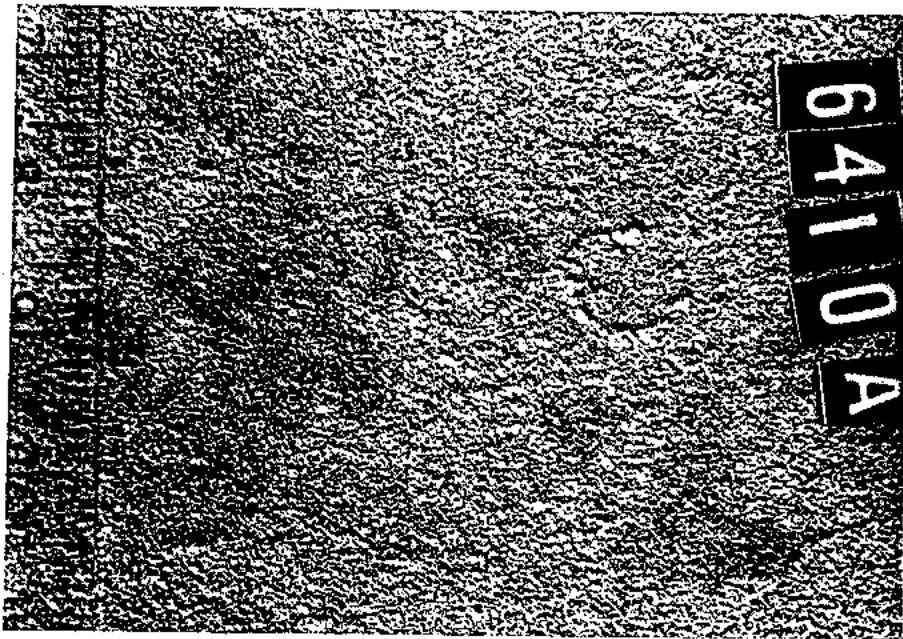
3.1 Panel 6137, with a chlorinated rubber system after 7 months immersion.



3.2 Panel 6410 with a thin coaltar epoxy system and four anti-fouling trials, after 18 1/2 months immersion. Marine fouling has been removed. Note pattern of marine growth.



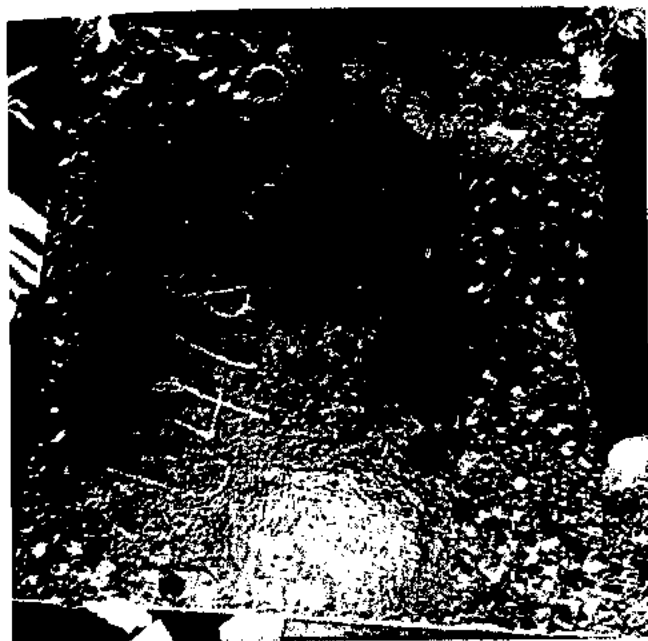
3.3 Panel 6410 some days after shotblasting. Note that corrosion pattern corresponds with marine growth in fig. 3.2.



3.4 Detail of panel 6410, which shows the attack on the places where barnacles had been attached (compare § 3.c)



3.5 Panel 6647. After shotblasting a low quality ships' bottom system has been applied (to accelerate the trial). Note that on about the same places blistering is found after two months immersion (compare § 3.d).



4.1 Three different coaltar systems, with different blistering after 18 1/2 months immersion.



4.2 Panel from figure 4.1, retouched with a coaltar primer over the whole surface, after 3 months immersion. Note that basically the same pattern returns.

Fig. 4. Panel 6418.

#### 4. DISCUSSION

O'Driscoll<sup>8</sup> showed already experimentally the phenomena of anodic and cathodic areas on steel panels, but he did not offer an explanation. On coated specimens the cathodic blisters were large; the coating was still elastic, the blisters becoming larger by creeping of the alkaline solution in the interface. The cause of the anodic and cathodic places may be understood from the following considerations.

The surface of steel is not homogenous, because of the different crystal planes. The planes themselves are irregular, and present different energy levels which result in potential differences. In addition the anodes created by the heavy stresses during cutting are important. Such circumstances are favourable, as Evans and Simnad<sup>1</sup> have found, to the development of anodes. But the panels as a whole must be in equilibrium, and the anodes must be compensated for by cathodes in the flats of the panels. Under normal conditions this will not mean that the steel is attacked, but as the electrical circuit is completed by a medium which transports electrons — e.g. seawater — the wellknown electro-chemical reactions start. Also crevices exist, and the alkali ions penetrate into the surface sufficiently deeply to render it permanently alkaline, even after shotblasting. An earlier paper from our laboratories describes troubles with a ship (2), which had been operated for several years under cathodic protection. The shotblasted steel surface was highly alkaline, and had to be neutralized with acids. The alkalinity was due to the absorption of hydroxyl ions. In turn it should be considered that these cathodic areas activate in subsequent trials the anodic areas.

It is important that we noticed that breakdown of panels after prolonged immersion (4 to 8 years) always starts with heavy anodic corrosion on the edges.

With this in mind it is possible to consider our observations more closely. That local stresses cause the creation of anodes is clearly shown on panel V 5706, where pitting indicates the most active anodic places. The coating is broken, and we observed corrosion here both before and after shotblasting.

Some areas of the flats also rust; the affected areas correspond to groups of small blisters, apparently anodic, noticed during the trial (fig. 1). We have always found some deviation at the edges from the general behaviour of the coating. We should consider this too.

The anodes on the edges activate the cathodes on the flat area, and consequently by electroosmosis, diffusion of water, ions, oxygen and alkaline solution fills the blister. The high pH (we noticed above 10) resulting in loss of adhesion due alkali creep during this process in this area is suppressed. The rather small area of the panel and the comparatively long edges result in completely different ratios from constructions in water, but the similarity remains: stresses, welds and rivets create potential differences there also.

Some investigations exclude the edges from the evaluation during exposure. However, if we look at the deformations at the edges, as discussed below, this appears to be poor practice.

In our second example (trial 5950/6350) the influence of the washprimer on steel was introduced. On the side indicated, one extra coat was applied, and lower permeability was expected with cathodes developing preferentially on the side with the higher permeability. It appears to us that the acid in the washprimer had repressed the cathodes. During and after immersion the steel was not attacked by alkaline solutions (fig. 2.1). On the lower part of this trial (6350) we observed the correlation between damage and the corrosion after shotblasting on what must have been anodic areas. Pitting and its influence on adjacent areas can be seen. At the edges the anodes, developed during the first trial, might have caused the loss of adhesion.

In our third example (fig. 3), the red lead has rendered the steel surface sufficiently passive, but the thin coating of coaltar epoxy was destroyed by the marine growth on the (inefficient) anti-fouling paint trials. The barnacle has isolated the surface, and formed an oxygen concentration cell. We have also found on this panel that the imprint of the barnacle is easily noticeable (fig. 3.4).

The imprints left by barnacles are clearly visible some days

after shotblasting. Also the blistering in a conventional system (fig. 3.5) points to a correlation on the cathodic places. We have also included an example of a panel which was patched on the damaged areas, as in dockyard practice.

In this trial blistering recurred after a few months. This may be considered from the point of the coating and of the permanent cathodes formed (see below). The anodes and cathodes are still active, and the electro-osmosis proceeds after immersion. Because of alkalinity of the surface under the blisters, adhesion fails. Consequently on these areas blistering will become more and more severe. This is very serious, and has to be considered with each ship treated in this way. It points also to consequences of the initial blistering of such systems and this is not limited to zinc primers, but found on many ship bottom systems.

To avoid these difficulties, all immersed steel should be treated adequately at once, with coatings of the lowest possible permeability to water, oxygen ions, etc., and the highest electrical resistance.

Singleton and Wilson (4) have pointed to the strong reactions of droplets on the blasted steel of old ships' hulls. In our laboratory we have never observed these droplets. But with agar, an indicator and potassium ferro-cyanide, and also with wet Universal pH paper, we have found both alkaline and acidic areas.

We also observed, that the more sophisticated systems — e.g. the chlorinated rubber (6137) and coaltar epoxy —, if properly applied, left less traces, compared with low grade and conventional hull paints.

We have even found the impressed corrosion effect on the steel in zinc-sprayed steel panels. The permeability of the

coating also influences the performance; if there are two systems on one panel, the one with the lower permeability will be more readily attacked. This has been confirmed by our observations.

## CONCLUSIONS

The mechanical treatment of steel creates anodic areas by preference, which influence the behaviour of coating system applied on the panel. Once the anodic and cathodic areas have been activated after immersion, it is very difficult, if at all possible, to remove the impressed corrosion effect by shotblasting. This is contrary to accepted ideas. To minimise these difficulties, sophisticated ships' bottom coatings should be used with the lowest possible permeability to water, oxygen and ions, and high electrical resistance.

## ACKNOWLEDGEMENT

The author wishes to acknowledge the permission to publish this paper by the management of Royal Paint & Varnish works Molyn & Co. N.V., Rotterdam and also the discussions with his colleagues in the Transocean Marine Paint Association.

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## DISCUSSION

TH. F. BIRKENHEAD (England): Dr. de Vlieger mentioned in his paper the action of red lead in chlorinated rubber passivating the surface of the metal. As red lead can not act in the normal way in chlorinated rubber, how does he explain this?

Dr. de VLIEGER: In my paper I have pointed out that red lead cannot act as in oil based vehicles: the formations of lead soaps which passivates the surface and influences the permeability. With chlorinated rubber binders this is not possible; but many trials have shown that red lead is also effective in this case. Also from our trials this can be noticed. I cannot fully explain this phenomenon.

Dr. WILSON (England): I think that one reason for the persistence of the rust patterns after shotblasting is certainly the presence of deep-seated rust pockets, but I should like to mention another possible cause. This is an effect similar to that mentioned in Dr. U. R. Evans' book where he observed that it is easier to preserve passivity on an anode that is already passive than to produce it on an anode that is active at the outset. We observed what we regard as a very pertinent consequence of this fact. When a ship was being launched the paint was slightly damaged in some areas by the drag chains. During the subsequent fitting-out DC welding was carried out while the ship was not properly earthed.

A heavy current passed from the ship to the sea water and severe pitting developed in the damaged areas. Unfortunately the corrosion did not stop when the welding current was switched off. The corrosion sites remained very active and within a few months the pits were so deep that the damaged areas had to be cut out of the ship and replaced. I regard this as a demonstration of the fact that once a corrosion site becomes active it is likely to remain active.

Dr. De VLIEGER: Well I have pointed out that first the anodic sites are created, then the cathodic ones are activated and then with the following system you get the reverse action.

I think that it is a very important question, I can also add Mr.

Wilson, that when we put these pannels in our laboratory the attack was much quicker if the salt spray cabinet worked, providing chloride ions in the laboratory atmosphere.

To this I may add that we never observed the formations of droplets with a low pH, as pointed out in your paper.

This is of course due to the conditions answer to Mr. Gabrillac.

C. CABRILLAC (France): Before I ask a question to the speaker I would like to confirm that Mr. Wilson recently said its a fact, it has been proved in laboratory its easy from the technological point of view that a ferritic steel 17% Cr with distorsions in the elastic range, which indicate potential variates more electronegative, showed a lower resistivity.

I would like to ask you what method did you use in order to identify the anodic and cathodic zones on your experimental plates.

Dr. De VLIEGER: It is somehow difficult to find the cathodic and anodic areas. We have done this in two ways. By visual inspections we find pitted areas, these must be anodic. We have also estimated the pH of fluids in the blisters. We observed in agreement with Driscoll; that the small blisters — if still present — contained a solution with a low pH, and the large ones with a pH of about 10. We have shown in one slide the bare metal, without corrosion products. Another method is to pour out an agar solution on the plate with potassium ferrocyanide and phenolphthaleine: anodic and cathodic areas are consequently marked by different colours (blue and red).

We have tried to immitate the measurements described by Driscoll with a small reference cell, but we did not manage to get this done in the proper way.

A.M. VAN LONDEN (Holland): I should like to make a little comment on the action of red lead in chlorinated rubber paint.

I think that in the first place red lead has a stabilizing effect on the chlorinated rubber itself. Secondly I presume that red lead is reacting with chloride ions which will penetrate the paint film, forming the more soluble lead chloride which may act as a passivator for steel.

**Séance - Meeting - Sitzung - Συνεδρίασις**  
**23.9.1968**

**Présidence - Presidency**  
**Präsidium - Προεδρείον**  
**Prof. F. ROGOWSKI (Deutschland),**  
**Prof. TH. KOUYOUMZELIS (Grèce).**

# EXPERIMENTAL SURFACE TREATMENT OF BLAST-CLEANED SHIP-PLATE

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British Steel Corporation.  
London, ENGLAND

## SUMMARY

It is nowadays common practice in the ship-building industry to blast-clean plates and sections before fabrication, and often the clean steel is primed immediately after blast-cleaning. As a result of this development, construction is usually on millscale-free steel, carrying a protective coating. Much greater use is also being made of prefabrication.

In these changed circumstances, many shipbuilders needed guidance in selecting the schedule of operations that would give the best long-term protection of the hull. Since weathering was no longer a necessity for the removal of millscale, it was decided to investigate possible alternative schedules for protection of the immersed outer-bottom plates.

The main objective of the research was to discover whether

better long-term protection of the hull would result from allowing the scale-free steel hull to rust on the stocks without any protection until just before launching; from delaying application of the primer until prefabrication was complete; or from coating the blast-cleaned steel with a prefabrication primer immediately after blasting.

Good protection against atmospheric corrosion was obtained with several prefabrication primers of known formulation. With each of the three schedules, and using either a conventional or a high-duty anticorrosive composition, it was found to be practical to protect the steel against sea water corrosion in the absence of heavy scaly rust.

## INTRODUCTION

The practice of shot-blasting to remove the millscale from steel plates that are to be used for the construction of ships has become almost universal. When the present work began, acceptable durabilities had been claimed for particular painting schemes applied over specified prefabrication primers on blast-cleaned steel for immersed outer-bottoms<sup>1</sup>. However, no direct experimental work had been published to show how the performance of any given anticorrosive composition varied with different possible fabrication and painting schedules.

The paper describes experiments carried out using three different orders of surface preparation; five prefabrication primers\*, and two anticorrosive paint schemes suitable for immersed outer-bottom plates.

The aims of the research were threefold:

- (i) To compare and evaluate three schedules for the surface treatment of blast-cleaned ship-plate for the outer-bottom plates of seagoing vessels.
- (ii) To compare surface treatments that can be applied on the stocks to millscale-free but rusted ship-plate before painting.
- (iii) To contribute, if possible, towards the development of prefabrication primers or other protective schemes for blast-cleaned ship-plate.

The three schedules considered in the main tests are listed below.

- (A) Blast-clean, prefabricate, construct on the stocks, then carry out the final surface preparation and painting.

- (B) Blast-clean and prefabricate, then prime the steel before it leaves the shop.

- (C) Blast-clean and prime immediately, prefabricate and then construct on the stocks.

Atmospheric weathering tests were carried out in two shipyards on the North East Coast of England, (Sunderland and Wallsend-on-Tyne). The sea-immersion trials were staged on a raft at Caernarvon, North Wales. The immersion tests continued for either one or two years. After this, maintenance repainting of successful schemes was undertaken. These will be reported upon separately at a later date.

The relative merits of a range of possible prefabrication primers was established by preliminary trials using the BISRA rotor apparatus<sup>2</sup>. These are described first.

## 2. ROTOR TESTS

### 2.1 Introduction

Mild-steel panels measuring 100 × 50 × 3 mm were used for the rotor tests. Nine prefabrication primers of known-compositions, representing types available commercially (1961), and two sprayed metals, were applied to prepared surfaces and weathered for five months before overcoating and testing in duplicate on the rotor. Replicate freshly-prepared specimens were also tested in the rotor at the same time.

### 2.2 Preparation of the Specimens

The specimens to be painted were shot-blasted by a technique that produced a surface profile similar to that obtained on ship-plate in British yards; those for metal spraying were grit-blasted.

The following paints were used as primers.

\* Three of these were paints and two were metal coatings.



BISRA  
Paint  
No.

Description

756	Two-pack pretreatment primer.
757	Two-pack phenolic-modified pretreatment primer.
758	Aluminium/epoxide ester primer.
759	Aluminium/chlorinated rubber primer.
760	Aluminium/isomerised rubber primer.
761	Zinc-rich/cold-cured epoxide primer.
762	Zinc-rich/polystyrene primer.
763	Polybutyl methacrylate lacquer.
764	Vinyl co-polymer lacquer.

Two sprayed metals (aluminium and zinc) were also used as primers their coating thickness being deliberately kept down to an unusually low value.

### 2.3 Weathering of Rotor Specimens

The eleven primers were applied by spray, and dry coating weights were recorded. A scratch was cut down the centre-line of the front face of each specimen before exposure. The specimens were then weathered for five months at an angle of 45°, facing South on the roof of the BISRA Battersea Laboratories in London. They were then removed, inspected and weighed.

After weighing, the specimens were cleaned by hand with a dry bristle brush, and were then painted with either three coats of BISRA anticorrosive composition No. 655 or two coats of paint No. 670. The former is in an oleoresinous medium, the latter in a coal-tar epoxide medium. Details of these two paints are given in the Appendix.

At the same time additional specimens were blast-cleaned and coated with the same complete schemes without an intervening weathering period. Fifty-nine of the specimens were bolted on the outer rings of the two BISRA rotors, and the rotors filled with artificial seawater of the following composition (g/litre).

Sodium chloride	36.1	Potassium chloride	0.93
Magnesium chloride	9.85	Potassium bromide	0.13
Magnesium sulphate	4.85	Sodium bicarbonate	0.13
Calcium sulphate	1.84		

The tests were continued (renewing the solution at intervals as necessary) for a total of six months. The rotors would not accommodate all the eleven schemes at once, so the preparation of specimens carrying the remaining schemes was scheduled to be completed by the end of the first test. When this time arrived, a second rotor test using the remaining schemes was started. This test was also continued for six months.

### 2.4 Discussion and Results

The BISRA rotor apparatus is believed to give a fairly good representation of conditions near the waterline on a moving ship. There is a tendency, however, for a greater amount of fine blistering to develop than in actual service conditions.

The most important result relates to the reference schemes, in which a prefabrication primer was omitted altogether and the outerbottom paints were applied directly to the freshly shot-blasted steel surface. On these, the only breakdown of the pitch epoxide paint No. 670 that occurred in the six months' rotor test was very fine blistering, while the BISRA paint No. 655 developed many fine blisters and some rust staining. Where paint No. 670 was applied over several of the prefabrication primers, especially if these were weathered, a poorer result was obtained. However, paint No. 670 was still virtually intact after six months over primers Nos. 756, 757, 761 and 763 irrespective of whether or not they had been weathered before over-painting. Paint No. 670 was, moreover, also virtually intact over weathered primers Nos. 759 and 764, and unweathered sprayed aluminium.

When paint No. 655 was used, primers Nos. 756, 757 and 761 all suppressed the fine blistering, even when they were weathered before completion of the painting, although on weathered primer No. 761 some flaking from a large broken blister occurred. An improved performance of paint No. 655 also resulted from the use of primer No. 759 (weathered or not), and from the use of unweathered sprayed aluminium. Several of the prefabrication primers led to a significantly poorer performance of paint No. 655 than when it was applied without a primer to freshly blastcleaned steel. These were primer No. 762 (weathered or not), unweathered primer No. 763, weathered sprayed aluminium, and sprayed zinc (weathered or not).

## 3. ATMOSPHERIC EXPOSURE AND SEA-IMMERSION TESTS

### 3.1 General

Three of the paint primers and the two sprayed metals, followed by one or other of the two outer-bottom paint schemes mentioned above were used for the main weathering and sea-immersion tests. The three practical schedules discussed in the introduction were simulated on 380 × 250 × 6 mm test panels of ship-plate quality mild steel, by blast-cleaning the steel to a texture resembling as closely as possible that obtained in shipyards, and either (A) weathering the specimens outdoors, then treating the rusted surface in a variety of ways before applying an anticorrosive paint; or (B) exposing the specimens indoors for 2 months (the prefabrication period), then cleaning and priming before weathering; or (C) coating the specimens immediately with a prefabrication primer or equivalent protective scheme followed by weathering. Three periods of outdoors weathering were used to simulate shipyard practice. These were one month, six months and twelve months. The schedule of tests can be seen from the Table of Results (Table I). All tests were conducted on duplicate specimens. Additional pairs of specimens, both in the bare condition, and in the primed condition were exposed on each occasion.

In May and June 1962, 184 specimens were prepared, painted and immersed in the sea at Caernarvon. These included specimens that had been exposed at Sunderland for periods of one or six months.

In April 1963, 38 specimens from Sunderland and 6 specimens from Wallsend-on-Tyne were removed from exposure. All these specimens had been weathered for one year. Thirty-eight of them were cleaned and painted in the BISRA laboratories Battersea then immersed in the sea at Caernarvon.

### 3.2 Preparation of Specimens

The specimens for the main tests were taken from a single heat of steel. The five prefabrication primers used for the weathering and immersion tests were No. 757 (phenolic-modified pretreatment primer), No. 758 (aluminium/epoxide-ester primer), No. 761 (zinc-rich/cold-cured epoxide primer), a thin coating of sprayed metallic aluminium, and a thin coating of sprayed metallic zinc. Details are given in the Appendix.

All specimens except those to be metal-sprayed were shotblasted in an airless centrifugal plant using S230 cast steel shot. The three priming paints were then applied using a conventional gravity-feed air spray gun. The specimens to be metal-sprayed were grit-blasted with grade No. 24 chilled cast iron grit using a 10 mm nozzle at 5 kg/cm<sup>2</sup>. They were then metal sprayed using 5 mm aluminium wire, or 3 mm zinc wire. Some difficulty was experienced in keeping the coating thickness down to the 13 microns specified. All coated specimens were then welded on one face near the edge with a hand electric arc to give a run of weld metal 20 mm long × 6 mm wide and a scratch was cut diagonally across one corner through the coating on the other face of the specimen.

**T A B L E I**  
**SUMMARY OF CONDITIONS OF PAINTS IMMERSERD AT CAERNARVON (AFTER 12, 22 OR 23 MONTHS IMMERSION)**

INDOOR WEATHERING PERIOD (UNPAINTED)	NONE												2 MONTHS																																								
	NONE						NONE						757		758		761		Zn*		Al		757		758		761																										
	0	1	6	6W	12	12W	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6	12	1	6
<b>INITIAL PROTECTION APPLIED:</b>  <b>OUTDOOR WEATHERING(1) PERIOD (MONTHS)</b>																																																					
<b>FURTHER TREATMENT</b> <b>OUTER-BOTTOM PAINT NO. 655</b> No cleaning Mechanically wire-brushed Hand wire-brushed Washed with fresh water Hand wire-brushed + phosphoric acid wash Hand wire-brushed + pretreatment primer 756 Hand wire-brushed + pretreatment primer 757																																																					
<b>OUTER-BOTTOM PAINT NO. 670</b> No cleaning Mechanically wire-brushed Hand wire-brushed Washed with fresh water Hand wire-brushed + phosphoric acid wash Hand wire-brushed + pretreatment primer 756 Hand wire-brushed + pretreatment primer 757																																																					

(1) 6W or 12W means 6 or 12 months' weathering at Wallsend-on-Tyne; all other weathering took place at Sunderland.  
 A = virtually intact  
 B = beginning to break down  
 C = considerable breakdown  
 \* = poor adhesion of top coats

Both bare and primed blast-cleaned steel specimens were exposed to the atmosphere at Sunderland at an angle of 45° facing the sea (approximately E.S.E.) with the scratch uppermost, for periods of one, six and twelve months. At the same time, additional specimens, similarly primed, were exposed to determine the ultimate durability of the coating. As it was suspected that the type of rust formed in some atmospheres might be more difficult to treat than that formed at Sunderland, a few bare specimens were exposed at Wallsend-on-Tyne for six and twelve months.

Panels of another set were shot-blasted and exposed in the prefabrication shop of a shipyard at Sunderland for two months. They were then hand wire-brushed and a prefabrication primer applied. Weathering outdoors at Sunderland followed for one or six months, again with additional specimens to determine the ultimate life of the coating. Just before weathering outdoors began, a 20 mm run of weld metal 6 mm wide was laid down on all these specimens too, near the edge of one face, and a scratch was cut diagonally across one corner of the other face of each coated specimen. They were then exposed with the scratch uppermost.

After atmospheric weathering, the primed specimens were cleaned either by hand wire-brushing, or by washing in fresh running water, or were not cleaned at all. Some additional metal-sprayed specimens were primed, by brush, with paint No. 757 after hand wire-brushing. The weathered bare steel specimens were cleaned either by mechanical wire-brushing or by hand wire-brushing followed by a phosphoric acid wash, or by brush application of primer No. 756 or primer No. 757.

The phosphoric acid wash was prepared according to British Defence Specification D.E.F. 36 and applied according to D.F.F. 38.

The specimens were then painted professionally using a 60 mm brush, either with three coats of BISRA paint No. 655 or two coats of coal tar epoxide paint No. 670. These gave total film thicknesses of 0.13 and 0.2 mm respectively. Successive coats were differently tinted to ensure complete coverage. One thick coat of Admiralty antifouling paint No. 161 P was brush applied on the day before immersion.

Weights of dry paint and other coatings were recorded and, where practical, wet paint weights were taken. Thinner coatings were applied to the specimens weathered for 12 months than to those weathered for 1 and 6 months prepared the previous year because the ambient temperature was higher, and the required thicknesses could not be obtained without sagging of the paint films.

### 3.3 Reference Specimens

At the same time as the set that had weathered at Sunderland for one month was completed and immersed, a small reference set was prepared in which no atmospheric weathering was involved. This set consisted of freshly shotblasted specimens to which paints Nos. 655 or 670 were either applied direct or after the application of pretreatment primer No. 757.

### 3.4 Measurement of Surface Roughness and Profiles of Blast-Cleaned Surfaces

Profiles of selected plates were measured with a plate roughness gauge kindly loaned by the British Ship Research Association. The surfaces were also photographed under standardized oblique lighting conditions at a magnification of twelve. The photographs of blast-cleaned surfaces reproduced in Figures 1 and 2 show the principal surface conditions used in this research.

### 3.5 Results of Weathering Tests on Primers at Sunderland

The Sunderland panels were inspected about every two months throughout the test. In general, the back faces deteriorated much less than the front faces. The durability of the set painted in April was generally better than that of the second set painted in December, but this cannot be wholly

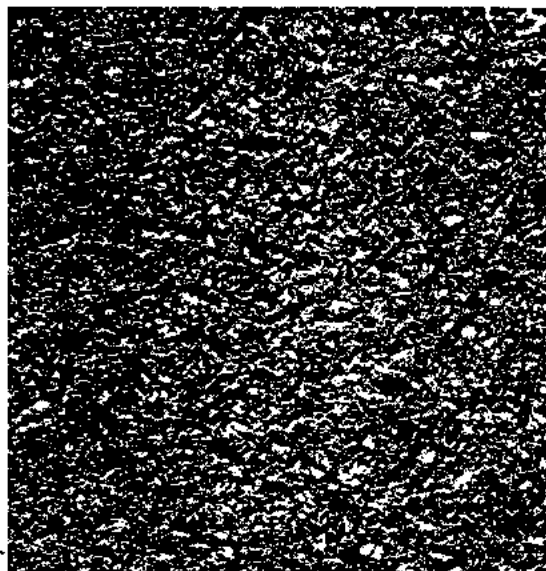


Fig. 1. Surface obtained on specimens to be metal sprayed, December 1961, with grade No. 24 (0.6-1.0 mm) chilled cast iron grit  $\times 12$ .

attributed to the better weather conditions because the thicknesses of the paint films were different for the two sets.

The presence, underneath the paint, of the rust formed by two months' exposure indoors had little effect on the durabilities of primers Nos. 757 and 758, but it was particularly harmful to primer No. 761, which flaked severely after six months' atmospheric exposure where applied over a rusty surface.

At Sunderland the best atmospheric protection of all was given by the thinly-sprayed 13-23 microns coatings of zinc. These allowed no rusting of the steel for one year.

### 3.6 Results of Immersion Tests at Caernarvon

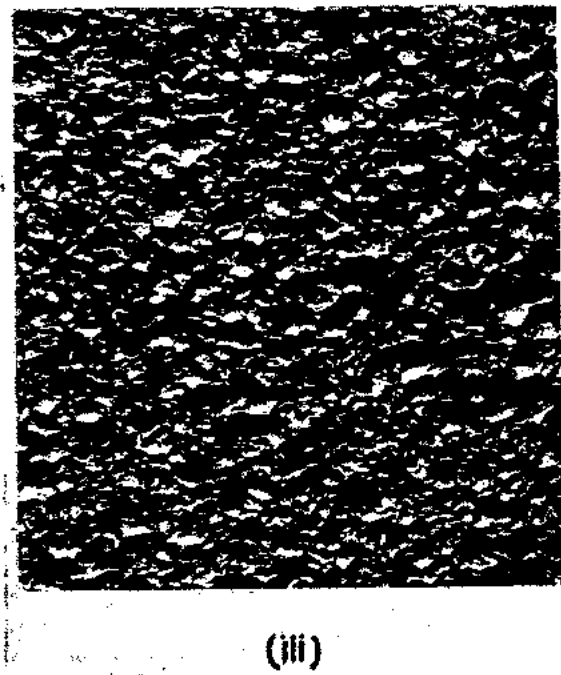
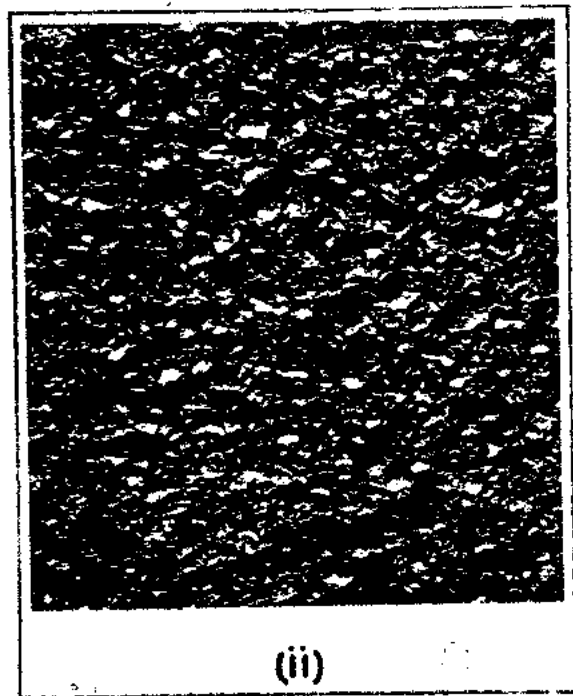
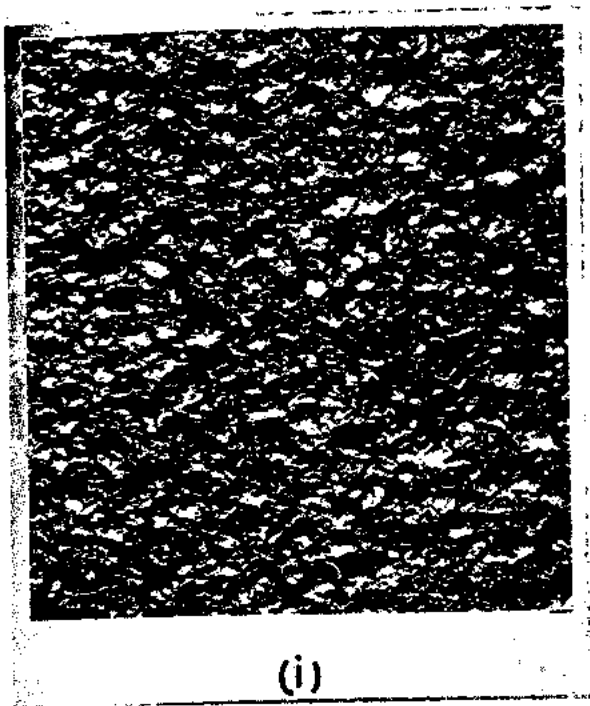
On the Caernarvon raft the anti-fouling paint prevented development of marine growth on all sets of specimens. Regular inspections at intervals of about two months were maintained throughout the test period.

The condition of all sets of specimens after immersion at Caernarvon is summarized in Table I.

*Specimens that had been weathered for one month; one-month sets:* After two years' immersion paint No. 670 was in better condition than paint No. 655. Paint No. 670 was virtually intact over almost all the primers used in this set, but over primer 758 the breakdown was severe. Paint No. 655 was not completely intact on any of the specimens in this set, but for about half the specimens the only breakdown was fine blisters.

*Specimens that had been weathered for six months; six-month sets:* After two years' immersion, paint No. 670 was generally in better condition than paint No. 655; but the range of performance, resulting from different surface conditions prior to application of the anticorrosive paint, was greater than with the one-month set, there being some badly failed as well as some almost intact coatings on specimens painted with either paint.

No breakdown was evident on any of the bare steel specimens which had been allowed to rust, outdoors for six months and were then either mechanically wire-brushed or hand wire-brushed followed by a phosphoric acid wash, or primer No. 756 or primer No. 757 before painting with paint No. 670 but the outer-bottom paint on specimens rusted indoors for two months then primed and weathered for six



**FIG.2 SURFACES OBTAINED ON THE PLATES FOR THE RAFT TRIALS, IN (i) OCTOBER 1961, (ii) DECEMBER 1961 AND (iii) FEBRUARY 1962, WITH GRADE S230 (0.6-1.0 mm.) CAST STEEL SHOT. X12**

months had broken down to differing extents. Prefabrication primer No. 758 was the best of the three primers under these latter circumstances, the use of Nos. 757 and 761 each having led to one moderate and one poor result. When the same three primers were applied directly to freshly shot-blasted steel then weathered for six months before application of paint No. 670, this paint remained virtually intact after two years' immersion. Over the two sprayed metals, some blistering had occurred.

On the specimens carrying paint No. 655, fine blisters had

developed in two years in many instances. If fine blisters (less than 2 mm diameter) are ignored when they cover less than 2 per cent of the surface (since past experience shows this amount to do little harm), it can again be said that no appreciable breakdown of the outer-bottom paint had occurred over bare steel allowed to rust for six months before being painted. With specimens rusted indoors before priming, paint No. 655 had developed some degree of failure over all three paint primers, but failure was less advanced for primers Nos. 758 and 761 than for primer No. 757, over which the

outer-bottom paint was in very poor condition. Application of the same three primers directly to freshly shot-blasted steel, followed by six months' weathering, led to mixed results in the immersion trials. The use of sprayed aluminium and sprayed zinc on the freshly blast-cleaned steel, followed by six months' weathering, led to blistering of paint No. 655 during immersion.

*Specimens that had been weathered for twelve months: twelve-month sets:* There was little to choose after one year's immersion between paints No. 655 and 670 in this small set. Paint No. 670, showed poor adhesion and massive flaking to bare metal after immersion, where it had been applied over specimens that had been weathered in the bare condition then hand wire-brushed and primed with No. 756. The corresponding specimens weathered bare and then hand wire-brushed and primed with No. 756 before finish painting with paint No. 655, behaved similarly to those painted with paint No. 670. Where, however, the specimens had been treated after weathering by mechanical wire-brushing or hand wire-brushing, followed by either a phosphoric acid wash or primer No. 757, the breakdown that occurred of paint No. 655 was less than that of paint No. 670. The paint on specimens weathered bare at Wallsend behaved similarly to that on those weathered at Sunderland. No breakdown of either of the two outerbottom paints had occurred on specimens that had been primed with Nos. 758 or 761 then weathered, but there was some blistering of specimens that had been primed with No. 757 then weathered. Flaking of both outer-bottom paints had occurred on specimens which had been sprayed with metallic aluminium or zinc then weathered.

### 3.7 Discussion and Results for Individual Primers

Results for the five individual prefabrication primers are summarized and discussed below.

#### (a) Phenolic-modified pretreatment primer (Primer No. 757)

The performance of the outer-bottom paints was good over this primer if it had been weathered for one month only. Moreover, with such a short period as this on the stocks, pre-rusting of the steel indoors before priming appears to be acceptable. Where pre-rusting indoors was followed by six months' outdoor weathering in the primed condition, however, it led to poor performance of the anticorrosive paints. In practice, therefore, if the steel has become rusty indoors, it may be better to defer the application of this pretreatment primer until the outdoor weathering is complete, since this primer gave good results in conjunction with both outer-bottom paints when applied to bare steel that had been weathered for six months then treated by any of several different methods.

When this primer was applied directly to freshly blast-cleaned steel, it gave a satisfactory basis for finish painting after six months' weathering provided it was hand wire-brushed.

The good result obtained for outer-bottom paints applied to primer No. 757 after one year's weathering possibly arises from the virtual loss of the primer followed by a short period of rusting.

It should be noted that application of primer No. 757 straight on to freshly blast-cleaned steel followed by the application of one of the outer-bottom paints without delay, as might occur in repair work, gave a better result than was obtained by omitting the primer, but neither gave such a good result as was obtained by allowing the primer to weather for one or six months before application of the outer-bottom paint.

#### (b) Aluminium/epoxide-ester primer (Primer No. 758)

Provided it had been thoroughly wire-brushed before being over-painted, this primer gave satisfactory results, (although, from supplementary observations, its adhesion to the steel in

service appears to have been only just sufficient). When used over steel rusted indoors for two months, it gave a better performance with paint No. 670 than it did with paint No. 655. As with primer No. 757, the good result after one year's weathering may simply indicate virtual loss of the primer followed by a short period of rusting of the bare steel.

#### (c) Zinc-rich/cold-cured epoxide primer (Primer No. 761)

This primer, when applied over steel that had been allowed to rust indoors for two months, flaked after six months' atmospheric weathering, and had to be removed before over-painting, i.e. an uncleaned surface could not be tested. In the subsequent immersion test, both outer-bottom paints gave only moderately good results on these samples, unless the primer was washed down before over-painting.

Good immersion-test results were obtained, with one exception where this primer was applied to freshly blast-cleaned steel and then weathered for one, six or twelve months.

#### (d) Thinly-sprayed aluminium

With one exception, (a weathering period of one month followed by hand wire-brushing and primer No. 757) this did not give good results under paint No. 655 when immersed. However, when used in conjunction with paint No. 670 better results were obtained, and up to six months weathering appeared acceptable.

#### (e) Thinly-sprayed zinc

Although averaging less than 25 microns in thickness, not very evenly applied, the sprayed zinc completely protected the steel in the atmosphere for at least a year. It was, therefore, disappointing that poor immersion-test results were generally given by this surface preparation when used in conjunction with paint No. 655. The exception was a long weathering period followed by the use of pretreatment primer No. 757. As with thinly-sprayed aluminium, better results were obtained when used under paint No. 670, but priming with paint No. 757 appeared to be advisable before over-coating.

## 4. DISCUSSION AND CONCLUSIONS

Although all five prefabrication primers gave satisfactory weathering protection to the steel for at least six months, the thin coatings of sprayed metallic zinc were the most effective. Unfortunately, the erratic performance of the outer-bottom paints subsequently applied over the sprayed zinc make it impossible to recommend this scheme for use at present.

Somewhat better results were obtained, in the immersion tests with the thicker pitch-epoxide coating No. 670 (approx. 0.2 mm) than with paint No. 655 (approx. 0.13 mm).

The condition of the surface to which these paints were applied had a profound effect on their life, especially from the point of view of loss of adhesion during immersion.

Application of either of the two paints (No. 655 or No. 670) direct to freshly shot-blasted steel did not give satisfactory results. The use of pretreatment primer No. 757 in this condition, however, improved matters, and, with paint No. 670, gave complete protection to the steel for two years. In normal shipyard practice, however, it is only during repair work that the above circumstances are likely to apply. During ship construction a period of atmospheric weathering before or after priming is almost inevitable.

The first possibility is to build the ship in descaled, but uncoated, steel. In these experiments, when the bare shot-blasted steel was allowed to weather for one or six months and was then cleaned with a mechanical wire-brush, or by a hand wire-brush followed either by a phosphoric acid wash, or by either of the two pretreatment primers, Nos. 756 or 757, both of the anticorrosive paints (Nos. 655 and 670) gave complete protection to the steel for two years. When the initial weather-

ing period was extended to one year, however, both anticorrosive paints had failed within a year after immersion. Whether this was due to the extended initial weathering period, the condition of the rust at the time of painting or to the thinner coatings (0.08 mm and 0.13 mm respectively) of anticorrosive paint applied at this time cannot be determined.

The second possibility is to leave the steel unpainted until after prefabrication, then to wire-brush and protect it before it is taken outdoors. The present experiments included one such period of indoor rusting before priming. When, after priming the rusted and wirebrushed steel, only one month's weathering elapsed before the anticorrosive paint was applied, reasonable or even good performance of the anticorrosive paint was achieved. When six months' atmospheric weathering preceded the final painting, however, the performance of the anticorrosive paints varied from good to bad, with no clear correlation with the type of primer used or the method of preparation for the final painting. On the whole, paint No. 670 tended to be better than paint No. 655, yet one of the worst results in this group was with paint No. 670 (over primer No. 761), hand wire-brushed).

The third possibility is to apply a prefabrication primer immediately after blast-cleaning. Although good results have been obtained by applying paint over rusty steel not only in these but in other trials, this procedure cannot be recommended because of the inherent dangers: no control of the form, amount or chemical composition of the rust is possible. An equally good and far more consistent performance was obtained from the anticorrosive paints when the primers tested were applied to the steel immediately after blast-cleaning. These primers, however, varied in their ability to protect the steel in the atmosphere, and the treatment after weathering affected their performance when immersed, and deserves further study.

Good protection against atmospheric corrosion was obtained in these trials with several of the primers tested, and with suitable selection of the treatment at each stage it appears to be possible, provided heavy scaly rust is removed to protect outer-bottom plates immersed in sea water by whichever schedule is preferred.

Nevertheless because no control is possible, the formation of rust is best avoided at all stages of construction. This implies the application of at least the priming coat before the hull plates are exposed to the weather.

When the immersion tests described in this paper were completed, the specimens on which the coatings had not failed were retained for maintenance painting trials so as to confirm that the adhesion of the systems to the steel remained adequate over extended periods. The surviving specimens have now been repainted twice, and have been immersed for a total of either 4 or 5 years, specimens with more than 2% breakdown being withdrawn at each repainting.

A report on these trials will be published separately.

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3. K.A. Chandler and J.F. Stanners: «Preparing the surface of steel for painting» (in French). *Peint. Pig. Ver.*, 1965, 41, 532.
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## APPENDIX

### PAINT FORMULATIONS

Paint No. 756. Two-pack pretreatment primer  
(This paint conforms to Mil-C-15328A)

Base	Composition	% by weight
	Polyvinyl butyral resin	7.2
	Zinc tetroxychromate	7.0
	Asbestine	1.0
	n-Butanol	16.1
	Industrial methylated spirits	48.9

#### Activator

Phosphoric acid (S.G. 1.5)	3.6
Industrial methylated spirits	16.2
	100.0
	====

#### Properties

Pigment/binder ratio by weight	0.78/1
Total volatile content (S.G. 0.815) by weight	81.2%
Density	(0.9 kg/l)
Drying time: Surface dry (B.S.I. method)	10 min
Hard dry	30 min

Paint No. 757. Two-pack phenolic-modified pretreatment primer

Base	Composition	% by weight
	Polyvinyl butyral resin	4.7
	Bakelite resin R-17620 (A heat-hardening phenolic resin soluble in methylated spirits (m.p. 44-55°C))	4.7
	Methyl ethyl ketone	25.85
	Methylated spirits (68 O.P.)	26.6
	Zinc tetroxychromate	8.6
	Asbestine	1.4

#### Activator

Butyl alcohol	25.85
Phosphoric acid (S.G. 1.7)	2.3
	100.0
	====

#### Properties

Pigment/binder ratio by weight	0.88/1
Total volatile content (S.G. 0.8) by weight	78.65%
Density	(0.91 kg/l)
Drying time: Surface dry (B.S.I. Method)	30 min
Hard dry	—

**Paint No. 758. Aluminium/epoxide ester primer**

Composition	% by weight	
	1st batch	2nd batch
Leafling aluminium paste (65% in white spirit)	20.0	25.3
D4 epoxide ester medium	43.0	54.4
6% cobalt naphthenate	0.2	0.25
Xylol	36.8	20.05
	100.0	100.00
	===	===

**Properties**

Pigment/binder ratio by weight	0.605/1	0.505/1
Total volatile content (S.G. 0.86) by weight	65.5%	56.15%
Density	(1.04 kg/l)	(1.04 kg/l)
Drying time: Surface dry (B.S.I. method)	30 min	30 min
Hard dry	5 h	5 h

**D4 Epoxide ester medium**

Composition (both batches)	% by weight	
Di-epoxide resin (epoxide equiv. 870-1025)	30.4	
Dehydrated castor oil fatty acids	19.6	
Xylol	50.0	
	100.0	
	===	

**Method:** Components mixed and heated together at about 238°C., then thinned.

**Paint No. 761. Zinc-rich/cold-cured epoxide primer**

Composition	% by weight	
<b>Base</b>		
Di-epoxide resin (epoxide equiv. 450-525)	4.0	
Bentonite amine derivative	0.5	
Ethyl glycol	4.0	
Xylol	4.73	
Zinc dust	82.6	
<b>Curing agent</b>		
Ethylene diamine adduct of the di-epoxide resin	1.67	
Ethyl glycol	1.25	
Xylol	1.25	
	100.00	
	===	

**Properties**

Pigment/binder ratio by weight	14.5/1
Total volatile content (S.G. 0.901) by weight	11.23%
Density	3.5 kg/l
Drying time: Surface dry (B.S.I. method)	15 min
Hard dry	1 h

**Anti corrosion Paint No. 655. Basic lead sulphate/aluminium powder/Burntisland red in modified phenol-formaldehyde/stand oil/tung oil medium**

Composition	% by weight
Basic lead sulphate (B.S. 637:1935)	19.14
Aluminium powder, non-leafling grade, (metallic content 65%)	14.74
Burntisland red	9.57
Barytes	9.57
Medium	34.65
White spirit	1.38
Lead naphthenate (6% Pb) drier	0.26
Manganese naphthenate (6% Mn) drier	0.09
Naphtha	10.60
	100.00
	===

**Properties**

Pigment/binder ratio by weight	3.6/1
Total volatile content (S.G. 0.808) by weight	28.8%
Density	1.40 kg/l

**Medium**

Composition	% by weight
Modified phenol-formaldehyde resin	22.3
Stand oil (60-poise)	22.3
Tung oil	22.3
White spirit	32.2
Lead-manganese driers	0.9
	100.0
	===

**Method:** Heat the stand oil with half the resin to 280°C in 3/4 h and hold to a long string. Add the remainder of the resin and dissolve this at 240°C. Add the tung oil and hold at 240°C to a long string (approx. 1/2 h). Cool to 180°C, thin with the white spirit and add the driers.

**Anticorrosive Paints Nos. 669 and 670. Two-pack coal-tar epoxide paint.**

(N.B. The undercoat was called No. 669, the top coat No. 670)

Composition	% by weight	
	Undercoat (669)	Top coat (670)
<b>Base</b>		
Di-epoxide resin (epoxide equiv. 450-525)	10.6	10.6
Coal tar fraction («U.C.C. No. 3 pitch»)	31.7	31.7
Asbestine	10.9	21.8
Red oxide	10.9	—
«Aerosil»	0.8	0.8
Xylol	11.0	11.0
Ethyl glycol («Oxitol»)	11.1	11.1

**Curing agent**

Ethylene diamine adduct of the diepoxide resin	5.2
Toluene	2.6
n-Butanol	2.6
Ethyl glycol («Oxitol»)	2.6
	100.00
	===

*Properties*

Pigment/binder ratio by weight	1.2/1
Total volatile content (S.G. 0.895) by weight	29.8%
Density (No. 699)	(1.28 kg/l)
(No. 670)	(1.27 kg/l)

*Admiralty Anti-Fouling Paint No. 161 P.*

*Composition*

Cuprous oxide	57.88
Asbestine	2.39
Chlorinated diphenyl (54% chlorine)	5.38
Medium	5.38
Rosin WW grade	16.14
Solvent naphtha	13.33

100.00  
===

*Medium*

*Composition*

	% by weight
Modified phenol formaldehyde resin	32.25
Medium stand oil (50 poise)	64.50
Lead naphthenate (24% lead)	1.95
Manganese naphthenate (6% manganese)	0.81
Cobalt naphthenate (6% cobalt)	0.49

100.00  
===

DISCUSSION

M. BARRILLON (France): If I have correctly understood Messrs Stanners and Watkins, leave the choice between the methods B. and C. It exists a combined method, consisted in using a shop primer, applied, immediately after gritblasting and in applying one or more layers of final paint, when the prefabricated element is still in the workshop. This method seems especially economical for tankers where we paint the insides and the outsides. Naturally care must be taken to leave zones without paint at the ends of the prefabricated elements for welding. I would like to know what Messrs Stanners and Watkins think about this method.

K. WATKINS: Thank you Mr. Barrillon. If you can blast clean and apply the primer immediately or even go farther and apply some of the covering paints in the shop this is good practice. The biggest problem however is the necessity for a large shipyard because your painting shop needs to be much the same size, as your priming and prefabricating shop and have similar handling facilities. If, however, you prime immediately in smaller parts then prefabricate in the shop touching up the welded and damaged areas, but carry out the cover painting on the stocks you will not need so large a space.

I hope I have answered your question.

Dr. HOAR (England): What was the composition of the zinc-rich epoxide primer? Did it give a zinc-rich conducting film, that would need 94% or more zinc metal in the final dried film. From the figures you give here, it would be less than 90%. Could you tell us whether the film was in fact electrically conducting when dry, or was it not? There are zinc primers that we sometimes use with as little as 60% zinc; these are frequently non-conducting but nevertheless are extremely good primers. Zinc in epoxy resin primers is really more as a filler than having any cathodic protection action: It is the epoxy resin that is the real protective.

K. WATKINS: Thank you Dr. Hoar. I have always understood that this particular type of zinc rich paint acted initially to give cathodic

protection to the steel. At a later date it is though to become inert and act as a barrier coating. This is perfectly acceptable however since one of the essential jobs of any coating is to keep the environment from the metal.

T. BIRKENHEAD (England): I would like to ask Mr. Watkins a practical point. I got the impression from his paper that all the paints were brush applied, is that so?

Mr. WATKINS: Thank you Mr. Birkenhead. The cover paints and the primers applied after weathering were brush applied, but the initial primers were spray applied.

T. BIRKENHEAD (England): From my own work on chlorinated rubber primer application to poorly prepared surfaces we found that brush application can, in general, give a better result than spray application. Unfortunately this is out of line with modern shipyard practice since brushing is too slow. Would Dr. Watkins agree that if he had sprayed his paints, particularly the primer, he would have got inferior results?

K. WATKINS: I would expect the results we obtained to be rather better than those obtained in practice however the paints were applied, since the painting was carried out on relatively small plates and obviously much greater control can be exercised under these conditions than in a shipyard.

Dr. KENWORTHY (England): Mr. Chairman, I would like to ask Mr. Watkins what was the thickness of primer he applied. As you know, in practice the primer is applied very thinly to facilitate quick drying and to ease the welding problem.

K. WATKINS: Thank you Mr. Kenworthy. All the primers were applied between 12 and 25 microns thickness.

T. BIRKENHEAD: I notice there was little evidence of fouling on your plates. Were antifouling paints used throughout the series?

K. WATKINS: We use Admiralty antifouling paint 161P over our specimens and this keeps them free of fouling.



# DEVELOPMENT OF ANTICORROSIVE PAINT BASED ON METALLIC MANGANESE PIGMENT AGAINST SEA WATER CORROSION

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## SUMMARY

The paper describes the physical and chemical characteristics of finely divided metallic manganese powder, which have been determined to ascertain its suitability as an anticorrosive pigment in the preparation of paints. The inhibitive property due to lower electronegative potential is enhanced by the ability of the metal powder to scavenge dissolved oxygen and also cause increase in pH to a certain extent.

The protective property of metal pigmented paints based

on manganese powder and zinc powder (control) have been determined by a) electrochemical studies of paint films coated on mild steel and b) raft trials. The electrochemical as well as protective properties of manganese rich paint have been found to be similar to that of zinc rich paint. Incorporation of manganese to the extent of 50 percent in a zinc rich paint has been found to improve remarkably the corrosion resistance and electrochemical property of the paint films.

## INTRODUCTION

The major defence against corrosion of metals in sea water has been the application of paints. The conventional compositions are known to confer protection by processes that have been categorised as, barrier protection or resistance inhibition and anodic passivation. The development of metal pigmented anticorrosive paints, provided a new dimension to the protective action of paints, as these coatings offer cathodic protection to a steel substrate at a certain stage. Development work on metallic primers has been largely restricted to the use of more commonly available metal powders such as zinc, lead and aluminium.

Recently it was shown that finely divided metallic manganese possesses definite anticorrosive properties and could protect steel in sea water<sup>1</sup> and in inland atmosphere<sup>2</sup> when used as a pigment. Moreover, the pigment could be produced indigenously in large quantities unlike zinc or lead. Its possible application as an anticorrosive pigment would be interesting from academic as well as economic point of view.

The present paper describes some of the more important properties of manganese pigment and paint in inhibiting corrosion of steel in sea water. The protective action of zinc rich paints is now generally accepted. A paint formulation with manganese and zinc dust was prepared as suggested by Evans<sup>3</sup> and its protective action based on potential/time study is also reported.

Since mild steel is a leading engineering material in the marine environment, it was selected for studying the protective action of the experimental paints. Moreover, if the protection is effective, then it could be extended to other metals/alloys having similar electrochemical behaviour as steel in sea water.

## EXPERIMENTAL

*Materials and methods:* Powder prepared by disintegrating electrolytic manganese flakes of 99.95% purity, was passed through 300 B.S.S. sieve, and was used in this investigation. The particle size distribution and the specific surface area was

determined by sedimentation process and the air permeability method respectively. An average value for the specific surface obtained was 0.09 sq.m/g and that for the particle size 8-10 $\mu$ . A microscopic examination of the powder revealed the irregular shape of the particles. A typical photomicrograph is shown in fig. (1). The powder floats on water forming a film like layer on the surface. The dark areas seen in the photomicrograph fig (2) are portions of water when the layer formed was broken.

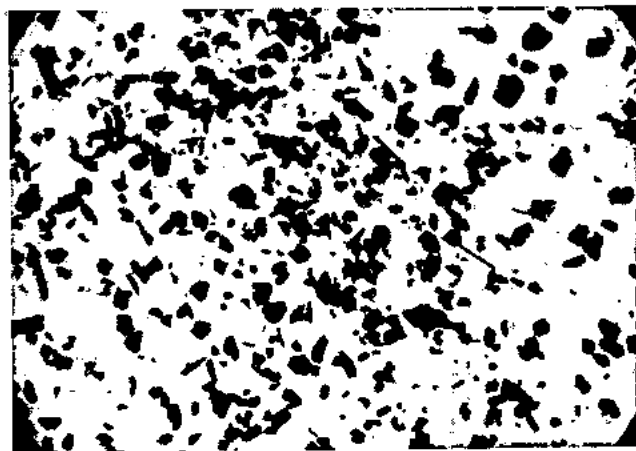


Fig. 1. — Photomicrograph of manganese powder  $\times 200$ .

The paints were formulated with chlorinated rubber medium and plasticized with chlorinated paraffin using xylene as solvent. Weighed quantities of chlorinated rubber and the plasticizer with proportionate amount of xylene were placed in a ground glass stoppered bottles and was slowly rotated with glass balls, on a mill till the dissolution was complete.

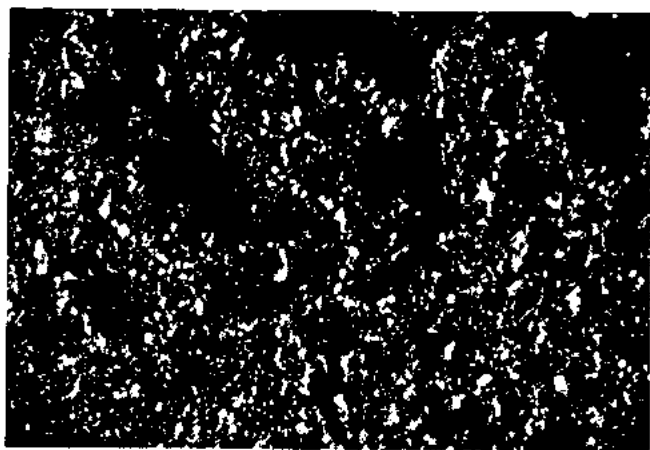


Fig. 2. — Photomicrograph of manganese powder on water. Dark areas seen are portions of water when the layer is broken  $\times 200$ .

A requisite amount of pigment was than added and the rotation was continued till the agglomerates disappeared.

Two types of compositions were formulated. The first was based on manganese powder at 70% pigment volume concentration (P.V.C.) and the second based on the manganese-zinc dust, composite pigment, at similar P.V.C. The addition of antissettling agent was avoided as it may adversely affect the anticorrosive behaviour of the paint. A zinc rich paint was prepared to serve as control in potential measurement. The details of the compositions are shown in table (1). The paints thus prepared could be conveniently applied by brush after thinning with the solvent as necessary.

TABLE 1

Composition of paint formulations based on manganese and zinc dust

Sl. No.	Paint ingredient	% Parts by Wt.		
		Manganese Paint	Manganese-zinc dust paint	Zinc dust paint
1.	Manganese powder	78.4	38.3	—
2.	Zinc dust	—	36.6	76.5
3.	Chlorinated rubber	3.8	3.8	4.0
4.	Chlorinated Paraffin	2.5	2.5	2.6
5.	Xylene	15.3	18.8	16.7
		100	100	100

*Change in electrode potential with time of painted mild steel in sea water:* Mild steel electrodes  $5\text{cm} \times 4\text{cm} \times 0.3\text{cm}$  cut with a  $10\text{cm} \times 0.5\text{cm} \times 0.3\text{cm}$  strip at the top edge centre, were freed from millscale in 5% sulphuric acid and thoroughly rinsed under running tap water and dried. The specimens were then abraded with Oakey emery No. 1 G till a uniform surface was obtained. Degreasing was carried out with benzene and the specimens were stored in a desiccator before use.

Two coats of experimental paints were applied by brush on the duplicate specimens and dried for a period of seven days. The film thickness measured was between 4-5 mils.

The thin strip of the specimens that served as a terminal for electrical measurements, was inserted in the perspex lid

of a beaker and the specimens were immersed in one litre of sea water. Care was taken to keep the upper edge below one inch of the open surface of sea water. Electrode potential of each specimen was determined against a saturated calomel electrode through an agar salt bridge, on a direct reading potentiometer.

Potential readings were recorded at rapid intervals on the first day. Subsequently they were recorded daily. As there was little change subsequently, the potentials were recorded at longer intervals. The immersion was continued for a period of 14 months. Results on potential measurement are shown in Figure 3.

The paint films showed blistering with the exception of manganese rich paint. However in all the cases the specimens showed no signs of visible corrosion for 12 months when manganese rich paint films showed brown spots. All the specimens were removed and examined for any signs of underfilm corrosion. The substrate surface was free from any signs of corrosion fig. (4).

*Reaction of manganese powder with sea water:* Different quantities manganese powder from (0.04 to 1.0g) were separately added to 100 ml of sea water and stirred with a magnetic stirrer. The change in hydrogen ion concentration was recorded using a pH meter and a pair of standard electrodes. Generally, maximum pH value was reached within 20 minutes from the addition of the powder. Similar measurements were made with distilled water.

The quantity of powder added with the corresponding maximum pH value reached is shown in Table 2.

TABLE 2

Effect of manganese powder on pH of Sea water

Sl. No.	Quantity of manganese powder	Maximum pH recorded	
		sea water	distilled water
1	0	8.14	5.66
2	0.04	9.10	8.82
3	0.10	9.28	9.00
4	0.30	9.32	9.22
5	0.50	9.42	9.50
6	1.00	9.52	9.80

The change in the dissolved oxygen content in sea water by manganese powder was determined by standard winkler's method.

One gram of manganese powder was added to 2 litres of clean seawater contained in a 2 liter aspirator bottle fitted with a rubber tube and a pinch cock at the outlet. The mouth of the bottle was quickly stoppered leaving no air bubble inside. The water was stirred with a magnetic stirrer for five minutes and allowed to settle. The dissolved oxygen content was determined. Average of duplicate determinations of oxygen content before and after addition of manganese powder to three different samples is given in Table (3).

*Change in potential over a partially painted mild steel surface in sea water:* Freshly abraded (Oakey No. 1G) degreased mild steel strip  $8\text{cm} \times 3\text{cm} \times 0.2\text{cm}$  was soldered with an electrical lead and painted half area on one side. The other side was thickly coated with an epoxy resin. The paint was dried for a period of seven days in a desiccator and the strip was placed horizontally, in a small perspex tray, the painted surface facing upwards. The electrical lead was connected to a direct reading potentiometer and a tubulus of a standard saturated calomel electrode, mounted on a travelling mechanism, was held just above the painted edge of the strip. Sea water was placed in the tray covering the strip about 3mm above the paint surface and the potential

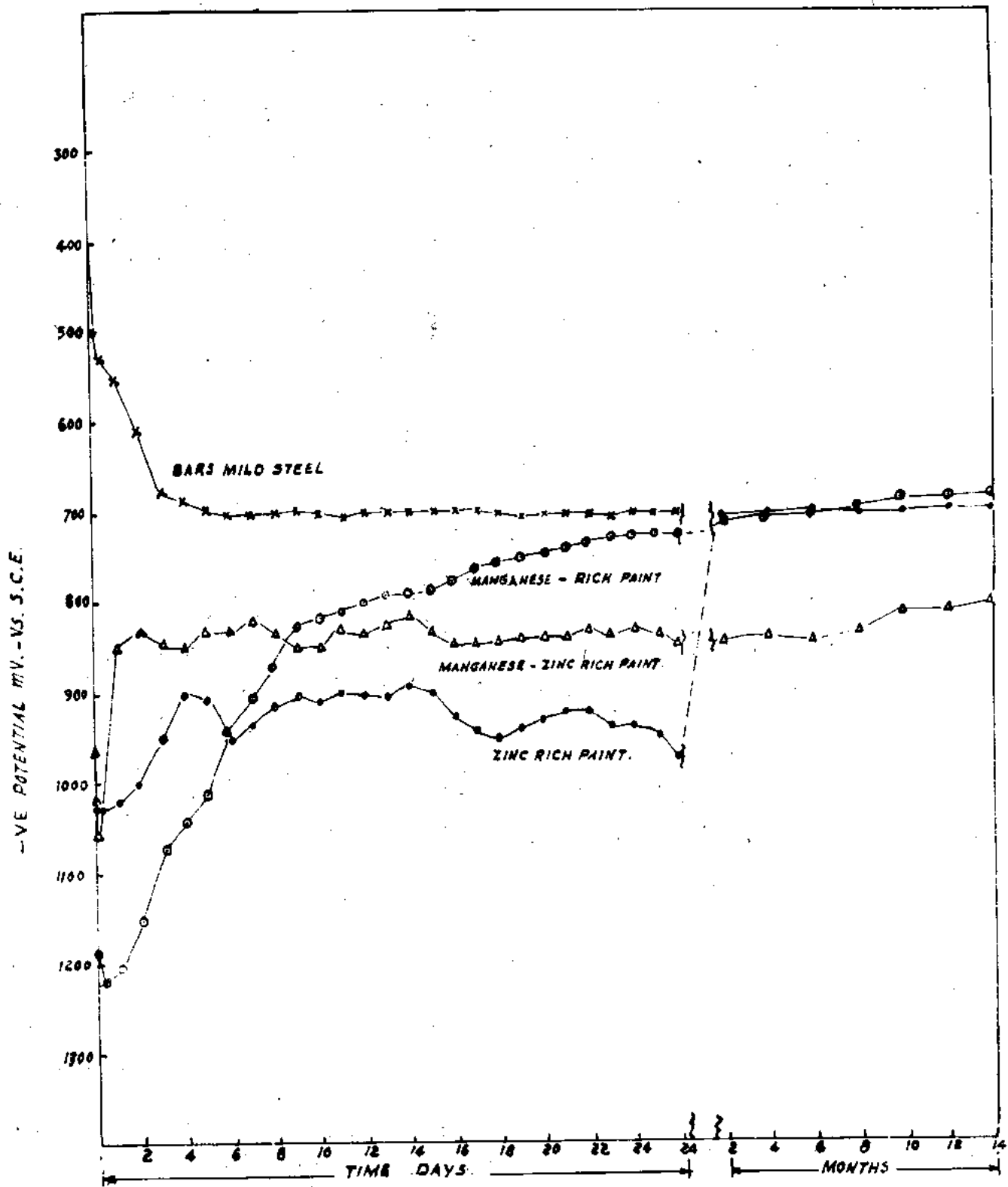


FIG. 3 CHANGE IN ELECTRODE POTENTIAL OF PAINTED MILD STEEL IN SEA WATER.



Fig. 4. — View of the electrodes after 14 months in sea water (upper row) left to right, electrodes painted with manganese-zinc rich, zinc rich and manganese rich paints, (lower row) same specimens after removing the paint film from the lower side.



TABLE 3

Effect of manganese powder on dissolved oxygen in sea water

Sl. No.	Type of sea water	Dissolved oxygen content p.p.m.	
		Before addition of Manganese Powder	After addition of Mn powder
1.	Freshly collected	4.93	0.176
2.	Sample from a storage tank	2.22	0.088
3.	Sample after aeration	7.02	0.176

was determined. The tip of the tubulus was carried forward and the potentials with distance were quickly determined as the probes travelled from the painted end to the bare end.

Measurements were carried out after 0, 5, 10, 20 minutes immersion in sea water.

The change in the potential of mild steel with time is graphically presented in fig. (5).

*Raft trials:* The manganese rich paint was applied on 10" x 6" x 3/16" pickles mild steel panels (3 coats) in duplicate and the paint was allowed to dry for 7 days. The thickness of the paint film was 8 mils. The panels were bolted to an angle iron frame which was electrically insulated using bakelite washers and sleeves. The panels were lowered in sea water to a depth of 1' and 4' from a raft moored off Bombay harbour.

Regular inspection of the panels was made for a period of 15 months. The panels got fouling settlement after a period of 3 months. No visible corrosion was observed for over 14 months when the lower panel showed corrosion towards the lower edge. The panels were, withdrawn after 15 months of immersion. Assessment of the substrate was made after removing the fouling settlement and the paint. The panels were free from corrosion except at the lower edge of the lower

- VE POTENTIAL IN MV VS. S.C.E.

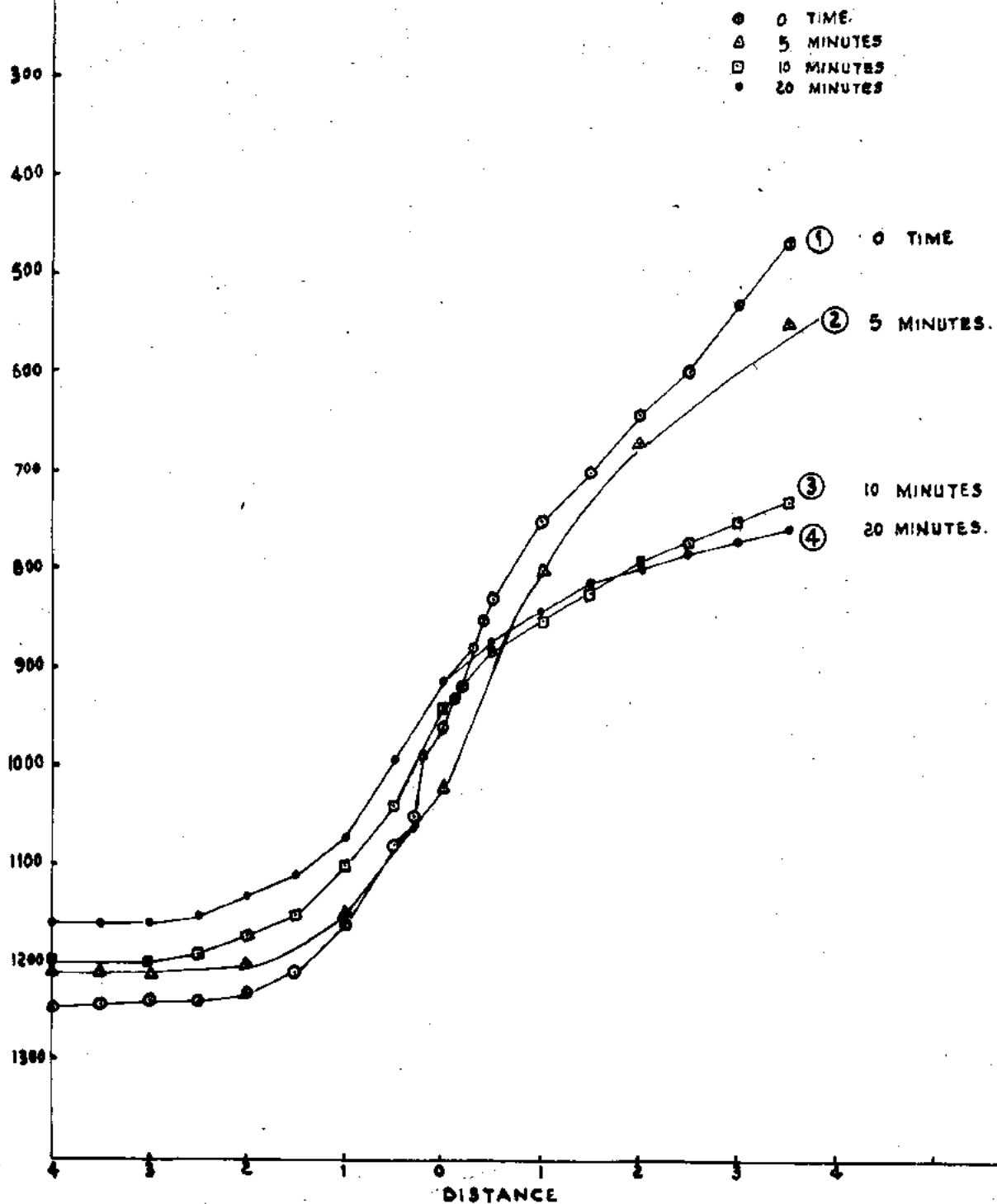


FIG. 5. CHANGE IN ELECTRODE POTENTIAL OVER A PARTIALLY PAINTED SURFACE IN SEA WATER.

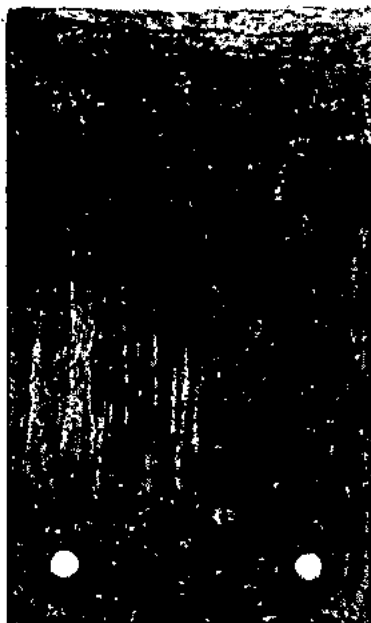


Fig. 6. — 10'' x 6'' mild steel panel removed from raft, after 15 months' of sea water exposure. Panel showed freedom from corrosion before (left) and (right) after removing of the paint film. Adherent dark spots were found to be comprised of manganese salts (right).

panel. Adherent blisters comprising mainly of precipitated manganese salts were observed, fig. (6).

#### DISCUSSION

The electrochemical behaviour of manganese and zinc-rich paints shows that initially the potential of the painted electrodes is similar to that of the pigment metal in sea water<sup>4,6</sup> indicating that the pigment particles are in metallic electronic contact with the substrate. With the penetration of the paint film by water and electrolytes the metal pigment may react with the environment. The products of reaction may isolate the metallic manganese pigment electrically from the substrate metal leading to an increase of the electrode potential.

The reactivity of manganese is more than that of zinc. In the composite primer, metallic manganese scavenges the dissolved oxygen as well as offers cathodic protection to the finely divided zinc pigment. The protective current requirement for cathodic protection of zinc may be reduced by the scavenging of dissolved oxygen<sup>6</sup> by manganese. This leads to maintenance of more negative potential of electrodes coated with zinc-manganese primer during the period of immersion (Fig. 3). The maintenance of the more negative potential facilitates the corrosion protection of the substrate mild steel. The corrosion resistant property of zinc rich paint has been improved by incorporation of manganese powder. The bare surfaces of the painted electrodes show that all the paints possess adequate protective property (fig. 4).

Potential measurements carried out over painted/bare metallic surface in sea water (fig. 5) show, that the area

receiving cathodic protection extends beyond the painted surface. The area also increases with time due to progressive polarisation of the bare metal.

The painted panels exposed to sea water from raft were fouled. However the corrosion protection to the substrate was clearly evident for a period of 14 months of sea water immersion (fig. 6).

Results of the investigation indicate that finely divided manganese has shown promise as corrosion inhibitive pigment in underwater anticorrosive paint formulations.

#### ACKNOWLEDGEMENTS

The author is grateful to Shri S.K. Ranganathan, Director of Scientific Research (Navy), and Shri C.P.De, Director, Naval Chemical and Metallurgical Laboratory, for taking keen interest in this investigation, which forms part of post graduate work. The guidance of Prof. S.V. Puntambekar, University Department of Chemical Technology, Bombay, is gratefully acknowledged.

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#### DISCUSSION

Dr. KENWORTHY (England): Is there any possibility that with these manganese-rich paints, weathering may be accompanied by brown staining which may not only be displeasing aesthetically but may be mistaken for corrosion of the underlying steel.

C. P. DÉ: Manganese paints have been formulated for environ-

ments like immersed condition in seawater etc. where aesthetic considerations are not of importance. The paint develops a near black appearance after several days exposure to seawater. Brown iron rust is clearly distinguished against this background and difficulties have not been experienced in assessment of the paint performance.

# SPECIAL PRETREATMENT FOR THE REPAINTING OF CATHODICALLY PROTECTED SHIPS' HULLS

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## RÉSUMÉ

Le comportement dans l'eau de mer de l'acier peint ou repeint, qui est protégé cathodiquement, se laisse avantageusement investiguer dans le laboratoire en eau de mer artificielle. Les résultats peuvent être confirmés par une expérience dans l'eau de mer naturelle.

On décrit un arrangement d'expérience pour investiguer le comportement d'un certain nombre d'éprouvettes peintes avec ou sans application de protection cathodique. On donne les résultats de recherches préliminaires concernant des traitements initiaux pour la repeinture des coques de navires, qui ont eu une protection cathodique.

## SUMMARY

The behaviour of cathodically protected painted or repainted steel in sea water can advantageously be investigated in the laboratory in artificial sea water. The results may be conformed by an experiment in natural sea water.

A test set for investigation of the conduct of a number of painted test panels with or without application of cathodic protection is described. Results are given of preliminary investigations as to special pretreatments for the repainting of cathodically protected ships' hulls.

## I. INTRODUCTION

Many factors determine the behaviour in seawater of paint layers on cathodically protected ships' hulls e.g. the installed cathodic protection system, the nature of the applied paint system, the application method of this system, the pretreatment that is given to the steel.

Of the named factors our attention is specially directed to the pretreatment. A ships' hull does not undergo in all circumstances the same pretreatment over the whole surface when it is repainted. The paint layer on that hull may be damaged locally. An installed cathodic protection system does not act on the whole hull surface with the same current density. On damaged spots a chalk layer is often deposited by this system.

If such a ships' hull has to be repainted one has to reckon with the fact that the condition of parts of the hull differs from the rest and that special pretreatments are necessary for these parts. The chalk layer has to be removed and also the alkaline substances that have been formed on the ships' hull during the cathodic protection action. In most cases this is done by washing the hull with an acid solution. The surplus acid has to be removed by a washing or a neutralizing operation. In practice difficulties often arise, especially with paint layers on places, where a chalk layer was present before the repainting. It turns out that on these places blisters are sometimes formed, when the cathodic protection is reinstalled on the repainted surface. The blistering takes place inspite of the pretreatments that are applied and points to an insufficient paint adherence. Possibly, insufficient attention during the repainting treatments causes the defects in the paint layer, but it is also possible that the proposed pretreatment is insufficient to forestall these defects.

To investigate the behaviour of paint layers on ships' hulls the following two investigation methods are often applied, viz.

- A. the placing of test panels on a raft under sea-level;
- B. a special treatment of parts of one or more ships'

hulls, which parts can be considered as a special kind of test panels, undergoing the same influences as the ships' hull itself.

Both investigation methods are costly and, if possible, they should be replaced or preceded by less expensive investigations.

Moreover, the results of the investigations sub B can often difficultly be interpreted, because comparable conditions for the different test parts of one ships' hull (and surely for more ships' hulls) can difficultly be created. Also, the inspections of the test parts cannot be performed at arbitrary times but only during docking periods.

Besides the mentioned investigation methods laboratory investigations of such a kind may be performed that the practical conditions are more or less simulated. In those investigations natural or artificial seawater (or eventually an other solution) can be used.

The main purpose of our research is to investigate the behaviour of repainted damaged spots of ships' hulls in seawater by the reinstallation of the cathodic protection system. Of course, the composition of the sea-water influences this behaviour, but this influence is of second order. The influence of the change, produced in the sea-water at the painted surface by the cathodic protection, preponderates. Thus, natural sea-water is not absolutely necessary for our experiments, but one can do with artificial sea-water. If necessary, the final results can be checked by a special experiment in natural sea-water.

Underneath follows a description of our test arrangement (sub II) and a review of some preliminary experiments (sub IV, V and VI).

## II. TEST ARRANGEMENT

The experiments are performed with painted steel panels (steel 52) of dimensions 300 × 120 × 5 mm. The painting had taken place on both sides of the panels over a length of 250 à 260 mm. 15 different groups of panels were prepared for the preliminary investigations, each group comprising

panels pretreated and painted in the same way. A detailed description of the preparation of the panels is given underneath (sub III).

The panels are placed in a vertical position with the unpainted part at the top along the long side of open cisterns of dimensions  $2,25 \times 0,40 \times 0,25$  m (depth). Of each group two panels (with an unpainted panel between them for current adjustment) are linked up in parallel connection; each set of 3 panels is linked up in series connection with an adjustable resistance. Totally 15 groups are investigated, requiring 15 resistances and 45 panels (30 painted and 15 unpainted). They are placed in 3 cisterns. The 15 resistances are connected with the negative pole of a rectifier with adjustable voltage. The positive pole of this rectifier is linked up with 9 parallel-connected siliconiron anodes, placed in flower-pots along the second long side of the 3 cisterns. The flower-pots are used to forestall the leaching into the cisterns of acid substances, freed by the protection current at the anodes.

Along the long side of a fourth cistern one painted panel of each group is placed without electrical connections.

The 4 cisterns and the 9 flower-pots are filled with artificial sea-water of the composition of table 1. The sea-water is recirculated in the cisterns (not in the flower-pots) by means of pumps and siphons.

In the filled cisterns cathodic protection was installed on the 45 connected panels. The current density on the panels was regulated by adjusting the resistances in such a manner that a definite potential of the surfaces against a saturated calomel reference electrode was established.

This potential was checked daily; if necessary it was adjusted to the desired value. The adjustment could be easily accomplished, because of the included unpainted panels.

TABLE 1

COMPOSITION OF THE ARTIFICIAL SEA-WATER

Add to every liter domestic water:		
30	gr	NaCl
8,4	gr	MgSO <sub>4</sub> ·7aq
2,35	gr	MgCl <sub>2</sub> ·6aq
2,0	gr	CaCl <sub>2</sub> ·6aq
0,20	gr	NaHCO <sub>3</sub>

The arrangement in two cisterns is shown in fig. 1. The 10 resistances are visible; they are all placed at one long outside of the foremost cistern, the other long outside of the cisterns being inaccessible.

The 15 panels (10 painted and 5 unpainted) along the long side of the foremost cistern are visible and also the 15 unpainted tops of the panels in the cistern behind. The 6 siliconiron anodes in the flower-pots are visible in the two cisterns, also the pump and siphons used for recirculation and the cables used for electrical connection.

Fig. 1 gives a part of figure 2 in greater detail.

Fig. 3 shows a scheme of the experimental set-up and the wiring diagram.

III. PREPARATION OF TEST PANELS

At first the surfaces of the 45 painted test panels, needed for the preliminary experiments, were brought in a reproducible start condition.

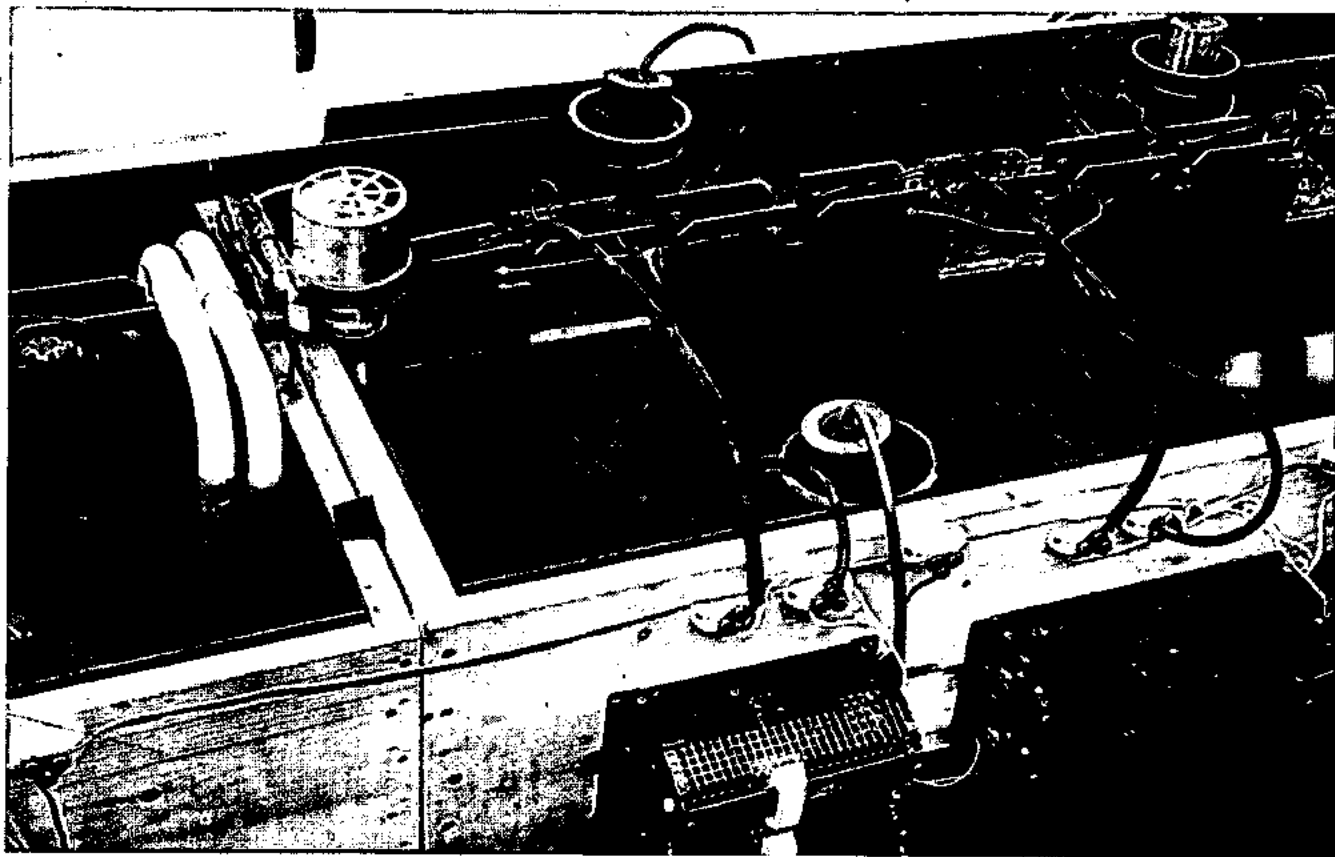


Fig. 1.



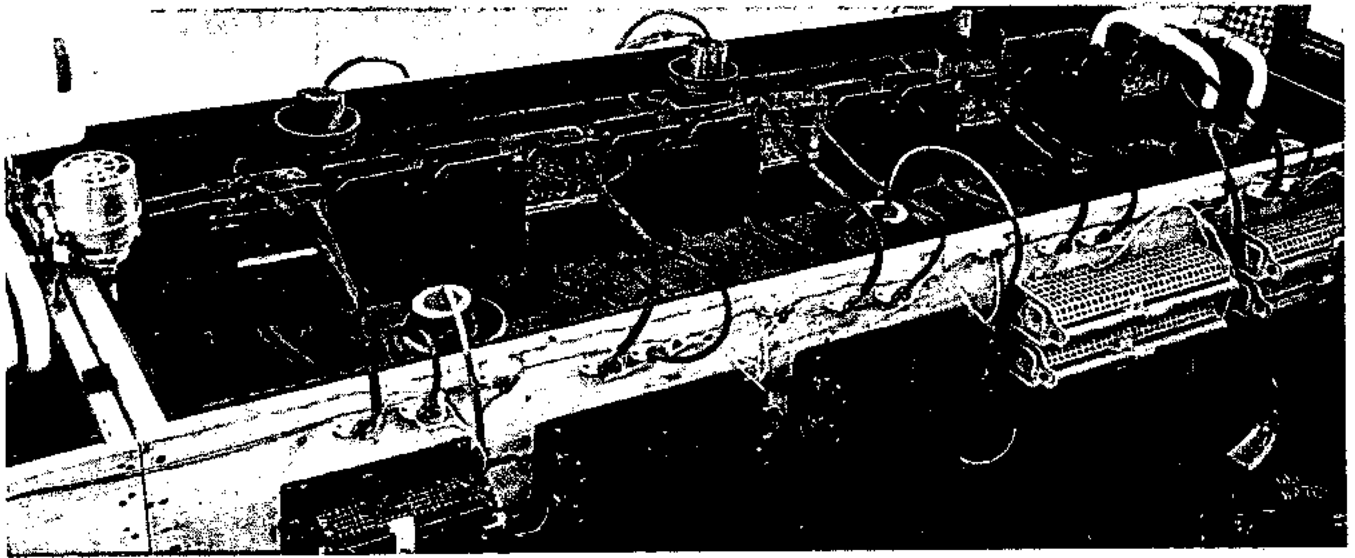


Fig. 2.

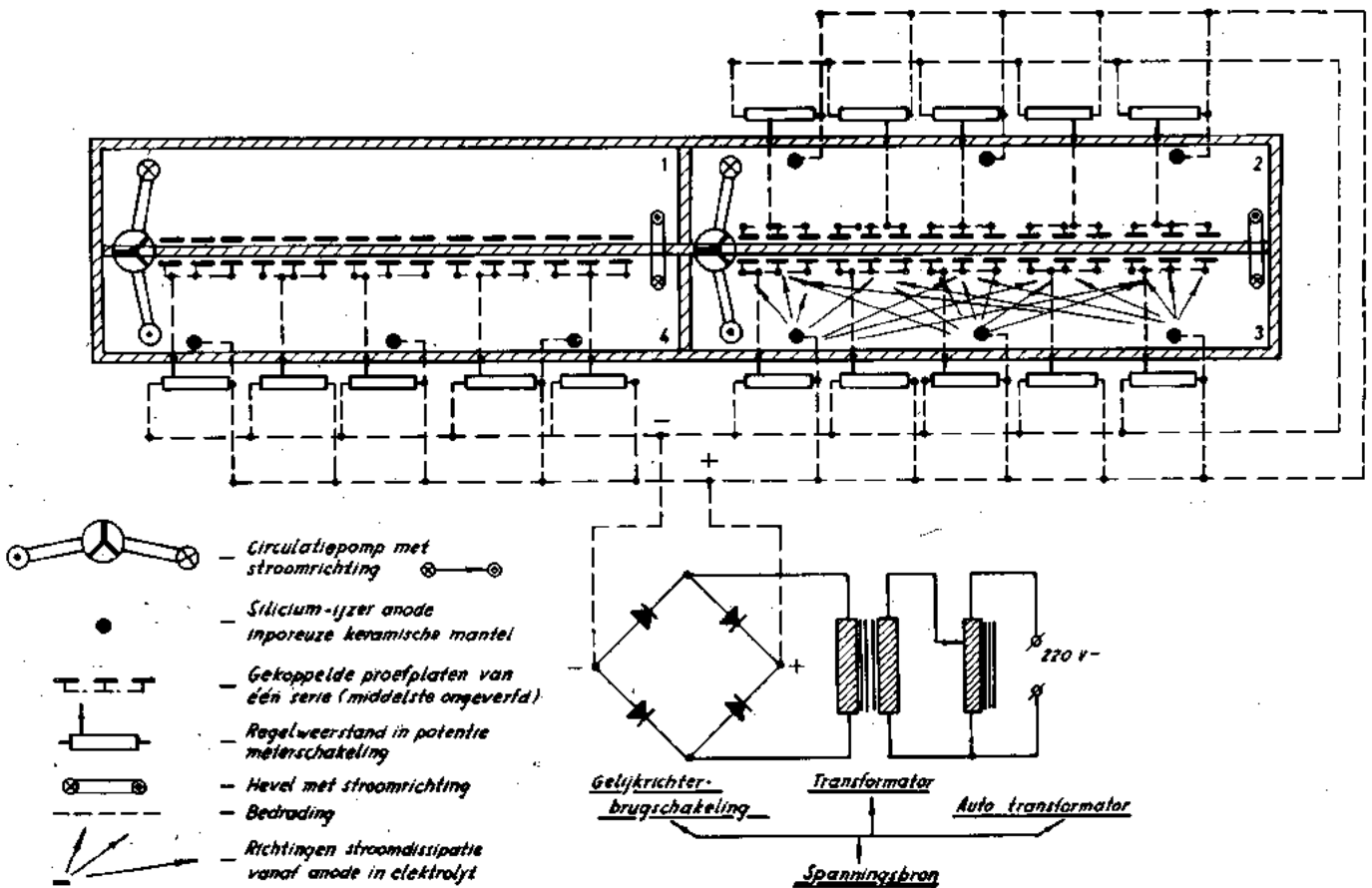


Fig. 3.

For that purpose the panels were pickled in a sulphuric acid solution, thereafter rinsed by domestic water of room temperature, then dipped in boiling distilled water during a few minutes and finally dried in the air.

This sequence of treatments was performed directly before the further preparation of the panels took place.

18 pickled panels were cathodically protected during 35 days in the artificial sea-water to a potential of  $-1000\text{mV}$  sat. cal. to form a chalk layer on their surface.

After that the panels (included the ones that were temporarily protected) were divided in 15 groups of 3 panels.

Every group was pretreated and painted according to the scheme of table 2. The groups are small to have the possibility to include many combinations in the preliminary experiments, so that much information is gathered about the possibilities of the test arrangement.

TABLE 2  
PREPARATION OF THE PANELS\*

Group no.	Successive treatments <sup>1</sup>								
	Pickling	Previously applied cathodic protection	Cold phosphoric acid	Mechanical cleaning	Water rinse <sup>2</sup>		Drying at a relative humidity of		Painting
					pH ~ 5	pH ~ 6,5	~90%	~55%	
1	x	x	x	—	x	—	x	—	x
2	x	x	x	—	—	x	x	—	x
3	x	x	x	—	x	—	—	x	x
4	x	x	x	—	—	x	—	x	x
5	x	—	x	—	x <sup>2</sup>	—	x	—	x
6	x	—	x	—	—	x	x	—	x
7	x	—	x	—	x <sup>2</sup>	—	—	x	x
8	x	—	x	—	—	x	—	x	x
9	x	x	—	x	—	—	—	x	x
10	x	x	x	—	—	—	x	—	x
11	x	—	x	—	—	—	—	x	x
12	x	—	—	—	—	—	x	—	x
13	x	—	x	—	x <sup>2</sup>	—	x	—	x
14	x	—	x	—	—	x	x	—	x
15	x	—	x	—	x <sup>2</sup>	—	—	x	x

\* For details see under III.

1 x means: treatment applied; — means: treatment not applied.

2 The rinsing is continued till the water trickles down with a pH 5 or 6,5. The groups 1 to 8 and also group 14 are rinsed with domestic water (pH ~ 7,0); the groups 13 and 15 are rinsed with demineralized water (pH ~ 5,7).

The various pretreatments, applied or not applied on the pickled test panels according to table 2, are:

1. a cathodic protection treatment of the bare panel (already mentioned above);
2. a dip in a cold phosphoric acid solution;
3. a mechanical cleaning of 3 cathodically protected panels;
4. a rinsing operation with more or less water (viz. the water that trickles down, has the pH 5 or 7);
5. a drying operation in the air at room temperature for 24 hours at different relative air humidities (50% and 90%), directly before the painting of the panels.

The different treatments 1 to 5 are chosen, because they represent important factors of the condition of the repainted ships' hull.

Treatment 1 is necessary to simulate damages on cathodically protected ships' hulls. The treatments 2 to 4 are deemed necessary to get a good condition of the cathodically protected hull for repainting. The water rinse may be strong or weak, therefore 2 different pH's of the water that trickles down, are included. Treatment 5 is included because in practice the painting may take place on a nearly dry or a slightly humid surface.

After pretreating the panels, they are all painted in the same way, viz. first a primer is brushed on and left to dry for 2 days at room temperature and a relative humidity of 55%, then an epoxytar coating is brushed on and left to dry under the same conditions as the primer.

The panels are weighed before the primer is applied and after each of the two coatings has dried. The primer layer proved to weight 5,5 to 8,0 grams on a panel (most weights between 6,5 to 7,3 grams) and the epoxytar layer 12 to 16 grams with exceptions of 10 grams (in the groups 4,8 and 10) and 20 grams (in the groups 13 and 14).

The data about the treatments are schematically summed up in table 2.

#### IV. TEST AND TEST RESULTS

The test was performed in the way described sub II. At first the potential of the 45 cathodically protected panels (30 painted and 15 unpainted) was fixed at  $-1000$  to  $-1050\text{mV}$  sat. cal. during nearly 100 days; then the panels were inspected. After that the cathodic protection was resumed, but now at a potential of  $-1150$  to  $-1200\text{mV}$  sat. cal. during nearly 85 days, after that a final inspection of the panels followed.

No cathodic protection was applied on the 15 panels in the fourth cistern, but these panels were inspected together with the other ones.

Only a general review of the results will be given and not a detailed description. The first inspection after a stay of 100 days in the cisterns showed the presence of a small number of very small blisters on some panels of the groups 11, 12 and 14.

In the final inspection more defects could be detected, viz. blister formation on the edges and (or) the flat part of the panels and loosening of the paint cover on or near the edges. The defects had dimensions from small to big and their number could go from zero to many. Table 3 sums up the defects for all groups; thus, both for the 30 panels that underwent cathodic protection in the filled cisterns (experimental condition A) and for the 15 panels that only underwent a stay in the artificial sea-water in the fourth cistern (experimental condition B).

Many of the blisters proved to be filled with an alkaline solution (pH ranging from 8,2 to 10, the value 10 mainly occurring in blisters on panels that underwent experimental condition A).

#### V. CONCLUSIONS

From table 3 the following conclusions can be drawn.

A. The damages of the paint layer at experimental condition A (with cathodic protection) are more extensive than at experimental condition B (without cathodic protection).

This may be an indication of the fact that the applied paint coatings are not or only difficultly proof against the applied cathodic protection conditions or that small defects in the paint coatings, under normal conditions only leading to damages of the coatings after a long exposition period, become visible in a fast and obvious way if cathodic protection is applied. We suppose the latter.

In the literature an investigation into the detection of defects in paint coatings by cathodic protection is known (R.W. Turnbull, Metal Progress 88 (6) 102 (1965)).

B. At the experimental condition A the groups, dried at high relative humidity (90-95%) (no. 1 - 2 - 5 - 6 - 10 - 12 - 13 - 14) generally show extensive defects. In all the mentioned groups, excepted group 12, big blisters or big spots with loosened paint layer were visible. In group 12 only small blisters were

TABLE 3  
REVIEW OF FINAL DEFECTS

Group, no. °	Experimental condition A <sup>1</sup>						Experimental condition B <sup>1</sup>		
	Blisters			Spots with losened paint cover			Blisters		
	Dimension <sup>2</sup>	Number	Place <sup>3</sup>	Dimension <sup>2</sup>	Number	Place <sup>3</sup>	Dimension <sup>2</sup>	Number	Place <sup>3</sup>
1	++++	some	a;(b)	++++	some	a	—	none	—
2	—	none	—	++++	2	a	—	none	—
3	+	many	b	—	none	—	(+)	fairly	b
4	+	some	b	—	none	—	(+)	many	b
5	++++	fairly )	a	++++	fairly )	a	—	fairly )	—
6	++	many )	a;b	—	none	—	—	none	—
7	++	some	b	—	none	—	—	none	—
8	—	none	—	—	none	—	—	none	—
9	+++	fairly )	b	—	none	—	+	many	b
10	++++	many )	a	++++	4	a	+	some	b
11	—	none	—	—	none	—	—	none	—
12	++	fairly )	b	—	none	—	++	many	b
13	—	none	—	++++	some	a	—	none	—
14	++	2	b	++++	3	a	—	none	—
15	+	5	b	—	none	—	—	none	—

° See table 2 for details.

1 Condition A : stay in artificial sea-water and application of cathodic protection following the data of IV;

Condition B : stay in artificial sea-water without cathodic protection.

2 Dimensions : +++++ very big;  
++++ big;  
++ medium (diameter 3 to 5 mm);  
+ small;  
(+) very small (pinhole).

3 Place : a. on or near the edge or originating from the edge;  
b. on the flat part of the panel;  
(b) a small quantity on the flat part of the panel.

visible on one of the two cathodically protected panels; the other panel was intact (just as one of the 2 cathodically protected panels of group 2).

Group 12 is a special group (see table 1); all defects in the paint layer must be attributed to a bad drying operation.

The groups dried at low relative humidity (50%) (no. 3 - 4 - 7 - 8 - 9 - 11 - 15) only showed small defects at the experimental condition A.

At the experimental condition B blisters are also found (in the groups 3 - 4 - 9 - 10 - 12), but all of them are small. Only the group 10 and 12 were dried at high relative humidity. Thus, these results do not give a clear indication as to the cause of the defects.

Properly speaking, drying at high relative humidity is no drying and one does not expect good results by doing this.

Experimental condition A (with cathodic protection) clearly shows this.

C. A comparison of the results of the group 1 - 3 - 5 - 7 - 13 (all of them washed to pH ~ 5) with the results of the group 2 - 4 - 6 - 8 - 14 (all of them washed to pH ~ 7) gives a faint impression of stronger defects in the uneven groups.

Thus, there is a faint indication that washing to pH ~ 7 (in practice this means longer washing) is more favourable than washing to pH ~ 5.

For the pairs 1 - 2, 5 - 6, 13 - 14 this conclusion is doubtful. These groups are all dried at high relative humidity, which fact leads to considerable damage of the paint layers. It is highly questionable if the weak influence of the washing method can be detected under these circumstances.

D. Of the groups 1 - 2 - 3 - 4 - 9 - 10, all of them cathodically protected before the other pretreatments took place, only the groups 3 and 4 showed good results.

Of the other groups (5 - 6 - 7 - 8 - 11 - 12 - 13 - 14 - 15) the results in no 8 and 11 were very favourable and in no 15 favourable.

For the groups 1 - 2 - 10 - 12 - 13 - 14 we do not expect good results because of their drying at high humidity.

Thus, there is a weak indication that previously installed cathodic protection may have a noxious effect on paint layers that are applied afterwards. However, an expert pretreatment before the painting may counteract this noxious effect (groups 3 and 4). The conclusion is doubtful because of the lack of sufficient data to confirm it.

E. The mechanical removal of the layer, formed during cathodic protection, does not take away the noxious effect of this action on paint layers applied afterwards (group 9).

F. The applied treatment with phosphoric acid, followed by proper washing and drying treatments, may lead to a surface with no disadvantages for paint application, independent of

the fact if a previous cathodic protection treatment has taken place or not (groups 4 - 8 - 11 - 15).

If unsuitable washing or drying treatments are applied, a bad or only a moderate good result can be expected (groups 1 - 2 - 3? - 5 - 6 - 7 - 10 - 13 - 14)

G. No significant difference in behaviour can be detected between the groups 5 and 13 and only a doubtful difference between the groups 6 and 14. According to table 1 each pair of groups is treated in the same way (also group 5 like group 13 and group 6 like group 14), except for the kind of water used for the washing operation.

The groups 5 and 6 are rinsed with domestic water, the groups 13 and 14 with demineralized water.

The groups 13 and 14 had a relatively thick paint coating, the groups 5 and 6 a normal one (see under III).

Presumably only the noxious influence of the bad drying operation is the only influence that can distinctly be detected. The observed differences are of doubtful value.

## VI. FINAL DISCUSSION

From the experimental results it follows, that application of cathodic protection on painted test panels placed in sea water is a suitable means to bring to light in a clear and rapid way small defects of the steel surface that has to be painted, and small defects in the application method of the paint system or the application conditions during the painting. Without cathodic protection such defects generally come to light after much longer exposition time (see under V sub A).

Therefore, it is necessary that surfaces, that will be cathodically protected after painting, are prepared with the utmost care, especially as far as pretreatment operations and paint application is concerned.

One can say that such surfaces in principle demand more care than painted surfaces that will not be cathodically protected.

E.g. drying the surfaces at high relative humidity before painting proved to have an unfavourable influence on the paint layers, that were applied after the drying (see under V sub B).

The other conclusions of V are of a provisional nature. In most cases they are based on very few results or the established differences between the compared results are so small that a statistical investigation to their significance is necessary.

However, it is established that the described investigation method is full of meaning and can rapidly lead to important results.

Therefore the investigation will be continued.

Less variations will be included and each variation will comprise more panels so that, if necessary, statistical evaluation of the results can be performed.

## ACKNOWLEDGMENT

We wish to thank RVO - TNO (Rijkswerdedigingsorganisatie TNO) for their permission to publish the above mentioned data.

## DISCUSSION

J.A.H. CARSON (Canada): Although our observations are not based on controlled test like those of Dr. Boon, we have observed many instances of steel protected in sea water at about -1.0 volt vs Ag/AgCl (the potential with a saturated calomel electrode is essentially the same) and do not find any significant cathodic deposits on the steel at this potential. Dr. Boon, on the other hand, finds that there is a considerable chalk deposit on steel maintained at -1.0 volt. I believe that similar deposits have been found on cathodically protected steel in a natural sea water exposure at Den Helder in the Netherlands. Apparently then, small differences in sea water conditions can make a fairly large difference in cathodic effects.

Dr. BOON: I do not object to the findings of Mr. Carson. They are different from our experience. We have to acknowledge this.

T. BIRKENHEAD (England): I have seen examples of ships which have been cathodically protected where extensive blistering has resulted. This has tended to be blamed on the paint and the paint maker, but I believe that variation in current density is the more probable explanation. Would Dr. BOON like to comment on this?

Dr. BOON: There are many possibilities for a bad behaviour of a cathodically protected ship. Beside a bad application or use of a bad paint, the applied protection potential and cathodic protection installation may cause damage in the paint layer. The potential may cause overprotection, the installation may locally cause a too high or a too low potential.

Differences of temperature and composition of the seawater, the speed of the ship and the possibility of fouling may also have influence.

J.A.H. CARSON (Canada): If I may comment on that point, we have found that in sea water cathodic protection at a potential of -1.2 volt (vs Ag/AgCl) has a much more drastic effect on coated steel than does protection at -1.0 volt. I believe that Dr. Boon used potentials more negative than -1.0 volt to produce paint damage.

Dr. BOON: Indeed, a lower potential was used to bring to life the desired effects.

Dr. PETROCOKINO (France): Is it possible Dr. Boon to mention the current densities used in these experiments? Because the current density is a fundamental point in cathodic protection and directly connected with paints behaviour.

Dr. BOON: Indeed, the current density is the vital point, but in most cases the current density is directly connected to the resulting potential. Mostly, only the protection potential is named without any indication about the current density. I cannot say the current density on our panels. As we did our experiments with painted panels, there is no possibility to calculate the current density for there is no notion about the effective surface area.

C. CABRILLAC (France): I was surprised to hear Dr. Boon saying that the choice between artificial and natural seawater was not very important. I wonder if there is no influence of the water altering during the experiments on the damage occurring in the paint films. The water changes during the experiments and I should like to know if you were obliged to add buffer solutions to stabilize the phenomena on the panel surface; I should also like to know if you measured the oxygen content of the water and the variations of this content.

Dr. BOON: We did not measure the oxygen content, but because of the circulation of the water in the open cisterns we are convinced of having used water that was saturated with oxygen.

We measured the pH and found it lowering after a short time (one or two weeks). We tried to restore the original potential by adding some sodiumbicarbonate. That did not work in the desired manner and therefore we renewed the artificial seawater two times during the experiments.

# WAXY SLUDGE DEPOSITS, A CAUSE OF PITTING CORROSION IN CARGO TANKS OF CRUDE OIL TANKERS

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## SUMMARY

Pitting corrosion in bottoms of tanks in crude-oil carriers has in the last few years become a serious problem. A laboratory investigation has shown that sea-water is responsible for the corrosion but that waxy sludge deposits on the steel surface cause it to become localized, which eventually results in pitting.

Corrosion experiments and electrochemical measurements have clearly shown that in sea-water steel covered with waxy sludge originating from crude oil achieves a nobler potential than bare steel, i.e. it forms a cathode and bare steel becomes the anode. The potential difference between sludge-covered

and bare steel provides the emf that drives the corrosion current in this corrosion cell, which is a large «differential aeration cell». The corrosion cell is characterized by a stable emf ranging from 50-300 mV and a low electric resistance, which allows considerable currents to flow over relatively large distances.

The mechanism of pitting attack established and the results of laboratory corrosion tests were found to fit in with the experience gained in crude-oil tankers. Mitigation of this attack by cathodic protection is being considered.

## 1. INTRODUCTION

Corrosion and pitting corrosion of tanks in crude oil carriers is not a new phenomenon. It has been observed for many years, but not until recently has it been of much concern and, hence, the object of careful attention by the corrosion specialists.

Regular carriage of crude oil for lengthy voyages did not become general practice until after 1948. In the 1950's the crude carriers were small by the standards of today and wastage of the bulkheads of the ships could be kept low by washing with cold water instead of hot and by the use of magnesium anodes in cargo/ballast tanks. Towards the end of the 1950's the encouraging experience gained with «EPI-KOTE»-coated tanks in ships carrying products (= distillates) lead to considering similar methods for crude-oil tankers. This idea was given added impetus when it was proved that magnesium anodes were a potential explosion hazard.

The increase in size of crude carriers — as illustrated in Fig. 1, which gives an impression of number and size of new tankers added to the fleet of the Royal Dutch-Shell Group in the years from 1959 to 1968 — and the corresponding increase in cost of complete painting of tanks, together with other considerations, gave rise to a system of protection that was less costly. Under this system, the so-called «selective painting scheme», also recommended by the Crude oil Corrosion Group of the Tanker corrosion research project of the American Petroleum Institute,<sup>1</sup> only the tank bottoms and stringer tops were painted, because previous experience in crude carriers had shown that corrosion concentrates mainly on the bottoms.

After only one year of service, however, in a number of selectively painted tankers widespread and very severe pitting of painted bottoms and stringer tops was found, pitting depths of up to 9 mm being measured. Fig. 2 shows a typical example of such pitting. Although the attack was severest in selectively painted tanks — the degree of pitting

depending on paint and primer systems employed — entirely painted tanks used for crude oil service were found not to be free of pitting corrosion either. The fact that pitting corrosion was more severe in cargo/ballast tanks — i.e. tanks regularly ballasted during the ballast trip — than in cargo-only tanks, which carry ballast only occasionally and then for a relatively short time, seemed to suggest that sea-water was responsible for the attack, rather than any constituent of the crude oil. Since such pitting was never found in unpainted or entirely painted product carriers, we had to assume that crude oil left behind in tanks influences the corrosion of steel in a particular way. The aim of our investigation was to prove this, to enable us to explain the mechanism of pitting corrosion in crude oil tankers and to find an appropriate remedy for it.

## 2. EXPERIMENTAL

### 2.1. Corrosion experiments

#### 2.1.1. Unpainted steel

Screening experiments showed that different corrosion patterns are obtained when unpainted steel is exposed to sea-water as such or covered with crude oil or crude oil sludge (waxy deposits on tank walls of crude oil carriers): Whilst steel as such corrodes rather regularly all over the surface, waxy-sludge-covered steel corrodes locally, and at these places at a high rate. This is shown in Fig. 3, where the thick rust pockets on the waxy-sludge-covered specimen indicate the vehement corrosion taking place.

To obtain quantitative information on the influence of oil or wax deposits on local corrosion we made the following experiment. Steel wires were completely covered with oil deposits and exposed to aerated seawater. To assess the influence of coverage with oil or waxy sludge a few of these wires had been welded to a strip of unpainted steel, which had

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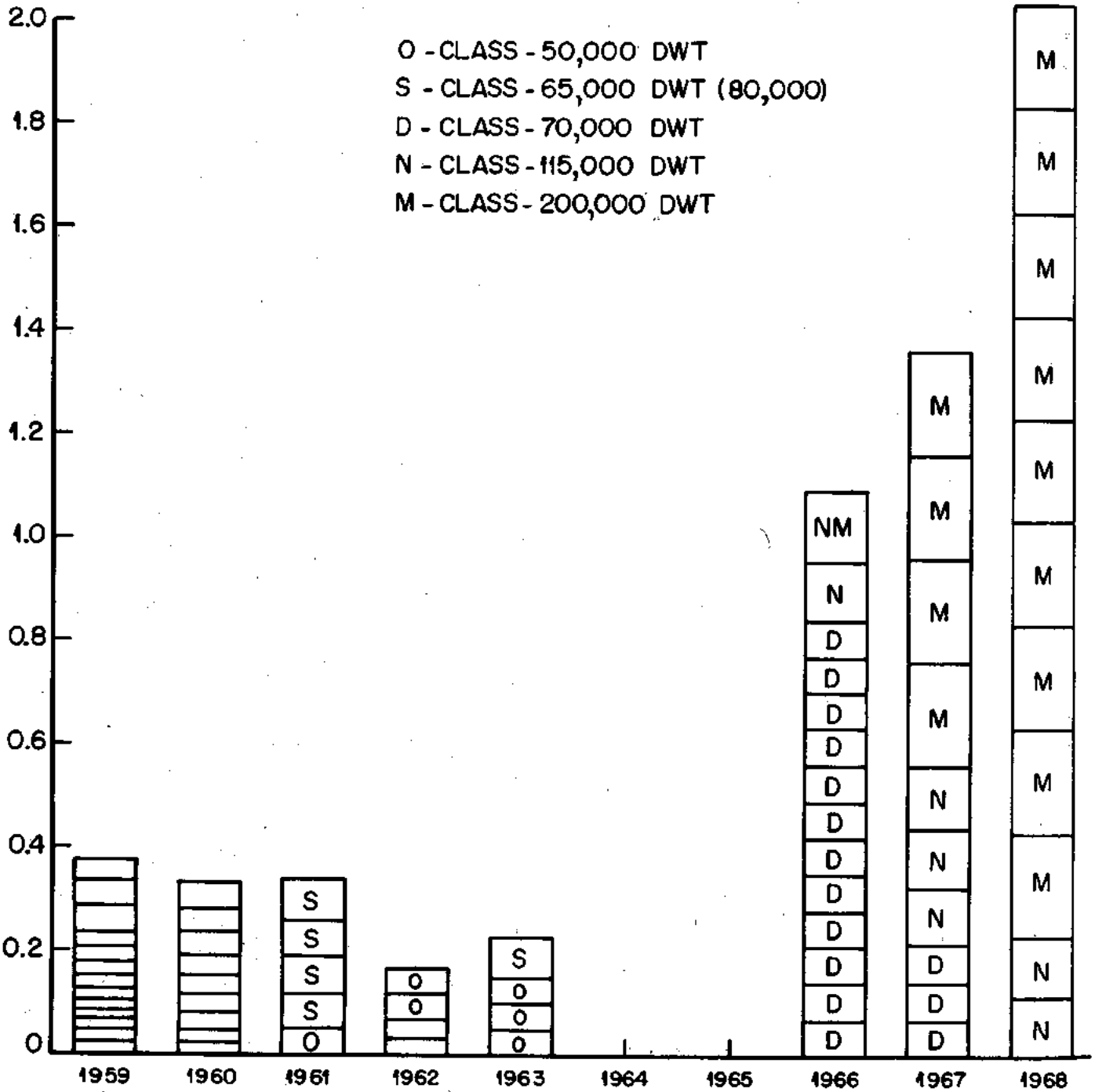


Fig. 1. New tankers put in service for SHELL TANKERS from 1959 to 1968.



Fig. 2. Typical pitting in «EPIKOTE»-coal-tar painted bottom after 2 years' service. Pitting depth: 8 mm.

a surface area 20 times as large as the test wire and which had not been covered with waxy sludge. For this experiment, whose duration was from 1 to 5 weeks, two types of waxy sludge recovered from crude oil carriers and a low-viscous crude oil were employed. After the test the weight losses of the wire specimens were determined and the local corrosion rates established by measuring the thickness profile of the wire by a novel technique. The results of these tests are compiled in Table I.

Severe pittinglike local corrosion with corrosion rates up to 10 mm/year was found on all specimens which were completely sludge-covered at the start of the test. It is interesting to note that with these specimens the unaffected part of the surface remained bright. Steel wires connected to strips of bare steel thus resembling a specimen incompletely covered with waxy sludge did not display any pronounced local attack, the corrosion pattern being similar to that obtained with bare steel in sea-water. In Fig. 4 some of the specimens are shown.

#### 2.1.2. Painted and partly (selectively) painted steel

The corrosion experiments with (partly) painted steel were based on two facts established in the preceding tests, viz. the strong promoting effect of waxy sludge deposits on pitting corrosion and the probable long-action range of this effect. The latter was suggested — although in the reverse sense — by the tests in which waxy-sludge-covered steel specimens (wires) were not attacked by pitting corrosion when the specimen was coupled to a strip of bare steel which was relatively remote.

For these tests we used steel strips, 20 mm wide, 1 mm thick, 500-1000 mm long and painted with «EPIKOTE». On one side of the strip spots of 5 mm diameter had been left unpainted at regular intervals of about 50 mm. These spots were intended to serve as defects in the paint coat. The tests, which were run with 28 days' exposure to aerated sea-water, comprised specimens of three types:

- (a) The painted test strips as such, as a reference for corrosion to be expected at defects in paint coating upon sea-water exposure only.

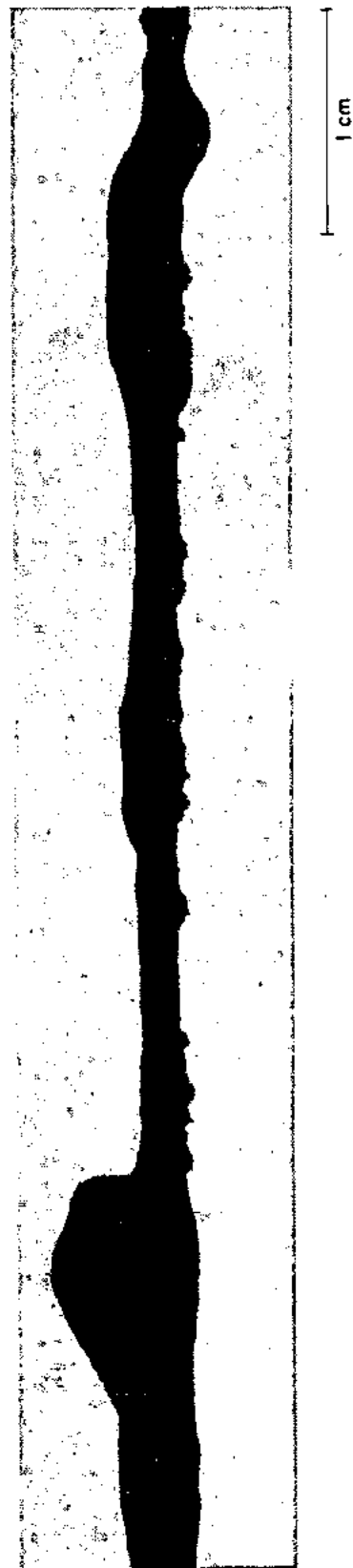


Fig. 3. Waxy-sludge-covered steel wire after exposure in sea-water.

TABLE I

## PROMOTION OF LOCAL CORROSION OF UNPAINTED STEEL BY WAXY-SLUDGE DEPOSITS

Test specimens: wires Exposure in 25-mm-diameter glass tubes Medium: synthetic sea-water

Type of waxy-sludge deposit	Waxy-sludge-covered wires coupled to unpainted steel strips	Exposure time, d	Length of wire, cm	Weight loss g/100 cm	% of length of wire with corrosion rate (mm/yr) of															
					1.5-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10	10-11						
Sludge ex tank 13C of ss «SITALA»		7	100	0.062	1	2	4	7	5											
		14	100	0.555	1	4	34	3												
		28	100	0.685	15	12	0	1												
		34	100	1.024	15	22														
	yes	8	50	0.108	14	20														
	yes	15	50	0.233	5															
	yes	15	50	0.262	5	5														
	yes	34	50	0.188	0															
Sludge ex tank 14C of ss «SITALA»		7	100	0.213	0															
		14	100	0.456	8	30	3													
		28	100	0.773	4	17	3	3												
		33	100	1.016	3	14	0	6												
	yes	7	50	0.171	0															
	yes	14	50	0.279	20															
	yes	27	50	0.346	0															
	yes	33	50	0.488	7															
Ijsselmonde crude		10	100	0.238		2	13	5	2	3	1									
		17	100	0.430		2	3	5	5	6										
		30	100	0.848		3	4	0	9											
		30	100	0.776	2	0	14	7	4											
		36	100	0.970		7	10	5												
	yes	8	50	0.100				5	0	4										
	yes	14	50	0.352	6	0	6													
	yes	21	50	0.674	9	11	6													
	yes	28	50	0.776	5															
	yes	35	50	not measured	6	6														

(b) Strips covered with waxy sludge in such a way that the unpainted spots were covered about 4/5, to establish the local stimulation of corrosion by waxy sludge.

(c) Strips of which half had been left unpainted but covered with waxy sludge. In the painted part of the strip unpainted spots were present as for (a).

The results of these tests are given in Table II. They clearly show that the corrosion-stimulating effect of waxy sludge deposits can act not only locally, but also over considerable distances (long-cell actions).

To gain an insight into the role played by the sludge itself we carried out a number of additional tests on painted wires, left uncoated at regular intervals (intended to serve as painted steel with paint defects) and coupled to strips of unpainted steel covered with waxy sludge.

In these tests the type and condition of the waxy sludge were varied. As regards the type of sludge the impression was gained that all sludges promote pitting corrosion, but that the sludges containing considerable quantities of water show the most pronounced effect.

To assess the influence of the condition of the sludge layer on pitting corrosion we performed similar experiments in which unpainted strip and painted wire were connected electrically outside the sea-water, which allowed electrochemical measurements to be made on the system (to be discussed later on). The following observations were made (see Table III)

The physical state of waxy sludge layers changed considerably upon exposure to sea-water. After some time holes and cracks appeared and subsequently local corrosion occurred on these strips, as shown in Fig. 5. Curiously enough, the severe local corrosion on the strip itself had little effect in reducing its long-cell action to the painted part of the test specimen to which it had been connected. Thick layers of waxy sludge did not allow long-cell action to start. Air drying of the waxy sludge layer at about 60°C, resulting in volatilization of light components, was found to suppress long-cell action to a large degree. In this case the waxy sludge layer did not reach the same degree of porosity as fresh sludge. Some local corrosion still occurred on the unpainted strip, however.

## 2.2. Electrochemical measurements

These measurements were made with the test systems consisting of two electrodes, viz. a painted steel wire (with defects in the paint coat) and waxy-sludge-covered unpainted steel strips, as mentioned before. The measurements, which were performed at least once a day, comprised the following parameters:

- open circuit potential of electrodes
- corrosion potential of system
- emf between electrodes
- corrosion current between electrodes
- overall resistance of corroding system.



WIRE No.	EXPOSURE TIME, DAYS	REMARKS
1	7	
2	8	
3	34	
4	28	
5	34	COUPLED TO BARE STEEL STRIP



Fig. 4. Waxy-sludge-covered steel wires after exposure in sea-water.

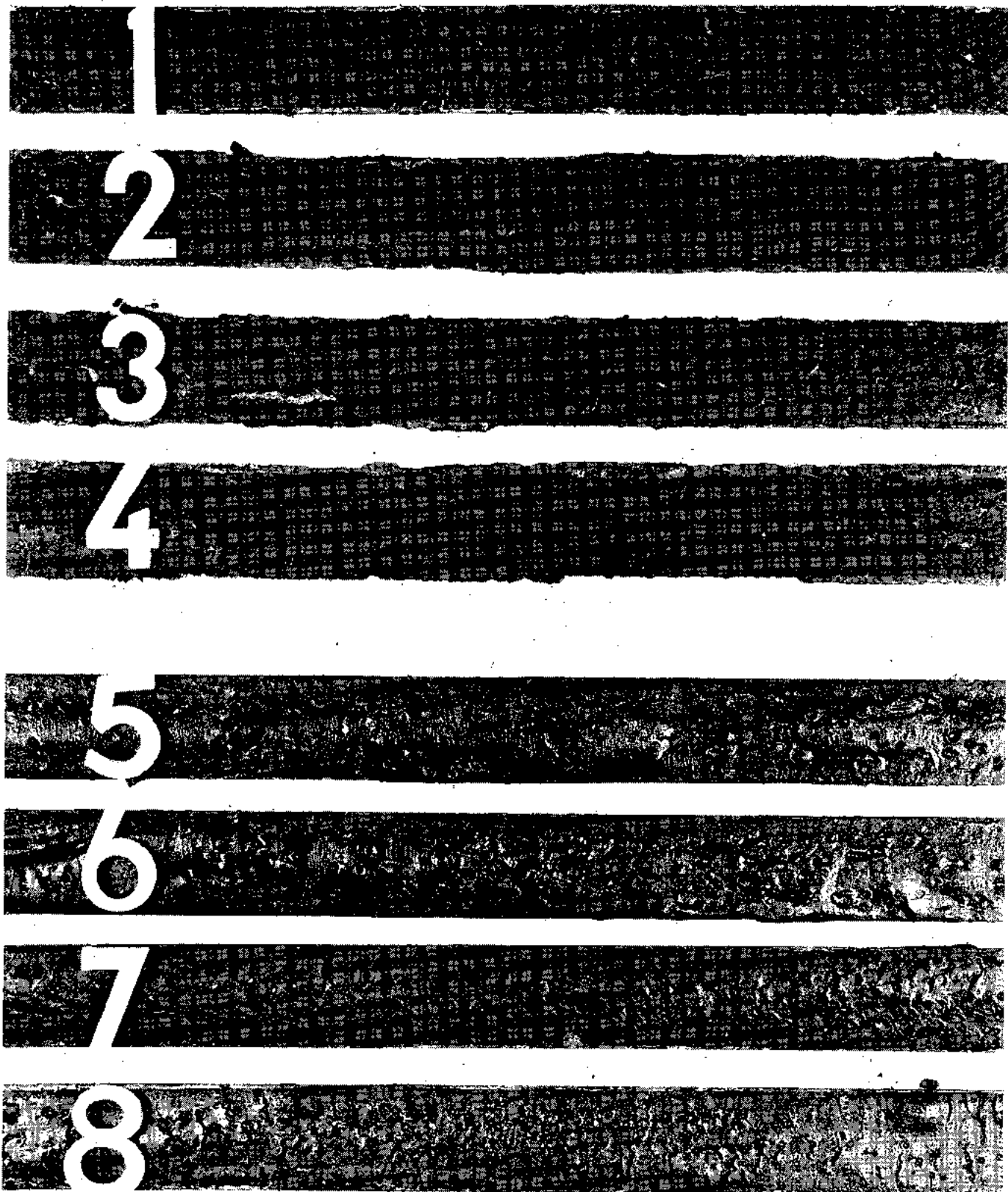


Fig. 5. Unpainted sludge-covered steel strips after exposure in seawater.  
1-4: covered with waxy sludge ex No. 8 starboard tank of ss «SITALA».  
5-8: covered with oil ex slops tank of ss «SITALA».

TABLE II

## PROMOTION OF PITTING CORROSION OF PAINTED STEEL IN SEAWATER BY WAXY SLUDGE DEPOSITS

Test specimens: «EPIKOTE»-painted steel strips with unpainted test spots exposure in 25 mm glass tubes,  
medium: aerated seawater at ambient temperature  
exposure time: 28 days

Type of test	Number of unpainted areas measured	Average corrosion rate, mm/year	Maximum corrosion rate, mm/year
Test spots as such; } no sludge present }	10	1.0	1.9
	10	1.1	1.5
Test spots 4/5 } covered with waxy } sludge }	20	1.6	5.2
	20	2.1	3.8
Half of test strip } unpainted but covered } with waxy sludge. Test } spots as such. }	10	2.8	3.4
	10	3.1	4.4

Potentials were determined versus a copper/copper sulfate half cell ( $E_h = -0.316$  V). For potential, emf and current measurements we used a Hewlett Packard dc vacuum tube voltmeter model 412 A/AR. The resistances were measured both with a dc and an ac instrument.

Typical results are given in Table III. The general trends derived from several thousand measurements are discussed in some detail below.

*Potential*

The potentials of (corroding) painted wires reached, after some fluctuations during the first few days, a stable potential of about  $-725$  to  $-750$  mV vs. Cu/CuSO<sub>4</sub> (sat.). The potentials of the waxy-sludge-covered unpainted steel varied widely, depending on the type of sludge used. In general they were 50-300 mV higher (nobler) than those of corroding steel, but even larger (over 500 mV) potential differences were recorded. The corrosion potentials of the complete system (both electrodes connected) were generally 20 to 50 mV higher than those of wires (corroding steel).

*emf*

The electromotive forces measured were similar to those computed from (open) potential measurements, provided the resistance of the waxy-sludge-covered steel electrode had already dropped from its initial high value (see Resistance).

*Corrosion current*

Immediately after the start of the exposure tests hardly any current could be measured. In most cases current in-

TABLE III

## PROMOTION OF PITTING CORROSION OF PAINTED STEEL IN SEAWATER BY WAXY SLUDGE DEPOSITS

Test specimens: painted wires with bare spots connected to bare steel strips covered with waxy sludge

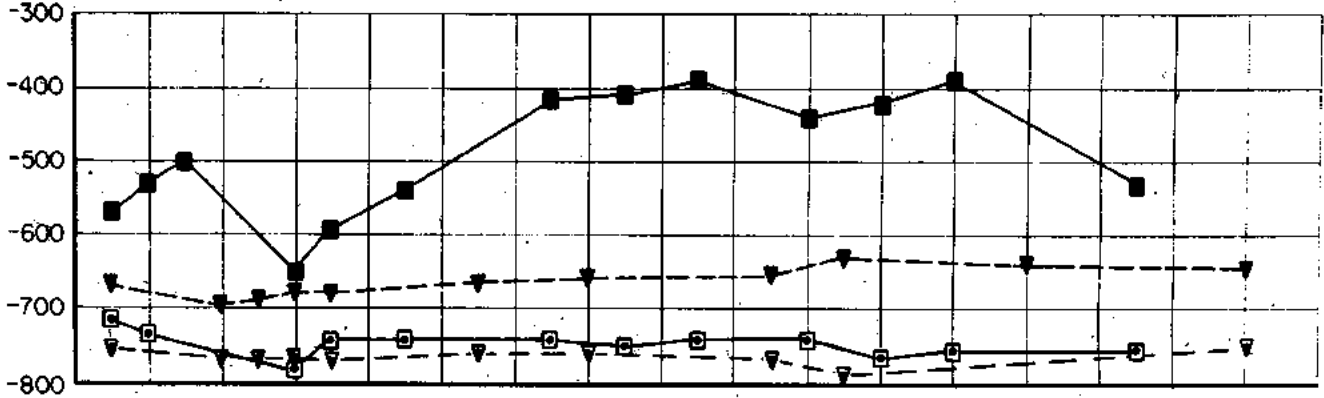
Particulars of test	Corrosion data			Electrochemical data						Exposure time, days
	Corrosion rate mm/yr		Pitting on strip	emf range, mV		Corr. current, mA, max.	Calcul. corr. rate, mm/yr	Resistance, $\Omega$		
	av.	max.		av.	max			initial	final	
Slops ex 13 C «SITALA» 3mm	3.5	3.9	no <sup>1</sup>	340	380	2.30	3.3	3000	130	54
Slops ex 13 C «SITALA» 3mm	2.6	2.8	yes <sup>2</sup>	100	160	0.9	1.6	310	110	54
Waxy sludge ex 8 S «SITALA» 10mm thick	< 0.5	< 0.5	no	450	545	< 10 <sup>-4</sup> A	nil	45 × 10 <sup>6</sup>	7 × 10 <sup>6</sup>	30
Waxy sludge ex 9/10 S «SITALA» 10mm thick	< 0.5	< 0.5	no	55	180	< 10 <sup>-5</sup> A	nil	18 × 10 <sup>6</sup>	2 × 10 <sup>6</sup>	30
Waxy sludge ex 8 S «SITALA» 3mm air-dried	1.7	2.0	yes	130	220	0.27	0.4	900	460	24
Waxy sludge ex 9/10 S «SITALA» 3mm, air-dried	0.9	1.8	yes	220	370	0.11	0.1	16500	2400	24

1. based on visual judgment
2. max. measured rate: 7,4 mm/yr.

POTENTIALS  
OF

	SLUDGE-COVERED UNPAINTED STEEL	PAINTED STEEL WITH DEFECTS	CURRENT
SYSTEM I	—■—	—□—	□
SYSTEM II	- - -▼-	- - -▼-	▼

POTENTIAL vs. Cu/CuSO<sub>4</sub>, mV



CURRENT,  $\mu$ A

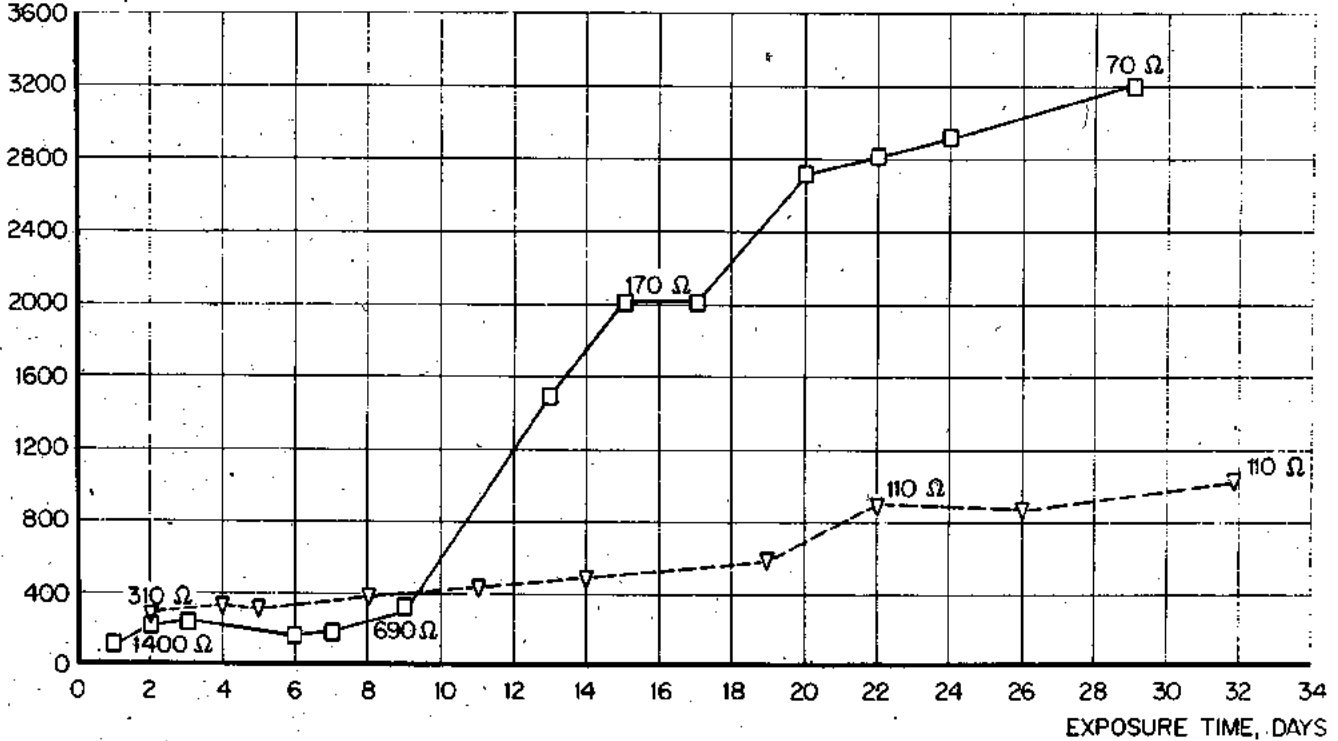


Fig. 6. Typical current-time and potential-time relationships for coupled waxy-sludge-covered steel/steel in aerated sea-water.

creased with time, whilst the emf remained constant. The increase and rate of increase varied widely with the type of deposits. In Fig. 6 typical examples for current-time and potential-time relationship is shown. As indicated in Table III there was satisfactory agreement between the measured corrosion rates and those computed from corrosion current data.

#### Resistance

The initially measured resistances in our test systems (200 cm<sup>2</sup> unpainted steel covered with about 3 mm waxy sludge or crude oil coupled to a painted wire with about 1 cm<sup>2</sup> unpainted area) were of the order of 10<sup>6</sup>-10<sup>7</sup> Ω, which agrees with the specific resistivities of the sludge (~10<sup>10</sup> Ω cm). A sharp drop in resistance of the system was measured at the moment when also a corrosion current began to flow. The measured resistances tallied very well with those computed from the emf's and corrosion currents.

We further established the following points:

- (1) the rate of resistance drop depends on the type of sludge and seems to be due to formation of water-logged deposits;
- (2) the thinner the sludge layer, the quicker the resistance drop;
- (3) small bare areas in the sludge layer makes a very large difference to the resistance but hardly any difference to the emf driving the corrosion cell between sludge-covered bare steel and small defects in painted steel.

### 3. DISCUSSION

The corrosion experiments as well as the electrochemical measurements have clearly established that steel covered with waxy sludge or crude oil achieves a nobler potential in sea-water than bare steel, i.e. it forms a cathode and the bare steel becomes the anode. According to Engell(2,3) this effect is due to a suppression of the anodic reaction underneath oil films, whereby the cathodic reaction becomes dominant and makes oil-covered steel in aerated sea-water more cathodic. The cathodic reaction, i.e. the reaction with oxygen is possibly enhanced by the high solubility of oxygen in hydrocarbons, which is higher than that in water. The stability of the noble potential of the sludge-covered steel is probably linked up with the alkalization as a consequence of the cathodic reaction.



In the Pourbaix diagram for iron<sup>4</sup> it is indicated that in aerated solution there is a sharp increase of the potential of an Fe electrode at a pH of 8. The corroding, that is, the anodic areas of steel tend to attain a potential close to the equilibrium potential of the non-aerated Fe/Fe<sup>++</sup> electrode, because oxygen is consumed by the oxidation of ferrous hydroxide to ferric hydroxide and the film of corrosion products prevents access of further oxygen to the liquid between it and the anodic areas.

The potential difference between sludge-covered steel and bare steel provides the emf to drive the corrosion current.

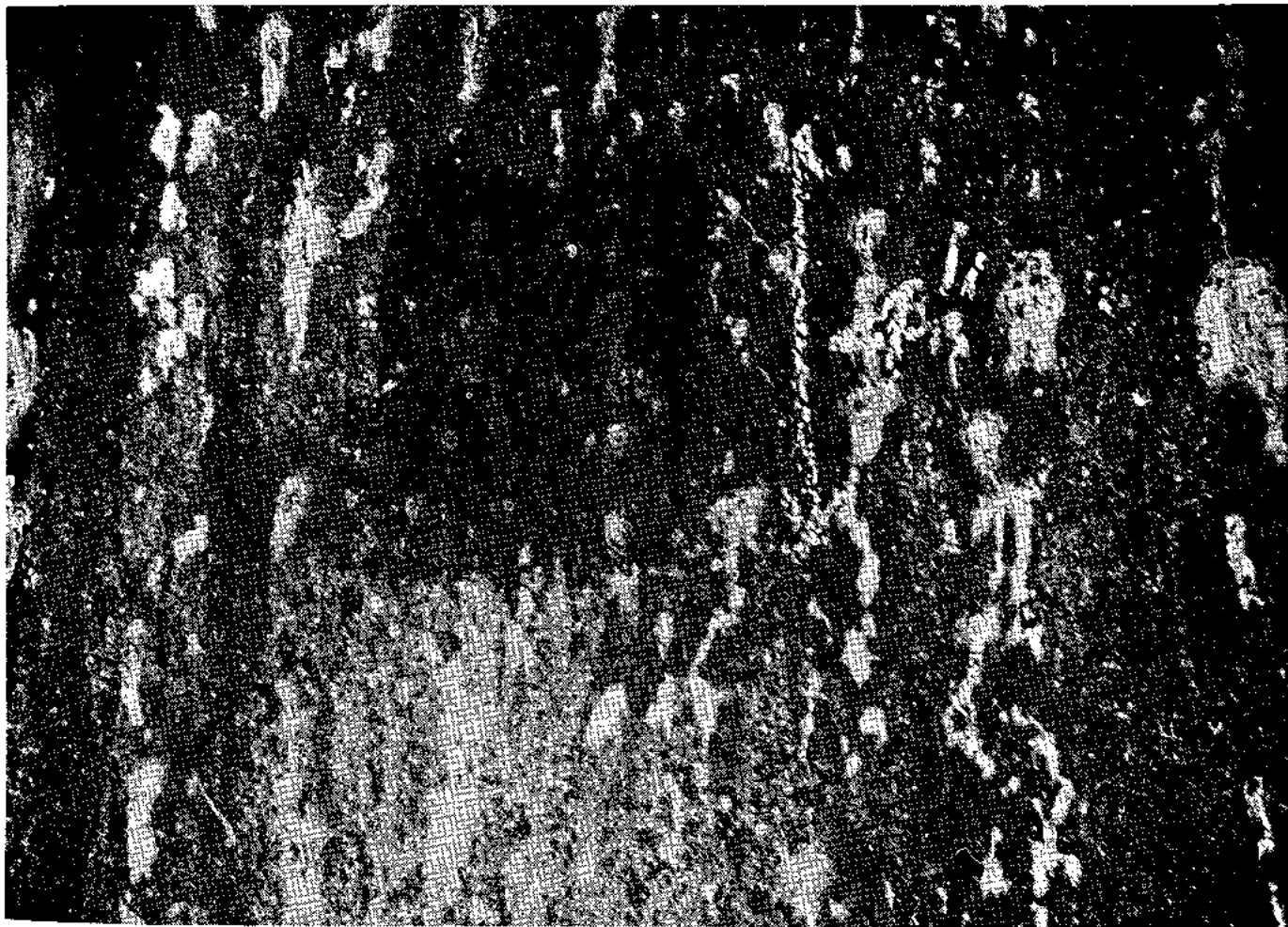


Fig. 7. Shallow pitting on unpainted verticals.

The corrosion cell is thus a large «differential aeration cell». The extent to which this driving force can act depends on the resistance in the circuit, which is the sum of the resistance of the sea-water, the resistance imposed by the sludge layer, and the back-emf of the anodic and cathodic polarization reactions. The resistance of sea-water is negligible, that of the sludge drops sharply when pores are formed and, although its specific resistance is still of a high order, the sludge-covered area is usually very large and its actual overall resistance is low enough to permit the corrosion process to operate. Thus, the rate-controlling factors for this differential aeration cell are the resistances imposed by anodic and cathodic polarization. Whether the corrosion process is under anodic or cathodic control depends on the degree of coverage with waxy sludge.

Predictions about the amount of corrosion to be expected can be made on the basis of the tests with the waxy-sludge-covered unpainted wires (see Table I). On account of the constant weight loss per unit time we can assume that the overall rate-controlling reaction, viz. oxygen transfer and consumption, proceeded at a steady rate. From the average metal wastage of the test specimens we calculated the cathodic current to be 240 mA/m<sup>2</sup>, taking into account the percentage of surface area not attacked. This means that 1 m<sup>2</sup> of steel entirely covered with waxy sludge can provide as much corrosion current as is necessary for the anodic dissolution of 2.1 kg steel per year. In case of partial coverage of a steel surface with waxy sludge the local corrosion rate would amount to about 0.3, 3 and 30 mm/year for 50, 90 and 99% coverage, respectively. Fortunately, in the case of a very high ratio of cathode to anode—the situation in «selectively painted» tanks with

very large bare steel bulkheads covered with crude oil deposits and a scatter of small defects on a painted tank bottom — the anodic reaction cannot keep pace with the cathodic reaction and becomes rate-limiting. This appears to happen at a pitting rate of 9-10 mm/year, which tallies closely with the rate encountered in actual practice in tankers, i.e. 4 mm/year with a ballast residence time of, on an average, 30 to 40% of the total time.

#### 4. CONCLUSION

Our laboratory experiments adequately explain the pitting phenomenon encountered in crude-oil tankers. The corrosion is of an electrochemical nature and is caused by oxygen in sea-water, which is abundantly available. A «differential aeration cell» is formed between surfaces covered with waxy sludge deposits (cathode) and surfaces in direct contact with sea-water (anode). This corrosion cell is characterized by a stable emf, which ranges from 50-300 mV, and a low electric resistance, which allows considerable currents to flow over large distances.

This corrosion process has the following consequences for crude-oil tankers. In unpainted tanks there is wide-spread shallow pitting on verticals because of non-uniform sludge thickness (see Fig. 7), but pitting tends to concentrate on poorly drained horizontals — the flat bottom and wide stringers — because of scattered pools of water (see Fig. 8). In selectively painted tanks the large sludge-covered bulkheads serve as cathodes to the small defects in the paint coat on the bottom which become anodes. Since the cathode is very large, pitting attack will be severe. In the fully painted tanks de-

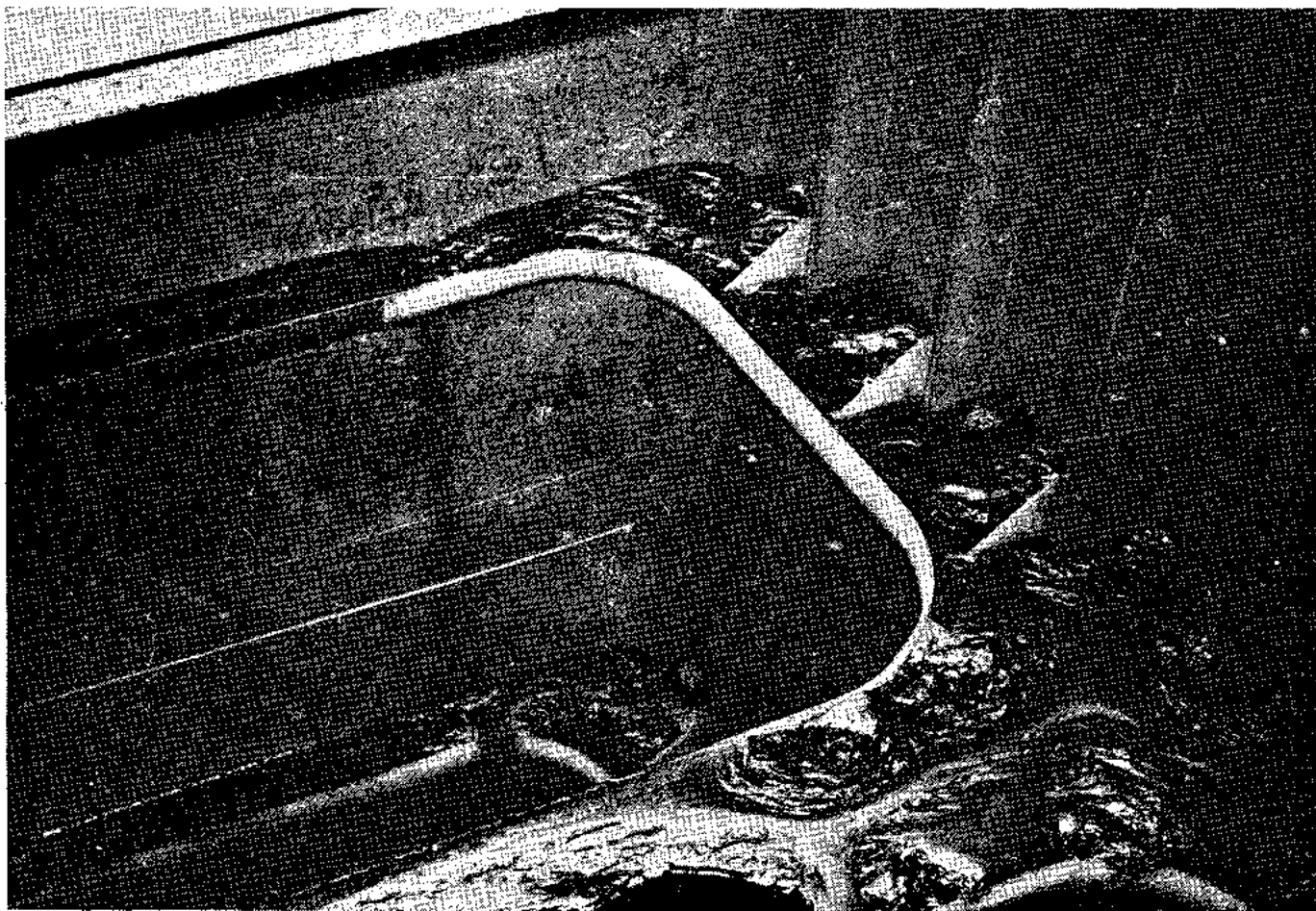


Fig. 8. Accumulation of sludge on horizontal stringers.

fects in the coating can act as anodes, depending on the degree of wax coverage. In this case pitting will be more likely to occur according as there are more defects. In any case, once a pit has formed on a horizontal it remains as a sink collecting water and providing a ready site for further attack as soon as the nearest cathode is immersed in water and capable of forming a corrosion cell.

Mitigation of this corrosion by cathodic protection seems feasible because of the purely electrochemical nature of this corrosion phenomenon.

#### ACKNOWLEDGEMENT

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#### DISCUSSION

Prof. ENGELL (Germany): Dr. Posch you have reminded me one of our old papers which was concerned with the problems mentioned. The results of this research work coincide absolutely with what you said. I am very glad because our old results have been verified by you. It is obvious that in an unpainted tank, corrosion is controlled cathodically.

Therefore we proposed at a discussion of the Society of Naval Architects, to coat the side walls up to the height of water line to reduce the cathodic reaction.

According to my opinion there is no doubt that the cathodic reaction is taking place at the height of waterline preferential, because there of course oxygen is dissolved preferentially.

Dr. POSCH: I should like to observe that in large companies certain faults are due to some policy decisions, which are difficult to change within a short time. I can share your opinion that the cathodic reaction should take place mainly in the upper part of the tank, but would think that this will not have a dramatic effect on pitting corrosion in tank bottoms. Pitting corrosion can occur in aerated sea-water at low oxygen concentrations. It is claimed that concentrations as low as 10-20 ppb  $O_2$  — as measured by the USA — developed oxygen meter — can cause pitting corrosion.

As we had some doubts about this, we made experiments to assess the corrosion potentials of steel in seawater as a function of oxygen content. We found that they keep a rather constant noble value down to an oxygen content of 0.1 p.p.m., below which value they drop to the potential of the non-aerated Fe electrode. At this concentration pitting also ceases. From this we can assume that at all places, also at the bottom of a tank, the oxygen concentration is high enough to cause pitting corrosion.

Secondly I would like to mention some experience gained in experiments in tankers with painted bottoms. Although an unpainted vertical bulkhead can be initially, i.e. in clean condition, less noble than a painted bottom, the opposite becomes true immediately when the dirty tank is ballasted, the verticals acting as cathode and the bottom as anode.

As regards your remark concerning filling tanks completely I should like to mention that in the Dutch Shell fleet the top of the tanks (deckhead verticals 2-3 m down) is painted, but this has, of course, no effect on the pitting corrosion at the bottom.

S. BARTHA (Sweden): I turn with my question to Prof. Engell and Dr. Posch: It is known that many ships and especially tankers are not painted at all, but they are protected cathodically only, and after unloading they are washed with sea-water at 80° to 85° degrees.

How much  $H_2SO_4$  and  $H_2SO_3$  may be evolved from the remaining sludge?

I had the opportunity to make some measurements, unfortunately some days later after the butterworthing, — and by the newly rusted surfaces it has shown that pH values were only 4.9 to 5.6, while on the other places the pH values were about 7. With lower pH value on the surfaces it was possible to notice hydrogen evolution. We measured at these places the potentials with reference electrode  $Cu/CuSO_4$ .

There, where pH was low, we found 400-450 mV, while at other places where pH was 7, we found 600-650 mV, which for unprotected surfaces is normal. Chlorides have certain influence, because the protective layer is destroyed very quickly. It must be taken into account not only the cathodic control but the reactions taking place between iron and sulphuric or sulphurous acid. The above mentioned surfaces

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can not be cathodically protected with these anodes, because the anodes are located too high so the layer of the sludge with a depth of 5-6 cm up to 10 cm by no means can be act as electrolyte.

Dr. POSCH: I cannot say directly what may happen at different pH values but I should like to emphasize that with pH measurements at places where corrosion takes place and in the presence of corrosion products the pH measured is not the primary one, but a secondary one, viz that developed at the spot due to the corrosion reaction. Therefore one must be very careful in interpreting the results of such measurements.

Whereas the salt concentration is an important parameter in pitting corrosion, we feel that mineral acids as such are of little influence. One can easily show that for corrosion of a given volume of steel, e.g. a 5 mm deep pit, one needs at least a hundredfold volume of dilute mineral acid to produce such corrosion.

S. BARTHA (Sweden): Is the phenomenon a question of aeration, i.e. an aeration cell?

Dr. POSCH: It is a large aeration cell acting as follows: The areas which are covered to a larger extent by waxy sludge become more noble than those covered to a smaller extent and then act as cathode and anode.

D. PETROCOKINO (France): Finally in order to conclude Dr. Posch speech, I call him to confirm in the following way. We know that some times in the tankers the bottom was corroded and the vertical surfaces not, it was attributed to the protective properties of crude deposits, it was thought that was resistant and consequently it neutralized the action of vertical surfaces of tankers which has been so important to day.

I think that Dr. Posch has established a new fact in this congress and that the deposits are resistant, I believe that the values of the resistance are indicated in the work which I read and which staying resistant has a property in case of oxygen deficiency and in this oxygen capture offers a cathodique situation on the enormous vertical surfaces.

These is new and the explanation at the same time of small problems that the expert which is occupied with the protection of tankers, does not understand, it brings an explanation to many of these small problems, which were not solved up the present, and which are completely solved.

I want to put the following question to Dr. Posch: This is that in the oil there is equally residual water which contains a lot of sulphur. Has Dr. Posch studied separately and parallel the influence of this sulphur, on the depolarization of cathodes of vertical surface to have an idea of the relation of the effect of oxygen or the effect of sulphur.

Mr. Raclot in France made the following experiment. He had in the laboratory a product of  $H_2S$  in water. It was sea water taken near to the coast and he found an increase in potential, that is, by doubling at the same time the parts of the specimen.

Have you any idea about the relation of the two phenomena?

Dr. POSCH: I think I may say the following: The amount of hydrogen sulphide lost during storage at the places of production is in general so high that we do not have difficulties in tankers. I must admit that we have not made a special study of this subject. I do know from experience with crude oil wells producing salt water containing hydrogen sulfide that traces of oxygen can cause very severe pitting corrosion, ten to twenty times as rapidly as without hydrogen sulfide. In this case one has to keep out oxygen completely.

Séance - Meeting - Sitzung - Συνεδρίασις

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Présidence - Presidency

Präsidium - Προεδρείον

Prof. J. YAHALOM (Israel),

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# LA PROTECTION CATHODIQUE DES CANALISATIONS SOUS-MARINES

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## RÉSUMÉ

Jusqu'à ces derniers temps, les protections cathodiques prévues pour des conduites sous-marines ont été systématiquement calquées sur le modèle de celles réalisées avec succès pour des canalisations enterrées; les deux techniques mises en œuvre à la mer étant le soutirage de courant et les anodes réactives.

Dans le cas du soutirage de courant, le courant de protection, produit par un redresseur implanté sur le rivage, se répartit sur la longueur de la conduite suivant une densité de protection à croissance exponentielle depuis l'origine de l'ouvrage, au large, jusqu'à son extrémité, à terre. L'émission du courant de protection s'effectuant par un seul déversoir, (association en parallèle de plusieurs anodes), celui-ci prend à sa charge la totalité de la longueur de la conduite, nécessairement.

Le fait n'est pas sans inconvénients: les revêtements des tubes deviennent, à la mer, du fait de leur porosité naturelle et des blessures reçues en cours de pose, de mauvais isolants. L'amortissement exponentiel du courant et du potentiel imposé au tube en résulte et limite à une portée très réduite sur une canalisation sous-marine, l'efficacité du redresseur à déversoir unique.

Certes, la portée protectrice d'une anode réactive est faible, mais l'amortissement du courant et du potentiel sur des longueurs minimales peut être confondu avec une ligne droite de faible coefficient angulaire. Ainsi, en multipliant le nombre des blocs d'anodes réactives est-il possible d'assurer, sous une densité de courant quasi constante, la protection intégrale d'une canalisation, aussi longue soit-elle.

L'inconvénient du système est, cette fois, la faible longévité d'une anode en service. Si les blocs réactifs ne peuvent être aisément renouvelés après usure, cette technique est sans issue dès qu'un ouvrage sous-marin est prévu pour durer plus de cinq ans.

Un système de protection cathodique de conduite sous-marine doit être, dans la mesure du possible doté d'une caractéristique d'amortissement:  $(\sin. h \times \# \times, \text{chx} \# 1)$  de profil aussi linéaire qu'il se puisse. Ainsi la solution des anodes réactives serait la perfection si la durée de service du système pouvait être portée à 10, 15 ou 20 ans.

Du fait du développement des réseaux de canalisations sous-marines, par suite de la croissance de l'industrie Pétrolière et notamment des forages sous marins, il était logique que l'on tendit à réaliser un jour des protections cathodiques à la mer s'inspirant du principe des émetteurs de courant multiples, tels que sont les anodes réactives, mais en dotant le système d'une autonomie de fonctionnement considérable, en tout cas supérieure à 10 années.

Les études, les recherches, ont donné naissance, dans cet esprit, à trois nouveaux procédés: pour les deux premiers l'auteur a remplacé, purement et simplement, les anodes réactives habituelles par des redresseurs et déversoirs immergés, couplés, alimentés en courant alternatif depuis la côte. Le système No 3 est, en fait, une évolution, assez élaborée, du soutirage classique. Le redresseur unique, implanté

à terre et le déversoir unique immergé, sont remplacés par une série de redresseurs et déversoirs immergés, portés par un câble électrique.

### 1er SYSTÈME

Les viroles étanches contenant les redresseurs et constituant chacune, une cellule de protection unitaire, sont solidaires de la conduite.

Les enveloppes qu'elles forment et le tube auquel elles sont accolées, constituent le pôle (-) du système électrolytique réalisé. Les pôles (+) unitaires sont les déversoirs portés par chaque cellule. Ils sont évidemment isolés du pôle (-) général.

Chacune des cellules unitaires de protection remplace ainsi les barillets d'anodes réactives que l'on fixe aux conduites immergées à intervalles réguliers. Un câble électrique traverse les cellules, assure leur alimentation et constitue la ligne de protection.

Les déversoirs peuvent, sans difficulté, assurer un service de 15 ans.

Nous donnerons à ce système breveté l'appellation INTEG, la ligne de protection étant INTEGRIE à la conduite et, lancée avec elle. Chacune des cellules prend en charge, moyennant un calcul de base établi avec discernement, une section bien définie de la conduite.

### 2ème SYSTÈME

La ligne de protection, analogue à la précédente dans sa conception, est, cette fois, indépendante de la conduite et lancée parallèlement à elle. Le pôle (-) général du système électrolytique est la conduite, reliée aux viroles des cellules de protection unitaires par des connexions transversales mises en place par une équipe de plongeurs.

Ainsi l'utilisation du procédé est-elle limitée aux petits fonds.

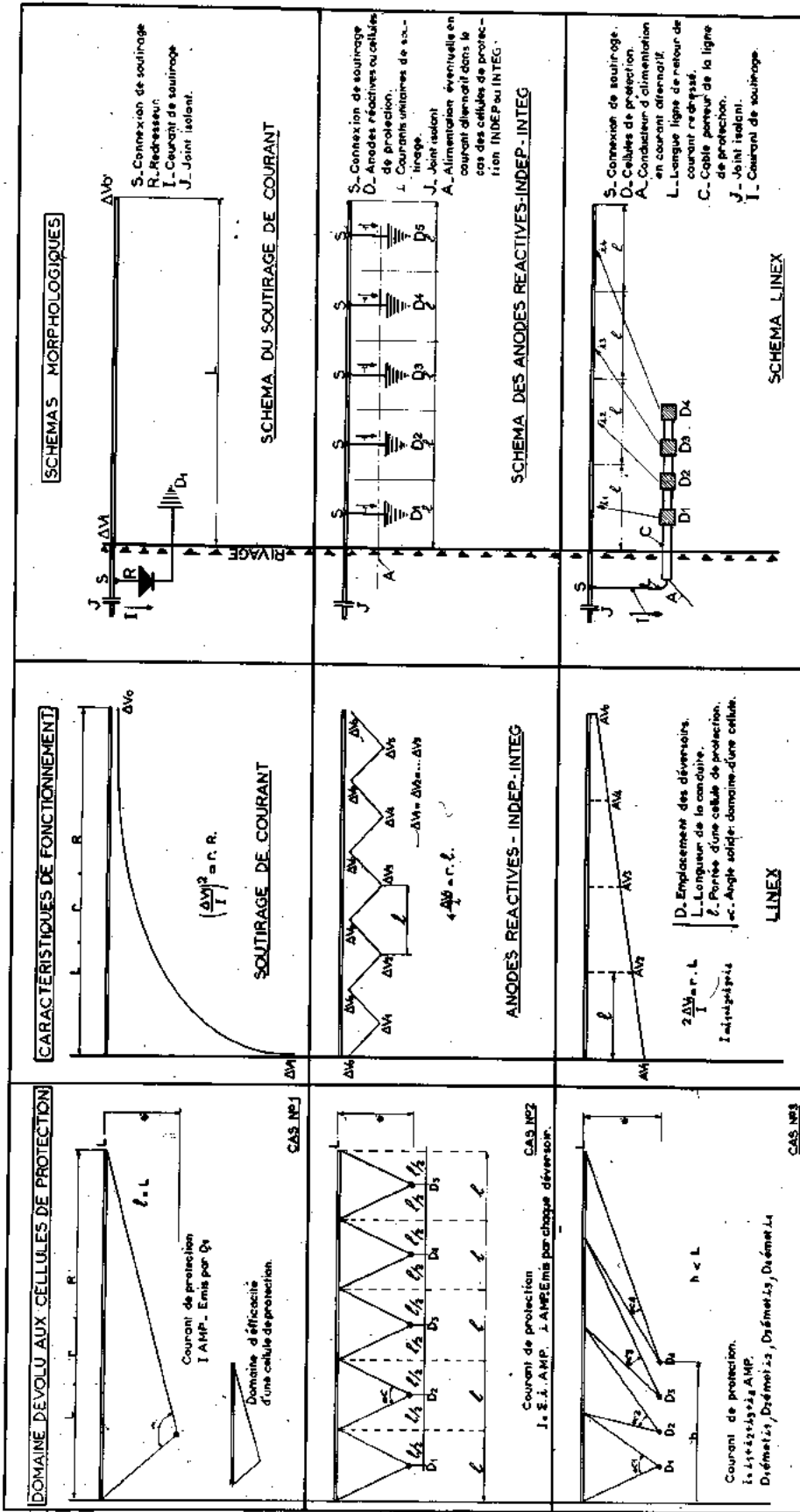
Nous donnerons à ce système breveté l'appellation INDEP, la ligne de protection étant INDEPENDANTE de la conduite, et, lancée après coup, en ce qui concerne les cellules et leurs déversoirs portés par le câble électrique même constituant la ligne de protection.

### 3ème SYSTÈME

On lance à la mer, après l'immersion de la conduite, un câble électrique portant les cellules de protection unitaires tout à fait analogues aux précédentes.

A l'intérieur du câble portant les cellules, un conducteur supplémentaire, de section appropriée, dit «conducteur de retour» est relié en un seul point, à terre, à la conduite et sert de retour au courant de soutirage assurant la protection cathodique du tube immergé.

Les redresseurs immergés, contenus à l'intérieur des cellules de protection, sont connectés, par leur pôle (-), au dit



conducteur de retour, et, par leur pôle (+), au déversoir porté par la cellule; ce déversoir est, évidemment, isolé électriquement de la virole de la cellule.

Chaque cellule prend, comme ci-dessus, en charge, une section bien définie de la conduite.

Nous donnerons à ce système breveté l'appellation LINEX en ce sens que, la ligne de protection est EXTÉRIEURE à la conduite et la prolonge, alors que l'amortissement du courant de protection et du potentiel imposé au tube se rapproche d'une caractéristique LINÉAIRE, ligne droite affectée d'un coefficient angulaire faible.

L'étude présente les différents systèmes de protection, classiques ou nouveaux, auxquels il a été fait allusion. Elle précise les différences doctrinales qui les séparent, fait ressortir leurs avantages et inconvénients, précise la marche à suivre pour les calculer convenablement.

L'influence du système de protection sur la valeur de l'isolement apparent que l'on peut attendre du revêtement est mise en évidence.

En fine, à propos d'une réalisation récente, il est donné un élément de comparaison entre le système de protection conformiste dit «soutirage de courants», ne comportant qu'un seul émissaire de courant (un seul déversoir) et celui, dit «LINEX» mettant en œuvre plusieurs émetteurs et émissaires de courant couplés, sous réserve d'assigner à chacun d'entre eux la

charge de la protection d'une section, bien définie, de l'ouvrage à protéger, délimitée par le calcul liminaire.

On fixe a priori, formellement, sans chevauchement, mais avec précision, la zone d'action impartie à chaque cellule de protection.

Les mesures permettent de confirmer la justesse relative des hypothèses du calcul.

Les différents systèmes de protection sont, également, classés au cours de l'étude, en fonction des facilités qu'ils offrent pour le contrôle permanent de l'efficacité de la protection offerte.

Enfin, quelques remarques sont faites, concernant l'évolution possible de la technique de protection, pour les années à venir.

Il semble possible, sinon probable, que pour les futures conduites sous-marines, seront substitués au système de soutirage actuel, des systèmes de plus en plus évolués, comportant plusieurs émetteurs de courant immergés, solidaires d'un câble électrique d'alimentation immergé lui-même. L'émission de chaque cellule de protection s'effectuera sous une différence de potentiel particulière, de manière à ce que chaque émetteur prenne en charge la protection d'une longueur bien déterminée de l'ouvrage, sans chevauchement, mais sans solution de continuité dans le potentiel imposé au tube, depuis son origine au large, jusqu'à son extrémité au rivage.

## 1. LIMINAIRE

Ne nous trouvons nous pas, en fait de protections cathodiques de canalisations sous-marines, dans la situation qui était celle de la Marine dans la première moitié du XIX<sup>e</sup> siècle ?

On avait transposé à la mer l'usage de la locomotive en munissant les navires de roues à aubages. Cette mécanique fonctionnait bien et l'on s'en contentait provisoirement, bien que l'on admit que ces renflements, rapportés sur la coque, offraient de la prise au vent et à la mer et fussent, de surcroît, une cible de choix pour les canonnières d'en face.

Logiquement, l'hélice apparut, fit timidement son chemin, puis s'imposa.

L'usage des techniques globales de protection, utilisées à terre avec succès sur les conduites «à longue distance», soit: revêtement associé à la protection cathodique, a été étendu tout naturellement aux canalisations sous-marines sans que la technologie en usage à terre ait été modifiée; à peine osa-t-on toucher à la morphologie du système et si peu! Cela n'a pas été et n'est pas sans inconvénients parfois mineurs, souvent dirimants.

Nous nous prendrons à songer qu'avant de devenir ce qu'elle est, l'automobile avait la forme d'une voiture hippomobile et que nos fusées lunaires cousinent encore avec celles de l'Empire Chinois des années zéro de notre ère, ou avec nos fusées républicaines du feu d'artifice du 14 juillet...

Il apparaît, et cela ne sera pas pour nous surprendre, qu'une évolution soit en cours, concernant la morphologie des systèmes de protection cathodique propres à assurer la sauvegarde des canalisations sous-marines. Nous nous orientons en direction de systèmes de protection réellement conçus en vue d'une utilisation à la mer.

Nous nous proposons de faire le point sur ce sujet, tel sera notre propos.

## 2. LE REVETEMENT DES TUBES D'ACIER SOUDES

On constate que les épaves métalliques coulées sur des fonds importants demeurent intactes, longuement. On ignore encore comment se comportera, du fait de sa longueur, une canalisation nue immergée, ainsi mise en contact direct et progressivement avec des milieux différents: des profondeurs de plus en plus prononcées sur des fonds qui s'accroissent, l'eau agitée des atterrages, l'eau calme et froide des profondeurs.

Ainsi, à la fois par principe et prudence, l'homme s'ef-

force de séparer le tube de l'eau et fait tous ses efforts pour réaliser, sur les conduites, des revêtements étanches, isolants.

### 2.1. Notion de $R'/\rho$ .

Du fait de la présence du revêtement, le métal du tube est, électriquement, isolé de la mer.

On peut admettre, l'eau de mer étant de résistivité sensiblement uniforme, une valeur normale pour celle-ci de  $\rho = 25$  ohms. cm<sup>2</sup>/cm — L'isolement étant relié à la résistivité du milieu encaissant par un facteur numérique, cet isolement est pratiquement constant pour toute la conduite, à condition que le revêtement soit relativement intact, sans solutions de continuité dues à des excorations de grande surface.

soit  $R'$  ohms.m<sup>2</sup>, la valeur de cet isolement auquel correspond la valeur:

$$R = \frac{R'}{\pi D} \text{ ohm} \cdot \text{m}, \quad (I)$$

(D étant en mètres la valeur du diamètre extérieur du tube), on observe expérimentalement, quel que soit le milieu encaissant autour de la conduite: sol, eau douce, eau de mer, que l'on peut tabler pour la plupart des revêtements sérieux recouvrant des surfaces métalliques, sur une valeur  $R'$  d'isolement telle que:

$$R' = K \cdot \rho \quad (II)$$

$\rho$  est alors la résistivité du milieu encaissant dans lequel la surface métallique revêtue est enterrée ou immergée.

### 2.2. Valeurs pratiques des isolements des canalisations immergées, obtenues en service, à la mer.

Pour le classique revêtement 2 C, (primaire carbolac sur le tube, plus deux couches de complexe carboplast/fibre de verre, d'épaisseur totale 8 mm), la résistivité de l'eau de mer étant de 0,25 ohm.m<sup>2</sup>/m et le coefficient K de l'ordre de 3.000 dans le cas le plus favorable connu, il vient:

$$R' = 3500 \times 0,25 = 850 \text{ ohms} \cdot \text{m}^2 \quad (III)$$

Dans l'eau de mer, il est ainsi assez illusoire de tabler sur des valeurs d'isolement supérieures au chiffre ci-dessus valeur optimale, exceptionnelle, assez théorique jusqu'ici, mais nous le savons personnellement, réalisable en prenant des précautions assez inhabituelles.

Aux aléas du lancement à la mer de l'ouvrage, peuvent en effet correspondre des excoriations de la garniture de protection. On se donne toutes les chances, en ne préparant point avec soin les différentes phases du lancement, si celui-ci est de longue durée, multipliant les possibilités de contact et frottement de la conduite avec des obstacles divers, (les flins de balise notamment); de n'observer que des isollements faibles, de 100 à 120 ohms.m<sup>2</sup>, pour le revêtement 2 C. Cela correspond à K = 400 environ, mais à 40 ou 50 ohms/m<sup>2</sup> seulement pour le revêtement C, d'épaisseur 4 mm à 5 mm. Ces constatations doivent-elles inciter au pessimisme? - Non.

«Et, on voit déjà apparaître l'influence de la technique du lancement sur le calcul de la protection cathodique, calcul étroitement lié à la résistance d'isollement de l'ouvrage à protéger».

### 2.3. Notion de «Résistance apparente» d'isollement.

En admettant que l'on se trouve en présence d'un revêtement sans solutions de continuité ni blessures, la valeur de l'isollement d'une telle garniture est, de toute évidence, liée à la répartition statistique des anfractuosités capillaires inhérentes à sa mise en œuvre et inévitables (porosité).

En l'absence de protection cathodique l'eau percole et l'isollement s'amenuise. Sous protection cathodique, la pénétration de l'eau semble être favorisée mais on constate les phénomènes suivants:

soit  $V_x$  volts, la différence de potentiel imposée (polarisation cathodique totale) relevée en un point quelconque de la conduite, entre le métal et une électrode de référence:

Si  $V_x \geq 7$  volts, les anfractuosités du revêtement laissent échapper des bulles d'hydrogène, bien visibles et peut à peu s'élargissent au point de devenir des fissures ou des orifices.

Si  $V_x$  est de l'ordre de 1,5 à 3 volts on ne constate aux anfractuosités, ni bulles, ni modification visible de l'état de surface du revêtement.

Si  $V_x$  est de l'ordre de 1 volt ou moins le revêtement tend à devenir une éponge bien que le métal sous jacent demeure encore intact, exempt de corrosion, à 0,9 volt, malgré la présence d'eau de mer, mais on doit, régulièrement, avec le temps, augmenter le débit de la protection pour maintenir  $V_x \neq 1$  volt.

Il nous a été donné de constater, au cours d'une carrière de cathodicien dépassant notablement 25 années, tant à terre qu'à la mer, que, pour des revêtements de même nature et même posés, les meilleurs isollements correspondaient toujours à des potentiels imposés moyens  $V_m$  de l'ordre de 2 volts.

Qu'est-ce que  $V_m$ , le potentiel imposé moyen découlant de la protection cathodique? Quand on mesure les potentiels locaux  $V_1, V_2, \dots, V_n$ , sur une conduite protégée cathodiquement sur une longueur  $l$ , en  $n$  points de cotes  $x, x_1, x_2, \dots, x_n$  distants les uns des autres de  $l_1, l_2, \dots, l_n$  et à condition que les valeurs  $l$  soient assez faibles, nous définissons  $V_m$  par l'expression:

$$V_m = \frac{\frac{(V_1 + V_2)}{2} l_1 + \frac{(V_2 + V_3)}{2} l_2 + \dots + \frac{(V_{n-1} + V_n)}{2} l_n}{L} \quad (IV)$$

Nous proposons l'explication suivante au sujet de l'existence d'un isollement apparent maximal pour  $V_m \neq 2$  volts.

Pour les valeurs  $V \geq 7$  volts, le rH caractérisant la couche limite eau/métal, (auquel correspond une pression  $H_2$  élevée) permet le dégagement d'hydrogène gazeux et l'élargissement de toute fissure par abrasion mécanique, à la longue.

Pour les valeurs  $V$  voisines de 2 volts, l'hydrogène réduit est seulement absorbé sur le métal et sur les parois du métal; la blessure est ainsi comatée.

Pour les valeurs  $V$  inférieures au volt, l'eau n'est pas électrolysée, la gaine d'hydrogène réduit ne se forme pas, l'eau pénètre le revêtement, par capillarité et percole plus

avant. L'hydrogène absorbé étant un très bon isolant électrique, il sera ainsi normal de constater, sur une même conduite, des isollements différents selon la valeur  $V_m$  caractérisant la protection. L'isollement a des chances d'être maximal pour une valeur  $V_m$  convenable, et un écart minimal entre les valeurs extrêmes  $V_x$  à l'origine et à l'extrémité de la conduite.

On ne devrait, en aucun cas, dire:

— isollement d'une conduite, mais  
Isollement apparent d'une conduite.

«Le système de protection cathodique adopté par une conduite immergée a une influence notable sur la valeur de l'isollement apparent de l'ouvrage, la valeur du potentiel moyen imposé  $V_m$  est liée à la forme du profil en long de la caractéristique d'amortissement de la d.d.p. métal/eau de mer sur l'ensemble de l'ouvrage».

### 2.4. Revêtement «MONOBLOC»

Le revêtement «Monobloc» est un revêtement tel que, s'il était «autopsié», après sa mise en œuvre, il soit impossible de distinguer les couches successives ou les spires qui ont servi à le constituer. De tels revêtements, tels les garnitures classiques C ou 2C, ne sont pas structurées et sont de ce fait relativement étanches et isolants.

### 2.4. Revêtement «SPIRALE»

Le revêtement spirale est un revêtement tel que, s'il était «autopsié» après sa mise en œuvre, il soit possible de distinguer encore les couches ou les spires qui ont servi à le constituer: par exemple bandes plastiques ou bandes adhésives. De tels revêtements, sous certaines conditions, peuvent être étanches et silants.

L'homogénéité de structure, l'adhérence de la garniture au tube, l'imperméabilité de la chape sont les qualités que l'on doit exiger de tout revêtement. Tous les revêtements, à sec, sont isolants, l'essai en laboratoire est, en général, sans signification et aussi les essais à grande échelle mal inspirés. Est à proscrire absolument toute occasion de cheminement capillaire de l'eau. Ainsi, pour les revêtements spirales, l'adhérence des spires entre elles doit être absolue et ne laisser subsister aucun vide dans la zone où finit le chevauchement de deux épaisseurs de revêtement.

En outre, la résistance mécanique et l'isollement de la garniture de protection ne doivent en aucun cas souffrir des opérations de lancement, ni du séjour au soleil, ni du stockage sur l'aire de lancement, ni du passage sur les diabolos de mise à l'eau.

Bien qu'ayant personnellement réalisé pour les revêtements le premier détecteur de défauts à ressort circulaire, déjà moins destructif que ses aînés, nous sommes maintenant hostiles à cette technique qui engendre sous l'effluve, sans qu'elles soient décelables, plus de porosité qu'elle ne décèle de défauts. Ne sont détectés que les fissures ou trous francs, généralement visibles et que la protection cathodique colmatra sans peine. . . quelque défauts échappés à la vigilance d'observateurs ne sont pas graves (1).

Tant il est vrai que la régression des opinions, avec le temps, dont Montaigne nous donna l'exemple, est un fait général.

### 3. La protection cathodique est une application de la loi d'Ohm types et systèmes de protection pouvant être imaginés. Avantages et inconvénients de chaque solution.

Sur une conduite immergée, un coupon de conduite de un mètre de longueur, quelconque, de cote  $x$  (\*), draine un

\* Nous prendrons  $x = 0$  à l'extrémité de la conduite la plus éloignée de la terre. Pour une conduite de longueur  $L$ ,  $x = L$  à la terre,  $x = 0$  au large. Pour un tronçon de conduite de longueur  $l$ ,  $x = 0$  pour l'extrémité la plus éloignée de la terre,  $x = l$  pour l'extrémité la plus rapprochée du rivage.

courant de protection  $i_x$  amp. On mesure en ce point, en intercalant un voltmètre approprié entre le tube et une électrode de référence (de tension propre  $e_v$  entre ses extrémités) une différence de potentiel  $V_x$  correspondant à l'isolement ohm.m dû à la présence de l'isolement.

$$V_x = R \cdot i \quad (V)$$

Cette différence de potentiel  $V_x$  est la somme de:

$e_v$  — voisine de 0,600 volt — d.d.p. aux bornes de l'électrode de référence.

et  $V'_x$  — d.d.p. entre le métal et l'eau de mer, au travers du revêtement.

$V'_x$  elle-même est la somme de:

$V_s$  — d.d.p. spontanée entre le métal et l'eau de mer, en l'absence de protection cathodique soit  $V_s \neq 0,0$  volt

et de  $\Delta V_x$  abaissement de potentiel dû à l'action de la protection cathodique, en sorte que:

$$V_x = Ri = v + V'_x = (v + V_s) + \Delta V_x = 0,6 \text{ volt} + \Delta V_x \quad (V')$$

En prenant à  $x = 0$ , la valeur minimale  $\Delta V_0 = 0,4$  volt le potentiel minimum minimum de sécurité d'une conduite protégée cathodiquement il doit être trouvé, à son origine côté mer, au moins égal à 1 volt ( $V_x = 1$  volt — pour  $x = 0$ ).

On distinguera entre elles, les différentes solutions de protection cathodique, d'une conduite immergée par la forme de l'expression:

$$\Delta V_x = f(x) \quad (VI)$$

Cette fonction peut être exponentielle ou se rapprocher d'une fonction linéaire, être une fonction unique sans discontinuité de  $x = 0$  à  $x = L$  ou se composer de plusieurs fonctions successives juxtaposées de  $x = 0$  à  $x = l$ , la valeur  $\Delta V_l$  de la section N (de côté l) étant égale à la valeur  $\Delta V$  de côté ZERO de la section N + 1, la section N = 1 étant celle située le plus au large.

Les solutions que l'on peut donner au problème de la protection cathodique d'une canalisation sont données aux chapitres (3.1), (3.2), (3.3); elles sont conformistes et du domaine public ou nouvelles et récemment brevetées.

### 3.1. Solution conformiste du soutirage de courant (fonctions exponentielles)

Le courant de protection prenant en charge une conduite de longueur L, soit I ampères, croît exponentiellement depuis l'extrémité immergée ( $x = 0$ ) ( $i_0$ ) de la conduite jusqu'au point unique de soutirage S ( $x = L$ ) situé à terre. Il en est de même pour l'accroissement de potentiel  $\Delta V_x$  qui passe de  $\Delta V_0$  pour  $x = 0$  à  $\Delta V_L$  pour  $x = L$

$$\text{ainsi: } I_x = f(e^x) \quad \Delta V_x = f(e^x)$$

Le courant I est produit en général par un redresseur de courant connecté par le pôle (—) à la conduite et par le pôle (+) à un système de déversoirs immergés (Fig. 1).

Les expressions donnant I et  $\Delta V_L$  sont celles bien connues:

$$I = \frac{a}{r} \cdot \Delta V_0 \cdot \text{shal} + i_0 \cdot \text{chal} \quad (VII)$$

$$\Delta V_L = \Delta V_0 \cdot \text{chal} + \frac{r}{a} \cdot i_0 \cdot \text{shal} \quad (VIII)$$

$i_0$  est la densité de courant de protection unitaire à  $x = 0$  (ampères)

r est la résistance longitudinale du tube en ohms.m

$$r = \frac{522}{Dm \cdot e} \times 10^{-4} \text{ ohm.m (tube en acier)} \quad (IX)$$

Dm est en centimètres, le diamètre moyen du tube d'épais-

seure (cm)

$$a = \left(\frac{r}{R}\right)^{1/2} \quad (X)$$

R est la notation habituelle

$$R = \frac{R'}{\pi \cdot D}$$

$\Delta V_0$  est l'abaissement de potentiel à  $x = 0$  (volt) auquel correspond une densité de courant

$$i_0 = \frac{\Delta V_0}{R} \quad (i_0 \text{ est relatif au dernier mètre de la conduite, vers le large}) \quad (XI)$$

I est le courant de soutirage débité par le redresseur (ampères)

$\Delta V_L$  est l'abaissement de potentiel à la connexion de soutirage  $x = L$  (volt) (Au rivage).

Le système conformiste schématisé à la fig. (1) possède les avantages de la simplicité, l'accessibilité aux appareillages est parfaite; les déversoirs usés sont aisément renouvelés.

Au chapitre des inconvénients, qui peuvent être dirimants, notons que pour des isollements R' de l'ordre de 100 ohms.m<sup>2</sup>, une longueur de tube de 10 Km requiert une protection d'un débit de plusieurs centaines d'ampères auxquels correspond une valeur  $\Delta V_L$  beaucoup trop élevée, que le revêtement admet avec difficultés et, tension déjà dangereuse pour l'être humain (20 volts au minimum).

### 3.2. Solution conformiste ou nouvelle selon le cas. (fonctions à caractéristiques quasi linéaires).

Cette solution a déjà ses lettres de noblesse sous la forme des anodes réactives (fig. 2) mais deux réalisations évoluées, de même esprit, de morphologies différentes ont vu récemment le jour; ce sont les solutions comportant:

«une ligne de protections» intégrée à la conduite (Fig. 3).  
ou «une ligne de protections» parallèle à la conduite (Fig. 4).

Dans tous les cas, chacune des anodes réactives A ou chacune des cellules de protection C doit protéger une section l d'une conduite L.

Le courant 2 i débité par chaque anode réactive ou cellule de protection correspond à un potentiel  $\Delta V_0$  à  $x = 0$  et  $\Delta V_l$  à  $x = \frac{l}{2}$ , soit:

$$2i = 2 \left( \frac{a}{r} \cdot \Delta V_0 \cdot \text{sha} \frac{l}{2} + i_0 \cdot \text{cha} \frac{l}{2} \right) \quad (XII)$$

(on admet que le point de soutirage s est au milieu de la section protégée).

$$\Delta V_l = \Delta V_0 \cdot \text{cha} \frac{l}{2} + \frac{r}{a} \cdot i_0 \cdot \text{sha} \frac{l}{2} \quad (XIII)$$

Les notations  $\Delta V_0$ , r, a,  $i_0$  sont identiques à celles du paragraphe (3.1).

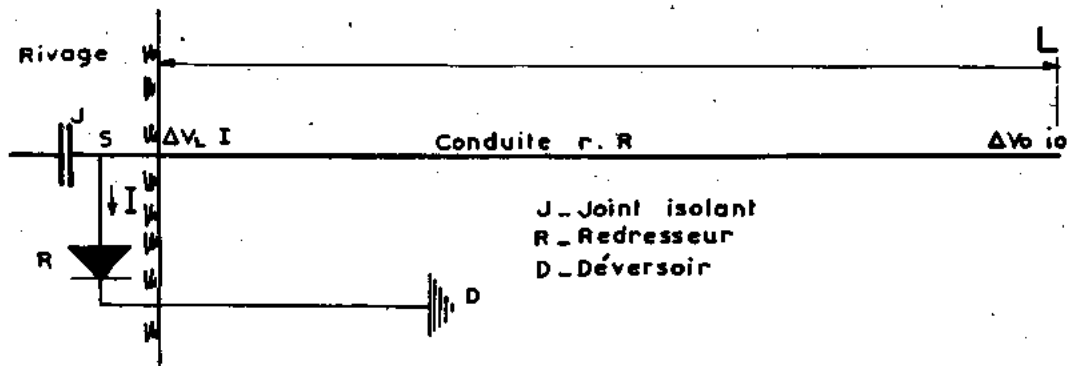
#### 3.2.1. Solution conformiste: les anodes réactives.

Les anodes réactives en zinc, magnésium ou aluminium sont connectées à la conduite à intervalles convenables par des conducteurs de liaison (fig. 2) ou intégrées à la conduite (fig. 2a).

Le dispositif de la Fig. 2 est utilisable pour les faibles profondeurs d'immersion, les plongeurs ferment les connexions après le lancement de la conduite, le dispositif de la fig. 2a ne tient pas compte des fonds.

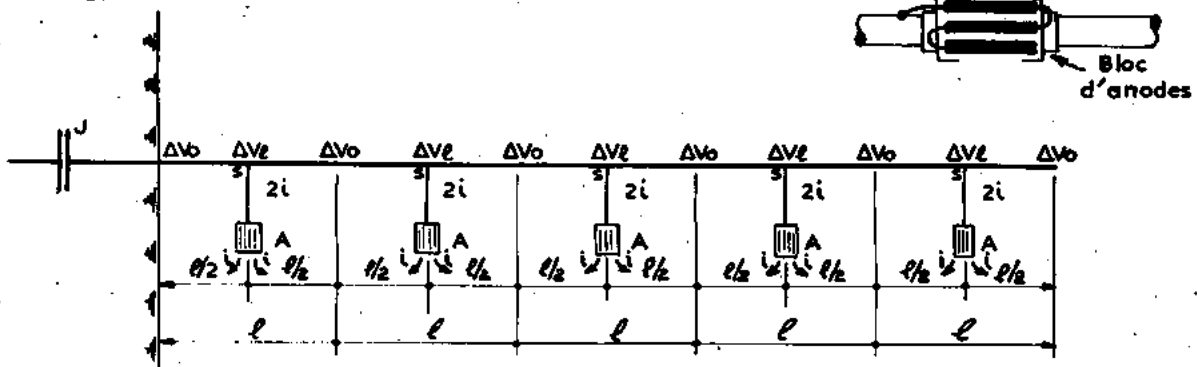
L'inconvénient général des anodes réactives est leur disparition rapide par usure totale (3 à 5 ans) et, la difficulté ou l'impossibilité de leur remplacement. En outre, l'isolement apparent de la canalisation, est, toutes choses égales d'ailleurs, à sa valeur minimale ( $V_m \leq 1v$ ) il y a toujours lieu de mettre en œuvre des tonnages importants de blocs réactifs.

# Fig. 1 — SOUTIRAGE DE COURANT

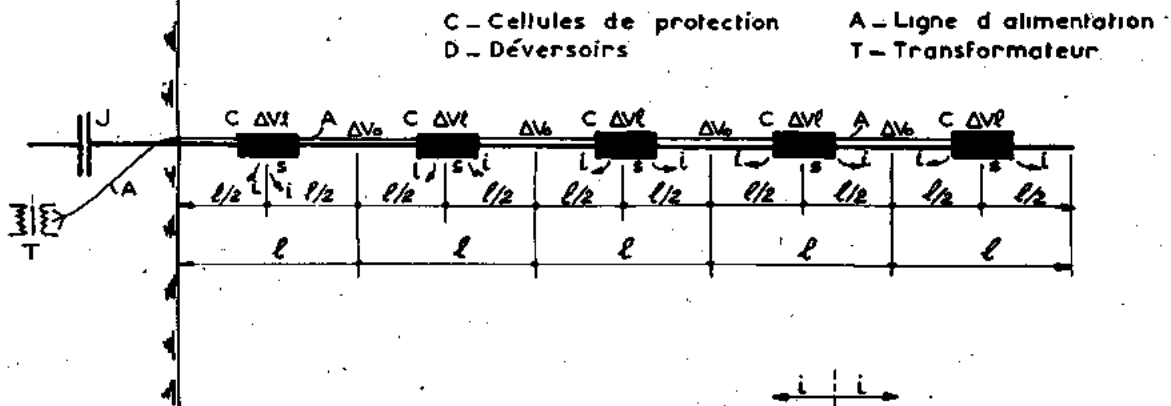


# Fig. 2 — ANODES REACTIVES

## Fig. 2a



# Fig. 3 — LIGNE DE PROTECTION INTEGREE A LA CONDUITE.



## Fig. 3a

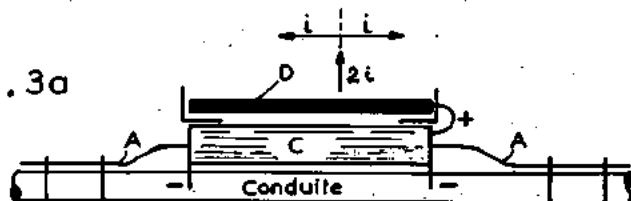
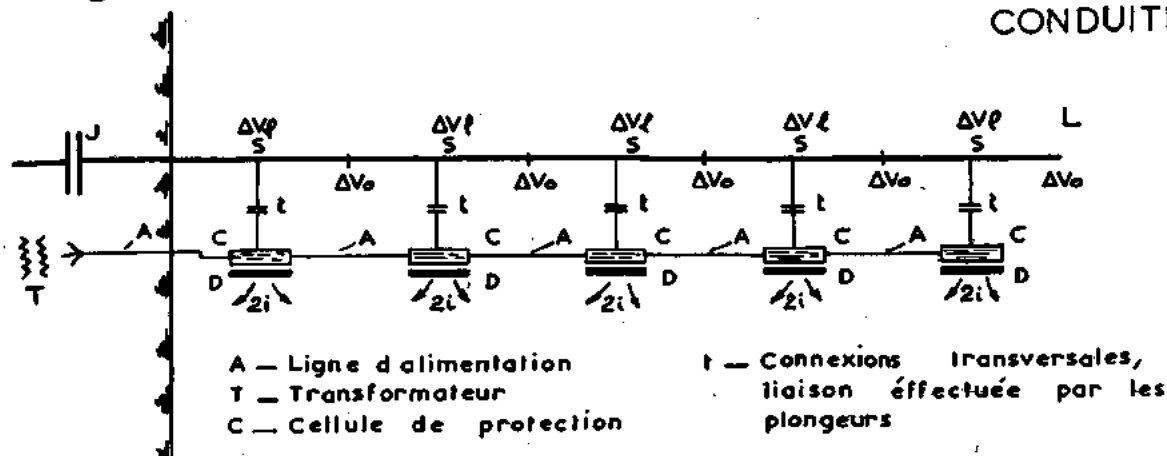


Fig. 4 - LIGNÉ DE PROTECTION PARALLÈLE A LA CONDUITE



«Par contre, lorsque la conduite est de faible longueur, de petit diamètre, peu profondément immergée, les anodes réactives constituent la solution de choix si toutes les dispositions ont été prises pour rendre aisé le renouvellement des blocs de protection».

Cette dernière condition étant remplie, on peut même envisager de protéger, avec les anodes réactives, une conduite de grande longueur, à condition de tenir les anodes très rapprochés.

3.2.2. *Solution nouvelle: ligne de protection intégrée à la conduite (Fig. 3).*

Dans ce système, on remplace les blocs d'anodes de la fig. 2 a intégrés à la conduite, par des cellules C étanches, contenant un redresseur et surmontées d'un déversoir, (pole +) du système, le pole (-) étant constitué par la virole contenant le redresseur, celle-ci étant soudée à la conduite. De la sorte, le tube est protégé cathodiquement. Un cable d'alimentation, triphasé par exemple, traverse successivement les cellules de protection C. Il est amarré à la conduite, entre les cellules. La durée de service d'un tel système est de 15 ou 20 ans, le procédé s'accommode de toutes longueurs de tubes.

L'avantage du système est son indépendance totale vis-à-vis de la profondeur d'immersion, son autonomie sans révision. L'inconvénient est la complication du mode de lancement du fait de l'alourdissement local du tube; d'autre part, la ligne de protection n'étant pas relevable, il faut, au départ, prévoir large. Il est des cas pour lesquels ce procédé est le seul valable.

3.2.3. *Solution nouvelle: Ligne de protection parallèle à la conduite (Fig. 4).*

Dans ce système, on remplace les blocs d'anodes de la Fig. 2 par des cellules de protection analogues à celles du paragraphe 3.2.2., la liaison conductrice entre le tube et la virole de la cellule est assurée par une connexion fermée par les plongeurs. On est ainsi dans l'obligation de «dancer à la mer» la ligne de protection (pratiquement presque aussi longue que la conduite), après l'immersion du tube. L'avantage de la durée de service sans révision, place celui-ci dans une situation favorable vis-à-vis des anodes réactives; son utilisation est cependant limitée aux immersions sur les hauts fonds du fait de la nécessité d'intervention des plongeurs.

La longueur de la conduite n'intervient pas; elle peut être aussi longue que possible sans inconvénients d'ordre technique.

«Ajoutons que l'avantage commun aux solutions 322. 323 sur la solution 321 est la possibilité d'obtenir une valeur  $V_m$  supérieure à 2 volts (voir chapitre 23)».

3.3. *Solution nouvelle: Ligne de protection en prolongement de la conduite, à caractéristiques intermédiaires entre celles, exponentielles ou linéaires, du courant et du potentiel sur la conduite. (Fig. 5-et 5a).*

Soit XX (L) une conduite immergée; on prolonge cette conduite, à partir du point de soutirage par un conducteur immergé LL, de section appropriés. Appelons ce conducteur LL: ligne de retour, ou longue ligne de retour par laquelle on soutire, à terre, le courant I amp, assurant la protection intégrale de la conduite.

Sur ce conducteur LL sont disposés, à des intervalles  $(l_1)$ ,  $(l_2-l_1)$ ,  $(l_3-l_2)$ ... des capacités étanches ou cellules de protection unitaires  $C_1, C_2, C_3, \dots (n \text{ cellules})$ . A l'intérieur des cellules, également traversées par une ligne d'alimentation en courant alternatif, on trouve un transformateur (ou plusieurs) et des diodes redresseuses S et R.

Le conducteur LL et les conducteurs d'alimentation (4 conducteurs par exemple) constituent un cable armé, l'ensemble des cellules de protection et du cable formant une ligne «monobloc» ou «ligne de protection» qui est lancée à la mer ou peut en être remontée sans dommages du fait de la résistance mécanique du système à la traction.

Les diodes  $S_1, S_2, S_3, \dots, S_n$  jouent le rôle de survolteurs pour annuler la chute de tension sur le conducteur ininterrompu = conduite immergée,  $S, l_1, (l_2 - l_1), (l_3 - l_2) \dots (l_n - l_{n-1})$  (Fig. 5).

Les diodes  $R_1, R_2, R_3, \dots, R_n$  sont les redresseurs de protection cathodique de chacune des cellules de protection  $C_1, C_2, C_3, \dots, C_n$  dont les pôles (-) sont reliés à LL et les pôles (+) à chacun des déversoirs  $D_1, D_2, D_3, \dots, D(n)$  portés par les cellules.

Ajoutons que les cellules sont éloignées les unes des autres de  $(l_2 - l_1), (l_3 - l_2) \dots$  (dans le cas de 3 cellules donné en exemple). Chacune des cellules (protection unitaire) prend à sa charge une longueur de conduite telle que  $\lambda_1$ , pour  $C_1$ ,  $\lambda_2$  pour  $C_2$ ,  $\lambda_3$  pour  $C_3$ ; la longueur de la ligne  $l_3$  est notablement inférieure à la longueur L de la conduite.

Dans l'exemple schématique de la fig. 5 le courant  $i_2$  émis par la cellule  $C_2$  protège, nous l'avons dit, une section de longueur  $\lambda_2$  de la conduite soit:

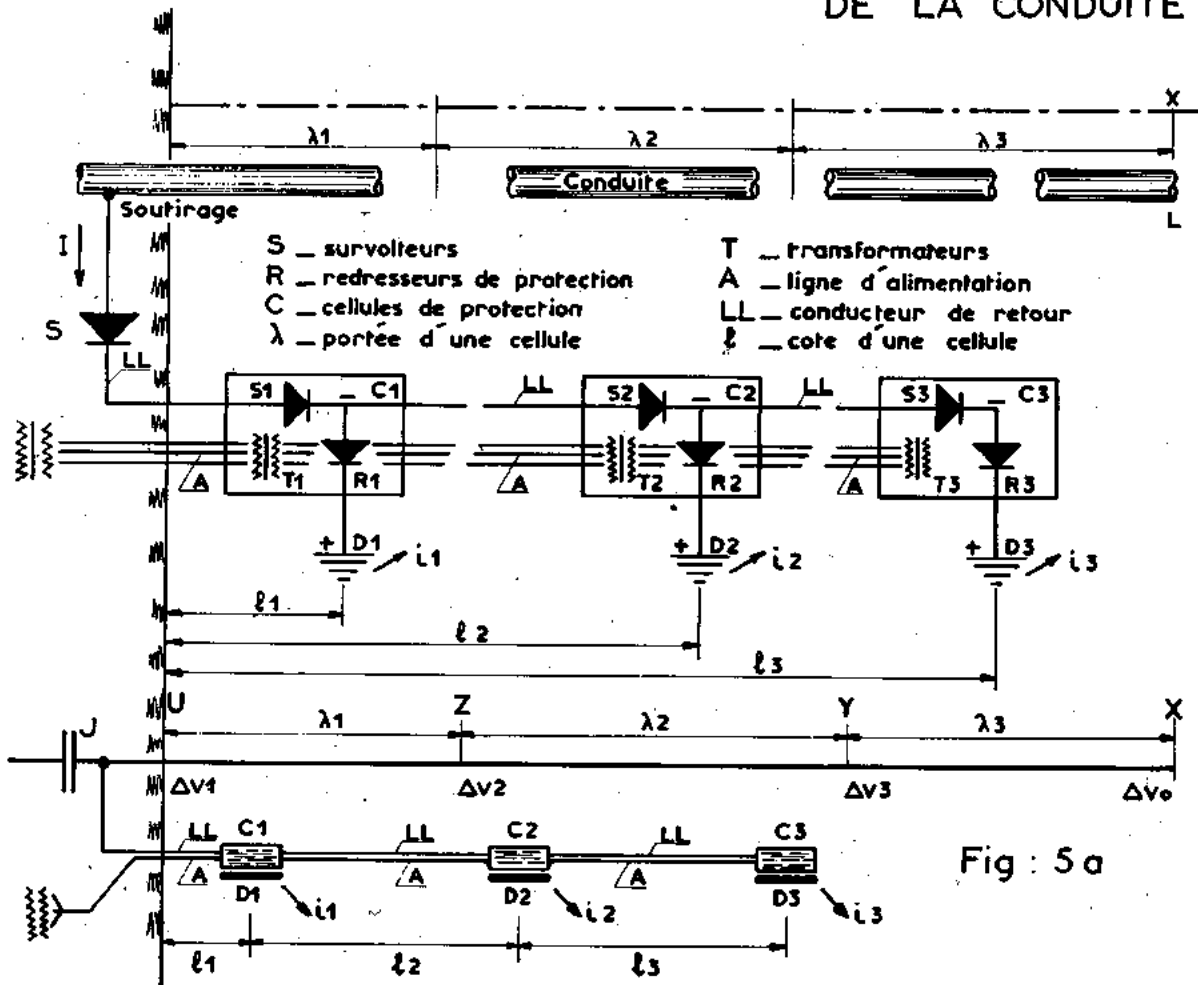
$$i_2 = \frac{\alpha}{r} \cdot \Delta V_0 \cdot \text{sh } a \lambda_2 + i_0 \text{ chal } (i_0 \text{ chal est négligeable}) \quad (XIV)$$

$i_0$  est la densité de courant sur le premier mètre, à l'origine de la conduite (= 1m) en x, en y:

$$\Delta V_s = \Delta V_0 \cdot \text{cha } \lambda_s + \frac{r}{a} i_0 \text{ shal } (l = 1m \text{ en } x) \quad (XV)$$

Le courant  $i_2$  émis par la cellule  $C_2$  protège, nous l'avons

# Fig. 5 LIGNE DE PROTECTION EN PROLONGEMENT DE LA CONDUITE



dit, une section  $\lambda_2$  de la conduite.

$$i_2 = \frac{a}{r} \Delta V_2 \cdot \text{sha } \lambda_2 + i_1 \text{ cha } \lambda_2 \quad (\text{XVI})$$

en z :

$$\Delta V_2 = \Delta V_2 \cdot \text{cha } \lambda_2 + \frac{r}{a} i_2 \text{ sha } \lambda_2 \quad (\text{XVII})$$

Le courant  $i_1$  émis par la cellule  $C_1$  protégée, nous l'avons dit une section  $\lambda_1$  de la conduite.

$$i_1 = \frac{a}{r} \Delta V_1 \text{ sha } \lambda_1 + i_2 \text{ cha } \lambda_1 \quad (\text{XVIII})$$

en U

$$\Delta V_1 = \Delta V_1 \cdot \text{cha } \lambda_1 + \frac{r}{a} i_1 \text{ sha } \lambda_1 \quad (\text{XIX})$$

$$I = i_1 + i_2 + i_3 \quad (\text{XX}) \quad \Delta V = \Delta V_1 \quad (\text{XXI})$$

RIVAGE

Une question vient aux lèvres: pourquoi la longueur de la ligne  $\ell_3$  est elle inférieure à la longueur L de la conduite,

pourquoi les cellules de protection sont elles décalées vers la terre par rapport à leur zone d'influence?

La réponse est simple et directe: par raison d'économie sur la longueur du câble.

Comment cela est-il réalisable sur le plan de fonctionnement du système, avec assignation d'une zone d'influence propre à chaque cellule zone d'action du reste très éloignée de la cellule?

L'auteur du système s'en est déjà expliqué et les résultats obtenus permettent de considérer l'explication comme admissible.

Dans un système électrolytique tel que celui schématisé à la fig. 1 la résistance ohmique du circuit extérieur à la somme de courant R se compose de :

- la résistance ohmique s'opposant au passage vers la mer du courant I émis par le déversoir, de,
- la résistance ohmique du volume de l'électrolyte (eau de mer) dans lequel se dilue le courant I, de,
- la résistance ohmique s'opposant au passage du courant I, de la mer vers le métal de la conduite, au travers de l'isolement qu'offre le revêtement.



De ces trois éléments d'une somme, celui concernant la mer elle-même est négligeable; la résistance globale du circuit se concentre au déversoir et à la conduite.

Dans ces conditions, le déversoir peut se trouver éloigné du rivage et de la conduite d'une manière quelconque, sans que la protection en soit modifiée. En pratique, le déversoir est éloigné de 100 ou 200m de la conduite.

Lorsqu'on utilise plusieurs déversoirs, soit plusieurs cellules unitaires de protection, les déversoirs seront d'autant plus éloignés du rivage, qu'il prennent en charge une section de conduite elle-même plus distante de la terre. Dans le même esprit, les différences de potentiel aux bornes des redresseurs de protection cathodique s'accroîtront d'une unité à l'autre lorsqu'on parcourt la ligne de protection du large vers la côte.

«Bien que ressortissant à la formule de calcul de base pour les soutirages de courant, le calcul particulier des systèmes «nouveau style» précédemment décrits, exige quelque discernement».

### 3.4. Propositions en vue d'une terminologie.

Nous conserverons, puisque l'usage les a consacrés, les termes «SOUTIRAGE DE COURANT» et «ANODES REACTIVES».

Nous proposerons en accord avec leur auteur, : système «INTEG» pour le procédé qui consiste à intégrer les cellules de protection et le cable d'alimentation à la conduite (322).

Nous proposerons : système «INDEP» pour le procédé qui consiste à utiliser une ligne de protection indépendante de la conduite, mais parallèle à celle-ci (323).

Nous proposerons : système «LINEX» pour le procédé qui consiste à utiliser une ligne de protection prolongeant la conduite. La ligne de protection est simplement Extérieure à la conduite et les caractéristiques d'amortissement du courant et du potentiel de protection se rapprochent de la «Linéarité» (1) (2).

### 4. CALCUL D'UNE PROTECTION CATHODIQUE DE CANALISATION IMMERGÉE - EXEMPLES

Précisons d'abord trois données liminaires:

L (mètres) est la distance comptée à partir du rivage, à laquelle un système à un seul déversoir impose un abaissement de potentiel  $\Delta V = 0,4$  V; à  $x = 0$ , origine, correspond  $\Delta V_0$ , à  $x = L$  correspond  $\Delta V_L$ .

De même, l (mètres) est la longueur, comptée à partir de l'extrémité côté terre, d'une section de conduite à la protection de laquelle est affectée 1 unité quelconque des cellules de protection d'un système de protection global. La section la plus éloigné du rivage est la section n; en se rapprochant du rivage, on rencontre les sections (n-1), (n-2), ..... 1.

Pour la section n, à  $x = l$ , correspond  $\Delta V_n$ , à  $x = 0$ , correspond  $\Delta V_n$  pour la section (n-1) à  $x = 0$  correspond  $\Delta V_{n-1}$ , à  $x = l$  correspond  $\Delta V_{(n-1)}$  etc. ....

$\Delta V_0$ , par sécurité, ne doit en aucun cas, être inférieur à 0,4 v (chapitre 3).

Deux cas seraient à considérer:

— La conduite «fait bout» à L mètres, c'est le cas d'un émissaire d'évacuation à la mer de résidus d'une usine.

— La conduite relie deux rivages distants de 2 L mètres; dans ce cas, on installe, généralement, sur chaque rivage où à partir de chaque rivage, un système de protection cathodique de portée L, capable d'imposer un potentiel  $\Delta V_0 = 0,4$  volt à égale distance de chaque rivage.

Nous admettrons ensuite que le cathodicien a su, au cours de sa carrière, acquérir assez de poids et de métier pour se permettre d'influencer le projet général de l'ouvrage et imposer des données qui lui sont propres, telles que: choix du revêtement, épaisseur et diamètre du tube, car il se sent

(1) le lecteur nous pardonnera de prendre des libertés avec les enseignements de Litté. D'autre part l'adjectif linéaire est pris ici dans le sens de «ligne droite».

(2) les systèmes LINEX, INTEG, INDEP font l'objet de brevets exploités par la Société Française C.A.M.O.M.

capable de justifier les éléments du compromis le meilleur en tenant compte des pertes de charge, des pompes, du coût et des charges annuelles de la protection globale dont il assume la responsabilité.

Dans certains cas, en effet, la protection cathodique et le revêtement peuvent valoir, au départ, chacun, 10% des dépenses de premier établissement, Il est utile de chercher à obtenir un meilleur résultat.

Il est certain que pour établir un projet indiscutable, il faut ne point se contenter de choisir à la billebaude, l'un des systèmes précédemment décrits. Certains s'éliminent d'eux-mêmes, à priori..... une canalisation de 200 m et de diamètre 200 mm est protégée logiquement par des anodes réactives... mais on n'a pas toujours la main guidée; en général, plusieurs solutions peuvent être envisagées et il est ainsi nécessaire d'étudier autant de projets pour une seule conduite, que de solutions offertes. On ne tranche, en définitive, à posteriori, que pièces indiscutables en main.

Nous ferons, pour ce qui suit, selon le cas, deux hypothèses, soit qu'il s'agisse, étant donné la conjoncture, du système reconnu comme le plus avantageux, soit qu'il s'agisse de déterminer les portées maximales à attendre d'un système déterminé qui vous est sinon imposé, du moins suggéré pour des raisons diverses et pour lequel on désire justifier un refus.

### 4.1. Cas de l'amortissement exponentiel (3.1) (Soutirage de courant).

Les expressions générales du courant et du potentiel sont déjà connues :

$$I = \frac{a}{r} \Delta V_0 \cdot \text{shal} + i_0 \cdot \text{chal} \quad l = 1m \quad (\text{VII})$$

$$\Delta V_L = \Delta V_0 \cdot \text{chal} + \frac{r}{a} i_0 \cdot \text{shal} \quad (\text{VIII})$$

$$\text{avec } \Delta V_0 \geq 0,4 \text{ volt et } i_0 = \frac{\Delta V_0}{R} \quad (\text{XI})$$

Les données du problème sont :

L en mètres, la longueur de la canalisation: exemple  
L = 3000 m

Dm, diamètre moyen du tube en cm: exemple  
Dm = 18,65 cm

e - épaisseur du tube en cm: exemple  
épaisseur 0,65 cm, pour De = 19,3 cm

Pour cet exemple :

$$r = \frac{522}{Dm \cdot e} 10^{-6} = \frac{522 \cdot 10^{-6}}{18,65 \times 0,65} = 43 \cdot 10^{-6} \text{ ohm.m} \quad (\text{IX})$$

Supposons que nous n'ayons pu, pour impossibilité matérielle, réaliser le revêtement sur le chantier; nous avons ainsi provisionné des tubes revêtus à l'Usine, ils ont été soumis aux aléas du voyage, des chargements, déchargements, manutentions, gerbages, bardages et débardages divers. Nous ne devons pas compter sur une valeur R' (ohm.m<sup>2</sup>) supérieure à 50, d'autant plus que la canalisation est déjà immergée quand nous pouvons songer à la protection cathodique.

Dans ces conditions :

$$R = \frac{50}{\pi \cdot 0,193} = 83 \text{ ohms.m} \quad (\text{XXII})$$

$$a = \left(\frac{r}{R}\right)^{1/2} = \left(\frac{43 \cdot 10^{-6}}{0,83 \cdot 10^2}\right)^{1/2} = 7,18 \cdot 10^{-4} \quad (\text{XXIII})$$

$$al = 7,18 \cdot 10^{-4} \times 3 \cdot 10^4 = 2,154 \quad (\text{XXIV})$$

$$\text{shal} = 4,25 \quad (\text{XXV})$$

$$\text{chal} = 4,35 \quad (\text{XXVIII})$$

$$\frac{a}{r} = \frac{7,18 \cdot 10^{-4}}{43 \cdot 10^{-6}} = 16,47 \quad (\text{XXVIII})$$

$$\frac{r}{a} = 0.06 = 6.10^{-2} \quad (\text{XXIX})$$

$$i_0 = \frac{\Delta V_0}{R} = \frac{0.4}{83} = 48.10^{-4} \quad (\text{XXX})$$

Les expressions (VII) et (VIII) deviennent :

$$I = 16,7 \times 0,4 \times 4,25 + 48.10^{-4} \times 4,35 = 28,4 + \varepsilon \text{ AMP} \quad (\text{XXXI})$$

$$V_L = 0,4 \times 4,35 + 6.10^{-2} \times 48.10^{-3} \times 4,25 = 1,74 + \varepsilon \text{ VOLTS} \quad (\text{XXXII})$$

#### OBSERVATIONS :

Il faut ainsi pratiquement, 30 Amp pour protéger 3.000 en diamètre extérieur de 193 mm.

Le gain de potentiel aux atterrages, pour  $\Delta V = 0,4$  v est de 1,74 volt ce qui permet de mesurer  $V_L = 1,74 + 0,6 = 2,34$  volts au point de soutirage.

On doit noter que, tant pour un mauvais revêtement et une valeur L faible, que pour un bon revêtement et une valeur L élevée, shal  $\neq$  chal.

En outre, dans les deux cas, on peut négliger le second terme des expressions VII et VIII.

Quoi qu'il en soit, et quel que soit l'isolement, fut-il excellent, il apparait qu'il est extrêmement malaisé de protéger par un soutirage de courant, une conduite de 6 à 10 km selon le diamètre nominal, du fait des limitations imposées à  $\Delta V_L$ . Une valeur  $\Delta V_L$  de 6 à 7 volts n'est pas admise par tous.

En conclusion,

« Pour un soutirage de courant, les expressions utilisées pour les calculs de l'intensité et du potentiel se réduisent, le plus souvent à :

$$I = \frac{a}{r} \times \Delta V_0 \times \text{shal} \quad (\text{VII})'$$

$$\Delta V_L = \Delta V_0 \times \text{chal}, \text{ avec} \quad (\text{VIII})'$$

$\Delta V_0 \geq 0,4$  volt  $\Delta V_L \leq 7$  volts (maximum maximum sur une plage non fréquentée par les baigneurs, sinon  $V_L \leq 3V$  En général shal  $\neq$  chal

Le soutirage de courant, solution conformiste, qui constitue les errements habituels, ne convient réellement qu'aux canalisations de faible développement, quelle que soit la valeur de l'isolement du tube vis-à-vis de la mer.

#### 4.2. Cas de l'amortissement quasi linéaire (paragraphe 3.2)

Trois solutions techniques, nous l'avons dit, sont à notre disposition, les anodes réactives (321), la ligne de protection intégrée à la conduite (322), la ligne de protection parallèle à la conduite (323).

Reprenons l'exemple précédent : une conduite de  $\varnothing_e = 193$  mm d'épaisseur 6,5 mm, isolée à 50 ohms.m<sup>2</sup> mais dont le développement atteint 12000 m. Il vient immédiatement à l'esprit, en s'inspirant des résultats exposés au paragraphe 4.1 de réaliser la protection suivant la fig. 6.

On peut aisément, en y mettant poids et prix, réaliser deux blocs d'anodes, chacun débitant 60 A, mais on ne pourra atteindre  $\Delta V_L = 1,74$  v ( $V_L = 2,34$ ), la valeur  $V_x$  maximale atteinte étant de l'ordre de 1.1 volt. Il sera nécessaire de rapprocher les blocs en les faisant débiter moins, la durée de service de cette réalisation sera de l'ordre de 3 à 5 ans. Mais le programme schématisé à la fig. 6a ou à la fig. 6b sera facilement respecté, soit dans le cas de la protection intégrée à la canalisation, soit dans le cas de la ligne parallèle à la conduite : dans les deux cas, les anodes réactives sont remplacées par des redresseurs immergés.

« Dans les exemples évoqués aux paragraphes (4.1) et (4.2), pour la portée L ou l, invoquée, on peut estimer que les courbes exponentielles d'amortissement, (sur L ou l), soit  $V_x = f(L)$  et  $I_x = f(L)$  sont suffisamment peu concaves

pour que l'on puisse les assimiler à des amortissements linéaires.

En général, un soutirage de courant, pour lequel l'amortissement de  $\Delta V_x$  ou  $I_x$  serait très accentué (exponentielle réelle) au voisinage du rivage, n'est pas, techniquement acceptable.

#### 4.3. Cas intermédiaire (paragraphe 3.3)

C'est le cas de la ligne de protection disposée en prolongement de la conduite (Fig. 7); avant que d'appliquer les formules de base il est bon de fixer les limites à l'intérieur desquelles nous allons opérer, numériquement parlant.

Nous voulons que les caractéristiques  $\Delta V_x = f(x)$  et  $I_x = f(x)$  soient aussi peu bosselées que possible, en les composant de caractéristiques partielles, section de conduite par section de conduite, elles-mêmes aussi plates que possible : de vraies lignes droites en prolongement les unes des autres. Chaque caractéristique partielle est le propre d'une cellule de protection particulière.

Dans ces conditions, et pour le domaine d'action de chaque cellule (en supposant pour simplifier qu'ils soient identiques), on adoptera la valeur uniforme  $a^2 = 0,46$  à laquelle correspond shal = 0,47 chal = 1,1 (al  $\neq$  shal chal  $\neq$  1).

Conservons l'exemple précédent : L = 12.000 m,  $\varnothing_e = 193$  mm  $e = 6,5$  mm,  $r = 43.10^{-3}$  ohm.m

Nous sommes autorisés à choisir le revêtement.

Sur la fig. 7, les portées l des cellules de protection sont cotées  $\lambda$ .

de :

$$a = \left(\frac{r}{R}\right)^{1/2} \text{ nous tirons :} \quad (\text{X})$$

$$R = \frac{r}{a^2} \quad (\text{XXXIII})$$

En fonction de  $\lambda$  nous connaissons les valeurs  $a^2$  limites pour  $a \cdot \lambda_n = 0,46$

$\lambda$  est, rappelons le, la portée d'une cellule de protection sur la conduite, chaque cellule étant distante d'une autre cellule de  $l_n$

$$a = \frac{0,46}{\lambda_n} = \frac{46.10^{-3}}{\lambda_n} \quad (\text{XXIV})$$

Ce qui nous permet d'établir le tableau No. 1.

TABLEAU No. 1

$\lambda$ mètres	$a = \frac{0,46}{\lambda}$	$a^2$
1.000	$46.10^{-4}$	$2.116.10^{-10}$
2.000	$23.10^{-4}$	$530.10^{-10}$
3.000	$1.535.10^{-4}$	$235.10^{-10}$
4.000	$1.15.10^{-4}$	$103,2.10^{-10}$
5.000	$0,92.10^{-4}$	$84,8.10^{-10}$

Nous opérons par essais successifs :

1. Prenons  $\lambda = 4.000$ m ce qui correspond à l'utilisation de trois cellules de protection.

$$a^2 = 103,2.10^{-10} \quad (\text{XXXV})$$

$$R = \frac{r}{a^2} = \frac{43.10^{-3}}{103,2.10^{-10}} = 4.170 \text{ ohms.m} \quad (\text{XXXVI})$$

Cette valeur R correspond à :

$$R' = \pi \times D_e \times R = 3,14 \times 0,193 \times 4170 = 2.540 \text{ ohms.m}^2 \quad (\text{XXXVII})$$

Dans l'état actuel de la technique des revêtements, cette valeur R' ne peut être envisagée.

# Fig:6. ANODES REACTIVES

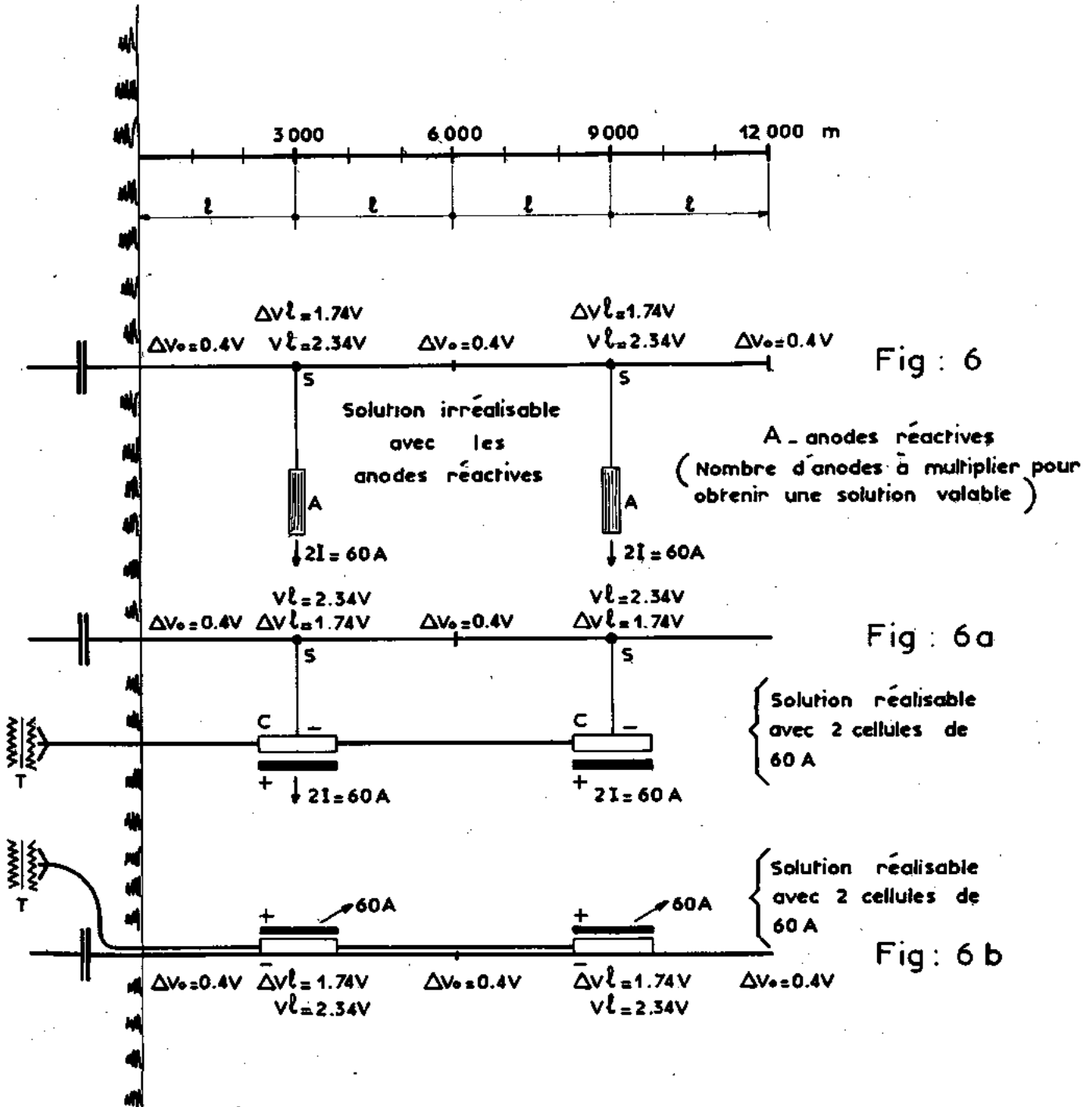
(6)

LIGNE DE PROTECTION PARALLELE A LA CONDUITE

(6A)

LIGNE DE PROTECTION INTEGREE A LA CONDUITE

(6B)



# Fig:7 LIGNE DE PROTECTION EN PROLONGEMENT DE LA CONDUITE

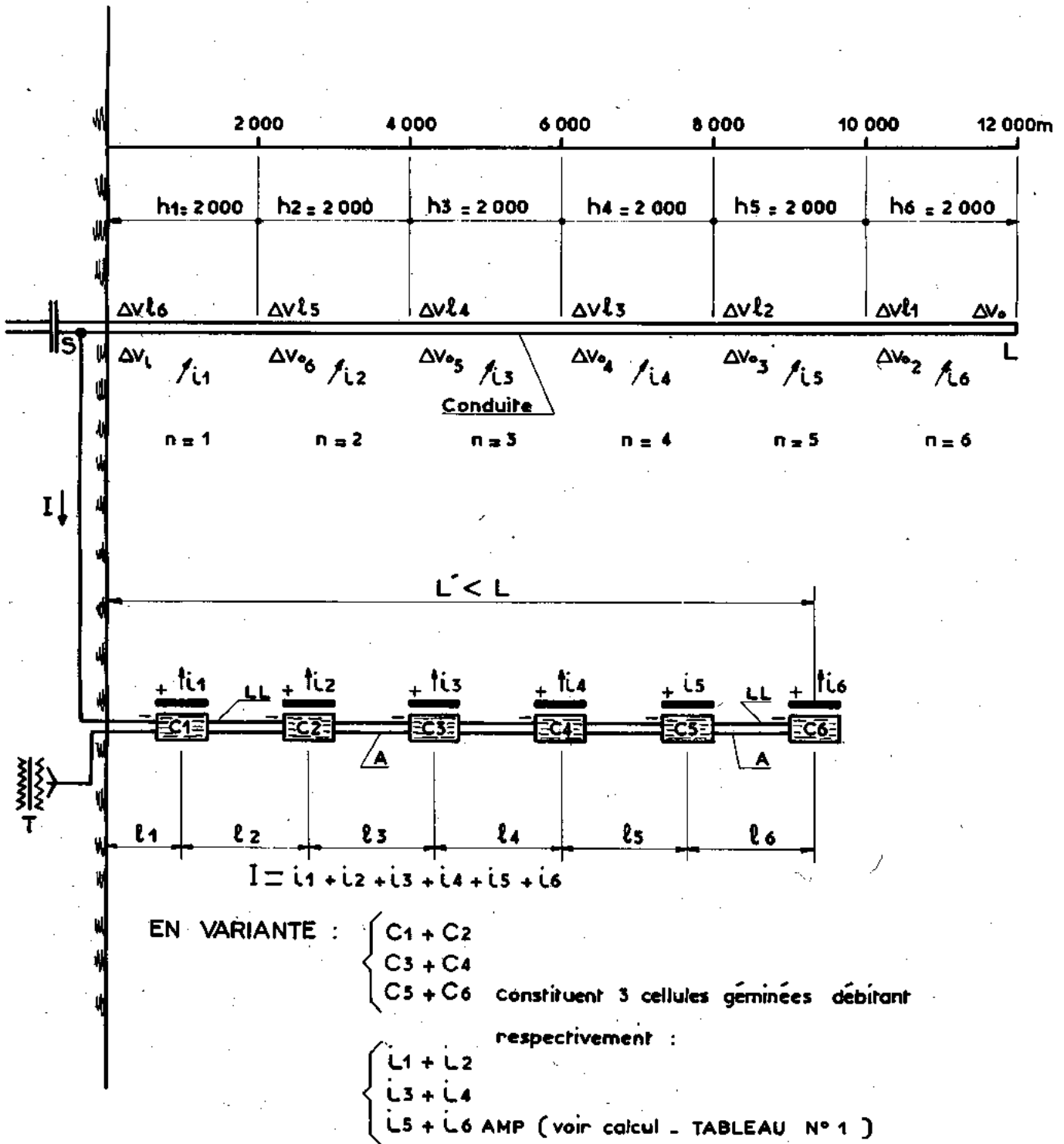


TABLEAU N° 2

Sections considérées (L-x) · (L-x)-2000 metres	ΔV <sub>o(n-1)</sub> volt	1 · 1ΔV <sub>o(n-1)</sub> volt	2 · 52 ΔV <sub>o(n-1)</sub> volt	i <sub>(n-1)</sub> Amp.	1 · 1 i <sub>(n-1)</sub> Amp.	0,88 i <sub>(n-1)</sub> Amp.	i <sub>n</sub> = 2,52 ΔV <sub>o(n-1)</sub> + + 1 · 1 i <sub>(n-1)</sub>		ΔV <sub>Ln</sub> = 1 · 1 ΔV <sub>o(n-1)</sub> + + 0,088 i <sub>(n-1)</sub> volt
							in cumulé AMP	in AMP	
12000 - 10000	0,4	0,44	1,02	ε	ε	ε	1,02	1,02	0,44
10000 - 8000	0,44	0,48	1,12	1,02	1,12	0,089	2,24	1,22	0,57
8000 - 6000	0,57	0,62	1,44	2,24	2,47	0,197	3,91	1,67	0,82
6000 - 4000	0,82	0,90	2,06	3,91	4,30	0,344	6,36	2,45	1,25
4000 - 2000	1,25	1,37	3,16	6,36	7	0,615	10,16	3,80	1,98
2000 - 0	1,98	2,18	4,98	10,16	11,20	0,895	16,18	6,02	3,06

A terre ΔV<sub>L</sub> = ΔV<sub>p</sub> = 3,06v (V<sub>L</sub> = 3,65v) pour Δv<sub>o</sub> = 0,4v, soit V<sub>o</sub> = 1 volt à l'extrémité.

Il y a lieu de réduire la portée h de chaque cellule unitaire.

- Pour λ = 3.000m (4 cellules de protection)  
= 1840 ohms.m R' = 1120 ohms.m<sup>2</sup>  
Nous devons encore réduire nos prétentions.
- Pour λ = 2.000m (6 cellules de protection)  
(à la rigueur 5 seulement)  
R = 810 ohms.m R' = 495 ohms.m<sup>2</sup>

De tels résultats sont jouables, nous en verrons plus loin, un exemple.

Dans le projet de protection, on considérera que chacune des cellules simples (deux cellules simples font une cellule geminée) protège 200m de conduite.

Soient ΔV<sub>on</sub> et ΔV<sub>ln</sub>, respectivement, les abaissments de potentiel à x = 0 et x = λ pour chaque section de conduite λ considérée (x = 0 est l'extrémité de chaque section la plus éloignée de la terre).

Soient i (n - 1) et i<sub>n</sub> les courants de protection circulant dans deux sections consécutives (de la mer vers la terre) d'ordre (n - 1) et n; les expressions générales (VII) et (VIII) deviennent.

$$i_n = \frac{a}{r} \Delta V_{o_{n-1}} \operatorname{sh} a\lambda + i_{(n-1)} \operatorname{ch} a\lambda. \quad (\text{XXXVIII})$$

$$\Delta V_{ln} = \Delta V_{o_{n-1}} \operatorname{ch} a\lambda + \frac{r}{a} i_{(n-1)} \operatorname{sh} a\lambda. \quad (\text{XXXIX})$$

$$\text{pour } n = 1 \quad i_{(n-1)} = i_0 \text{ et } \Delta V_{o_{n-1}} = \frac{i_0}{R}.$$

Dans notre CAS particulier,

$$a = \left(\frac{r}{R}\right)^{1/2} = \left(\frac{43 \cdot 10^{-4}}{8,1 \cdot 10^2}\right)^{1/2} = 2,3 \cdot 10^{-4} \quad (\text{XL})$$

$$\frac{a}{r} = \frac{2,3 \cdot 10^{-4}}{43 \cdot 10^{-4}} = 5,35 \quad (\text{XLI})$$

$$\operatorname{sh} a\lambda = 0,47, \operatorname{ch} a\lambda = 1,1, \frac{r}{a} = 0,187. \quad (\text{XLII})$$

$$\text{soit: } i_n = 5,35 \Delta V_{o_{(n-1)}} + 0,47 + 1,1 i_{(n-1)} = 2,52 \Delta V_{o_{(n-1)}} + 1,1 i_{(n-1)} \quad (\text{XLIII})$$

$$\Delta V_{ln} = 1,1 \cdot \Delta V_{o_{(n-1)}} + 0,187 \times 0,47 \times i_{(n-1)} = 1,1 \Delta V_{o_{(n-1)}} + 0,088 i_{(n-1)} \quad (\text{XLIV})$$

En prenant ΔV<sub>o(n-1)</sub> = 0,4 volt pour (n-1) = 6, on peut construire le tableau n° 2.  
— pour ΔV<sub>o</sub> = 0,4 volt à x = 0

Ainsi la protection intégrale de l'ouvrage est assurée pour 17 AMP. environ. Le tableau N° 3 résume les données, cellule par cellule, ces données conduisant au calcul du redresseur.

TABLEAU N° 3

N° de la cellule	zone d'action de la protection assurée par la cellule m.	débit à assurer Amp.	Abaissment de potentiel à assurer à (l-x) metres		
			volts	metres	
C6	h6=2000	1,02	16,18	0,44	10000
C5	h5=2000	1,22		0,57	8000
C4	h4=2000	1,67		0,82	6000
C3	h3=2000	2,45		1,25	4000
C2	h2=2000	3,80		1,98	2000
C1	h1=2000	6,02		3,06	0

La longue ligne ramènera ainsi quelque 17 A.

Dans ce cas particulier, les portées λ des cellules sont identiques, mais on peut, si la conjoncture le demande, réaliser une protection de ce type avec des valeurs λ différentes pour chacune des cellules.

5. Contrôle permanent de l'efficacité d'une protection cathodique de conduite sous marine.

Nous distinguerons entre les diverses solutions de protection exposées au cours de cette étude, selon que le contrôle permanent de l'efficacité du système requiert ou non des dispositifs auxiliaires de contrôle.

5.1. Contrôle direct, depuis la côte, sans dispositif accessoire.

Il s'agit, en général, de conduites longues bien isolées, ou de canalisations courtes mal isolées.

5.1.1. Elément de contrôle ΔV/I

Nous reprendrons les expressions générales du calcul de la protection, dans les conditions du soutirage de courant, on peut admettre (41)  $\operatorname{ch} a\lambda \neq \operatorname{sh} a\lambda$

$$\Delta V_L = \Delta V_o \cdot \operatorname{ch} a\lambda \quad (\text{VIII})$$

$$I = \frac{a}{r} \cdot \Delta V_o \cdot \operatorname{sh} a\lambda \quad (\text{VII})$$

soit:

$$\frac{\Delta V_L}{I} = \frac{r}{a} \quad (\text{XLV}) \quad \text{et} \quad \left(\frac{\Delta V_L}{I}\right)^2 = \frac{r^2}{a^2} = rR \quad (\text{XLVI})$$

$$R = \left(\frac{\Delta V}{I}\right)^2 \times \frac{1}{r} \quad (\text{XLVII})$$

Le contrôle d'une installation consistera à évaluer R (ohms.m) aussi souvent qu'il est jugé nécessaire.

En disposant d'un abaque établi pour l'installation à

contrôler, il est possible d'ajuster périodiquement et rapidement, le débit à l'isolement en respectant les conditions:

$$\Delta V_0 \geq 0,4 \text{ volt.}$$

### 5.1.2. Système à soutirage de courant

On applique directement les indications du paragraphe 511.

### 5.1.3. Système LINEX

On applique directement aussi les indications du paragraphe 511 mais il est possible, en même temps de vérifier la valeur du «facteur de mérite» de l'installation, que nous définirons comme étant «de degré de rectitude» des caractéristiques  $V_x = f(x)$  et  $I_x \times f(x)$ .

Soit  $I_{AMP}$  le courant total soutiré par le système LINEX. En admettant que la caractéristique  $I_x = f(x)$  soit une ligne droite, c'est-à-dire si l'accroissement de courant est constant de  $x = 0$  à  $x = L$ , on a:

$$\Delta V_L = V_L - 0,6 = r \cdot L \cdot \frac{1}{2} \quad (\text{XLVIII})$$

$$2 \cdot \frac{V_L}{1} = r L \quad (\text{XLIX})$$

$r$  et  $L$  conservent les notations précédentes: ohm.m et mètre.

$$\frac{2 \Delta V_L}{1} < 1 \rightarrow \text{la protection est renforcée vers la côte}$$

$$\frac{2 \Delta V_L}{1} = 1 \rightarrow \text{la protection est réellement uniformément croissante}$$

$$\frac{2 \Delta V_L}{1} > 1 \rightarrow \text{la protection est renforcée vers le large.}$$

### 5.1.4. Comparaison chiffrée, à propos d'une même conduite des résultats obtenus grâce aux deux systèmes de protection précédents.

Nous nous référerons au cas d'un émissaire sous marin réalisé par la firme française CAMOM, dans le golfe de Corinthe. Le tube d'acier de (180 x 193) ( $r = 43.10^{-6}$ ), se développe sur 12600m, jusqu'à atteindre la cote (-350m). On a utilisé le revêtement 2 C réalisé en chantier et procédé au lancement rapide (44h) de l'ouvrage selon une technique garantissant l'intégrité du revêtement.

Une protection cathodique provisoire, par soutirage de courant, a été mise en service par nos soins dès le début du lancement, il lui a été substitué par la suite une protection LINEX à 5 cellules. Ainsi, il nous a été possible de comparer les résultats que procurent les deux procédés, SOUTIRAGE d'une part, LINEX d'autre part.

La protection cathodique provisoire fut caractérisée par un «effondrement» du rapport  $\frac{\Delta V}{I}$ , 30 jours après le lancement de la conduite, nous n'avions plus, pour  $\Delta V \neq 4$  volts et  $I = 23$  Amp qu'une valeur  $\frac{\Delta V}{I} = \frac{4}{23}$  soit 0.174.

Dans ces conditions, la résistance apparente d'isolement était (pour  $r = 43.10^{-6}$ ).

$$R = \left(\frac{\Delta V}{I}\right)^2 \times \frac{1}{r} = 0,0305 \times 23.300 = 710 \text{ ohms.m} \quad (\text{L})$$

Cela correspond à une valeur  $R' = 430$  ohms.m<sup>2</sup> (contre 2.900 ohms.m<sup>2</sup> à la fin du lancement), chiffre cependant excellent après 30 jours d'immersion, succès dû pour la plus grande partie aux soins du personnel applicateur et pour le reste à l'étude préalable approfondie des opérations de lancement et à la mise en œuvre d'un matériel de chantier spécial

prévu pour mener à bien les opérations.

Dans ces conditions, pour un même débit de 23 Amp, 72 H après sa mise en service, le procédé LINEX conduit à

$\Delta V = 5,65$  v, ce qui caractérise une valeur  $\frac{\Delta V}{I} = 0,244$  et à une valeur  $R$

$$R = \left(\frac{\Delta V}{I}\right)^2 \times \frac{1}{r} = 0,0598 \times 23.300 = 1.390 \text{ ohms.m} \quad (\text{LI})$$

Cela correspond à une valeur  $R' = 840$  ohms.m<sup>2</sup>, valeur exceptionnelle, inespérée et jamais, à notre connaissance, réalisée jusqu'ici.

Un mois après le neuvage du système LINEX  $R$  atteint la valeur 1600 ohms.m (965 ohms.m<sup>2</sup>) et ces chiffres se maintiennent depuis:

Si nous recherchons le «facteur» de mérite de la protection LINEX, il vient pour:

$$\frac{2 \Delta V}{1} = r L \quad (\text{XLIX}) \quad (\text{LII})$$

$$\frac{2 \Delta V}{1} = \frac{2 \times 5.65}{32} = \frac{11.30}{23} = 0,492 \quad (\text{LIII})$$

$$r L = 43.10^{-6} \times 1.26.10^4 = 0,542 \quad (\text{LIV})$$

Le facteur de mérite du système LINEX est ainsi de:

$$\frac{0,492}{0,542} = 0,9$$

Ce chiffre de 0.9 qui caractérise LINEX est à comparer à celui de:

$$\frac{0,348}{0,542} = 0,64 \text{ qui caractérise le soutirage de courant.}$$

Nous sommes très proches de la caractéristique linéaire recherchée en utilisant le système LINEX.

Ajoutons que pour le soutirage,  $\Delta V_0 \neq 0,4$  volt pour une intensité de 23 A. On ne pouvait, par conséquent, réduire l'intensité de protection pour ce procédé, mais  $\Delta V_0 \neq 1.1$  volt pour le procédé LINEX débitant la même intensité, on pouvait ainsi réduire l'intensité débitée par LINEX.

En fait, en se contentant, avec le procédé LINEX de  $\Delta V_0 = 0,4$ v le débit des cellules n'aurait pas dépassé 9 A et  $\Delta V_L$  serait resté inférieur à 1,85 volt.

Ajoutons enfin, que le procédé LINEX absorbe 9 A triphasés sur 220 volts pour débiter 23 A et que l'installation supporte aisément une alimentation d'intensité double; le coefficient de sécurité est élevé, l'isolement du système est prévu pour 1500 volts et l'autonomie pour atteindre 12 à 15 ans.

La fig. 8 schématise l'installation réalisée, nous retrouvons au paragraphe 75 une photographie de la ligne de protection levée sur la barge de lancement.

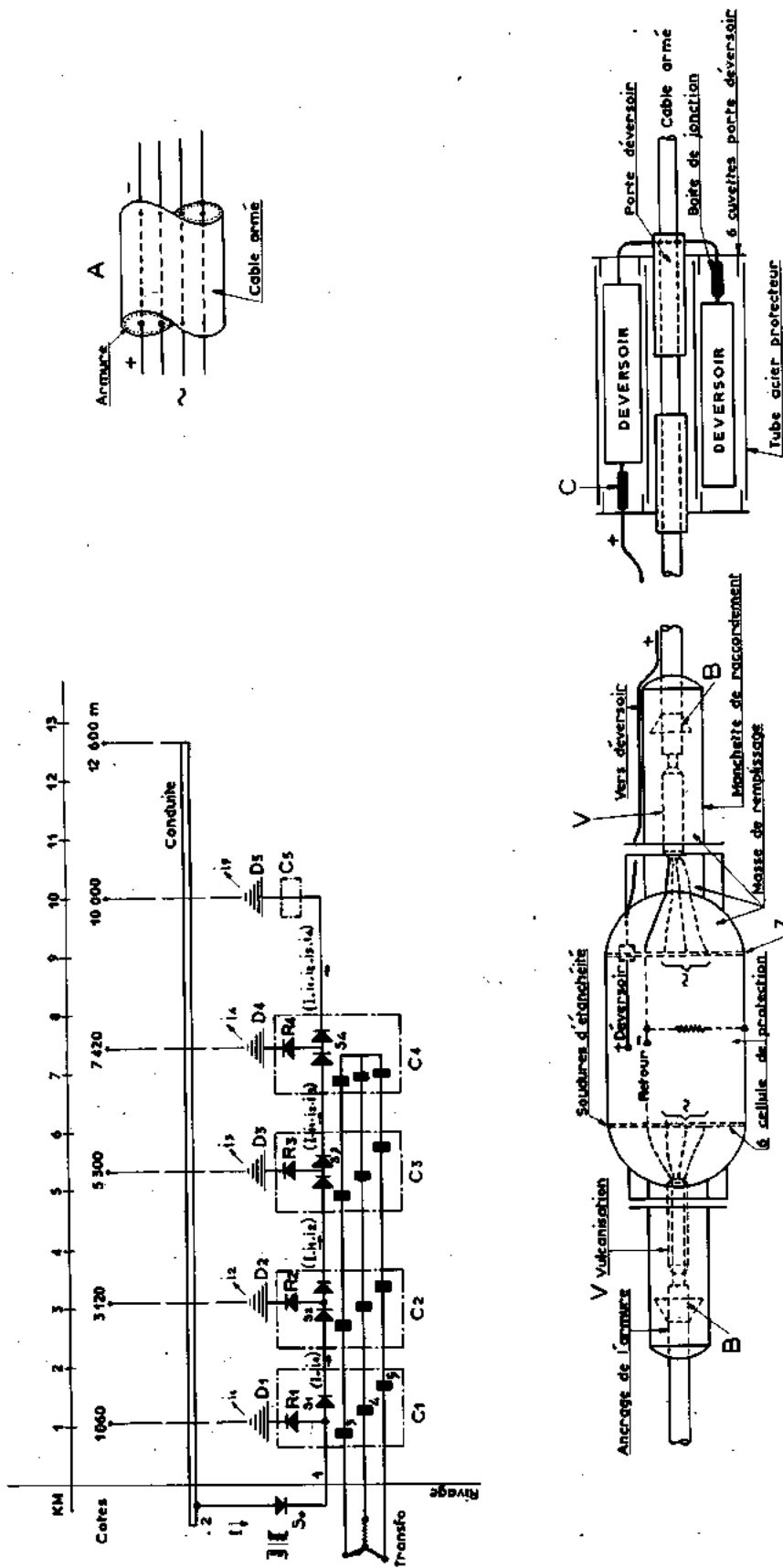
«L'intérêt du système LINEX réside dans l'augmentation spectaculaire de la valeur apparente de l'isolement si on prend pour référence le «soutirage, de courant» débitant la même intensité. Cette valeur dans le cas particulier évoqué, a doublé et même a été au delà. On peut estimer que pour un même revêtement, la portée du système LINEX est de 1,5 à 2 fois plus forte, peut être davantage, que celle d'un soutirage de même intensité».

### 5.2. Contrôle indirect, depuis la côte, recours aux télémesures.

Il y a lieu, dans tous les cas, d'établir les connexions nécessaires, ce qui ne présente pas de difficultés en les incorporant au câble d'alimentation des systèmes INTEG et INDEP.

#### 5.2.1. Système INTEG.

On reporte à terre, la valeur  $\Delta V$  ( $x = \lambda$ ) au droit de



**FIG: 8**

chacune des cellules de protection et on contrôle  $\Delta V_0$  à terre ( $x = 0$ ).

### 5.2.2. Système INDEP

La technique de contrôle est identique à la précédente.

### 6. Possibilités éventuelles de combinaisons entre les différents systèmes de protection.

On peut évidemment, combiner l'usage du soutirage et des anodes réactives. Telle école anglo-saxonne préconise ce système pour lequel on dispose, au large, les blocs d'anodes pour améliorer la portée du soutirage.

Il apparait comme plus intéressant de combiner le système LINEX avec celui du soutirage de courant. On implante le redresseur de soutirage à terre et on immerge une ligne de protection ne portant que les seuls déversoirs. Le réglage du débit unitaire des déversoirs et celui de la d.d.p.; entre déversoirs et conduite, est obtenu simplement par la chute de tension dans la ligne, ce qui fixe les intervalles entre les déversoirs en fonction de leurs dimensions. Cette solution simple et sûre, n'est pas obligatoirement économique du fait de sections de cuivre à mettre en œuvre.

### 7. Quelques aspects de la technologie et de la morphologie des protections cathodiques de type nouveau. — nous donnons quelques détails sur la protection LINEX réalisée à METOXI.

#### 7.1. Câbles de lignes

Le câble d'alimentation est de marque SILEC; il comprend 4 conducteurs en cuivre de  $16 \text{ mm}^2$ , sa longueur est de 7420m. Autour de l'isolement-gaine est disposée l'armure, sous forme d'une nappe de fils d'acier à 110 kgs, torsadés et maintenus en place par une garniture continue, étanche, en matière plastique résistante. L'armure est, par précaution, reliée aux négatifs de chaque cellule par l'intermédiaire de résistances de limitation de courant disposées à l'intérieur des cellules de protection. Le diamètre extérieur de câble est de 32mm.

#### 7.2. Jonctions et raccords

La ligne de protection, d'une longueur de 7420m monobloc, a été assemblée à terre, puis, chargée sur la barge qui a servi au lancement.

Entre les extrémités de deux tourets consécutifs ont été disposées des boîtes de jonction, aux extrémités de cellules traversées par la ligne de protection ont été boulonnées des manchettes de raccordement.

A l'intérieur des boîtes de jonction et des manchettes de raccordement, l'ancrage mécanique de l'armature évasée, puis prise entre deux mors coniques, réalise la continuité mécanique de la ligne qui admet sans rompre une traction de l'ordre de 10 tonnes. En outre, la connexion des câbles, conducteur par conducteur est effectuée par brasures, l'ensemble est recouvert par un manchon isolant vulcanisé sur place et rétablissant la continuité de l'isolant sur toute la longueur de la ligne (fig. 10 in fine).

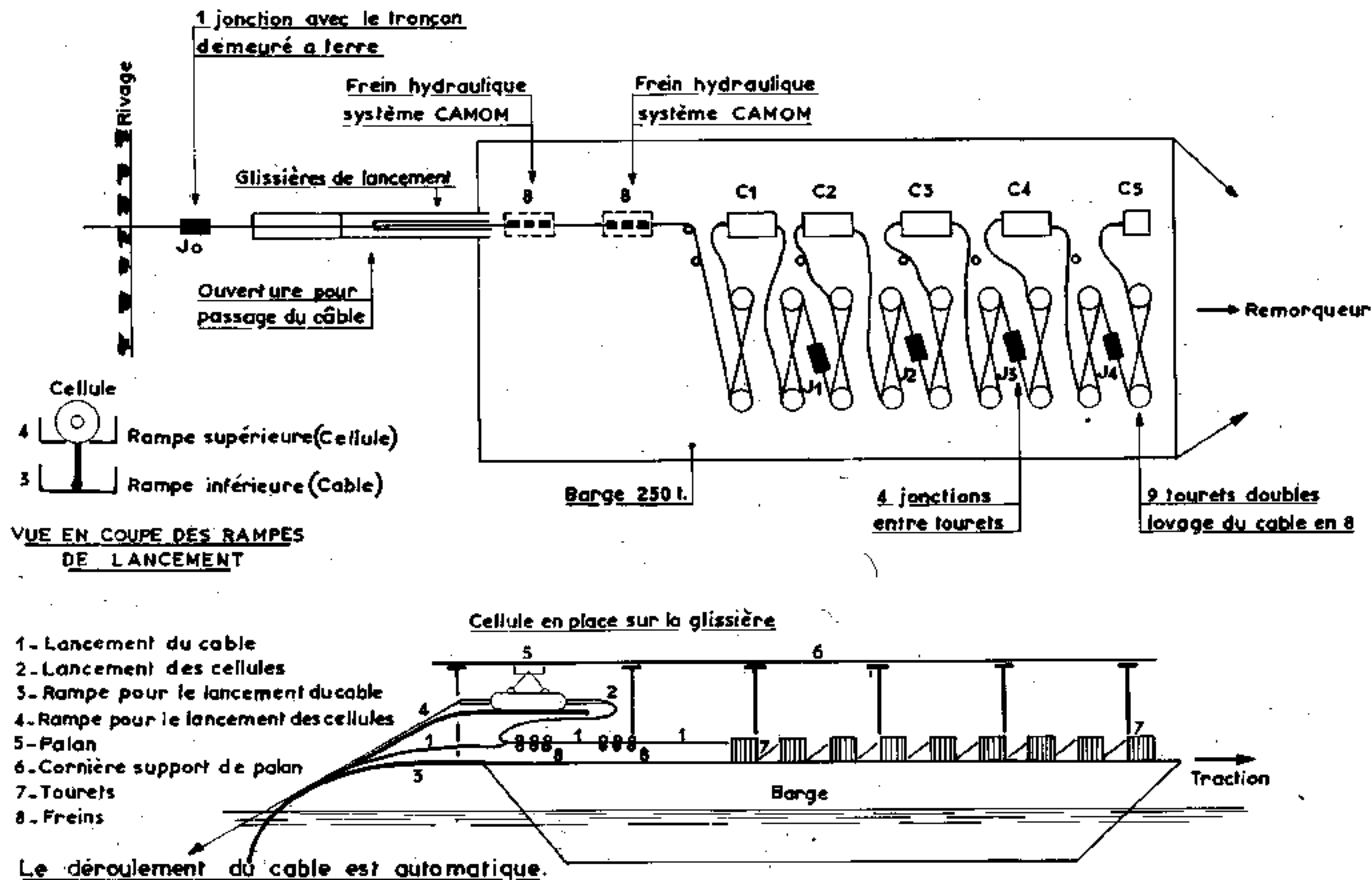


Fig. 9. — au schéma de lancement de la ligne levée sur des tourets à tête double chargés à bord d'une barge de 250 T tirée par un remorqueur de 350 cv.



### 7.3. Redresseurs et survolteurs — DDP AUX BORNES

Les diodes constituant les ponts des redresseurs de protection et des survolteurs sont alimentés par des transformateurs d'intensité — ref. 3.4.5. de la fig. 8.

Il était aisé de calculer les survolteurs en fonction de la chute de tension dans la conduite et la ligne de retour du courant (LL fig. 5).

Il a été plus délicat de fixer les d.d.p. aux bornes des redresseurs de protection cathodique car il fallait tenir compte, en équilibrant les phases, de la résistance ohmique du circuit électrolytique déversoir — mer — conduite, et de la valeur  $\Delta V\lambda$  à l'extrémité  $x = \lambda$  de chacune des sections protégées.

### 7.4. Déversoirs

Le schéma de montage des déversoirs sur la ligne est indiqué à la fig. 8.

Des anodes «DURICHLOR» de 28 kg en fonte au silicium chrome, manganèse ont été disposées, proportionnellement au débit de chaque cellule, sur un barillet centré sur le câble, à la sortie de chaque cellule; la durée du service à attendre de cette installation est de l'ordre de 12 à 15 ans, comme nous l'avons dit.

### 7.5. Schéma de lancement de la ligne.

La fig. 9 et les photographies fig. 10, 11, 12 sont relatives.



Fig. 10. — Sur la cellule C4, l'épissure réalisant l'extrémité de la ligne triphasée vient de sortir du moule de vulcanisation.

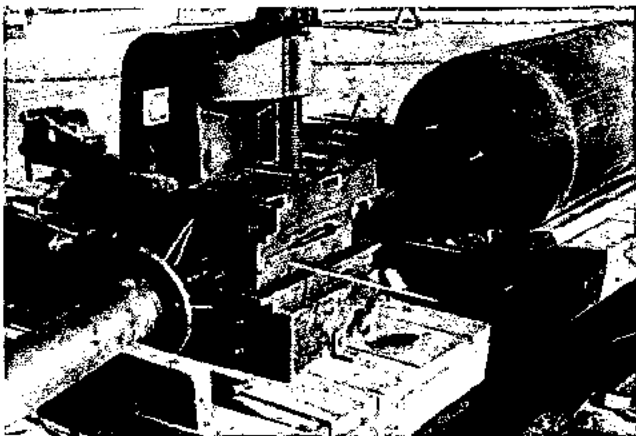


Fig. 11. — L'amont de la même cellule.

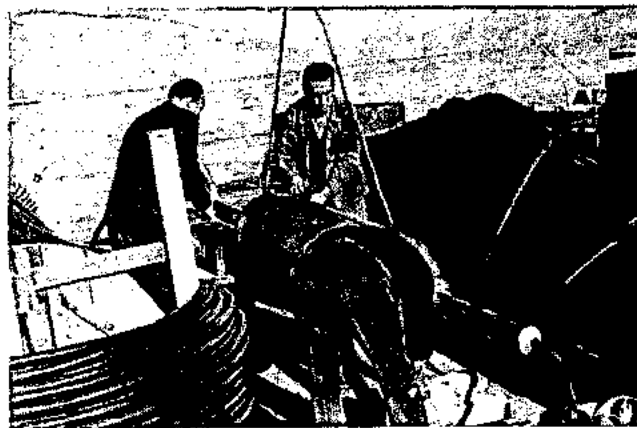


Fig. 12. — La ligne de protection a été chargée sur la barge. On aperçoit une cellule en place, un des tourelis...

Les fig. 10, 11, 12 montrent l'évolution du montage des cellules:

### 8. Tentative de prévision de l'évolution logique de la technique de protection globale: Revêtements et protections cathodiques des canalisations immergées.

Pour les canalisations de petits diamètres et faibles longueurs, il apparaît que la technique des anodes réactives conservera tout son attrait, à condition toutefois, étant donné qu'elles se «fanent» vite que toutes dispositions utiles soient prises pour que leur remplacement soit aisé.

Il ne semble pas que les revêtements évoluent beaucoup dans un proche avenir; ne nous apparaissent comme valables que les revêtements dotés d'une porosité certaine, infime peut-être, mais réelle. Il est nécessaire que le courant de protection soit uniformément réparti et qu'il ne hante pas seulement les joints des spires puisque, dans ces conditions, il ne peut accéder qu'à des portions infirmes de métal réparties hélicoïdalement.

Bien des cahiers des charges, et cela se généralise — à tort ou à raison — précisent que la valeur  $V_L$  maximale ne doit pas excéder 2 volts pour éviter le décollement des garnitures et ne pas gêner plongeurs ou baigneurs. Cette limite nous paraît un peu faible, mais elle s'impose peu à peu.

C'est ainsi, par conséquent, la condamnation sans appel des soutirages de courant classiques au profit des systèmes à plusieurs exutoires de courant permettant l'obtention d'une caractéristique linéaire ou quasi linéaire à coefficient angulaire nul ou très faible.

«On peut ainsi prévoir, sans trop de risques, la disparition de l'exutoire de courant unique (soutirage) au profit des exutoires multiples à polarisation uniforme (anodes réactives, INTEG, INDEP) ou à polarisations différentes liées à la zone d'action dévolue à l'émissaire considéré (LINEX).»

Nous serions particulièrement satisfaits si les nouveaux systèmes de protection décrits pouvaient être considérés comme les prototypes de procédés beaucoup plus évolués, à l'exemple de notre poste de Boussens mis en service à la RAP en 1946, et des anodes au magnésium de la Courneuve (1945) qui ont été les ancêtres de la lignée perfectionnée des quelques 1800 postes de protection cathodique existant actuellement en Gaule.

9. Est-il possible et dans quelles limites souhaitables de lancer à mer des tubes non revêtus?

Est-il possible de lancer à la mer des tubes nus et de les protéger cathodiquement? la réponse est OUI, à condition d'accepter de mettre en œuvre des systèmes de protection comportant des sources de protection multiples à gros ampérages.

Dans quelles limites est-il souhaitable?

Uniquement dans les cas pour lesquels se trouvent réunies les deux conditions suivantes:

1. — L'installation de protection, au moment de sa mise en

service, doit être moins onéreuse que le revêtement plus le système de protection convenant au cas traité.

2. — La charge annuelle découlant des KWH dépensés ou des anodes à remplacer pour la protection du tube ne doit pas excéder la charge annuelle de même genre propre au tube protégé par un revêtement, augmentée de l'amortissement de la valeur du revêtement. Pour ce dernier calcul on peut admettre de tenir compte d'un taux d'intérêt marginal assez élevé.

(1) Manuel d'Anticorrosion de l'Auteur vol. No. 1, page 286.

#### DISCUSSION

B. HEUZÉ (France): Dans le système Linex, vous n'avez qu'un seul point de soutirage du courant sur la canalisation donc, j'en déduis que la chute de tension dans la canalisation est maximale et que cela conduit à une limitation de la longueur que l'on peut protéger avec un système Linex.

D. ECONOMOU (Grèce): Avec un système Linex vous pouvez protéger n'importe quel longueur, sans inconvénients d'ordre technique, il suffit d'avoir un courant convenable. En ce qui concerne le voltage, ceci est faible. Aussi, le potentiel imposé moyen peut être supérieur à 2 V.

B. HEUZÉ: Cela n'évite pas la nécessité des connections en mer. Quel sera donc l'espacement de ces connections?

D. ECONOMOU: Non, il n'y a qu'un seul point de soutirage. En ce qui concerne l'espacement des cellules de protection c'est un problème de calculs.

Par ailleurs les systèmes différents de protection peuvent être combinés. Ainsi on peut combiner le soutirage et les anodes réactives. On dispose au large les blocs d'anodes pour améliorer la portée du soutirage. On peut effectuer d'autres combinaisons également. C'est encore un problème de calculs.

B. HEUZÉ: Oui je pense que dans les autres systèmes présentés, dont chaque poste anodique comporte une connection négative la chute de tension dans la conduite est convenablement divisée mais je ne comprends pas très bien les résultats avec du systèmes Linex si l'on n'a toujours qu'un point de soutirage.

D. ECONOMOU: On a un seul point de soutirage. Sur la ligne de protection nous avons plusieurs cellules. Chacune des cellules prend à sa charge une section de la conduite déterminée. La cellule a une zone d'action éloignée de celle-ci.

B. HEUZÉ: Mais vous avez dit que les chutes de tension sont négligeables dans l'eau de mer.

D. ECONOMOU: Oui. Pour l'exemple que nous avons donné, nous

avons à terre  $DV_L = 3,06$  V. Sur le système électrolytique défini par le déversoir, la mer et la zone correspondante de la conduite la résistance ohmique de l'électrolyte (eau de mer) dans lequel se dilue le courant est négligeable par rapport à la résistance ohmique opposée au passage du courant par le déversoir vers la mer et de la mer vers le métal de la conduite.

B. HEUZÉ: Mais pratiquement vous avez des résultats sur les conduites existantes?

D. ECONOMOU: Oui.

B. HEUZÉ: Quel est le potentiel de la conduite par rapport à la mer, son potentiel d'électrode, son potentiel réel de protection cathodique à l'extrémité en mer?

D. ECONOMOU: Je vous ai donné le chiffre de 5,55 V 72 heures après la mise en service du procédé Linex. Un mois plus tard cette valeur n'a pas trop changé. Le potentiel à l'extrémité en mer est égal à 1 V.

B. HEUZÉ: Pour quel longueur de conduite?

D. ECONOMOU: 1200 mètres environ.

J.A.H. CARSON (Canada): Avez-vous trouvé un seul cas où la protection cathodique des tuyaux nus soit plus économique que celle des tuyaux revêtus? Moi, je n'ai jamais entendu parler d'un tel cas.

D. ECONOMOU: Vous avez raison. Je vous ai donné la réponse de l'auteur de ce rapport à la question de «il est possible, de lancer des conduites sous-marines nues». La réponse est oui à condition que le système de protection soit bien calculé et que la consommation des KWh et des anodes soient telles que le coût annuel soit inférieur de l'amortissement du capital nécessaire pour le revêtement avec un taux d'intérêt marginal assez élevé.

# EXPOSURE TO AIR OF THE INTERTIDAL ZONE IN THE MARACAIBO ESTUARY

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## SUMMARY

The amount of time spent daily out of the water due to tidal oscillation, is an important factor in the survival of intertidal organisms, including those promoting corrosion. In the present contribution an attempt is made to define that amount of time for a tropical estuary.

In the Maracaibo estuary, Venezuela, tidal range decreases progressively from 110 cm at the mouth to 40 cm at Maracaibo, 35 km inside the estuary. This decrease follows a law of the form:

$$A = Ne^{-kD}$$

(A = tidal range in cm at a given point; N = value of A in cm when D = 0; k = damping coefficient in  $\text{cm}^{-1}$ ; D = distance measured from the first tide gauge in cm).

From the previous equation it is possible to obtain other

equations for the percentage of time that a plane, normal to water surface, will be exposed to the air due to tidal oscillation, at any locality inside the estuary. For levels below -17.8 cm from the datum of the tide gauges, the relation will be:

$$y = \left( 8.765 + \frac{80x + 1424}{A} \right) + 0.27A - 8.7$$

For levels above -17.8 cm, the relation will be

$$y_1 = 0.57x + (0.188 + 6.44)$$

(x = distance from the datum of tide gauge).

In both cases the variable used is the tidal range, which can be easily obtained from the first equation.

## INTRODUCTION

Most of the research on the intertidal zonation has been of a descriptive nature. Very little work has been done to evaluate the daily exposure of the organisms to the air, although this could be an important factor in the corrosion of aquatic structures.

During a survey of ecological factors in the Maracaibo estuary it became apparent the need to evaluate exposure in a rigorous way. The principles used here could be of application under similar conditions in other estuaries.

The fresh water of Lake Maracaibo is in free communication with the marine waters of the Gulf of Venezuela through a shallow bay, Bay of Tablazo which is 25 km long (figure 1). A navigation channel has been dredged to connect the deep waters of the lake with those of the Gulf of Venezuela.

Redfield (1961) and Redfield et al. (1954) have made studies of the tidal system in the Maracaibo area. The structure and composition of the communities in Tablazo Bay have been analyzed by the author in a previous paper (Rodriguez, 1963).

## MATERIAL AND METHODS

An analysis of the tidal system in Tablazo Bay was made using the tidal records from five tide gauges located on a line between Malecon and Maracaibo. The portion of the records studied covers from January 1960 to July 1963, in 24-hour periods as follows: Malecon tide gauge, 944 periods; Punta Diablo tide gauge, 844 periods; Tablazo tide gauge, 533 periods; Punta Palams tide gauge, 1053 periods; Maracaibo tide gauge, 657 periods.

The maximum and minimum levels for each day of all periods available were taken from each tide gauge to determine the average range of the tide. The differences between the highest and the lowest water level in each 24-hour period were grouped in 6 cm intervals for each tide gauge thus ob-

taining the monthly mean and annual mean. The water levels for all the tide gauges in Tablazo Bay are referred to as 'monthly mean level of lowest waters'.

The mean tide level was calculated as the mean of the highest and lowest level in 24-hour intervals. These values were grouped in 2 cm intervals for each month and each tide gauge, thus obtaining the monthly and annual means.

The percentage of exposure to the air for each tide gauge was calculated for 24-hour periods taken in June and September for spring and neap tides. The means of these periods were plotted and counted in 5 cm intervals as percentage exposure in 24 hours.

## RESULTS

*The general type of the tide.* The tides in the estuary are of the mixed type. The inequality between successive tides diminishes from the mouth to the Maracaibo tide gauge (figure 2). The differences between maxima and minima are small.

*The range of the tides.* The tidal range diminishes progressively throughout the estuary, from 110 cm at Malecon tide gauge to 40 cm at Maracaibo tide gauge, as shown in Table 1. This decrease follows a regular law (figure 3). The curve of best fitting is an exponential of the form:

$$A = Ne^{-kD} \quad (1)$$

Where A is the tidal range in cms at a given point, N is the value in cms of A for D = 0, k is the damping coefficient in  $\text{cm}^{-1}$  and D is the distance measured from the first tide gauge in cm. The values calculated from the graph (figure 3) for this equation are:

$$A = 110e^{-2.95 \cdot 10^{-7}D} \quad (2)$$

which allow us to predict the mean annual range of the tide at any point on a line whose origin is Malecon tide gauge.

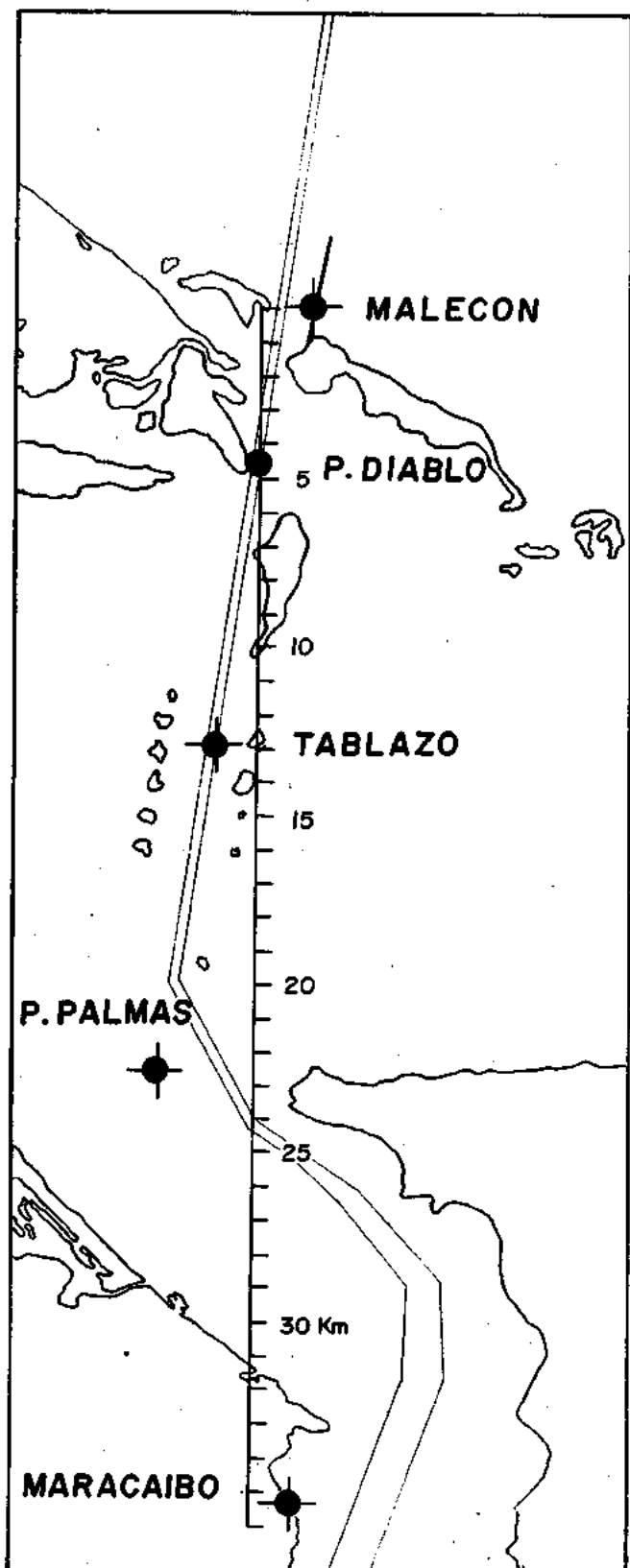


Fig. 1.

TABLE 1  
TIDAL AMPLITUDE OVER THE PERIOD 1960-1963

	Annual mean cm	Jan. - April mean cm $\pm$ SE	May - August mean cm $\pm$ SE	Sept. - Dec. mean cm $\pm$ SE
Malecon	110	110 $\pm$ 4.7	111 $\pm$ 5.7	108 $\pm$ 5.4
Punta Diablo	89	91 $\pm$ 4.2	88 $\pm$ 4.2	87 $\pm$ 4.2
Tablazo	70	71 $\pm$ 3.5	69 $\pm$ 4.4	69 $\pm$ 3.1
Punta Palmas	57	59 $\pm$ 3.2	56 $\pm$ 3.3	55 $\pm$ 3.0
Maracaibo	40	45 $\pm$ 3.8	37 $\pm$ 2.8	35 $\pm$ 2.4

The equation is valid only in the estuary, but inside the lake as well. The theoretical value calculated for the town of La Salina, on the east coast of the lake and 75 km from the mouth, is 11.98 cm. The value obtained from tidal records over three years (1956-1959) by Cockroft (1961) is 10.9 cm which is only 10% in defect of our theoretical value.

In Table I is shown the average tidal range for each tide gauge in 4-month periods. In almost all cases the standard errors are larger than the differences between the 4-month periods means and the annual mean. These values indicate that there is no significant variation in the tidal amplitude throughout the year. In the period September-December for Maracaibo, the difference is 2.1 times the standard error and may be considered significant.

*Mean water level.*

In Table 2 is shown the water level for each tide gauge referred to a datum at the entrance of the estuary. These values indicate that there is a gradient throughout the estuary of 1 cm per km. Redfield (1955) has found that the gradient throughout the Gulf of Venezuela, from Zapara to Las Piedras, is 0.16 cm per km.

TABLE 2  
MEAN WATER LEVEL OVER THE PERIOD 1960-1963

	cm
Malecon	79
Punta Diablo	83
Tablazo	94
Punta Palmas	103
Maracaibo	112

*The seasonal variation of the water level.*

The water level fluctuates throughout the year in all tide gauges. In Malecon, Punta Diablo, Punta Palma and Maracaibo there is a fall during the first months of the year, a rise in March, a fall in September and a rise again in December (figure 4). These fluctuations follow the general pattern of Curacao (de Haan & Zaneveld, 1959) and other localities on the Venezuelan coast (Patullo et al., 1955).

At Tablazo tide gauge there is an anomaly during the years under study: the level descent from July to November, while in other gauges it rises to peak values. The records however are incomplete and do not allow any definite conclusion.

The afore mentioned gradient throughout the estuary undergoes alterations corresponding to these variations in water level.

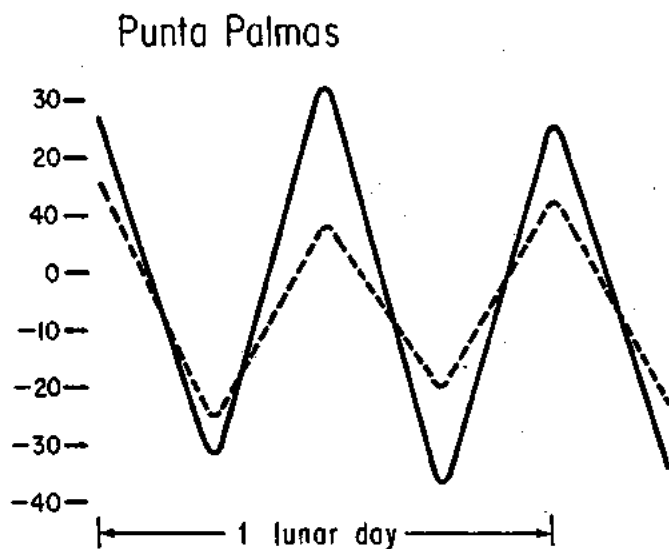
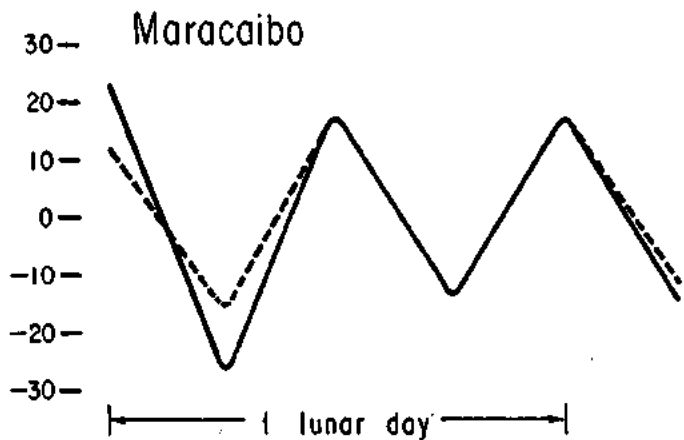
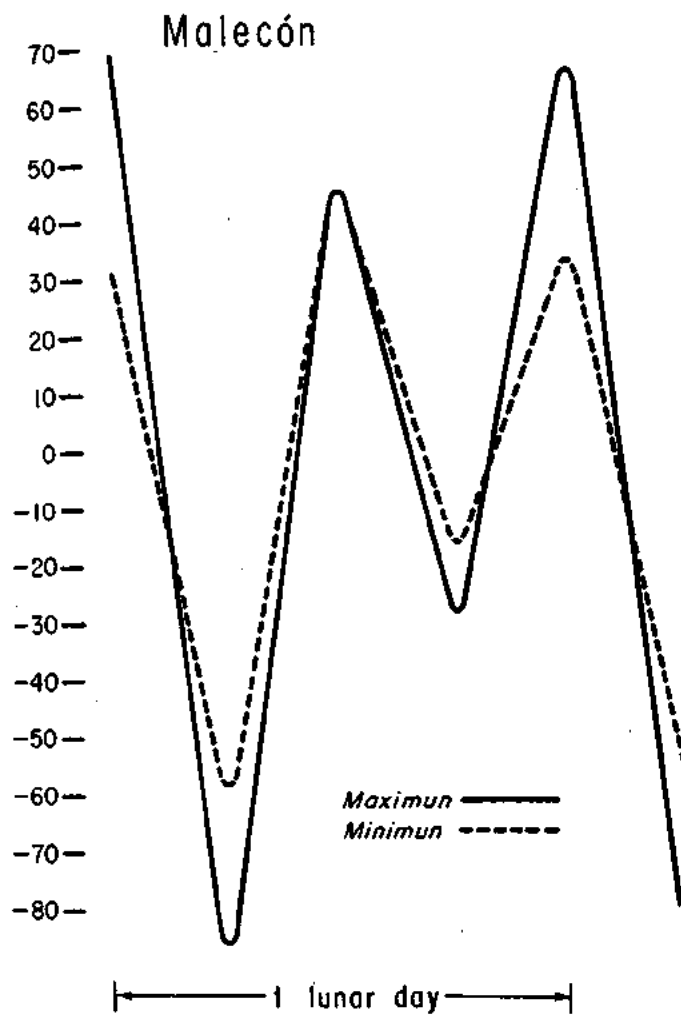


Fig. 2.

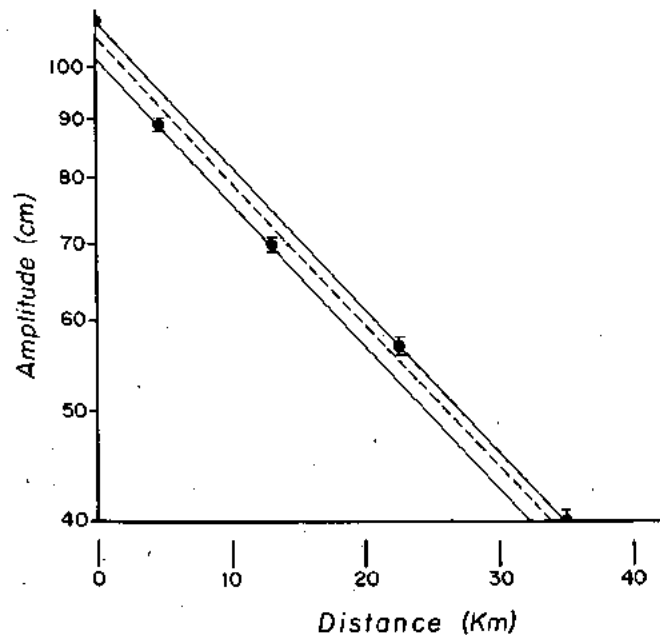


Fig. 3.

*Exposure to the air in the tidal zone.*

The values of percentage exposure plotted against levels (figure 5) gives a discontinuous function of  $x$  that could be defined by two straight lines.

$$y = mx + b \quad (3)$$

$$y_1 = m_1x + b_1 \quad (4)$$

in which  $y$  is percentage of exposure, calculated for 24 hours, for levels above the inflexion point,  $y_1$  is percentage of exposure, calculated for 24 hours, for levels below the inflexion point,  $m$  and  $m_1$  are the slope of the two straight lines in  $\text{cm}^{-1}$ ,  $b$  and  $b_1$  are the intersection of the lines with the  $y$ -axis and  $x$  are the levels in  $\text{cm}$ .

If the slope of these lines and the  $y$ -intersect could be determined by a general equation the problem of determining the percentage of exposure for any location and at any level in the estuary will be solved.

a. Position of the inflexion point. Since the two straight lines from each tide gauge have different values for  $m$  and  $b$ , the value of  $x$  at the inflexion point should be determined first. This is shown in Table 3 to be constant value,  $-17.8 \pm 2.0$  (S.E.)  $\text{cm}$  from the mean water level in all tide gauges.

As stated before, different values of  $m$  and  $b$  should be used for  $x > -17.8$  and  $x < -17.8$ .

b.  $m$  and  $b$  when  $x > -17.8$ . If the values of  $m$  for the five tide gauges are plotted against the tidal amplitude  $A$ ,

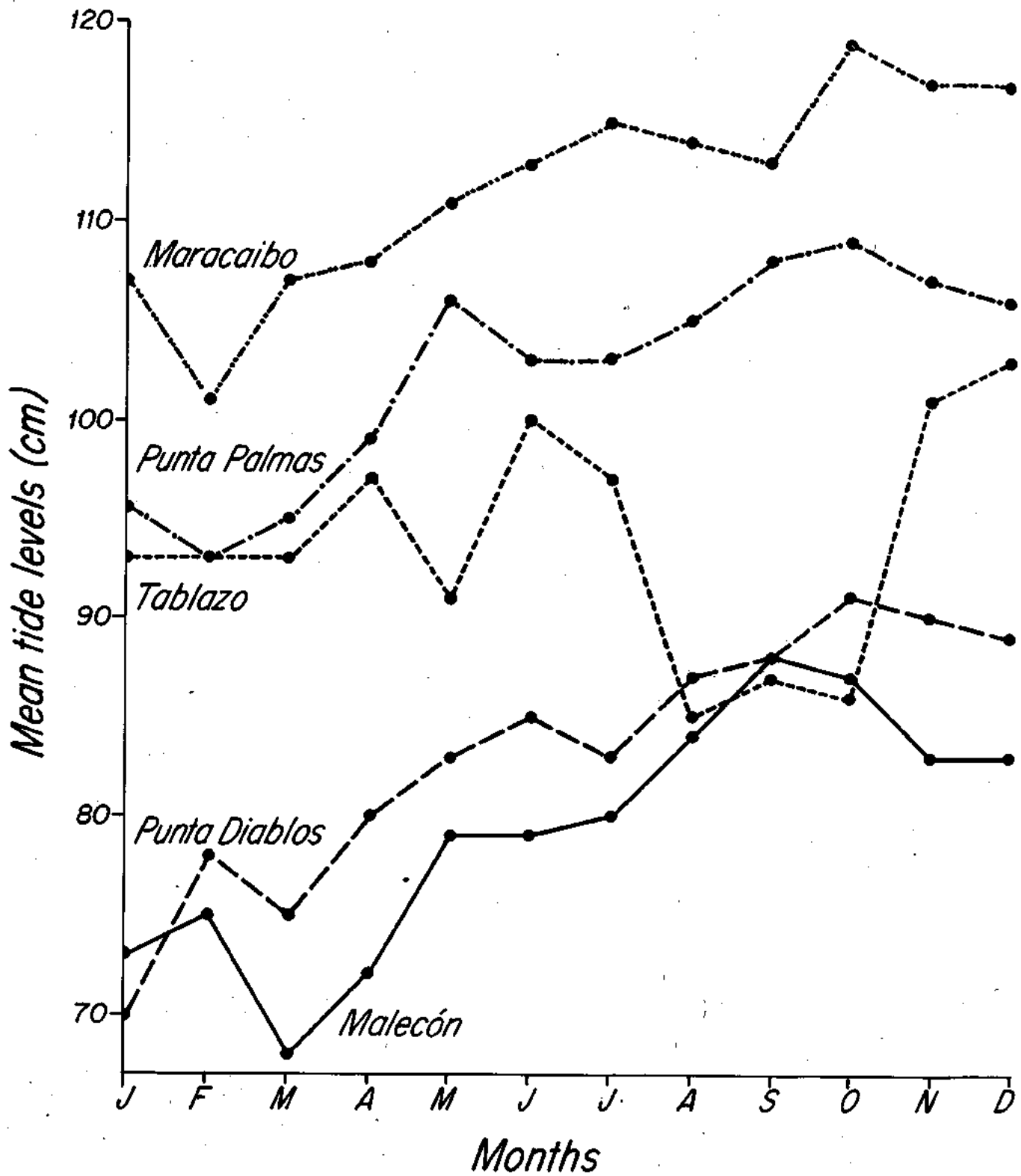


Fig. 4

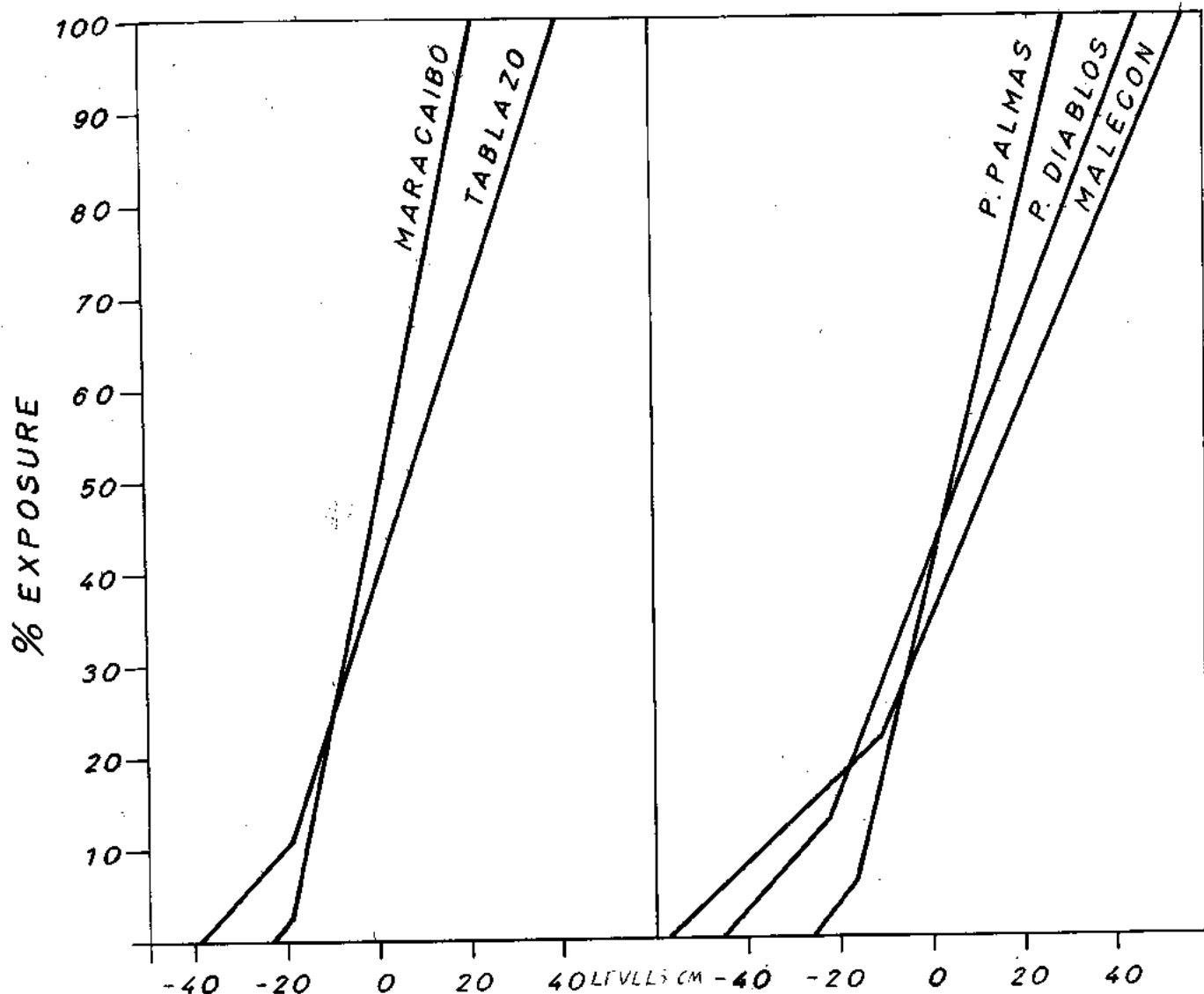


Fig. 5.

TABLE 3  
VALUES FOR THE INFLEXION POINT

Malecon	-11
Punta Diablo	-23
Tablazo	-17
Punta Palmas	-19
Maracaibo	-19

we obtain an hiperbolic relation such as the one illustrated in figure 6, whose equation is

$$m = 0.465 + \frac{80}{A} \quad (5)$$

To obtain 'b', 17.8 is added to the values of x. Thus the values of b become equal to the projection of the inflexion point over the y-axis. These values for each tide gauge plotted against tidal amplitude A, gives the equation

$$b = 0.27A - 8.7 \quad (6)$$

and thus equation (3) becomes

$$y = \left[ \left( 0.465 + \frac{80}{A} \right) (x + 17.8) \right] + 0.27A - 8.7 \quad (7)$$

which can be simplified to

$$\left( 8.765 + \frac{80x + 1424}{A} \right) + 0.27A - 8.7 \quad (8)$$

Replacing A for its value given in equation (2) the previous equation becomes

$$y = \left( 8.765 + \frac{80x + 1424}{110e^{-2.95 \cdot 10^{-7D}}} \right) + 29.16e^{-2.95 \cdot 10^{-7D}} - 8.7 \quad (9)$$

which gives the general relation of the percentage exposure to the levels referred to the mean water level and to the distance from the mouth of the estuary for levels above -17.8 cm.

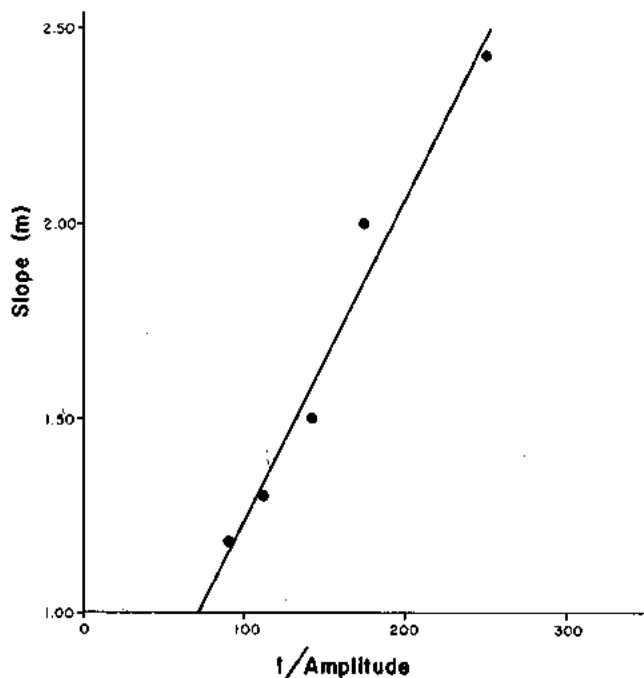


Fig. 6.

TABLE 4  
VALUES OF  $m$  WHEN  $x < -17.8$  cm

Malecon	0.47
Punta Diablo	0.48
Tablazo	0.63
Punta Palmas	0.63
Maracaibo	0.63

c.  $m_1$  and  $b_1$  when  $x < -17.8$  cm. As shown in Table 4 the values for  $m_1$  is a constant,  $m_1 = 0.57 \pm 0.08$ , and the equation for this line becomes

$$y_1 = 0.57x + b_1 \quad (10)$$

If the value of  $b$  below the inflexion point are plotted against the tidal amplitude we obtain the equation

$$b_1 = 0.188A + 6.44 \quad (11)$$

Combining equation (8) and (11) and substituting  $A$  for its value in equation (2) we have

$$y_1 = 0.57x + 20.7e^{-2.95 \cdot 10^{-7}D} \quad (12)$$

which gives the general relation of the percentage exposure

to the levels referred to the mean water level and to the distance from the mouth of the estuary for levels below  $-17.8$  cm.

## DISCUSSION

To obtain the percentage of exposure to the air in 24 hours for any level on a plane normal to the surface of the water in a place with a tidal system such as the described for Maracaibo estuary, the problem is reduced to find the slope and the  $y$ -intersect of the straight lines described in equations (9) and (11). These lines intersect each other at a point of inflexion whose value is  $-17.8$  cm.

If the level investigated is above the inflexion point the value of the slope is obtained from equation (5) and is multiplied by the sum of the values of the levels plus the value of the inflexion point. The value of the  $y$ -intersect is obtained from equation (11).

If the level investigated is below the inflexion point the slope is a constant value 0.57. The value of the  $y$ -intersect is obtained from equation (11).

Both the slope and the  $y$ -intersect in all the equations have being described as functions of the amplitude of the tide at the locality chosen. Since the amplitude is an exponential function of the distance of the locality from the mouth, it can be easily introduced by means of equation (2).

The value of the particular level investigated is measured from the mean water level, but since it changes seasonally, corrections should be applied for each month of the year. The graph presented in figure 4 makes these corrections possible.

In this method it is considered only the exposure due to tidal action. When the tide amplitude is small the wave action overcomes the tide action (Mokyevsky, 1960). The method outlined permit the calculation of the tide action, thus isolating the wave action and facilitating its analysis.

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## DISCUSSION

D. PETROCOKINO (France): For what reason this excellent, this magnificent research has been initiated? One feels that you are examining the fouling and corrosion factor, but for what specially case?

G. RODRIGUEZ: Lake Maracaibo, as I mentioned, is our most important oil producing area and it is in communication with the sea by a narrow strait that has being dredged. The dredging has produced

changes in all this area, in which are located our main fishing grounds. For the last five years we have been doing a survey to determine the effects that the dredgings have had on the aquatic organisms. One aspect that we were interested was the settlement of fouling organisms on oil towers and other aquatic structures. Now, one of the main factors in the settlement is the amount of time that the organisms spend under the water during a tidal cycle. Since there is no general equation in the literature to determine these percentages of submergence, we had to work out one for this particular tidal system.



# PEINTURES ANTICORROSION A LA POUDRE DE ZINC AVEC DES LIANTS ORGANIQUES

## II) INFLUENCE DE L' ALUMINIUM INCORPORE ET DE L' UTILISATION DE PEINTURES DE FINITION A HAUTE RESISTANCE ELECTROCHIMIQUE

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### RESUMÉ

Des essais préliminaires effectués sur des formules de peintures riches en zinc (zinc rich primers), en radeau et à l'extérieur aux bords de la mer, avaient montré les problèmes posés par les produits de corrosion formés par l'action de l'électrolyte sur le zinc. Ces produits traversaient les pores de la couche de finition et dans quelques cas donnaient lieu à la formation de soufflures et au décollement de la peinture des couches de surface. Cette attaque permettait celui de l'acier de base. Le pouvoir anticorrosion d'une des peintures était notamment amélioré par l'utilisation de petites quantités de poudre d'aluminium incorporé au zinc.

Dans une deuxième série d'expériences, actuellement en exécution, on a essayé comparativement des peintures au zinc pure et avec l'incorporation de 5 et 10% d'aluminium. Les deux pigments ont des caractéristiques lamellaires. Les liants utilisés ont été préparés avec des résines époxydes, des esters de résines époxydes avec des acides gras de l'huile de lin, caoutchouc chloré et isomérisé, et avec un vernis de résine formophénolique pure-huile de bois de Chine. Toutes les peintures ont été préparées au laboratoire.

Les essais programmés comportent l'immersion partielle (ligne de flottaison) ou complète (carène) de plaques peintes dans notre radeau à Mar del Plata, dans la côte de l'Atlantique; des essais aux intempéries, un desquels se développe en climat marin; des essais de laboratoire, spécialement du vieillissement accéléré (Weather-Ometer), expositions dans la chambre de brouillard salin et l'immersion dans des solutions d'eau de mer artificielle.

Les peintures furent appliquées à la brosse sur des plaques d'acier doux, sablées et nettoyées avec des solvants. L'épais-

seur de la peinture de zinc est de l'ordre de 40-50 microns; celui des peintures de finition, 80-100 microns. Les peintures pour les couches de finition comportent l'utilisation comme liant d'un vernis de résine formophénolique pure-caoutchouc chloré, et d'une résine époxyde avec une polyamide comme agent de durcissement. Dans les plaques de carène, la peinture antisalissures est appliquée directement sur le zinc ou en utilisant une couche intermédiaire à haute résistance.

Après une immersion de six mois, une observation a été faite, sans retirer le film de peinture (les expériences continuent pour compléter au minimum le délai d'un an). On a vérifié l'excellente tenue des systèmes comportant l'utilisation de la peinture de finition au vernis formophénolique-caoutchouc chloré. Il n'y a pas de produits de corrosion du zinc visibles sur le film, comme conséquence de la bonne étanchéité donnée par les peintures de surface. Dans toutes les plaques protégées avec la peinture époxydique on trouve des ampoules dans la zone immergée.

Dans les plaques de carène, l'utilisation de la peinture intermédiaire semble complètement nécessaire; on trouve de décollements de la peinture antisalissures appliquée directement sur le zinc.

C'est impossible, jusqu'à présent, d'obtenir des conclusions définitives referentes à l'efficacité des formules essayées.

Des essais de laboratoire ont été faits dans le but d'établir les caractéristiques d'application à la brosse, de stabilité ou des propriétés de sustentation du pigment pendant l'emmaillage. Pour les essais accélérés, on pourra faire un jugement des résultats seulement après avoir établi le comportement en service.

### 1. INTRODUCTION

Ce travail a été programmé tenant compte les nombreux problèmes posés par l'utilisation des peintures riches en zinc (zinc rich primers), spécialement face aux milieux agressifs (par exemple des électrolytes).

Ces peintures sont bien connues d'après les travaux de Evans et Mayne (1, 2). La poudre de zinc finement dispersée dans un liant organique agisse comme une protection cathodique sur l'acier (3 à 8). Metal moins noble que le fer, il possède un potentiel anodique par rapport à celui-ci. Lorsque les particules de zinc sont en contact électrique entre elles ou avec le fer ou l'acier, il se forment des piles dont le zinc se comporte comme anode et se dissout avec la formation de sels de zinc; de cette façon la peinture agisse comme pas-

sivant cathodique du fer. Il y a, peut-être, formation d'une couche d'hydroxide de zinc sur la cathode, ou de carbonate basique de zinc en présence de  $CO_2$ . Le contact intime entre les éléments des piles doit être assuré par une très faible proportion de liant dans le film sec.

Il faut considérer aussi la possibilité de réactions chimiques entre le zinc et les acides provenant de la dégradation des huiles au cours de leur vieillissement, pour former des savons zincifères. Ces savons renforcent l'adhérence, la durée et l'imperméabilité du film.

Les différents chercheurs ne sont pas d'accord avec les possibilités réelles d'application des peintures riches en zinc. Tandis que Pass et Meason (6) nous indiquent qu'elles sont des peintures appropriées pour la protection de l'acier en milieu marin, Floyd et Glaser (2) soutiennent la thèse d'une faible résistance à la corrosion et une très grande tendance des films à la formation d'ampoules. D'Ans et Schuster, de

1) Travail réalisé avec des crédits accordés par le Consejo Nacional de Investigaciones.

son côté, indiquent un pouvoir protecteur supérieur à celui des peintures anticorrosion classiques.

Les expériences présentées ont été faites en différentes conditions, ce qui impossibilité d'obtenir des conclusions valables sur le problème.

## 2. ESSAIS PRÉLIMINAIRES

Nous avons fait antérieurement des expériences isolées sur des formules de ce type. Sur la base des résultats obtenus et de ceux présentés par la bibliographie sur le thème, on a fait un programme d'expériences à courte durée, nous permettant de fixer notre point de vue particulier sur le problème d'une façon rapide, spécialement du point de vue de la protection des carènes. Le programme définitif pour 1966/67, actuellement en exécution, a été rédigé à partir de ces résultats.

Pour des essais préliminaires (11) on a préparé neuf échantillons (Tableau I) en employant des poudres de zinc de différent origine: un produit de notre industrie, deux échantillons français (Vieille Montagne et Baudier fils) et un anglais (Amalgamated Oxides Ltd.). Ils furent dispersés dans des différents liants: résines époxydes, caoutchouc chloré et isomérisé, et dans un vernis de résine formophénolique pure-huile de bois de Chine. Le zinc représente le 93-94% en poids des solides, et quelques formules contiennent aussi une faible proportion de Bentone pour retarder la sédimentation de la poudre de zinc ou pour donner, en tout cas, des dépôts mous et faciles à remettre en suspension par agitation. Dans une des peintures on remplaça le 5% du zinc par la poudre d'aluminium type haut «leafing».

Les essais préliminaires ont été faits sur des plaques d'acier peintes. On réalisa une immersion dans l'eau de mer (radeau à Mar del Plata), une exposition aux intempéries à La Plata et à l'air salin à Mar del Plata, et des essais de laboratoire (immersion, vieillissement accéléré et chambre de brouillard salin).

La peinture de finition utilisée pour la couche de surface avait comme liant du caoutchouc chloré plastifié (avec de la paraffine chlorée); elle était pigmentée à l'oxyde de fer rouge-baryte. Pour le revêtement des plaques en immersion totale on utilisa une peinture antisalissure.

Les peintures de zinc furent appliquées avec une épaisseur moyenne de 100 microns; les couches de finition avaient entre 30 et 50 microns.

Ces essais (spécialement l'essai en radeau) nous ont donné une bonne connaissance sur le problème de l'attaque du zinc par les électrolytes, suivi dans tous les cas par l'apparition des produits d'oxydation du zinc, qui traversaient les pores de la couche de finition. Dans quelques cas on trouve aussi

formation de soufflures et décollement de la peinture. Il y a un correspondance entre les zones d'attaque du film et celles de l'acier de base.

Ces résultats nous remarquent l'importance des caractéristiques des couches de surface et de son épaisseur (ce qui a été utilisé semble être très faible) sur le comportement de tout le système. Ce type d'attaque se reproduit dans la chambre de brouillard salin et dans l'immersion dans les solutions de chlorure de sodium. Un comportement pareil est trouvé aux intempéries à l'air salin.

Le comportement est notamment différent à La Plata (climat de type rural) et au Weather-Ométer: Pas d'attaque, même dans les films qui ont été exposés depuis un an sans protection de couches de finition.

L'incorporation de l'aluminium (Zn-IX) semble réduire notamment la tendance à la formation de soufflures et améliore les propriétés anticorrosion des peintures riches en zinc.

Toutes ces considérations nous indiquent l'importance de la présence des électrolytes en contact avec telles peintures, et son influence sur leur échec.

## 3. PROGRAMME ACTUEL DE RECHERCHES. CARACTÉRISTIQUES DES PEINTURES. ESSAIS.

Sur la base des expériences préliminaires on a fixé un programme de travail à fin d'étudier l'amélioration des propriétés des films des peintures riches en zinc, en utilisant des quantités croissantes d'aluminium (type haut «leafing»). On modifie aussi la composition et l'épaisseur des couches de surface.

On a préparé au laboratoire 21 formules (tableau II), en employant seulement des poudres de zinc et d'aluminium d'origine nationale, avec des caractéristiques lamellaires et de la composition suivante:

Poudre de zinc:	Zn .....	99,7 %
	Pb .....	0,23 %
	Caractéristiques granulométriques: passe le tamis 325.	
Poudre d'aluminium:	Al .....	97,7 %
	Fe .....	0,5 %
	Caractéristiques granulométriques: 0,4% retenu sur le tamis 325.	

Pour tous les essais on utilisa des plaques d'acier doux, sablées et dégraissées avec des solvants avant peinture.

Les peintures à la poudre de zinc furent appliquées à la brosse avec une épaisseur de 40-50 microns (on a diminué l'épaisseur de la couche anticorrosion et augmenté celui de la peinture de finition).

TABLEAU I  
COMPOSITION DES PEINTURES DE ZINC DANS LES ESSAIS PRÉLIMINAIRES  
(Proportion de zinc: 94% sur les solides totales)

Peinture	Liants	Type de poudre de zinc
Zn - I	Résine époxyde/poliamide	National (Fca. Argentina Pigmentos) Français (Vieille Montagne)
Zn - II		
Zn - III	Caoutchouc chloré/paraff. chlor.	National (Fca. Argentina Pigmentos) Français (Vieille Montagne) Français (Baudier Fils) Anglais (Amalgamated Oxides) National, avec 5% d'aluminium
Zn - IV		
Zn - V		
Zn - VI		
Zn - VII		
Zn - VIII	Caoutchouc isomérisé/dyphénile chloré	National (Fca. Argentina Pigmentos)
Zn - IX	Vernis de résine formophénolique pure/huile de Bois de Chine	National (Fca. Argentina Pigmentos)

**TABLEAU II**  
**COMPOSITION DES PEINTURES RICHES EN ZINC (ESSAIS 1966/1967)**  
 Proportion de zinc (national): 93-94% sur les solides

Peinture	Liant	Pigment
Z - 1	Résine Epikote 1001/poliamide	Zn (x)
Z - 2	Résine Epikote 1001/poliamide	Zn; 5% Al
Z - 3	Résine Epikote 1001/poliamide	Zn; 10% Al
Z - 4	Résine Epikote 1004/poliamide	Zn (x)
Z - 5	Résine Epikote 1004/poliamide	Zn; 5% Al
Z - 6	Résine Epikote 1004/poliamide	Zn; 10% Al
Z - 7	Caoutchouc chloré/paraffine chlorée	Zn (x)
Z - 8	Caoutchouc chloré/paraffine chlorée	Zn; 5% Al
Z - 9	Caoutchouc chloré/paraffine chlorée	Zn; 10% Al
Z - 10	Caoutchouc isomérisé/diphényle chloré	Zn (x)
Z - 11	Caoutchouc isomérisé/diphényle chloré	Zn; 5% Al
Z - 12	Caoutchouc isomérisé/diphényle chloré	Zn; 10% Al
Z - 13	Vernis formophénolique/huile bois de Chine	Zn (x)
Z - 14	Vernis formophénolique/huile bois de Chine	Zn; 5% Al
Z - 15	Vernis formophénolique/huile de bois Chine	Zn; 10% Al
Z - 16	Ester epoxy (1001)/acides gras huile de lin	Zn (x)
Z - 17	Ester epoxy (1001)/acides gras huile de lin	Zn; 5% Al
Z - 18	Ester epoxy (1001)/acides gras huile de lin	Zn; 10% Al
Z - 19	Ester epoxy (1004)/acides gras huile de lin	Zn (x)
Z - 20	Ester epoxy (1004)/acides gras huile de lin	Zn; 5% Al
Z - 21	Ester epoxy (1004)/acides gras huile de lin	Zn; 10% Al

Nota. Dans les peintures marquées (x) on utilise 1% de Bentone

Les systèmes complets utilisés comprenaient:

a) *Ligne de flottaison*: plaques en immersion partielle, en radeau:  
 Peinture de zinc, 40-50 microns  
 2-3 couches des peintures A et B, avec une épaisseur de 80-100 microns  
 Les mêmes systèmes sont utilisés pour l'exposition aux intempéries et pour les essais de laboratoire.

b) *Plaques de carène*: immersion totale, en radeau:  
 Peinture de zinc: 40-50 microns.  
 1 couche intermédiaire de peinture C: 30-40 microns.  
 2 couches de peintures antisalissures: 90-110 microns.  
 Une deuxième série de carène a été préparée sans l'utilisation de l'intermédiaire. On appliqua la peinture antisalissures directement sur la couche de zinc.

Dans tous les cas on a fixé en 24 heures le temps de séchage entre les différentes couches. La mise en service sur le radeau a été faite 24 heures après l'application de la dernière couche de peinture.

#### 4. CONSIDÉRATIONS SUR LES RÉSULTATS

*Caractéristiques générales des peintures:*

Toutes les peintures essayées sont aisément applicables à

**TABLEAU III**  
**COMPOSITION CHIMIQUE DES PEINTURES POUR LES COUCHES DE FINITION**

Peinture A	
Fe <sub>2</sub> O <sub>3</sub> .....	230
Baryte .....	120
Liant A .....	544
Solvants .....	106
<i>Liant A</i> : Résine formophénolique pure Huile de Bois de Chine Parlon 20 cP Dyphénile chloré Solvants et diluants	
Peinture B	
<i>Base</i> :	
Fe <sub>2</sub> O <sub>3</sub> .....	230
Baryte .....	120
Epikote 1001 .....	250
Oxytol .....	65
MEK .....	65
Xylene .....	70
<i>Agent de durcissement</i> :	
Versamid 115 .....	100
Isopropanol .....	50
Toluène .....	50
Peinture C (intermédiaire, mat)	
Fe <sub>2</sub> O <sub>3</sub> .....	231
Baryte .....	89
Estearate Al .....	30
Liant A .....	544
Solvants .....	106
<i>Liant A</i> : Résine formophénolique pure Huile de Bois de Chine Parlon 20 cP Dyphénile chloré Solvants et diluants	
Peinture D (antisalissures)	
Pigments: Cu <sub>2</sub> O - HgO - As <sub>2</sub> O <sub>3</sub> - ZnO - Fe <sub>2</sub> O <sub>3</sub>	
Liant: Colophane plastifiée - Solvants	



Peinture Z-1



Peinture Z-3



Peinture Z-13

Dans les trois cas la photo de gauche correspond à la peinture anti-salissures appliquée directement sur le zinc; dans celle de droite on utilise un intermédiaire.

la brosse. Les liants à base de caoutchouc chloré et isomérisé (Z-7/Z-12) donnent les films les plus uniformes. L'incorporation de l'aluminium dans la plus haute proportion (10%) fait paraître des traits de la brosse sur le film.

Un essai de stabilité dans leurs récipients pendant 4 mois nous indique les meilleures caractéristiques pour les peintures au caoutchouc chloré (Z-7/Z-9), liant inerte. Pour les autres liants, plus actifs, il y a dégagement de gaz.

Les conditions de sustentation du pigment sont notamment améliorées par l'utilisation de Bentone. L'aluminium n'est pas si efficace dans ce but.

#### Essai en radeau.

C'est le plus important par rapport à l'utilisation de ces peintures dans la protection des carènes de navires. Après six mois d'immersion on a fait une observation des plaques sur le radeau même, sans éliminer le film de peinture. Une étude plus approfondie sera faite au bout d'un an, pour établir le comportement des peintures en rapport avec les exigences des spécifications argentines pour les peintures anticorrosion.

Les plaques en immersion partielle (ligne de flottaison), protégées dans les couches de finition par la peinture préparée avec le vernis formophénolique-caoutchouc chloré (A) comme liant, sont exemptes d'oxydation visible. Il n'y a pas de passage des produits de corrosion du zinc à travers de la couche de finition. Alors, cette couche de surface présente une bonne étanchéité et une excellente résistance électrochimique vis-à-vis le milieu marin qui entoure la plaque. Dans le cas des plaques terminées avec de la peinture au liant epoxydique (B), on trouve des ampoules dans la zone immergée, mais pas de produits de corrosion visible.

Les plaques de carène, dans lesquelles la peinture antisalissure fut appliquée directement sur la peinture à base de zinc se caractérisent par la formation d'ampoules et par zones de décaillage de la peinture toxique. On trouve aussi des zones d'oxydation.

Une autre série de plaques a été protégée par une peinture intermédiaire C pigmentée à l'oxyde de fer rouge (sans pigments inhibiteurs) et avec un liant au vernis formophénolique-caoutchouc chloré. Il faut remarquer l'influence de la couche intermédiaire pour protéger le zinc de l'action de l'électrolyte; les plaques de cette série ne présentent pas d'attaque visible (excepté les peintures Z-10, Z-13 et Z-15).

#### Essais aux intempéries

Jusqu'à présent toutes les plaques placées à La Plata sont en excellent état, ce qui confirme les résultats des essais préliminaires qui ont été faits dans le même emplacement. Les peintures de zinc ont une bonne tenue même sans l'application des couches de finition.

Face à l'air marin cette protection est indispensable: les plaques montrent des produits d'oxydation du zinc (chlorures, oxydes, etc.), dans la zone exposée directement, mais pas de corrosion dans celle protégée avec la peinture de surface.

#### Essais de laboratoire

Des essais en Weather Ometer, chambre de brouillard salin et l'immersion en solution 3,5% de chlorure de sodium sont actuellement en exécution. Ils sont réalisés à fin d'établir des correspondances avec le comportement en service.

Les résultats obtenus nous indiquent une excellente tenue au bout de 700 heures dans le Weather-Ometer et 1200 h. dans la chambre de brouillard salin.

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#### DISCUSSION

Dr. GUILLEN (Espagne): J'aimerais bien poser deux questions Monsieur le Docteur Rascio. La première question, est savoir la préparation de surface utilisée dans les expériences et deuxièmement si ils ont fait des essais comparatives avec les peintures riches en zinc avec de différents préparations de surfaces.

Dr. RASCIO: J'ai oublié de vous dire que tous les essais ont été faits sur des plaques sablées; vous connaissez le problème posé par la mauvaise adhérence des peintures riches en zinc quand on emploie des surfaces très lisses (p. exemple la tôle d'acier après décapage chimique). Pour la deuxième question la réponse est non; on a essayé seulement sur des plaques sablées; on a maintenant la possibilité d'utiliser des plaques grenillées, et dans une autre série on va comparer des résultats obtenus dans ces deux conditions. Avant le prochain Congrès on espère communiquer ces résultats. Merci bien.

J.A.H. CARSON (Canada): Puisqu'il paraît que la peinture riche en zinc fraîchement appliquée fournit elle-même une protection cathodique qui devient par la suite de moins en moins efficace, je voudrais demander à Monsieur le Docteur Rascio s'il a jamais songé à renforcer la protection que fournit cette peinture en utilisant en même temps un système de protection cathodique distinct?

Dr. RASCIO: Ce que vous demandez est seulement pour le cas des peintures riches en zinc ou pour toutes les peintures en général?

J.A.H. CARSON: Je parle des peintures riches en zinc.

Dr. RASCIO: On effectue maintenant une série d'expériences sur le problème de la compatibilité entre la protection cathodique (anodes de sacrifice, en zinc et magnesium) et les différents types de

peintures (epoxy coal-tar, vinyliques, caoutchouc chloré, à liants gras, etc.), mais on n'a pas effectué des essais pour vérifier le comportement de la protection cathodique face aux dites peintures.

Du point de vue du mécanisme d'action des peintures riches en zinc, immergées dans l'eau de mer, on a beaucoup de doutes. Peut-être, dans le début de l'exposition, il y existe une protection cathodique par le zinc; mais après une période de contact avec l'eau de mer, les produits de corrosion formés colmatent le film et donnent une couche imperméable et isolante. Si l'immersion continue, on peut avoir une détérioration importante du film, et dans toutes les places où le même est enlevé commence l'attaque de l'acier. C'est pour cette raison que dans les cas des carènes il faudra employer une couche intermédiaire, isolante, et après appliquer la couche antisalissure.

A. GUILHAUDIS (France): Je voudrais vous poser deux questions. Je vois que vous avez utilisé de la poudre d'aluminium. Or la poudre d'aluminium, tout au moins celle qui est sous forme lamellaire, est généralement enrobée de stéarine et de stéarate d'aluminium. Ces corps gras protègent l'aluminium.

- 1°) La poudre de zinc que vous avez utilisée était-elle grasse?
- 2°) Pensez-vous que l'action bénéfique de la poudre d'aluminium est due à une propriété d'ordre chimique ou au contraire d'ordre mécanique, les paillettes jouant un simple rôle de barrière?

Dr. RASCIO: Pour la première question, je vous indique qu'on a utilisé des pigments non gras; pour la deuxième question, je pense que c'est une protection mécanique; l'aluminium contribue à la formation d'un film qui protège les particules de zinc. C'est de l'aluminium à haut leafling.

# EFFECT OF 5 YEAR MARINE ATMOSPHERE EXPOSURE ON SOME METALS AND ALLOYS USED AS ELECTRICAL CONDUCTORS AT THE EASTERN VENEZUELA AND THE DELTA OF ORINOCO

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## SUMMARY

In 1963, specimen of all standard I.P.C.E.A. Armored cables — as well as some experimental types were exposed for a long time — weather exposure test at various points of the eastern coast of — Venezuela and the Delta of Orinoco. (Piritu, Pto. La Cruz, Guanta, Cumana, Carupano, Pedernales, Tucupita and Barrancas). Some metals and alloys used as armor were very susceptible to intergranular —

corrosion and rapid desintegration in some of the before mentioned points. The galvanized steel wire increased the corrosion resistance of the alloys more than certain protective paints but in hot cases we have loss in weight and losses in tensile strength also insufficient was the asphaltic protection.

Almost complete protection was afforded by an extruded polyethylene film coating.

## I. CORROSIVE ENVIRONMENTS IN THE ZONE.

Generally speaking this coast on the Atlantic ocean is a zone of about 1,700 kilometers, partially is formed by the Delta of Orinoco this tremendous river which sends to the ocean from 60 to 120.000m<sup>3</sup> of water each second, bounded in the eastern part by older formations, these older formations attain a height in some places of from 50 to 100 metres above sea level and consist mainly of tertiary and diluvial sand mixed with gravel, haphazardly interspersed with lenticular pockets of clay and peat layers; in some places they are intersected by fairly large rivers with the resultant deposit of river clay, sporadically covered by peat.

These higher areas are bounded in the west and north by lower areas consisting of holocene sand, clay and peat, for the greater part deposited in seawater, the top layer of which is of ten below sea level, so each year during the rain season (May to November) the zone of the Orinoco's Delta presents big inundations, to prevent these inundations are now developing a system of dykes called cano Manamo.

It is obvious, therefore, that the ground-water level in such geologically contrasting areas also varies considerably. In the higher eastern and southern areas, which consist mainly of sand deposits, this level is sometimes some tens of metres below the surface. As a result the armored cables in the parts are nearly always above ground-water level.

The situation in the west and north is quite different, as the ground-water level in these parts of the country is often only a few decimetres below the surface. The armored electrical conductors in the areas are either permanently or, depending on the season, alternatively above and below ground-water level this water has a variable salinity and all type of microorganisms of a tropical climate also, as is very near to petroleum wells, is very rich in hydrocarbons which include as impurities various sulphates these impurities have as consequence one corrosive process which is the so called sulphate reduction, first recognized in Holland by von Wolzogen Kuhr as a source of corrosion. In the absence of oxygen by the intermedation of certain bacteria (sporovibrio desulfuricans), the function of the oxygen necessary for the cor-

rosion process may be taken up by the sulphate oxygen. At the same time a certain quantity of ferrous sulphide is formed. When conditions have altered and oxygen again renders the soil aerobic, these sulphides are oxidized forming sulphuric acid which leads to further corrosion-damage.

The conditions which must be fulfilled to bring about this electro-biological corrosion are, apart from the presence of sporovibrio desulfuricans, absence of oxygen, presence of organic matter and other physiological compounds necessary for the growth of the bacteria, presence of soluble sulphates and neutral or nearly neutral medium.

As we have comprobate only the presence of strong quantities of tannic solutions stops this phenomenon which was observed in the areas where «mangle» woods are locate (the mangle is a plant like the Argentinian Quebracho with a big percentage of tannic acid in his external structure).

The composition of the ground-water also varies considerably. In the higher areas in the east south, this water is generally fresh. In the lower districts in the west and north the ground-water is very much affected by the proximity of the sea; here large tracts are brackish, whereas in other places the original salt and brackish water have been displaced by the fresh water that has seeped through. The chemical composition of the ground-water varies considerably, e.g., in so far as this affects reaction to metals. In many areas, especially in the west and north, either unprotected or insufficiently treated iron and steel wires are severely affected as a result of the aggression of the soil and ground-water. Such areas have received the nickname of «dangerous». In a number of cases it was necessary to renew entire cables not older than one or two years, which were protected in the then prevailing way, e.g., for iron wires a coating of coal-tar pitch and for steel wires an immersion of the same material, provided with an impregnated hessian wrapping.

## II. PRESENT CONDITIONS AND NEAR FUTURE REQUIREMENTS OF ARMORED SUBMARINE CABLES.

The vastly increased demand for Venezuelan petroleum products following the first and second Suez crisis, gave im-

petus to a tremendous demand of auxiliary wells equipment and between them of armored cables which are used to supply electrical energy from the coast or the electrical generating equipment to the wells pumping system. The Oriental Zone of Venezuela is one of the principals in the country's oil production in 1968 is producing daily more of 1,000,000 Barrels day from the 4,000,000 which is the all country's production.

The armored cable is composed from three stranded conductors (each one, in accordance to the proper standards and dimensions, is composed from 19 to 364 wires) insulated with high voltage conventional or cross linked polyethylene, or butyl rubber, over each insulated conductor is a metallic (copper alloy) shiling tape all three conductors are cabled together and in the interstices a yute bedding is applied the overall is covered with a helicoidal bronze tape to called «teredo» tape because is applied to protect the organic insulation from the attacks of the Teredo's a type of termites of the Tropical seas over the Teredo tape is applied a Jacket of Polyvinyl Chloride. This kind of cable has normally a tensile strength about 40-56,000 P.S.I. but as is supposed to resist from mechanical point of view very rigorous conditions, needs a special external protection so called «armor» is normally composed from about 24-72 iron, steel, cooper or copper weld wires which they can increase its tensile strength up to 80,000 P.S.I. as this armor was not protected against corrosion normally esapears in time intervals from 8 to 14 months and as continuously the same fatigue was applied by the external factors the life of these cables was in 1965 of 16 months as

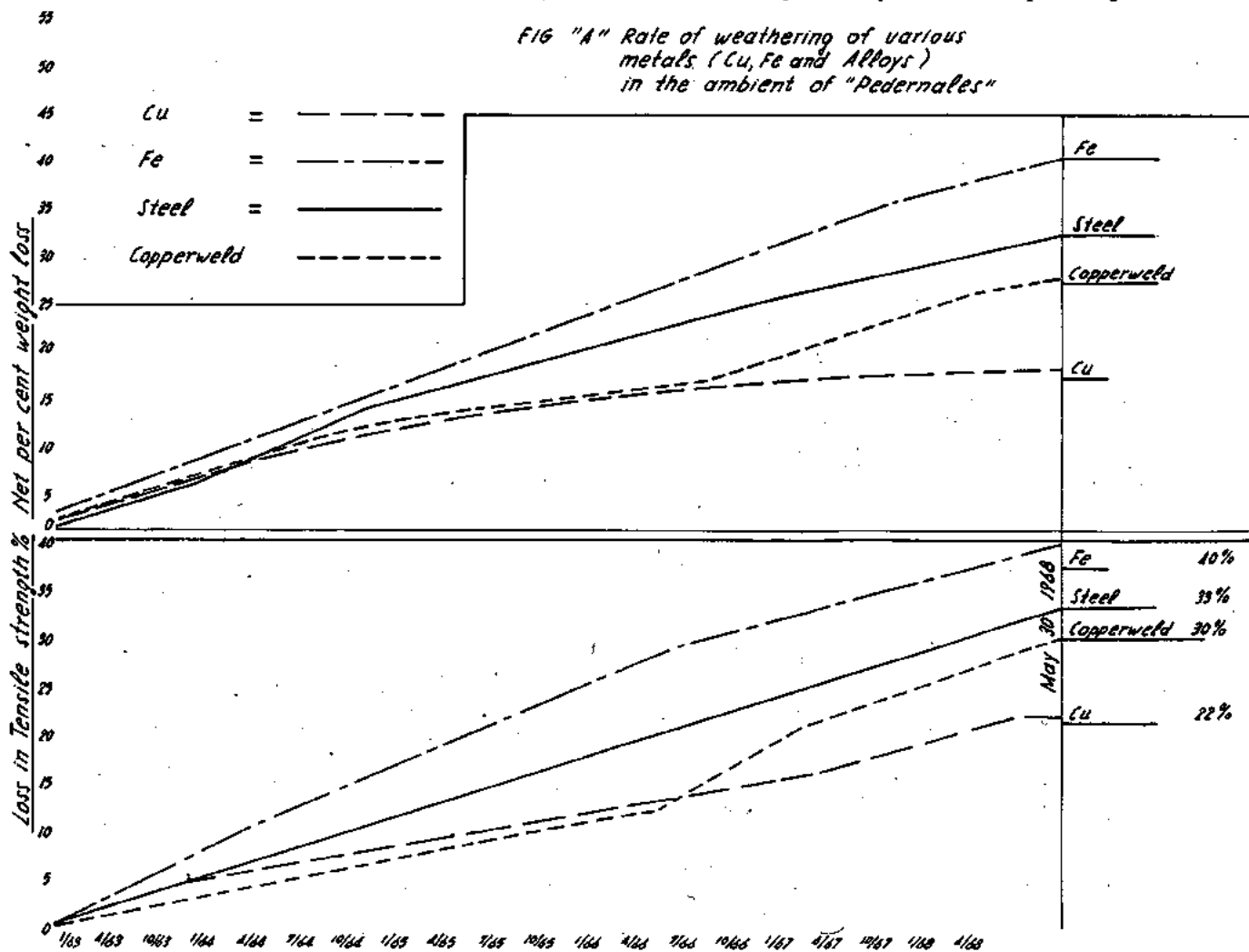
tent of the soil, as well as the presence of carbon particles. The sulphate, sulphide and polysulphide content are important in connexion with the sulphate reduction process, whereas a high chloride content promotes corrosion by contributing to the electrical conductivity. The presence of lime prevents the formation of acid corrosion products.

**Acidity:** The pH value is determined in a sample by means of a glass electrode; for that purpose a special type of penetration electrode strong enough to be pressed into the soil, is used. A calomel-electrode with asturated KCl solution of a specially designed type for the purpose of soil measurements serves as a reference electrode. The pH is established by means of a standard type laboratory potentiometer.

**Electrical conductivity:** The measurement of soil resistivity is carned out with the Shepard apparatus, as designed for field use. Two electrodes are thrust into the soil and connected with the poles of a battery; a milliammeter, graduated in ohm-centimetres shows the resistivity of the soil, from which the conductivity may be calculated.

**Redox-potential:** The redox-potential must be measured in undisturbed soil, without exposing the soil to the air. Because the establishment of equilibrium at the electrodes takes much time, a special procedure is followed in which the testing in situ is replaced by sampling. The measurements are made within six hours after sampling. The determination is carried out in the same way as described under «Acidity» however, the glass electrode is replaced by two platinum-electrodes, to duplicate the test. The electrodes are made of 1-millimetre platinum plate with sharpered edge to facilitate

FIG "A" Rate of weathering of various metals (Cu, Fe and Alloys) in the ambient of "Pedernales"





the penetration in the soil.

## V. EXPERIMENTAL WORK.

### Materials and Testing Procedure

The exposed materials have commercially Standard (A.S.T.M. - I.P.C.E.A. N.E.M.A. and U.L.) Copper wire, iron wire, steel wire and copperweld all No 12 Awg. same as the used for armoring purposes all of them without any covering or other protection.

Various tests have been also done with the same wires, covered with asphalt, paints, and plastics (Chloroprene called commercially Neoprene, P.V.C., polyvinil acetate, polystyrene, conventional, polyethylene, cross-linked polyethylene, A.B.S., poly-butadiene etc.) a resume of these results loss in tensile strength and weight can be appreciate on figures «A», «B» and «C».

As you can observe in these results the best results have been obtained with the polyethylene protected wires.

### Interpretation of data

The foregoing data in themselves are of considerable value in illustrating the relative performance of these metals in different types of environments. There still exists the problem of translating data on specific metals in specific environments to applications involving those of related alloys to related en-

vironments. Several ways of analyzing the data are suggested so that the information can have the far-reaching effects intended.

Consider first installations at the sea-coast. If the alloys are to be exposed close to salt water, continually subjected to salt spray or salt mist, without the cleansing action of they are cables of full lengths of 1-4 km and after the first interruptor was not more use for them the damage for the oil companies was very significant at the same time under the pressure of the demand they — have being study to perforate new wells for which they need to triplicate the existing equipment in 1965 from this need come the present paper.

## III. EXPERIMENTAL WORK FOR PROTECTIVE COATINGS.

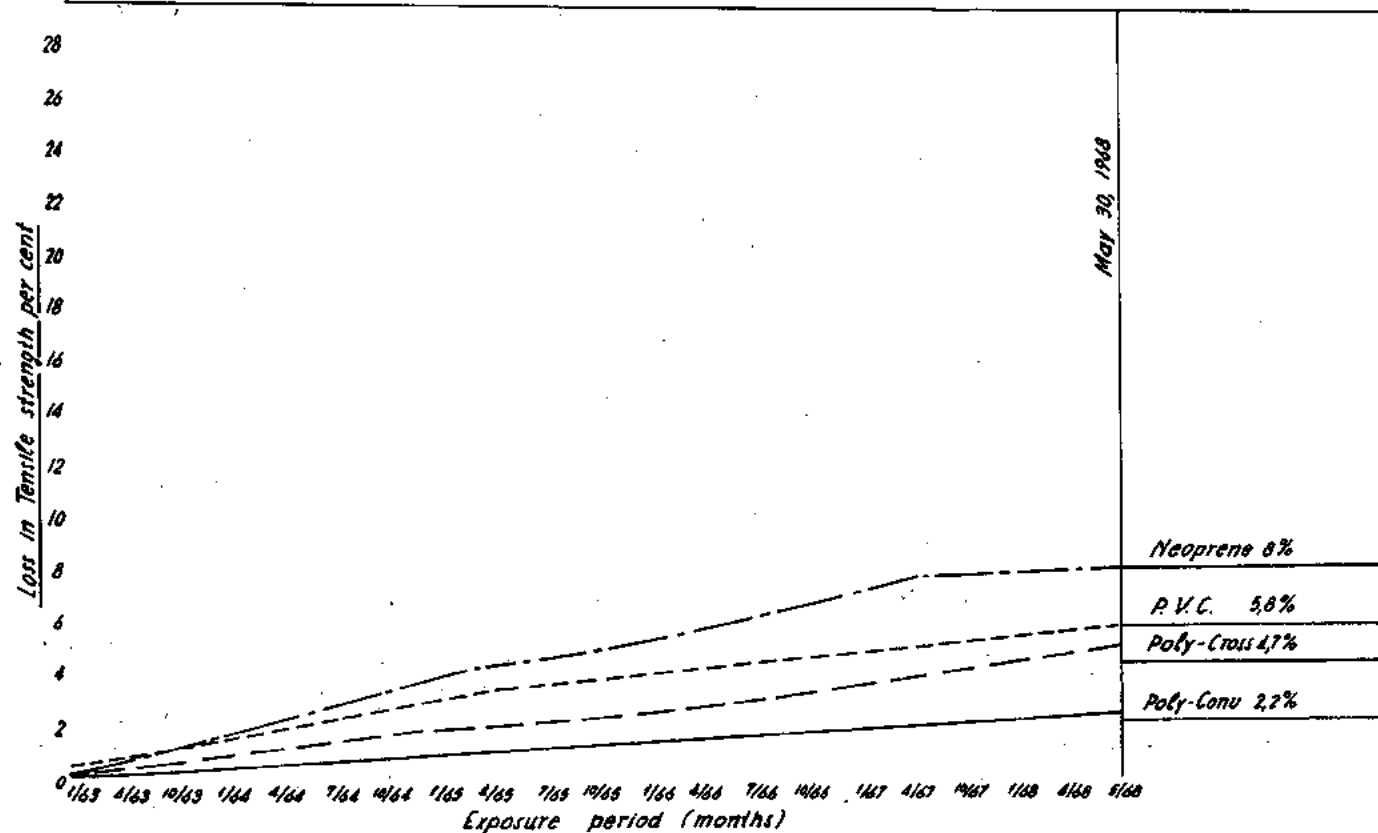
The main constituent of the systems of protection relative is blown asphaltic bitumen, chosen because of its chemical stability and special mechanical properties, four classes of protection are specified light medium, heavy and extra heavy for use in soils and waters, of increasing corrosiveness.

### Specification of systems of protection classes I-IV.

*Class I, light:* One coating of blown asphaltic bitumen with a minimum thickness of 0.5 mm.

*Class II, medium:* First coating: Primer of blown asphaltic bitumen to ensure adhesion of second coating. Second

*Poly-Conu* ————— *FIG "B" Rate of Weathering of Metals (Cu, Fe)*  
*Poly-Cross* - - - - - *protected with various plastic*  
*P.V.C.* - - - - - *coatings (Polyethylene, Cross linked,*  
*Neoprene* - - - - - *P.V.C. and "Neoprene"*  
*in the ambient of "Pedernales")*



coating: blown asphaltic bitumen with filler. Minimum total thickness: 2.5 mm., first coating maximum 0.5 mm.

*Class III, heavy:* First and second coating as for class II. Third coating impregnated fibre cloth for mechanical reinforcement. Fourth coating, top coating of blown asphaltic bitumen with filler; minimum thickness: 2 mm.

*Class IV, extra heavy:* First and second coating as for classes II and III, but with a minimum total thickness of 6 mm.

Third to fifth coating: two impregnated fibre cloth wrappings, separated by a mm. coating of blown asphaltic bitumen with filler. Sixth coating; top coating: top coating as for class III. Seventh coating: crepe paper covering. Eighth coating: straw cord wrapping, specially meant for protection of coating during transport and construction.

Specifications are given for the blown asphaltic bitumen to be used, as to softening point Ring and Ball, Penetration and Fraass Breaking Point; in addition, the material with filler must meet the requirements of a severe steel ball drop test, a flow test and a plunger load test. The finished coatings must show no pinholes when tested by a high voltage spark test and meet the requirements of a conductometric test.

Actually (May 1968) this standard is under discussion of the Venezuelan Standard Committee (Codelectra) which will decide how will be recommended the use of each of the before mentioned four classes of asphaltic protection. Unfortunately the asphalt which is produced in Venezuela has a percentage of sulphates up to a 4% as consequence the sulphate reduction can be a factor of corrosion of the armor wires so that relating to this matter must be included.

#### IV. TESTING OF THE SOIL AND THE WATER WITH REGARD TO CORROSIVENESS.

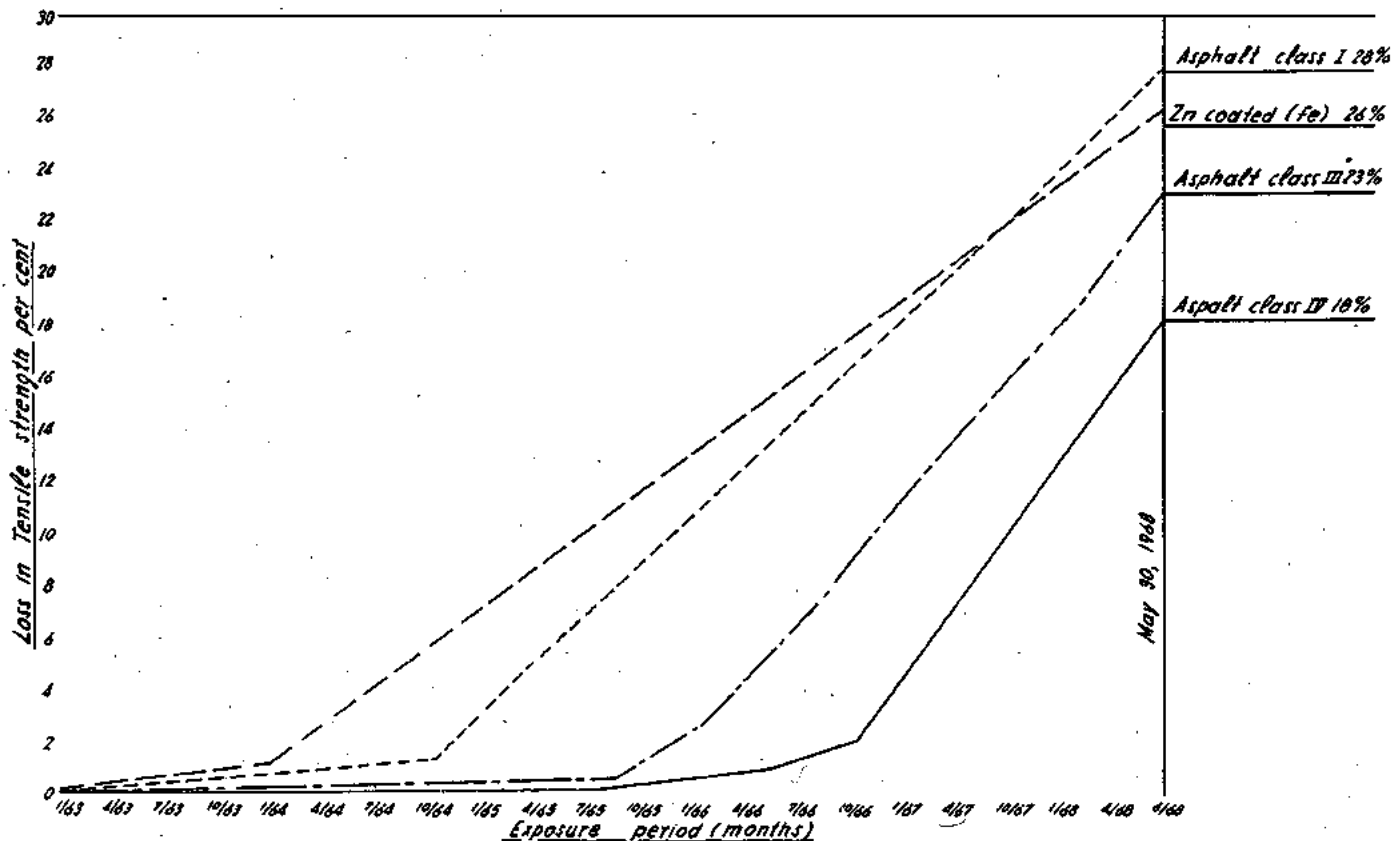
The investigation consists of the following determinations:  
 Chemical analysis of the soil;  
 Acidity, by pH measurement;  
 Electrical conductivity;  
 State of oxidation with respect to reductions of the soil, by measurement of the redox-potential.

*Chemical analysis:* The analysis includes determination of the sulphate, sulphide, polysulphide, chloride and lime con-rainfall but with salt fogs to wet the surfaces, then the data obtained at Cumana might best apply.

Other seacoast exposures, even in the immediate vicinity of the ocean, may be much less corrosive because of several factors, such as (1) frequent or periodic rains to cleanse the surfaces of salt and soil, (2) reduced amounts of salt mist in air because of the direction of prevailing winds, magnitude of the surf, and effects of certain barriers, and (3) general absence of fogs. For such situations, the data obtained at Pto. La Cruz would be more useful.

Results secured on specimens exposed close to the ocean would indicate what might be anticipated along beach or boardwalk exposures. The corrosivity decreases markedly with increasing distance from the ocean. Conditions just a few hundred meters from the ocean are much less adverse than those at the beach. In fact, at points beyond 1/2 to 4 km. from the ocean, the corrosivity of the atmosphere to aluminum alloys generally may not be any different from that of

*Zn coating*      — — — —      *FIG "C" Rate of Weathering of Metals (Cu, Fe and Alloys)*  
*Class I asph*      - - - - -      *protected with Zinc and asphalt Coatings in the ambient*  
*" III "*      — · — · —      *of "Pedernales"*  
*" IV "*      — — — —



many nonindustrial, inland localities. Although a town or city may be classified as a seacoast community, the great bulk of structures may be substantially beyond the corrosive influences of the marine atmosphere.

## VI. SOME ECONOMIC ASPECTS OF CORROSION CONTROL AND PROTECTION IN ELECTRICAL CONDUCTORS.

### *Corrosion costs and Corrosion control*

It is surely opportune to reaffirm the importance of corrosion in relation to metal conservation. It should be borne in mind, however, that wastage of metal is by no means the only economic factor to consider. Frequently, corrosion may lead to heavy losses of other materials or heavy increases of power necessary to maintain supplies. An important example of this indirect effect is the reduction of carrying capacity of cables through the formation of insoluble corrosion product, to quote from a recent article, «the indictment against corrosion is by no means exhausted in the premature replacement of material rendered unserviceables; it should include, for example, the indirect costs of damage due to corrosion failures in service, and the incidental losses of productivity and human life. Like production interruptions and accidents due to broken conductors.

In our particular case a good protective method, is the use of one polyethylene extruded film.

On this question, much depends upon the life of the cable as determined by factors other than corrosion, and the initial cost of protection must be balanced against the number of years the installation is expected or required to last.

## VII. CONCLUSIONS

1. The exposures used represented a wide range of conditions, not only with regard to type of atmosphere sea coast industrial, or nonindustrial but also in severity for each type of environment. It is very likely that these cover the range of atmospheric conditions to which the bulk of metallic structures are normally subjected.
2. For copper and alloys in all environments, the effects of weathering when based on measured depths of attack and loss in tensile strength, generally decreased with time.
3. The outstanding performance of Copperweld is noteworthy as it demonstrates the excellent over-all resistance.
4. The protection of the zinc coating is very relative.
5. The application of asphaltic products presents satisfactory results but in some times the presence of sulphates as impurities of the asphalt has contraproductent results.
6. The plastics like P.V.C. and the polyethylenes when applied by extrusion are the best protection of this kind of armoring for aerial, underground or undersea uses.

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## DISCUSSION

Dr. KENWORTHY (England): I would like to ask the speaker, if he could give us the composition of the metals involved in his tests.  
Prof. G. PETRIDES: I mentioned that it was the American Society for Testing Material, that means the copper is pur 99.9 the type of hard ground copper, now the steel is specified by the British Standards and the American Standards, for the Protection of Cables. This is a low carbon steel, naturally with small Hardness because we need a big elasticity. This is a cable and needs relative elasticity; now about the copper well is the 40% high strength copper weldy.

C. CABRILLAC (France): I would like to ask the speaker about his conclusion. He said that the best product was polyester or conventional polyethylene. I would like to ask him to define the tendency of protections the cables of telecommunications or the cables of transportation of power especially in the under water sea cables and of having used the polyethylene with the need of using smooth jackets.

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There is a tendency to avoid these cables with armatures because of their fragility, their high cost, the difficulty of installation, while smooth sheaths or corrugated ones present a high interest because they are very adherent and hence they hinder the migration of water between the metallic sheath and the plastic envelope.

A second question, you spoke about Neoprene and you didn't give any conclusion. Is it the Zypalon or the Neoprene comparatively inferior than PVC or polyethylene?

Prof. G. PETRIDES: First on the question of Neoprene, you find on the table about Neoprene that it is partially permeable and inferior of polyethylene. There you can observe the effect on Neoprene. Now we prefer this system because is more resistant than the others. On the fact of permeability, there is not any problem because there is the plastic jacket, which is made of PVC and it is an exceptional protection. In this case this is used all over America as a standard.

# ELECTROLYTIC INHIBITION IN SEA WATER

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## SUMMARY

Laboratory investigations of an electrolytic treatment for reducing the corrosion of mild steel piping in sea water are described. A significant reduction in corrosion in cold sea water was achieved by treatment with aluminum, zinc, steel or magnesium anodes. With both aluminum and zinc anodes the corrosion was reduced to as little as one-fifth

that in untreated water. The beneficial effect of electrolytic treatment appears to result from combined cathodic and anodic inhibition by the metallic anode reaction products in the form of gelatinous hydroxides. For a given ratio of anode current to sea water flow rate, the degree of corrosion reduction was found to increase with time and water velocity.

## INTRODUCTION

In an earlier paper<sup>1</sup> it was shown that electrolytic treatment with aluminum or steel anodes could make sea water markedly less corrosive to mild steel piping, and it was concluded that both the aluminum and steel corrosion products were acting as cathodic inhibitors. Further investigations to be described in this paper have shown that electrolytic treatment with zinc or magnesium (alloy) anodes also results in inhibition of steel in sea water.

In the scientific literature, there does not appear to be any reference to the benefits of aluminum corrosion products in reducing the corrosion of steel in water, but apparently as early as 1881 Parker<sup>2</sup> recognized that zinc anode corrosion products were inhibitive to steel in boiler water. In 1924 Evans<sup>3</sup> reported that zinc sulphate inhibited the corrosion of steel in aerated fresh water, and his observations led him to suggest that the zinc was deposited as the hydroxide on cathodic areas; i.e., the zinc acted as a cathodic inhibitor. His observations were confirmed and extended by Thornhill<sup>4</sup> in 1945.

One would expect that a cathodic inhibitor would be just as effective in sea water as in fresh water since in both cases the corrosion of steel is primarily under cathodic control. Vernon and Wormwell, in the discussion of Thornhill's paper, reported that zinc corrosion products inhibited mild steel in moving, intermittently heated sea water, but that if the zinc was added as a salt (chloride or sulphate) under otherwise the same conditions, corrosion was accelerated. On the other hand, Hatch and Ralston<sup>5</sup> reported that a combined zinc-polyphosphate salt addition in the order of 25 ppm acted as a cathodic inhibitor and provided good inhibition of steel in sodium chloride brines.

There does not appear to be any direct reference in the scientific literature to the effects of iron corrosion products on the corrosion of steel in sea water. Iron corrosion products have, however, been recognized<sup>6,7</sup> as beneficial in reducing the corrosion of copper alloys in sea water, and Bostwick<sup>8</sup> reported that the periodic addition of around 1 ppm of ferrous sulphate dramatically reduced impingement attack of aluminum brass tubes in brackish water. It is also probable that some of the benefits to ships' sea water cooling systems, attributed to cathodic protection by Cumberland,<sup>9</sup> were in fact the result of inhibition by iron corrosion products.

Bregman<sup>10</sup> refers to the beneficial effects of magnesium salt additions with polyphosphates in fresh water. In contrast to aluminum, zinc, and iron however, whose concentrations in sea water could be markedly affected by an addition of around 1 ppm of the respective ions, the magnesium content of sea water is already so high (1300 ppm) that it is hard to understand why the addition of 1 ppm more should make any difference to the sea water corrosivity.

The present paper describes, in addition to the investigations of electrolytic treatment with different anode materials, a study of the effects of a number of variables on the inhibition achieved specifically with aluminum and steel anodes.

## EXPERIMENTAL TECHNIQUE

The experimental set-up shown in Figure 1 (with either 1/4" or 3/4" nominal Schedule 40 pickled mild steel pipe specimens) was used throughout our investigations, with the exception of Runs 13, 14 and 15. In these latter runs with the 3/4 inch piping system, the basic set-up was the same but the number of pipe specimens on each side of the treatment tank was increased from 10 to 40, and provision was made for the insertion of electrical resistance probes for measuring the corrosion rate. In addition, in Run 15, provision was made during the initial part of the test period for fitting 3/8 inch diameter concentric zinc anodes running the full length of the pipe assemblies. In all runs the pipe specimens in a group were coupled to each other with malleable iron fittings but were not metallically coupled to the reaction tank. Earlier work<sup>1</sup> had shown that metallic coupling did not affect the inhibitive action.

Weir boxes were used to measure flow rates of the sea water, which was supplied fresh on a once through basis from the sea adjacent to the laboratory. The sea water temperature ranged between 7° and 14°C during the trials, with an average close to 10°C.

The anode current was supplied by filtered rectifiers, and was determined from the potential drop measured across fixed precision resistors ( $R_m$  in Figure 1).

Gas accumulation in the top of the 3/4 inch system treatment tank was eliminated by the installation of a small bleed line. No bleed was necessary in the 1/4 inch systems.

In Run 34, in which aluminum was introduced as a salt, the experimental set-up was essentially the same as that

shown in Figure 1 except that the aluminum chloride as a fresh water solution (containing 158 gms/litre of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) was introduced by means of the low pressure tap of a venturi located in the pipe run just upstream of the treatment tank. The venturi pressure drop was applied across a rubberized bag containing the aluminum chloride solution. A length of capillary tube between the outlet from this bag and the low pressure tap of the venturi served as a flow control resistance. The instantaneous rate of aluminum chloride addition could be estimated by counting the drop rate from the end of the capillary, but the overall chemical addition rate was determined from the volume of chemical used.

At the end of an exposure period (the usual period was 60 days) the pipe specimens were degreased, mechanically cleaned, pickled in inhibited hydrochloric acid, dried and weighed.

## RESULTS AND DISCUSSION

### General

In all instances electrolytic treatment with aluminum anodes resulted in a reduction of the corrosion in the pipes carrying the treated water (downstream of the treatment tank) when compared to the corrosion of the pipes carrying raw sea water (upstream of the treatment tank). In some instances (see Figure 2) there was considerable scatter and a slight overlap of upstream and downstream weight losses, but on the average there was a beneficial effect of the treatment and in many instances (see Figure 3) the protective effect was very marked.

In general, as can be seen in Figures 2 and 3, the absolute scatter became greater as the weight losses increased. It was therefore concluded that most of the deviations were random effects and not the result of experimental errors. There did appear to be a tendency, particularly upstream, (see Figure 3) for the weight losses of the first and last specimens in an assembled run to show wide deviations from the average. In such instances these end specimen weight losses were ignored in selecting the average weight loss line.

The experimental conditions, the graphically averaged weight losses and the linear\* corrosion rates of all the runs completed since publication of the previous paper<sup>1</sup> are given in the Table.

### Effect of Anode Material

The purpose of Runs 16-29 inclusive (with the exception of Runs 19 and 27) was to determine the effect of electrolytic treatment with different readily available anode materials. The control anode material was the same 99.9% wrought aluminum used throughout the investigations. The other anode materials were pure zinc (0.003% iron), a magnesium alloy (6% Al 0.5% Zn), mild steel, and graphite. The nominal sea water flow was 5.5-5 fpm and the ratio of anode current to flow rate (I/U ratio) was approximately 0.4 amps/US gallon per minute throughout. At 100% anode efficiency this ratio would result in the following concentration of the respective metals in the sea water: aluminum 0.6 ppm; zinc 2.1 ppm; magnesium 0.8 ppm and iron (ferrous) 1.8 ppm. Actual anode efficiencies\*\* for these runs were as follows: aluminum 86% and 88%\*\*\*; zinc 112% and 114%; magnesium (based on pure Mg) 69% and 74%; and iron 120% and 128%.

From Figure 4(A) it can be seen that at an I/U ratio of

\* Linear corrosion rate as used here is the apparent corrosion rate obtained by dividing the corrosion penetration for a given time period by the time (as opposed to the true corrosion rate which is the slope of the corrosion penetration vs time curve at any given time).

\*\* Anode efficiency =  $\frac{\text{Actual Amp Hours} \times 100}{\text{Theoretical Amp Hours (from Wt. Loss)}}$

\*\*\* Throughout all the trials aluminum anode efficiency varied between the extremes of 68% and 144% but usually ranged between 77% and 87%.

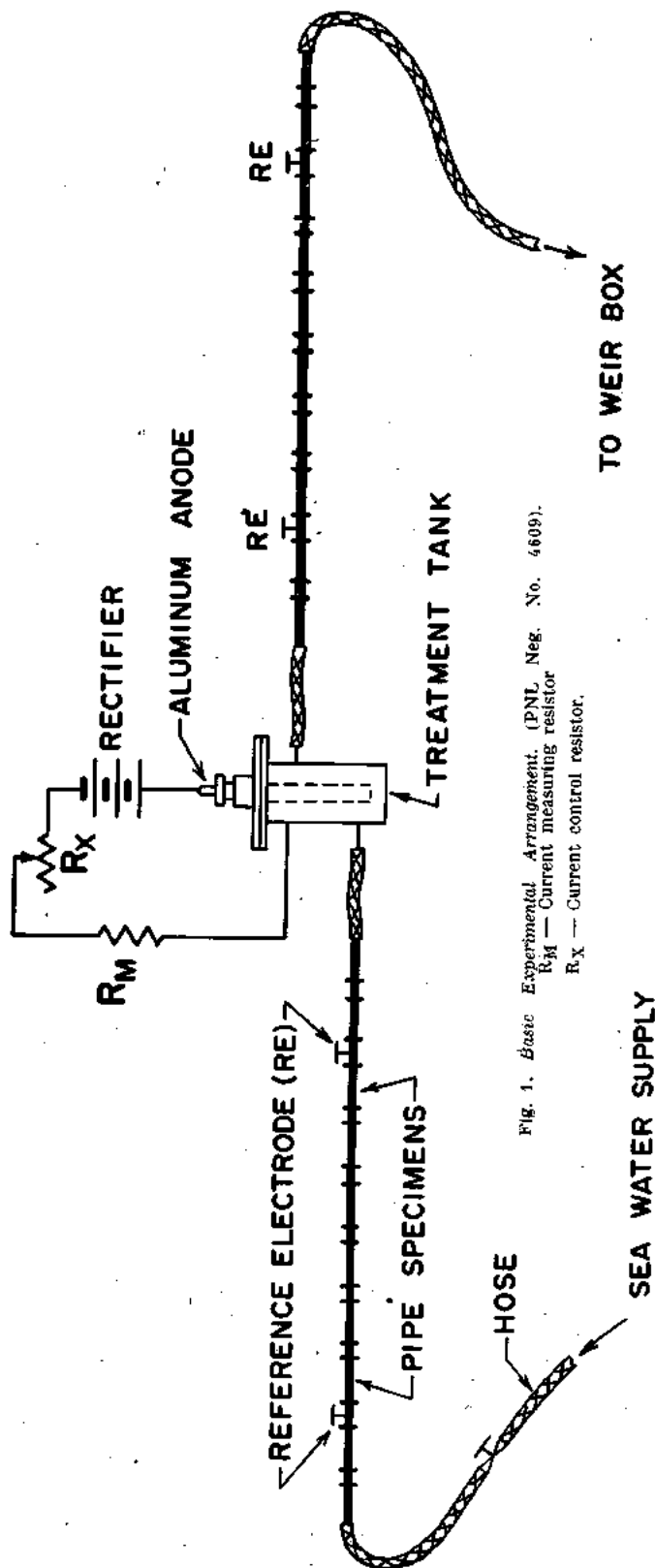


Fig. 1. Basic Experimental Arrangement. (PNL, Neg. No. 4609).  
 $R_M$  — Current measuring resistor  
 $R_X$  — Current control resistor.

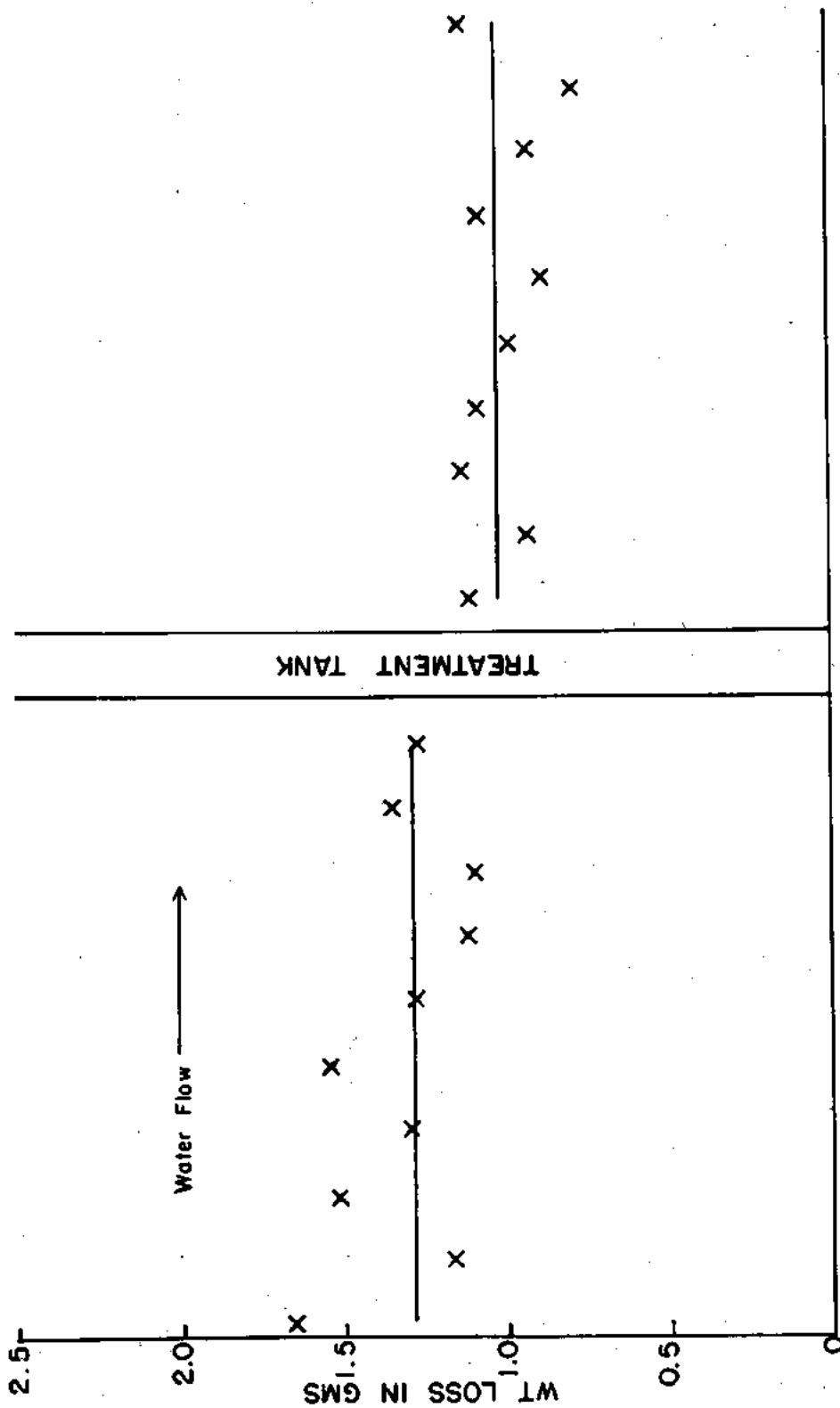


FIG. 2. Example of Run with Bad Scatter and Overlap of Upstream and Downstream Weight Losses. (Run 27). (PNL Neg. No. 4610)

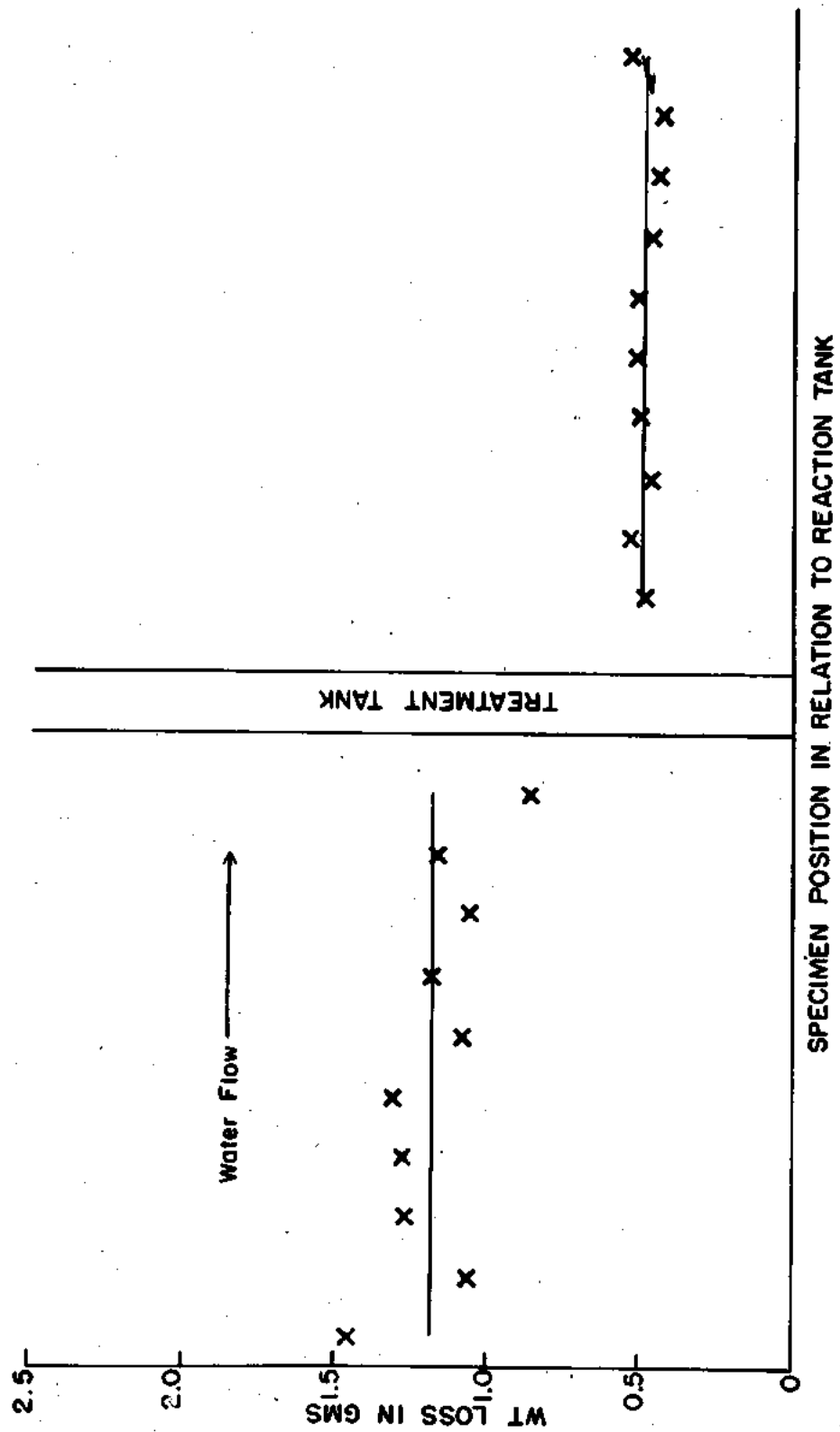


Fig. 3. Example of Run with Minimum Scatter of Weight Losses and Pronounced Effect of Treatment. (Run 31). (PNL Neg. No. 4611)

TABLE

Run. No.	Anode Material	Size of Pipe Specimens	No. of Pipes each side of Treatment Tank <sup>a</sup>	Exposure Period (days)	Water <sup>1</sup> Flow (fps)	Anode <sup>2</sup> Current (amps)	I/U <sup>3</sup> amps gpm(US)	Weight Loss and Linear Corrosion Rate			
								Upstream		Downstream	
								Wt. Loss (gms)	Corrosion Rate (mils/yr)	Wt. Loss (gms)	Corrosion Rate (mils/yr)
13	Mild Steel	3/4" x 6"	40(5)	35	5	3.0	0.36	3.0	15.6	1.9	9.9
			(5)	46	5	3.0	0.36	3.25	12.9	1.9	7.5
			(5)	123	5	3.0	0.36	5.75	8.5	2.6	3.9
			(5)	346	5→0	3→0.5		8.8	4.6	3.5	1.8
			(5)	347	"	"		8.7	4.6	3.5	1.8
			(5)	350	"	"		9.2	4.8	3.6	1.9
			(5)	355	"	"		10.3	5.3	4.1	2.1
			(5)	355	"	"		7.9	4.1	3.9	2.0
14	Aluminum	3/4" x 6"	40(5)	27	5	0.3 <sup>b</sup>	0.036	2.3	15.6	1.25	8.4
			(5)	59	5	0.3	0.036	3.8	11.7	2.0	6.2
			(5)	139	4.9	0.3	0.037	5.9	7.8	3.8	5.0
			(5)	188	4.8	0.3 <sup>a</sup>	0.038	7.0	6.8	4.7	4.6
			(10)	220	4.7	0.28 <sup>b</sup>	0.036	7.8	6.5	5.2	4.3
			(5)	369	4.6	0.27 <sup>a</sup>	0.036	10.9	5.4	6.0	3.0
			(5)	371	4.6	0.27	0.036	10.6	5.2	7.6	3.7
15	Aluminum	3/4" x 6"	40(5)	88 <sup>c</sup> (33)	5	0.3 <sup>a</sup>	0.036	1.50	8.3	0.70	3.9
			(5)	138(83)	5	0.28	0.033	3.10	6.8	1.70	3.7
			(5)	202(147)	4.9	0.26	0.032	4.75	5.9	3.10	3.8
			(25)	258(203)	5	0.28 <sup>a</sup>	0.034	7.5	6.7	4.25	3.8
16	Magnesium	3/4" x 4"	10	63	4.5	0.65	0.45	1.12	11.0	0.82	8.1
17	Zinc	"	10	65	4.5	0.65	0.45	1.33	12.7	0.27	2.6
18	Mild steel	"	"	65	4.5	0.65	0.45	1.30	12.4	0.67	6.4
19	Aluminum	"	"	65	4.5	1.6	1.10	1.30	12.4	0.25	2.4
20	Aluminum	"	"	64	4.5	0.65	0.45	1.20	11.6	0.25	2.4
21	Graphite	"	"	64	4.5	0.65	0.45	1.17	11.3	0.90	8.7
22	Mild steel	"	"	60	5	0.65	0.41	1.26	13.0	0.65	6.7
23	Magnesium	"	"	61	5	0.65	0.41	1.18	12.0	0.70	7.1
24	Zinc	"	"	61	5	0.65	0.41	1.20	12.2	0.20	2.0
25	Graphite	"	"	62	5	0.65	0.41	1.10	11.0	1.40	14.0
26	Aluminum	"	"	62	5	0.65	0.41	1.38	13.8	0.40	4.0
27	Aluminum	"	"	62	5	0.15	0.093	1.28	12.8	1.01	10.1
28	Graphite	1/4" x 4"	10	80	4.5	0.65	0.45	1.35	10.5	1.91	14.8
29	Graphite	"	"	80	4.5	0.65	0.46	1.34	10.4	1.42	11.0
30	Aluminum	"	"	79	2.5	0.39	0.48	1.07	8.4	0.57	4.5
31	"	"	"	79	5.5	0.78	0.44	1.18	9.3	0.50	3.9
32	"	"	"	78	8.5	1.15	0.42	1.46	11.6	0.17	1.4
33	"	"	"	78	12	1.55	0.40	1.50	11.9	0.080	0.64
34	AlCl <sub>3</sub> salt	3/4" x 6"	"	63	5	— <sup>10</sup>	— <sup>11</sup>	4.40	12.7	2.60	7.5
35	Aluminum	1/4" x 4"	"	61	2	0.31	0.48	1.12	11.4	0.390	4.0
36	"	"	"	62	4.5	0.63	0.43	1.02	10.2	0.080	0.80
37	"	"	"	62	7	0.95	0.42	1.03	10.3	0.070	0.70
38	"	"	"	62	9	1.3	0.45	0.82	8.2	0.060	0.60
39	"	"	"	62	12	1.5	0.39	0.76	7.6	0.050	0.50
40	"	"	"	62	15	1.9	0.39	0.90	9.0	0.080	0.80
41	"	"	"	57	2	0.63	0.38	0.90	9.8	0.20	2.2
42	"	"	"	57	5	0.63	0.39	0.96	10.4	0.28	3.0
43	"	"	"	57	7.5	0.63	0.26	0.94	10.2	0.29	3.2
44	"	"	"	59	9	0.67	0.23	0.98	10.3	0.32	3.4
45	"	"	"	59	12	0.65	0.17	1.18	12.4	0.35	3.7
46	"	"	"	59	15	0.67	0.14	1.60	16.8	0.47	4.9

- Where there is more than one exposure period per Run, then the figures given for Flow Rate, Anode Current and I/U Ratio are averages over the period since the previous specimens were removed.
- Numbers in brackets give number of specimens removed for that particular time period.
- Current maintained at 15 amps first 11 days.
- Current inadvertently maintained at 1.5 amps for 10 days in intervening period between 139 and 188 days. 1.5 amp period not included in average.
- Current off for several days between 188 and 220 days. Off period not included in average.
- Current off for 22 days between 220 and 369 days. Off period not included in average.
- Total exposure period. Corrosion rate figures are based on period starting with removal of zinc rod anodes. This latter exposure period given in parentheses.
- Anode current inadvertently maintained at 1.2 amps for 10 days in period between 88 and 138 days. 1.2 amp period not included in average.
- Anode current off for 22 days between 202 and 258 days. Off period not included in average.
- Equivalent anode current at 80% efficiency = 2.9 amps.
- Equivalent I/U ratio = 0.35 amps/gpm (US).



approximately 0.4 amps/gpm all four of the metallic anode materials produced a corrosion inhibitive effect. The corrosion reduction was around 80% for aluminum and zinc, 50% for mild steel and 40% for the magnesium alloy anodes. Because of the uncertainty of the effect with the graphite anodes (slight inhibition in Run 21 and corrosion stimulation in Run 25) two further runs with graphite anodes (Runs 28 and 29) were made in a later series. In both of these later runs corrosion was slightly accelerated (see Figure 4(B)) and therefore it can be concluded that electrolytic treatment with graphite anodes is detrimental

*Effect of Addition of Aluminum as a Salt*

In order to confirm that the beneficial effect of treatment with aluminum anodes arose from the introduction of dissolved aluminum into the sea water, in Run 34 the aluminum

was added as a salt solution. The system used for introducing the aluminum chloride, which was described earlier, proved difficult to control and the introduction rate of aluminum varied from 0-1.2 ppm. However, the overall average rate of addition of the chemical was about 0.6 ppm aluminum which, at 80% anode efficiency, corresponds to an I/U ratio of 0.35 amps/gpm. The reduction in the linear corrosion rate to 7.5 mils/year (see Table) downstream was not as great as would have been expected at an I/U ratio of 0.35 amps/gpm (see Figure 5), but was still very appreciable and indicates that in the electrolytic treatment the anodically produced aluminum salts play an important inhibitive role.

*Effect of I/U Ratio*

In the earlier paper<sup>1</sup> the data indicated that the protective effect of electrolytic treatment with aluminum anodes

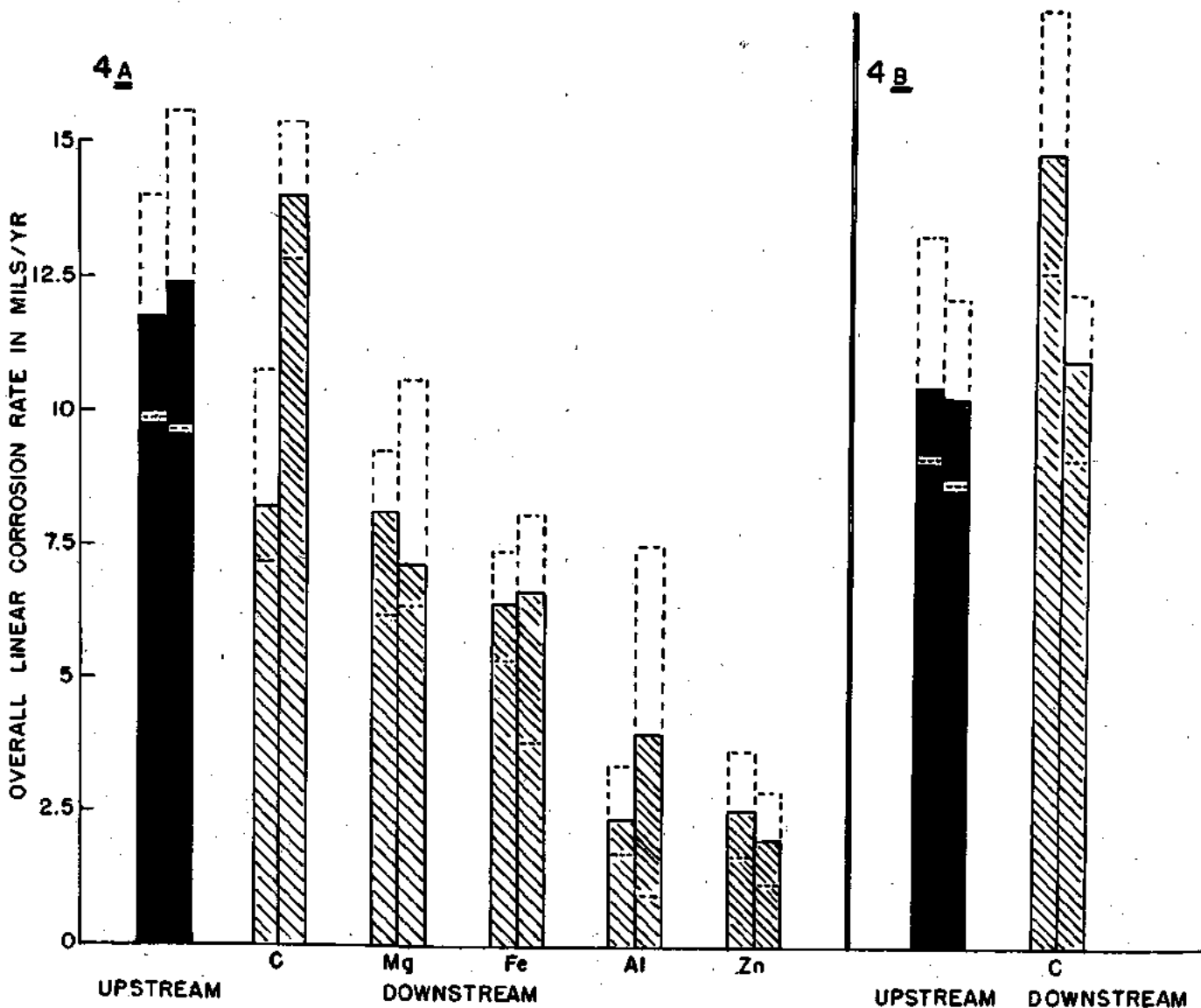


Fig. 4. Effect of Anode Material: (DREP Neg. No. 10,267).  
 Flow Velocity: 4.5-5 fps;  
 I/U Ratio: 0.41-0.46 amps/gmp (US);  
 Exposure Period: (A) 60-65 days, (B) 80 days.  
 N.B. Dotted lines indicate range of results.

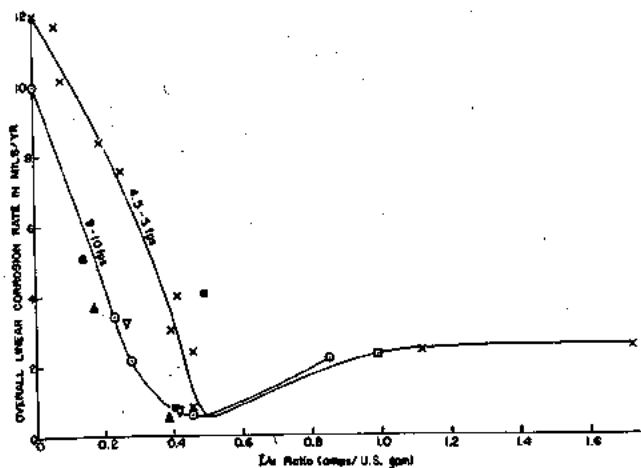


Fig. 5. Effect of I/U Ratio with Aluminum Anodes: (PNL Neg. No. 4613)  
Exposure Period: 57-67 days  
 ■ 2 fps  
 × 4.5-5 fps  
 ▽ 7-7.5 fps  
 ○ 9-10 fps  
 ▲ 12 fps  
 ● 15 fps

increased as the ratio of anode current to flow rate (I/U ratio) increased. Such a relationship would be expected for an inhibitive type of action since by Faraday's Law the concentration of aluminum salts in the treated sea water is directly proportional to the I/U ratio.

Figure 5 shows the relationship between the I/U ratio and the linear corrosion rate for 1/4 inch mild steel pipe for runs of approximately 60 days duration. Data points from the earlier investigations<sup>1</sup> are included. Curves have been drawn only for the 4.5-5 fps and 9 to 10 fps data since not enough points were available to define the curves for other velocities. It will be noted that at I/U ratios of less than about 0.5 amps/gpm there is a marked improvement in protection as the flow velocity is increased from 5 to 10 fps. This effect is discussed further in the following section.

The minimum in the curves was unexpected and is not fully understood. Increased corrosion at the higher I/U ratios may possibly be due to the erosive effect of the larger quantities of hydrogen gas bubbles and/or solid cathodic reaction products that would be produced in the treatment tank at the higher cathodic current densities involved. If this assumption is correct, then the location of the minimum would probably depend upon the geometry of the anode and reaction tank.

#### Effect of Water Velocity

The beneficial effect of increased velocity for a given I/U ratio is apparent from Figure 5. Specific corrosion rate vs. velocity data for a constant aluminum concentration was obtained in Runs 30-33 and 35-40 (I/U ratio of approximately 0.4 amps/gpm) and is plotted in Figure 6. The improved protection at higher velocities is very pronounced and similar to the effect of velocity obtained by Hatch and Rice<sup>11</sup> with a polyphosphate (cathodic) inhibitor in a hard tap water, and by Cohen<sup>12</sup> with a sodium nitrite (anodic) inhibitor in Ottawa tap water.

A probable explanation of the velocity effect was given in the earlier paper<sup>1</sup>, and is based on the assumption that the inhibitive agent forms an oxygen barrier at the solid film-liquid interface. (The solid film will be composed of steel corrosion products, aluminum hydroxide, etc.). Increased

velocity thins the laminar liquid diffusion layer next to the corrosion product films and, for a given inhibitor concentration in the bulk of the water (i.e. for a given I/U ratio), results in an increased rate of diffusion of inhibitor to the solid film-liquid interface.

In Figure 6 the divergence of the linear corrosion rate curves for the pipes passing untreated water appears to be

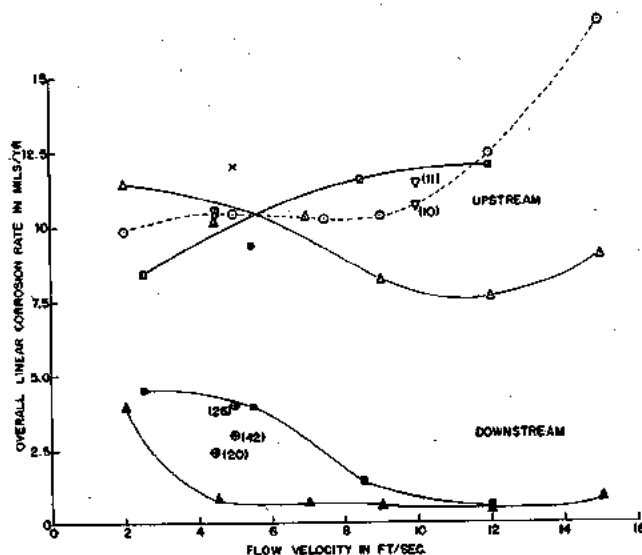


Fig. 6. Effect of Velocity with Aluminum Anodes and Constant I/U Ratio of 0.38-0.48 amps/gpm. (PNL Neg. No. 4614).  
 □ Upstream — Runs 28-33  
 ▲ " — Runs 35-40  
 ○ " — Runs 41-46  
 × " — Average for all runs at 4.5-5 fps  
 ▽ Downstream — Runs 30-33  
 ● " — Runs 35-40  
 Numbers in parentheses refer to Runs not included in specific velocity tests.

the result of passivation at the higher velocities in the series of Runs 35-40. A similar reduction in corrosion rate with increased velocity was found by Cohen<sup>12</sup> in untreated low chloride fresh water. It is not surprising that some passivity should occur in well aerated low chloride fresh water, but it certainly is surprising to find even partial passivity of steel in sea water. It seems probable that the very low corrosion rates found downstream in Runs 35-40 could be attributed to this passivity effect added to the inhibitive effect.

The comparative effects of velocity and concentration can be deduced from the plot in Figure 7 of the data from Runs 41-46. All runs in this series were made with the same anode current, and therefore the concentration of the inhibitive aluminum salts would be inversely proportional to the flow rate. Since the data shows that the downstream corrosion rate increases only slightly with velocity, the beneficial effect of increased velocity comes close to completely counteracting the adverse effect of decreased inhibitor concentration.

#### Effect of Time

Run 13, a year long run with 3/4 inch mild steel piping, was undertaken to determine whether the protective effect of electrolytic treatment increased or decreased with time. This particular run was made with a steel rather than an aluminum anode because of an error at the start of the run. In interpreting the results the authors have assumed that if an aluminum anode had been used the results would have differed only in magnitude.

The details of the run and the weight losses for the various time periods are given in the Table. The overall average

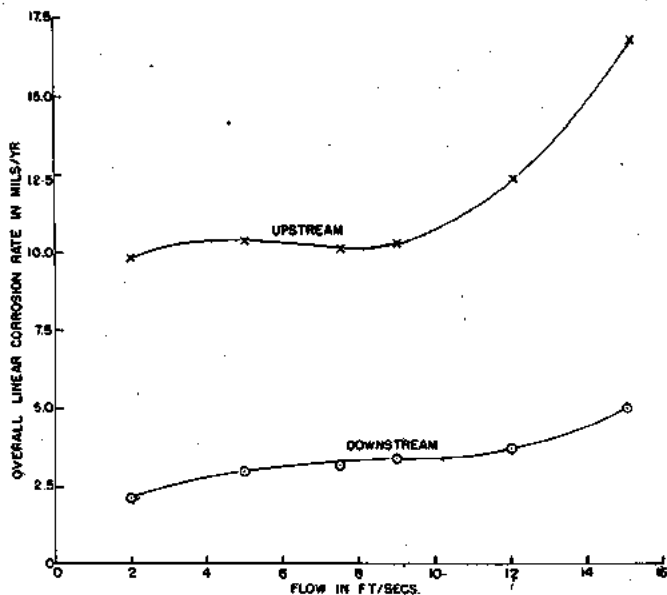


Fig. 7. Effect of Velocity with Aluminum Anodes at Constant Current. (Runs 41-46). (PNL Neg. No. 4615).  
I approximately = 0.65 amps

corrosion penetration vs. time curves as determined from both the weight loss and the electrical resistance corrosion probe data are plotted in Figure 8. The correlation between the weight loss and probe data is poor upstream but fairly good downstream.

In Figure 9 the corrosion rate data for Run 13 was obtained from the slopes of curves plotted with linear scales from data points taken from the straight line plots in Figure 8. It should

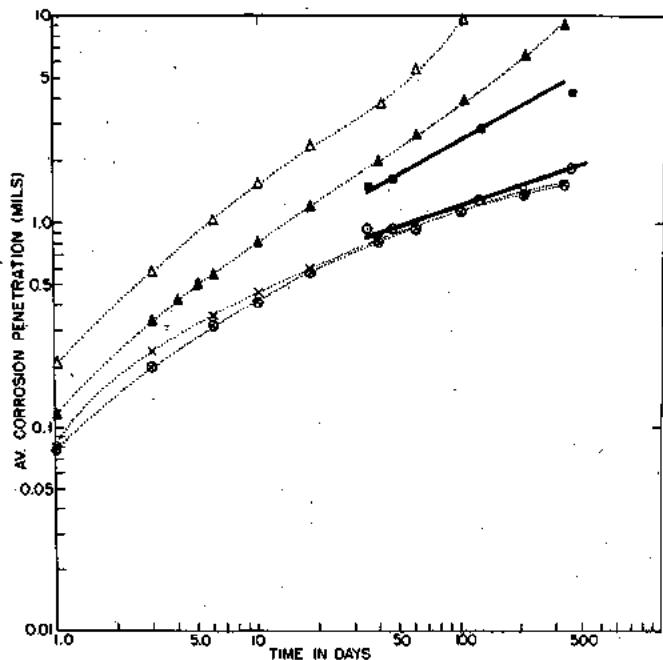


Fig. 8. Effect of Time with a Steel Anode (DREP Neg. No. 10,268).  
 UPSTREAM — by weight loss  
 " — by Electrical Resistance Probe # 1  
 " — by Electrical Resistance Probe # 2  
 DOWNSTREAM — by weight loss  
 " — by Electrical Resistance Probe # 3  
 " — by Electrical Resistance Probe # 4

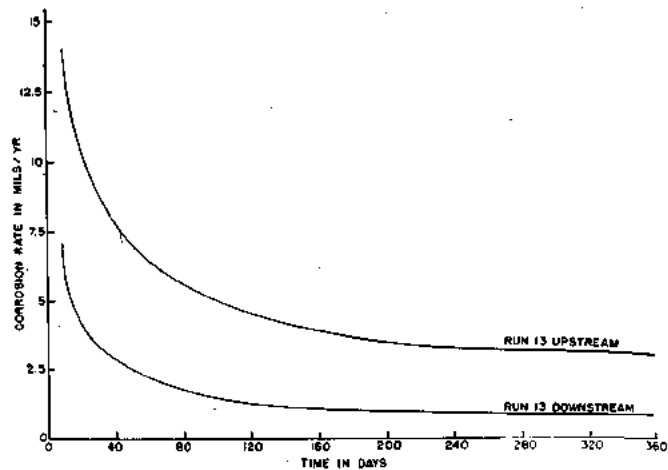


Fig. 9. Corrosion Rate vs. Time for Run 13 (DREP Neg. No. 10,269).

be noted that this is true corrosion rate data and that the values so obtained are considerably lower than the linear corrosion rates obtained from a weight loss measurement for a single period as given in the Table. For example, the corrosion rate obtained from the slope of the downstream corrosion time curve at 120 days is 1.3 mils per year, whereas on the basis of weight loss at 120 days, the linear corrosion rate would be 3.9 mpy, i.e. three times as great.

It can be concluded from the results of Run 13 that for periods up to at least 120 days the protective effect increases with time. The reduction in corrosion rate of 62% at 30 days compares with 66% at 60 days and 71% at 120 days.

#### Effect of High Initial I/U Ratio

On the basis of a reduction in corrosion of 60% using an aluminum anode at a continuous I/U ratio of 0.4 amps/US gpm, the treatment is only marginally economical for a 3/4 inch mild steel sea water piping system. The economics can be expected to become less favourable as the size of the piping system is increased because the cost in terms of aluminum to maintain this I/U ratio would be proportional to the square of the diameter whereas the cost of the piping system can be expected to vary nearly linearly with the diameter.

To improve the economics of the treatment it was thought it might be possible to achieve substantial protection by using a high inhibitor concentration (I/U = 1.8 amp/gpm) for the first few days of the run in order to establish a protective film rapidly, and subsequently maintain this film at a relatively low inhibitor level (I/U = 0.036 amps/gpm).

The above technique was tried in Run 14. The experimental details are given in the Table, and the weight loss data converted to total average penetration is plotted against time in Figure 10. From Figure 10 it can be concluded that this particular treatment technique is only marginally effective in the first few months and that the beneficial effect decreases with time. For example, the reduction in corrosion rate of the pipes dropped from 36% at 30 days to 31% at 120 days. It is probably unwise, however, to conclude from the above results that this high initial I/U — low maintenance I/U treatment technique can never be successful. The technique has been most successful with chemical inhibitive treatment. Further investigations using initial I/U ratios closer to the optimum indicated in Figure 5 and somewhat higher maintenance I/U ratios might prove profitable.

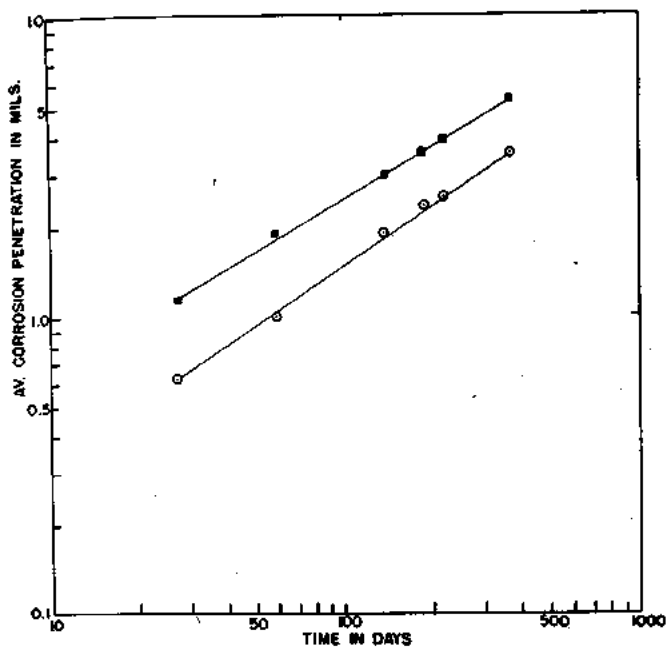


Fig. 10. Effect of High Initial I/U - Low Maintenance I/U Using an Aluminum Anode (PNL Neg. No. 4818).  
 ■ Upstream — by weight loss  
 ○ Downstream — by weight loss

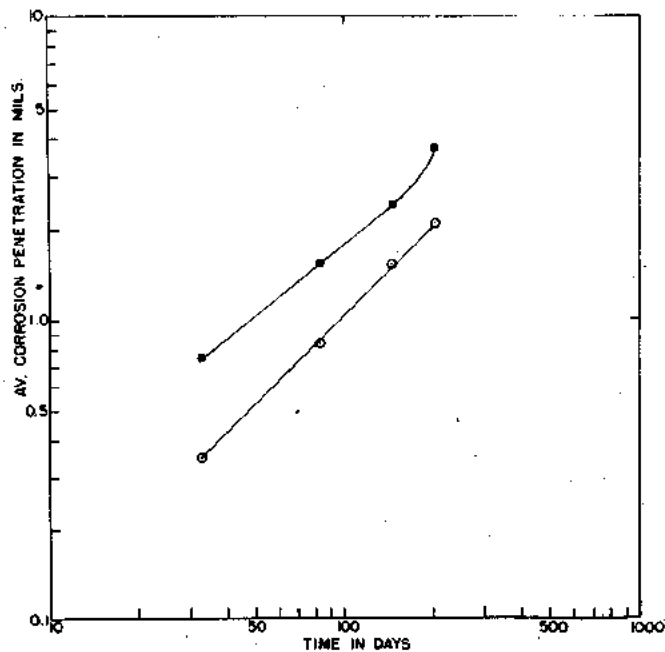


Fig. 11. Effect of Initial Cathodic Protection (PNL Neg. No. 4619).  
 ■ Upstream — by weight loss  
 ○ Downstream — by weight loss  
 Note: Time period considered as starting at zero when zinc anodes removed.

### Effect of Initial Cathodic Protection

Run 15 was undertaken to determine the effect of keeping the mild steel pipe specimens under cathodic protection during the first two months of the electrolytic treatment. It was speculated that there were two ways in which initial cathodic protection could improve the inhibitive effect. One benefit could be to provide a corrosion-free period in which to build up a protective film. Another possible benefit, similar to that obtained by Hatch<sup>13</sup> with glassy polyphosphates, would be the enhancement of the deposition of the positively charged<sup>14</sup> aluminum corrosion products by making the steel cathodic. With the improvement of the inhibitive effect by one or both of these mechanisms it was hoped that use of a relatively low I/U ratio (0.036 amps/gmp) would become practical.

The weight loss results from Run 15 are given in the Table and average corrosion penetration vs. time curves in Figure 11. It should be noted that the data has been plotted in Figure 11 as if the time started at zero when the zinc anodes were removed, i.e. 55 days after the commencement of the trial. This zero time was chosen because potential readings indicated that corrosion of both the upstream and downstream pipes did not start until the zinc anodes were removed.

From Figure 11 it appears that there is no benefit in the combined cathodic protection-inhibitive treatment used in this trial. Within four months of the removal of cathodic protection, the corrosion rate of the pipes carrying treated water is greater than that normally found in raw sea water. It is possible of course, that the combination of cathodic protection and inhibition would prove effective at a higher inhibitor concentration, i.e. higher I/U ratio.

### DISCUSSION - MECHANISM OF PROTECTION

The evidence obtained to date strongly supports the conclusion that the beneficial effect of the electrolytic treatment results primarily from inhibition by the anode reaction products. The evidence is as follows:

- (1) The addition of aluminum as a salt produces a protective effect similar to that obtained by electrolytic treatment with an aluminum anode.
- (2) In the case of graphite anodes, where the electrolytic treatment does not produce anode products containing metal salts, no protective effect is found.
- (3) Where protection was achieved (with aluminum and zinc anodes) there was a marked increase in the concentration of the material of the anode in the films on the pipes.

Figures 12 and 13 illustrate the contrast between the rust films formed in untreated sea water and the whitish protective films formed in water to which aluminum has been added either electrolytically or as a salt. The white appearance apparently is the result of aluminum salts depositing on top of the initially formed rust. Not enough of the white portion of the films was obtained to make a quantitative analysis on this part of the film alone. Iron was always the major metal ion in the complete film. Nevertheless, the concentration of aluminum in the samples of complete films increased from a small fraction of a percent upstream to 5-10% downstream. The aluminum salt was not identifiable by X-ray diffraction and therefore must be amorphous.

When zinc was the anode material, the downstream films were a greyish colour mottled with rust. The zinc content varied from 2-4% compared with a negligible amount in the upstream films. The zinc salt also appeared to be amorphous.

It may be that in instances such as those depicted in Figure 12, where the pipe films appear nearly completely white, corrosion has almost ceased. The steel weight loss from which the linear corrosion rate was determined for these runs could have occurred during the early part of the trial while the protective film was forming. Unfortunately, no such whitish films were formed in any of the long term trials where the true corrosion rate could be checked.

Whether or not the beneficial action of the anode reaction products can be attributed solely to cathodic inhibition, as suggested in the earlier paper,<sup>1</sup> is now in doubt. The more

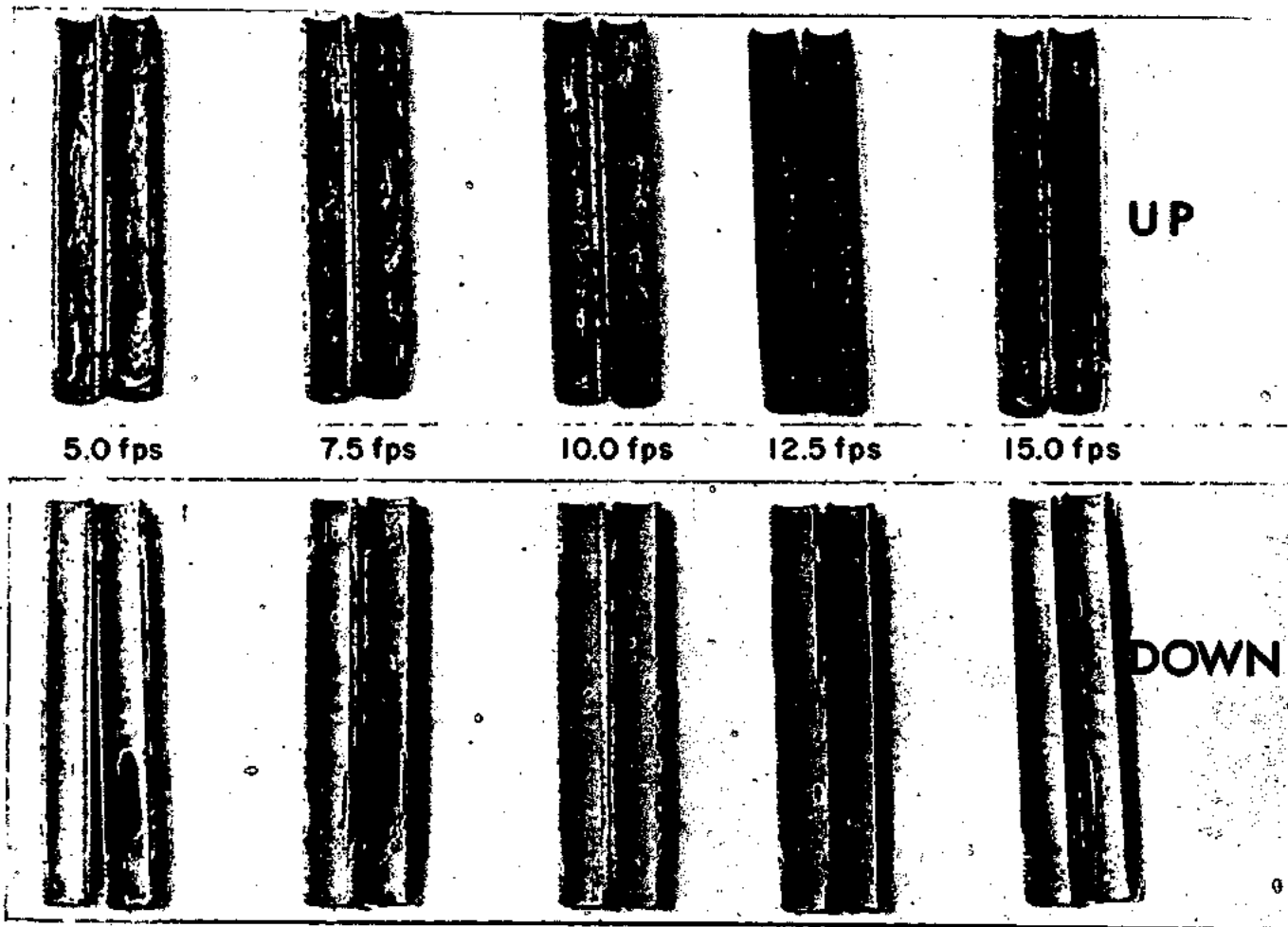


Fig. 12. Comparison of Upstream and Downstream pipe. Films -  
Runs 36-40 - Aluminum Anode (PNL Neg. No. 4265).

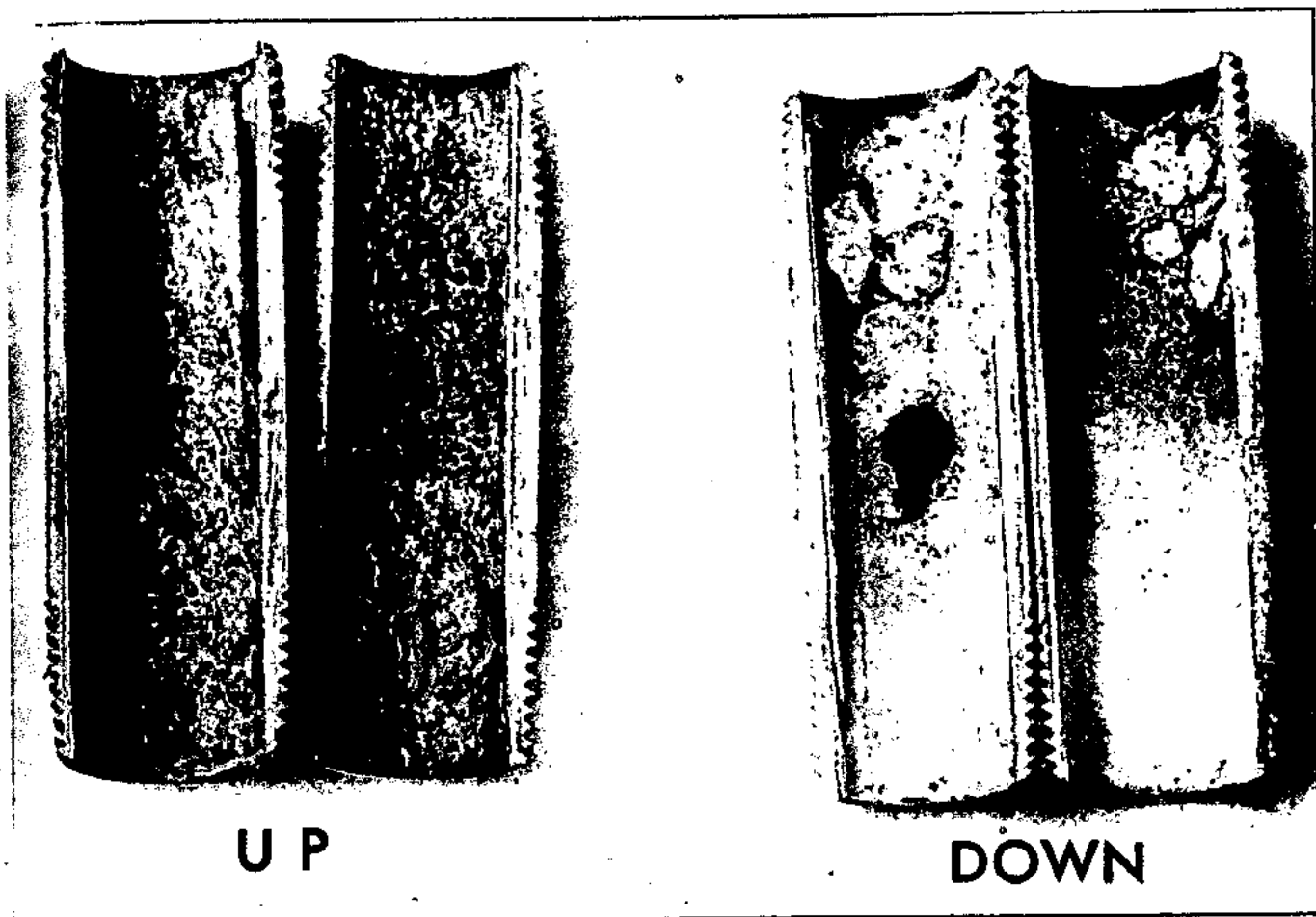


Fig. 13. Comparison of Upstream and Downstream pipe. Films -  
Run 34 -  $\text{AlCl}_3$  Addition. (PNL Neg. No. 4266).

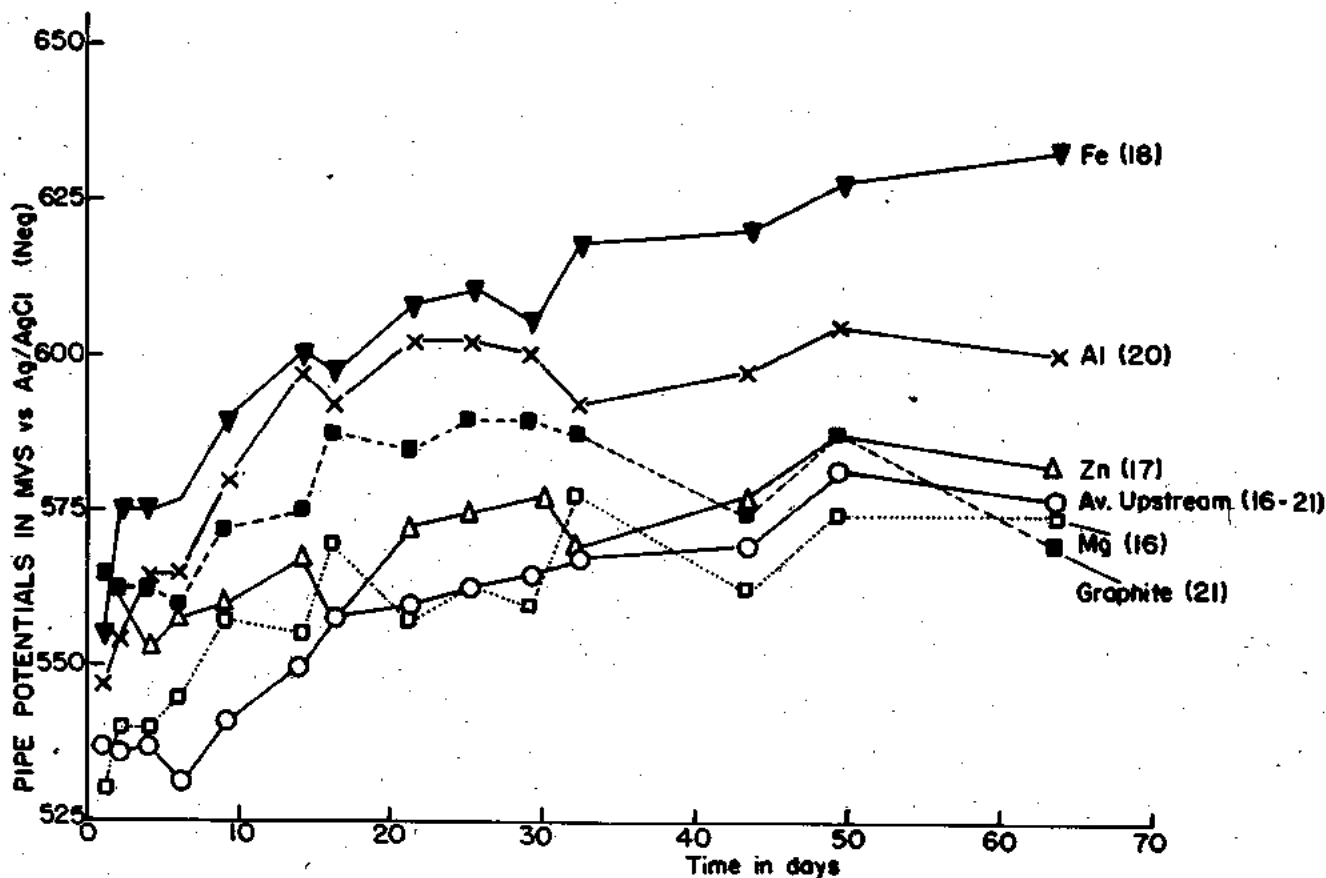


Fig. 14. Effect of Anode Material on pipe potentials. (PNL Neg. No. 4620).

Average Flow Velocity: 4.5 fps.

I/U Ratio: approximately 0.45 amps/gpm (US).

N.B. Numbers in parentheses are numbers of respective Runs.

negative potentials of pipes passing water treated with aluminum, zinc or iron anodes certainly indicate cathodic inhibition. However, there does not appear to be any correlation between the protective effect and either the absolute magnitude of the pipe potentials or the difference in potentials between the upstream and downstream pipes. As can be seen in Figure 14, treatment with steel anodes produced the biggest difference in pipe potentials yet resulted in markedly less protection than treatment with aluminum and zinc. With magnesium anodes there was little difference between the upstream and downstream potentials, yet an appreciable protective effect was achieved. These differences in effect on potentials indicate that the protective effect results from varying combinations of cathodic and anodic inhibition.

#### CONCLUSIONS

1. Electrolytic treatment of cold sea water with aluminum, zinc, steel or magnesium (alloy) anodes can make it markedly less corrosive to mild steel. Electrolytic treatment with graphite anodes tends to be detrimental. With a ratio of anode current to flow (I/U ratio) of approximately 0.45 amps/gpm (US), treatment with aluminum or zinc anodes is the most effective, reducing corrosion to one-fifth of that in untreated sea water.

2. The electrolytic treatment appears to reduce corrosion of mild steel through a combination of cathodic and anodic inhibition by the gelatinous anode reaction products.

3. For electrolytic treatment with aluminum anodes, the optimum I/U ratio is about 0.5 amps/gpm (US).

4. On the basis of the results for continuous treatment

with a steel anode at an I/U ratio of 0.35 amps/gpm, it can be concluded that the beneficial effects of electrolytic treatment improve with time.

5. For an I/U ratio of around 0.4 to 0.5 amps/gpm, electrolytic treatment of cold sea water with aluminum anodes increases in effectiveness with velocity in the range 2.5-12 fps.

#### ACKNOWLEDGEMENT

The authors are indebted to the Defence Research Board of Canada for permission to publish the results of this work. The opinions expressed are those of the authors.

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#### DISCUSSION

D. PETROCOKINO (France): I believe that in these protection the aluminium could present a double advantage and I would like to have Mr. Carson's opinion on the subject.

First advantage, the trivalency of aluminium ion is permitting to have lighter electrodes and of longer life and second, an interesting property, which is that the aluminium ion flocculates the sludges, if you treat water containing sludges, which have the tendency to be deposited at certain points and give trouble. Aluminium is able to flocculate these sludges and I have observed that personally in many installations. What is your opinion Mr. Carson?

J. CARSON: In reply to your first question, although aluminum does have a very much higher electrochemical equivalent than zinc, by weight it is more expensive, and therefore for a given protective effect the cost is about the same for aluminum or zinc anodes.

In reply to your second question, I am not sure whether or not the flocculating ability of aluminum salts is important to the protective effect. The aluminum may assist in the precipitation of suspended mud in the sea water. Unfortunately, shortly after these experiments were commenced, our originally clear sea water supply periodically became contaminated with suspended mud. Possibly a mud layer itself can act as a cathodic inhibitor and this would explain the rather low corrosion rates we have experienced in untreated water.

B. KENWORTHY (England): I have followed Mr. Carson's work on this subject for many years and I would like to congratulate him on the success he has achieved. I wonder if he could now tell us what practical application is being made of these techniques in naval and merchant ships as regards both the prevention of corrosion and the prevention of marine fouling. Incidentally, I think it is perhaps worth mentioning that in work I carried out a long time ago on the problem of copper and zinc components in the same water system, the injection of zinc salts was found to be beneficial in suppressing corrosion.

J. CARSON: Thank you Mr. Kenworthy. I would be interested to see your data on the effect of additives of zinc salts on the corrosion in domestic water systems with galvanized steel tanks and copper pipes.

With regard to the results from use of this kind of treatment in ships, the picture is still not clear to me, although several local commercial ship operators and two or three governmental operators using galvanized steel sea water systems appear to be happy with it. Our own laboratory's research ship has some galvanized sea water piping and this electrolytic treatment process. The results after two and one-half years operation

are still difficult to evaluate because we do not have an untreated system to compare with. I might comment, however, that in a galvanized sea water system with a lot of bronze fittings, such as this one, I would have expected more failures than we have had. In the laboratory we have also found that the electrolytic treatment markedly reduces corrosion in galvanized steel-bronze galvanic couples.

Your second question was about the effect of this treatment on marine fouling. The particular commercial process which operates in our area uses aluminum anodes for corrosion control and copper alloy anodes for control of fouling. We have not investigated the fouling control aspects because Naval ships normally use copper alloy sea water piping and these alloys appear to be inherently antifouling. However, we see no reason to question the effectiveness of a system which provides sufficient dissolved copper in the water.

B. HEUZE (France): Have you had disturbing deposits on the cathode, how did you eliminate these, and finally if you use a limiting current density, what is that limit?

J. CARSON: I am sorry Mr. Heuzé, but I do not have the exact current densities. Very hard cathodic deposits are sometimes formed in the reaction tank, but we have not found that removal of these deposits affects the results (other than occasional blockage of the pipes with spalled cathodic deposit). In the commercial system the reaction tanks are descaled at approximately yearly intervals.

T. HOAR (England): As you have said, Dr. Carson, the process of cathodic inhibition by alumina and other hydroxides is not new. I recall a paper by Herzog in 1932 where he showed the inhibitory effects, of heavy metal ions such as nickel that produce insoluble hydroxides. In this case, what you are sending along the tubes on the downstream side must be largely colloidal aluminium hydroxide, because of the hydroxylion that is produced at the tank cathode. This will give rise to precipitation of aluminium hydroxide within the reaction chamber, from the positively charged colloidal aluminium hydroxide, at cathodic zones.

J. CARSON: I believe the film to be colloidal aluminum hydroxide (or oxide) but I have forgotten whether the charge is positive or negative [Author's Note: According to Weiser (Reference 14 in the paper) it is positive as Dr. Hoar suggests]. We have found that it is not necessary to have metallic coupling between the cathodic reaction tank and the pipes in order to get the protective effect. However, the colloid could very well be precipitated (cathodically) by local cells within the pipe.



# CAVITATION EROSION OF MATERIALS

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## SUMMARY

Investigations of the resistance to cavitation erosion of several metallic alloys in sea and fresh water are described. The alloys studied include copper base, corrosion-resistant and non-corrosion resistant steel and titanium alloys. The effects

of corrosivity of liquid and cathodic protection on the cavitation erosion of ferrous alloys are described. The use of elastomeric coatings in preventing cavitation erosion of structural materials is also discussed.

## INTRODUCTION

The successful accomplishment of the primary missions of merchant marine and naval vessels is dependent to a large extent on their resistance to deteriorating and other natural effects of the environment in which they operate. Structural materials have to be designed to resist the mechanical stresses of operation, such as stresses in the hull, propeller shafting and propeller blades. Non-corrosion resistant structural materials also have to be protected against corrosion. This may be accomplished by the use of protective coatings or galvanic

or impressed current cathodic protection systems. Immersed structures also have to be protected against biological effects of the environment, namely fouling, which increases the drag of the vessel and result in decreases in maximum speed and increases in fuel consumption.

In addition to the above, a serious deteriorating effect of the environment which occurs in only isolated areas of ships' structures, is cavitation erosion. Cavitation erosion is the localized damage and removal of a material resulting from exposure to a cavitating liquid environment. It is normally associated with high velocity liquid flow systems such as

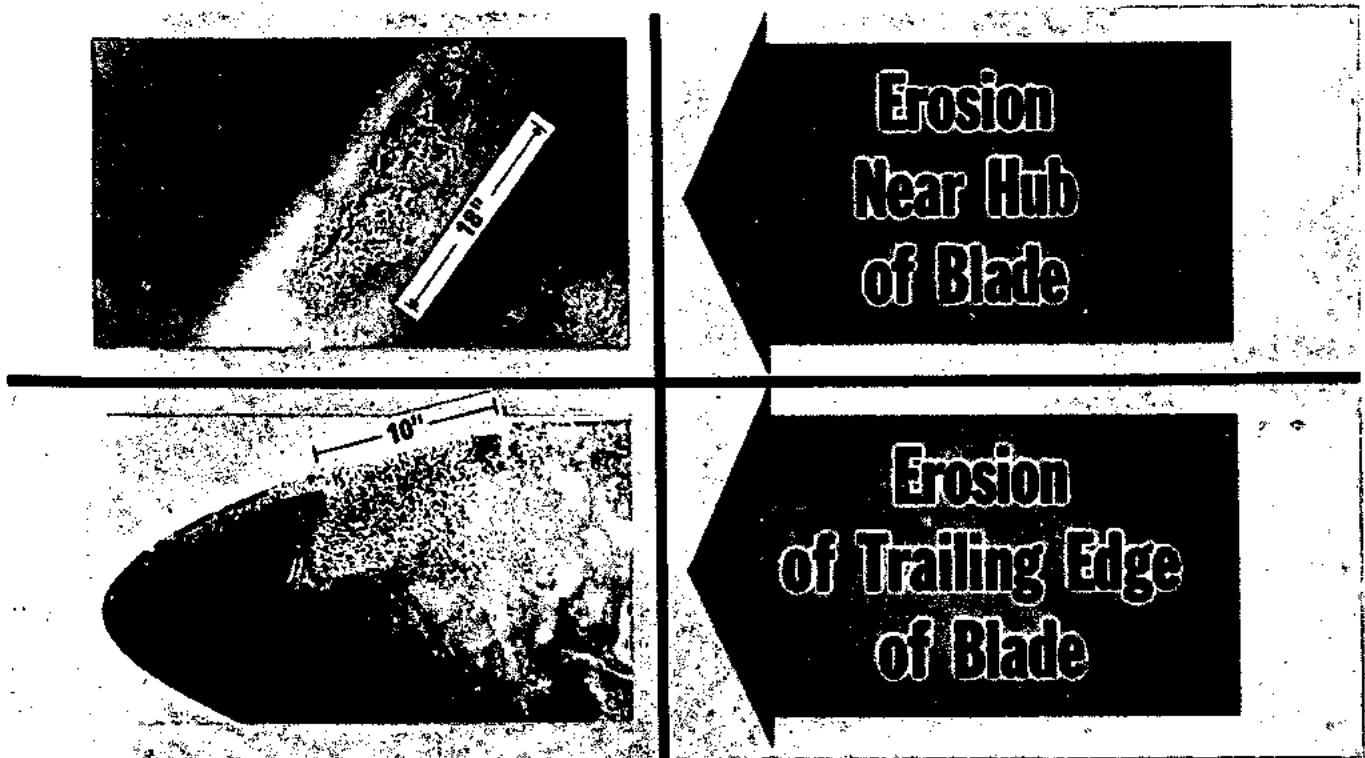


Fig. 1. (Photo No. L 19930-65). Cavitation Erosion of Propeller.



**A. Starboard Strut  
Inboard, Aft**



**B. Port Strut  
Inboard, Aft**

Fig. 2. (Photo No. (20030 - 96). Erosion of Vinyl Coatings of Hydrofoil Struts, Nacelles and Foils After 20 minutes of Foilhorn Operation.

propellers, hydraulic turbines, pumps and hydrofoils. Typical erosion of propellers and corrosion-resistant, vinyl coatings on hydrofoil structures are shown in Figures 1 and 2. Cavitation erosion may also occur at relatively low flow rates if a high frequency vibrating condition exists. Such conditions are found at sonar transducer faces and sonar domes; and in internal combustion engine cylinders as the result of high frequency pressure fluctuations in the adjacent liquid.

Cavitation occurs in a rapidly moving liquid because of a localized decrease in pressure in the liquid below its vapor pressure and the presence of nucleating sources such as minute foreign particles or gas bubbles.<sup>1</sup> As a result, a vapor bubble is formed and continues to grow until it reaches a region of pressure higher than its vapor pressure when it will collapse. Cavitation may likewise occur in a liquid-immersed high frequency vibrating system when cyclically recurring pressure fluctuations produce a vapor condition during the low pressure cycle and vapor cavity collapse during the high pressure cycle.

It has been theorized<sup>2</sup> that, when the vapor bubbles collapse, high intensity shock waves are produced which radiate to the boundary and result in mechanical damage (yield or fatigue damage) of the material. In more recent investigations of erosion mechanisms<sup>3,4</sup> it has been theorized that material damage and erosion is caused by the unsymmetrical collapse of the vapor bubbles at the boundary surface, and a reentrant liquid jet flow into the collapsing bubble, impinging on the boundary surface. The behavior of materials in cavitating liquids and theories of erosion mechanisms, including mechanical erosion and electrochemical corrosion have been reported, reviewed and summarized by investigators listed in the bibliography<sup>(1,5,6,7,8)</sup> and by numerous others.

The mechanisms of cavitation erosion have been a source of controversy among investigators of this phenomenon for many years. The association of cavitation erosion with mechanical effects of stress intensities predicted and observed as described above, causes deformation and erosion of low yield metals, Fig. 3, and the damage to nonmetallic materials<sup>(7,9)</sup>. The erosion resistance of alloys is related to mechanical and metallurgical properties, including strain energy, hardness,

tensile strength, fatigue strength, grain size, and cold working properties<sup>(1,5,8,10)</sup>.

The strain energy, which represents the energy-absorbing capacity per unit volume of a metal up to fracture, has been calculated<sup>(8)</sup> using three methods, including integration of the engineering stress-strain diagram, and equations based on the true fracture strength, and ultimate tensile strength. The percentage deviation between the three methods was  $\pm 10\%$ .

In general erosion resistance increases with increase in strain energy, hardness, tensile strength, and fatigue strength, and with decrease in grain size. Cold working resulting in increase in hardness (strain hardening) also tends to increase erosion resistance. The erosion resistance of polymeric materials has been shown<sup>(7,9)</sup> to be related to the elasticity (related to the hysteresis or relaxation time), tensile strength, tear strength, and extensibility, the cavitation erosion resistance increasing with increase in these properties. High strength elastomeric materials are observed to be more erosion-resistant than metallic and plastic materials, and serve effectively as erosion-resistant coatings when adequate adhesive strength is provided.

The significance of corrosion in contributing to cavitation erosion has been demonstrated by Leith<sup>(11)</sup>, Plesset<sup>(12,13)</sup>, and Wheeler<sup>(14)</sup>. Relationships between erosion rates and corrosivity of the liquid were determined as shown in Fig. 4. Investigations<sup>(11,12)</sup> of the application of cathodic protection to suppress cavitation erosion in corrosive liquids have shown a decrease in erosion rate with increase in current density, Fig. 5. However, it was observed in these investigations and those of Plesset<sup>(13)</sup>, that hydrogen bubble generation accompanied such cathodic protection. As aeration of water also has been found to be effective in decreasing cavitation erosion<sup>(15)</sup>, it is believed that decrease of erosion by application of cathodic protection is associated with the formation of hydrogen bubbles. These bubbles increase the compressibility of the liquid and tend to cushion the cavitation bubble collapse. Plesset<sup>(13)</sup> has confirmed this hypothesis by using anodic currents sufficiently high to generate oxygen on the specimen surface. He then observed a similar decrease in erosion rate with increasing oxygen evolution. Corrosion may



Fig. 3. (Photo No. 21483-4). Cavitation Damage of Aluminum 1100-O  
(10 Sec. exposure in rotating disk apparatus at 150 ips and 15 psig).

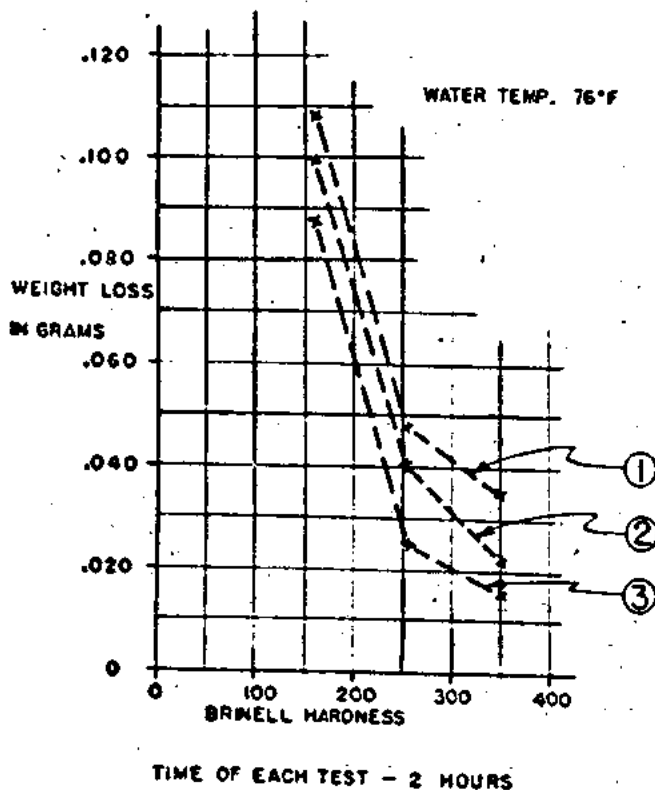


Fig. 4. (Photo No. 21185-80). Effect of Liquid Corrosivity and Metal Hardness on Cavitation Erosion of Ductile Iron. Leith (11).  
 (1) Halifax Sea Water; (2) Montreal Tap-water; (3) Distilled Water.

also contribute to metallic damage in areas exposed to cavitation bubble collapse because of galvanic potentials resulting from velocity and stress gradients. Galvanic potentials may result from continual removal of corrosion product films in regions of cavitation. These bared surfaces are anodic to the adjacent filmed surfaces which will exhibit a more noble (cathodic) potential. Galvanic effects may also result from an increase in anodic potential caused by impingement stresses. Adjacent unstressed areas will be cathodic to the stressed area. Removal of corrosion products also permits corrosion to proceed at higher rates on the bared surfaces. The increased rate of deterioration and weakening by corrosion increases the rate of mechanical erosion due to cavity bubble collapse, and stress impingement.

The feasibility of diminishing the contribution of corrosion to cavitation erosion by the use of chromate inhibitors was investigated by Rheingans<sup>26</sup>. The laboratory studies, using cast iron alloys, including those regularly used in diesel engine cylinder liners, indicated that in the case of a hardened low-alloy cast iron the addition of the chromate was effective in reducing erosion. Under the conditions of Rheingans' tests, unhardened low-alloy cast iron and high alloy cast irons were not similarly affected by chromate. It has been suggested by Speller and LaQue<sup>26</sup> that the effectiveness of the chromate inhibitors in diesel engine service may indicate that corrosion tends to predominate over the mechanical cavitation erosion process in the damage to liners in service and differs from the laboratory conditions in this respect. Since the conditions of Rheingans' tests were selected to maximize cavitation damage, the contribution of corrosion may not be as evident as in an actual service test.

Other means of suppressing erosion, in addition to the use of corrosion and erosion resistant alloys and weld overlays, elastomeric coatings and aeration, include pressurization to

prevent the liquid pressure from dropping below its vapor pressure and design of the flow system to prevent cavitation itself by avoiding severe local pressure drops.

Although some structural materials have shown considerably higher resistance to cavitation erosion than others, none of those evaluated in the laboratory have shown resistance as high as some high strength elastomeric coatings<sup>(7,9,17,18,19)</sup>. A major problem with successful use of erosion-resistant elastomeric coatings has been adhesion failure under service conditions<sup>(7)</sup>. Recent investigations have shown successful adhesion performance of erosion-resistant cured sheet elastomeric coatings using epoxy and solvent-based adhesives under high speed flow conditions in the laboratory<sup>(19,20,21)</sup> and under service conditions<sup>(22)</sup>.

This paper is concerned with the resistance to cavitation erosion of representative structural materials and the protection against erosion of such materials. The effectiveness of a galvanic cathodic protection system and elastomeric coatings in minimizing erosion of structural materials are also examined and discussed.

## OBJECTIVES

The objectives of the investigations described in this paper were as follows:

a. To determine the cavitation erosion resistance of several structural alloys in sea water. These include propeller bronzes and alloys intended for hydrofoil structures.

b. To determine the effect of corrosivity of the liquid on erosion

c. To determine the effectiveness of galvanic cathodic protection in minimizing the contribution of corrosion to erosion of high strength steels in sea water.

Supplementary objectives were as follows:

a. To determine the comparability of different cavitation erosion test procedures, including high velocity flow (rotating disk) and vibrational (magnetostriction) apparatuses, based on evaluations of several structural materials.

b. To determine the effect of vibration amplitude of the vibratory (magnetostriction) facility on erosion intensity.

## EXPERIMENTAL

### Materials:

The metallic alloys used in this program included the following:

### Structural materials:

Manganese bronze  
 Manganese nickel bronze  
 Cu-Ni-Si-Be alloy (Cunisibe 18)  
 High yield steel (HY80)  
 High yield steel (HY100)  
 High yield steel (HY130)  
 Alloy steel 17-4 PH (1025)  
 Titanium 621 - 0.8 Mo

### Anode material

Zinc. Mil Specification MIL-A-18001

### Facilities:

The test facilities at NASL used in evaluating the resistance of structural materials and protective coatings to cavitation erosion include both high velocity flow and high frequency vibrating facilities. The former simulate high velocity liquid flow systems, such as propellers, pumps and hydrofoils. The latter simulate high frequency vibrating environments such as sonar transducer faces and sonar domes. The facilities used in the present investigation are described in the following paragraphs.

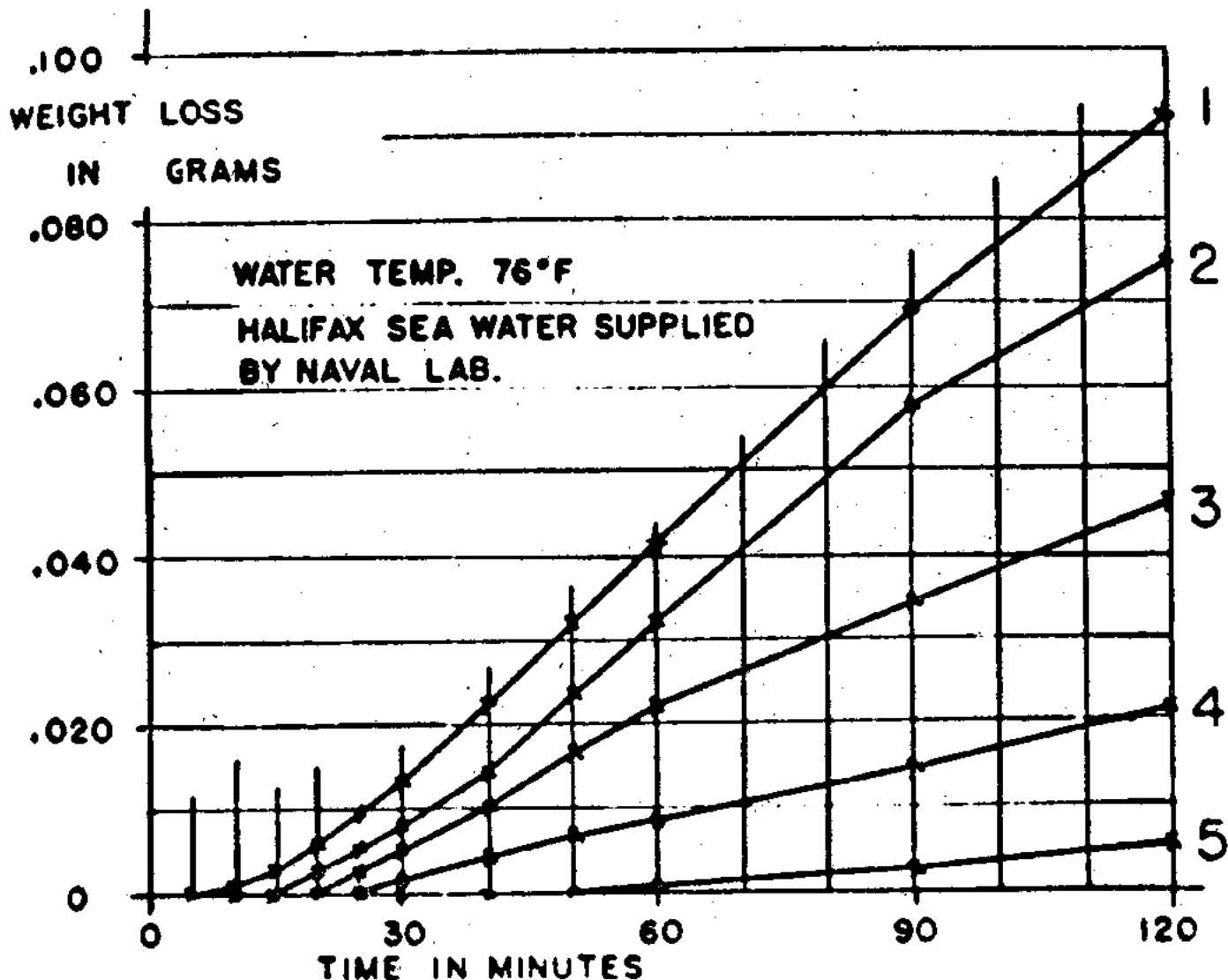


Fig. 5. (Photo No. 21185-81). Effect of Cathodic Protection on Cavitation Erosion of Cast Steel in Sea Water. Leith (11).  
(1) No Current; (2) 0.032 Amps Cathodic Protection; (3) 0.130 Amps Cathodic Protection; (4) 0.360 Amps Cathodic Protection; (5) 0.500 Amps Cathodic Protection.

#### Rotating Disk Apparatus

The rotating disk apparatus is similar to one used by Rasmussen(15). Its design and operation has been described by Lichtman et. al.(7,9,18,19). It consists essentially of a cylindrical test chamber in which a 12 inch diameter by 1/8 inch thick disk is mounted on a shaft which is co-axial with the cylinder. The shaft is driven at speeds up to 3200 rpm with a 30 hp vari-drive motor. Water fills and flows through the test chamber at an observed flow rate under controlled pressure and temperature. Fig. 6 shows the essential details. The removed forward section in Fig. 6 shows the radially positioned stilling vanes which are intended to minimize the rotational flow induced by the rotating disk. In operation, the location of the disk in the test chamber provides 5/8 inch clearance between the disk surfaces and the respective front and rear stilling vanes. Fig. 7 shows a test disk, with a 3/8 inch diameter hole which serves as the cavitation source; and a typical erosion pattern. Test disks may be prepared with several hole sources

and test sites located at various radial distances to establish velocities up to 90 knots at 3200 rpm. Other features of the apparatus include a 280-gallon open stilling tank which serves as a means for controlling air content of the recirculating water; heat exchangers for controlling water temperature; and water flow controls for maintaining pre-set pressures in the test chamber.

#### Magnetostriction Apparatus

The magnetostriction apparatus is in the class of vibratory devices which generates the cavitation condition through a low-amplitude, high-frequency displacement of an immersed element. Unlike water tunnel and rotating disk devices, the magnetostriction apparatus operates with no water flow other than that developed adjacent to the driven element. The cavitation generated by the rapid fluctuations of pressure under the-driver face is very similar to that generated at the face of a sonar transducer or at the water jacket side of an

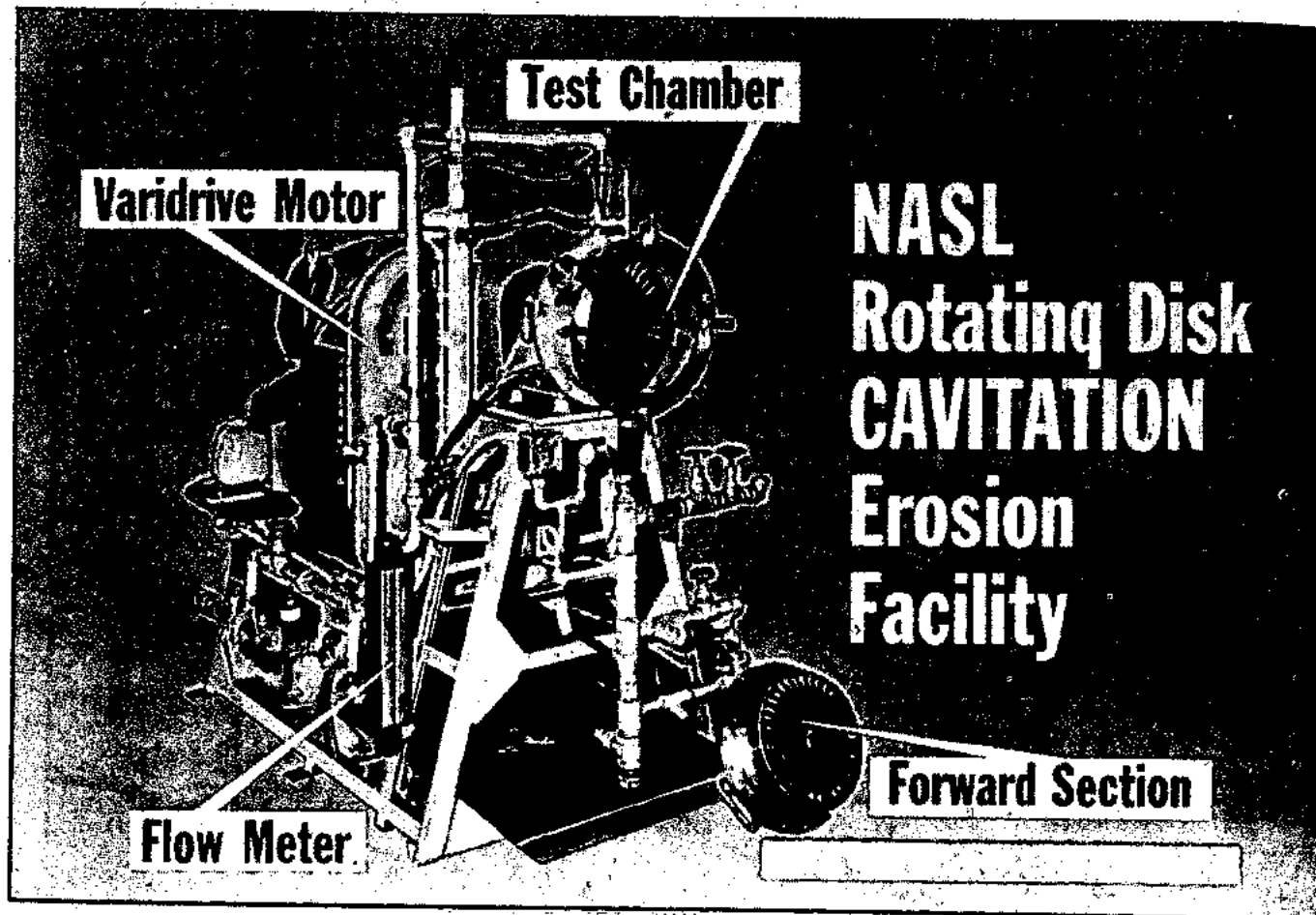


Fig. 6. (Photo No. 19930-70). NASL Rotating Disk Cavitation Erosion Facility.

internal combustion engine cylinder liner.

The NASL magnetostriction apparatus includes two sets of transducer assemblies for operation at either 6.5 or 13 kilocycles per second; electronic driving and monitoring equipment; cooling baths; and specimen plugs. The transducer assembly consists of a laminated nickel stack, a driving coil and a stainless steel mechanical transformer (horn). The driving equipment is an audio oscillator operated through a power transformer. The monitoring equipment to measure and record displacement amplitude at the specimen end of the horn is a pick-up coil and a voltmeter and recorder. The use of an oscilloscope to determine wave-form of the pick-up coil voltage has been found helpful for detecting faulty drive or loose mechanical connections in the transducer system.

A frequency counter also monitors the signal output of the coil pick-up. A mercury thermometer is used to determine the test liquid temperature in both the test beaker and surrounding constant temperature bath. The complete assembly is shown schematically in Fig. 8. During tests the specimen beaker is immersed in a thermostatically controlled bath for maintaining specific test temperatures. The mechanical transformers available for either transducer assembly are of the exponential and stepped horn types. A material under study is attached to or consists of a cylindrical plug which is screwed into the end of the horn before test.

In conducting an erosion study the cylindrical plug itself may be machined out of the material to be tested, or a specimen to be tested is attached to the face of a metallic plug.

Coatings, overlay materials and some cladding metals are tested by adhering the test specimen to a plug machined from the intended substrate material. The immersed test end of the plug is 5/8 inch in diameter and flat. The weight of the plug is approximately 15 grams. Measurements are made at 6.5 or 13 kilocycles per second, at double amplitudes of up to 3.0 mils at the specimen face, with the specimen immersed approximately 1/8 inch. Degree of erosion of structural materials is determined by weighing the test plug before exposure and after various intervals of exposure to establish an erosion-time relationship. The degree of erosion of coating materials is determined on the basis of the nature and extent of damage after exposure. The erosion resistance is determined by nature and extent of damage, and time of exposure at which damage occurs under specific test conditions.

A comparison of the NASL rotating disk and magnetostriction apparatuses is given in Table 1.

#### Method:

Rotating disk tests. Mild steel disks of Type 3 as shown in Fig. 9 were used. Inserts 1/16 inch thick  $\times$  1 inch diameter of the test alloys were bonded into the recesses rotating at 150 fps, using an ambient temperature curing non-conductive adhesive. In the cathodic protection tests, inserts of the anode material and the test materials were mounted as shown in Fig. 10. Granular zinc (30 mesh) was added to the adhesive, as described by Geld and Miller<sup>(23)</sup> in bonding the 1/16 inch

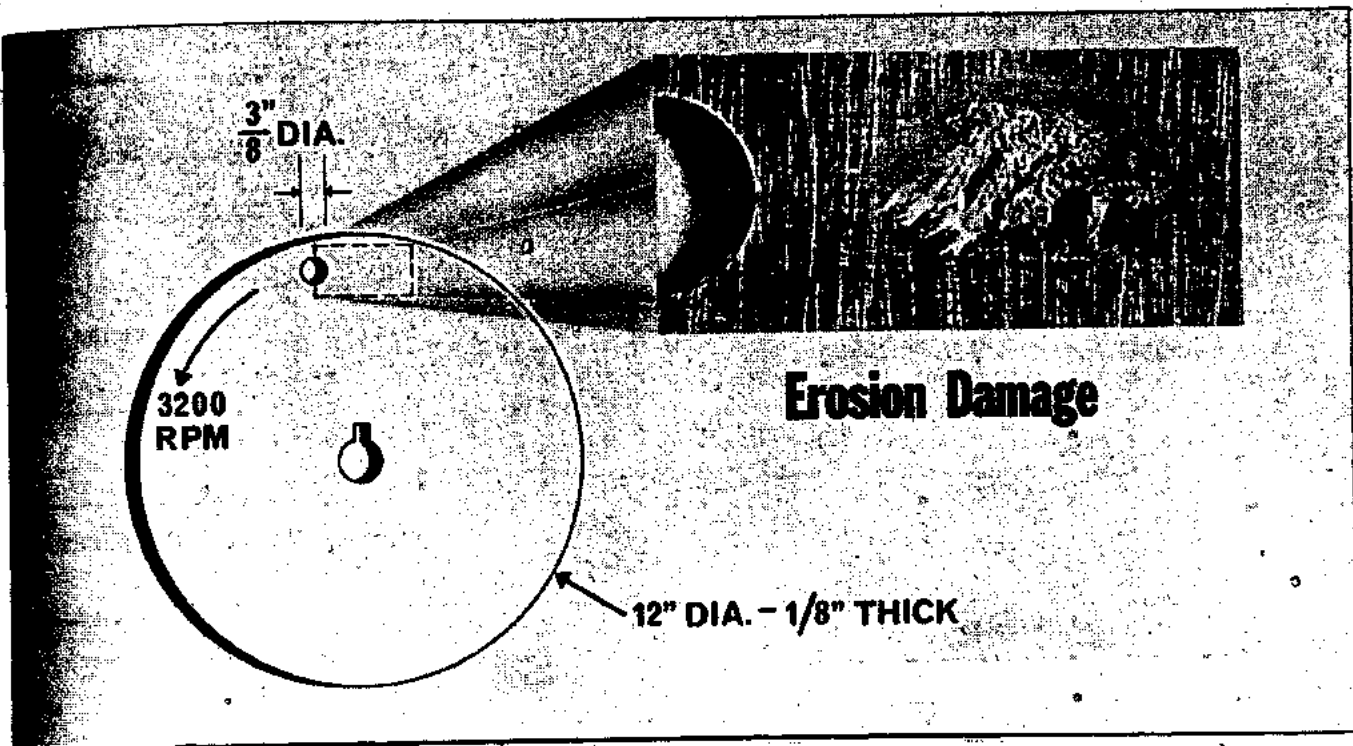


Fig. 7. (Photo No. 19930-69). Typical Erosion Damage of metal in Rotating Disk Apparatus at 150 Ips.

TABLE 1  
COMPARISON OF CHARACTERISTICS OF  
NASL CAVITATION EROSION FACILITIES

Characteristic	Facility	
	Rotating Disk	Magnetostriction
Water pressure	0 to 30 psig (controlled)	Liquid at atmospheric pressure.
Water velocity relative to specimen-ips	60 to 150	No appreciable flow
Area occupied by facility	100 sq ft	50 sq ft
Cavitation exposure	Continuous	Continuous
Liquid medium	Fresh or sea water	Fresh or sea water
Frequency of vibration	(not vibrated)	6.5 or 13 keps
Temperature of liquid	65 to 80F	Controllable in range of 40 to 125F
Liquid capacity of apparatus	50 gal minimum, 230 gal maximum	400 cc

thick  $\times$  1 inch diameter zincs and test materials into the recesses for the cathodic protection tests. C-clamps were used to apply pressure to the inserts during cure of the adhesive, and obtain metallic contact between the inserts and the 12 inch diameter steel disk through the granular zinc in the adhesive. The resistance between the zinc and steel inserts was 0.00004 ohms before and after test. The top and bottom surfaces of the 12 inch diameter disk of Fig. 10 were coated with an epoxy coating to minimize the cathode area. The test insert and cavitation source (drilled hole) areas were left bare as shown in this figure.

Magnetostriction tests. Disks 1/16 inch thick  $\times$  5/8 inch in diameter of the test materials were bonded to threaded mild steel base pieces using the non-conductive epoxy adhesive. Tests were conducted using a 13 keps transducer and exponential horn. In the cathodic protection tests, the 1/16 inch thick zinc anode and test material were bonded as a sandwich to the threaded bases piece as shown in Fig. 11. As described above, granular zinc was added to the epoxy adhesive used to bond the test material to the zinc anode disk to obtain metallic contact between the zinc anode and test material through the zinc granules. C-clamps were used during cure of the conductive adhesive, to apply pressure between the zinc and HY80 or HY130 disks and obtain metallic contact through the zinc granules.

#### Erosion volume measurement.

Rotating disk tests. The measurement of the volume of material eroded during a test exposure was made by measuring the volume of a liquid required to fill the eroded region. The liquid used was a silicone oil of 50 cs viscosity. It was injected into the eroded region using a micrometer microsyringe of 250 mm<sup>3</sup> capacity graduated to 0.02 mm<sup>3</sup>. The oil

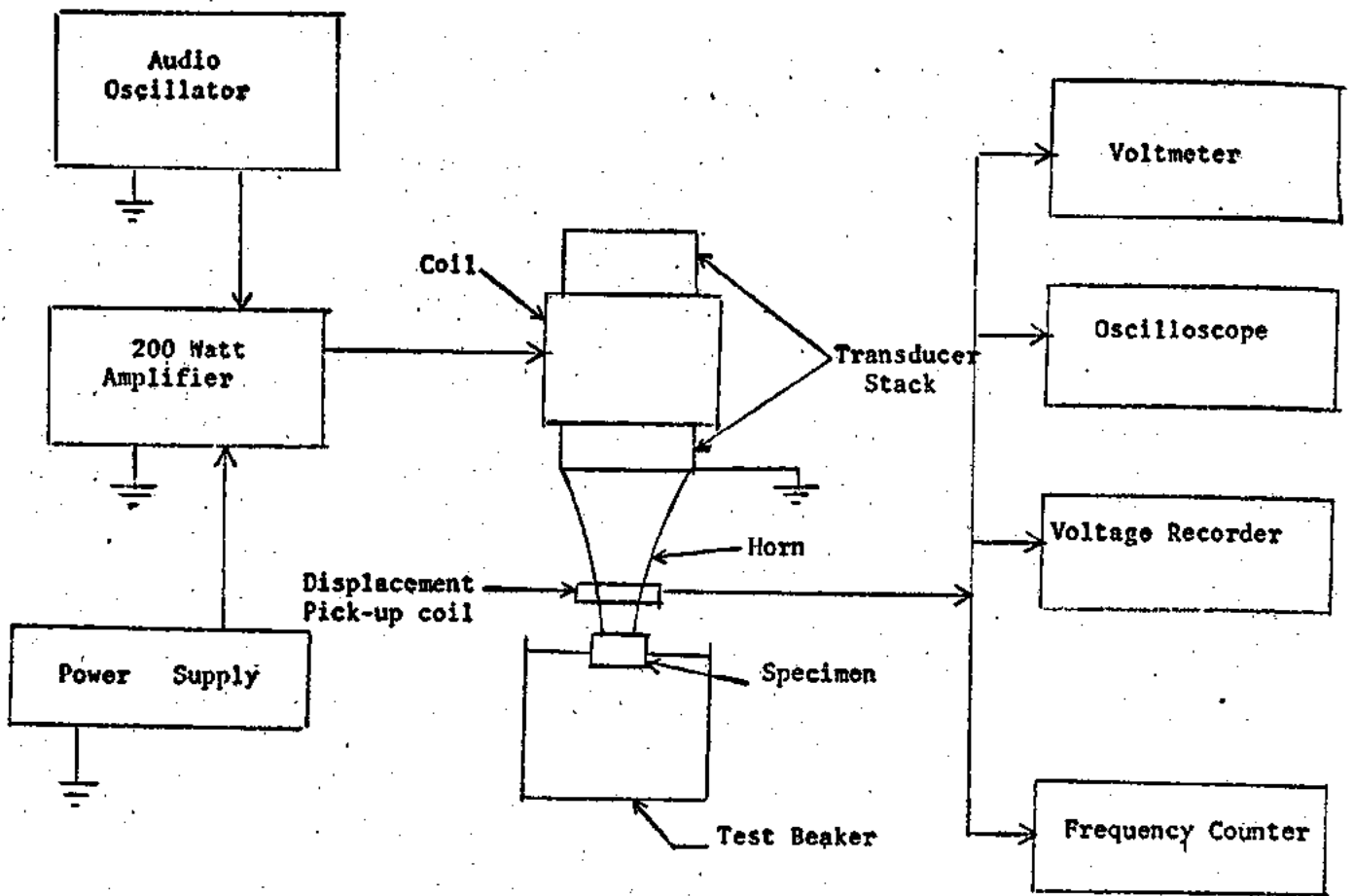


Fig. 8. Magnetostriction Cavitation Erosion Apparatus.

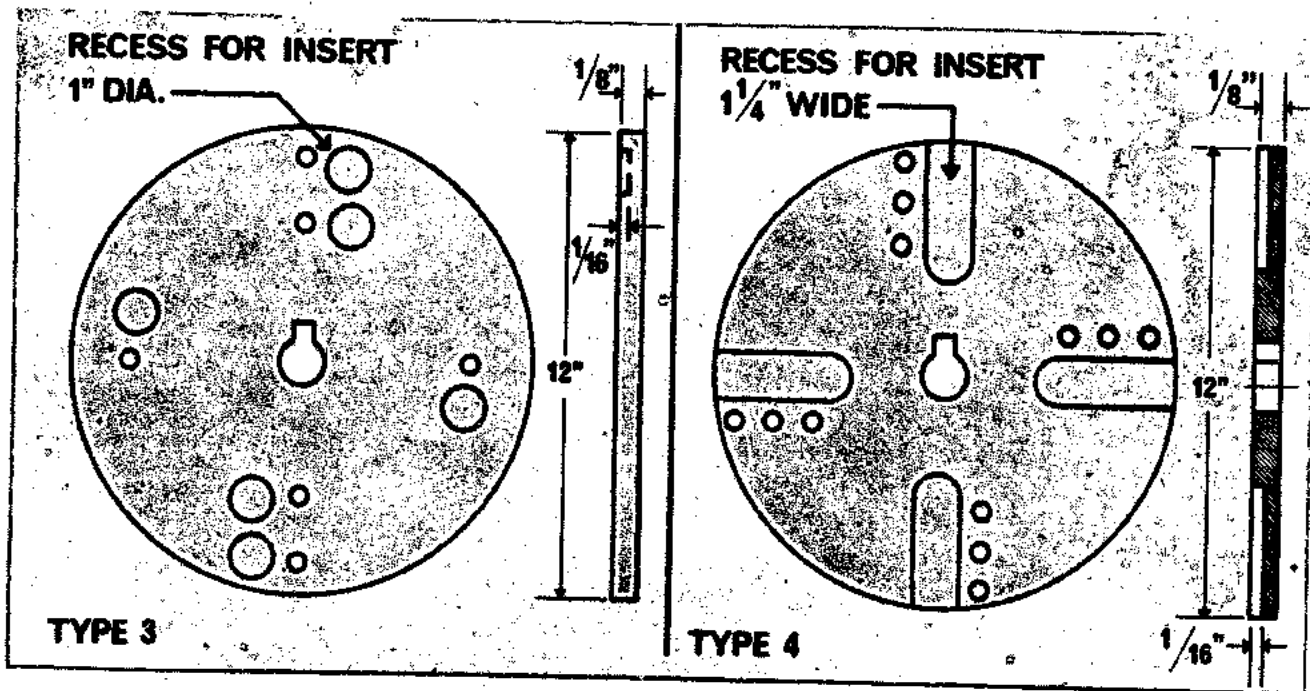


Fig. 9. (Photo No. 21046-36). Cavitation Erosion Test Disk.



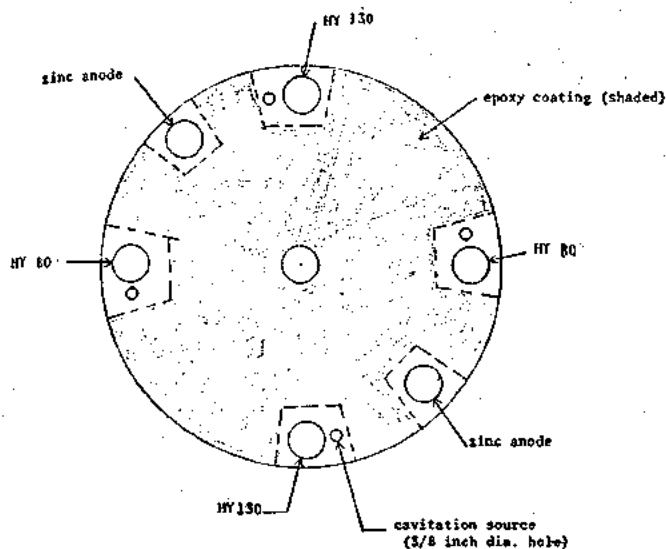


Fig. 10. Cathodic Protection Test Disk.

was injected until its surface was level with the horizontal disk surface as shown by contact with a surface gage set to the disk surface.

**Magnetostriction tests.** The measurement of volume of material eroded during a test exposure was made by weighing the specimen before and after exposure, and converting the weight loss to volume loss on the basis of the specific gravity of the test material. An analytical balance graduated to 0.0001 grams was used for the weight measurements.

## RESULTS

**Cavitation Erosion Resistance.** The erosion resistance of the structural alloys evaluated using the NASL magnetostriction apparatus and natural sea water as the test liquid was determined at a frequency of 13 kcps and double amplitude (Sine wave peak-to-peak) of 1.9 mils (.0019 in.) The erosion volume-time characteristics of the alloys are shown in Fig. 12. The metals show a range in resistance (inverse of the erosion volume at the same exposure time, e.g. 6 hours) of approximately 3:1. The most resistant was the titanium 621-0.8 Mo alloy and the least resistant was the HY 80 alloy.

**Liquid Corrosivity.** The influence of liquid corrosivity on the erosion of alloys was determined by testing selected corrosion-resistant and non-corrosion resistant alloys in sea and fresh water. The erosion volume-time characteristics of ferrous, titanium and copper base alloys as determined in these liquids are shown in Figures 13, 14, 15, and 16. The degree of erosion of non-corrosion resistant alloys HY 80 and HY 130 was larger in sea water than in fresh water, while other more corrosion-resistant alloys, including Ti 621-0.8 Mo, MnNi bronze and 17-4 PH (1025) steel, showed no significant difference.

**Effects of Cathodic Protection.** The effectiveness of sacrificial zinc anodes in controlling the erosion of the HY 80 and HY 130 steels was determined, using the NASL magnetostriction and rotating disk apparatuses. Sea water was used as the test liquid. Polarization measurements at the anode and cathode were not made under the test conditions. The turbulent cavitating clouds obscured these regions and prevented observations of hydrogen generation at cathode areas under test conditions. Hydrogen evolution at cathode areas of both the rotating disk and magnetostriction specimens was observed under quiescent conditions. On the basis of the degree of corrosion of the zinc anodes during the cavitation exposure of the rotating disk specimens, the average current density at the zinc anodes was calculated to be 300 ma/ft<sup>2</sup>. The average current density in the cathode (bare steel) areas was calculated to be 20 ma/ft<sup>2</sup> (cathode/anode area ratio of 15/1).

As shown in Figures 13 and 14, erosion of protected HY 80 and 130 was slightly lower than the unprotected fresh water erosion, indicating no significant cushioning by evolved hydrogen. Cathodic protection apparently minimized the effect of corrosion in sea water on the degree of erosion of these steels. With cathodic protection the resistance of the HY 130 alloy was within the range of the Ti 621-0.8 Mo alloy, the most resistant of the alloys shown in Figure 12. Plesset<sup>12</sup>, using impressed current systems, has observed hydrogen evolution at a current of 1 milliamp in salt solutions (equivalent to a current density of 300 ma/ft<sup>2</sup> on the cathode surface, calculated on the basis of the immersed area of the specimen). However, he obtained a decrease of only approximately 30% in the erosion of 4340 steel in 3% salt solution with currents as high as 100 milliamp (equivalent to a current density of 30 amp/ft<sup>2</sup>), which is approximately the percentage decrease indicated by cathodic protection of HY 80 in Figure 13. In view of the uncertainty of the significance of hydrogen evolution on the degree of erosion of non-corrosion resistant ferrous alloys under sacrificial anode cathodic protection, further studies are underway using corrosion-resistant alloys under

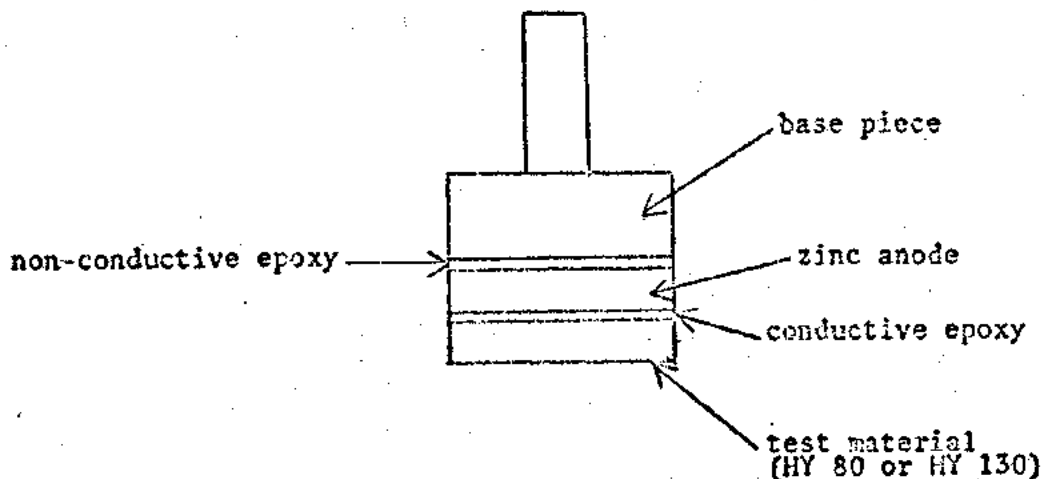


Fig. 11. Cathodic Protection Magnetostriction Specimen.

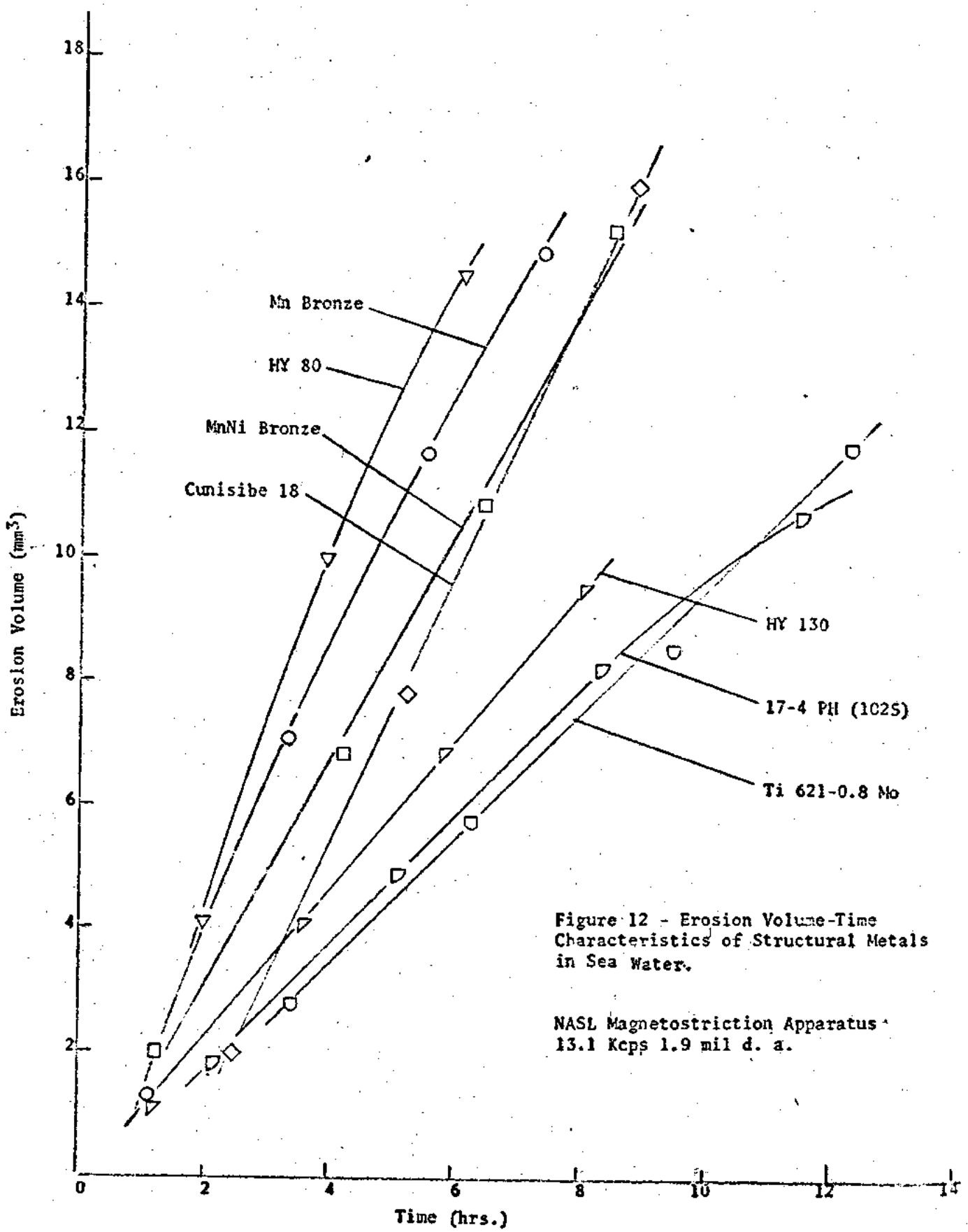


Figure 12 - Erosion Volume-Time Characteristics of Structural Metals in Sea Water.

NASL Magnetostriction Apparatus  
13.1 Kcps 1.9 mil d. a.

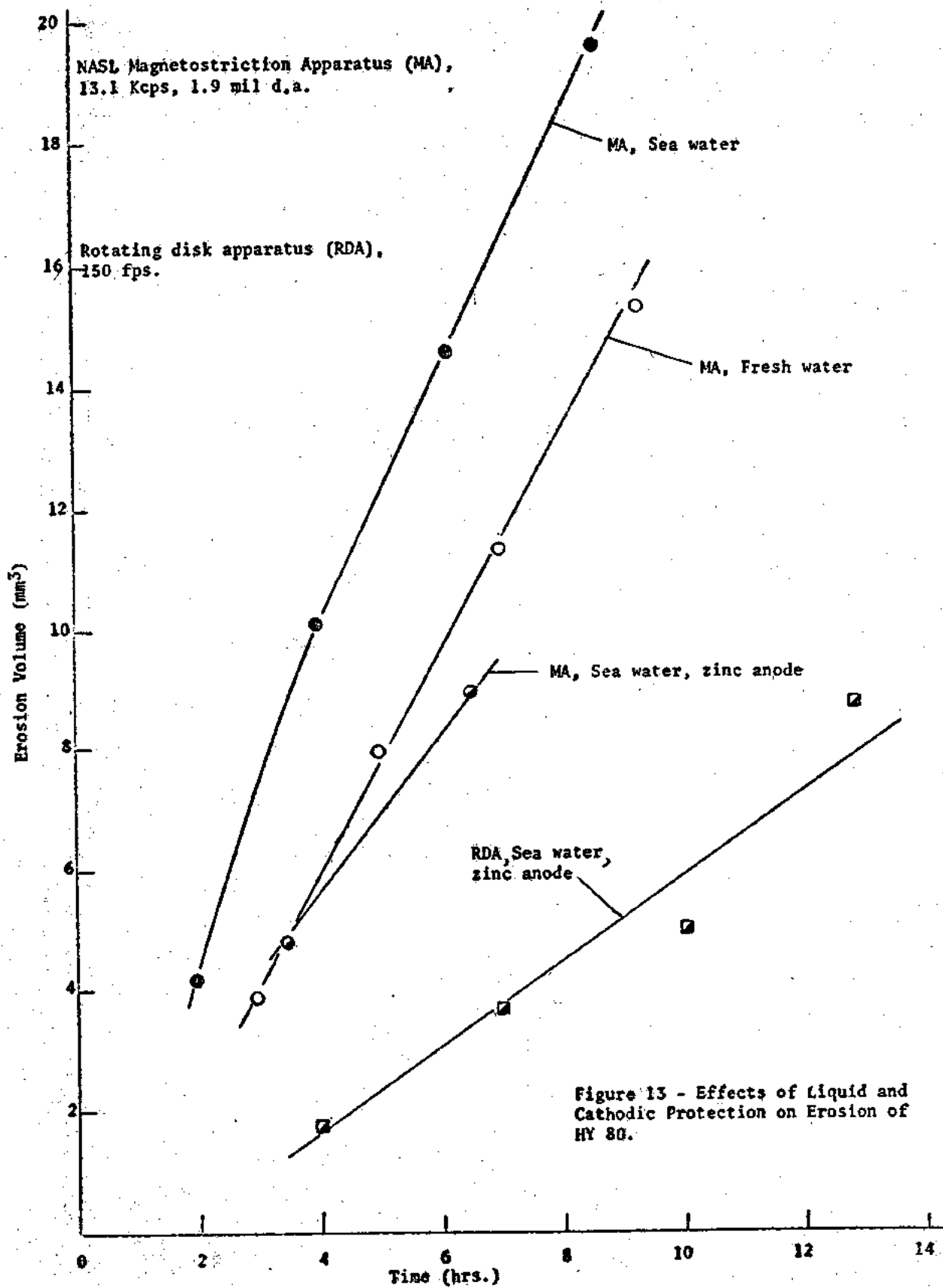
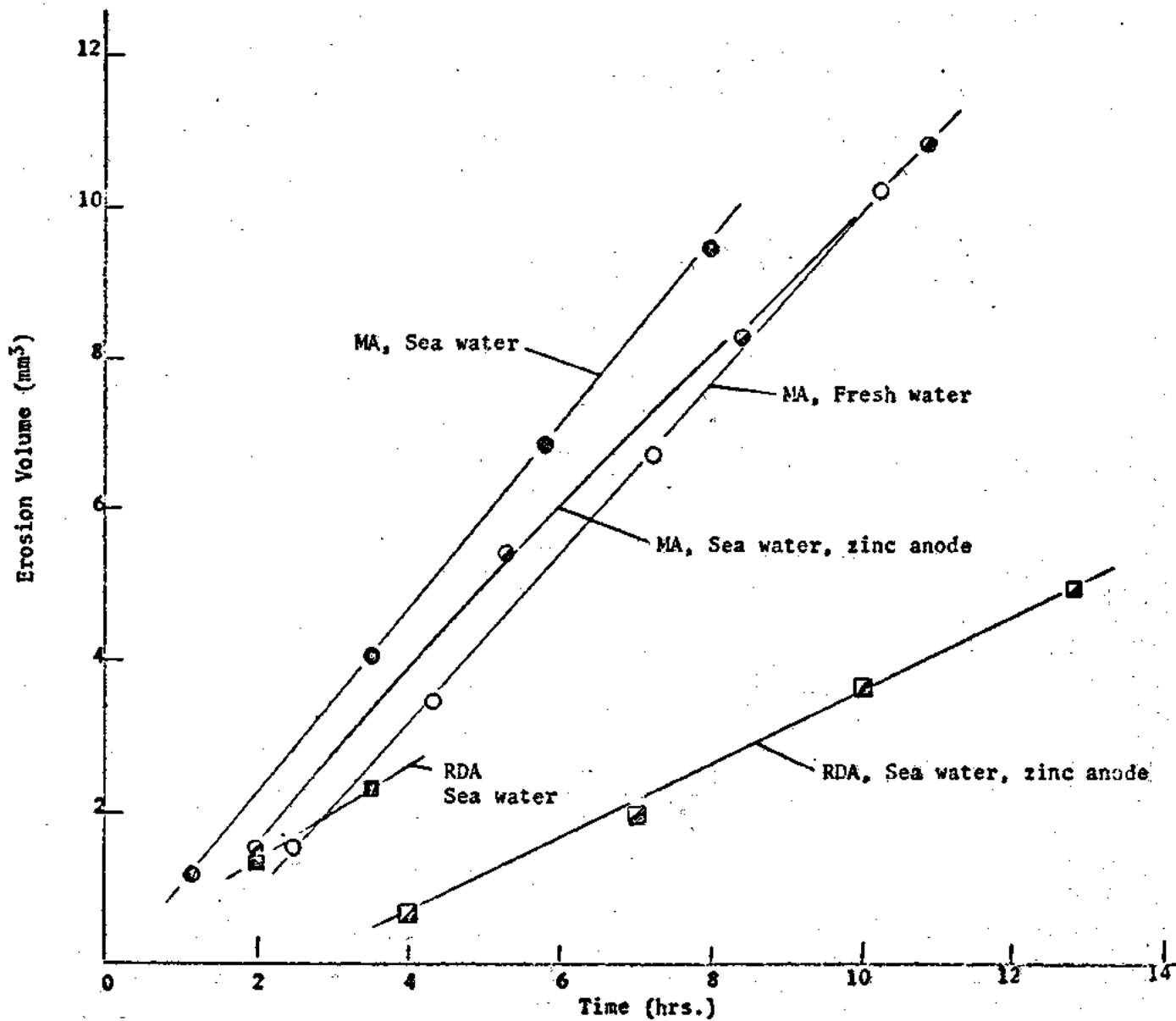


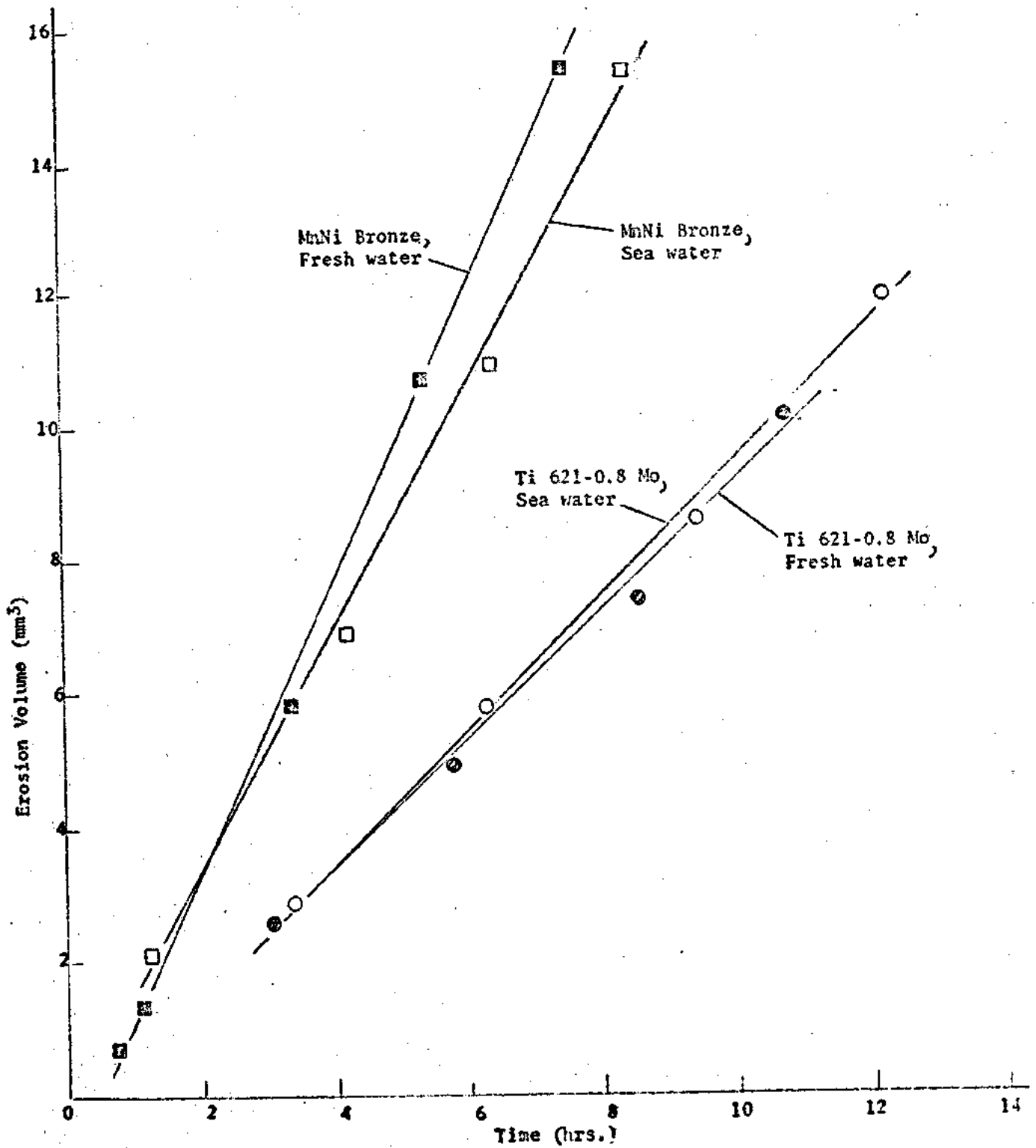
Figure 13 - Effects of Liquid and Cathodic Protection on Erosion of HY 80.



NASL Magnetostriction app. (MA), 13.1 Kcps, 1.9 mil d. a.

Rotating Disk App. (RDA), 150 fps

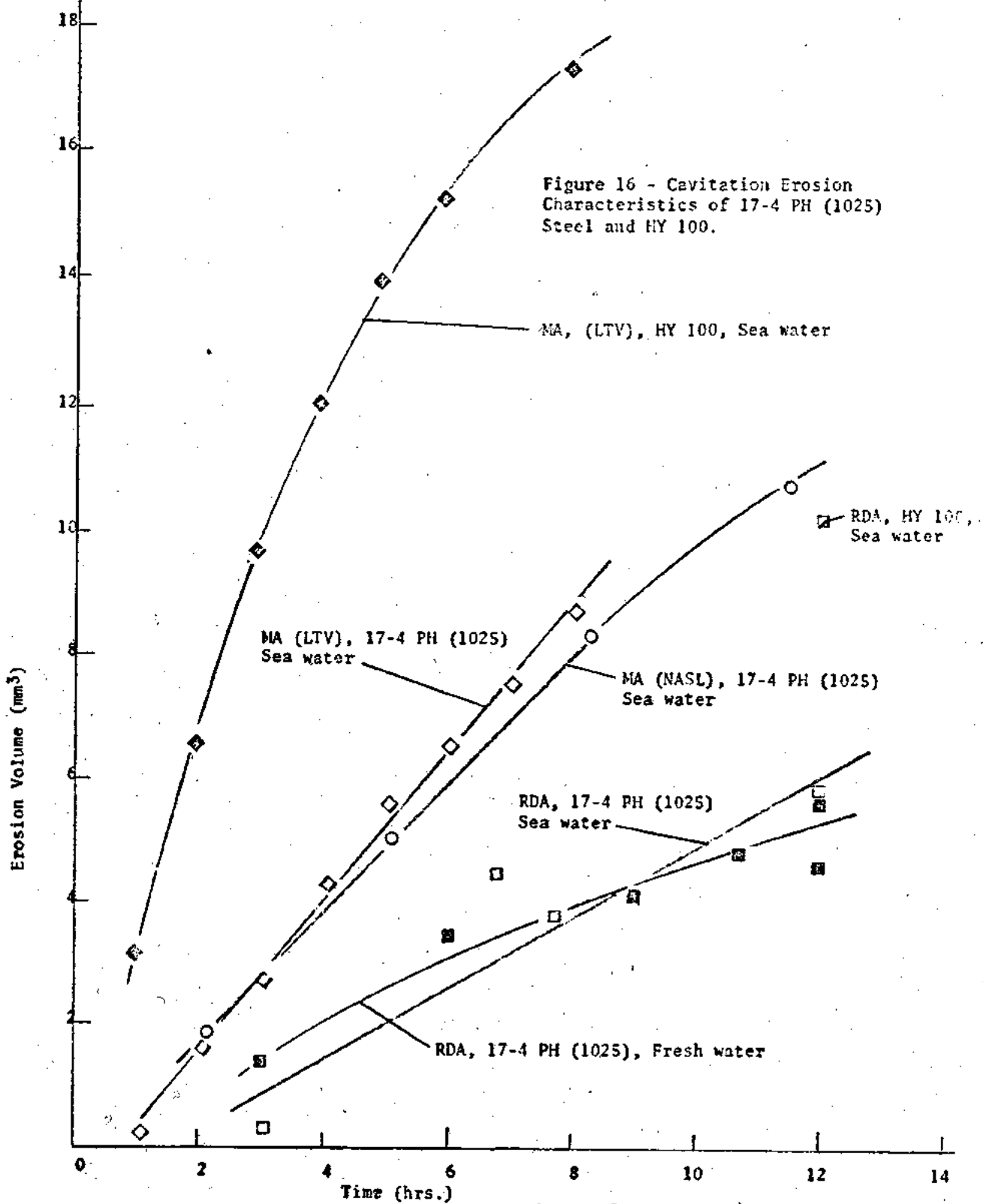
Figure 14 - Effects of Liquid and Cathodic Protection on Erosion of HY 130.



NASL Magnetostriction Apparatus 13.1 Kcps, 1.9 mil d. a.

Figure 15 - Effect of Liquid on Erosion of Ti 621-0.8 Mo and MnNi Bronze.

Magnetostriction 13.1 Kcps 1.9 mil d. a. (NASL)  
 App. (MA) 22 Kcps 1.0 mil d. a. (LTV)  
 Rotating Disk App. (RDA), 150 fps



NASL Magnetostriction App. (MA), 1.9 mil double ampl., 13.1 Kcps.

Rotating Disk App. (RDA), 150 fps.

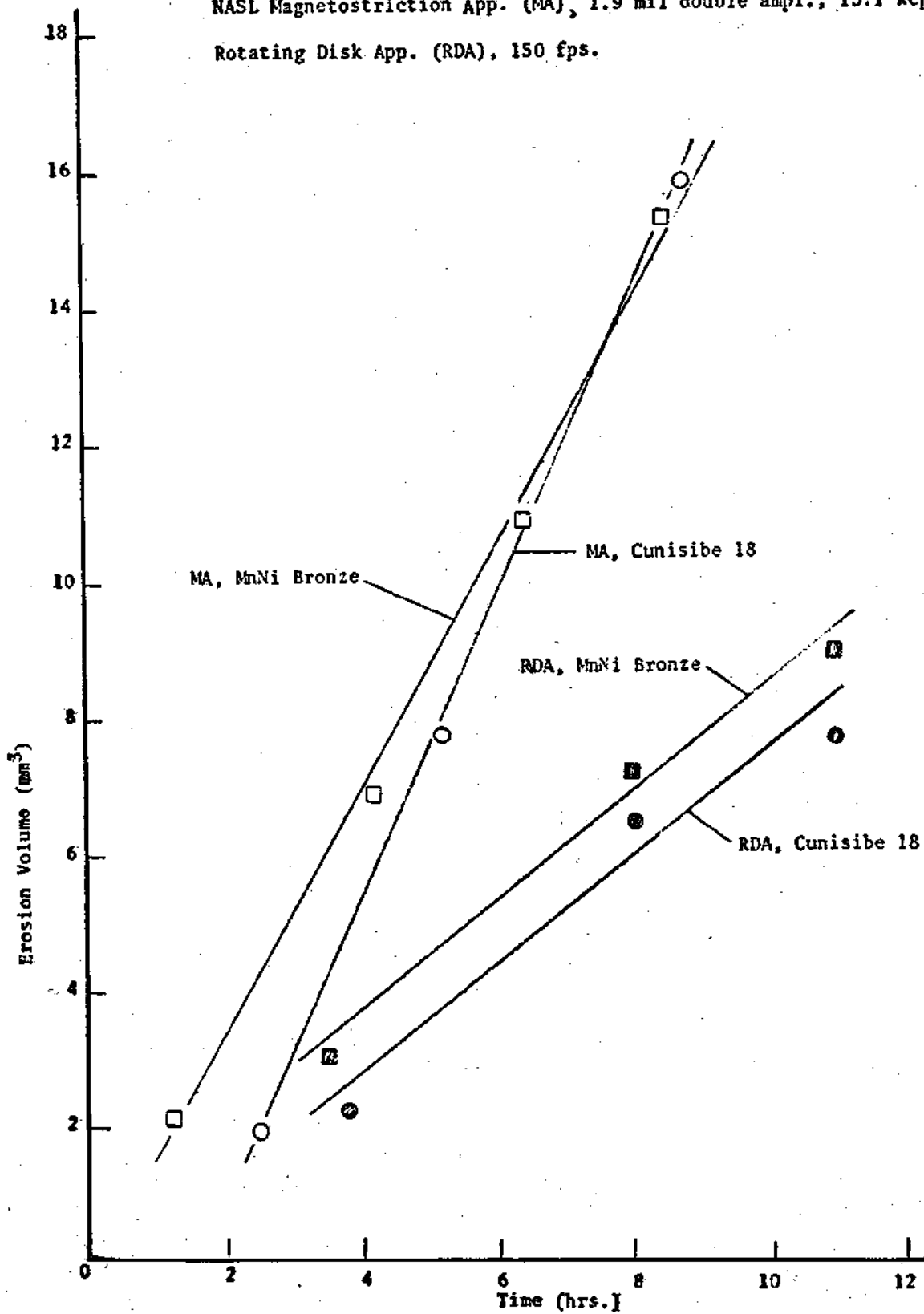


Figure 17 - Cavitation Erosion Characteristics of Copper Base Alloys in Sea water.

Apparatus

Frequency (Kcps)

Double Amplitude (mils)

NASL  
A-C

13.1  
6.5

1.9  
3.4

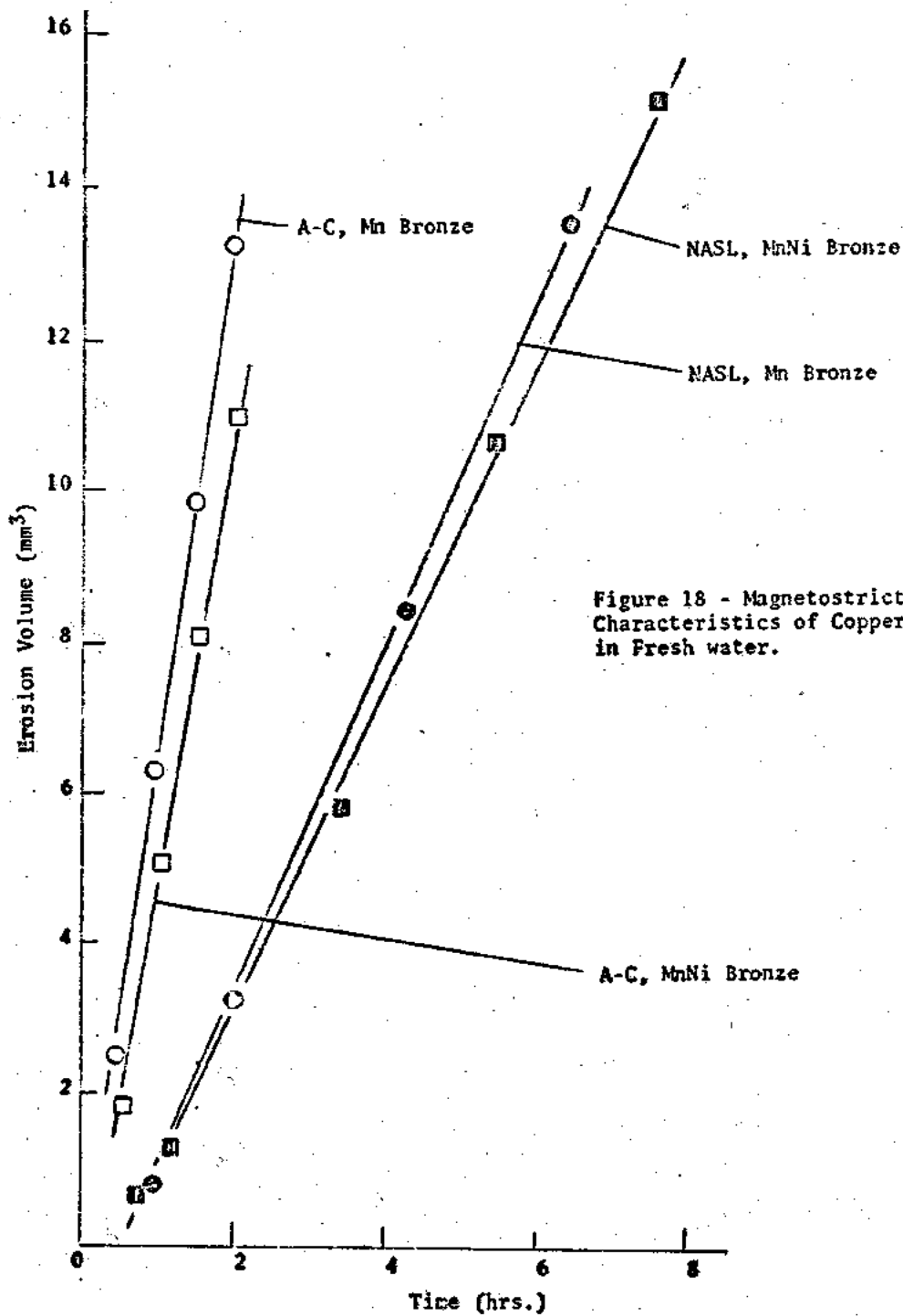


Figure 18 - Magnetostriction Erosion Characteristics of Copper Base Alloys in Fresh water.



such protection. If such protection will result in a decrease in erosion, it would indicate that hydrogen evolution probably contributes to a decrease in erosion.

**Comparability of Erosion Test Procedures.** NASL rotating disk and magnetostriction methods were compared with each other, and with magnetostriction methods as used by Rheingans<sup>14</sup> and Hohman, and others<sup>24,25</sup>. The characteristics of the vibratory facilities are given in Table 2. Results of comparison tests are shown by erosion volume-time characteristics of the same alloys and liquids in Figures 13, 14, 16, 17 and 18.

TABLE 2  
CHARACTERISTICS OF  
MAGNETOSTRICTION TEST FACILITIES

Characteristic	NASL	Rheingans <sup>(16)</sup>	Hohman et al <sup>(24,25)</sup>
Frequency (keps)	13	6.5	22
Double Amplitude (mils)	up to 1.9	3.4	1
Specimen	Flat, 5/8 in. dia.	Flat, 5/8 in. dia.	Dished, 5/8 in. dia.
Test liquid	Fresh, Sea water	Fresh water	Sea water

Note: Rheingans tests at Allis-Chalmers Co. (A-C)  
Hohman tests at Ling-Temco-Vought (LTV)

**Vibration Amplitude.** The effect of vibration amplitude on erosion intensity is shown by the erosion volume-time characteristics of the HY130 and Ti 621-0.8 Mo alloys in Figure 19. The plots of erosion volumes after eight hours exposure of these alloys vs. double amplitude is shown in Figure 20. The indicated increase in intensity with increase in amplitude is in agreement with observations of Eisenberg<sup>8</sup>, Leith<sup>11</sup>, Plesset<sup>12</sup>, and Rheingans<sup>14</sup>.

### CONCLUSIONS

**Cavitation Erosion Resistance.** The results of the magnetostriction erosion tests of the structural alloys in sea water, Figure 12, indicate a broad range in erosion resistance under the described test conditions. The most resistant was the Ti 621-0.8 Mo alloy and the least resistant was the HY80 alloy. The order of resistance of the test alloys based on the results shown in Figures 12 and 16 are summarized in Table 3. None of the structural materials tested has erosion resistance values comparable with high strength elastomeric materials<sup>(7,9,19)</sup>. For optimum performance of structural materials in cavitating environments it may be necessary and feasible to protect isolated areas showing erosion, by overlaying or inlaying such areas with suitably applied elastomeric coatings or patches<sup>(19,21)</sup>.

**Liquid Corrosivity.** The cavitation erosion resistance of metallic alloys is influenced by the electrochemical characteristics of the alloy-liquid system. The less corrosion-resistant low alloy HY80 and HY130 steels show a significant increase in erosion in sea water as compared to fresh water, while the more corrosion resistant titanium, ferrous and copper-base alloys show no significant effect of the liquid on the degree of erosion, the erosion of the latter alloy being even slightly higher in fresh water than in sea water.

**Effects of Cathodic Protection.** The coupling of the non-corrosion resistant HY80 and HY130 steels to sacrificial zinc anodes during exposure to cavitation is effective in reducing the observed degree of erosion of these alloys in sea

TABLE 3  
ORDER OF RESISTANCE OF TEST MATERIALS IN  
SEA WATER WITHOUT CATHODIC PROTECTION

Order of Resistance(*)	Material
1.	Ti 621 - 0.8 Mo
2.	17-4 PH (1025) steel
3.	HY130
4.	Cunisibe 18
5.	MnNi bronze
6.	Mn bronze
7.	HY80
8.	HY100

(\*) 1 - highest resistance, 8 - lowest resistance

water. The observed decrease is due primarily to a decrease in corrosion of the steels in sea water due to cathodic protection by the sacrificial zinc anode, and, to a minor extent, to possible cushioning of the cavitation bubble collapse energy by hydrogen evolved at the cathode surfaces. The second factor may explain the slightly lower erosion of the protected HY80 magnetostriction specimen in comparison with the fresh water specimen.

**Comparability of Erosion Test Procedures.** Based on the comparable characteristics of Figures 13, 14, 16, 17 and 18, the relative intensities of the test procedures in descending order of intensity are as follows:

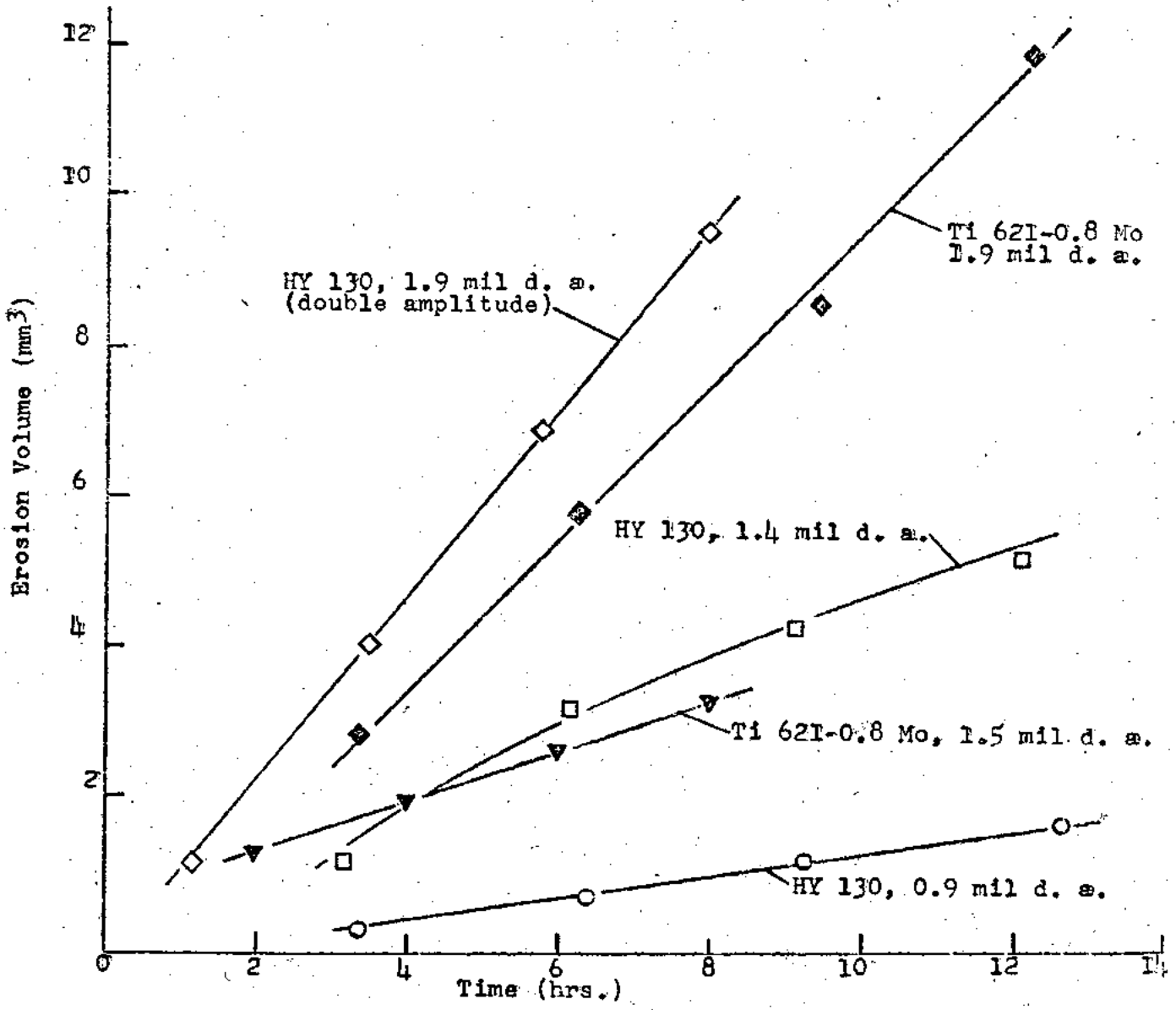
Order of Intensity	Test Procedure	Relative Erosion Intensity
1.	Rheingans <sup>(16)</sup> magnetostriction	1.0
2.	NASL magnetostriction (1.9 in. d.a.)	0.25
2.	Hohman <sup>(24,25)</sup> magnetostriction	0.25
3.	NASL Rotating Disk Apparatus (150 fps linear velocity source)	0.1

The relative order of erosion resistance of the test materials fall in the same order of resistance when tested by different procedures as shown in Figures 13, 14, 16, 17 and 18, and as summarized in Table 3.

**Vibration Amplitude.** The erosion intensity of the NASL vibratory (magnetostriction) apparatus is highly dependent on the amplitude of vibration, increasing with increase in amplitude as indicated in Figures 19 and 20. This relationship is in agreement with investigations of Eisenberg<sup>8</sup>, Leith<sup>11</sup>, Plesset<sup>12</sup> and Rheingans<sup>14</sup>.

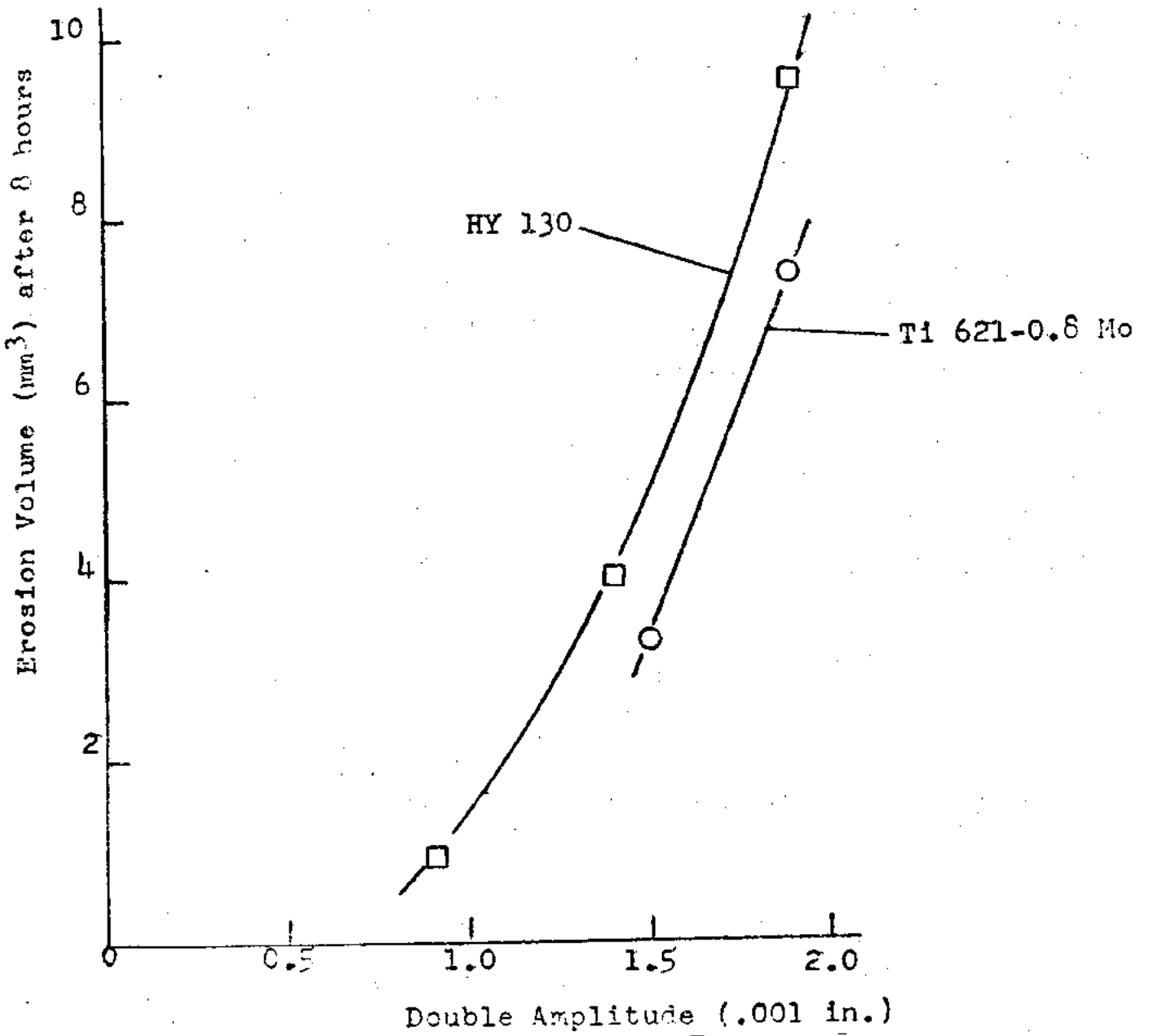
### SUMMARY

The resistance to cavitation erosion of several ferrous and non-ferrous metallic alloys has been determined by using high velocity (rotating disk) and vibratory (magnetostriction) apparatuses, and rated on the basis of their relative resistance. None of the structural materials were as resistant as high strength elastomeric coatings, inlays or overlays, suggesting the use of elastomeric patches in local areas where erosion of structural materials occurs. The erosion of non-corrosion resistant ferrous alloys was increased significantly in sea water, in comparison with fresh water exposure due to electrochemical (corrosion) effects in the former liquid. The use of a sacrificial zinc anode cathodic protection system decreased the erosion of these alloys to values within the range associated with fresh water exposure. The comparability of erosion intensities of the NASL rotating disk and magnetostriction facilities and two other vibratory facilities was determined



NASL Magnetostriction App., 13.1 Kcps, Sea water.

Figure 19 - Effect of Vibration Amplitude on Erosion Volume-Time Characteristics.



NASL Magnetostriction App., 13.1 Kcps, Sea water.

Figure 20 - Erosion Volume-Amplitude Characteristics.

on the basis of the erosion characteristics of the test materials. The effect of variation of the vibration amplitude of the NASL magnetostriction apparatus was determined and was similar to that shown by other vibratory facilities.

#### ACKNOWLEDGEMENT

The authors wish to express their appreciation to W. L. Miller and I. Geld for reviewing portions of this manuscript, and their helpful observations and suggestions. These investigations were conducted under the sponsorship of the U.S. Naval Ship Systems Command.

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#### DISCUSSION

J. BOTHWELL (U.S.A.): You have discussed in this paper erosion on screws of various compositions. Let us take for a moment the two extreme cases. A vessel of minimum draft and a vessel of maximum draft. Now, as maximum draft you consider a submarine down in several hundred meters depth and here you design a screw, with many blades, in fact one approaching a helix, thus you eliminate the cavitation problem. By the design on a minimum draft. (You might assume as an example a racing hydroplane), and here you overcome the cavitation problem, with the supercavitating screw. Now, my question, the point I like to invite you to comment on, is a twofold one. What consideration are you giving in your studies to the design of the screw and secondly what indicators are you considering for possible use by the ships' operators to determine or indicate the existence of cavitation and so to try to conduct their ship's manoeuvres around the cavitation?

D. KALLAS: Before answering your questions, you have brought up something that might be touched on. A submarine is operating at a depth. Now the cavitation phenomenon, as the depth increases, becomes less and less, and cavitation damage becomes less and less, with increasing pressure for several reasons. One reason is that there is a less nucleation in the water to cause cavities to form, but the other reason more important is the vapor cavity cannot form if the surrounding pressure is too great. So in a submarine operating at some depth cavitation is not a problem.

Now, the solution of the problem of cavitation, in my mind rests in design. The only time we should concern ourselves with cavitation resistant material is when our designers have not been able to avoid the cavitation phenomenon, this is essential in answer to your first question.

What we do in design? Now, our designers try not to design in a way that you will get a cavitation effect as we have noted in the U.S. Navy's PCH 1. In the PCH1 we put a propeller on a forward end of the nacelle,

the propeller cause the formation of cavities which we call travelling cavities. These cavities travel downstream from the propeller and they collapse down on the nacelle where we got damage. This is a design problem and it is not really a material problem. The materials engineer was called in to solve the problem after the designer have done a poor job of design in my opinion. Now some times the designers have no alternative and therefore we have to resort to materials. The materials engineer has not been too successful in solving this problem, despite the beautiful coloured slides that I showed you. If you are discriminating enough, you would see that we really have not solved this problem. Your second question deals with using the cavitation noise as an indicator. Sound is an excellent indicator and the reason that you can use sound as an indicator is if you have collapsing cavities, these make noises, which you can hear. Knowing you as an ex-Submarine commander I realize that your questions are based possibly on personal experience I don't know if you can tell the difference in an operating submarine, but if you can tell then sound is the way to answer your problem. No we have not considered the possibility of building in an indicator so that the ship's commander will know that he is getting cavitation. We have not.

J. BOTHWELL: Trying to transfer naval experience to instances like the new supertankers, where you do have your screw down quite deep in the order of 70 feet or so, but you also have the screw somewhat removed from the ship's control station, possibly an indicator on the bridge, which will indicate the onset of cavitation and allowing the revolutions to increase speed to built up slowly, could be used by the ship's control point, captain's as well, and there by minimize the effect of cavitation, when you are building up speed.

D. KALLAS: We have not thought of this and we might consider your suggestion, I will go back to our laboratory and bring it up to every body and see what they think.

# PROTECTION OF SEA WATER DESALTING EQUIPMENT BY OXYGEN SCAVENGING

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## SUMMARY

Corrosion behaviour in many sea water desalting plants indicates systematic decrease of corrosion as the dissolved oxygen concentration level is reduced. For complete elimination of corrosive attack, very low oxygen level such as 1 ppb or lower in the sea water has to be achieved. However, by mechanical deaeration alone as is being practiced in desalting plants, such low oxygen level cannot be reached. Sodium sulfite is a powerful scavenger for oxygen and is suitable for sea water systems. The calcium sulfite solubility in sea water, unknown so far, has been found high enough to enable the use of adequate sulfite concentration without the risk of causing precipitation. A novel process is being designed in which the acidification pretreatment of sea water for decomposing the bicarbonates and expulsion of carbon dioxide will be carried out by using sulfur dioxide rather than the conventionally used sulfuric acid. This process provides ample concentration of sulfite ion to act as a scavenger dispensing with the need to have a supply of sodium sulfite as such. The reaction of oxygen with the sulfite ion in sea water is

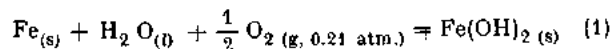
very fast, particularly at high temperatures. Complete elimination of corrosion by oxygen depolarization of carbon steel and copper base alloys is expected.

The large scale production of potable water from sea water has relied almost exclusively up to the present time and apparently will rely in the near future on distillation type processes. Estimates of the tubing costs alone range from 30 to 60% of the total cost of the plant<sup>1</sup>. Increasing the expected life of this equipment by preventing corrosion is therefore a major consideration in the design and operation of the plant.

The metals mostly used are carbon steel for the shells and tube sheets, and copper-base alloys for the tubing. Considerable corrosion attack has been reported to occur in sea water desalting installations both to the copper alloy and steel components. If corrosion of steel could be prevented so that it can be used also for tubing, large savings in the investment required in desalination equipment could be made. A process is being proposed in this paper aimed to contribute towards this goal.

## THE ROLE OF DISSOLVED OXYGEN AND THE FERROUS HYDROXIDE FILM.

Past experience with sea water has shown that oxygen content ranks highest in importance among the many factors that affect the corrosiveness of sea water. The pH of the brine in contact with the metal in distillation equipment is between 7 and 8 and the main corrosion takes place through oxygen depolarization. The overall reaction



involves a free energy change of -58.5 kcal, which means a great thermodynamic spontaneity of the corrosion reaction even at a very low oxygen concentration in the order of ppb (parts per billion). Bearing in mind, however, the kinetics of the cathodic reduction of oxygen which is determined by the ability of oxygen to reach the cathodic sites, it may be stated that the actual corrosion promoted by oxygen reduction should decrease linearly together with oxygen concentration.

The oxygen reduction process is diffusion-controlled and its overpotential is therefore brought about by concentration polarization, while the whole corrosion circuit is cathodically controlled. A value for the limiting current density for oxygen reduction was given by Bockris<sup>2</sup> for an unstirred solutions as

$$i_L = 0.14 \times C' [\text{Amp/cm}^2] \quad (2)$$

where  $C'$  is the oxygen concentration in gram-moles per

liter, when a diffusion coefficient of  $1.8 \times 10^{-5}$  ions/sec was assumed. The cited  $i_L$  would seem to indicate very low corrosion rates (up to 1 mpy) if the oxygen level is kept below 500 ppb\*. The diffusion coefficient (and therefore the corrosion rate) would, however, increase exponentially with temperature and also by agitation, and, therefore, much lower oxygen concentration would be allowable at, say, 250°F under turbulent flow conditions. Contrary to tap water, no passivity is reached in sea-water by increasing the flow-rate, and no decrease of corrosion-rate may be expected by increasing the flow-rate<sup>3</sup>.

The ferrous hydroxide formed at the metal surface acts as a protective film by slowing down diffusion of oxygen to the metal surface, and keeping a high pH adjacent to the metal surface. The saturated solution of  $\text{Fe}(\text{OH})_2$  has a pH of about 9. Any influence of the environment on this film will bear upon its effectiveness as a protective film. The film will dissolve faster with the increase of acidity, temperature and the velocity of the water flow. The addition of salt to water decreases the activity coefficients of the ions in solution, hence increases the solubility of the ferrous hydroxide. Different salts vary in their action in reducing the activity of coefficients. The electrolytic conductivity of the solution permits operation of anode and cathode areas farther removed from each other and the anode and cathode reaction products

\* These figures are approximately in line with early results of Cox and Roethel<sup>4</sup>.

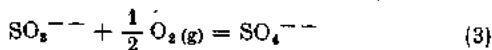
can then combine at a place removed from the iron surface and hence precipitate a less protective corrosion product layer. Sometimes cations are also assigned catalytic capacity in promoting the cathodic depolarization by oxygen.

An additional effect of the oxygen is the oxidation of the more soluble ferrous hydroxide (150 ppb in water) to the much less soluble ferric hydroxide (0.05 ppb), thereby destroying the saturation of the brine with the ferrous hydroxide and encouraging faster dissolution of the protective ferrous hydroxide film. Similarly to oxygen also the ferric ion and hydroxide cause cathodic depolarization, thereby promoting corrosion. The phenomena of passivity by highly-oxidized protective films produced sometimes in environment rich in oxygen, and the effect of various anions by penetrating such films, are of lesser interest for well designed desalination plants in which large efforts are made to deaerate the water and reduce oxygen content to the lowest possible level.

## INDUSTRIAL PRACTICE OF OXYGEN REMOVAL

It is a customary practice with various industrial processes to remove oxygen from the water in order to combat corrosion. In hot water supply systems it has been considered allowable to have oxygen concentration of about 100 ppb. For low pressure steam boilers (under 250 psi) the desirable maximum should not exceed 30 ppb. For high pressure boilers, practically «zero» oxygen is required, which usually means below 5 ppb. Steam-operated deaerators at power plants are sometimes capable of reducing the oxygen content to this low level<sup>6-7</sup>. This operation is quite expensive. For further reducing the oxygen concentration a chemical scavenger is added. Sodium sulfite has been used with success for many years for the complete removal of oxygen from boiler and cooling water systems<sup>4-12</sup>.

The effectiveness of the sulfite as a scavenger for oxygen results from both the thermodynamics and the kinetics of the reaction.



The free energy change of this reaction is -61.3 kcal from which it can be calculated that as long as some sulfite is present, even of a small concentration (e.g. 1 ppm), the equilibrium oxygen concentration would be a great many orders of magnitudes below 1 ppb. However, the thermodynamic spontaneity of the corrosion reaction (Eq. 1) is about the same as that of the scavenging reaction (Eq. 3), and the main objective is to achieve a high reaction rate for the scavenging reaction, so that any dissolved oxygen that may leak into the system will be consumed by the sulfite much faster before it can diffuse through the protective ferrous hydroxide film and react with the metal.

The kinetics of the auto-oxidation of sulfite in aqueous solutions have been studied extensively<sup>13</sup>. The reaction is considerably accelerated by the amount of sulfite in excess of the oxygen present and is catalysed by minute amounts of polyvalent cations, notably are cobalt, copper and iron. As an example: in the absence of catalyst only 30% of the 10 ppm oxygen in cold water reacted with about an equivalent amount of sulfite in 10 minutes. With the addition of 0.01 ppm  $\text{Co}^{++}$ , a 100% completion of the reaction took place in less than 20 seconds<sup>14</sup>. At elevated temperatures, the reaction rate is much faster. For the purpose of corrosion protection, the sulfite indeed acts faster exactly where it is mostly needed in the water-system: at points vulnerable to oxygen attack, where the metallic ions delivered at the anodic areas serve as catalyst, and at the higher temperatures, where corrosion is known to be several-fold more severe than at the cooler parts of the system.

The use of sulfite is beneficial by several functions. Not only does it reduce the oxygen content of the feed water much below the limit obtainable by mechanical means, but also, by keeping a certain concentration of sulfite in the system, it serves as a safe-guard against in-leakage of air at various

parts of the system during operation or shutdowns. Furthermore, the occurrence of air in-leakages and various kinds of failures in the system can be detected by the decrease of the sulfite concentration in the water which is easy to check by simple analysis. Therefore, some experience in boiler practice indicated that considerable concentration of sodium sulfite should be maintained in the water, e.g. 20-50 ppm for operation and 100 ppm for idle periods<sup>4-8</sup>.

There are, however, some limitations in the use of sodium sulfite in very high pressure power-plant boiler systems. However, these limitations are dictated by specific power-plant conditions and do not apply to sea water desalting conditions. (Because of suspected decomposition of the sulfite at very high temperature and pressure prevailing at power-plant boilers, the concentration of sodium sulfite in the water has been limited to about 10 ppm at 1400 psi and 3 ppm at 1800 psi<sup>9</sup>. Also, power-plant boilers require highly pure deionized water; and the use of sodium sulfite has a disadvantage as it increases the salt content of the water. Accordingly hydrazine, which does not leave any salt residue, has been replacing the sodium sulfite. In addition, a very high pH, above 9, is maintained in power-plant boilers and the hydrazine evolves ammonia which helps to keep a desirable high pH at the generator turbine).

Other reducing agents have been successfully employed in industrial water conditioning to combat corrosion: The addition of ferrous hydroxide or sulfate and pretreatment of the water with expanded iron. However, the sludge that iron compounds leave may be objectionable. It may also be undesirable to have ferric ion and hydroxide that result from such treatment, as these are known to be effective cathodic depolarizers acting similarly to oxygen, in promoting corrosion.

## THE NEED FOR OXYGEN SCAVENGING IN SEA WATER DESALTING EQUIPMENT.

Pilot plants for distilling sea water are often constructed of inexpensive steel. Experience has shown that the corrosion rate of steel is substantially reduced by reducing the oxygen content in hot sea water<sup>14</sup>. The effect of even low oxygen concentration can be demonstrated by the results obtained at the Freeport desalination plant<sup>15</sup> where corrosion tests on carbon steel specimens showed the following corrosion rates (for 156 day runs) in mils per year:

Dissolved O <sub>2</sub>	Temperature		
	130°F	200°F	250°F
40 - 600 ppb	8 mpy	21 mpy	32 mpy
«Nil»	3.5 mpy	7 mpy	13 mpy

Similarly, at the San Diego Plant (90 days runs)<sup>14</sup>

5 ppb «No dissolved oxygen»	130°F	200°F
	12.5 mpy	20 mpy
9 mpy	12.5 mpy	

It has also been reported that carbon steel tubes showed practically no corrosion in deaerated (5 ppb oxygen) five percent brine at 140°F (60°C)<sup>14</sup>.

Here we arrive at the core of the problem. It is evident from experimental results that even very low oxygen concentrations within the range of 0-10 ppb are reported to cause significant corrosion rate of carbon steel, especially at the higher temperature stages. However, with the regular mechanical deaeration of sea water, adequate elimination of oxygen is not attainable in existing plants. In fact, it is also quite difficult to set up in a plant a procedure for measuring oxygen at levels below 10 ppb in hot sea water. Similarly, it is not generally possible to keep such extreme deaeration

for long durations with complete prevention of leaks at various parts of the systems, faults in gasketing and the evacuating systems, and admission of air at shut-downs. It is therefore necessary to consider statements of «Nil» oxygen concentration or «No dissolved oxygen» as only expressions describing the present practical lowest oxygen concentration limit attainable at the specific reported desalination plant.

There has been, though, an interesting experience with connate brines (found in oil producing fields, originating deep down in the earth and under high pressure), that are not only completely oxygen-free but occasionally will also chemically react with small amounts of oxygen that may be inadvertently introduced during handling. Such brines, as has been found, do not attack carbon steel even at 250°F (121°C)<sup>17</sup>. This may indicate that if a real 0.00 or, say, 0.01 ppb oxygen concentration, is attained in sea water brine at the desalination plant, the desired prevention of corrosion of carbon steel may be achieved. Furthermore, the behavior of the connate brine indicates that it contains a natural scavenger, similar in its affect to the sulfite as in industrial use mentioned above. This makes it practically possible to attain a zero concentration of dissolved oxygen in solution.

This holds the clue for the practical prevention of corrosion in desalination plants, namely, by using a scavenger in the water. Following the pattern of use of scavengers in various industrial processes, sodium sulfite seems then to be very beneficial to check corrosion also in desalination plants. Scrutinizing the various operating conditions of the processes involved also leads to the conclusion that none of the disadvantages of sodium sulfite in connection with very high pressure power-plant boilers seem to be relevant for desalination plants. Furthermore, except for the higher temperature used in power plants, all the other factors at desalination plants are of a more corrosive character: lower pH (it must not exceed 7.5) and higher salt content. This may enhance the role of sodium sulfite in desalination plants.

#### THE USEFULNESS OF TREATMENT FOR SEA WATER.

Sea water contains 10 mM (millimoles/liter) calcium, and the available data<sup>18</sup> indicates that calcium sulfite is only sparingly soluble in water: 0.42 mM at 30°C, 0.20 mM at 90°C and 0.081 mM at 100°C. Based on these values and assuming an increased solubility of calcium sulfite in sea water similar to the behavior of calcium sulfate, some reported calculations indicate the limits of solubility of CaSO<sub>3</sub> in 15 part per thousand chlorinity brine to be: 3.75 ppm CaSO<sub>3</sub> at 50°C, and only 0.145 ppm CaSO<sub>3</sub> at 100°C<sup>18</sup>. This would mean severe limitations on the possible use of adequate concentration of sulfite as scavenger in sea water.

We have considered the subject worthy of further investigation. As the sulfite exists both as sulfite and bisulfite ions in solution, the solubility of calcium sulfite should be pH-dependent. In aqueous solutions at 25°C.

$$\log \left[ \frac{(\text{SO}_3^{2-})}{(\text{HSO}_3^-)} \right] = -6.36 + \text{pH} \quad (4)$$

(which indicates that at a pH of 6.36 the sulfite/bisulfite ratio is unity). Data for 1 molar NaClO<sub>4</sub> solution<sup>20</sup> (which seems to be closer to sea water conditions than data for water) is used. (For water the value -7.26 rather -6.36 is known). No data on this and on the solubility of calcium sulfite in sea water is known. Therefore we have launched experimental work on this problem. Our present findings indicate quite high solubility values for calcium sulfite in Mediterranean sea water at a pH of 7: at least 2 mM at 25°C and 1.5 mM at 90°C. At a pH of 8 the solubility has been found to decrease by a magnitude less than 0.5 mM. No great change is marked for concentrated (2X) sea water.

When adding sodium sulfite to sea water there is a marked effect of supersaturation. Therefore the experiments involved dissolving solid calcium sulfite in sea water and analysing for the total sulfite content of the filtered solution. To avoid oxidation of the sulfite by air, the experiments were conducted under inert atmosphere and other precautions were taken.

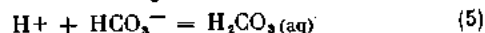
In order to prevent interference by calcium carbonate precipitation upon heating, the sea water was pretreated to eliminate the bicarbonate content by acidifying, expelling the carbon dioxide, and correcting the pH to the desired value. The relatively high solubility of calcium sulfite in sea water is connected to the reduced activity coefficients of the calcium and sulfite ions. This may involve also complex equilibria of the divalent ions including also ion-pair formation<sup>21</sup>. Work continues at our laboratory on this project.

#### PROVISION OF SULFITE ION THROUGH A NEW ACIDIFYING PROCESS.

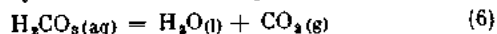
From the new experimental data obtained it is now evident that from the consideration of calcium sulfite solubility there would be no hindrance on the use of sulfite as scavenger in sea water desalting plants. The next question is about the cost of the sulfite treatment. As huge quantities of sea water are involved which after partial distillation are drained back to the sea, the sodium sulfite treatment might considerably increase the yearly expenditure for chemicals. This drawback can be overcome by a new process modification being investigated now at our laboratories.

The usual practice in desalination plants is to pretreat the fresh sea water by sulfuric acid in an equivalent amount to the bicarbonate content of the sea water. The acid decomposes the bicarbonate ion into carbon dioxide gas most of which is expelled out to the atmosphere in a degassifier. The remaining gas is removed in a stripper by application of vacuum and heat.

The acidification process instantly converts the bicarbonate ion to carbonic acid according to

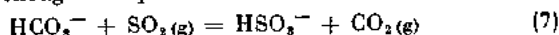


After this step there is not any sulfuric acid left in the sea water, and the pH of the solution is dependent only on the dissociation of the carbonic acid. The latter is decomposed at a slower rate to yield carbon dioxide gas:



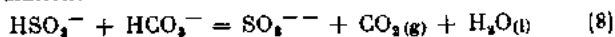
This treatment removes the bicarbonate ion from the water. Without such a treatment, the bicarbonate would decompose thermally when the water is heated and the pH would rise and cause precipitation of calcium carbonate and magnesium hydroxide.

In the new process modification, sulfuric acid is replaced by sulfur dioxide gas. This gas upon dissolution in sea water produces an acid, which, though weaker than sulfuric acid, is strong enough to replace the bicarbonate ion. The reaction



has an equilibrium constant of  $10^{6.51}$  at 25°C in a 1M NaClO<sub>4</sub> solution<sup>20</sup> (pertinent data for sea water is not fully available). Namely, the reaction will proceed from left to right well enough to decompose the bicarbonate ion. This would also be expected from merely knowing that the first ionization constant of sulfurous acid is approximately equal ( $10^{-2}$ ) to the second ionization constant of sulfuric acid.

Concerning the second ionization of the H<sub>2</sub>SO<sub>3</sub> acid, calculations for the reaction



based on data<sup>20</sup> for the relevant equilibria indicate an equilibrium constant of  $10^{1.91}$ . This constant is quite close to the value of  $10^{1.51}$ , the constant of the equilibrium for Eq.(6)<sup>20</sup>. From this it may be expected that about the same magnitude of efforts (scrubbing, evacuating and heating) used in the procedure to drive off the carbon dioxide after acidification with sulfuric acid will also suffice after acidification with an equivalent amount of sulfur dioxide.

The important achievement concerning the sulfur dioxide treatment is that simultaneously with the action of the sulfur dioxide gas in decomposing the bicarbonate, the application of this gas supplies the solution ample concentration of sulfite

(namely, sulfite and bisulfite ions) which is the desired oxygen scavenger.

The practical application of sulfur dioxide in desalination plants should be quite simple. Sulfur dioxide is very readily absorbed in sea water and the scrubbing towers of degasifiers often used in desalination plants for expelling the carbon dioxide following the acidification step should be capable of effecting both absorption of  $\text{SO}_2$  and release of carbon dioxide at the same time. For the purpose of absorbing tower considerations the low vapour pressures of sulfur dioxide over the sea water constitute practically zero back-pressure. Calculations show that no more than 5 transfer units<sup>22</sup> are required to absorb 99% of the sulfur dioxide gas from sulfur combustion gas, which indicates a light task for the absorption equipment. The feasibility and simplicity of such an absorption can be demonstrated by many reported industrial processes. For example, Kelly<sup>23</sup> described a scrubber for the removal of sulfur dioxide from combustion gases by using river and sea water for washing. The packing was made of wood. A run with 99% absorption of the  $\text{SO}_2$  showed a pressure drop of only 0.32" w.g.

Costwise, sulfur dioxide gas is considerably cheaper than sulfuric acid. The gas can be easily produced at site at the bottom of the tower by burning sulfur using commercially available sulfur burners, and the cost of the produced gas is substantially no more than the cost of the sulfur used. For producing the gas, low grade sulfur, unsuitable for sulfuric acid production, can be made use of, and even industrial wastes that contain sulfur such as refineries acid sludge. This might reduce costs even lower. The process should be more economical than the conventional one with sulfuric acid for eliminating alkaline scale, while the supply of sulfite to the sea water to act as oxygen scavenger is obtained cost-free, as a by-product of the acidification process.

#### SOME PROCESS FEATURES

Experiments in our laboratory using natural Mediterranean sea water indicated very fast reaction showing completion of the reaction of the dissolved oxygen with sulfite in a short time in the order of a minute at room temperature. Similar results on oxidizing sulfite with dissolved oxygen in Atlantic Ocean water (collected several miles out from Boston, U.S.A.) was reported<sup>18</sup>. In fact, the reaction in sea water is several times faster than in distilled water, which indicates the activity of some of the ionic metals in the sea water as catalysts. At elevated temperature the reaction is much faster and is completed in sea water in seconds.

Sea water has a pH of about 8, arising from the existence of 2.4 mM bicarbonate ion. Therefore, no more acid is required than 1.2 mM  $\text{SO}_2$  to neutralize that alkalinity. The vapour pressure of sulfur dioxide over the sea water containing 1.2 mM  $\text{HSO}_3^-$  should be very low. From the relation

$$\log \left[ \frac{(\text{HSO}_3^-)}{(\text{PSO}_2)} \right] = 1.34 + \text{pH} \quad (9)$$

derived from equilibria at an ionic environment of 1 M  $\text{NaClO}_4$ <sup>20</sup>, it obtains that for 1.2 mM  $\text{HSO}_3^-$  in solution the vapour pressure of sulfur dioxide is  $2.0 \times 10^{-4}$  mm Hg at a pH of 7, and  $2.0 \times 10^{-3}$ , at a pH of 4. (For water the figure 5.0 replaces 2.0). If the total original sulfite content is 1.2 mM and a fraction X has been oxidized, the sulfur dioxide pressure would decrease by a factor 1-X. To account for the sulfite-bisulfite ratio (by Eq. 4) another factor should be introduced, 0.1 for a pH of 7.3, and 1 for a pH of 6.3 or lower (down to a pH of 4). For example, for 50% of the total sulfite oxidized and a pH of 7.3, the sulfur dioxide pressure would be  $1.0 \times 10^{-7}$  mm Hg. At higher temperatures encountered in desalination this pressure would increase to  $10^{-6}$  or  $10^{-5}$  mm Hg. Such low pressures are  $10^{-6}$  to  $10^{-8}$  smaller than the water vapour pressure and are not expected to cause any appreciable pH change in the condensate, hence they would not cause any attack on the vapour side of the heat transfer surfaces.

The corrosiveness of carbon dioxide is tied up to the exis-

tence of oxygen<sup>24</sup>. In the complete absence of oxygen carbon dioxide would exert its effect mainly by reducing the pH. However, here the presence of sulfite should be useful also in an additional way, by the  $\text{SO}_3^{2-} \leftrightarrow \text{HSO}_3^-$  equilibrium which acts as a buffer and opposes pH changes.

Another potential contribution of the sulfite ion is the possible deposition of  $\text{FeSO}_4$  or  $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  at the iron surface induced by the higher pH of the ferrous hydroxide film. Such effects are yet to be investigated.

No hydrogen-ion reduction is possible on copper in sea water from which oxygen has been completely removed, and since no other cathodic reaction is feasible in such conditions, corrosion should be entirely prevented. This has recently been experimentally illustrated in sea water by Bromley<sup>25</sup>. The use of sulfite as an oxygen scavenger for this purpose should be most effective. For carbon steel, too, it is as well expected that corrosion by oxygen-depolarization can be similarly eliminated.

The question whether corrosion by hydrogen evolution can appreciably take place on carbon steel in sea water at a pH around 7.5 has yet to be ascertained. Shreir<sup>26</sup> estimated that iron in aerated sea water can corrode with 95% of the cathodic process consisting of oxygen reduction and 5% of hydrogen-ion reduction. The non-corrosivity of connate water even at 250°F<sup>17</sup> seems to suggest no corrosion of any kind. For the case of sea water desalination conditions it has to be investigated what effect would be exerted by the absence of oxygen and by a sulfite-modified protective layer. In such conditions it seems, also, that the load on cathodic protection (in as much as it is found necessary) would be low.

#### CONCLUSION

The saltiness of sea water is not a cause of corrosion by itself but does accelerate the action of oxidizing agents which do cause corrosion. With the radical elimination of oxygen by adequate sulfite scavenging, no corrosion of copper-base alloy should occur in sea water desalting plants and also the corrosion of carbon steel should be mostly suppressed. The new process proposed can materialize the technological and economical feasibility of such scavenging.

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#### DISCUSSION

Prof. Dr. SKOULIKIDIS (Grèce) : If I have correctly understood Prof. Yahalom said that the rate of corrosion depends on the diffusion rate of oxygen in the metal.

Prof. Dr. YAHALOM : No, I said that the rate of corrosion depends on the diffusion of oxygen to the metal surface, from the solution. And so it will depend some how on the temperature apart from the concentration and of the velocity of water.

Prof. Dr. SKOULIKIDIS : Thank you. Because the corrosion rate depends on the diffusion of metal ions to metal surface, which means, that is independent of oxygen pressure. Now I have understood that Prof. Yahalom has spoken about the diffusion of oxygen to the interface.

C. CABRILLAC (France) : I would like to ask two questions. First I shall refer to the influence of the velocity and I would like to ask if in the tubes of condensers the factor velocity was studied and if you have determined the optimum velocity as a function of tube diameter? The second question which I would like to ask is on the diagram which you projected before i. e. the diagram concerning the reduction of hydrogen. You mention that the copper alloys were satisfactory, could you tell us the nature of these copper alloys. Thank you.

Prof. Dr. YAHALOM : We have not conducted any experiments so far and no dynamic experiments. This particular development is in its preliminary state and what we have conducted was only experiments to determine the rate of reaction of ethyl 2 with oxygen, in hot sea water, and also the solubility of calcium sulfate. We are now going to start series of corrosion experiments in such a set up but we have not any details, yet. For this reason I cannot tell you anything about the alloys which will be eventually used. The diagrams, which I have shown, were drawn by Dr. Prayer, and taken from his paper. They are theoretical.

HEUZÉ (France) : Can you imagine Prof. Yahalom the possibility of using concrete for the construction of tubes, in order to reduce the cost.

Prof. Dr. YAHALOM : That is of course considered and I think some more experiments should be done on the resistance of the various concretes on hot sea water but I think this is a very healthy approach. What we are most concerned about are the tubes which as I said consist about the 60 % of the cost and we want to try to reduce corrosion there.

Séance - Meeting - Sitzung - Συνεδρίαση

24.9.1968

Présidence - Presidency

Präsidium - Προεδρείον

Prof. E. MOR (Italie),

Prof. A. KALOGERAS (Grèce).

# FICHE SIGNALÉTIQUE pour PROTECTION CATHODIQUE MARINE

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## RÉSUMÉ

L'établissement de fiches signalétiques facilite l'exposé des problèmes de protection contre la corrosion et clarifie les

solutions proposées, notamment en matière de protection cathodique et de revêtement.

### 1. EXPOSÉ

Autrefois empirique et relativement méconnue, la protection cathodique est aujourd'hui une science exacte que ni le constructeur, ni l'utilisateur ne doivent ignorer.

D'une façon générale, c'est en effet au stade de la conception, c'est-à-dire du projet de construction, que se jouent la simplicité et l'efficacité des divers moyens de protéger contre la corrosion les ouvrages métalliques ou en béton armé, à savoir: protection cathodique, revêtement, nature des matériaux principaux et auxiliaires, éléments de continuité ou de séparation électrique, et même choix des formes réduisant les risques de corrosion de certaines parties de l'ouvrage ou facilitant leur protection. La coordination judicieuse de ces différents moyens d'action est la meilleure condition de réussite.

Dans son domaine d'application, la protection cathodique offre de nombreux avantages mais elle ne doit pas être considérée comme une panacée susceptible de sauver les situations les plus délicates, ni surtout de rattraper les erreurs de conception.

C'est pourquoi il est devenu courant de l'envisager dans les projets d'exécution, soit pour la réaliser d'emblée, soit pour aménager simplement l'ouvrage en vue de la mettre en œuvre facilement si elle s'avère justifiée par l'observation d'un taux de corrosion inacceptable.

Cependant, dans les appels d'offres, les problèmes de protection cathodique sont parfois posés avec trop peu de données et de précision pour que les spécialistes consultés puissent les apprécier avec justesse et, a fortiori, proposer des solutions valables à moins de faire des hypothèses qui risquent de se révéler inexactes.

Il est donc souhaitable que les demandeurs, bien que ne pouvant connaître à fond les techniques et modalités d'application de ce type de protection, fournissent sinon un cahier des charges, du moins un minimum de renseignements sur la constitution, les conditions d'exposition à la corrosion et les sujétions d'exploitation de l'ouvrage à équiper. Cela s'impose notamment en matière de génie civil.

Réciproquement, le spécialiste doit exposer sans ambiguïté les critères et les solutions qu'il préconise ainsi que les résultats escomptés tant sur le plan technique qu'économique.

A cet égard, il semble que l'utilisation de fiches signalétiques n'omettant aucun renseignement essentiel, soit de nature à favoriser la bonne compréhension mutuelle, d'une part en clarifiant les données du problème et le but recherché, d'autre part en facilitant le jugement et la comparaison des solutions en présence.

La fiche signalétique ne remplace évidemment pas un

projet d'exécution: elle n'est qu'une introduction à l'étude ou un résumé de ce projet.

L'exemple d'application consacré ici aux ouvrages maritimes en pieux ou palplanches métalliques comporte le modèle d'une fiche en blanc prête à être complétée en rattachant point par point chaque spécification à une notice exposant les principes généraux et les règles particulières adoptées.

### 2. PRINCIPES GÉNÉRAUX

#### 2.1. Dangers de corrosion

Dans les ouvrages maritimes, la corrosion des pieux et des palplanches métalliques n'est jamais uniforme, mais dépend des différents milieux environnants: sous-sol, remblais, eau salée, atmosphère. Elle se renforce là où l'air et l'eau se superposent, c'est-à-dire sur les parties soulevées au marnage, à la houle, aux éclaboussures et aux embruns.

Ailleurs, sur les parties toujours immergées, elle peut se localiser à certains niveaux par suite de phénomènes d'aération différentielle, ou de couples galvaniques dus à la juxtaposition de métaux différents.

Pour les ouvrages situés dans un estuaire, les variations permanentes de la salinité du milieu ambiant, dues à l'influence conjuguée du fleuve et de la marée, ajoutent à ces phénomènes des effets de piles de concentration pouvant augmenter dans des proportions sensibles le taux de corrosion.

Exceptionnellement, la corrosion a pour origine les bactéries sulfato-réductrices vivant dans certains fonds vaseux ou véhiculées par les eaux polluées.

L'attaque de l'acier par le soufre est alors dangereusement rapide.

S'il est bon d'avoir conscience de ces divers dangers de corrosion, il ne faut cependant ni les généraliser ni en exagérer les conséquences car l'acier leur oppose une résistance naturelle d'autant plus importante qu'il est de meilleure qualité et que son taux de travail est modéré. De plus, il peut être immunisé au besoin par protection cathodique.

L'expérience montrant d'ailleurs que la corrosion est généralement insignifiante en fiche et au contact des remblais, cette protection n'est requise, sauf exception, que pour les surfaces purement immergées; les parties enterrées en bénéficient cependant par contre-coup, du fait de la conductibilité électrique de l'ouvrage et des différents milieux ambiants.

Il faut donc tenir compte de cette dispersion et distribuer le courant de protection cathodique de façon à optimiser sa répartition sur les différentes parties à protéger.

## 2.2 Principes de la protection cathodique

Les applications de la protection cathodique et leur réussite sont aujourd'hui suffisamment connues pour qu'il n'y ait pas à justifier leur intérêt: la protection cathodique constitue une défense absolue contre la corrosion quelle qu'en soit la cause. Elle ne peut cependant s'exercer que dans un milieu ambiant conducteur et n'a donc aucun effet contre la corrosion atmosphérique: il faut toujours la compléter dans la zone de marnage et au-dessus, par un revêtement d'excellente qualité à moins que l'on puisse abaisser le couronnement en béton de l'ouvrage pour éviter ce revêtement et les sujétions d'entretien qu'il implique.

L'efficacité totale de la protection cathodique permet de réaliser des économies substantielles sur le coefficient de sécurité des parties enterrées et immergées, aussi devient-il courant de l'intégrer aux projets de construction, sinon en la réalisant d'emblée, du moins en aménageant spécialement les ouvrages pour les équiper en cas de besoin.

Le comportement des pieux et palplanches est alors jugé d'après des éprouvettes-témoins qui, examinées et pesées périodiquement, indiquent les taux de corrosion et permettent de décider ultérieurement de la protection cathodique en toute connaissance de cause.

Bien qu'il soit possible de surveiller, puis d'équiper un ouvrage existant non préparé, il est évidemment plus avantageux de prévoir les aménagements spéciaux à inclure dans la construction, en étudiant au besoin la protection cathodique sur modèle réduit, au bassin électrique.

L'immunité de l'acier est réalisée à un potentiel négatif de l'ordre de 0,85 volt par rapport au milieu ambiant, le potentiel de référence étant celui de l'électrode standard  $\text{Cu}/\text{SO}_4\text{Cu}$ ,\* mais il est d'usage de rechercher un potentiel un peu plus important, par exemple 0,90 ou 1 volt pour disposer d'une marge de sécurité.

La densité du courant électrique consommé dans ces conditions par les surfaces rendues négatives dépend essentiellement de leur dépolarisation, c'est-à-dire de l'oxygène frais diffusant à travers le milieu ambiant. Sauf exception, elle est donc beaucoup plus importante à la surface qu'au fond de l'eau, de même qu'elle atteint un minimum dans les argiles compactes et s'accroît avec la porosité des terrains ou la vitesse des courants d'eau.

Le projet de protection cathodique doit donc tenir compte de l'ambiance autant que de l'ouvrage lui-même pour distribuer aux différentes mailles de l'infrastructure les densités de courant localement nécessaires. La solution de ce problème implique une répartition appropriée des anodes engendrant le courant.

La nature des anodes à choisir dépend principalement de cette répartition et surtout de considérations économiques.

Les anodes dites «sacrifiées», en zinc ou en aluminium, qui ont détrôné celles de magnésium pour les applications maritimes, s'avèrent généralement moins coûteuses à installer, mais tout compte fait plus chères à renouveler fréquemment que les anodes à très longue durée alimentées par redresseur. Ces anodes «sacrifiées» peuvent néanmoins s'imposer si le réseau de distribution électrique fait défaut ou bien pour de petites installations demandant peu de courant ou encore lorsqu'il est suffisant de réaliser une protection cathodique très locale.

Cependant, l'énergie électrique du réseau est toujours plus avantageuse que celle d'origine électrochimique, et si l'on a le choix, on a généralement intérêt à l'utiliser pour alimenter des redresseurs fournissant le courant continu à des anodes appropriées.

Parmi celles qui résistent le mieux à l'électrolyse que tend à produire le courant qu'elles émettent, citons principalement les anodes en ferro-silicium, en titane ou tantale platiné, en plomb platine, en plomb argent, en graphite.

Certaines anodes en ferro-silicium et en titane platiné peuvent être enfilées et bloquées par des coins de cuivre sur

\* Ou 0,82 volt avec l'électrode  $\text{Ag}/\text{ClAg}$  généralement préférée en milieu marin.

un câble électrique sans coupure dont la résistance mécanique est éventuellement renforcée par une âme en acier.

Les solutions sont donc relativement nombreuses et permettent de résoudre au mieux tous les problèmes.

Quant aux redresseurs, ils sont généralement constitués de cellules fer/sélénium ou de diodes au silicium, à refroidissement naturel.

## 3. CAS PARTICULIER DE LA PROTECTION DANS LA ZONE DE MARNAGE ET AU-DESSUS

Comme il a été dit la protection cathodique ne peut se réaliser que dans un milieu ambiant conducteur et n'a aucun effet contre la corrosion atmosphérique. Elle a donc une efficacité intermittente dans la zone de marnage, mais, comme la dépolarisation n'est pas immédiate après le retrait de l'eau et que, par conséquent, l'oxydation n'a pas le temps de se produire, la protection cathodique assure une immunité suffisante à des niveaux pourtant découverts à marée basse.

En fait, le comportement des ouvrages existants montre que l'on peut compter sur la protection cathodique jusqu'à la cote moyenne des marées.

Au-dessus de cette cote, le revêtement est indispensable et ne peut être évité qu'en abaissant suffisamment le couronnement en béton, ce qui d'ailleurs est généralement la meilleure solution.

En matière de revêtement, le goudronnage habituellement pratiqué en usine n'a aucune valeur définitive: il n'assure qu'une protection temporaire pour le transport et le stockage.

Comme le goudron peut gêner par la suite l'accrochage d'un revêtement de qualité, il est recommandé de choisir le système de revêtement dès la fabrication, afin que l'application des premières couches puisse être exécutée en usine; ceci permet de préparer la surface par sablage ou grenailage dans des conditions beaucoup plus satisfaisantes et avantageuses. Il ne reste ainsi à exécuter sur le chantier que la réparation des premières couches endommagées par la manutention et à appliquer les couches de finition.

Il faut évidemment que le revêtement soit compatible avec la protection cathodique sans risquer de cloquer ou de se saponifier.

Les produits bitumineux, qu'ils soient simples, modifiés au chlorure de vinyle ou alliés aux résines époxy, et certaines peintures vinyliques par exemple font parfaitement l'affaire.

La métallisation au zinc, ou à défaut diverses peintures riches en zinc, constituent une protection des plus durables contre la corrosion atmosphérique tout en supportant parfaitement la protection cathodique dans la zone de marnage. Ce revêtement est généralement profitable jusqu'à la cote des basses mers, surtout lorsque le marnage est important, mais il est toujours inutile plus bas que cette cote car, faute de pouvoir être entretenu sous l'eau, il est inévitablement détruit un jour ou l'autre et l'installation de protection cathodique doit être prévue de toute manière pour être efficace malgré cette disparition. La rubrique F 11 de la fiche signalétique indique la décomposition et l'aire totale des surfaces à revêtir dans le cas présent.

## 4. CALCUL DU COURANT DE PROTECTION CATHODIQUE

### 4.1. Aires à protéger et densité de courant

L'évaluation des aires à protéger découle simplement de la constitution de l'ouvrage décrit au paragraphe F 3 de la fiche signalétique annexée à la présente notice.

On distingue différents types de surfaces selon la nature du milieu ambiant auquel elles sont exposées: sous-sol, immersion permanente, marnage moyen, et éventuellement houle si celle-ci est importante.

Cette décomposition est motivée par le fait que la densité du courant nécessaire à la protection cathodique dépend, comme il a été dit précédemment, de la dépolarisation par l'oxygène qui est elle-même conditionnée par le milieu ambiant.

Le revêtement éventuel pourrait jouer un rôle modérateur important, mais il n'est pas durable, à moins de dépenses prohibitives qui sont toujours injustifiées puisque la protection cathodique est autosuffisante et qu'elle est relativement peu grevée par le surcroît de courant électrique qu'entraîne l'absence du revêtement.

Sauf cas particulier, on admet donc que la protection cathodique s'applique à l'acier nu et on évalue la consommation sur la base des densités de courant qui se vérifient sur les installations de protection cathodique existantes à savoir:

- .0,04 A/m<sup>2</sup> en fiche ou en remblai
- .0,06 A/m<sup>2</sup> en immersion permanente
- .0,10 A/m<sup>2</sup> au marnage, et éventuellement à la houle.

#### 4.2 Courant utile et majorations

La détermination du courant nominal de protection cathodique figure à la rubrique F 5 de la fiche signalétique.

On calcule tout d'abord le courant total utile qui est la somme des courants partiels appropriés aux aires des différentes surfaces discriminées selon leur exposition.

S'il s'agit d'un ouvrage en palplanches, ce résultat est ensuite majoré des pertes sur les faces arrière de ces dernières.

Ces pertes sont dues aux flux de courant qui passent sous les rideaux grâce à la conductibilité électrique du sous-sol et des remblais.

Leur densité est parfois suffisante pour modifier le potentiel des parois correspondantes et exercer sur elles une certaine protection cathodique. Cette protection est inutile car en présence de fonds et d'un remblai hydraulique exempt de vase, les palplanches ne subissent de toute façon aucune corrosion dangereuse, mais elle est inévitable du fait que la propagation de ces flux de courant est liée à la conductibilité électrique des fonds marins et de l'ouvrage lui-même.

Au stade de l'avant-projet, il suffit généralement d'évaluer approximativement la majoration correspondante d'après des exemples connus.

Pour plus d'exactitude, on peut recourir à une étude analogique sur modèle réduit, au bassin électrique.

Il faut enfin remarquer que le courant total à fournir, compte tenu des pertes, est ainsi évalué en tant que ration d'entretien de la protection cathodique, mais que celle-ci ne se réalise pas immédiatement sans un surcroît de courant.

On prévoit donc une majoration supplémentaire pour obtenir rapidement l'immunité dès la mise en service ou la retrouver aisément après les arrêts qui interviennent inévitablement, ne serait-ce que pour certaines vérifications ou opérations d'entretien.

C'est ainsi que l'on aboutit finalement au courant nominal sur lequel repose toute la technologie de la protection cathodique.

## 5. CONSTITUTION DE L'EQUIPEMENT

### 5.1. Schéma électrique

La rubrique F 6 de la fiche signalétique et le plan qui s'y rapporte indiquent schématiquement la répartition du dispositif anodique et le principe des circuits leur distribuant le courant continu à partir de transformateurs - redresseurs munis d'une régulation automatique.

### 5.2 Redresseurs

Les caractéristiques des transformateurs-redresseurs sont précisées à la rubrique F 7.

Le choix du nombre de phases, du type standard ou anti-déflagrant, de la nature des éléments redresseurs, du mode de réglage et de la régulation éventuelle, découle de diverses considérations où interviennent notamment la sécurité, le rendement, la fiabilité et le prix de revient.

Un dispositif de régulation agissant sur la tension d'alimentation des redresseurs est indispensable pour faire face aux modifications permanentes de la résistance électrique du

circuit, dues aux variations de salinité de l'eau dans le cas d'un estuaire.

Comme il se base sur le potentiel de l'ouvrage, (garantie de l'efficacité de la protection cathodique), il règle également le débit des redresseurs en fonction des besoins réels qui dépendent de l'agitation de l'eau, du niveau de la marée et de la force des courants marins.

La protection est ainsi assurée en permanence, mais sans excès qui conduirait à une dépense inutile.

Les transformateurs-redresseurs sont généralement installés dans les bâtiments existants, ou dans des abris extérieurs, ou en chambres souterraines, ce qui nécessite des systèmes de refroidissement appropriés.

Quand l'évacuation des calories est problématique, on peut recourir au refroidissement naturel par l'eau de mer, en immergeant les transformateurs-redresseurs qui sont alors gainés d'une enveloppe étanche appropriée.

### 5.3. Dispositif anodique

Si l'on peut rendre l'ouvrage pratiquement équipotentiel moyennant les précautions spéciales exposées au paragraphe suivant, il n'en va pas de même du milieu conducteur environnant car la hauteur de l'eau de mer est insuffisante par rapport à la longueur de l'ouvrage pour que sa résistance électrique puisse être négligée.

Les fonds n'apportent aucune amélioration car ils sont spécifiquement beaucoup moins conducteurs. Autrement dit, la propagation du courant de protection cathodique entre le dispositif anodique et l'ouvrage subit des chutes de tension qui peuvent conduire à une inégalité des potentiels réalisés sur les surfaces à protéger.

Il faut donc répartir les anodes de façon à limiter ces chutes de tension et à obtenir dans toute la mesure du possible une distribution de courant uniforme, d'où la spécification de la rubrique F 9.

La nature des anodes est choisie en considérant principalement leur robustesse, leur résistance éventuelle à l'érosion et, dans une certaine mesure, la longévité que l'on en attend avant d'avoir à les renouveler.

Leur forme et leurs dimensions dépendent des mêmes facteurs et aussi d'un rapport optimum ou maximum admissible courant/surface.

La tension maximale de fonctionnement évaluée en tant que potentiel d'électrode est également limitative, par exemple dans le cas du titane platiné.

Le nombre total d'anodes est calculé pour le débit nominal des redresseurs, mais en fait elles fonctionneront la plupart du temps au débit d'entretien qui est nettement inférieur et cela leur confère une marge de sécurité appréciable.

### 5.4 Continuité électrique

Dans ce qui précède, l'ouvrage est supposé équipotentiel, ce qui est une hypothèse nécessaire en dehors de laquelle les solutions de protection cathodique et de régulation seraient infiniment complexes.

Or, bien que les palplanches soient en contact métallique les unes avec les autres, les rideaux existants ne s'avèrent pas suffisamment conducteurs du fait de la multiplicité des serrures. Il faut donc améliorer leur continuité électrique et il suffit pour cela de souder en tête des palplanches ou sur les agrafes un fer filant de 100 x 10 mm.

Au passage de chaque gabion un fer de même section remonte verticalement jusqu'à la plate-forme pour y recevoir la connexion du circuit négatif de la protection cathodique.

S'il existe un couronnement en béton, il est parfois avantageux d'utiliser ses armatures pour assurer ou renforcer la continuité électrique.

La marche à suivre est précisée à la rubrique F 4 de la fiche signalétique.

### 5.5. Consommation d'énergie électrique

L'optimisation des circuits de distribution de la protection

cathodique réalisée avec ce type d'anode, c'est-à-dire notamment l'espacement des redresseurs et la section des câbles de distribution, conduit généralement à une tension de l'ordre de 8 volts au départ des redresseurs.

La consommation annuelle est évaluée pour la ration moyenne d'entretien de la protection cathodique qui correspond approximativement aux 2/3 de la puissance nominale. Ceci conduit au calcul de la rubrique F 10.

## 6. DISPOSITIFS DE CONTROLE ET DE REGULATION

On sait que l'efficacité de la protection cathodique est une question de potentiel de l'acier par rapport au milieu avec lequel il est en contact: eau de mer, fond sableux et éventuellement remblai.

Elle est certaine lorsque la valeur de ce potentiel qui est bien entendu négatif, atteint au moins 0,85 volt par rapport à l'électrode de référence standard Cu/SO<sub>4</sub>Cu.

En général, on cherche à atteindre de préférence 1 volt pour disposer d'une marge de sécurité suffisamment large.

Pour vérifier l'efficacité obtenue, on peut donc installer à poste fixe des voltmètres permettant de mesurer instantanément le potentiel de l'acier ou tout au moins une valeur globale représentative autorisant à conclure que le potentiel réel est suffisant en tout point de l'ouvrage considéré.

Le voltmètre de contrôle est donc installé à demeure dans un coffret étanche. Il est connecté entre la masse de l'ouvrage métallique et une ou plusieurs électrodes de référence dont la nature et l'emplacement doivent être déterminés dans l'étude du projet.

En milieu marin, on utilise couramment des électrodes de zinc pur ou des cellules du type Ag/ClAg.

Le potentiel effectif de protection cathodique ainsi mesuré peut être utilisé pour régler automatiquement le courant débité par les anodes.

Les dispositifs de régulation classiques sont constitués de transducteurs, de thyristors, d'autotransformateurs à curseur ou même, tout simplement, de contacteurs pouvant régler par tout ou rien le débit des anodes à son maximum, à zéro, ou à un niveau intermédiaire, selon les exigences de l'ouvrage protégé.

La surveillance du potentiel et la régulation automatique qu'elle autorise, sont toujours souhaitables pour les ouvrages de quelque importance.

À plus longue échéance, l'efficacité de la protection cathodique peut, en outre, être observée d'après l'état de surface d'éprouvettes-témoins.

## 7. TEMOINS DE CORROSION

Les éprouvettes-témoins sont des plaquettes ou des cylindres d'acier, usinés de préférence dans les chutes du métal entrant dans la construction des ouvrages.

Il ne faut pas les polir: il faut et il suffit qu'elles présentent initialement un bon état de surface correspondant à une potée 00.

Avant leur mise en place, elles sont pesées au milligramme près, puis montées sur des supports spéciaux qui sont fixés verticalement le long de certaines palplanches.

Etant disposées, par exemple de mètre en mètre, sur toute la hauteur de l'ouvrage, ces éprouvettes-témoins permettent de suivre l'évolution de la corrosion.

Elles sont récupérées après 2 ou 3 ans d'exposition, puis pesées.

Leur état de surface et leur perte de poids permettent de juger en toute connaissance de cause si la protection cathodique est nécessaire.

Dans le cas où cette protection est réalisée, les mêmes éprouvettes-témoins permettent de vérifier son efficacité car alors, elles ne doivent subir aucune corrosion supplémentaire.

L'exécution, le montage et la répartition de ces témoins peuvent être effectués suivant la rubrique F 12 de la fiche signalétique.

## 8. CONCLUSION

La protection cathodique est à même d'éliminer totalement les dangers de corrosion des parties immergées sans nécessiter le moindre revêtement complémentaire.

Par contre, seul un revêtement de qualité peut exercer une protection efficace contre la corrosion atmosphérique au-dessus du niveau moyen des marées, et pour éviter les sujétions d'entretien des peintures, la meilleure solution consiste à munir les palplanches d'un couronnement de béton s'abaissant jusqu'à ce niveau.

Le problème de la corrosion étant ainsi résolu, la fiabilité de cette construction métallique sera en tout point satisfaisante, comme en font preuve les ouvrages similaires dont le comportement, excellent après 10 à 20 ans d'existence, promet une sécurité totale pour de très nombreuses années.

Référence

Date

FICHE SIGNALÉTIQUE pour  
PROTECTION CATHODIQUE  
ÉTUDE d'AVANT-PROJET

F 1) — Client:

F 2) — Désignation de l'ouvrage:

F 3) — Constitution de l'ouvrage:

- longueur totale:
- structure uniforme ou mixte:
- pieux tubulaires acier:  $\Phi$
- palpieux:
- palplanches en gabions:  $\Phi$ ; nombre:
- avec ou sans voiles de raccordement:
- rideau droit palplanches Larssen: type
- longueurs extrêmes des pieux ou palplanches:
- résistivité ambiante ohm-mètre:
- particularités:

F 4) — *Continuité électrique :*

- existe par construction :
- à établir au moyen de :

F 5) — *Courant de protection cathodique*

Aires des surfaces métalliques	Densité de courant	Courant partiel
	$m^2 \times A/m^2 =$	A
En fiche	0,04	
Immersion permanente	0,06	
Marnage	0,10	
Houle	0,10	

Courant total utile.....  
 % pertes sur faces AR .....

Courant total à fournir .....

% de surcharge transitoire .....

Courant nominal de l'équipement .....

F 6) — *Schéma électrique de la protection cathodique, cf. plan de principe*

F 7) — *Transfos - Redresseurs :*

- nombre :
- caractéristiques nominales :
- alimentation mono - triphasé volts Hz
- type standard - antidéflagrant
- cellules Fe-Sé - diodes silicium
- réglage par barrettes - commutateurs
- régulation automatique, commandée par :
  - le potentiel effectif de protection cathodique,
  - le courant,
  - technique utilisée: transducteur, thyristor, régulateur à curseur, contacteurs, autre technique.
- particularités

F 8) — *Electrodes de référence*

- nature : zinc, Ag/ClAg, autre :
- plan de construction et de montage :
- nombre :

F 9) — *Anodes :*

- nature :
- poids unitaire :
- plan de construction et de montage :
- intervalle :
- nombre total :
- position verticale - horizontale :
- câble porte-anodes conventionnel :
- câble porte-anodes spécial :
- mode de fixation du câble :
- durée escomptée avant renouvellement :

F 10) — *Consommation annuelle d'électricité :*

- Valeurs moyennes, en régime permanent  
 — puissance fournie au départ des redresseurs : kw  
 — puissance absorbée sur le réseau : kw  
 — consommation annuelle (8.750 heures) : kwh

F 11) — *Aires des surfaces à revêtir :*

1/2 zone de marnage	
— côtes à	: m <sup>2</sup>
— houle et atmosphère	: m <sup>2</sup>
<hr/>	
Total des aires à revêtir	m <sup>2</sup>
Observations sur le revêtement	

F 12) — *Témoins de corrosion :*

- nature :
- plan de construction et de montage :
- nombre de règles verticales :
- nombre de témoins par règle :
- nombre total de témoins :
- délai des observations :

DISCUSSION

Dr. POSCH (Pays-Bas) : Est-ce que vous avez utilisé des courants continus ou des courants alternatifs pour les études modélisées ?

B. HEUZÉ : Nous utilisons toujours du courant continu pour représenter le mieux possible la réalité.

En effet, s'il est exact que le courant électrique suit les lois d'OHM et de LAPLACE, il ne faut pas oublier que le potentiel de la polarisation cathodique a souvent une incidence considérable sur l'atténuation et, par conséquent la propagation du courant dans l'électrolyte.

Plutôt que d'éliminer cette incidence, dans le cas où l'analogie est difficile à respecter, nous préférons modifier convenablement d'autres paramètres: si par exemple le modèle réduit est à l'échelle 1/50 et si la résistivité réelle est de 10 ohms-mètre, il faudrait maintenir autour du modèle un électrolyte de 500 ohms-mètre. Ceci n'est pas impossible, mais peut présenter certaines difficultés.

Or, il est parfaitement correct d'utiliser pour le modèle réduit une résistivité plus faible, à condition d'augmenter proportionnellement les densités de courant.

Le modèle réduit est un instrument de travail qui permet précisément ce genre de transposition et en utilisant le courant continu on ne perd pas de vue l'influence de la polarisation.

J.A.H. CARSON (Canada) : Je m'étonne que les armatures dans les structures en béton précontraint soient reliées métalliquement. Est-ce que vous pouvez me fournir des précisions quant au gradient minimum de potentiel qui conduira à la corrosion des armatures dans un ouvrage en béton armé situé dans un champ de courants vagabonds ?

B. HEUZÉ : Dans les structures en béton précontraint il faut évidemment comme dans tous les autres cas de protection cathodique, éviter les différences de potentiel intrinsèques et il est donc toujours recommandable de relier métalliquement toutes les armatures.

Lorsque cela est possible, il est intéressant d'utiliser comme armature du treillis soudé, afin de réduire les travaux de soudure à effectuer sur le chantier.

Cependant, dans le cas général, il n'est pas indispensable de souder toutes les armatures entre elles car les ligatures assurent par elles-mêmes une certaine continuité métallique: il suffit alors de souder un quadrillage d'armatures suivant une loi déterminée pour obtenir une interconnexion suffisante.

Nous avons eu l'exemple d'ouvrages en béton armé dans lesquels les armatures n'étaient pas d'une qualité soudable. Pour les besoins de la protection cathodique, il a fallu leur superposer un maillage d'acier soudable et relier ces armatures par des nombreuses ligatures.

Tout ceci doit être évidemment étudié dans chaque cas particulier, compte tenu d'une densité de courant qui est relativement faible dans le béton puisqu'elle dépasse rarement un mA/m<sup>2</sup>.

Ceci me conduit à souligner qu'il est toujours bon d'étudier les projets de protection cathodique avant construction afin de pouvoir imposer les aménagements et parfois même le type de ferrailage.

En ce qui concerne les différences de potentiel tolérables dans le béton précontraint, il faut évidemment être extrêmement pondéré car l'acier sous tension mécanique est plus susceptible de se corroder et parce que la masse spécifique d'acier qui peut être détruite sans compromettre la structure est beaucoup plus faible dans le béton précontraint que dans le béton armé.

Néanmoins, dans les conduites terrestres ou sous-marines en béton précontraint, nous admettrons couramment des différences de potentiel de 50 mV sur des longueurs de plusieurs mètres.

Ces différences de potentiel n'apparaissent donc pas entre les armatures voisines: elles résultent de l'atténuation et non pas de la discontinuité électrique.

Lorsque cette atténuation est progressive, on peut tolérer, sans inconvénient, 100 mV pourvu que cela ne nuise pas à l'efficacité de la protection cathodique.

Dans le domaine des potentiels anodiques sous l'influence d'un champ électrique extérieur, par exemple dans le cas de courants vagabonds, l'élévation de potentiel admissible dépend essentiellement de la qualité du béton.

En présence d'un bon béton de couverture très faiblement perméable à l'air et à l'eau, cette élévation peut atteindre plus de 200 mV sans aucun risque à partir d'un potentiel d'électrode compris couramment entre 0 et -100 mV par rapport à l'électrode standard au sulfate de cuivre.

Dr. ANTONIOU (Grèce) : Est-il possible de réaliser une protection cathodique lorsque les potentiels électriques des ouvrages à protéger sont perpétuellement modifiés par des courants vagabonds comme c'est le cas par exemple dans certains chantiers navals ?

B. HEUZÉ : La protection cathodique a généralement des possibilités limitées et il est bien entendu que si les courants de soudure se chiffrent par milliers d'ampères, avec des potentiels de plusieurs volts ou même de dizaine de volts, elle sera incapable de les maîtriser à moins d'envelopper complètement la structure à protéger avec un dispositif anodique.

Cette enveloppe anodique, qui est d'ailleurs brevetée, ne s'applique cependant qu'à des cas particuliers et dans l'exemple des courants vagabonds en question, la première chose à faire est d'assainir la situation par une conception et une surveillance appropriées de façon à réduire les perturbations provoquées par ces courants vagabonds. C'est un problème lié aux chutes de tension dans les installations de soudage et par conséquent aux calibres des connexions, aux mises à la terre de sécurité ou intempêtes, etc.

Il n'y a aucune raison pour que la protection cathodique ne puisse être normalement réalisée après cet assainissement.



# EINFLUSS DER OFFENEN POROSITÄT AUF DIE BESTÄNDIGKEIT VON MÖRTELN UND BETONEN GEGEN AGGRESSIVE LÖSUNGEN

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## ZUSAMMENFASSUNG

1. Anhand von graphischen Darstellungen wird der Einfluss der offenen Porosität — gemessen mit Hilfe der Gasdurchlässigkeit — auf die Beständigkeit von Mörteln gegen den Angriff sulfathaltiger Lösungen aufgezeigt. Dabei wirkt sich erwartungsgemäss eine geringe Gasdurchlässigkeit günstig aus.

2. Als Ursache geringerer Aggressivbeständigkeit ist die Bildung von ettringitähnlichen Phasen, Gips und Brucit zu nennen.

3. Die Ursache der Sulfatbeständigkeit von  $C_2A$ -freien Portlandzementen liegt zunächst in der geringen Hydrata-

tionsgeschwindigkeit der eisenoxidreichen Calciumaluminatferrite, die von hütten sandreichen Hochfenzementen in dem geringeren Kalkangebot. Bei beiden Zementarten muss jedoch die Tatsache Berücksichtigung finden, dass nicht nur Sulfationen in den Mörtel eindiffundieren, sondern in gleicher Weise Calcium- und Hydroxylionen aus dem Zementstein des Mörtels herausdiffundieren, so dass schliesslich — wie beim Sulfathüttenzement — die zur Bildung des treibend wirkenden Ettringites erforderliche Calcium- und Hydroxylionenkonzentration nicht mehr vorhanden ist.

## 1. EINLEITUNG

Neben der chemischen und mineralogischen Zusammensetzung des Zementsteines in Mörteln und Betonen ist die offene Porosität für die chemische Widerstandsfähigkeit und beständigkeit, für die Festigkeiten und die Wärmeleitfähigkeit von besonderer Bedeutung.

Unter der Beständigkeit soll insbesondere die Widerstandsfähigkeit gegen angreifende Flüssigkeiten und Gase sowie gegen wechselnde Temperatur- und Witterungseinflüsse verstanden werden.

Für die Widerstandsfähigkeit gegen aggressive Lösungen und Gase sind die Poren, die von Flüssigkeiten oder Gasen durchdrungen oder durchströmt werden können, von besonderer Bedeutung.

Auf die Messung und Beurteilung der offenen Porosität kann hier leider nicht eingegangen werden. Es wird auf die bereits erschienenen Veröffentlichungen verwiesen (1, 2, 3, 4).

## 2. EINFLUSS DER OFFENEN POROSITÄT AUF DIE BESTÄNDIGKEIT VON MÖRTELN UND BETONEN GEGEN AGGRESSIVE LÖSUNGEN

### 2.1. Methoden der Aggressivbeständigkeitsuntersuchung

Zur Beurteilung der Aggressivbeständigkeit werden sowohl Untersuchungen an Purzementen als auch an Mörteln oder Betonen durchgeführt. Einen Überblick über die bekannten Verfahren gibt die Tabelle 1, aus der auch die entsprechenden Literaturstellen zu entnehmen sind. Bei den einzelnen Versuchsverfahren wird zwischen Prüfungen an Betonkörpern, an Mörtelprismen sowie an Zementsuspensionen unterschieden. Die unter 4. angegebenen Untersuchungen werden an hydratisierten Purzementen durchgeführt. Die Dauer der verschiedenen erforderlichen Prüfzeiten liegt zwischen 3 Stunden und 60 Jahren. Daraus folgt, dass neben Langzeitversuchen Prüfverfahren entwickelt wurden, die nach kurzen Prüfzeiten Aussagen über die Aggressivbeständigkeiten der untersuchten Zemente gestatten sollen.

Ein genormtes Verfahren liegt bisher nicht vor. Es werden in Deutschland sowohl Laborversuche an Mörtelprüfkörpern als auch Langzeitversuche an Betonprüfkörpern durchgeführt.

Eine Zusammenstellung der am Institut für Gesteinskundetechnik angewendeten Untersuchungsverfahren zur Bestimmung der Aggressivbeständigkeit von Mörteln zeigt die Tabelle 2. Es wurden Untersuchungen an Kleinprismen  $1 \times 1 \times 6$  cm, an Flachprismen  $1 \times 4 \times 16$  cm, an Normenprismen  $4 \times 4 \times 16$  cm und an Prismen der Abmessungen  $5 \times 5 \times 25$  cm durchgeführt.

Das Kleinprismenverfahren wurde in Anlehnung an das Verfahren von Koch- und Steinegger angewendet. Dabei wurde auf ein Nachtitrieren mit  $2n-H_2SO_4$  verzichtet, da nach unserer Ansicht die Zemente mit unterschiedlicher Kalk- oder Alkaliabspaltung bei der Hydratation verschiedenen Sulfatkonzentrationen ausgesetzt werden. Aufgrund der grossen Bedeutung der Vorlagerung und der Dichtigkeit sind die Werte für die durchströmbare Porosität bei Beginn der Aggressivlagerung mit in die Tabelle aufgenommen worden, wobei das Verfahren der Gasdurchlässigkeit angewendet wurde, mit dem die Poren  $> 0,1 \mu m$  erfasst werden.

Als Aggressivlösungen wurden vor allem Sulfatlösungen verwendet, daneben Natriumformiat- und Essigsäurelösungen. Die Dauer der Aggressivlagerung lag zwischen 17 und 72 Wochen. Die Beurteilung erfolgte bei den Kleinprismen nach der relativen Biegezugfestigkeit, die sich aus dem Quotienten aus Biegezugfestigkeit bei Sulfatlagerung und Biegezugfestigkeit bei Wasserlagerung errechnet. Die Prüfkörper wurden anschliessend bei 20 bis 30°C getrocknet, im Mörser zerkleinert und durch Absieben des Quarzsandes der Bindemittelanteil angereichert. In den angereicherten Bindemittelanteil wurden infrarotspektroskopisch die Gips- und Ettringitgehalte ermittelt.

Bei den  $1 \times 4 \times 16$  cm Flachprismen wurden sowohl die Änderung der Resonanzfrequenz als auch die lineare Ausdehnung zur Beurteilung herangezogen.

Die  $4 \times 4 \times 16$  cm Normenprismen wurden nach der

TABELLE 1  
 UNTERSUCHUNGSVERFAHREN ZUR BESTIMMUNG DER AGGRESSIVBESTÄNDIGKEIT

1 Betonprüfkörper 1.1. Feldversuch										
Verfahren	Prüfkörper (cm)	Zuschlag	Zementanteil Mischungsverh.	W/Z	Verlager. Ig	Aggr. Medium	Lagerungsart	Prüfdauer	Beurteilung	Literatur
Portl. Cement Association	Würfel, Platte, Balken	verschieden	220, 300, 390 kg Zement je m <sup>3</sup>	verschieden	n.b.	Aggr. Böden, künstlich herg. aggr. Lsg.	halbgetaucht bzw. vollst. in aggr. Böden	60 Jahre	Jahrl. Beurteilung n. Augenschein	J. Americ. Concr. Inst., 1953 March, S. 601
Dtsch. Aussch. für Stahlbeton	Würfel	Weserkies-sand 0-30mm	1,5, 1,4, 1,3	0,66 0,56 0,44	2	Seewasser	im Seehafen (Durch Gezeiten teilw. trockenleg.)	19 Jahre	Druckfestigkeit	Edvard, A. Kronsbein, W. D. Aussch. f. Stahlb. 1950, H. 102
1. Betonprüfkörper 1.2. Laborversuche										
Ungarisches	4 x 4 x 16	Donaukies-sandmauerm.	250 kg/m <sup>3</sup>	0,8	7	Mg-u. Na <sub>2</sub> SO <sub>4</sub> -Lsg. n/2100 b/12500 i Lsg.	In der Lösung	1 Jahr	Festigkeit	Bizák I. Betonkorrosion-Beton-schutz Verl. f. Bauw. Berlin, 1950/5. 98
2. Zementmörtelprüfkörper 2.1. Mittlere Prüfkörpergröße										
Arbeitskr.-Sulfatbeständigkeit	Prismen 4 x 4 x 16	NS	1:4	0,7	28	0,15m MgSO <sub>4</sub> -Lsg.	In der Lösung	10 Monate	Relat. Biegezugf. n. 9Mon. Sulfatlagerung	Nicht veröffentlicht
Ausdehnung n. Miller u. Snyder	Prismen	Ottawasand	1:5	n.b.	7	2%-ige Na <sub>2</sub> SO <sub>4</sub> -Lsg.	In der Lösung	35 Tage	Längenänderung	D.G. Miller u. C.G. Snyder, Proc. Amer. Soc. Test. Mat. 45 (1945), 165-194
Ausdehnung n. Wolachow	Prismen 254 x 254 x 254	Ottawasand	1:4	n.b.	7	5%-ige Na <sub>2</sub> SO <sub>4</sub> -Lsg.	Senkrecht i. d. Lösung	35 Tage	Längenänderung	Wolachow, D. Proc. Amer. Soc. Test. Mat. 45 (1945), 250-266
Ausdehnung ASTM C62-601	Prismen	NS	1:2,75	0,53	7	Zement-Gips-Misch SO <sub>4</sub> gesamt: 70%	In Wasser	-3 Monate	Längenänderung	Bull. Amer. Soc. Test. Mat. Nr. 273 (1956), 37-44
E-Modul-Messungen	5 x 5 x 25	n.b.	1:5	n.b.	n.b.	10%-ige Sulfatlösung	In der Lösung	3 Monate	Änderung d. E-Moduls	Hornbrook, F.B. Am. Soc. Test. Mat. Bull. (1939), 12
Vorschlag 1) Wittekindt	Prismen 1 x 4 x 16	NS	1:3	0,6	7	0,15m Na <sub>2</sub> SO <sub>4</sub> -Lsg.	Hochkant auf Fläche 1 x 16 cm in der Lösung	Monate	Nach Augenschein Längenänderung	Wittekindt, W. ZKG 12 (1960), 571
2) Dyckerhoff	Prismen 1 x 4 x 16	NS	1:3	0,6	21	n.b.	In der Lösung	Monate	Nach Augenschein Längenänderung	Nicht veröffentlicht
2. Zementmörtelprüfkörper 2.2. Kleinprüfkörper										
Koch und Steinegger	Prismen 1 x 1 x 6	NS	1:3	0,6	21	10%-ige Na <sub>2</sub> SO <sub>4</sub> -Lösung	In der Lösung	77 Tage	Relat. Biegezugfestigk.	Koch A. Steinegger, H. ZKG Nr. 7 (1960), 5317-324
GOST und ČSN	Prismen 1 x 1 x 3	NS	1:3,5	n.b.	14 bzw. 28	0,2-10%-ige MgSO <sub>4</sub> -Lösung	In der Lösung	6 Monate	Relat. Zugfestigkeit	GOST 4798-49 ČSN 732-023
3. Suspensionen										
Flockenbildung n. Paul	Wasser-Zement-Suspension	-	-	100	-	-	-	8 Tage	Loslichkeit	D.G. Miller u. C.G. Snyder, Proc. Amer. Soc. Test. Mat. 45 (1945), 165-194
Zuckerloslichk. nach Merriman	Zuckerlösung-Zement-Suspension	-	-	ca. 6	-	-	-	3 h	Loslichkeit des C <sub>3</sub> A	Rock Products 41 (1938), Jan. S. 86-88
Sulfatempfindl. n. Taylor, Bogue	Zement-Sand-Walkwasser-Suspension	-	-	-	-	-	-	1-2 Tage	Gebund. SO <sub>4</sub> in % bezogen auf Gesamt-SO <sub>4</sub> -Gehalt	Taylor, W.C. u. Bogue, R.H. J. Res. Nat. Bur. Stand., 45 (1950), 223
4. Weitere Verfahren										
n. Anstett	Zylinder d=8, h=3	-	hydr. Zement-Gips = 100:50	0,06	1	Gips	Auf feuchtem Filterpapier	28 Tage	Volumenänderung	Blondiau, L. Tonind-Zig 59 (1935), 571-73
n. Anstett - Le Chatelier	Le Chatelier-Ring	-	hydr. Zement-Gips = 100:50	Normerstein	1	Gips	In Wasser	28 Tage	Volumenänderung	Lieber, W., Bleher, K. ZKG, Nr. 7 (1960), 312
nach Merriman	Platte 5-10	-	Purzement	0,43	2	10%-ige Na <sub>2</sub> SO <sub>4</sub> -Lsg.	Halbgetaucht in die Lösung	28 Tage	Nach Augenschein	D.G. Miller u. C.G. Snyder, Proc. Amer. Soc. Test. Mat. 45 (1945), 165-194

Entwicklung der Druck- und Biegezugfestigkeiten beurteilt. Gleichzeitig wurden Kern und Randzone der Prismen mit Hilfe der Röntgenfluoreszenzanalyse auf ihre chemische Zusammensetzung und der angereicherte Bindemittelanteil dieser Zone auf die mineralogische Zusammensetzung untersucht. Das Verhalten der unterschiedlich dichten 5 x 5 x 25 cm Prismen gegenüber der Magnesiumsulfatlösung wurde durch Messungen der Resonanzfrequenz verfolgt. Zur Klärung der Zerstörungsursache wurden die angereicherten Bindemittelanteile röntgenographisch und die Mörtelbruchstücke lichtmikroskopisch untersucht.

Wie der Tabelle 2 weiter zu entnehmen war, wurden die Untersuchungen der Aggressivbeständigkeit unter anderem an Mörtelprismen mit hüttensandreicherem Hochofenzement sowie C<sub>3</sub>A-armen Portlandzement durchgeführt.

### 2.2. Aggressivbeständige Zemente

Die chemische Zusammensetzung von aggressivbeständigen Zementen sowie deren mineralogische Zusammensetzungen zeigt die Tabelle 3. Die C<sub>3</sub>A-armen bzw. die C<sub>3</sub>A-freien Zemente sind durch einen niedrigen Tonerdemodul gekennzeichnet.

Bei den Hüttenzementen mit Hüttensandgehalten > 70% fallen die hohen Kieselsäure- und Tonerdegehalte sowie die relativ geringen Kalkgehalte auf. Ähnlich ist die chemische Zusammensetzung der Sulfathüttenzemente.

Völlig anders dagegen ist die Zusammensetzung des Tonerdeschmelzementes. Die Tonerde- und die Kalkgehalte machen mit jeweils etwa 40% den wesentlichen Anteil dieser Zemente aus.

Bekanntlich wird die Sulfatbeständigkeit von Portlandzementen überwiegend durch den Anteil an Tricalciumaluminat herabgesetzt. Die wird in der amerikanischen ASTM-Norm C 150-63 dadurch berücksichtigt, dass der C<sub>3</sub>A-Gehalt von Zementen mittlerer Sulfatbeständigkeit den Wert von 8% und bei Zementen mit hoher Sulfatbeständigkeit den Wert von 5% nicht überschreiten darf. Bei der Bestimmung des C<sub>3</sub>A-Gehaltes muss darauf hingewiesen werden, dass die übliche Berechnungsweise nach Bogue nicht immer der wahren Zusammensetzung entspricht. Besser ist die Bestimmung des C<sub>3</sub>A-Gehaltes röntgenographisch mit Hilfe des Counting-Rate-Computers oder mit Hilfe mikroskopischer Untersuchungsverfahren<sup>2</sup>. Das C<sub>4</sub>AF als Mischkristallglied der Calciumaluminatferrite ist insbesondere bei der Hydratation zu

TABELLE 2  
 UNTERSUCHUNGSVERFAHREN ZUR BESTIMMUNG DER AGGRESSIVBESTÄNDIGKEIT

Prüfkörperabmessungen [cm]	Verwendete Zemente	Mischungsverhältnis	Verw. Prüf-sand	W/Z	Vor-lager. Dauer [Tg.]	Durchström-bare Poros. z. Beginn d. Aggrlg. [pPm]	Aggressivlösg.	Konzentration	Aggress. Lager. [Tage]	Beurteilung
1x1x6 <sup>1)</sup>	PZ, HOZ, Spezialzem.	1:3	DIN 1164	0,6	21	n. b.	Na <sub>2</sub> SO <sub>4</sub> , MgSO <sub>4</sub>	0,3m	14,28,56, 90,180	rel. Biegezugfestgk. Infrarotspektroskop. Unters.
1x4 x 16	PZ, EPZ HOZ, Tr. Z	1:3 1:4,5 1:6	Ritem-Cem	0,5 und 0,6	14	1-3 30-16000 3-95 · 10 <sup>3</sup>	Na <sub>2</sub> SO <sub>4</sub> , MgSO <sub>4</sub>	0,3m	7,14,21,28, 35,42,49,63 77,91,105	Resonanzfrequ. lineare Ausdehnung
4x4x16	HOZ Spezialzem.	1:4	Ritem-Cem	0,6	28	0,5-0,8	Na <sub>2</sub> SO <sub>4</sub> , MgSO <sub>4</sub> , Na-Formial, Essigsäure, Ca-Sulf.(ges.)	0,15m	2,4,12,24, 36,48,72 Wochen	rel. Druckf. u. Biegezugfestigkeit Röntgenograph. u. chem. Unters.
4x4x16	HOZ mit abgest. Klinkerant.	1:4	DIN 1164	0,6	28	0,1-7,9	Na <sub>2</sub> SO <sub>4</sub>	0,15m	2,4,12,24, 36,48,72 Wochen	Druck- u. Biegezugfestigkeit Resonanzfrequ. Röntgenograph. u. chem. Unters.
5x5x25	PZ, HOZ Spezialzem.	1:4 <sup>2)</sup>	DIN 1164	0,4... ...7 <sup>3)</sup>	28	0,55-18000	MgSO <sub>4</sub>	0,15m	342	Resonanzfrequ. Röntgenograph. u. lichtmikroskop. Unters.

1) In Anlehnung an Verf. v. Koch u. Steinegger

2) NS.I : NS.II = 0:4 bis 2:2 (zur Erzielung unterschiedl. Porositäten)

3) gleiche Verarbeitbarkeiten

den sogenannten Hydrogranaten unter zusätzlichem Einbau von Kieselsäure gegenüber sulfathaltigen Lösungen beständig, wie von Schwiete und Iwai experimentell nachgewiesen werden konnte<sup>9</sup>.

Die Calciumsilicate sind gegenüber Sulfatangriff am wenigsten empfindlich. Von den beiden im Portlandzementklinker auftretenden Calciumsilicaten wird das C<sub>2</sub>S schneller angegriffen als das C<sub>3</sub>S, doch wirkt sich die höhere Anfangsfestigkeit der C<sub>3</sub>S-reichen Zemente günstig aus. Bei den klinkerarmen Hochofenzementen, den Sulfathüttenzementen und den Tonerdezementen wirkt sich der geringere Kalkgehalt dieser Zemente günstig auf die Sulfatbeständigkeit aus, da hier ein Ettringitreiben wegen der etwas geringeren pH-Werte nicht zu erwarten ist.

### 2.3. Sulfatbeständigkeit von Normenzementen in Abhängigkeit von der Gasdurchlässigkeit

#### 2.3.1. Normale Normenzemente

Sehr deutlich zeigt sich der Einfluss der Dichtigkeit auf die Sulfatbeständigkeit beurteilt durch die Resonanzfrequenz und die lineare Ausdehnung von 1 x 4 x 16 cm Flachprismen aus der Abb. 1. Für diese Untersuchungen wurde ein normaler

Hochofenzement 375 mit 40% Hüttsand verwendet. Zur Erzielung unterschiedlicher Porositäten wurden Mischungsverhältnisse von 1:3, 1:4, 5 und 1:6 bei W/Z-Faktoren von 0,5 und 0,6 gewählt. Die Sulfatlösung bestand aus 0,15 m Na<sub>2</sub>SO<sub>4</sub> und 0,15 m MgSO<sub>4</sub>-Lösung. Aus der Abbildung erkennt man das spiegelbildliche Verhalten der linearen Ausdehnung und des Abfalles der Resonanzfrequenz. Daraus folgt, dass beide Verfahren gleich gut für eine Beurteilung der Aggressiveinwirkung geeignet sind.

Die Abb. 2 zeigt das Ergebnis, wenn man die Gasdurchlässigkeit nach 14 Tagen Vorlagerungsdauer direkt über der Sulfatlagerungsdauer aufträgt, nach welcher 10% der maximalen Resonanzfrequenz unterschritten bzw. 3 mm/m linearer Ausdehnung überschritten wurden. Wir erkennen eine eindeutige Beziehung zwischen der Gasdurchlässigkeit und der Sulfateinwirkung auf die Mörtelprüfkörper.

Unter den gleichen Bedingungen wie der eben genannte HOZ 375 wurden noch 6 weitere normale Normenzemente untersucht und es zeigt sich, dass auch diese Zemente in Abhängigkeit von ihrer Porosität im Bereich bis zu 110 Tagen Sulfatlagerungsdauer 10% der maximalen Resonanzfrequenz unterschritten bzw. 3 mm/m linearer Ausdehnung überschritten hatten (Abb. 3).

TABELLE 3  
CHEMISCHE UND MINERALOGISCHE ZUSAMMENSETZUNG VON ZEMENTEN MIT ERHÖHTER  
SULFATBESTÄNDIGKEIT

	PZ C <sub>3</sub> A-arm bzw. frei [%]	HOZ (>70% HÜS) [%]	SHZ [%]	TZ [%]
SiO <sub>2</sub>	20 - 21	26 - 29	23 - 26	3 - 11
Al <sub>2</sub> O <sub>3</sub>	2,5- 4	10 - 14	12 - 15	35 - 44
Fe <sub>2</sub> O <sub>3</sub>	6,5- 7,5	0,5- 0,7	-	4 - 12
FeO	-	0,8- 1	0 - 1	0 - 10
MnO	-	0,2- 1,5	0,4- 1,4	-
CaO	63 - 65	46 - 52	42 - 46	35 - 44
MgO	2 - 3	0,5- 6	3 - 4	ca. 1
SO <sub>3</sub>	1,5- 3	1 - 4	8 - 9	0 - 1,2
<b>Mineralbestandteile</b>				
	C <sub>3</sub> S C <sub>2</sub> S C <sub>3</sub> A C <sub>2</sub> (A,F) CaO <sub>frei</sub> MgO CaSO <sub>4</sub> CaSO <sub>4</sub> ·2H <sub>2</sub> O	C <sub>3</sub> S C <sub>2</sub> S C <sub>3</sub> A C <sub>2</sub> (A,F) CaO <sub>frei</sub> MgO CaSO <sub>4</sub> CaSO <sub>4</sub> ·2H <sub>2</sub> O Glasanteil	C <sub>3</sub> S C <sub>2</sub> S C <sub>3</sub> A CaSO <sub>4</sub> CaSO <sub>4</sub> ·2H <sub>2</sub> O Glasanteil	CA <sub>2</sub> CA C <sub>12</sub> A <sub>7</sub> C <sub>2</sub> AS C <sub>2</sub> (A,F) C <sub>2</sub> S

Vorlagerung: 14 Tage Lösung: 0,15m Na<sub>2</sub>SO<sub>4</sub> + 0,15m MgSO<sub>4</sub>  
 Bindemittel HOZ 375

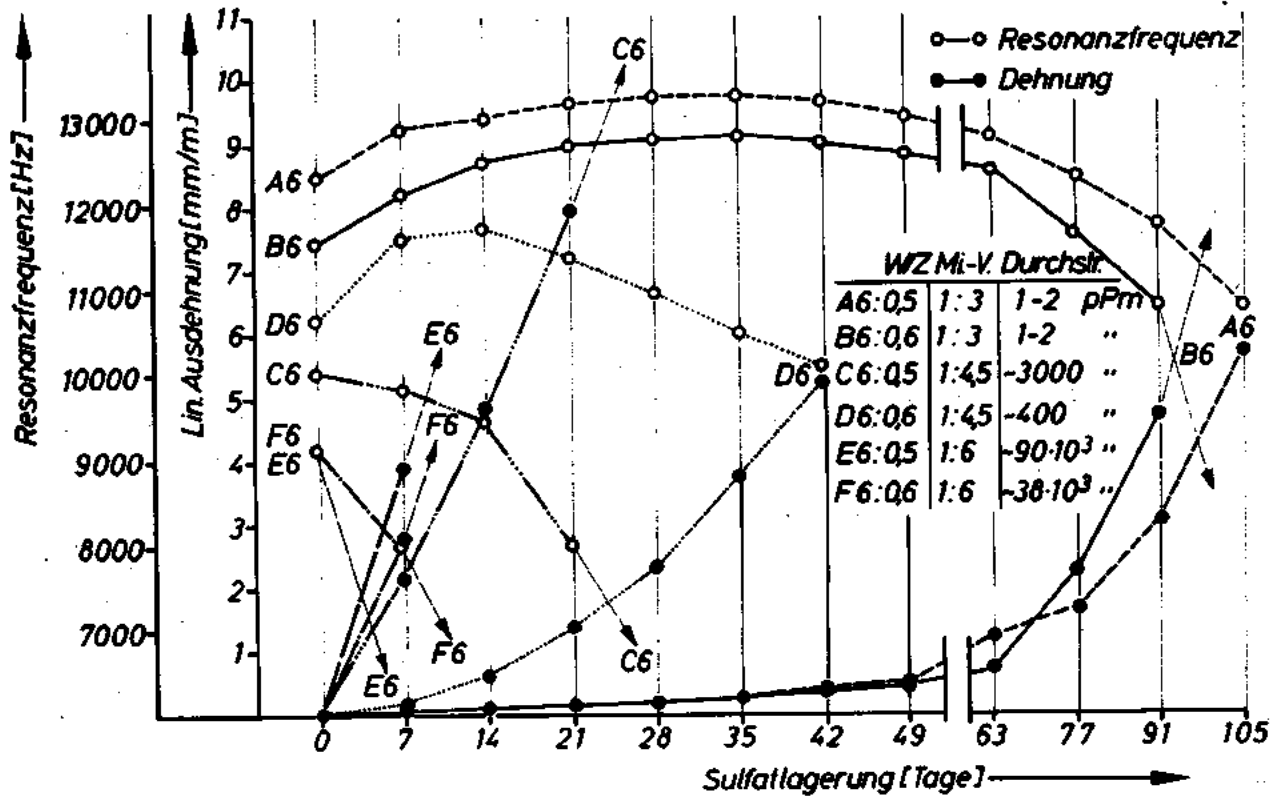


Abb. 1 Resonanzfrequenz und lineare Ausdehnung in Abhängigkeit von der Sulfatlagerungsdauer (1×4×16 cm Mörtelprismen).

### 2.3.2. Zemente mit steigenden Hüttensandgehalten

Nach dem modifizierten Verfahren von Koch und Steingger wurden von uns Zemente mit Hüttensandgehalten zwischen 50 und 90% auf ihre Sulfatbeständigkeit untersucht. Die Abb. 4 zeigt die relative Biegezugfestigkeit, die über der Natriumsulfatlagerungsdauer aufgetragen wurde. Aus der Abb. 4 ist zu erkennen, dass die relativen Biegezugfestigkeiten nach 56 Tagen nur von dem Zement mit 50 Teilen Hüttensand den Wert 1 leicht unterschreitet. Bei 60% wird die relative Biegezugfestigkeit von 1 nach 90 Tagen und bei 70% Hüttensand erst nach 180 Tagen erreicht.

Weitere Untersuchungen wurden an Mörteln 1:4 bei einem Mischungsverhältnis von Normensand 1 zu Normensand 2 wie 1:2 durchgeführt. Der W/Z-Faktor betrug für alle Mischungen nur 0,6. Nach einem Tag feuchter und 27 Tagen Wasserlagerung wurden die Prüfkörper bis maximal 72 Wochen in 0,15 m Na<sub>2</sub>SO<sub>4</sub>-Lösung gelagert. Die Gasdurchlässigkeit im Zeitpunkt der Einlagerung in die Natriumsulfatlösung lag zwischen 0,1 und 7,9 Pikoperm. Untersucht wurden Hüttensandzemente mit von 50 auf 90% ansteigenden Hüttensandgehalten, wobei der Hüttensand einmal nass und einmal trocken granuliert worden war. Ausserdem wurde der Hüttensand einmal auf 3500 und einmal auf 5000 Blaine vermahlen. Nach 72 Wochen Natriumsulfatlagerungsdauer waren

nur an den Zementen mit 50 bzw. 60% Hüttensand feine Risse zu erkennen bzw. es zeigten sich abfallende Tendenzen der untersuchten Mörtelfestigkeiten.

### 2.3.3. Aggressivbeständige Zemente

Als aggressivbeständige Zemente wurden ein Hochofenzement mit 40% Hüttensand und 60% C<sub>3</sub>A-freiem Klinker sowie ein C<sub>3</sub>A-freier Portlandzement in Mörtelmischungen 1:4 untersucht, wobei zur Erzielung einer unterschiedlichen Dichtigkeit das Verhältnis von Normensand I zu Normensand II im Bereich von 0:4 bis 2:2 variiert wurde. Die erforderlichen W/Z-Faktoren variierten zwischen 0,42 und 0,69 bzw. 0,46 und 0,73. Nach einem Tag feuchter Lagerung und 27 Tagen Wasserlagerung wurden die 5 × 5 × 25 cm Mörtelprismen in 0,15 Molare MgSO<sub>4</sub>-Lösung eingelagert. Die maximale Sulfatlagerungsdauer betrug 370 Tage. Die Abb. 5 gibt eine erste Auswertung der Änderung des dynamischen E-Moduls und der Gasdurchlässigkeit über dem Mischungsverhältnis der beiden Normensande wieder. Es zeigt sich, dass die Mischung IV die dem Normensandverhältnis der derzeitigen DIN 1164 entspricht, die geringste Gasdurchlässigkeit und den höchsten dynamischen E-Modul erreicht, also am dichtesten ist und die höchsten Festigkeiten erzielt. Die feinsandärmeren bzw. feinsandreicheren Mischungen werden durchlässiger und sind

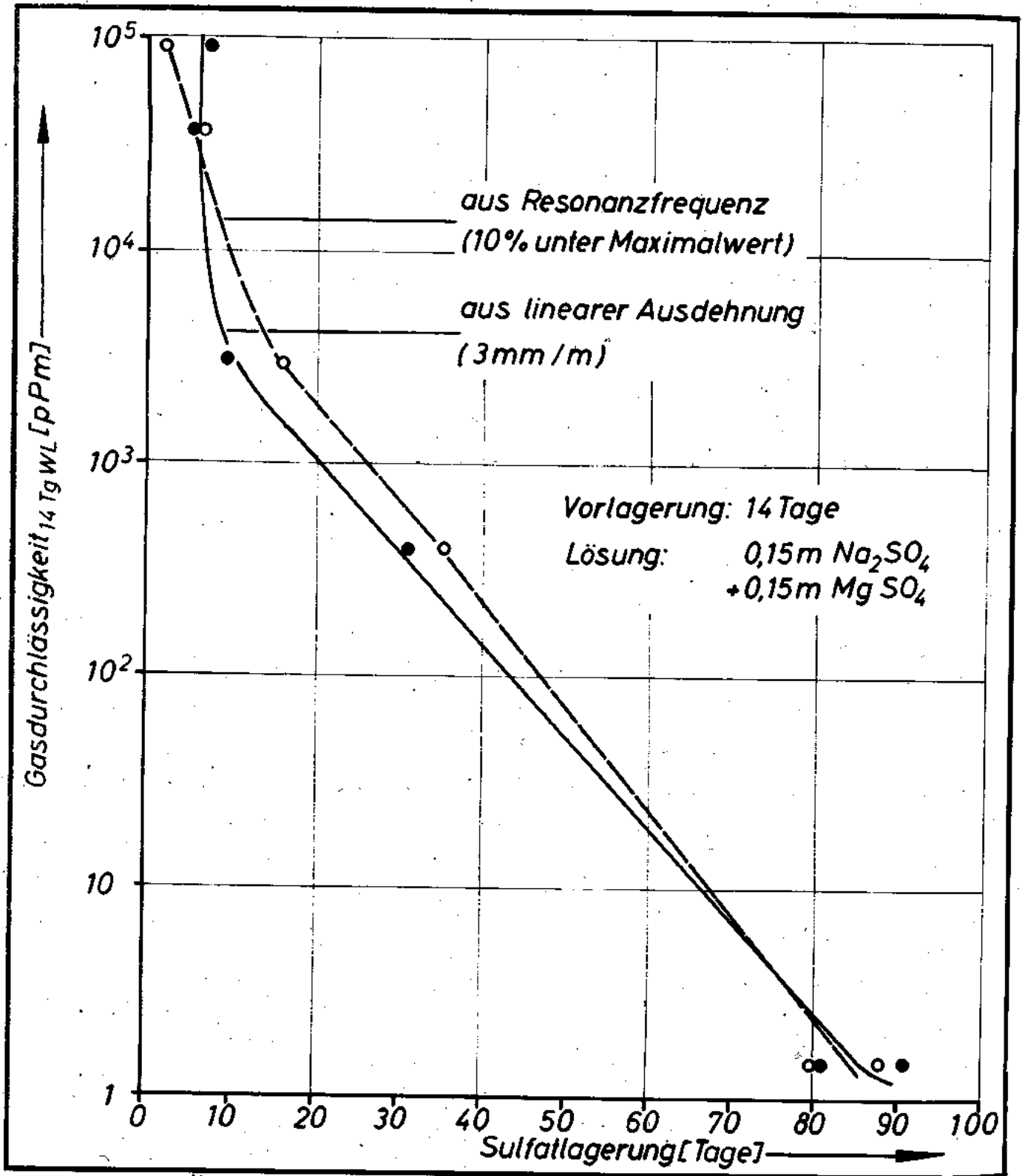


Abb. 2 Aggressivbeständigkeit eines HOZ 375 (40% HOS) in Abhängigkeit von der Gasdurchlässigkeit.

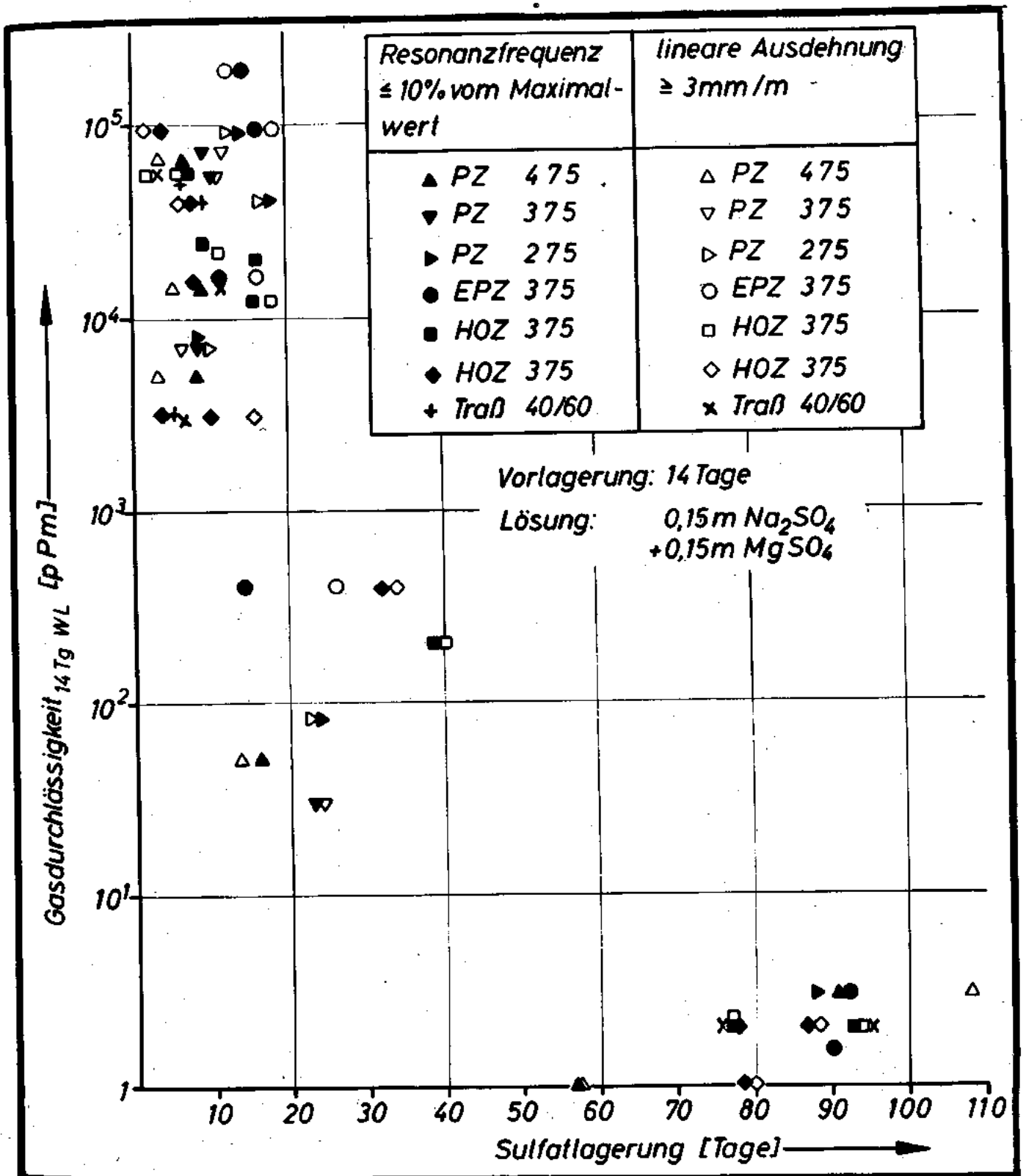


Abb. 3 Aggressivbeständigkeit verschiedener Zemente in Abhängigkeit von der Gasdurchlässigkeit.

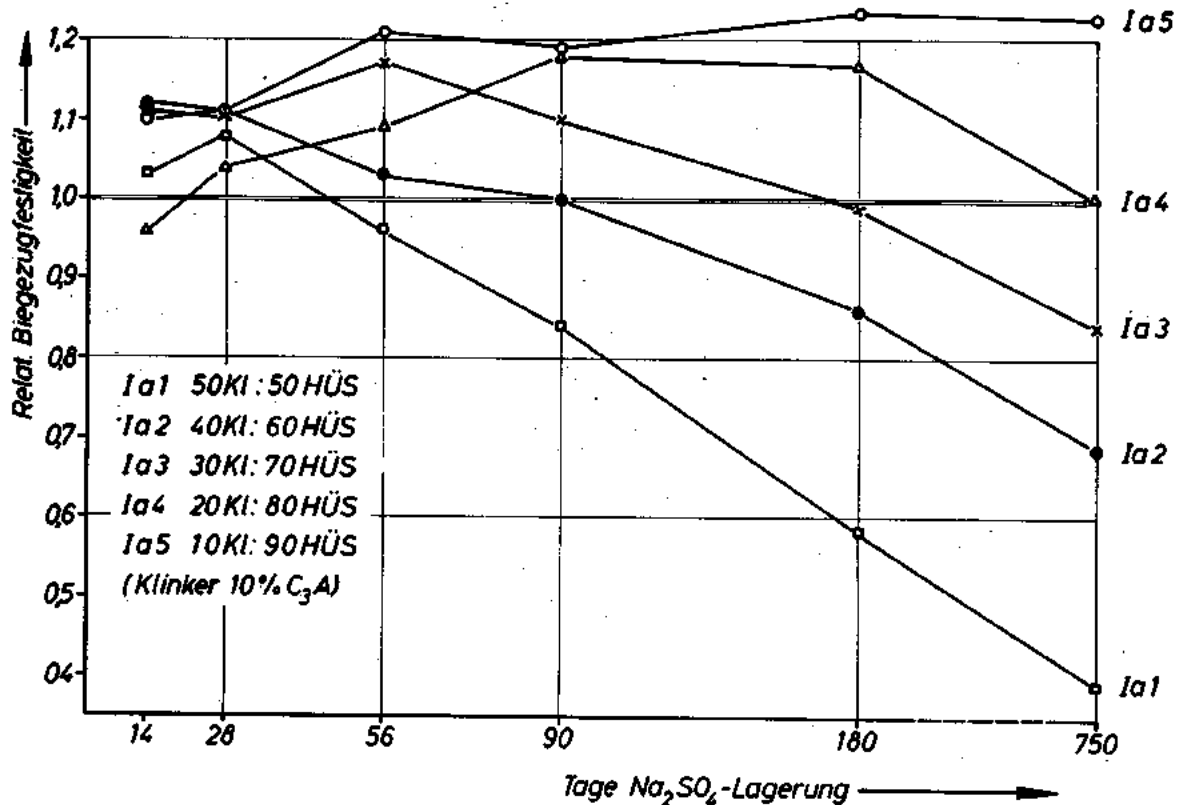


Abb. 4 Relative Biegezugfestigkeit in Abhängigkeit von der Na<sub>2</sub>SO<sub>4</sub>-Lagerung.

weniger fest. Zusätzlich ist der Darstellung zu entnehmen, dass die Gasdurchlässigkeit der Prüfkörper parallel zur Verdichtungsrichtung geringer ist als senkrecht zur Verdichtungsrichtung. In die Abb. 5 wurden noch die E-Module der Prüfkörper nach 160 Tagen Magnesiumsulfatlagerung mit eingetragen. Wir erkennen aus der Darstellung, dass nur die E-Module der beiden feinsandärmsten Mischungen (mit höchsten Gasdurchlässigkeiten) gegenüber denen abgefallen sind, die nach 28 Tagen Wasserlagerung gemessen wurden.

In der Abb. 6 wird nochmal das Verhalten sämtlicher Prüfkörper in Abhängigkeit von der Gasdurchlässigkeit über der Sulfatlagerungsdauer wiedergegeben. Die Prüfkörper mit Gasdurchlässigkeiten > 500 Pikoperm zeigen mit zunehmenden offenen Porositäten verminderte Aggressivbeständigkeiten. Dabei ist das Verhalten der Hochofenzementmörtel etwas günstiger als das der Portlandzementmörtel.

In einer weiteren Versuchsreihe wurden 4 Hochofenzemente mit 75% Hüttensand und 17% Klinker sowie 8% Anhydrit vermahlen. Ein weiterer Hochofenzement bestand aus 40% Hüttensand und 60% C<sub>3</sub>A-freiem Klinker. Zusätzlich wurden zwei C<sub>3</sub>A-freie Portlandzemente der Güteklassen 275 und 375 untersucht. Das Mischungsverhältnis der Mörtel war ein Teil Zement auf vier Teile Rilem-Cem-Sand-Mischung. Der W/Z-Faktor betrug 0,6. Die Mörtel wurden in Abhängigkeit von der Dauer der Aggressivlagerung auf Druck- und Biegezugfestigkeit geprüft. Nach 28 Tagen Vorlagerungsdauer

lagen die Gasdurchlässigkeiten zwischen 0,3 und 2,8 Pikoperm. Als aggressive Medien wurden 0,15 m Na<sub>2</sub>SO<sub>4</sub>-Lösung, 0,15 m MgSO<sub>4</sub>-Lösung, 0,15 m Na-Formiat-Lösung, 0,15 m Essigsäure-Lösung und gesättigte Gipslösung verwendet. Das Ergebnis dieser Untersuchungen kann wie folgt zusammengefasst werden:

Gegen die Natriumsulfatlösung waren alle Zemente beständig mit der Ausnahme, dass der Hochofenzement mit 60% C<sub>3</sub>A-freiem Klinker während der Versuchsdauer zwischenzeitlich eine abnehmende, dagegen später wieder eine zunehmende Festigkeitstendenz zeigte.

Gegen die Magnesiumsulfatlösung waren zwei hüttensandreiche Hochofenzemente über die Versuchsdauer beständig, während der Hochofenzement mit 60% C<sub>3</sub>A-freiem Klinker nach 48 Wochen und die restlichen vier Zemente nach 72 Wochen eine abnehmende Festigkeitstendenz zeigten.

In der Natriumformiatlösung waren alle Zemente beständig, dagegen in der Essigsäurelösung unbeständig, d.h. dass bereits nach 2 bzw. 4 Wochen Lagerung in der Essigsäurelösung die Festigkeiten der wassergelagerten Prüfkörper um 10% unterschritten wurden.

Gegen die gesättigte Gipslösung waren alle Zemente mit Ausnahme des Hochofenzementes mit 60% C<sub>3</sub>A-freiem Klinker beständig, der nach 48 Wochen Aggressivlagerungsdauer deutlich abnehmende Biegezugfestigkeiten zeigte.



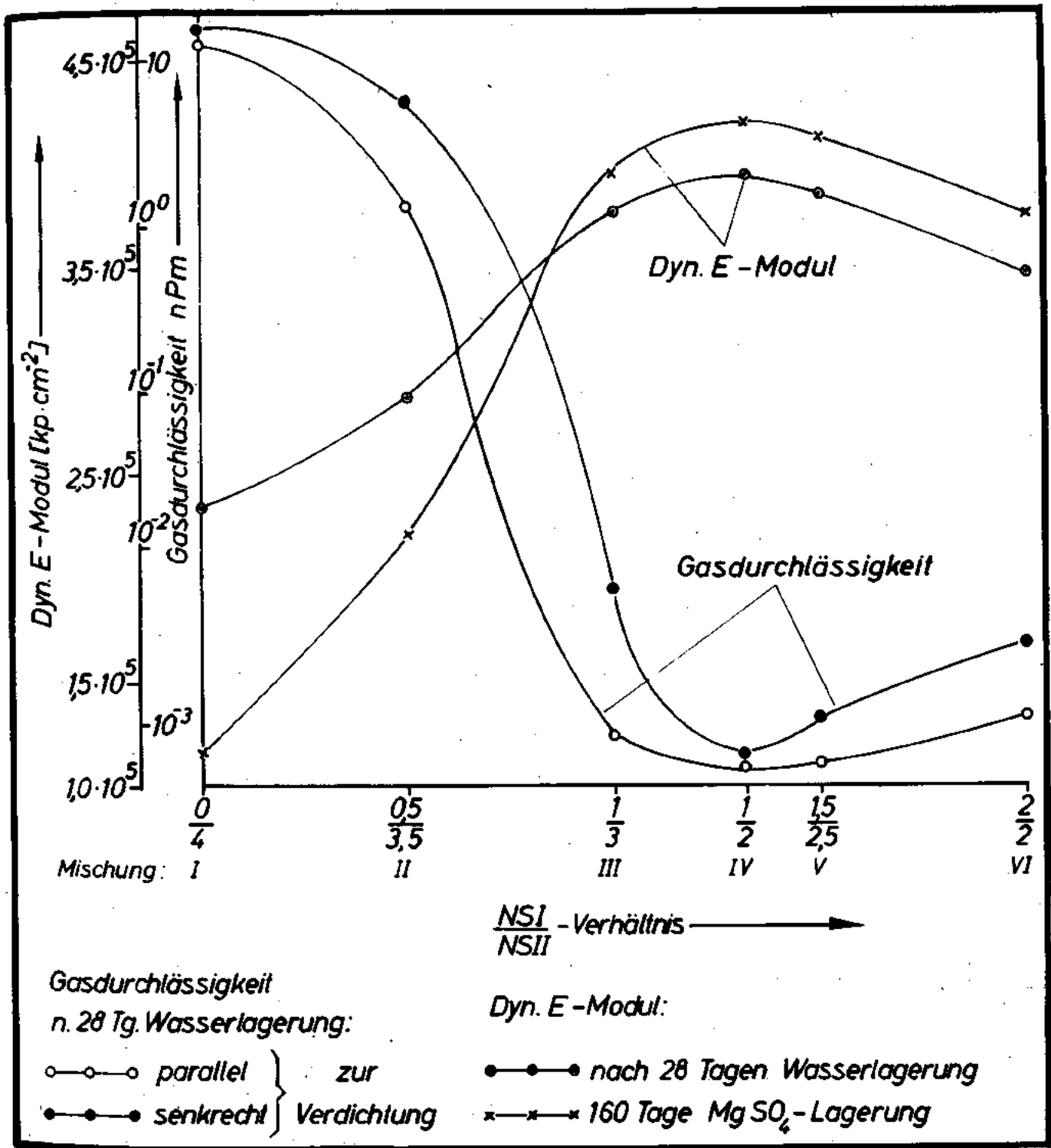


Abb. 5 Gasdurchlässigkeit und dynamischer Elastizitätsmodul in Abhängigkeit vom Normensandverhältnis in Mörtelprüfkörpern.

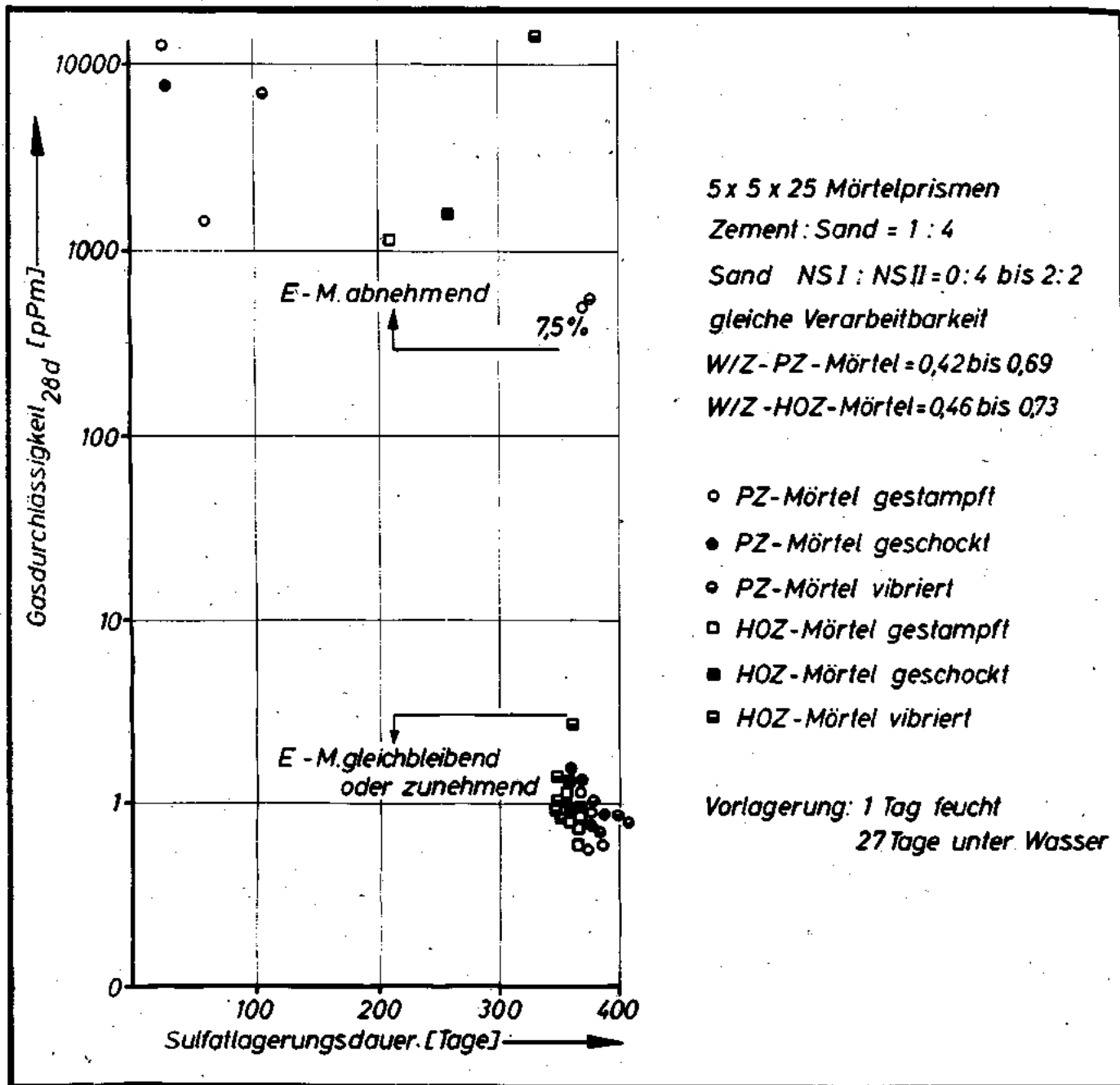


Abb. 6 Einfluss der offenen Porosität auf die Beständigkeit von Mörteln mit C<sub>3</sub>A-freiem PZ bzw. HOZ (60% C<sub>3</sub>A-freier Klinker) gegen 0,15 m MgSO<sub>4</sub>-Lösung.

#### 2.4. Art des Sulfatangriffes

Bei der Einwirkung von Natriumsulfat auf Zemente ist mit einer Reaktion zwischen Natriumsulfat und Calciumhydroxid unter Bildung von Gips und Natronlauge zu rechnen, wobei der Gips mit den Tonerde- bzw. Eisenoxidkomponenten zu ettringitähnlichen Phasen zu reagieren vermag.

Bei der Reaktion von Magnesiumsulfat mit Zementstein reagiert ebenfalls das Calciumhydroxid des Zementsteines, wobei Magnesiumhydroxid ausfällt und zusätzlich Gips gebildet wird. In einer weiteren Reaktion setzt sich der Gips zu

ettringitähnlichen Phasen um. Die Ausscheidung des Magnesiumhydroxides erfolgt ohne eine Verfestigung.

Bei dem Angriff von Gipslösungen ist entsprechend den zuvor gemachten Ausführungen die Ettringitbildung als Ursache der Zerstörung anzusehen.

#### 2.5 Ursachen der Sulfabeständigkeit

Als Ursache der Sulfatbeständigkeit von Zementen, die an sich mit den Sulfaten unter Bildung treibender ettringitähnlicher Phasen zu reagieren vermögen, muss in erster

TABELLE 4

ZUSAMMENSTELLUNG DER GRENZWERTE FÜR DIE ETTRINGITBILDUNG, DIE PRÜFKÖRPERBESCHAFFENHEIT UND DIE TENDENZ DER FESTIGKEIT

Mischung	Kli:HÜS-Verh.	Prüfkörperbeschaffenheit	Festigkeit		Grenzwert $G = \frac{CaO/56}{1,5 \frac{SiO_2}{60} + 3,0 \frac{Al_2O_3}{102}}$	p <sub>H</sub> Wert
			BZ	D		
A1	50:50	feine Risse	a <sup>1)</sup>	gl <sup>2)</sup>	0,93	12,2
A2	40:60	feine Risse	a	Z <sup>3)</sup>	0,83	12,1
A3	30:70	nicht korr.	gl.	Z.	0,77	12,1
A4	20:80	nicht korr.	gl.	Z.	0,70	12,0
A5	10:90	nicht korr.	gl.	Z.	0,63	12,0
B1	50:50	feine Risse	a	gl.	0,93	12,1
B2	40:60	feine Risse	a	Z.	0,88	12,2
B3	30:70	nicht korr.	gl.	gl.	0,81	12,2
B4	20:80	nicht korr.	gl.	gl.	0,69	12,0
B5	10:90	nicht korr.	gl.	Z.	0,65	12,0
Klinkerarmer HOZ "A" ohne Molererde	20:67 (:13Anh.)	nicht raumbeständig	-	-	0,80	n.b.
Klinkerarmer HOZ "A" mit Molererde	20:57 (13A:10M)	raumbeständig	-	-	0,64	n.b.
SHZ	3:82(:15A)	-	-	-	0,77	n.b.
1) abnehmend, 2) gleichbleibend, 3) zunehmend						

Linie die geringe offene Porosität von gut verdichteten Mörteln und Betonen genannt werden. Dabei ist das wesentliche Merkmal, dass nicht nur eine Diffusion von Sulfationen oder anderen schädlichen Ionen in den Prüfkörper hinein stattfindet, sondern in gleicher Weise Calcium- und Hydroxyl-Ionen aus dem Prüfkörper heraus diffundieren. Dieses ist ein wesentliches Merkmal der Vorgänge beim Sulfatangriff.

Wenn wir zugrunde legen, dass die Diffusionsvorgänge einen wesentlichen Anteil an der Beständigkeit oder Unbeständigkeit der Mörtel- oder Betonprüfkörper mit verschiedenen Zementen haben, so muss die Lagerungsart von grossem Einfluss sein. Hier ist zu unterscheiden:

- 1) Angriff in ruhender Sulfatlösung oder Aggressivlösung
- 2) Angriff in bewegter Sulfatlösung oder Aggressivlösung und
- 3) Angriff mit zwischenzeitlicher Austrocknung d.h. dass ausser Diffusionsvorgängen auch die Kapillarität von grossem Einfluss für den Transport der aggressiven Salze in den Prüfkörper bzw. die löslichen Bestandteile des Zementes aus dem Prüfkörper heraus ist.

#### 2.5.1. Das Verhalten C<sub>3</sub>A-armer Zemente bei ruhender Sulfatlösung

Das besondere zusätzliche Merkmal C<sub>3</sub>A-armer bzw. C<sub>3</sub>A-freier Zemente ist die geringe Reaktionsgeschwindigkeit der aluminatisch-ferritischen Phase unter Bildung ettringit-ähnlicher Phasen. Die Abb. 7 zeigt die Bodenkörpergewichtszunahmen der auf gleiche spezifische Oberflächen umgerechneten Calciumaluminatferrite wobei das C<sub>3</sub>F nach einem Tag nur 50% des Umsatzes des C<sub>3</sub>AF, 30% des C<sub>2</sub>A<sub>2</sub>F und nur etwa 15% des C<sub>3</sub>A erreicht. Diese Darstellung charakterisiert sehr eindeutig die Reaktionsgeschwindigkeit der einzelnen Bestandteile der aluminatisch-ferritischen Phase. Hinzu kommt die Kalkbindung der Calciumaluminatferrite, d.h. dass zur Bildung von einem Mol Ettringit ein Mol Calciumhydroxid zusätzlich erforderlich wird. Auch bei den Zementen vom Portlandzementtyp ist damit zu rechnen, dass eine parallel dem Sulfateintritt verlaufende Kalkauslaugung zu einer Verhinderung der Ettringitbildung führt.

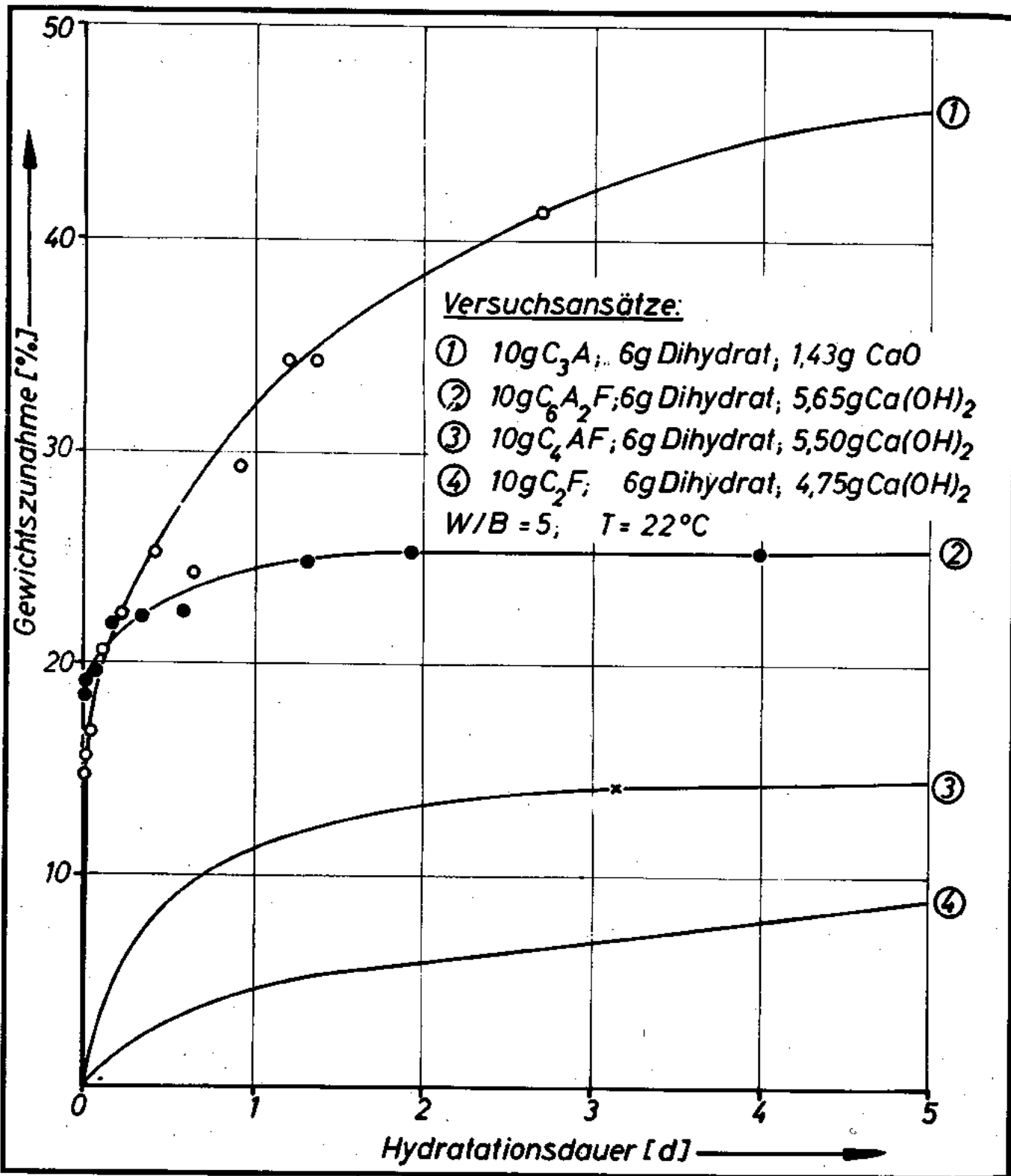


Abb 7 Zunahme des Bodenkörpergewichtes bei Hydratation der aluminatisch - ferritischen Phase bezogen auf eine spezifische Oberfläche von 1000  $cm^2/g$  (Blaine).

## Einfluß der Molererde auf die Raumbeständigkeit bei erhöhtem Sulfatanteil (mit Le Chatelier - Ringen)

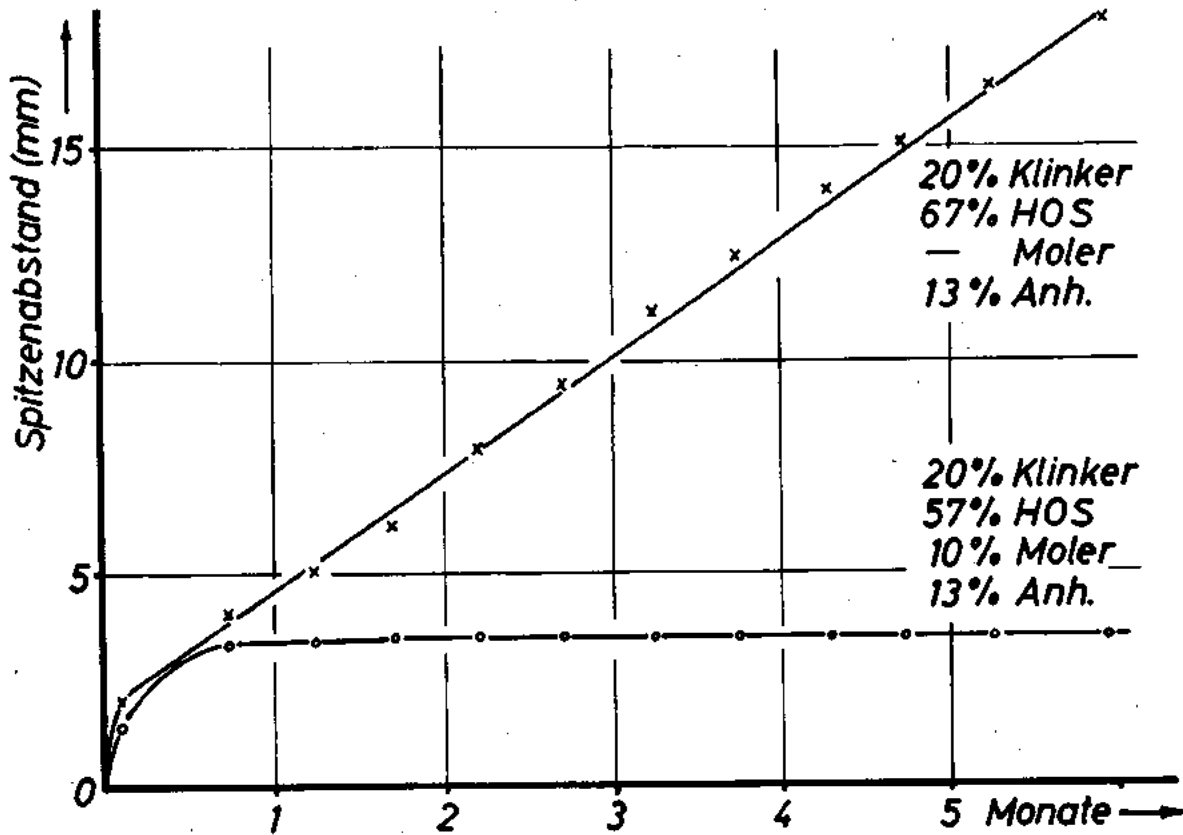


Abb. 8 Einfluss von Molererde auf klinkerarme Hochofenzemente.

### 2.5.2. Hüttsandreiche Zemente bei ruhender Sulfatlösung

In Anlehnung an in der Literatur bereits bestehende Formeln zur Charakterisierung der Aggressivbeständigkeit von Hüttenzementen (7, 8, 9) wurde auch von uns ein Grenzwert zur Charakterisierung sulfatbeständiger Zemente errechnet. Bei diesem Grenzwert werden nicht wie bei anderen Verfassern die prozentualen Verhältnisse, sondern die molaren Verhältnisse von  $\text{CaO}$ ,  $\text{SiO}_2$  und  $\text{Al}_2\text{O}_3$  berücksichtigt. Wir sind uns darüber im klaren, dass bei  $\text{MgO}$ -reichen Hüttsanden das  $\text{MgO}$  in die Formel mit aufgenommen werden muss.

Aus den Analysen der Mörtelrandschicht und des Mörtelkernes ergab sich eine Verschiebung in der Zusammensetzung. Wir haben die chemische Zusammensetzung des Zementes nach der Aggressivbeanspruchung in der Mörtelrandschicht unter Berücksichtigung des Sandanteiles berechnet und daraus den Grenzwert gebildet. Wie man aus der Tabelle 4 entnehmen kann, würde dann ein Zerstückung der Hüttenzemente beobachtet, wenn der Grenzwert  $\geq 0.80$  lag. Ausserdem wurden in dieser Tabelle die entsprechenden Koeffizienten für Hüttenzemente mitgeteilt, die mit 13% Anhydrit hergestellt wurden. Hier zeigt sich, dass der Wert 0,8 noch nicht ausreicht, um den Zement bei erhöhtem  $\text{SO}_2$ -Gehalt raumbeständig zu machen. Durch weitere Absenkung des Koeffizienten durch Zugabe von Molererde auf den Wert 0,64 wurde der Zement, wie in Bild 8 gezeigt, raumbeständig. Die Sulfatbindung und die Raumbeständigkeit eines Sulfat-

hüttenzementes zeigt die Abb. 9. Der Darstellung ist zu entnehmen, dass die Bindung des zugesetzten Calciumsulfates nach 3 Tagen im wesentlichen abgeschlossen ist. Zusätzlich ist zu erkennen, dass auch nach 90 Tagen Hydrationsdauer noch Anhydrit im Zementstein beobachtet wurde. Andererseits zeigt aber der Versuch mit dem Le Chatelier-Ring, dass sich kaum eine Ausdehnung der Probe zeigt, d.h. dass die Sulfatbindung ohne eine merkliche Änderung des Zementsteinvolumens abläuft.

Eine weitere Auswertung unter Einbeziehung von zwei weiteren Versuchsreihen und der Grenzwerte der Ausgangsanalysen der Hochofenzemente gibt die Abb. 10. In der Darstellung wurden die Grenzwerte, die aus den Zementanalysen berechnet wurden und die, welche nach 72 Wochen Sulfatlagerung an den Zementsteinanteilen der Prüfkörperaussonen zurückbestimmt wurden, über den Hüttsandgehalten aufgetragen. Man erkennt allgemein eine Abnahme der Grenzwerte während der Lagerung, d.h. in dem Masse, wie mit einer Diffusion von Calcium- und Sulfationen in den Prüfkörper hinein muss auch mit einer solchen von Calcium- und Hydroxyl-Ionen aus dem Prüfkörper heraus gerechnet werden. Diese Diffusionsvorgänge sind abhängig von den Konzentrationen, der offenen Porosität und der Temperatur. Es muss sich also für die Beständigkeit gegen sulfathaltige Lösungen ein Übergangsbereich ergeben, in dem je nach den Reaktionsbedingungen ein Ettringittreiben auftreten kann oder die Mörtel bzw. Betone raumbeständig sind. Gegen einen

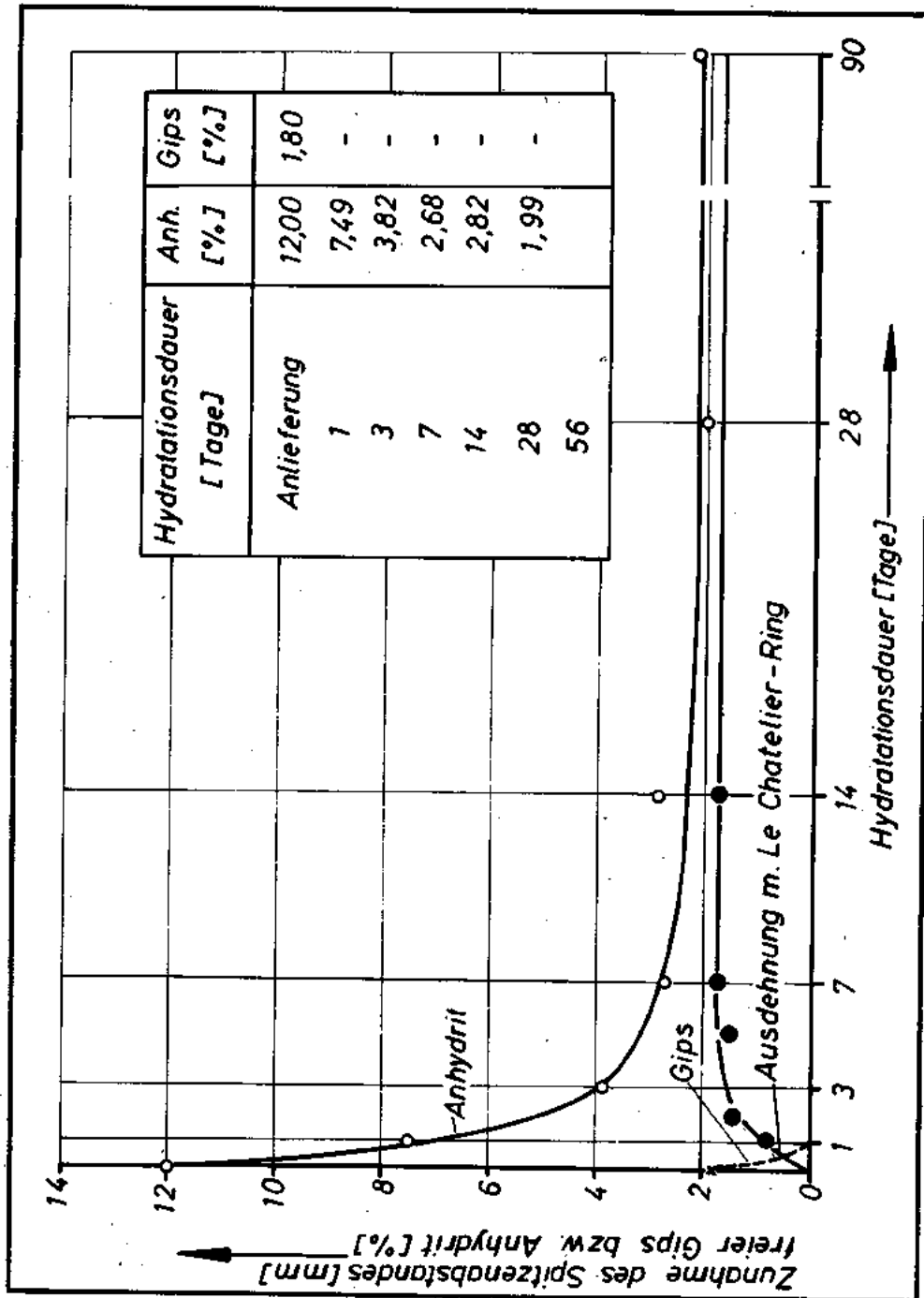


Abb. 9 Sulfatbindung und Raumbeständigkeit eines Sulfatbüttenzementes.

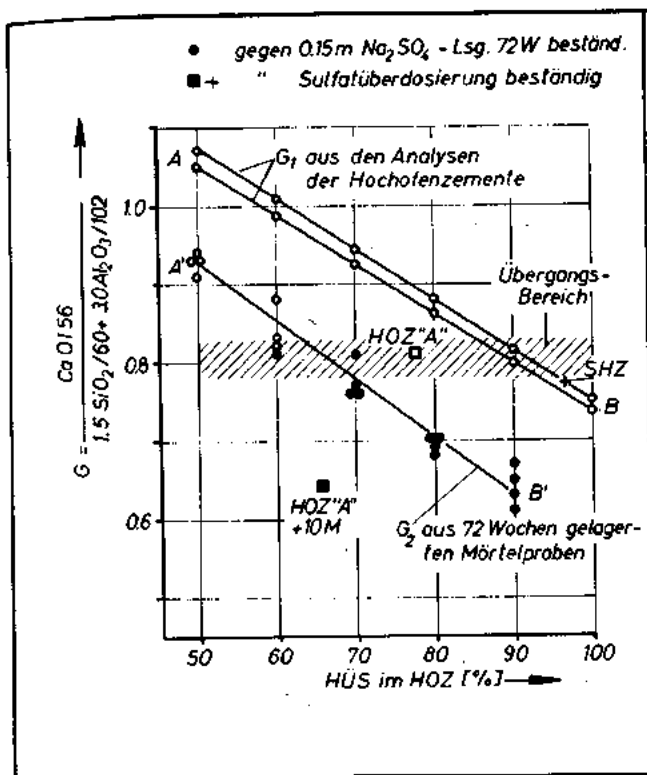


Abb. 10 Einfluss der Zusammensetzung auf die Sulfatbeständigkeit von Hüttenzementen.

inneren Sulfatgriff, z.B. bei einer Sulfatüberdosierung, muss der Grenzwert auf den der Sulfathüttenzemente herabgesetzt werden. Normal zusammengesetzte Hochofenzemente können (z.B. HOZ A) durch einen geeigneten Puzzolan auf einen niedrigeren Grenzwert gebracht werden. Man erkennt also aus den oben aufgezeigten Zusammenhängen, dass die Hochofenzemente im Mörtel oder Beton beim Angriff sulfathaltiger Wasser bei genügend hohem Hüttsandgehalt durch die

Kalkauslaugung in den Aussenzonen die chemische Zusammensetzung eines Sulfathüttenzementes annehmen, wenn die Calciumsulfatgehalte beider Zemente ausser Ansatz bleiben. Massgebend für die Sulfatbeständigkeit von Hüttenzement ist also der Calciumgehalt im Zementstein.

Für die Hilfe bei der Durchführung der Untersuchungen danken die Verfasser den Herren Dr.-Ing. H.P. Lühr und Dipl.-Ing. P. Otto. Dem Kulturministerium des Landes Nordrhein-Westfalen in Düsseldorf, der Deutschen Forschungsgemeinschaft in Bad Godesberg und der Arbeitsgemeinschaft Industrieller Forschungsvereinigungen in Köln danken wir für die Bereitstellung der Sach- und Personalmittel.

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# BESTÄNDIGKEIT VON BETON IM MEERWASSER UND IM SULFATHALTIGEN HALDENABWASSER

(Befundergebnisse nach acht- bis zehnjähriger Auslagerung)

Vom Dr. Ing. W. NIEBUHR

Ministerialrat im Bundesverkehrsministerium  
Bad Godesberg, DEUTSCHLAND

## ZUSAMMENFASSUNG

Die Versuchsergebnisse einer acht- bis zehnjährigen Auslagerung von Betonprismen verschiedener Zusammensetzung im Meerwasser (Nordsee) sowie in einem sulfathaltigen Haldenabwasser werden mitgeteilt. In die Untersuchung wurden sowohl handelsübliche Normzemente (Portlandzement, Hochofenzement und Sulfathüttenzement), wie auch Sonderzemente mit hohem bzw. mässigem Sulfatwiderstand einbezogen. Im ganzen sind 9 verschiedene Bindemittelarten und 4 Mischungen verschiedener Bindemittel zur Anwendung gekommen. Die Bindemittelmenge wurde variiert und zwar in den Abstufungen 270, 335 und 400 kg/m<sup>3</sup>. Auch der Einfluss von Betonzusatzmitteln, wie Betonverflüssiger und andere, sowie der Einfluss des Alters des Betons im Zeitpunkt der Auslagerung sind in entsprechenden Versuchsreihen untersucht worden. Der Wasserzusatz wurde so geregelt, dass alle Betone eine praxisnahe, möglichst gleiche Konsistenz aufwiesen. Hierbei ergaben sich je nach Bindemittelart und -menge Unterschiede im Wasserzementwert zwischen 0,34 und 0,62.

Die Auslagerung im Meerwasser erfolgte in zwei verschiedenen Zonen und zwar unter Tideniedrigwasser (UTNW) und in Höhe des Mitteltidewasser (MTW). Im Versuchsbecken mit dem Haldenabwasser (1200-1500 mg/l SO<sub>4</sub>) wurden die Betonprismen sowohl liegend (dauernd unter Wasser) als auch stehend (z. T. aus dem Wasser herausragend) gelagert. Im ganzen sind 3094 Probekörper angefertigt worden, davon 1826 für Auslagerungszecke.

Nach nunmehr zehn- bzw. achtjähriger Lagerung zeigen die Probekörper bemerkenswerte Unterschiede in ihrem Verhalten, abhängig von Bindemittelart und -menge, insbesondere aber auch abhängig vom Auslagerungsort. Während die Prismen der UTNW-Lagerung im Meerwasser bis auf eine mehr oder weniger ausgeprägte Rauigkeit der Oberfläche allgemein noch keine nennenswerten Veränderungen zeigen, sind in der MTW-Lagerung z.T. bereits erhebliche Abtragungen bis zum 30 mm-Korn festzustellen, und zwar bei den Portlandzement-Betonen mit 270 und 335 kg/m<sup>3</sup> Bindemittelgehalt, bei den Portlandzement-Trassgemischen und bei den Dreistoffgemischen (bestehend aus Portlandzement bzw. Hochofenzement, Kalkhydrat und Trass). Nur die Portlandzement-Serie mit 400 kg/m<sup>3</sup> Bindemittelgehalt hat sich bisher gut gehalten.

Die Hochofenzement-Betone und die Hochofenzement-Trassgemische haben dem Angriff des Meerwassers deutlich besser widerstanden. Aber auch bei diesen, insbesondere bei

den Hochofenzement-Trassgemischen, ist der Feinmörtel stellenweise bis zum 7 mm-Korn abgetragen worden, wieder mit Ausnahme der Serie mit 400 kg/m<sup>3</sup>, die nur geringfügig aufgeraut ist. Die übrigen Betone, mit Ausnahme der Sulfathüttenzement-Prismen, die ein für diesen Beton typisches Abtanden an allen Seiten zeigen, lassen noch keine nennenswerten Änderungen erkennen. Der Unterschied im Verhalten der Betone in der UTNW- sowie der MTW-Lagerung lässt darauf schliessen, dass die Schäden der MTW-Lagerung in erster Linie auf Witterungseinflüsse, wie Frost-Tauwechsel, zurückzuführen sind, und erst in zweiter Linie auf chemische Einwirkung des Meerwassers.

Die im Haldenabwasser gelagerten Probekörper unterlagen ausschliesslich dem chemischen Angriff des sulfathaltigen Wassers. Gegen Witterungseinflüsse waren die Körper weitgehend geschützt. Die Portlandzement-Betone zeigen typische Sulfatschäden, wie Aufwölben der Zementhaut, Ettringitbildung und im Zusammenhang hiermit starke Abtragungen an Ecken, Kanten und an den Oberflächen bis weit in die Mittelbereiche hinein. Besser gehalten haben sich die Portlandzement-Trassgemische; aber auch diese zeigen Sulfatschäden. Gut gehalten haben sich die Serien mit Hochofenzement sowie die Hochofenzement-Trassgemische und überraschenderweise auch die Dreistoffgemische, ferner die Betone mit den Sonderzementen, mit Ausnahme eines Portlandzementes mit etwa 3% Tricalciumaluminatgehalt, der gleichfalls beginnende Sulfatschäden aufweist.

Der Einfluss des Alters des Betons im Zeitpunkt der Auslagerung ist sowohl im Meerwasser wie auch im Haldenabwasser deutlich erkennbar. Während im allgemeinen die später ausgelagerten Prismen das bessere Aussehen haben, wirkt sich bei den Hochofenzement-Betonen die Vorlagerung im Klimaraum (Austrocknung) offensichtlich ungünstig aus. Die früh ausgelagerten Prismen sehen besser aus als die später ausgelagerten.

Der Einfluss der verwendeten Betonzusatzmittel ist z.T. positiv, z.T. negativ, im allgemeinen jedoch nur geringfügig, mit Ausnahme eines gleichfalls in die Untersuchung einbezogenen Dichtungsmittels, das sich allgemein ungünstig ausgewirkt hat.

Ein Vergleich zwischen Meerwasser- und Haldenabwasserlagerung zeigt, dass der Sulfatanteil im komplexen Salzgehalt des Meerwassers offenbar den hierfür anfälligen Beton weniger angreift als ein etwa gleich höher Sulfatgehalt im Haldenabwasser.



## ALLGEMEINES

Die Beständigkeit von Beton im Meerwasser hängt erfahrungsgemäss ausser von seiner Zusammensetzung nach Bindemittelart und -menge insbesondere auch von der Sorgfalt der Herstellung sowie den jeweiligen Umwelteinflüssen ab. Dass dichte Betone mit einem Bindemittelgehalt von 400 kg/m<sup>3</sup> und mehr sich unabhängig von der Bindemittelart im Meerwasser 40 Jahre und länger gut gehalten haben, war bekannt. Die in den letzten Jahrzehnten erzielten Fortschritte sowohl in der Betontechnologie als auch in der Herstellung von Zementen mit mässigen bzw. hohem Sulfatwiderstand warfen die Frage nach dem Mindestgehalt von Bindemitteln für einen meerwasserbeständigen Beton erneut auf. Vom Sonderausschuss «Betonschädliches Wasser» des Deutschen Ausschusses für Stahlbeton wurde daher im Jahre 1953 ein umfassendes Versuchsprogramm mit entsprechender Zielsetzung aufgestellt. Insbesondere sollten untersucht werden:

1. Einfluss der Bindemittelart und -menge mit dem Ziel, die Mindestmengen — abhängig von der Bindemittelart für einen Beton mit ausreichender Widerstandsfähigkeit zu ermitteln.
2. Einfluss des Alters des Betons bei der Auslagerung.
3. Einfluss von Betonzusatzmitteln.

Die Auslagerung sollte einmal im Meerwasser (Borkum, Nordsee) und zweitens vergleichsweise im Haldenabwasser des Versuchsbeckens Dortmund-Hörde mit etwa 1200 bis 1500 mg/l SO<sub>4</sub> erfolgen. Im einzelnen sah das Arbeitsprogramm vor:

- 13 verschiedene Bindemittelarten
- 3 Bindemittelmengen in den Abstufungen 270, 335 und 400 kg/m<sup>3</sup>. (S. Anl. 1).

Die Bindemittelmenge von 400 kg/m<sup>3</sup> blieb beschränkt auf die Meerwasserversuchsreihen mit Portlandzement und Hochofenzement. Alle in Dortmund-Hörde ausgelagerten Prüfkörper erhielten ausschliesslich 335 kg/m<sup>3</sup> Bindemittel, ebenso die Dreistoffgemische im Meerwasser.

An Betonzusatzmitteln wurden verwendet:

1. Betonverflüssiger Murasit (BV)
2. Luftporenbildender Betonverflüssiger Frioplast (LPV)
3. Luftporenbildner Mischöl — VR (LP)
4. Dichtungsmittel Ceresit (DM)

Der Tonerdeschmelzzement sowie die Sonderzemente des Zusatzprogrammes erhielten keine Zusatzmittel.

Als Zuschlagsstoffe wurde Rheinkies in vier Körnungen bis 30 mm, Sieblinie im besonders guten Bereich, verwendet. Der Anteil an Feinstkorn ( $\leq 0,2$  mm) wurde durch Zugabe von Quarzmehl so bemessen, dass die Feinstkornmenge einschliesslich Bindemittelgehalt betrug:

bei 270 kg Bindemittel/m<sup>3</sup> = 340 kg Feinstteile  
bei 335 kg » » = 400 kg »  
bei 400 kg » » = keine Zugabe von Quarzmehl.

Um auch den Einfluss der Vorlagerung zu untersuchen, wurden drei Auslagerungstermine festgelegt und zwar 7, 28 und 90 bzw. 365 Tage nach Herstellung der Probekörper. Die Probekörper wurden nach dem Ausschalen bis zu einem Alter von 7 Tagen unter feuchten Tüchern und anschliessend bis zur Auslagerung im Klimaraum bei 20° Celsius und 65% relativer Feuchte gelagert. Insgesamt sind 3094 Probekörper angefertigt worden, davon 1826 für Auslagerungszwecke.

Auf die Herstellung der Probekörper im einzelnen sowie auf die Ergebnisse der Laborprüfungen kann hier nicht näher eingegangen werden. Nur die wesentlichsten Kennzeichen des Betons, soweit sie für das Verständnis der Versuchsergebnisse von Bedeutung sind, sollen hier mitgeteilt werden.

Der Versuchsbeton sollte möglichst praxisnah, d.h. gut verarbeitbar sein. Um für alle Mischungen eine einheitliche,

vergleichbare Konsistenz zu erhalten, wurde der Wasserzusatzen solange variiert, bis die Mischung auf dem Rütteltisch ein vorher bestimmtes Ausbreitmass (50 cm) in einer bestimmten Rüttelzeit (20 s) erreichte. Hierbei ergaben sich je nach Bindemittelart und -menge, sowie nach Art der Zusatzmittel, natürlich unterschiedliche WZ-Werte, wobei im allgemeinen die mit V angemachten Betone die unteren Grenzwerte, die O-Serien die oberen Grenzwerte erreichten. Die WZ-Werte lagen:

bei der Mischung 270 kg/m<sup>3</sup> (Nr. 10) zwischen 0,52 und 0,62  
bei der Mischung 335 kg/m<sup>3</sup> (Nr. 20) zwischen 0,42 und 0,51  
bei der Mischung 400 kg/m<sup>3</sup> (Nr. 30) zwischen 0,34 und 0,41

Das Ausbreitmass auf dem Klapptisch, das auch gemessen wurde, lag im allgemeinen zwischen 28 und 36 cm.

Die Wasserdurchlässigkeit wurde nach DIN 1048 geprüft. Die Prüfung ergab mit wenigen Ausnahmen befriedigende Ergebnisse. Nur die Tonerdeschmelzzemente und die Dreistoffgemische waren wasserdurchlässig. Die Zugabe von Betonzusatzmitteln ergab keine erkennbare Verbesserung der Dichtigkeit.

Die Frostbeständigkeit wurde im Kristallisationsversuch geprüft. Durch laufende Messungen des dynamischen E-Moduls wurde hierbei der Zerstörungsverlauf verfolgt. Es zeigte sich, dass die Prismen geringerer Betongüte auch im Kristallisationsversuch am schlechtesten abschnitten. Eindeutige Ergebnisse konnten aber nicht erzielt werden.

Festigkeitsprüfungen wurden nach 28 und 180 Tagen durchgeführt. Bei einem Bindemittelgehalt von 270 kg/m<sup>3</sup> wurde mindestens ein B 225, zum grössten Teil sogar B 300 erzielt mit Ausnahme der Serie mit dem klinkerarmen Hochofenzement, deren Festigkeit nach 28 Tagen noch unter 225 kg/cm<sup>2</sup> blieb. Bei einem Bindemittelgehalt von 335 kg/m<sup>3</sup> wurden im allgemeinen die Festigkeiten eines B 300 überschritten, ausgenommen die Betone mit DM-Zusatz und die Dreistoffgemische, die nicht einmal die Festigkeiten eines B 225 erreichten. Eine Steigerung des Bindemittelgehaltes auf 400 kg/m<sup>3</sup> brachte keine wesentlichen Festigkeitserhöhungen. Sie blieb daher, wie bereits erwähnt, auf die Serie mit Portlandzement und Hochofenzement (Nr. 100 und 200) beschränkt.

Die Zugabe von Betonzusatzmitteln erbrachte nur bei den Serien mit BV eine Festigkeitssteigerung, die abhängig von der Mischung zwischen 14 und 18% betrug. Die übrigen Zusatzmittel ergaben nur in Einzelfällen eine Festigkeitserhöhung, in der Mehrzahl eine Abminderung der Festigkeit. Festigkeitsabfälle bei allen Serien brachte der Einsatz des Dichtungsmittels (DM).

## BISHERIGE ERGEBNISSE DER BEFUNDAUFNAHMEN AN DEN AUSGELAGERTEN PROBEKÖRPERN.

Die Probekörper des Hauptprogrammes liegen nunmehr 10 bis 12 Jahre, die des Zusatzprogrammes 8 bis 9 Jahre aus ein Alter bei dem jedenfalls in früher durchgeführten Versuchen schon deutliche Anzeichen einer beginnenden Zerstörung erkennbar waren. Des begrenzten Raumes wegen müssen die Angaben hier auf die Hauptserien sowie auf die wichtigsten charakteristischen Feststellungen beschränkt bleiben.

### A. HAUPTPROGRAMM

- 1) Auslagerung im Meerwasser; Borkum. Lagerung unter Tideniedrigwasser (UTNW)

Serien «100»; PZ 225

Der bereits im Fünfjahresbefund festgestellte starke Bewuchs durch Seepocken hat zu einer Konservierung der Oberflächen geführt, sodass die im Anfang beobachteten

geringen Unterschiede verschiedener Auslagerungstermine im Befund der Prismen sich jetzt verwischen.

Der Einfluss der Bindemittelmenge ist nur insoweit erkennbar, als sich bei den Serien mit 270 kg/m<sup>3</sup> eine Aufrauung der Kanten und Oberflächen zeigt, während die Prismen mit den Bindemittelmengen 335 und 400 kg/m<sup>3</sup> allgemein noch scharfkantig sind.

Ein Unterschied der Betone mit Betonzusatzmitteln gegenüber den O-Betonen ist nicht erkennbar.

#### *Serien «200»; HOZ 225*

Der Bewuchs des Betons ist nicht ganz so stark wie bei den PZ-Körpern. Die schon im Fünfjahresbefund festgestellte mässige Oberflächenaufrauung ist kaum verändert. Im Gegensatz zu den PZ-Körpern, bei denen die später ausgelagerten Prismen das bessere Aussehen hatten zeigen die früher ausgelagerten HOZ-Prismen ein besseres Aussehen als die später ausgelagerten. Die Empfindlichkeit des HOZ-Betons gegenüber Austrocknung bei der Vorlagerung im Klimaraum kommt hier deutlich zum Ausdruck. Der Einfluss der Bindemittelmenge zeigt sich nur in der Kantenstruktur und einer unterschiedlichen Oberflächenrauigkeit die bei den Prismen geringerer Bindemittelmenge grösser ist als bei den fetteren Mischungen.

Unterschiede zwischen O-Beton und den Prismen mit Zusatzmitteln sind kaum festzustellen. Nur bei der LPV-Serie mit 270 kg/m<sup>3</sup> ist die Oberfläche etwas stärker bis zum 3 mm-Korn abgetragen.

#### *Serien «300»; SHZ und «400»; TSZ*

Die SHZ-Prismen zeigen mit graduellen Unterschieden, abhängig vom Bindemittelgehalt, das für den SHZ typische Absanden der Oberfläche bis zum 15 mm-, teilweise bis zum 30 mm-Korn. Einflüsse der Auslagerungstermine sind nicht erkennbar. Die TSZ-Prismen sind dagegen noch unverändert.

#### *Serien «500»; 70% PZ + 30% Trass*

Unterschiede zwischen den Prismen mit verschiedenem Bindemittelgehalt sind unwesentlich. Sie zeichnen sich lediglich in einer etwas erhöhten Rauigkeit der Oberfläche und einer leichten Unebenheit der Kanten bei den mageren Mischungen ab. Auch der Einfluss des Auslagerungsalters ist unwesentlich. Eine negative oder positive Auswirkung der Zusatzmittel kann mit Sicherheit gleichfalls nicht festgestellt werden.

#### *Serien «600»; 85% HOZ + 15% Trass*

Der Beton dieser Serien verhält sich ähnlich wie der Beton der Serien «200» mit reinem HOZ. An den später eingelagerten Betonen ist abhängig von der Bindemittelmenge eine mehr oder weniger starke Rauigkeit und leichte Kantenbeeinträchtigung bemerkbar.

Systematische Unterschiede zwischen O-Beton und den Prismen mit Zusatzmitteln können nicht festgestellt werden.

#### *Serien «720» und «820»; Dreistoffgemische*

Die Prüfkörper haben sich über Erwarten gut erhalten. Die Prismen der Serie «720» mit PZ sind dabei besser als die der Serie «820» mit HOZ. Während bei letzteren das 7 mm-Korn (28 und 90 Tage-Körper) freigelegt ist, lassen die ersteren nur das 3 mm-Korn und vereinzelt das 7 mm-Korn sichtbar werden. Ein Einfluss der Betonzusatzmittel ist kaum erkennbar.

#### *2) Auslagerung im Meerwasser; Borkum. Lagerung Mittel-Tidewasser (MTW)*

#### *Serien «100»; PZ 225*

Bei den Serien mit PZ, zeigen sich nach zehnjähriger La-

gerung im Mittel-Tidewasser schon bemerkenswerte Veränderungen in Abhängigkeit von Bindemittelmenge, Auslagerungstermin und Zusatzmitteln.

Die Prismen mit 270 kg/m<sup>3</sup> PZ zeigen Abtragungen an den Schmalseiten, Kanten und Ecken, die das 7 mm-Korn erheblich, das 15 mm- und 30 mm-Korn teilweise freigelegt haben. Die Abtragungen gehen häufig von Abplatzungen über einem grösseren Einzelkorn aus. Die Mittelbereiche der Oberflächen sind jedoch im allgemeinen noch unbeeinträchtigt. Die früher ausgelagerten Prismen sind hierbei stärker verändert als die 90 und 365 Tage-Körper. Die Serien «110» bis «113» zeigen untereinander nur geringe Unterschiede. Stärker geschädigt ist die Serie «114» (DM), bei der sich die Abtragungen bis in die Mittelbereiche der Oberflächen erstrecken.

Die Prismen mit 335 kg/m<sup>3</sup>, die als Hauptreihe der Gruppe «100» vier Auslagerungsalter und vier Betonzusatzmittel erfassen, zeigen ein ähnliches, wenn auch weniger ausgeprägtes Schadensbild wie die entsprechenden Prüfkörper mit 270 kg/m<sup>3</sup>. Bei den Serien «120», «121» und «123» ist das 7 mm-Korn erheblich, das 15 bis 30 mm-Korn nur an Schmalseiten, Kanten und Ecken freigelegt, allerdings noch nicht so stark wie bei den Prismen mit 270 kg/m<sup>3</sup>. Am stärksten sind wieder die Schäden an den Körpern der Serie «124» (DM).

Die Prismen der Serien «130» mit 400 kg/m<sup>3</sup> sind noch gut erhalten; Ecken und Kanten sind noch unverändert, Aussprengungen sind kaum vorhanden.

#### *Serien «200»; HOZ 225*

Der Zustand der Prüfkörper unterscheidet sich deutlich von dem der Serien «100». Nur eine mehr oder weniger kräftige Aufrauung der Oberflächen und eine gleichmässig verlaufende Kanten- und Eckenabrundung ist bisher festzustellen. Auch hier ist der Einfluss der Auslagerungszeiten in der Gütereihenfolge von 7 über 90 nach 365 Tagen erkennbar.

Der Einfluss der Bindemittelmenge drückt sich in einem unterschiedlich starken Grad der Abtragungen aus. Bei den spät ausgelagerten Prismen mit 270 kg/m<sup>3</sup> ist im allgemeinen das 7 mm-Korn sichtbar, während bei den früher ausgelagerten Prismen höchstens das 3 mm-Korn und bei den entsprechenden Körpern der Serie mit 400 kg/m<sup>3</sup> nur das 1 mm-Korn sichtbar ist.

Die auch hier bei den Prismen der niederen Zementmengen regellos vorhandenen Aussprengungen sind im allgemeinen auf Bereiche begrenzt, in denen ein 15 mm-Korn unmittelbar unter der Oberfläche liegt.

Ein Einfluss der Betonzusatzmittel ist, abgesehen von dem Dichtungsmittel (DM) nicht erkennbar. Die Prismen mit DM zeigen auch hier eine höhere Anfälligkeit gegen Aufrauung und Absprengungen, wenn auch nicht in dem gleichen Masse wie bei den entsprechenden Körpern mit Portlandzement.

#### *Serien «300»; SHZ und «400»; PHZ*

In der MTW-Zone zeigen die SHZ-Prismen ein verstärktes Absanden an allen Seiten.

Die TSZ-Prismen sind wie bei der UTNW-Lagerung noch unverändert.

#### *Serien «500»; 70% PZ 225 + 30% Trass*

Die Prüfkörper mit der Bindemittelmenge 270 kg/m<sup>3</sup> zeigen bereits erhebliche Abtragungen an Kanten und Ecken sowie auch Flächenabtragungen. Der Einfluss der Vorlagerung ist im gleichen Sinne wie bei den reinen PZ-Serien wirksam. Die stärksten Veränderungen zeigen die 7 Tage-Körper; zum grossen Teil ist das 15 und 30 mm-Korn blossgelegt. Die Kanten und Ecken sind abgerundet, die Abtragungen erstrecken sich bis in die Mittelbereiche der Flächen. Bei den 28 Tage-Körpern, die im allgemeinen etwas besser aussehen, ist bisher in Abplatzungen das 7 mm-Korn und teilweise auch das 15 mm-Korn freigelegt. Besser haben sich die Prüfkörper mit 335 kg/m<sup>3</sup> gehalten. Die Schäden beschränken sich auf örtlich begrenzte Absprengungen.

Unterschiede der O-Betone gegenüber den Prismen mit Zusatzmitteln sind kaum erkennbar.

Bei diesen Serien sind die früher schon festgestellten, kraterförmigen Aplatzungen bei den Prismen mit 270 kg/m<sup>3</sup> nunmehr in zusammenhängende Abtragungen übergegangen, während sich bei den Prismen mit 335 kg/m<sup>3</sup> erst örtlich begrenzte Vertiefungen zeigen.

*Serien «600»; 85% HOZ 225 + 15% Trass*

Die Prismen dieser Serien zeigen gleichmässige, leichte Abrundungen an Kanten und Ecken sowie flächenhafte Abtragungen, die das 1 mm-Korn bis 7 mm-Korn freilegen. Einzelne Absprengungen über flach liegenden gröberen Körnern sind vorhanden.

Die Prismen mit 335 kg/m<sup>3</sup> sehen hierbei etwas besser aus als die mit 270 kg/m<sup>3</sup>, sind aber gleichwohl auch schon angegriffen.

Die früh dem Meerwasser ausgesetzten Prismen sehen besser aus als die mit längerer Vorlagerungszeit im Klimaraum.

Mit Ausnahme des Dichtungsmittels DM, das vermehrte und tiefergehende Aussprengungen bewirkt hat, zeigen die mit Zusatzmitteln versehenen Prismen keine Unterschiede zum O-Beton.

*Serien «720» und «820»; Dreistoffgemische*

Die Prismen beider Serien haben bereits ein waschbetonartiges Aussehen mit starken Abtragungen an Kanten und Ecken bis zum 30 mm-Korn. Die Unterschiede im Verhalten der Dreistoffgemische untereinander sind im Gegensatz zu den reinen PZ- und HOZ-Prismen nur gering. Bei den Gemischen mit PZ sind die nach 7 Tagen ausgelagerten Prismen erheblich stärker angegriffen als die später ausgelagerten, während die 7 und 90 Tage-Körper der Gemische mit HOZ fast das gleiche Abtragungsbild zeigen. Ein Einfluss der Zusatzmittel ist kaum feststellbar.

*3) Auslagerung Dortmund-Hörde; Haldenabwasser*

Die im Versuchsbecken Dortmund-Hörde ausgelagerten Prüfkörper unterlagen ausschliesslich dem chemischen Angriff durch das sulfathaltige Haldenabwasser. Gegen Witterungseinflüsse, wie Frost und Tauwechsel, waren die Körper geschützt. Die Prüfkörper waren einmal liegend, vom Abwasser völlig bedeckt, zum andern stehend, z.T. aus dem Wasser ragend, im Versuchsbecken gelagert.

*Serie «120»; PZ 225*

Sämtliche Prismen dieser Serie zeigen ausnahmslos Sulfatschäden. Unterschiede im Ausmass der Schäden sind auch hier wieder durch die verschiedenen Einlagerungstermine bedingt. Die 7 Tage-Körper zeigen Abrundungen der Ecken und Kanten, Blasenbildung auf Fertigungs- und Schalungsflächen — die gesamte Kornstruktur bis zum 30 mm-Korn ist an den abgetragenen Stellen freigelegt, und umfangreiche Ettringitbildung, die z.T. bereits eine Rückwandlung zu festem Gips erkennen lässt.

Die 90 Tage-Körper weisen demgegenüber einen besseren Zustand auf; dennoch zeigen auch sie bereits leichte Blasenbildung und Abrundungen an Ecken und Kanten. Die Prismen mit Zusatzmitteln sind deutlich schlechter als die O-Betone, und zwar in der Gütereihenfolge BV, LPV, LP und DM. Die Körper der Serie mit dem Dichtungsmittel DM sind z.T. bereits in völliger Auflösung begriffen.

*Serie «220»; HOZ 225*

Sämtliche Prismen sind nach zehnjähriger Lagerung im Sulfatwasser noch gut erhalten. An den ständig unter Wasser liegenden Prismen zeigen sich bisher keinerlei Schäden. Ecken und Kanten sind im allgemeinen noch scharfkantig.

Die stehenden Prismen zeigen im Bereich des Wasserspiegels und im Luftbereich eine Aufrauhung der Flächen,

die aber nicht über das 1 mm-Korn hinausgeht. Die 90 Tage-Prismen zeigen hierbei eine etwas stärkere Rauigkeit als die 7 Tage-Prismen. Ein Unterschied zwischen dem O-Beton und den Prismen mit Zusatzmitteln ist mit Sicherheit nicht festzustellen, mit Ausnahme der Serie «224» (DM), die in der Luftzone etwas rauher ist.

*Serien «300»; SHZ und «400»; TSZ*

Die SHZ-Prismen zeigen starkes Absanden an den Oberflächen, besonders an der Herstellungsfäche, bis zum 15 mm-Korn, wobei die Absandung bei den 90 Tage-Prismen stärker ist als bei den 7 Tage-Prismen.

Die TSZ-Prismen sind noch unverändert.

*Serie «520»; 70% PZ 225 + 30% Trass*

Die Prismen dieser Serie zeigen nach zehnjähriger Lagerung bereits echte Sulfatschäden, wenn auch in geringerem Ausmass als die reinen PZ-Betone. Eine beginnende Zerstörung macht sich in Kantenabplatzungen bemerkbar, Stossstellen, an denen das Gefüge gelockert worden war, sind offensichtlich von Ettringit unterwandert. Die Fertigungsflächen weisen Abplatzungen und leichtes Aufwölben der Zementhaut auf.

*Serien «620»; 85% HOZ 225 + 15% Trass*

Die Prismen zeigen einen ähnliche Zustand wie die Prismen der Serien «200» mit reinem HOZ. Die Ausmagerung durch Trass hat sich in etwas stärkerer Rauigkeit ausgewirkt. Ecken und Kanten können im allgemeinen noch als scharfkantig bezeichnet werden. Im Bereich des Wasserspiegels und der Luftzone ist das 1 mm-Korn, z.T. auch das 3 mm-Korn, freigelegt. Unterschiede zwischen O-Beton und den Prismen mit Zusatzmitteln sind kaum feststellbar. Nur die Prismen der Serie «624» (DM) zeigen wieder eine etwas kräftigere Aufrauhung.

*Serien «720» und «820»; Dreistoffgemische*

Der Zustand dieser Serien ist noch verhältnismässig gut. Bei den 7 Tage-Prismen ist die Zementhaut teilweise abgelöst. Bei den 90 Tage-Körpern ist das 1 mm-Korn freigelegt. Unterschiede hinsichtlich Einlagerungstermin und Zusatzmittel sind nicht erkennbar.

## B. ZUSATZPROGRAMM

*Serien «1100» bis «1500»*

Die Prüfkörper des Zusatzprogrammes haben sich im Meerwasser, soweit sie ständig vom Wasser bedeckt waren (UNTW-Lagerung), bisher noch kaum verändert.

In der Tidewechselzone (MTW-Lagerung) zeigen die Prismen mit C<sub>2</sub>A-freiem PZ (Serie «1100») nur z.T. geringfügige Veränderungen. Lediglich die 90 Tage-Körper mit 270 kg/m<sup>3</sup> sind in der Fertigungsfläche aufgeraut. Ähnlich haben sich die Prismen mit C<sub>2</sub>A-armen PZ (Serie «1200») verhalten, wobei die 90 Tage-Körper dieser Serie etwas rauher sind als die entsprechenden Prismen der Serie «1100».

Die Prüfkörper mit dem klinkerarmen HOZ (Serie «1300») lassen Einfluss von Zementmenge, wie auch vom Einlagerungstermin, deutlicher erkennen. Bei den 90 Tage-Prismen mit 270 kg/m<sup>3</sup> ist die Abtragung an der Fertigungsfläche und an den Schalungsflächen soweit fortgeschritten, dass das 7 mm-Korn etwa auf 75%, das 15 mm-Korn etwa auf 50% der Oberfläche freigelegt ist. Die 7 und 28 Tage-Körper sind demgegenüber weniger aufgeraut. Bei den 90 Tage-Körpern mit 335 kg/m<sup>3</sup> ist bisher nur das 1 mm-Korn freigelegt. Ecken und Kanten sind noch unbeschädigt.

Bei den HOZ-Prismen mit 35% Klinker (Serien «1400» und «1500») ist die Aufrauhung geringer als bei den entsprechenden Prismen der Serie «1300». So ist bei den 90 Tage-Körpern mit 270 kg/m<sup>3</sup> bisher nur das 3 mm-Korn allgemein sichtbar, während das 15 mm-Korn nur stellenweise freigelegt

ist.

Im Haldenabwasser zeigen die Prismen mit C<sub>3</sub>A-freiem PZ nach achtjähriger Lagerung noch keine Schäden, während an den Prismen mit C<sub>3</sub>A-armen PZ beginnende leichte Schäden durch Sulfatangriff zu beobachten sind.

An den HOZ-Prismen mit 19 und 35% Klinker sind die Kanten und Ecken nach achtjähriger Lagerung im Haldenabwasser noch unbeschädigt; ihre Oberflächen sind jedoch durch Ablösen des Feinmörtels, vor allem an der Fertigungsfläche, leicht aufgerauht.

### VERGLEICH ZWISCHEN MEERWASSER - UND HALDENABWASSERLAGERUNG

Die vorliegenden Versuchsergebnisse zeigen zwischen den im Meerwasser und im Haldenabwasser ausgelagerten Prüfkörpern bei gleicher Zusammensetzung des Betons doch bemerkenswerte Unterschiede im Schadensbild.

Bei der Meerwasserlagerung scheint der hohe Sulfatanteil innerhalb des Salzgehaltes des Meerwassers eine geringere Wirkung als im sulfathaltigen Haldenabwasser zu haben. Während sich im Haldenabwasser an einer Anzahl von Prismen einwandfrei Sulfatschäden gezeigt haben, machen sich bei den entsprechenden Prismen im Meerwasser Schäden bemerkbar, die vermutlich in erster Linie auf Witterungseinflüsse (MTW-Lagerung) zurückzuführen sind. Für diese Annahme spricht der ungünstige Befund bei den in der Tide-wechselzone gelagerten Prismen gegenüber den ständig vom Wasser bedeckten Körpern. Dies gilt insbesondere für die Trassbetone (Serien «510» und «610») sowie für die Dreistoffgemische (Serien «720» und «820»).

Im Haldenabwasser ist die Abhängigkeit der Widerstandsfähigkeit des Betons vom C<sub>3</sub>A-Gehalt des Bindemittels offensichtlich. Gut gehalten haben sich bisher die Serien mit HOZ und mit den HOZ-Gemischen sowie die Prüfkörper des Zusatzprogrammes, mit Ausnahme des C<sub>3</sub>A-armen PZ (Serie «1200»), das nach achtjähriger Lagerung bereits beginnende Sulfatschäden zeigt.

Im Meerwasser ist dagegen die Beständigkeit des Betons in erster Linie von der Betongüte, d.h. der Bindemittelmenge, und in zweiter Linie, insbesondere bei mageren Betonen, von der Bindemittelart bzw. dem C<sub>3</sub>A-Gehalt abhängig. Gut gehalten haben sich im Meerwasser bisher, unabhängig von der Bindemittelart, nur die Serien mit 400 kg/m<sup>3</sup> Zement sowie ferner in beiden verwendeten Bindemittelabstufungen von 270 und 335 kg/m<sup>3</sup> die Prüfkörper mit den Sonderzementen (Zusatzprogramm), sowie die TSZ-Betone.

Im Sulfatwasser hat die Zugabe von Trass die Widerstandsfähigkeit der PZ-Betone deutlich verbessert, während bei den HOZ-Betonen eine Veränderung weder im negativen noch im positiven Sinne bemerkbar ist. Im Meerwasser ist dagegen keine Verbesserung durch Trass festzustellen. Typisch für die Gemische mit Trass sind bei diesen Serien kraterförmige Absprengungen an den Oberflächen der Prüfkörper.

Ein Einfluss der Auslagerungstermine ist sowohl im

Meerwasser wie auch im Haldenabwasser deutlich festzustellen. Der Einfluss der Betonzusatzmittel ist z.T. positiv, z.T. negativ, im ganzen nur geringfügig, mit Ausnahme des Dichtungsmittels DM, das sich allgemein ungünstig ausgewirkt hat.

### A N L A G E

Prüfkörper des Versuchsprogramms 1953  
Abmessungen der Betonprismen 10 × 15 × 35 cm

#### Zementart:

Kurzbezeichnung: PZ = Portlandzement  
HOZ = Hochofenzement  
SHS = Sulfathüttenzement  
TSZ = Tonerdeschmelzzement  
C<sub>3</sub>A = Tricalciumaluminat

#### A Handelsübliche Zemente (Hauptprogramm):

Serie Nr.	100	PZ 225 «J»
	200	HOZ 225 «W»
	300	SHZ 225 «Rh»
	400	TSZ
	500	70% PZ 225 «J» + 30% Trass
	600	85% HOZ 225 «W» + 15% Trass
	700	45% PZ 225 «J» + 10% Kalkhydrat + 45% Trass
	800	45% HOZ 225 «W» + 10% Kalkhydrat + 45% Trass

#### B Sonderzemente (Zusatzprogramm):

Serie Nr.	1100	PZ 275 «S» (ohne C <sub>3</sub> A)
	1200	PZ 275 «WS» (etwa 3% C <sub>3</sub> A)
	1300	HOZ 275 «O» (19% Klinker)
	1400	HOZ 275 «M» (35% Klinker, tonerdearmer Hüttensand)
	1500	HOZ 275 «Rh» (35% Klinker, tonerdereicher Hüttensand)

#### Bindemittelmengen:

Serie Nr.	.10	270 kg/m <sup>3</sup>
	.20	335 kg/m <sup>3</sup>
	.30	400 kg/m <sup>3</sup>

#### Betonzusatzmittel:

Serie Nr.	.0	ohne Zusatzmittel (O-Beton)
	.1	Betonverflüssiger «Murasis» (BV)
	.2	Luftporenbildender Betonverflüssiger «Frioplast» (LPV)
	.3	Luftporenbildner «Mischöl-VR» (LP)
	.4	Dichtungsmittel «Ceresit» (DM)

# STANDARDISATION D'ÉPROUVETTES EN BÉTON ARMÉ SUR LA BASE DES MESURES DANS L'EAU DOUCE ET L'EAU DE MER AVEC OU SANS PROTECTION CATHODIQUE

## I. MESURE DU POTENTIEL DE CORROSION

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### RÉSUMÉ

Les valeurs du potentiel de corrosion des armatures du béton armé sont influencées par la forme des éprouvettes, l'isolation et la mode de leur préparation e.t.c.; il en est de même pour la reproductibilité de ces valeurs.

Ainsi les mesures du potentiel ont été faites dans l'eau douce et l'eau de mer sur des éprouvettes en béton armé sans protection cathodique avec section carrée, circulaire et triangulaire; de même on a modifié l'isolation des armatures et l'isolation de la surface des éprouvettes. De plus les mesures

pour les éprouvettes dans l'eau de mer ont été établies en fonction de l'intensité du courant sous une tension constante de la protection cathodique et sans protection en fonction du temps.

Nous avons pu ainsi déterminer les meilleures conditions pour la préparation des éprouvettes (forme, isolation etc.), afin d'obtenir une bonne reproductibilité et précision des mesures du potentiel.

### INTRODUCTION

Pendant les dernières années, la corrosion des armatures du béton armé a excité l'intérêt des hommes de science à cause du fait que les observations et les traitements théoriques de la corrosion des métaux par Wagner ont montré que cette corrosion dépassait les prédictions du passé.

D'autre part, le temps qui s'est écoulé depuis le début de l'utilisation du béton armé a donné des résultats plus concrets de la corrosion. C'est pourquoi un plus grand nombre d'hommes de science s'est occupé plus intensivement du problème et des méthodes de protection.

Au premier congrès des Cannes 1964 nous avons présenté les résultats des nos travaux sur la corrosion des armatures du béton armé en milieu marin et nous avons prouvé, à l'aide des éprouvettes des armatures pris de constructions démolies de différents âges, que l'épaisseur des oxydes augmente avec le temps selon la loi parabolique de Wagner.

Par le passé et à présent plusieurs hommes de science se sont aussi occupés du problème de la corrosion du béton armé.

Ces recherches ont soumi des données qui ne permettent aucun doute quant à l'acuité du sujet; il est indispensable de prendre des mesures convenable. Cela est naturellement plus nécessaire pour les constructions immergées dans l'eau de mer où les effets de la corrosion des armatures sont plus rapides et plus intenses.

Dans ces différents travaux, les essais de corrosion, entre lesquels la mesure du potentiel de corrosion, se réalisent sur des éprouvettes, de forme et de conditions de préparation différentes, de sorte que les résultats obtenus ne sont pas comparables entre eux.

Pour cela nous avons jugé nécessaire d'examiner, au point de vue de la précision et de la reproductibilité, les valeurs obtenues sur des éprouvettes de section carrée, circulaire et triangulaire, de forme usuelle où qui peuvent être utilisées,

en variant aussi l'isolation des armatures et de la surface des éprouvettes, laquelle comme nous avons prouvé dans des recherches précédentes joue aussi un rôle important.

Les mesures sont réalisées sur des éprouvettes immergées dans l'eau douce et l'eau de mer avec et sans protection cathodique.

Nous avons l'intention de standardiser ainsi les éprouvettes afin que les résultats de mesures des différentes chercheurs soient comparables entre eux.

### MESURES

#### A. MESURES QUALITATIVES

Nous avons constaté que le potentiel de corrosion des éprouvettes est influencé par les facteurs suivants:

##### 1. Influence de la forme, des qualités des matériaux, des conditions de préparation et de prise.

Le potentiel de corrosion est influencé par la qualité du ciment, du sable et de l'eau, par le pourcentage sable-ciment-eau, par les dimensions, la qualité et le traitement mécanique pour le nettoyage de la surface de l'acier utilisée comme armature, par l'environnement pendant la prise, par le temps qui s'écoule entre la préparation et la mesure et par la forme (forme de leur section, dimensions) des éprouvettes.

##### 2. Influence de la position des éprouvettes pendant la prise.

Le potentiel de corrosion est influencé par la position des éprouvettes (c'est-à-dire si l'acier de l'armature en dehors du béton est culminant en haut ou en bas ou s'il se trouve dans une autre position) pendant le temps s'écoulant entre leur préparation et les mesures, avec le même pourcentage sable-ciment-eau et la même qualité de sable.

### 3. Influence d'isolation.

Il a été établi très clairement que, pour une forme et un mode de préparation donnés, les potentiels de corrosion sont influencés par le mode d'isolation de l'armature et de la surface de béton.

### 4. Influence de la position d'électrode de référence.

De plus, le potentiel est influencé par la place et la distance du bout libre du tuyau capillaire de l'électrode de référence par rapport à l'armature d'acier de l'éprouvette.

## B. MESURES QUANTITATIVES

Etant donné les observations ci-haut mentionnées, nous avons préparé toutes les éprouvettes avec les mêmes qualités de ciment-sable-eau et pourcentage. Ainsi nous avons utilisé du ciment portland préparé en Grèce. Ses propriétés sont indiquées au tableau 1.

TABLEAU 1  
PROPRIÉTÉS PHYSIQUES ET CHIMIQUES DU CIMENT UTILISÉ

Propriétés Physiques		Resistances (Regl. Allemands)		
		Temps	Compression	Flexion
Surface spécifique 2971 cm <sup>2</sup> /g (Blaine)				
Finesse (4900)	25%	1er jour	96 kp/cm <sup>2</sup>	26 Kp
		3ème jour	231 »	49 »
Com. de la prise	1h 45 min	7ème jour	354 »	62 »
Fin de la prise	2h 20 min	28ème jour	482 »	77,5»
Constance de vol. (Chatelier)	2mm			
Analyse du Clinker (%)				
SiO <sub>2</sub>	21,65	SO <sub>3</sub>	1,80	
Al <sub>2</sub> O <sub>3</sub>	5,11	Chaux libre	0,80	
Fe <sub>2</sub> O <sub>3</sub>	3,59	K <sub>2</sub> O	0,40	
CaO	54,57	Na <sub>2</sub> O	0,30	
MgO	2,16	Insolubles	0,12	

Le sable utilisé était du sable normal standard anglais: Portland Cement Standard Sand B.S. 12:1958, Leighton Buzzard, traversant les mailles de 18 Mesh B.S. ainsi que les mailles de 25 Mesh B.S. moins de 10%.

L'eau utilisée provenait du cricuit de la ville d'Athènes et avait les propriétés indiquées au Tableau 2.

Le pourcentage ciment-sable-eau était toujours 1:3:0,45 (par poids).

TABLEAU 2  
QUALITÉS DE L'EAU UTILISÉ

pH	7,6	Al	1,1 mg/lit	Sulfates	21,3mg/lit
K	6,0mg/lit	O <sub>2</sub> libre	1,6 »	Carbonates	2,0 »
Na	50,8 »	Cl <sub>2</sub> libre	0,25 »	SiO <sub>2</sub>	6,3 »
		Residue			
Ca	56,8 »	à 105°C	426,0 »	Dureté per.	5,4of
Mg	27,3 »	Clorures	107,0 »	Dureté total	25,2of

Tous les éprouvettes portaient à leur axe géométrique de l'acier Siemens-Martin, préparé en Grèce, de section circulaire, d'un diamètre de 10 mm et d'une longueur de 100 mm, après traitement mécanique, pour le nettoyage de sa surface.

Le traitement mécanique consistait à une réduction du diamètre de l'acier de 12 mm à 10 mm (c'est-à-dire de deux millimètres) à l'aide d'une tour ayant une vitesse de rotation de 600 tours/min et un avancement de 0,05 mm/tour.

Les propriétés de l'acier sont indiquées au tableau 3.

TABLEAU 3  
QUALITÉS DE L'ACIER UTILISÉ

Analyse		Propriétés mécaniques	
Fe	99,23%	Résistance d'écoulement	22,5 Kp/mm <sup>2</sup>
C	0,11%	Résistance à la rupture	37,0 »
Mn	0,56%	Allongement spécifique	
P	0,03%	à la rupture	27,5%
S	0,07%		

Dans toutes les éprouvettes, l'épaisseur minimum du béton revêtant l'acier était de 1,5 cm et il était posé de façon que 1,5 cm de l'acier ressorte du béton.

Toutes les éprouvettes étaient préparées dans des moules en acier.

Le mélange ciment-sable-eau restait pendant 24 h dans les moules dans un milieu saturé d'humidité à la température ambiante (~ 20°C) et, après le démoulage, 24 h dans l'eau douce, à une hauteur de 3 cm moins celle du béton et à la température ambiante.

Pendant la préparation, l'acier d'armature restait toujours culminant avec le morceau d'acier ressortant du béton en haut.

De cette façon nous avons préparé 160 éprouvettes, sur lesquelles nous avons maintenu les conditions de préparation et de mesures ci-haut mentionnées constantes, mais nous avons modifié la forme et l'isolation. Ainsi, nous avons préparé des éprouvettes avec des sections carrées, circulaires et triangulaires (Fig. 1, A, B, C). Sur la figure 2 on voit les différentes isolations par «Araldite» employées pour toutes les formes d'éprouvettes.

La condition constante pour l'isolation était l'isolation d'une partie du béton ou de l'acier 3 cm au-dessous de la surface supérieure du béton.

Cette forme d'isolation est nécessaire parce que sans celle-là l'eau dans laquelle les éprouvettes sont immergées pendant les mesures entre en contact avec l'acier en dehors du béton grimant sur la surface du béton à l'aide de forces capillaires et superficielles. D'autre part, l'isolation de l'acier en bas s'est avérée nécessaire car le champ électrostatique pendant la mesure est différent en raison de l'effet du recoin.

Pendant les mesures, les éprouvettes étaient immergées dans l'eau (douce ou de mer) à une hauteur de 3 cm au-dessous de la surface supérieur du béton.

L'emplacement du bout libre du tuyau de l'électrode de référence (calomel saturé) est indiqué dans la figure 4 pour toutes les sortes d'éprouvette. Le point commun est que le bout libre était en contact avec le béton en des points se trouvant à 1,5 cm de l'armature et à une hauteur de 4,5 cm de la base de l'éprouvette.

Tous les mesures étaient effectuées à une température de 25°C, et pendant le temps nécessaire pour que le potentiel soit stabilisé.

Toutes les conditions ci-haut mentionnées étaient acceptées après de mesures pendant lesquelles on a modifié une condition chaque fois dans le but de déterminer les conditions meilleurs au point de vue précision et reproductibilité.

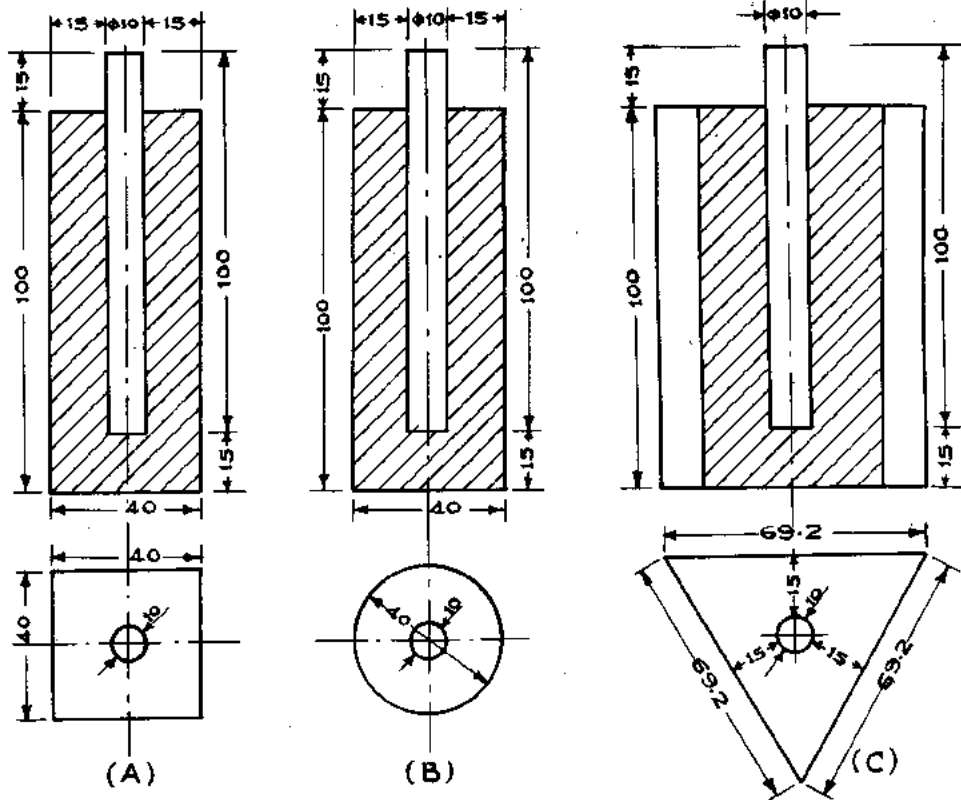
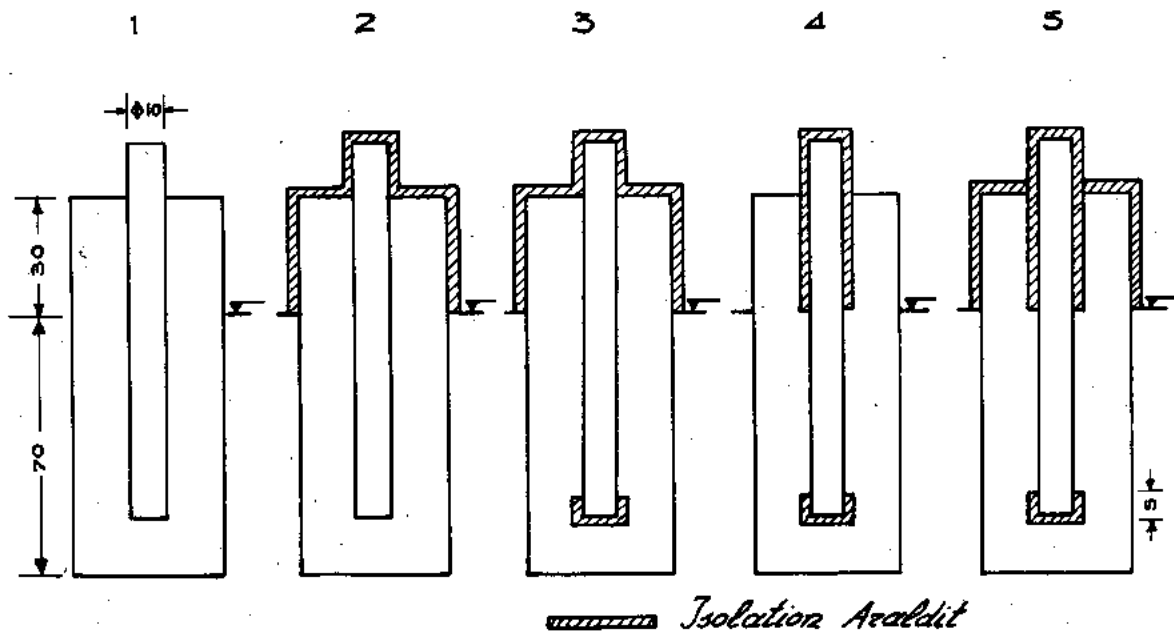


Fig. 1. Différents types d'éprouvettes utilisées.



*Isolation Araldite*

Fig. 2. Différentes isolations par araldite.

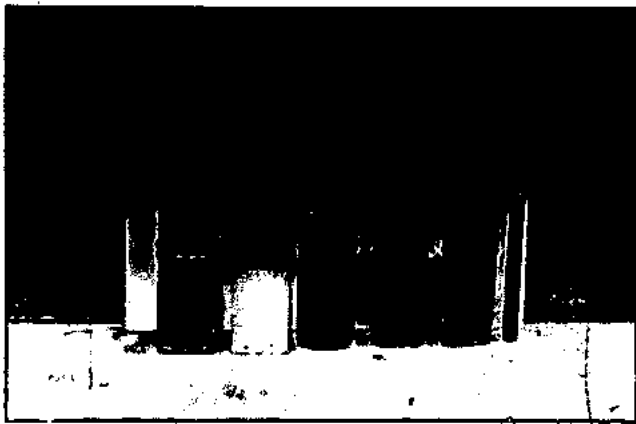


Fig. 3. Vue de différentes éprouvettes utilisées.

1ère série de mesures: Mesure de potentiel de corrosion (par rapport à l'électrode de calomel saturée) dans l'eau douce.

Pour chaque éprouvette, préparé selon les conditions ci-haut mentionnées, on a mesuré le potentiel par rapport à l'électrode de calomel saturée à des positions indiquées dans la figure 4.

Les mesures étaient effectuées à l'aide d'un voltmètre électronique avec enregistreur. Le dispositif de mesure est indiqué dans la figure 5.

Un certain nombre d'éprouvettes était préparé pour chaque type d'éprouvette pour contrôler la reproductibilité.

Les résultats des mesures sont donnés aux tableaux 4, 5, 6. Chaque valeur portée au tableau est la moyenne des mesures selon les positions différentes (Fig. 4) du bout du capillaire par rapport à l'éprouvette, mais à la même hauteur.

La seule façon d'interpréter les valeurs différentes indiquées aux tableaux pour les éprouvettes de différentes formes de section et de différentes isolations, est d'accepter l'influence de la surface libre de l'acier et de la forme du

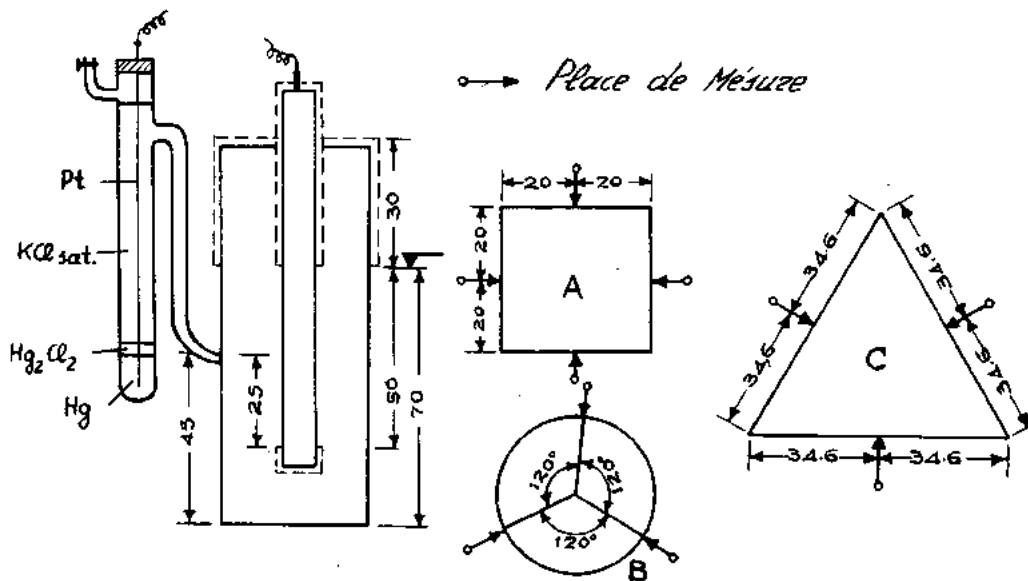


Fig. 4. Place de mesure sur les éprouvettes.

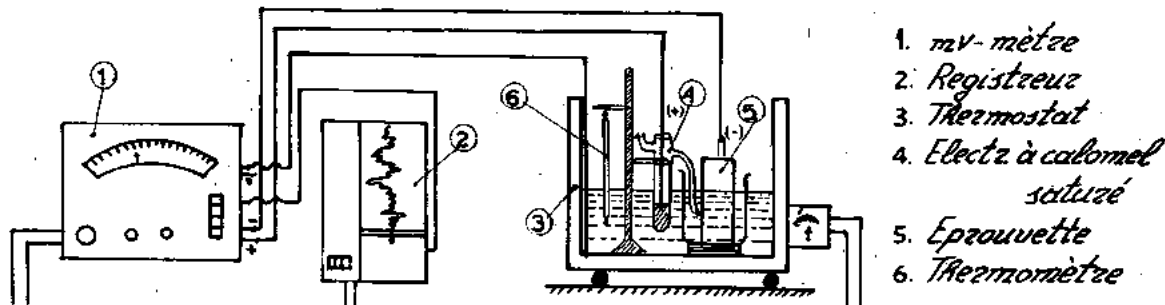


Fig. 5. Dispositives de mesure du potentiel.

1. *mv-mètre*
2. *Registreur*
3. *Thermostat*
4. *Electz à calomel saturé*
5. *Éprouvette*
6. *Thermomètre*



TABLEAU 4

MESURES DE POTENTIEL SUR LE TYPE A (FIG. 1) DIFFÉRENTES ISOLATIONS (1-5 FIG. 2) P. RAP. A CAL. SAT.

A1 mV	A2 mV	A3 mV	A4 mV	A5 mV
286	419	432	541	594
295	404	436	516	481
222	424	385	557	569
242	429	374	473	551
248	432	434		533
243	408	425		549
250		560		592
283		480		462
		319		428
		446		579
				567
259	419	430	522	537

TABLEAU 5

MESURES DE POTENTIEL SUR LE TYPE B (FIG. 1) DIFFÉRENTES ISOLATIONS (1-5 FIG. 2) P. RAP. A CAL. SAT.

B1 mV	B2 mV	B3 mV	B4 mV	B5 mV
324	197	309	548	405
236	125	299	520	448
386	126	232	500	362
180	130	379	530	426
374	323	315	365	395
274	448	358	160	398
	274	300	467	398
	384		287	435
	450			
	341			
	145			
	345			
	120			
	407			
	211			
	200			
296	262	313	422	408

champ électrostatique pendant la mesure entre le bout de capillaire et de l'acier. Par surface libre, on entend toute la surface libre (pas isolée) de l'acier dans le béton et non seulement la surface jusqu'à la hauteur de l'eau, étant donné que par des forces capillaires toute cette surface est en contact avec l'eau et influence par conséquent la mesure.

Pour cela, nous avons effectué des mesures sur de l'acier libre immergé dans l'eau douce à différentes hauteurs (surfaces différentes) et on a aussi modifié le temps d'immersion avant la mesure (temps 0 h - 72 h).

Le tableau 7 contient les mesures.

Les valeurs du tableau 7 sont portées au diagramme de la fig. 6.

TABLEAU 6

MESURES DE POTENTIEL SUR LE TYPE C (FIG. 1) DIFFÉRENTES ISOLATIONS (1-5 FIG. 2) P. RAP. A CAL. SAT.

C1 mV	C2 mV	C3 mV	C4 mV	C5 mV
144	373	171	375	164
276	327	430	355	256
205	380	180	412	247
335	180	390	120	257
188	200	420	405	367
345				
320				
300				
264	292	318	333	258

TABLEAU 7

POTENTIELS D'ACIER (P. RAP. CAL. SAT.) PAR RAPPORT AU TEMPS ET A LA SURFACE IMMERGÉE

Surface immergée	Temps d'immersion			
	0h	24h	48h	72h
1570 mm <sup>2</sup> (1)	469 mV	610 mV	687 mV	700 mV
581 » (2)	522 »	565 »	645 »	654 »
1838 » (2)	440 »	590 »	658 »	685 »
2278 » (2)	521 »	555 »	627 »	652 »
2700 » (2)	500 »	695 »	730 »	720 »

(1) Acier isolé du reste de sa surface.

(2) Acier sans isolation.

De ce diagramme, on conclut que le potentiel augmente par rapport au temps d'immersion, on conclut aussi que la surface immergée influence le potentiel d'une manière irrégulière mais, en général, pour les éprouvettes immergées pendant plus de 24 h, le potentiel augmente, subit une diminution pour la même surface pour toutes les éprouvettes et augmente de nouveau.

Sur la base des résultats des tableaux 4, 5 et 6, en tenant compte des résultats du diagramme de la fig. 6 pour immersion des éprouvettes pendant 48 heures (le même temps que pour les éprouvettes en béton armé des tableaux 4, 5 et 6) on a tracé le diagramme de la fig. 7.

La fig. 7 présente les potentiels pour des éprouvettes de forme et d'isolation différente en fonction de la surface libre d'acier, déjà cité plus haut.

De ce diagramme, on constate une diminution systématique des valeurs de potentiel, à l'exception d'une faible augmentation au commencement du diagramme pour le type C, provenant de différents champs électrostatiques (comparer les types d'isolation 5 avec 4 et 2 avec 1).

Si on compare entre eux les fig. 6 et 7 on conclut qu'il n'existe aucune liaison entre les valeurs des potentiels par rapport au temps dans les deux diagrammes parce que les potentiels des éprouvettes en béton armé diminuent tandis que les potentiels des éprouvettes en acier nue dans le même domaine des grandeurs des surfaces passent par un minimum. C'est une preuve que les valeurs des potentiels aux éprouvettes

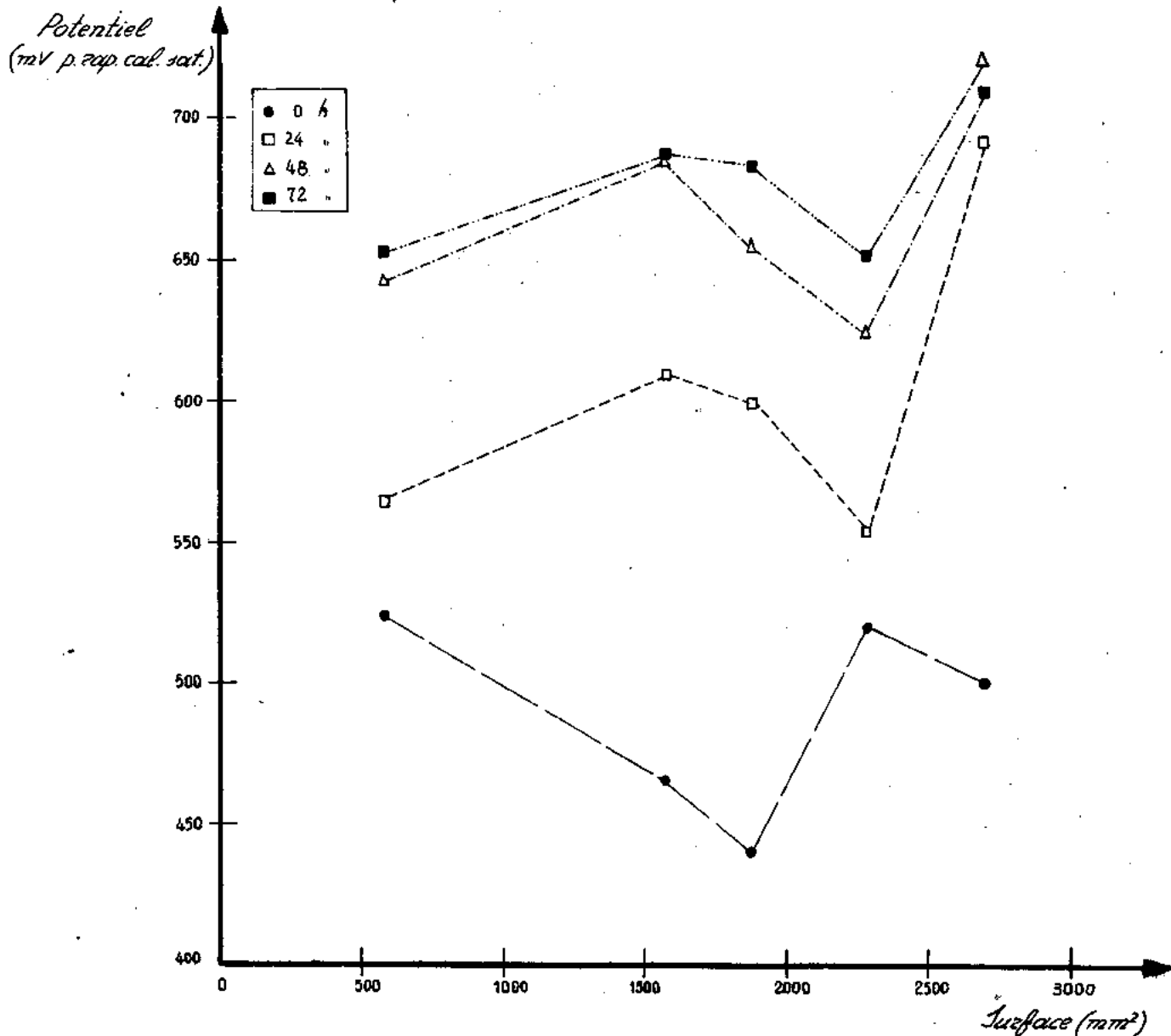


Fig. 6. Potentiel d'acier (p. rap. cal. sat.) par rapport au temps et de la surface immergée.

en béton armé ne sont pas influencés seulement par la surface mais aussi par le champ électrostatique pendant la mesure.

Au point de vue de la reproductibilité, les valeurs des éprouvettes (type-isolation) A4, B5, C5 semblent être les meilleures.

On constate aussi que pour tous les types d'éprouvette, les valeurs des potentiels sont identiques pour celles n'ayant pas d'isolation.

On conclut donc, en tenant compte des valeurs pour la même isolation pour différents types d'éprouvette, que sans isolation les valeurs ne sont pas réelles.

C'est pour cela, que nous proposons des éprouvettes de section circulaire avec isolation du type 5 (B5) pour lesquelles la reproductibilité et la réalité des valeurs semblent les meilleures, étant donné la distance des valeurs pour la même isolation et les différentes types d'éprouvettes.

*2ème série des mesures : Mesures du potentiel de corrosion (par rapport à l'électrode Ag/AgCl saturée) dans l'eau de mer.*

Avec des éprouvettes préparées sous les mêmes conditions que celles de la série 1 et avec les mêmes modifications de forme et d'isolation, les mêmes mesures dans de l'eau de mer ont été effectuées sous les mêmes conditions et les valeurs ont été rapportées à l'électrode de calomel saturée (Tableau 8).

A l'aide du tableau 8, on obtient dans les mêmes conditions que le diagramme de la fig. 7 le diagramme de la fig. 8.

Sur ce diagramme on constate qualitativement les mêmes résultats qu'au diagramme de la fig. 7, soit une diminution du potentiel par rapport à la surface et précisément plus intense, que celle dans l'eau douce.

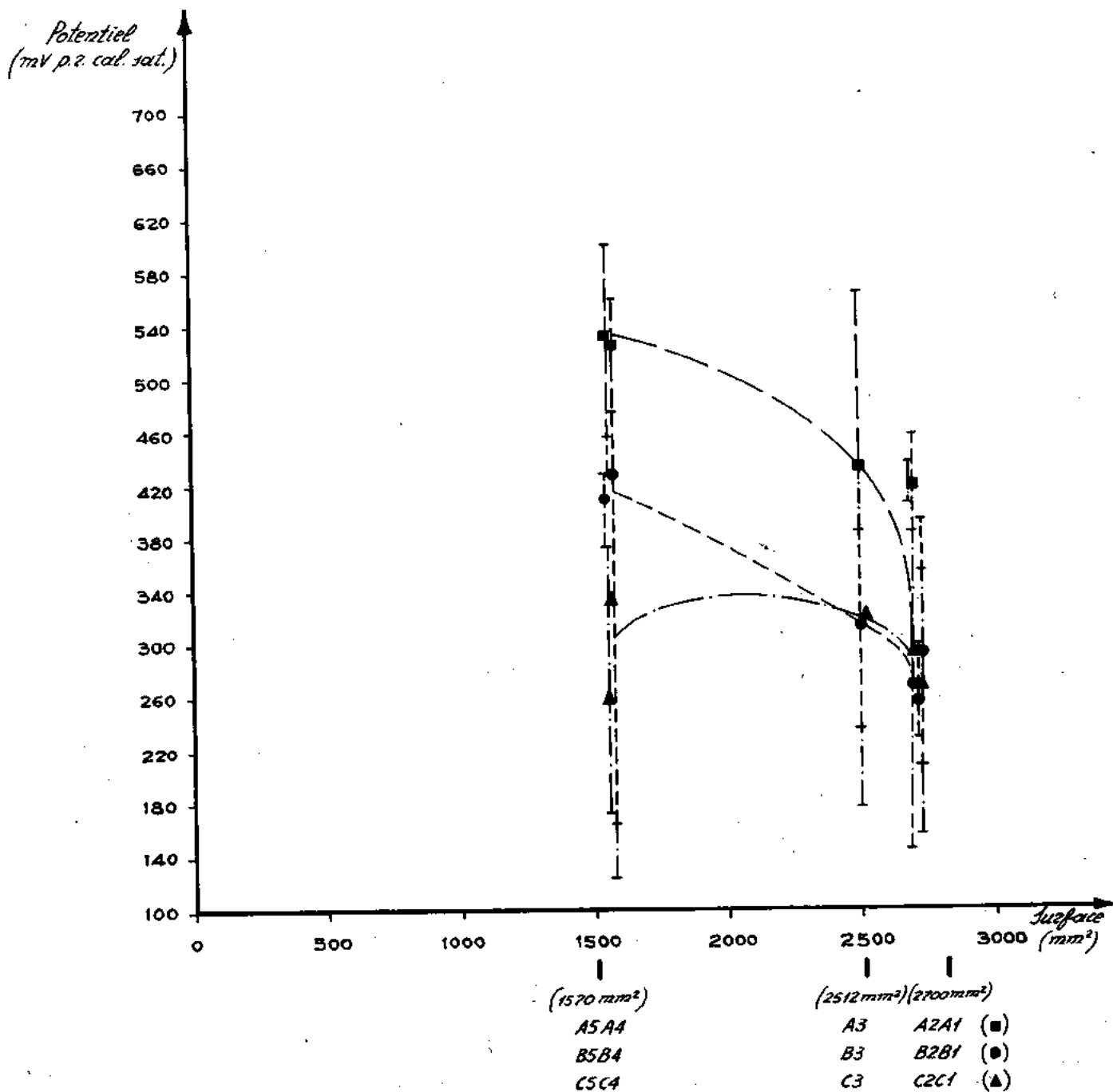


Fig. 7. Potentiels des différents types (A, B, C, Fig. 1) et différentes isolations (1-5 Fig. 2) p. rap. à cal. sat.

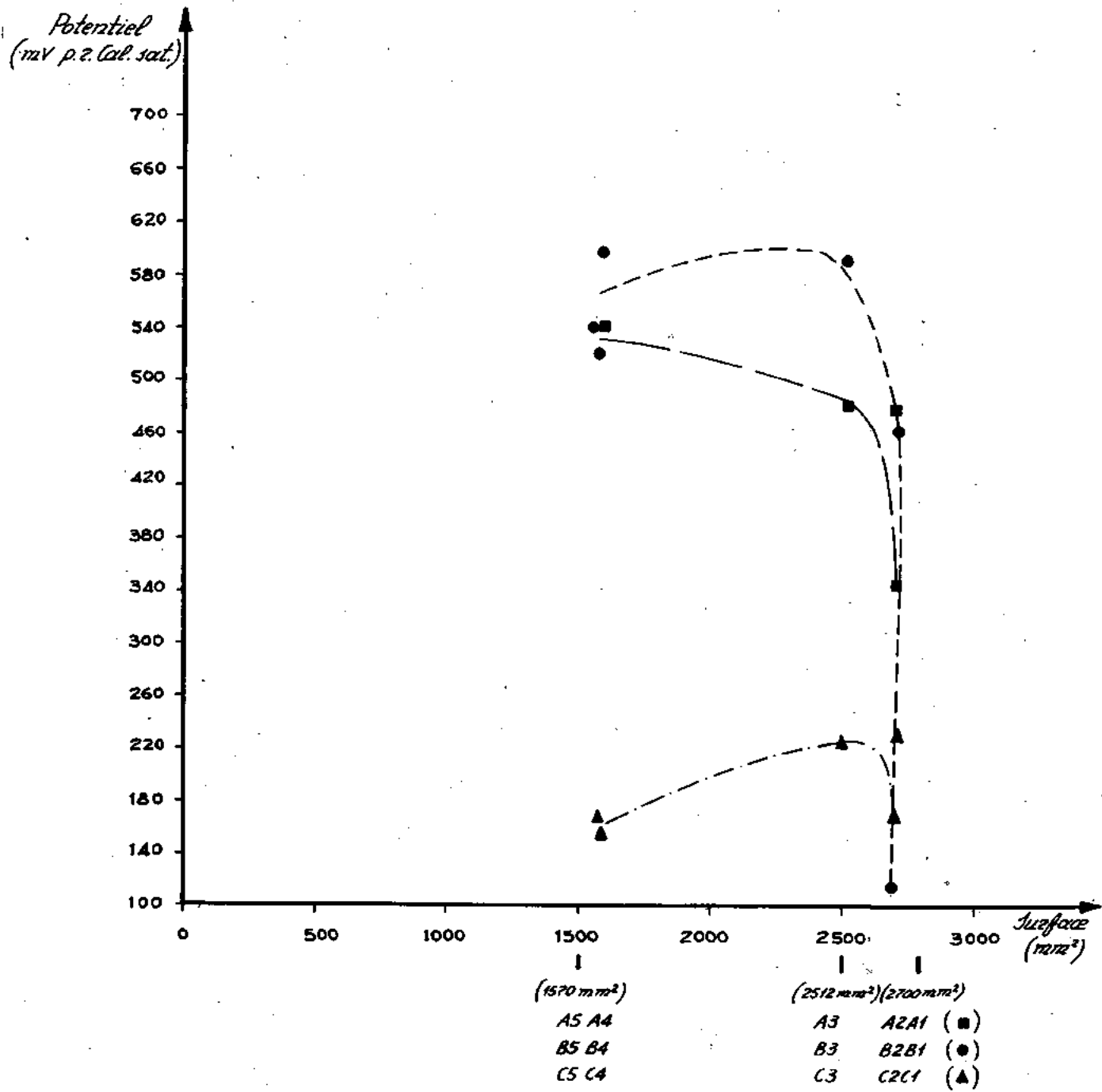


Fig. 8. Potentiels des différents types (A, B, C, Fig. 1) et différentes isolations (1-5, Fig. 2) rapporté par rap. à cal. sat. dans l'eau de mer.

TABLEAU 8

POTENTIELS DE DIFFÉRENTS TYPES D'ÉPROUVETTES (A, B ET C FIG. 1) ISOLATION 1-5 (FIG. 2) DANS L'EAU DE MER RAPPORTÉES PAR. RAP. A CAL. SAT.

Potentiel (mV)					
	Isolation				
Type	1	2	3	4	5
A	345	478	481	542	520
B	460	113	589	598	540
C	230	170	222	155	170

3ème série des mesures: Mesures du potentiel de corrosion (par rapport à l'électrode Ag/AgCl saturée) dans l'eau de mer par rapport au temps.

Nous avons mesuré avec des éprouvettes préparés sous les mêmes conditions que les séries 1 et 2 les potentiels par rapport au temps lorsque les éprouvettes étaient dans l'eau de mer circulante, se renouvelant toutes les 24 heures. Les résultats sont portés au tableau 9.

Les valeurs du tableau 9 sont portées aux diagrammes des fig. 9, 10, 11. Des diagrammes, on constate que les valeurs de potentiel pour toutes les formes d'éprouvette et tous les types d'isolation restent à peu près constantes où diminuent légèrement, à l'exception de deux types d'éprouvette où on constate une diminution de potentiel (cas A1) et une augmentation du potentiel (cas C4). Les valeurs pour les éprouvettes de section triangulaire sont toujours plus basses, comme on l'a constaté déjà au diagramme fig. 7.

4ème série de mesures: Mesures de l'intensité du courant par rapport au temps pour des éprouvettes immergées dans l'eau de mer circulante sous une protection cathodique d'une tension de -850 mV constante par rapport à Ag/AgCl saturée.

Un nombre d'éprouvette préparé dans les mêmes conditions de séries 1, 2 et 3 avec les mêmes variations de formes et quelques variations d'isolation (surtout celles qui selon les mesures précédentes donnent des résultats plus précis et plus reproductibles), a été immergé dans l'eau de mer circulante sous une protection cathodique de -850 mV. Quelques-unes des ces éprouvettes avaient des trous perpendiculaires à l'acier d'un diamètre de 5 mm jusqu'à la surface de l'acier.

Deux éprouvettes de chaque types étaient posées dans des cuves en matière plastique (chaque type d'éprouvette séparément).

Comme anode, nous avons utilisé du graphit à une distance de 32 cm.

Nous avons utilisé le groupe des dispositifs de la figure 12, 12a, 12b.

Ces ensembles expérimentaux disposaient tous les circuits électriques et instruments nécessaires pour la circulation de l'eau de mer, la protection cathodique et la mesure précise de l'intensité du courant pour chaque type d'éprouvette (couple) par rapport au temps.

De cette manière, nous avons obtenu les valeurs suivantes du tableau 10.

Les valeurs de ce tableau (Tabl. 10) sont portés aux diagrammes fig. 13, 14 et 15. De ces diagrammes, on a conclu que l'intensité diminue pendant cinq à dix jours à cause du fait que la résistance de la surface de l'acier augmente à cause de la formation d'oxyde et demeure ensuite constante. On constate aussi que pour les éprouvettes, pour lesquelles le potentiel de corrosion était bas (A>B>C, fig. 7), l'intensité du courant est plus grand (C>B>A), comme on l'entendait. Quand on compare entre eux les mêmes types d'éprouvettes (la même forme et la même isolation), avec et sans trous, on constate que l'intensité du courant pour les éprouvettes avec trous et pour toutes les formes d'éprouvette sans isolation (type 1 fig. 2) est plus basse que celle sans trous. Au contraire, pour le type d'isolation 5 (fig. 2), l'intensité du courant pour les éprouvettes avec trous est plus haute.

TABLEAU 9

POTENTIELS PAR RAPPORT A L'ÉLECTRODE Ag/AgCl SAT. DE DIFFÉRENTS TYPES (A,B,C, FIG. 1) ET DIFFÉRENTES ISOLATIONS (1-5, FIG. 2) PAR RAPPORT AU TEMPS DANS L'EAU DE MER.

Temps (jours)	A1 mV	A2 mV	A3 mV	A4 mV	A5 mV	B1 mV	B2 mV	B3 mV	B4 mV	B5 mV	C1 mV	C2 mV	C3 mV	C4 mV	C5 mV
0	30	17	45	34	45	40	36	36	150	10	55	125	225	105	98
2	305	438	441	502	480	420	72,8	549	558	500	190	130	182	115	130
5	250	400	345	490	445	405	78	435	510	490	62	110	132	125	155
6	220	395	340	470	415	400	64	380	510	440	50	117	127	125	153
10	136	400	335	460	365	355	34	435	495	425	45	111	110	175	230
12	140	395	335	435	380	380	32	430	500	405	44	110	133	155	170
14	95	390	345	435	405	315	30	430	485	405	42	106	123	240	155
16	108	380	330	440	405	335	30	430	450	405	45	104	110	260	150
18	95	375	335	425	405	320	27,5	435	445	395	36	100	108	270	146
21	105	370	330	410	395	390	29	450	430	390	65	97	110	270	150
23	97	370	310	385	390	340	27	455	440	380	45	85	115	280	148
25	87	375	320	375	400	310	26	455	440	390	35	90	124	290	148
28	109	380	320	335	365	345	24	460	455	385	36	86	111	300	148
31	96	380	310	310	315	325	22	470	410	378	38	81	101	305	145

Type A [□]

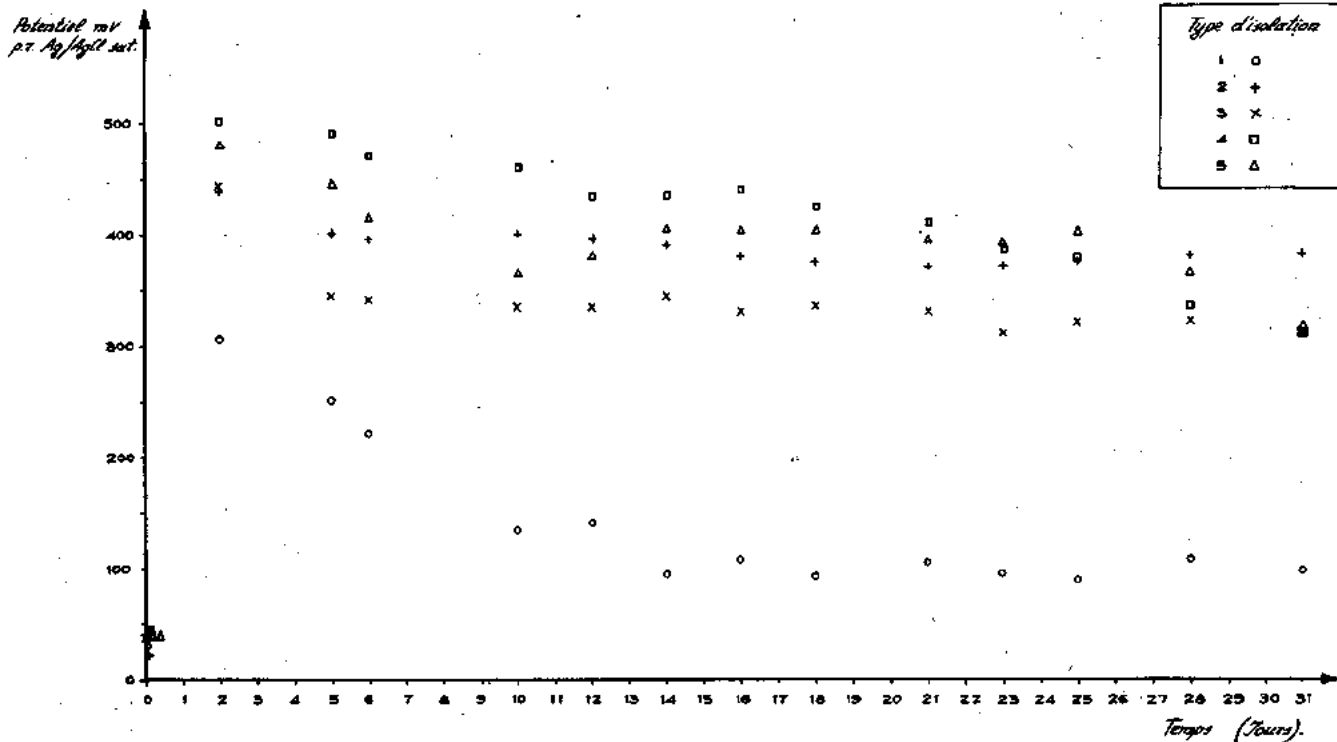


Fig. 9. Potentiels de type A (Fig. 1) et des différentes isolations (1-5 Fig. 2) des éprouvettes par rap. à élec. Ag/AgCl sat. dans l'eau de mer par rapport au temps.

Type B [○]

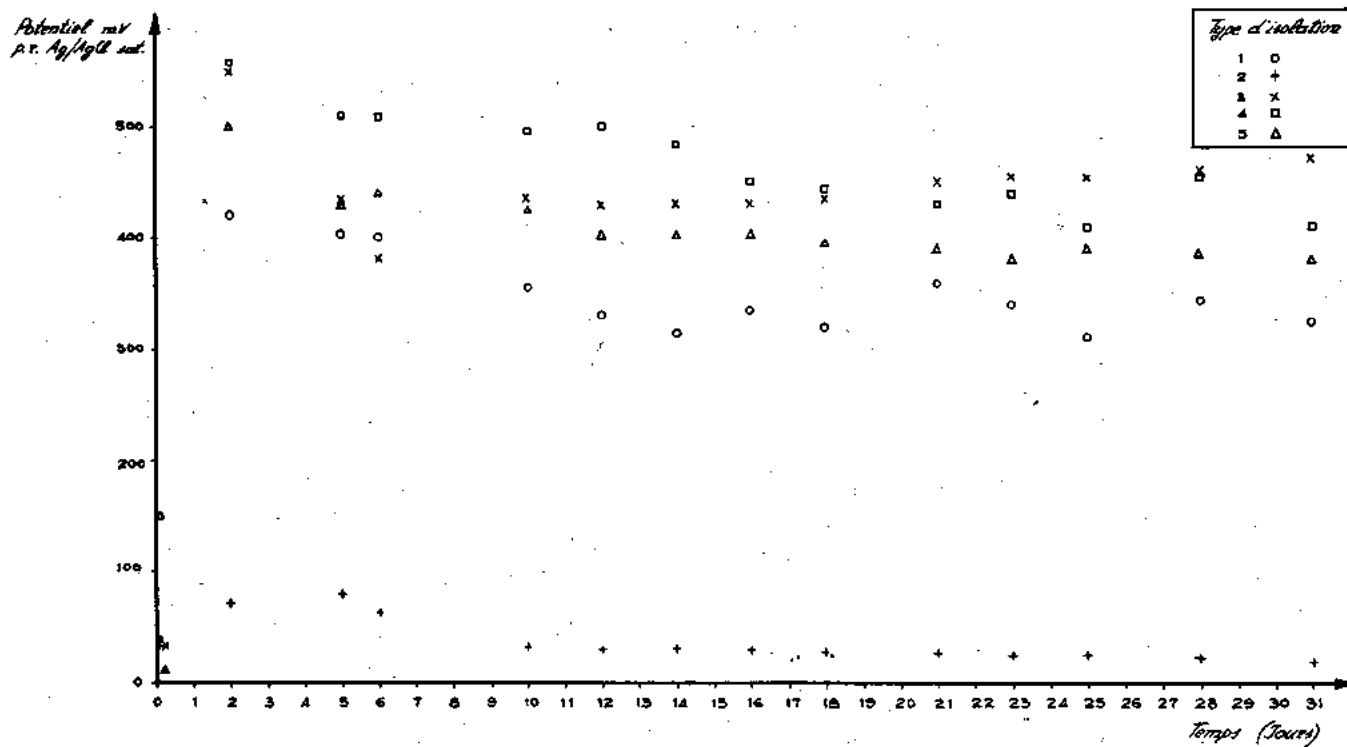


Fig. 10. Potentiels de type B (Fig. 1) et des différentes isolations (1-5 Fig. 2) des éprouvettes par rap. à élec. Ag/AgCl sat. dans l'eau de mer par rapport au temps.

Type C (A)

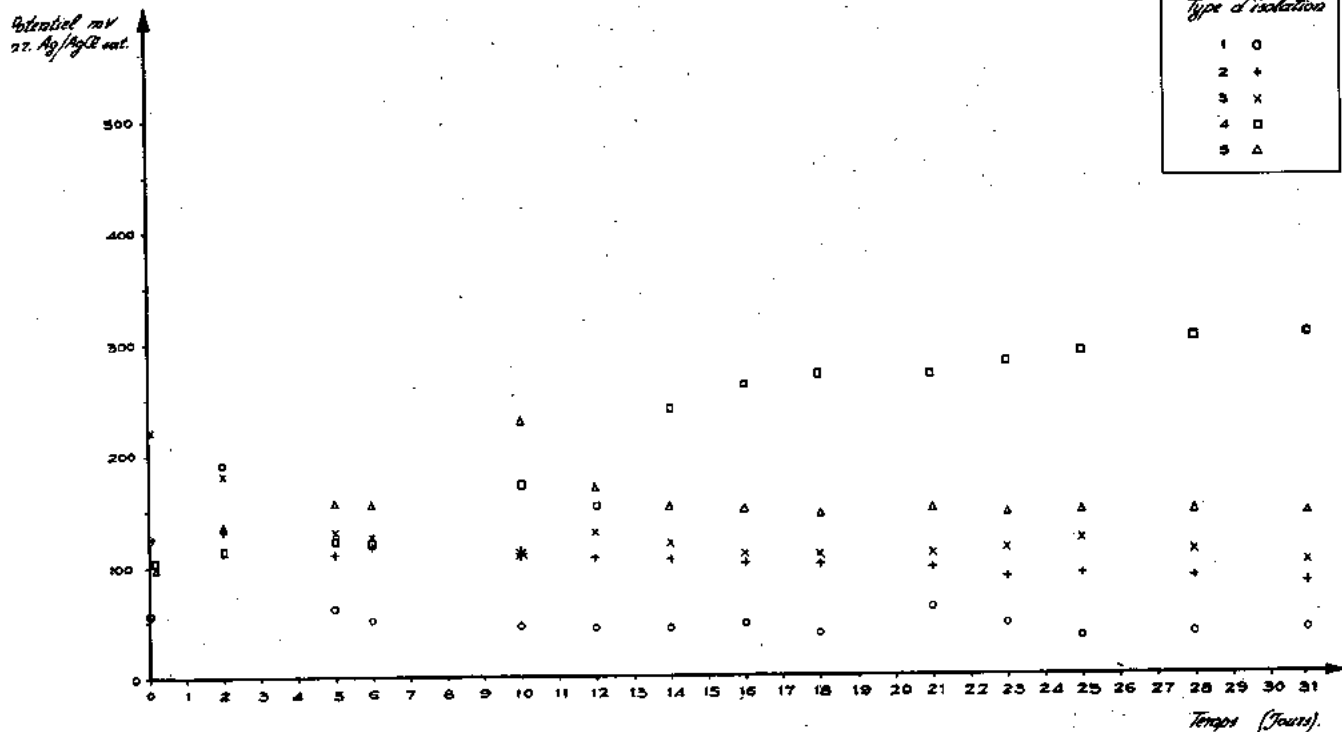


Fig. 11. Potentiels de type C (Fig. 1) et des différentes isolations (1-5 Fig. 2) des éprouvettes par rap. à élec. Ag/AgCl sat. dans l'eau de mer par rapport au temps.

TABLEAU 10

INTENSITÉ DU COURANT PAR RAPPORT AU TEMPS DANS DES ÉPROUVETTES DES DIFFÉRENTS TYPES ET ISOLATIONS DANS L'EAU DE MER SOUS PROTECTION CATHODIQUE, D'UNE TENSION CONSTANTE DE -850 mV PAR RAP. A L'ELECTRODE Ag/AgCl SAT.

Temps (jours)	A1 μA	A4 μA	A5 μA	Avec trou		B1 μA	B4 μA	B5 μA	Avec trou		C1 μA	C4 μA	C5 μA	Avec trou	
				A1	A5				B1	B5				C1	C5
				μA	μA				μA	μA				μA	μA
0	1100	300	340	800	700	1600	940	360	2500	900	900	1100	1700	1200	1500
0,125 (3h)	150	210	40	320	40	40	40	20	40	60	1000	600	1100	840	1800
2	40	40	10	40	10	70	10	10	35	20	500	50	100	300	950
5	40	70	5	5	40	120	5	40	20	10	410	170	3	400	180
6	45	80	2	60	110	115	5	40	25	25	400	130	380	380	160
10	50	120	40	20	55	200	40	60	40	50	360	160	100	330	210
12	50	100	100	35	60	190	20	45	35	45	360	155	170	320	210
14	50	110	60	30	60	200	35	55	35	55	350	165	150	290	215
16	60	125	80	30	60	200	35	55	35	55	340	165	150	290	210
18	60	120	80	40	65	190	25	50	30	60	340	170	150	280	210
21	70	120	60	50	65	210	25	50	50	60	340	180	160	300	230
23	70	140	120	35	70	200	30	45	25	65	340	180	160	260	230
25	70	130	70	35	70	180	25	45	35	60	340	180	155	250	230
28	80	130	80	45	75	190	30	45	35	80	340	180	160	240	230
31	70	140	100	40	70	180	30	40	35	75	320	175	155	220	240



Fig. 12.

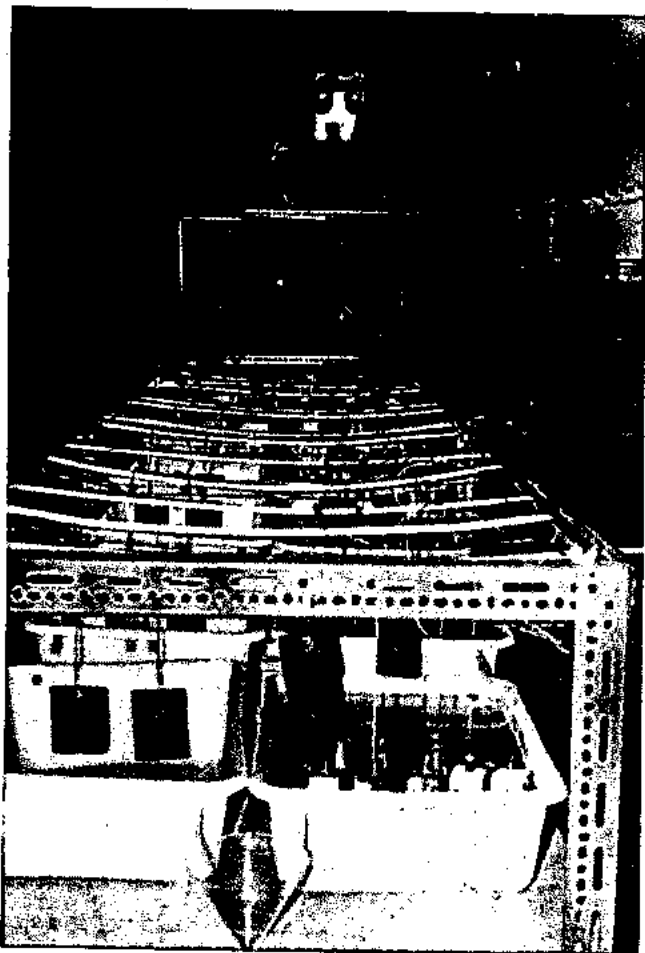


Fig. 12a. Groupe des dispositifs pour les mesures dans l'eau de mer avec ou sans protection cathodique.

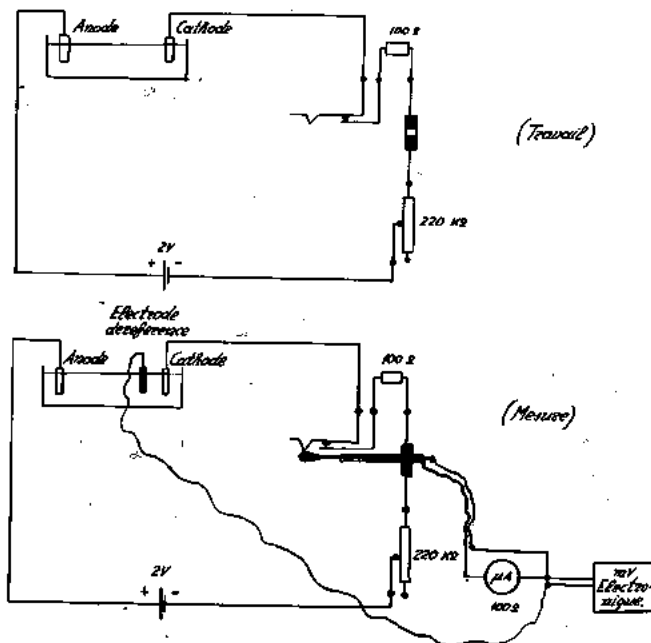


Fig. 12b. — Schéma du circuit électrique.



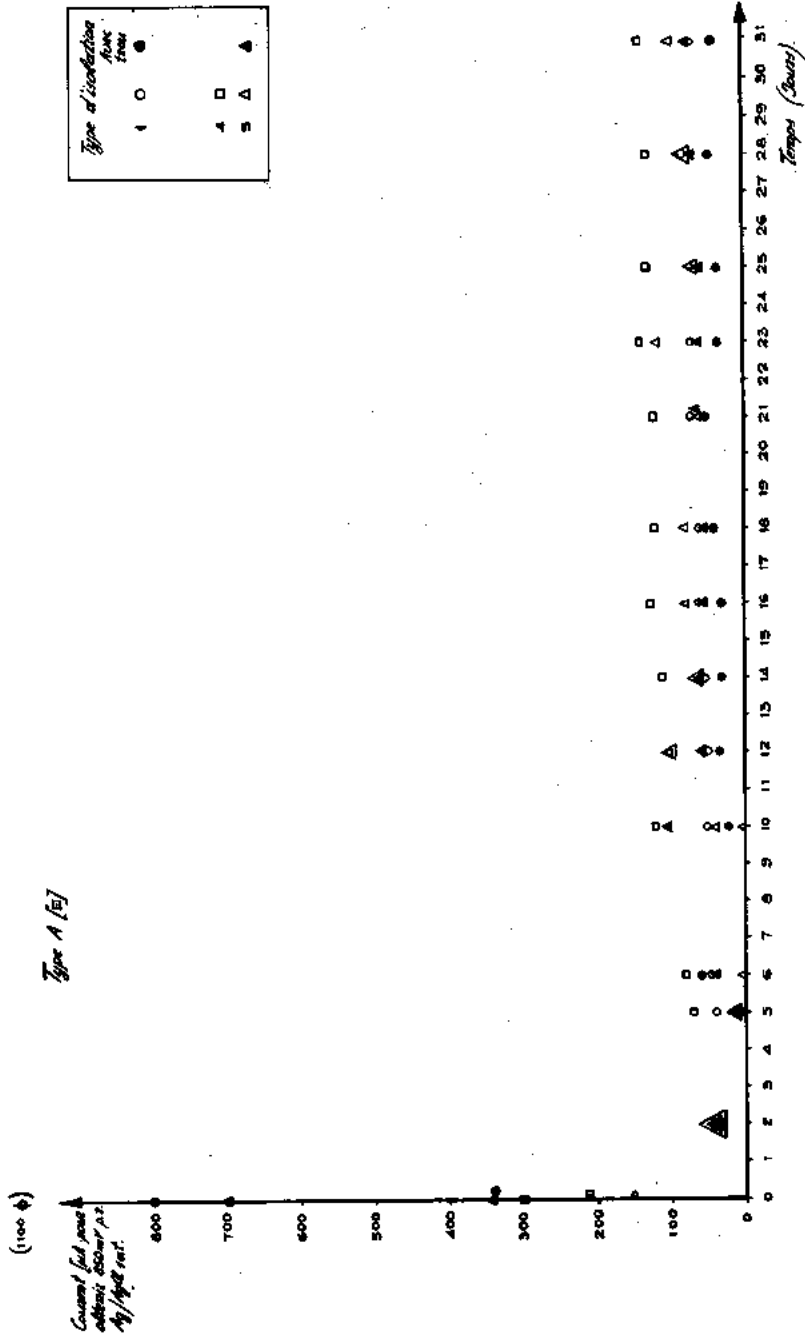


Fig. 13. Intensité du courant par rapport au temps à des éprouvettes de type A et différentes isolations, dans l'eau de mer sous protection cathodique d'une tension constante de -850 mV par rap. à l'électrode Ag/AgCl sat.

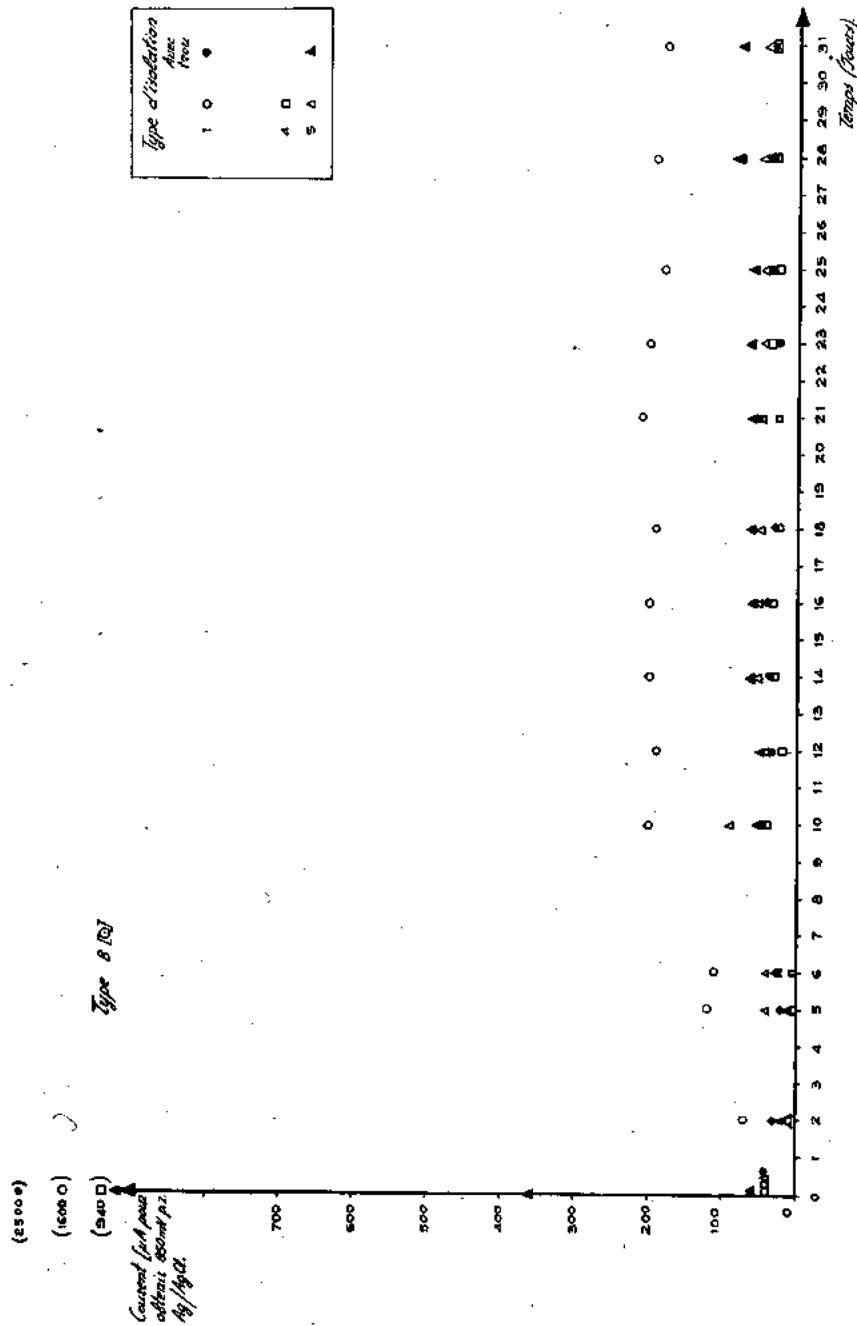


Fig. 14. Intensité du courant par rapport au temps à des éprouvettes de type B et différentes isolations, dans l'eau de mer sous protection cathodique d'une tension constante de -850mV par rap. d'électrode Ag/AgCl sat

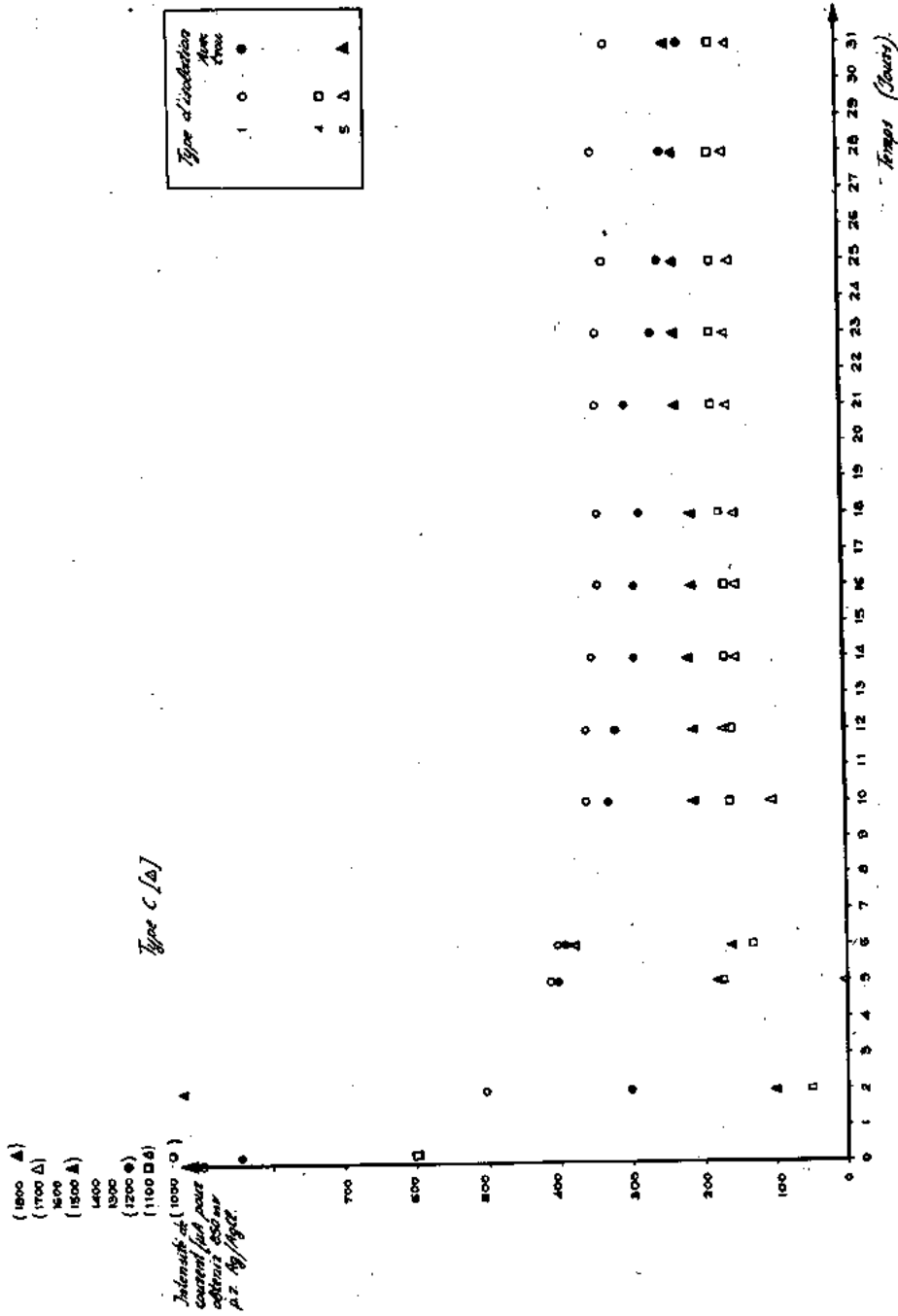


Fig. 15. Intensité du courant par rapport au temps à des éprouvettes de type C et différentes isolations, dans l'eau de mer sous protection cathodique à l'électrode Ag/AgCl sat.

## CONCLUSIONS

1. Les valeurs du potentiel pour le béton armé sont extrêmement sensibles aux conditions: qualité du ciment, du sable, de l'eau, et de l'acier, y compris le type de préparation de la surface de l'acier, proportion ciment-sable-eau-acier (la grandeur de la surface d'interface) et aux conditions de prise; elles dépendent aussi de la forme des éprouvettes, de l'isolation, de la position des éprouvettes pendant la prise, de la position de l'électrode de référence et du temps entre leurs préparation et les mesures; c'est pour cela que les valeurs du potentiel se reproduisent très difficilement.

2. Nous pensons que l'isolation des quelques parties des éprouvettes et de l'acier est indispensable à cause du fait que, sans isolation pour les éprouvettes de différents types, on trouve les mêmes potentiels, bien que les différents champs électrostatiques pour les différents types imposent un potentiel différent pour les éprouvettes avec isolation.

3. Par des mesures du potentiel effectuées quand les éprouvettes étaient immergées dans l'eau douce et l'eau de mer et des mesures de l'intensité du courant par rapport au temps,

nous avons conclu que les éprouvettes à section circulaire avec isolation du type 5 (B5) présentent la meilleure précision et reproductibilité des mesures.

4. En raison de la sensibilité mentionnée, il est nécessaire d'avoir un plus grand nombre d'éprouvettes que celles (160) qu'on a utilisées pour les mesures, afin de conclure avec une plus grande certitude sur le type d'éprouvette et la forme acceptables.

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## DISCUSSION

Dr. RASCIO (Argentine): Pour éliminer les effets de frange que vous appelez effet électrostatique, est-ce que vous avez essayé de faire de mesure de potentiel en coupant le courant.

Dr. SARROPOULOS: Non pas en coupant le courant pour les éprouvettes qui étaient sous une protection cathodique. C'étaient des éprouvettes sans protection cathodique où on faisait la mesure de potentiel.

Dr. ANTONIOU (Grèce): Je voudrais vous demander si on a fait des éprouvettes avec de l'eau de mer au lieu de l'eau douce parce que

dans des travaux maritimes d'un chantier on emploie souvent l'eau de mer au lieu de l'eau douce.

Dr. SARROPOULOS: Toutes les éprouvettes étaient préparés avec de l'eau douce, et après se sont immergés dans l'eau de mer.

Dr. ANTONIOU: C'est très intéressant de savoir ce qui se passe dans le béton qui se fait avec de l'eau de mer au lieu de l'eau douce.

Dr. SARROPOULOS: Oui, naturellement et nous sommes en train de le faire.

SECTION  
SEKTION-TOMEYΣ

II

Corrosion biologique et bactériologique. Salissures. Biologie et écologie des organismes sessiles. Organismes xylophages. Ouvrages en bois. Combination des sections I et II.

Biological corrosion. Fouling and its prevention. Biology (including physiology and biochemistry) and ecology of sessile organisms. Marine borers. Papers comprising a combination of subjects listed in I and II.

Biologische und bakteriologische Korrosion. Bewuchs und Bewuchsschutz. Biologie und Ökologie von Bewuchsorganismen. Marine Holzzerstörer. Schutz von Bauwerken aus Holz. Kombination von Sectionen I und II.

Βιολογική και βακτηριολογική διάβρωση και προστασία. Ρύπανσις τῶν ὑφάλων.

Βιολογία τῶν προκαλούντων διάβρωσιν μικροοργανισμῶν. Ὄργανισμοὶ ξυλοφάγοι. Κατασκευαὶ ἐκ ξύλου καὶ προστασία αὐτῶν. Συνδυασμὸς τῶν τομέων I καὶ II.

Séance - Meeting - Sitzung - Συνεδρίασις  
20.9.1968

Présidence - Presidency  
Präsidium - Προεδρείον

Prof. K. NIAVIS (Grèce).  
Dr. B. CALLAME (France).

Allocution de Mr ANARGYROU, représentant du Président de l'Organisation pour la Prévention des Accidents Archevêque d'Athènes et de Grèce Monseigneur IERONIMOS et Secrétaire Général de l'Organisation

Le Président de l'Organisation pour la Prévention des Accidents Archevêque d'Athènes et de Grèce entière Mr Ieronimos, m'a chargé de vous interpréter ses vœux pour la réussite de votre Congrès, ainsi que de vous déclarer son vif intérêt, car les travaux scientifiques qui ont été communiqués durant ce Congrès, (il en est de même pour les congrès précédents) constituent pour nous un sujet très intéressant.

Comme Secrétaire Général de l'Organisation, j'ai été chargé d'assister à votre Congrès, et de vous communiquer nos points de vue au sujet des dangers maritimes.

En ce qui concerne le sujet général du Congrès, outre les pertes économiques, dues à la corrosion et aux salissures il y a aussi un très grand danger pour l'équipage des bateaux, et pour l'homme, tout particulièrement.

On sait que les salissures et la corrosion des tuyauteries conduisent à des difficultés de manipulation, et, souvent, à de grands dangers.

Je vais vous expliquer cela pour bien comprendre. Les salissures qui s'installent sur l'hélice et sur le gouvernail des navires provoquent de grands dommages, et cela à cause d'un frottement continu sur les coussinets.

L'opinion des spécialistes sur ce sujet ce serait très intéressante.

En fin, je voudrais vous souligner un autre danger qui concerne les navires transatlantiques. C'est un danger très spécial; celui-ci apparaît sous forme de mollusques. Ces petits organismes de mer, ont une sorte d'oreille, dont ils se servent comme d'une voile, par conséquent l'action du vent leur donne une propulsion dans la direction des vagues.

Voici, donc, le danger: A l'océan, il y a le navire qui voyage, tranquille. Mais, hélas, il y a, aussi, ces petits organismes dangereux de mer, les mollusques, qui, allant toujours en masse, dans la direction des flots, et surnageant à la surface de l'eau vont quelquefois rencontrer le navire. C'est alors que la question anxieuse se pose: où iront-ils pénétrer? Car il y a bien le danger que les bouches des tuyaux par où pénètre et circule l'eau de la mer dans la tuyauterie du bateau-soient obstruées.

Notre devoir de vous nommer quelques-uns des dangers en mer termine ici. Maintenant, nous pensons que commence le vôtre, qui est celui de chercher la manière et les méthodes pour prévenir ces risques et dangers maritimes.

Nous vous remercions de tout.

# PARTICIPATION DES BACTERIES AEROBIES AUX PROCESSUS DE CORROSION DU CUIVRE ET DU NICKEL

Par J. BRISOU, G. VALENSI, H. CONSTANT et T. GUILLAUME

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Poitiers, FRANCE

## RÉSUMÉ

Si certaines bactéries participent à la corrosion, d'autres ont un pouvoir protecteur qui ne peut être mis en doute; on a voulu attribuer cette propriété à la consommation d'oxygène. D'autres facteurs doivent être pris en considération.

Les auteurs ont particulièrement étudié l'action des bactéries en milieux nutritifs sur le cuivre et le nickel. Ils ont pu établir qu'en présence de bactéries banales, il y avait arrêt total de la corrosion mais qu'en présence d'espèces protéolytiques l'attaque du métal n'était pas inhibée. Ceci les a conduit à étudier l'action de certains produits de la biodégradation des protéines sur les métaux notamment les amines. Certaines

amines protègent tandis que d'autres sont corrosives.

Il est conclu que théoriquement toutes les bactéries aérobies consomment de l'oxygène et réduisant de ce fait le potentiel Redox devaient protéger les métaux contre la corrosion. En fait c'est ce qui se produit, sauf pour les groupes microbiens capables de libérer des produits de dégradation tels que l' $\text{NH}_3$ , certaines amines et autres produits du métabolisme; cela indépendamment du pH et de la salinité. La qualité et la quantité des substrats nutritifs retiennent tout particulièrement l'attention. Il y a intervention certaine du nombre de fonctions amines et de la présence d'une fonction alcool primaire.

Dans une série de travaux qui ont fait l'objet des Diplômes d'Etudes Supérieures de LAGEOT (1964) de LEMAIRE (1965) et de CONSTANT (1967), il a été établi que si certaines bactéries participent activement à la corrosion des métaux, d'autres ont un pouvoir protecteur qui ne peut plus être mis en doute. Ces effets protecteurs ont été également signalés par les auteurs soviétiques ISCHENKO et ULANOVSKII à peu près en même temps que nous. En 1962, GARLAND avait montré qu'en présence de glucose oxydase bactérienne la désoxygénation du milieu entraînait une nette diminution de la corrosion des métaux.

Toutes les bactéries aérobies consomment de l'oxygène, si l'on voulait attribuer les effets protecteurs à cette seule réduction du taux d'oxygène, on devrait observer une inhibition de la corrosion avec toutes les bactéries aérobies, ce n'est pas le cas. Certaines sont indiscutablement protectrices alors que d'autres favorisent l'altération des métaux en expérience. D'autres facteurs entrent en ligne de compte, c'est à l'étude de certains d'entre eux que cette note sera consacrée.

Nous ne détaillerons pas la partie expérimentale qui a fait l'objet de développements dans les travaux cités. Rappelons simplement que les mesures de corrosion en fonction du temps ont été effectuées par dosage polarographique du métal passant en solution dans le milieu. Les métaux utilisés ont été le Cuivre, sous forme de plaques de métal ultra-pur et un alliage Cuivre-Nickel.

Les plaques de 2 mm d'épaisseur avaient 7 cm de long sur 2 cm de large. Elles étaient stérilisées dans un mélange d'alcool éther et rapidement flambées avant d'être introduites dans les liquides d'expérience et les cultures microbiennes. Nous avons observé les phénomènes de corrosion dans de l'eau douce, dans de l'eau de mer stérile, dans les mêmes milieux enrichis soit de peptone (1% et 10/100) soit d'hydrolysate de caséine, ou d'autres substrats nutritifs.

Les courbes et tableaux qui seront présentés illustrent les résultats expérimentaux, obtenus avec les souches microbiennes de laboratoire (26 souches).

## RESULTATS

Pour comprendre les résultats exposés, il est nécessaire de rappeler que l'un de nous a classé les bactéries en quatre ensembles A, B, C et D que gouvernent la protéolyse et la réduction des nitrates en nitrites. L'ensemble A correspond aux bactéries protéolytiques productrices de nitrites en milieu nitraté, l'ensemble B aux germes protéolytiques non producteurs de nitrites, en C nous trouverons les bactéries non protéolytiques mais réduisant les nitrates en nitrites, enfin l'ensemble D contient les microbes dépourvus de protéinases et de nitrates réductases.

Il n'est pas un germe qui ne puisse entrer dans une de ces catégories. Dans chacune d'elles on reconnaît un groupe de germes attaquant les glucides, on lui donne l'indice 1 avec la litre (a) si le lactose est acidifié et (b) si le glucose et d'autres glucides sont seuls attaqués, un groupe d'indice 2 caractérise les bactéries indifférentes vis-à-vis des sucres. Un germe A1a sera donc par définition protéolytique, réduira les nitrates en nitrites, attaquera le lactose, un D2 sera dépourvu de protéase, de nitrates réductase et sera dans action sur les glucides. Ces notions et cette systématique rendent de grands services en écologie. Nous en avons fait, en ce qui concerne le problème de la corrosion, une simple application qui comme on le verra ne manque pas d'intérêt pratique.

Dans les milieux choisis, nous avons en effet observé l'action de bactéries très variées, appartenant à tous les groupes, mises en présence de cuivre et de l'alliage cuivre nickel. Si l'on compare les tableaux et les courbes projetés, on constate les différences considérables dans la vitesse d'attaque du métal selon les bactéries utilisées. Nous avons rapidement été frappés par le fait que les bactéries protectrices se situaient plus volontiers dans les ensembles C et D, non protéolytiques tandis que les germes corrodants appartenaient aux groupes A et B, riches en protéases.

Nous avons pu vérifier que l'attaque aérobie ou anaérobie des sucres influait peu sur la vitesse de corrosion et sur son importance.



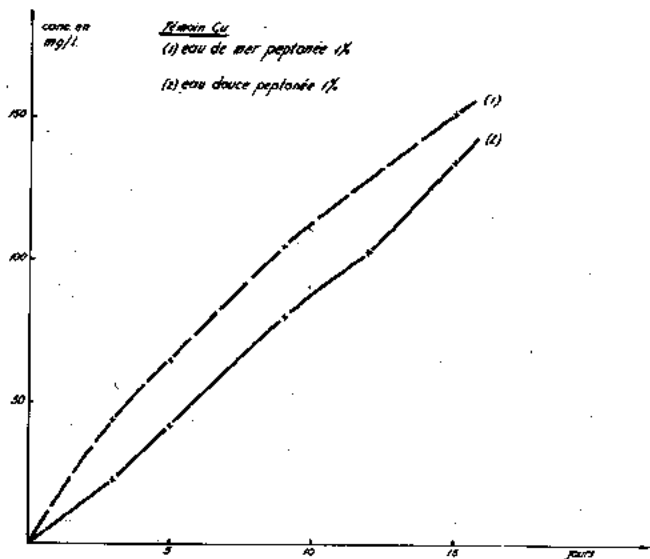


Fig. 1. — Courbes 5

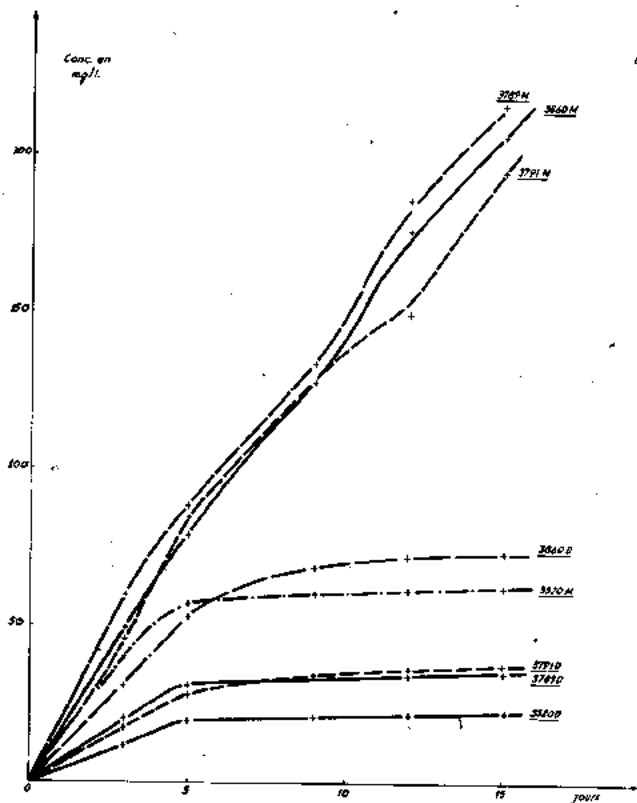


Fig. 3. — Courbes 7

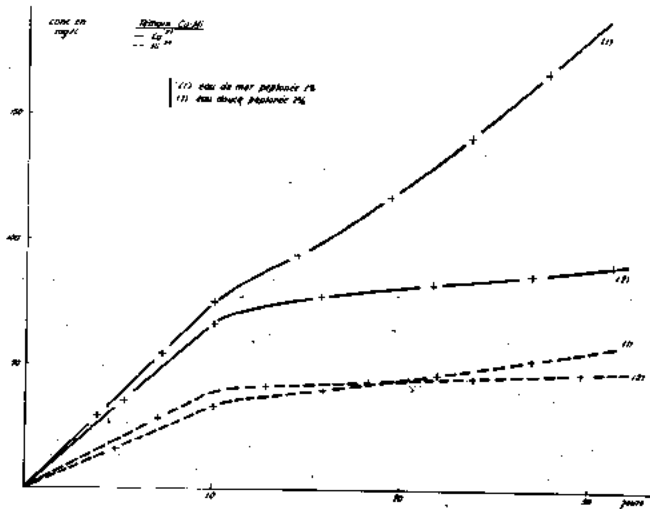


Fig. 2. — Courbes 6

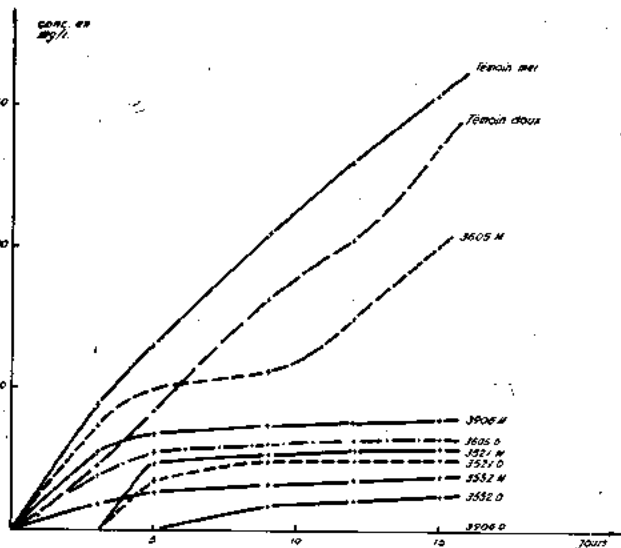


Fig. 4. — Courbes 7

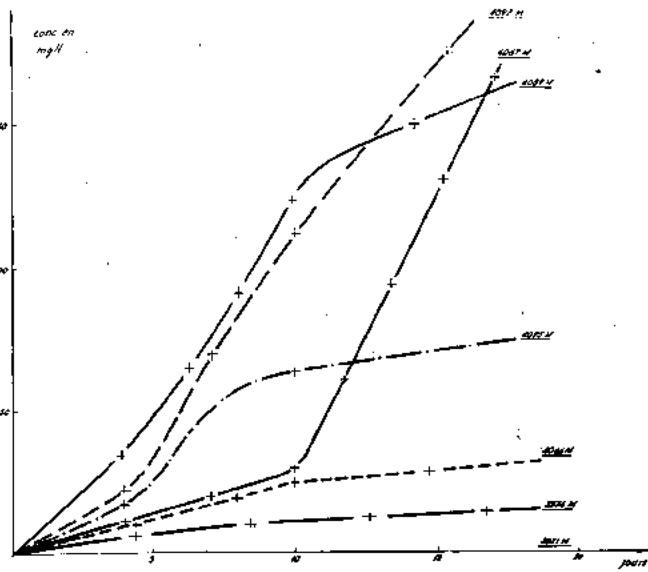


Fig. 5. — Courbes 8

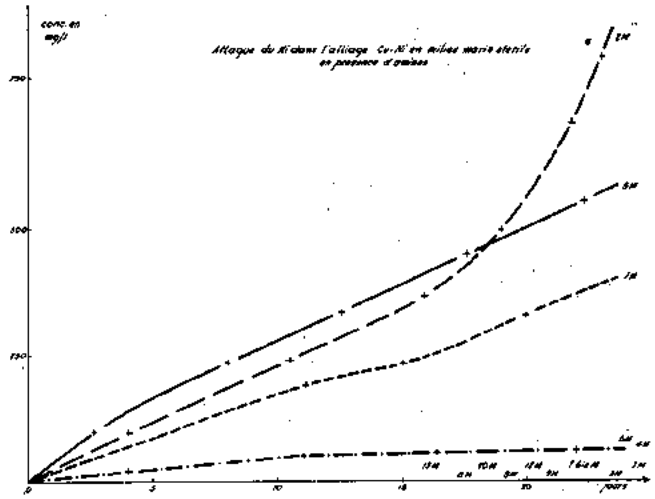


Fig. 7. — Courbes 10

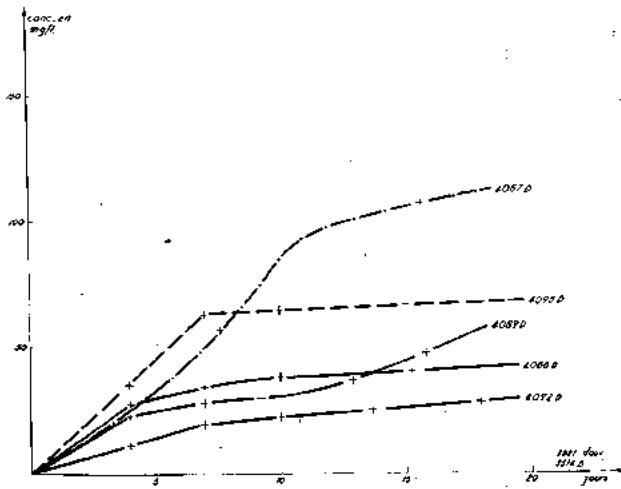


Fig. 6. — Courbes 8

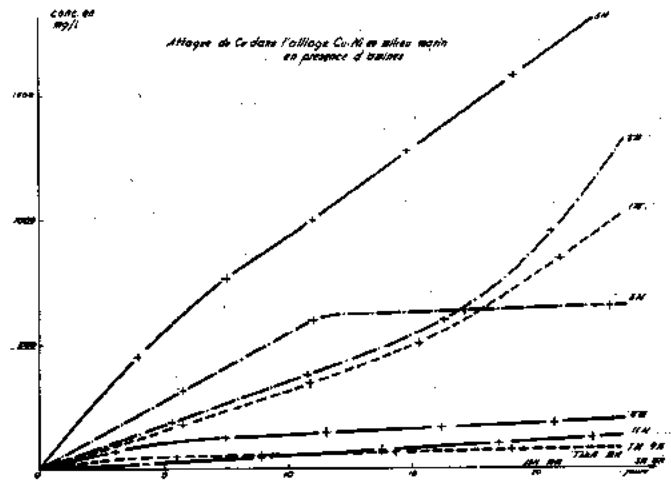


Fig. 8. — Courbes 10

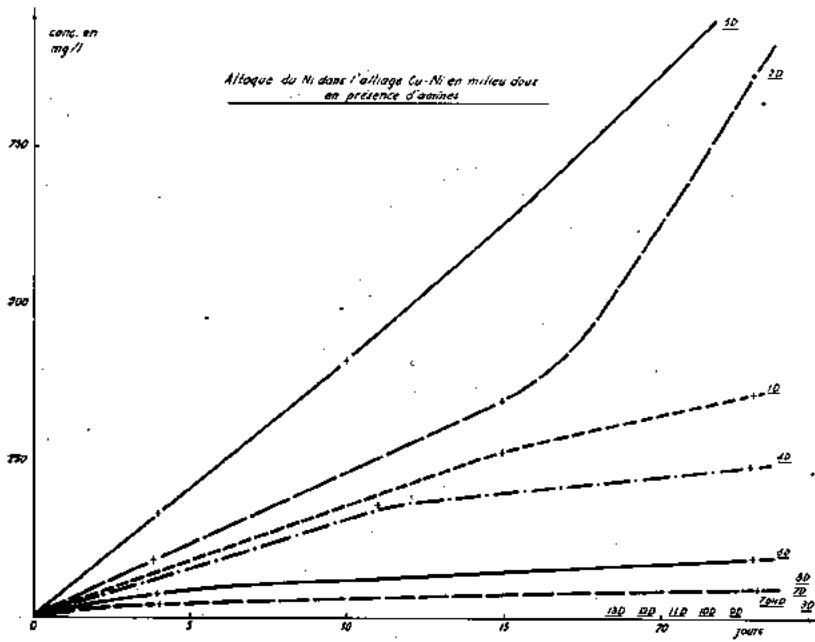


Fig. 9. — Courbes 10

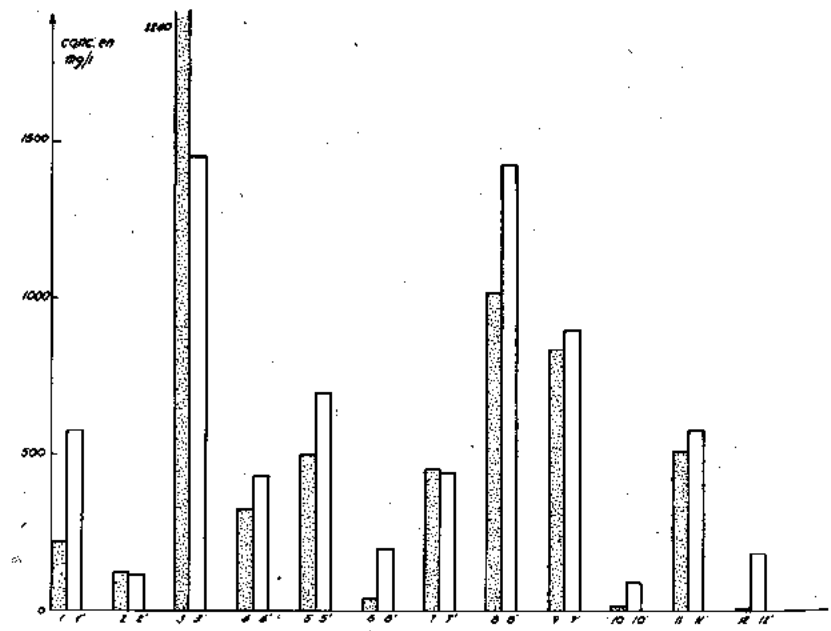


Fig. 10

Cette première constatation nous a alors invité à orienter les recherches vers les relations possibles entre les processus de corrosion et la protéolyse.

On sait qu'au cours de la protéolyse microbienne des peptides, puis des acides aminés sont mis en liberté. La dégradation se poursuit par l'attaque des acides aminés. Ceux-ci par des voies métaboliques bien classiques sont soit désaminés, soit décarboxylés, transaminés, dihydrolysés, oxydés ou réduits. Les produits terminaux ou intermédiaires de ces processus de dégradation sont avant tout l' $\text{NH}_3$ , des amines, des acides cétoniques ou des acides organiques.

Le rôle de l'ammoniaque dans les processus de corrosion est trop classique pour qu'il en soit discuté. Nous avons concentré notre attention sur les amines, en travaillant avec des produits purs et en milieux aussi simples que possible pour être à l'abri de réactions couplées.

Les amines utilisées ont été :

La triéthylène tétramine  
Éthylène diamine = diamino 1-2 éthane  
Tributylamine  
Triéthanolamine  
Diéthylène-triamine  
N-butyl diéthanolamine  
Isobutylamine  
Monobutylamine  
Méthylbutylamine  
Diisobutylamine  
Dibutylamine

Nous avons également effectué des expériences avec des acides aminés sur lesquels nous avons fait agir des bactéries possédant des aminoacide décarboxylases (*Pseudomonas*).

Les expériences effectuées avec 26 bactéries différentes: *Achromobacter*, *Pseudomonas*, *Phytobacterium*, *Esch. coli*, *Citrobacter freundii*, *Erwinia*, *Klebsiella*, *Bacillus*, *Innominitus*, *Acinetobacter* conduisent aux constatations suivantes:

Les bactéries les plus actives appartiennent aux ensembles protéolytiques acidifiant les sucres, viennent ensuite les protéolytiques non acidifiantes.

Les bactéries protectrices appartiennent pratiquement toujours aux ensembles non protéolytiques. Les plus actives sont glucidolytiques. Certaines possèdent un pouvoir protecteur considérable, au point qu'au 17<sup>ème</sup> jour, il n'y avait pas la moindre trace de métal en solution dans le milieu, qu'il s'agisse d'eau de mer ou d'eau douce. Dans les mêmes conditions l'éprouvette de cuivre libérait par exemple 150 mg de cuivre dans l'eau de mer et 130 dans l'eau douce. Il s'agit donc bien d'une *Protection totale*. Ces bactéries protectrices sont parmi les plus banales, la majorité des *Enterobactéries*: *Esch. coli*, *Klebsiella*, *Citrobacter*, par exemple en sont d'excellents représentants.

En étudiant directement et indirectement le rôle des amines dans la corrosion nous avons noté l'importance des polyamines primaires, tandis qu'il n'y a aucune attaque en présence de composés ne présentant qu'une fonction amine surtout lorsqu'elle est secondaire voir tertiaire. La notion d'encombrement spatial, d'avidité pour le métal s'impose donc.

Au cours de la décarboxylation microbienne des acides aminés on note là encore une intervention certaine du nombre de fonctions amines et de la présence d'une fonction alcool primaire.

On peut donc pour le moment estimer que tout germe protéolytique libérant des quantités notables d' $\text{NH}_3$ , ce qui est fréquent, et certaines amines se révèle plus corrosif que d'autres.

Tous ces germes consomment cependant de l'oxygène. Pour bon nombre d'entre eux, nous avons effectué des mesures manométriques du quotient respiratoire et de l'activité déshydrogénasique. Nous n'avons pas noté de relations précises entre les valeurs trouvées et l'activité vis-à-vis des métaux.

Les explications données par GALARD et les auteurs soviétiques sont donc incomplètes.

On peut penser que toutes les bactéries, du fait de la consommation d'oxygène qu'entraîne leur métabolisme, sont douées d'un indiscutable pouvoir protecteur vis-à-vis de la corrosion des métaux. Cela est vrai dans les conditions expérimentales, qui ne l'oublions pas se situent dans des espaces *clos, très limités, fermés*. Toutefois les bactéries qui d'autre part agissent sur les protéines pour libérer des amines, des polyamines, notamment, et l' $\text{NH}_3$ , deviennent corrodantes du fait de cette libération secondaire de produits nocifs résultant de leur métabolisme. Tous ces processus sont étroitement liés, comme nous l'avons montré à la nature des substrats, à leur quantité et à leur qualité. Ce sont là des résultats fondamentaux dont nous n'avons pas encore envisagé les applications pratiques. Mais il va de soi que dans certaines conditions elles pourraient être mises à profit.

Il est bien évident que toutes ces recherches ont été accompagnées de mesures nombreuses intéressant le pH des milieux et leur potentiel d'oxydo réduction. Les résultats ont été reportés sur les classiques diagrammes de POURBAIX.

Comme le révèlent les chiffres inscrits sur les tableaux, il n'y a pas de relations bien évidentes entre l'intensité de la corrosion et ces valeurs qui au cours de nos expériences effectuées en milieux peptonés et tamponnés variaient dans des limites assez étroites.

Toutefois lorsque nous avons expérimenté sur les amines, on notait que pour certaines avec un pH de 7,4 et un potentiel de 150 mV on se trouvait dans la zone de corrosion théorique du Nickel. Au contraire avec d'autres donnant un pH de 8,3-8,4 nous étions à la limite de la zone de passivation.

Rappelons que pour le Cuivre à 25°, la zone de passivation se situe entre pH 6 et pH 13 pour des potentiels de + 0,2 et la zone d'immunité à toutes les valeurs de pH si le potentiel redox est au dessous de 0.

Nos potentiels étaient constamment positifs et les pH entre 6,5 et 8. Ces valeurs n'expliquent donc pas tout, elles non plus, comme nous l'avons dit. La qualité et la quantité de substrats, les produits du métabolisme microbien semblent d'un intérêt digne de retenir l'attention et invitent à poursuivre les recherches.

Retenons donc en définitive le pouvoir protecteur souvent total des bactéries non protéolytiques. L'activité constante des germes aérobie possédant des protéases.

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# SOME SPECIAL FEATURES OF THE ANAEROBIC CORROSION OF STEEL BY ORGANISMS OF ESTUARINE ORIGIN

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## SUMMARY

Laboratory experiments have shown that pure cultures of sulphate-reducing bacteria isolated from estuarine waters and grown in anaerobic conditions in a synthetic medium can bring about corrosion much greater than is experienced in the natural environment. In the conditions employed, the corrosion products consisted of ferrous sulphide and ferrous carbonate in equimolecular proportions. Although no relation could be seen between rates of corrosion and the hydrogenase

activity of the cultures, there was some evidence that the more anaerobic the source of the isolate, the greater the rate of corrosion during the time of the experiments. There was also an indication that strains of *Desulfovibrio vulgaris* might be more corrosive than strains of *Desulfovibrio desulfuricans* from chemically similar environments. Further work would be necessary before definite conclusions could be drawn.

## INTRODUCTION

A comprehensive survey of the rate of corrosion of bare mild steel exposed to the tidal waters of the Thames estuary for periods of up to 5 years showed that the total corrosion was caused by a combination of anaerobic microbiological corrosion and aerobic corrosion. The latter arose from the exposure to saline water containing dissolved oxygen<sup>1,2,3</sup>, and was probably the more important contribution. This view was supported by comparative experiments in the estuary of the Afon Dyfi in mid-Wales<sup>4</sup>, a relatively unpolluted river, in which very high rates of corrosion occurred, mainly because of the high oxygen content and rapid rate of flow of the water. Nevertheless, it was apparent that even in these conditions, some contribution to the total corrosion arose from anaerobic microbiological effects, sulphur compounds being detected among the corrosion product. Sulphate-reducing bacteria were detected in both rivers; numbers varied from  $10^6$  to  $10^8$  cells/cm<sup>3</sup> in the Thames, the high populations tending to be in the more polluted reaches of the estuary; in the Afon Dyfi populations of  $10^6$  to  $10^8$  cells/cm<sup>3</sup> were found, the higher numbers occurring in the lower, (seaward) reaches.

It was considered of interest to determine whether the amount of anaerobic corrosion experienced in the rivers could be ascribed to the conditions in the water being unfavourable or to an intrinsic inability of the organisms to cause corrosion as severe in water as they commonly produce in the soil. Corrosion (weight loss) tests have been made in the laboratory using pure cultures of sulphate-reducing bacteria isolated from various parts of the estuaries and grown with as nearly optimal conditions as possible. The results have been compared with those obtained in the natural river conditions and show some striking differences, not only in the gross amount of corrosion occurring, but also in the nature of the products obtained.

## EXPERIMENTAL

### Preparation of bacterial cultures

Pure cultures of sulphate-reducing bacteria were isolated

from samples of river water taken from the estuaries of the Thames and Afon Dyfi at points indicated by the names given to the appropriate isolate. The methods used were those described by trs Butlin, Adams and Thomas<sup>5</sup> and the cultures were tested for purity by the method described by Postgate<sup>6</sup>. Stock cultures were maintained under nitrogen in Postgate's modification<sup>7</sup> of the 'Medium C' of Butlin, Adams and Thomas<sup>5</sup>, further supplemented by 0.5% w/v crystalline ferrous ammonium sulphate and adjusted to pH = 7 immediately before use. Growth in all the stock cultures was so vigorous that no prepoising of the redox-potential of the medium on subculture was required. All the isolates were hydrogenase and desulfoviridin positive, mesophilic and halotolerant. The isolates Woolwich (National Collection of Industrial Bacteria No. 8457) and Aberdovey (NCIB No. 9492) have been classified by Postgate and Campbell<sup>8</sup> as *Desulfovibrio vulgaris* and *Desulfovibrio desulfuricans* respectively. Using only the ability to metabolise choline (with the production of trimethylamine) as a diagnostic test<sup>9</sup>, we confirm this classification and, of the new strains, would tentatively classify Greenwich as *D. desulfuricans* and the rest as *D. vulgaris*.

### Hydrogen absorption coefficients

Resting cell suspensions of the various organisms were prepared from 3-day old batch cultures in 'modified Medium C' containing growth iron only, i.e. without the 0.5% supplement used in the stock cultures. In this way, a crop of cells could be harvested that was not grossly contaminated by ferrous sulphide. Suspensions were made in tris buffer at pH = 7, and hydrogen absorption coefficients for both sulphate and benzyl viologen reductions were determined in Warburg manometers by the method described by Postgate<sup>6</sup>.

### Preparations of test specimens

20 swg. mild steel sheet of the following analysis was used: C 0.06; Si 0.014; S 0.025; P 0.015; Mn 0.31; Ni 0.09; Cr 0.01; Cu 0.11; Al 0.002; Sn 0.007; Co 0.009 per cent. The

sheet was supplied «satin finished» and was cut into specimens  $2 \times 1$  cm. The surface was abraded with emery papers to No. 0 (Hubert). The specimens were degreased in liquid benzene, washed in methanol and dried in a stream of warm air. After weighing, the specimens were sterilized by passage through a flame immediately before use.

#### Corrosion experiments

The sterilized specimens were placed singly in sterile test-tubes closed with cotton-wool plugs. 10 cm<sup>3</sup> portions of iron-rich modified Medium C were added aseptically to each tube and inoculated with 0.1 cm<sup>3</sup> of a three-day old culture of one of the stock organisms. The tubes were incubated at 30°C in McIntosh and Fildes anaerobic jars under nitrogen. All tests were run in triplicate with sterile controls. At intervals of 3 or 4 days, the medium was removed aseptically from each tube and replaced with 10 cm<sup>3</sup> of fresh sterile medium. Traces of the old culture remaining on the specimens and on the walls of the test-tubes served as inoculum for the continuation of the experiment. After 1 and 3 months specimens were removed from the cultures, cleaned in inhibited HCl (Clarke's solution) as described by Champion<sup>10</sup> and reweighed. Corrosion rates were calculated in mg/dm<sup>2</sup>/day assuming constancy with time. Earlier laboratory work using a similar medium suggests that this assumption is justified<sup>11</sup>.

### RESULTS

When the laboratory specimens were removed from the cultures, they were found to be completely covered with a thick envelope of black granular material which was readily removed, to reveal a thin, black and extremely adherent film. Dispersions of both types of material in ethylene glycol, when examined at 50,000 magnification in the electron microscope, presented a similar finely microcrystalline appearance and gave electron diffraction patterns suggesting mainly siderite (FeCO<sub>3</sub>) with some troilite (FeS) and a little Fe<sub>3</sub>O<sub>4</sub>. X-ray diffraction patterns for the bulky envelope material, using unfiltered CoK $\alpha$  radiation indicated a composition of siderite and troilite with some  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O. Gravimetric chemical analysis of the bulked products showed that 99.8% of the material consisted of equimolecular proportions of FeCO<sub>3</sub> and FeS.

Examination of cleaned specimens under the optical microscope showed an even attack with no evidence of localization or pitting.

Table I gives the rates of corrosion brought about by pure cultures of the individual organisms after 1 and 3 months exposure. Corrections for corrosion by the sterile medium amounted to some 4% after 1 month and 1% after 3 months. The table gives also the rates of corrosion (aerobic and anaerobic) calculated for 6 months exposure of a similar steel to the natural conditions in the appropriate rivers at points from which the individual cultures were isolated. It is emphasized that, in the natural environment, part of the attack is due to aerobic corrosion by oxygen-bearing saline water and that only a proportion of the total corrosion can be ascribed to bacterial action.

Table II gives the hydrogen absorption coefficients (= hydrogenase activity) for the reduction of sulphate and of benzyl glucose for each of the bacterial isolates. In each case the maximum value obtained from several determinations is quoted. It is not to be expected that these should necessarily correlate with each other.

### DISCUSSION

The discovery of a high proportion of carbonate in the corrosion products was rather unexpected, as much of the early work on the corrosion of iron and steel by sulphate-reducing bacteria refers to the formation of the initial corrosion product as FeS + Fe(OH)<sub>2</sub> with a subsequent conversion of the Fe(OH)<sub>2</sub> to various hydrated oxides of iron.

TABLE I  
RATE OF CORROSION OF MILD STEEL BY  
LABORATORY CULTURES AND IN NATURAL  
ENVIRONMENTS

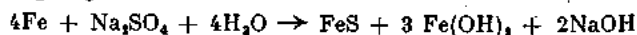
	Mean rate of corrosion mg/dm <sup>2</sup> /day			Mean redox-potential of river during 1960-65 V at pH=7
	Pure culture* 1 month	Pure culture* 3 months	River 6 months	
Richmond	76	72	8	0.70
Putney	86	96	5	0.53
Westminster	81	77	15	0.50
Greenwich	90	79	26	0.28
Woolwich	71	107	16	0.24
Crossness	77	98	52	0.29
Rainham	9	99	27	0.34
Aberdovey	50	51	43	0.44

\* Corrosion rates corrected for corrosion by sterile medium.

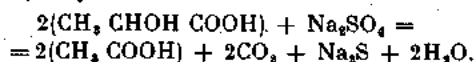
TABLE II  
HYDROGENASE ACTIVITY (HYDROGEN  
ABSORPTION COEFFICIENTS)  
OF BACTERIA ISOLATES

	Max. hydrogenase activity of organisms $\mu$ l H <sub>2</sub> /mg.dry wt. of cells/hr.	
	— Q <sub>H<sub>2</sub></sub> <sup>SO<sub>4</sub></sup>	— Q <sub>H<sub>2</sub></sub> <sup>BzV</sup>
Richmond	102	785
Putney	108	300
Westminster	162	1020
Greenwich	137	760
Woolwich	162	790
Crossness	210	740
Rainham	206	896
Aberdovey	185	795

The summary equation for the mechanism of the corrosion process proposed by von Wolzogen Kühr and van der Vlugt<sup>12</sup> gives



However, the presence of carbonate in the product from an iron-rich lactate medium is easily accounted for. Grossman and Postgate<sup>13</sup> give as summary equation for the oxidation of lactate by sulphate-reducers.



If the oxidation of the lactate were completely dissimilatory and the only substrate for sulphate reduction and if all the CO<sub>2</sub> and sulphide were trapped as iron-compounds, then a ratio of 2:1 would be expected for FeCO<sub>3</sub>:FeS. In the system used in this work, however, the cultures were actively growing and at least part of the lactate oxidation must be assimilatory. Since it is known that acetate is not assimilated, this would

result in a decrease in the ratio of  $\text{CO}_2$  to sulphide. Likewise, in the presence of the corroding metal some reduction of sulphate to sulphide by the utilization by the bacteria of cathodic hydrogen must result in an increase in the sulphide production. Hence a value for  $\text{FeCO}_3 + \text{FeS}$  of less than 2:1 must be expected. We have no means of telling whether the observed value of almost exactly 1:1 is more than coincidental. We have never detected significant amounts of carbonate in the products of «natural» corrosion by sulphate-reducers. It is clear from the corrosion rates (Table I) that the build-up of the corrosion product affords little, if any, protection to the corroding metal, and with one exception, all the strains gave very high rates of corrosion. In 1-month tests with the Rainham strain, it was observed that very poor growth of the organism occurred in all of the triplicate cultures. This accounts for the low rate of corrosion, but the poor growth is not explained. The rates of corrosion obtained, (50-100  $\text{mg}/\text{dm}^2/\text{day}$ ) in the very favourable conditions used, indicate that the low rates of microbiological corrosion that are experienced in the rivers themselves arise from the physico-chemical conditions obtaining in the rivers and not to any intrinsic inability of the organisms present to stimulate corrosion. There is no relationship observable between the rates of corrosion in either laboratory or river conditions and the hydrogenase activities of the organisms (for either sulphate or benzyl viologen reduction) (Tables I and II), and it is concluded that, in these conditions, hydrogenase activity is not rate-controlling. However, if the rates of corrosion by individual strains are plotted (Fig. 1) against the mean redox-potential of the rivers from which the strains were isolated and measured intermittently over a period of 5 years at the points from which the isolates came, an interesting relationship is revealed. From the eight organisms tested, the data for six lie on an approximate straight line of negative slope with increasing (more positive) redox-potential of source. All six of these were organisms of the *Desulfovibrio vulgaris* type. The other two, both *D. desulfuricans*, deviate widely from the six, and the corrosion was less in both cases than might have been anticipated. This suggests (a) that the intrinsic ability to cause corrosion of sulphate-reducing bacteria depends on the redox-potential of their natural habitat and that this property is retained for a period of at least three months when the bacteria are growing in the most favourable conditions (b) that *D. vulgaris* type organisms are more aggressive than *D. desulfuricans* types from the same source when transferred to optimal conditions, again for at least three months. All the strains had been stored in the freeze-dried condition since their isolation. Considerably more work would be required, however, before these conclusions could be firmly established.

#### ACKNOWLEDGEMENTS

We acknowledge the assistance given by Miss L. Elford and Mrs. P.M. Cooper in isolating and characterizing the organisms and by Mr. G.O. Lloyd in electron microscopy and electron diffraction of corrosion products. The work was done at the National Physical Laboratory, Teddington, Middlesex, England.

#### DISCUSSION

Dr. DE VLIÉGER (Holland): At the end of your communication you state that applicability of bacterial corrosion phenomena is not very high. Contrary I think that it is a very important point, which is worth further study. I have met very serious corrosion through anaerobic bacteria in water ballast tanks, which were almost a complete loss.

Dr. D. BOOTH: Thank you, sir. I would just like to add that, when I said that the practical applicability was not very high, I was referring to corrosion in open water where the amount of aerobic corrosion seems to swamp the anaerobic corrosion. In your particular application, where the aerobic corrosion is probably very small indeed, the anaerobic corrosion matters a hundred per cent.

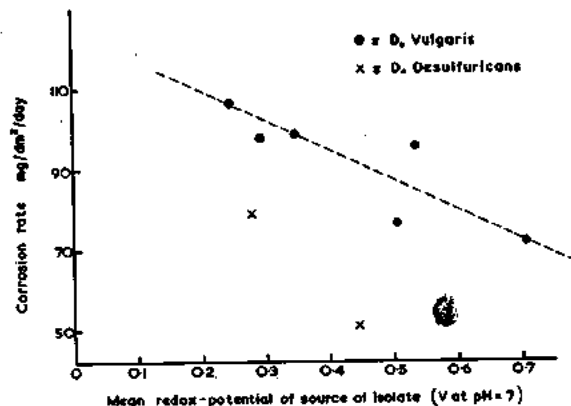


Fig. 1.

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J. DEPIREUX (Belgium): I would like to ask the speaker if he has had the opportunity to investigate the corrosion under anaerobic conditions of steel protected with a system, including antifouling paint based on copper oxide?

Dr. BOOTH: I am afraid not, sir. This was the beginning of a bigger investigation in which we hoped to proceed to other metals and to protectives. We were, in fact, unable to do more than the initial stages on bare steel. The work, unfortunately, has now been terminated and the research unit disbanded.

# THE PROBLEM OF TIMBER DESTROYING ORGANISMS ALONG THE INDIAN COASTS

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## SUMMARY

Two species of *Martesia*, 22 species of teredinids, 4 species of *Sphaeroma* and 9 species of *Limnoria*, besides the wood infesting bacteria and fungi, especially in the *Ascomycetes* and in the *Fungi imperfecti*, are known to be active along the coasts of India. The pattern of distribution of marine timber-borers along the coasts of India is described. The nature and activity of the different species of borers show variations in the different regions along the Indian coasts. Studies in the harbours indicate that each harbour has its own dominant set of species and an assemblage of less important forms. Data obtained with the aid of a planned system of test panels on the seasonal settlement of timber-boring organisms at Cochin Harbour are presented. The nature of damage by the crustaceans and the molluscs, and the role played by bacteria and fungi in the «conditioning» of timber, are explained. In Cochin Harbour, the existence of at least five species of wood-infesting fungi has been noticed, namely *Gnomonia longirostris*, *Halosphaeria quadricornuata*, *Torpedospora radiata*, *Corrollospora pulchella* and *Lulworthia* sp. The results of recent studies on the timber-borers at Cochin Harbour are briefly reviewed. The different species of borers have their

own characteristic preferences, life-histories and seasons of attachment, and a scheme evolved for one locality may prove ineffective for another, owing to different species composition in the different harbours even along the same coast.

A hitherto little known fauna of commensals, parasites and predators of timber-boring animals have been brought to light. Ciliates belonging to Boveridae, Urceolariidae, Thigmophryidae, Spirostomidae, Lichnophoridae, Hysteroecinetidae and Stentoridae; an undescribed and unique hydroid assignable to the genus *Eugymnanthea*; and a new species of entocytherid ostracod belonging to an interesting new genus *Microsyssitria*, have been collected from wood-boring organisms of the south-west coast of India. Besides these, as yet unidentified isopods and copepods have also been collected from wood-borers of this locality. The conditions under which these associates live, the exact nature of the relationship etc., are being investigated. The importance of detailed ecological information has been stressed since an understanding of the parasites, predators and other associates is likely to provide us with valuable information regarding the biological control of these pests.

## INTRODUCTION

There has probably never been a period in the history of developing countries when interest in the utilisation of timber and progress in this field have been greater than at present. Conservation and protection, have, therefore, become extremely essential for the effective utilisation of the limited resources. There are two approaches to the problem of the destruction of timber structures in sea-water exposures. One is discarding the home-grown, susceptible timbers as structural material for marine constructions and sea going craft, and using more expensive materials such as steel, concrete etc.; but even these are not exempt from the ravages of all types of deterioration and are vulnerable to one or more of the destructive processes. The utilisation of steel and concrete for all kinds of marine constructions will certainly be impracticable for a long time in developing countries like India. The other approach is the use of home-grown timber as building material, with the use of every device and technique calculated to prolong their service life. Careful conservation and scientific protection are integral parts of this reasonably sound approach. This involves among others, a precise understanding of the biology of the organisms which are responsible for the destruction. Successful control measures depend upon a knowledge of the nature of the organisms

against which the control is directed. Studies along these lines have been in progress in the University of Kerala.

## THE ORGANISMS THAT CAUSE DESTRUCTION OF TIMBER ALONG THE COASTS OF INDIA

Timber in sea-water exposures is threatened by decay through the action of bacteria, fungi, and marine boring organisms. The borers are chiefly active below the low water level and decay is mainly above this level. Both do damage in the inter-tidal zone. The borers chiefly belong to two groups the Mollusca and the Crustacea. The molluscs are represented by one genus of pholads namely *Martesia* (piddocks) and by the shipworms of the family Terebridae. The crustacean wood borers are mainly confined to the order Isopoda and are represented by two well known genera, *Sphaeroma* (pill bugs) and *Limnoria* (gribbles). Four species and a variety of *Sphaeroma*, and nine species of *Limnoria*, have so far been reported from the coasts of India. On the basis of the new classification proposed by Dr. Ruth D. Turner (1966), 22 species of shipworms can be recognised as active along our coasts, in addition to the two species of *Martesia* known to occur (Srinivasan, 1959) in these tropical waters. Thus the attack on timber is the concerted effort of a heterogeneous assemblage consisting of at least 36 different species of crustaceans and



molluscs, besides the bacteria and the fungi. These are engaged in a relentless destruction of valuable timber, thereby reducing its service life in the sea, in the brackish water and even in almost fresh water. According to Becker (1958) the cost of periodic replacement of fishing crafts alone as a result of the activity of marine timber-destroying organisms is estimated at 25,00,000 rupees. This does not include the damage done to the numerous water-front structures such as harbour constructions etc., the estimation of which is not easy. Therefore, the total property damage caused by these pests each year must be enormous. The problem is thus as important as that of coastal erosion and should, therefore, be treated with all the seriousness it certainly deserves.

Of the marine wood-borers that occur and are active along our extensive coasts, the shipworms, the piddocks and the pill bugs are responsible for most of the destruction. *Limnoria*, though present, have not yet assumed any great importance since they occur only sparsely. Though the majority of the borers hitherto studied were typically marine, recent investigations have shown (Nair, 1965, 1965 a, 1966) that certain species of *Nausitora*, *Martesia* and *Sphaeroma* account for serious damage to timber in the estuarine and other brackish water localities along our coasts.

The nature of damage by the molluscs and the crustaceans is different, producing different effects on timber. This enables them to share effectively, without serious competition, this common substratum which is limited in extent. The crustaceans work from the outside and the molluscs, particularly the shipworms, penetrate deep into the hearts of timber. The combined action of these two groups of borers converts the wood into a highly porous, weak and fragile mass. The crustaceans have the added ability to enter even the creosoted shell of treated timber which the shipworm larvae are unable to do.

Besides these wood-boring animals wood-infesting bacteria, and fungi, especially in the *Ascomycetes* and in the *Deuteromycetes* (*Fungi imperfecti*), actively participate in a sort of «conditioning» of the timber, preparing it for the subsequent attack by borers. This is a biological phenomenon, the importance of which has been stressed only recently (Kohlmeyer, 1963). The activity of these fungi leads to a kind of wood deterioration called «soft rot» which is a sort of superficial softening of the wood. These fungi, which are resistant to preservatives, release a strong cellulase which hydrolyses the unignified cell elements leading to the softening and disintegration of the outer tissues of timber. Even though the magnitude of damage by these is not spectacular, and may not even be noticed by the layman, the importance lies in the fact that their silent and steady activity soon after submergence of timber prepares it for attack by the crustaceans and the molluscs. The borers in turn help the fungi to spread deeper and deeper into the timber, thereby enabling them to expand the field of operation from superficial layers to its very core. The relation between gribbles and these fungi seems to be of a symbiotic type. The fungal infestation on light timbers of the catamarans, dugout canoes and other fishing crafts, according to Becker and Kohlmeyer (1958), is not of the usual superficial type, the penetration being deep, affecting the entire log. The periodic drying of these logs accelerates the spread of the fungal hyphae which get effective ventilation through the large vessels of these light timbers. Our studies in the Cochin Harbour so far have revealed the existence of the following species of marine fungi in the timber test panels. *Gnomonia longirostris* Cribb and Cribb, *Halosphaeria quadricornuata* Cribb and Cribb, *Torpedospora radiata* Meyers, *Corollospora pulchella* Kohlm., Schmit and Nair, and *Lulworthia* sp.

#### THE PATTERN OF DISTRIBUTION OF TIMBER BORERS ALONG THE COASTS OF INDIA

Studies on the incidence and activity of marine borers have been undertaken only in selected areas both along the east and west coasts of India. In Table I is presented

the important species of marine timber-boring molluscs and crustaceans that occur, along the coasts of India, classified on the basis of the recent revision of the shipworms by Dr. Ruth D. Turner, indicating the main region of their occurrence. It will be seen that while 33 species\* are active along the east coast of India (including the Andamans), only about 17 species\* are known to exist along the west coast (including Minikoi). Fourteen species are common for both the east and west coasts. Of these *Dicyathifer manni*, *Teredo furcifera*, *Lyrodus pedicellatus*, *Bankia campanellata*, *Bankia carinata*, *Martesia striata*, *Sphaeroma annandalei* and *Sphaeroma walkeri* (not an active wood-borer) seem to be continuously distributed along the coasts of India, being present in almost all areas from where records are available. Forms like *Bac-tronophorus thoracites*, *Teredora princesae*, *Teredo clappi*, *Nausitora hedleyi*, *Bankia rochi* and *Martesia fragilis*, though recorded from the east and west coasts of India, have not been collected from all the regions. Certain species collected from the east coast or the Andamans have not yet been noted along the west coast. Nineteen species come under this category namely *Teredothyra smithi*, *Teredothyra excavata*, *Uperotus rehderi*, *Uperotus clavus*, *Teredo fulleri*, *Teredo triangularis*, *Lyrodus affinis*, *Lyrodus massa*, *Nototeredo edax*, *Nausitora dunlopei*, *Bankia bipennata*, *Bankia nordi*, *Sphaeroma triste*, *Limnoria indica*, *L. tripunctata*, *L. septima*, *L. insulae*, *L. unicornis* and *L. platycauda*. Similarly three species *Limnoria bombayensis*, *L. pfefferi*, *L. biuberculata*, occurring along the west coast or in the Minikoi island, are conspicuous by their absence along the east coast.

At least seven species of borers are active in West Bengal. From the mangrove swamp forests of the Sundarbans, *Bac-tronophorus thoracites* has been reported as a serious pest (Roonwal, 1954) infesting both the living and dead trees, so weakening them mechanically that they break off before strong winds. From the same locality Rajagopalaingar (1961) has recorded a new species *Bankia* (*Neobankia*) *roon-wali* which according to Turner (1966) is a synonym of *Bankia rochi*. *Nausitora dunlopei* (Wright, 1864) *Bankia campanellata*, *Bankia carinata* (Roch, 1961) and *Bankia nordi* (= *Nausitora sajnakhaliensis*: Rajagopalaingar, 1964) are the other four species of shipworms reported as active in West Bengal. No systematic work on the boring animals has hitherto been undertaken from the environs of Calcutta, and our information is limited regarding the exact number of species that occurs there, and their biology. *Nausitora dunlopei* is a very interesting species reported in timbers exposed even to almost fresh water in the River Comer, a tributary of the Ganges, 150 miles up river (Wright, 1864). The ability of this species to live in almost fresh water is of special interest.

The marine wood-borers of the Andhra coast have been studied in detail by Dr. P.N. Ganapati and Dr. R. Nagabhushanam (see Nagabhushanam, 1958, 1960). According to the revised estimates, not less than 16 species of wood-borers seem to exist in that region of which *Bankia campanellata*, *Teredo furcifera* and *Martesia striata* are by far the most important from the point of destruction at the Visakhapatnam Harbour.

Along the Madras coast, 26 species are apparently active, of which only four species of shipworms and *Martesia striata* occur in abundance and, hence are of importance from the point of view of timber destruction. The most important form infesting the fishing floats are *Bankia carinata* and *Teredora princesae*, and along the coast *Teredo furcifera*, *Uperotus rehderi* and *Martesia striata* are destructive. All the four species of *Sphaeroma* known to occur in the Indian waters occur along the Madras coast. *Sphaeroma triste* which was recently recorded from Rameswaram (George 1963; 1964) has subsequently been collected in fair numbers from pillings at Tuticorin (Venkatakrishnan 1966). *Uperotus clavus* infests the floating mangrove seeds which are cast ashore during the monsoon period.

Nearly 10 species of wood-borers are active in and around

\* *Sphaeroma walkeri* not included.

TABLE I

THE PATTERN OF DISTRIBUTION OF THE MARINE TIMBER BORING MOLLUSCS AND CRUSTACEANS ALONG THE INDIAN COASTS

Serial Nr.	Name of borer	West Bengal	Andhra Coast	Madras Coast	Andamans	South West Coast	Bombay
1	<i>Bactronophorus thoracites</i> (Gould)	+	+	—	—	—	+
2	<i>Dicyathifer manni</i> (Wright)	—	+	+	—	+	+
3	<i>Teredothyra smithi</i> (Bartsch)	—	—	+	—	—	—
4	<i>Teredothyra excavata</i> (Jeffreys)	—	—	+	—	—	—
5	<i>Teredora princesae</i> (Sivickis)	—	—	+	—	+	—
6	<i>Uperotus rehderi</i> (Nair)	—	—	+	—	—	—
7	<i>Uperotus clavus</i> (Gmelin)	—	—	+	—	—	—
8	<i>Teredo furcifera</i> Martens	—	+	+	—	+	+
9	<i>Teredo fulleri</i> Clapp	—	—	+	—	—	—
10	<i>Teredo clappi</i> Bartsch	—	—	+	—	+	—
11	<i>Teredo triangularis</i> Edmondson	—	+	+	—	—	—
12	<i>Lyrodus affinis</i> (Deshayes)	—	+	—	—	—	—
13	<i>Lyrodus pedicellatus</i> (Quatrefages)	—	+	+	—	+	+
14	<i>Lyrodus massa</i> (Lamy)	—	+	+	—	—	—
15	<i>Nototeredo edax</i> (Hedley)	—	+	+	—	—	—
16	<i>Nausitora dunlopei</i> Wright	+	+	+	—	—	—
17	<i>Nausitora hedleyi</i> Schepman	—	+	+	—	+	—
18	<i>Bankia bipennata</i> (Turton)	—	+	+	—	—	—
19	<i>Bankia campanellata</i> Moll/Roch	+	+	+	—	+	+
20	<i>Bankia carinata</i> (Gray)	+	+	+	—	+	+
21	<i>Bankia Nordi</i> Moll	+	+	+	—	—	—
22	<i>Bankia rochi</i> Moll	+	+	—	—	—	+
23	<i>Martesia striata</i> Linn	?	+	+	—	+	+
24	<i>Martesia fragilis</i> Verril and Bush	—	—	+	—	+	—
25	<i>Sphaeroma terebrans</i> Bate	—	+	+	—	+	—
26	<i>Sphaeroma annandalei</i> Stebbing	+	+	+	—	+	+
27	<i>Sphaeroma triste</i> Heller ( <i>Sphaerona walkeri</i> Stebbing) not a true wood borer	—	—	+	—	—	—
28	<i>Limnoria bombayensis</i> Pillay	—	+	+	—	+	+
29	<i>Limnoria indica</i> Becker and Kampf	—	—	+	—	—	—
30	<i>Limnoria tripunctata</i> Menzies	—	—	+	—	+	—
31	<i>Limnoria pfefferi</i> Stebbing	—	—	—	—	(Minikoi)	—
32	<i>Limnoria septima</i> Barnard	—	—	—	+	—	—
33	<i>Limnoria bituberculata</i> Pillay	—	—	—	—	+	—
34	<i>Limnoria insulae</i> Menzies	—	—	—	+	—	—
35	<i>Limnoria unicornis</i> Menzies	—	—	—	+	—	—
36	<i>Limnoria platycauda</i> Menzies	—	—	—	+	—	—

Bombay (Palekar and Bal, 1955-1957; Palekar *et al.*, 1964). It is interesting to note that the dominant forms in this area are somewhat different from those that occur in other localities. According to the recent reports, most of the destruction is caused by *Dicyathifer manni*, *Bankia rochi* and also by *Teredo furcifera*.

Thirteen species of borers have so far been collected from the south west coast of India. In the environs of the Cochin Harbour which is a typical estuarine area, the most destructive species are *Nausitora hedleyi*, *Teredo furcifera*, *Martesia striata* and *Sphaeroma terebrans*. *Sphaeroma annandalei* also occurs in this locality but are numerically much less than *S. terebrans*. The other species that occur in the area have not assumed any importance owing to the smallness of their numbers.

#### THE NEED FOR INFORMATION ON MARINE BORERS

Information regarding species active in other regions along the coasts of India, and the adjacent islands like the Laccadives and the Andamans, is most inadequate. Similarly no data exist regarding the forms that occur in the deep off shore waters. Such data are specially significant since con-

siderable variations have been noticed in regard to the nature, the occurrence and the activity of borers even in two localities along the same coast. Further, it is of interest to note that all the 17 species of *Xylophaga*, a wood-boring genus collected from the deep sea during the Galathea Expedition (Knudsen, 1961), were new to science, thus showing that the forms in the deeper waters could be quite different from those that occur in drift wood or in the coastal waters. Essential information needed is regarding the range of distribution of the species, their relative abundance and regional differences etc., along the east and west coasts of India. This is a prerequisite for detecting new arrivals, if any, through drift wood etc., and to keep under surveillance the forms that are already present. The data for this can be gathered in many ways. An easy method is by examining submerged portions of wooden structures in water-front constructions, piles, wooden floats etc.

Submerged timber of any description which was in water for some months come under this category. Record of wood-borers can also be obtained from drift wood that are washed ashore and these are likely to contain either live specimens or the shells and pallets. Such material may be from a neighbouring locality or may be washed ashore from distant places.

TABLE II

A-SERIES, SHORT-TERM BLOCKS SHOWING THE MONTHLY SETTLEMENT OF MARINE WOOD BORERS AT THE THREE LEVELS NAMELY INTERTIDAL (IT), BELOW LOW WATER (T), AND ABOVE MUD-LINE (B). THE NUMBERS REPRESENT THE TOTAL NUMBER OF ENTRANCE HOLES COUNTED ON THE SURFACE OF TEST BLOCKS.

Block number and period of immersion	<i>Martesia striata</i>			<i>Teredo furcifer</i>			<i>Nausitora hedleyi</i>			<i>Sphaeroma terebrans</i>		
	IT	T	B	IT	T	B	IT	T	B	IT	T	B
PRE-MONSOON												
A1 - 14 Feb - 14 March	5	52	327	28	141	1080	0	0	0	0	0	0
A2 - 14 March - 14 April	8	22	8	0	46	64	0	0	0	0	0	0
A3 - 14 April - 14 May	1	23	37	4	12	146	0	0	0	0	0	0
A4 - 14 May - 14 June	0	83	30	0	1340	1685	0	0	0	0	0	0
Total for pre-monsoon	14	180	402	32	1539	2975	0	0	0	0	0	0
MONSOON												
A1 - 1 June - 1 July	0	0	5	0	0	104	0	0	0	0	0	0
A2 - 1 July - 1 August	0	0	0	0	0	0	0	0	0	0	4	0
A3 - 1 August - 1 Sept.	0	0	0	0	0	0	2	0	11	7	5	0
A4 - 1 Sept. - 1 Oct	0	0	0	0	0	0	0	0	0	0	0	0
Total for monsoon	0	0	5	0	0	104	2	0	11	7	9	0
POST-MONSOON												
A1 - 1 Oct. - 1 Nov.	0	0	0	0	0	0	0	54	54	1	0	0
A2 - 1 Nov. - 1 Dec.	0	0	0	0	0	0	0	0	0	14	0	0
A3 - 1 Dec. - 1 Jan.	18	12	18	0	0	0	3	0	0	15	0	0
A4 - 1 Jan. - 1 Feb.	23	84	384	0	0	372	0	0	1	2	0	0
Total for post-monsoon	41	96	402	0	0	372	3	54	55	32	0	0
Total for the year	55	276	809	32	1539	3451	5	54	66	39	9	0

Floating seeds and drift wood are cast ashore in fair abundance, with boring animals or their remains, along both the east and west coasts of India, during the monsoon season. By far the most satisfactory and reliable method of collecting data on boring animals is with the help of test panels. This is done by exposing untreated, knot-free, straight-grained timber pieces, preferably of a soft timber, for the settlement of the borers. A methodically operated system of panels easily facilitate the collection of data regarding the occurrence, distribution, extent of activity, seasonal settlement, period of maturity, growth rates, influence of external factors and a variety of interesting data on borers from widely separated localities. These panels must be examined at regular intervals and new panels introduced throughout the duration of the test. Such data collected from Cochin Harbour are presented in Tables II and III.

The conditions prevailing in an estuarine area like the Cochin Harbour provide an ideal habitat for the settlement, growth and breeding of forms like *Nausitora hedleyi*, *Martesia striata* and *Sphaeroma terebrans*. During the monsoon and the post-monsoon periods the salinity is low, providing conditions for the growth and breeding of characteristic estuarine species. During the hot, pre-monsoon period, the salinity creeps up (see Table IV) and the stage is set for the recruitment into the estuary, and the activity, of typical marine forms. Thus, timber structures within this habitat are almost continuously attacked by waves of different species of borers, and this unsparring attack all through the year in ceaseless cycles rapidly reduces their service life. It will be seen that *Martesia striata* and *Teredo furcifer* are the chief borers settling on the blocks during the pre-monsoon period. The blocks register no attack from either *Nausitora* or *Sphaeroma* during

this time. A feature of practical importance is the comparative freedom of timber structures from borer attack during the peak of the south-west monsoon. During the period of low salinity of the monsoon, *Nausitora hedleyi* and *Sphaeroma terebrans* begin their settlement which reaches a climax during the post-monsoon period.

Through an effective and complex adjustment, the borers occurring in this locality have reached inter-relationships in such a way that both inter-specific and intra-specific competitions are reduced to a minimum and a seasonal succession seems to be in operation. The distribution of borers also seems to be balanced. When two species compete for the same zone, their life histories exhibit different cycles, with variations in the breeding season, so that the settlement of one species alternates with that of the other without serious overlapping. Yet another interesting point is that *Nausitora hedleyi* grows to a comparatively larger size than *Teredo furcifer* and this enables the latter to settle and grow to maturity on the left-over spaces by the former, thus leading to the full exploitation of timber structures in this area.

The reactions of closely allied species are different, and even those of the same may vary, according to the peculiar hydrographic conditions prevailing in an area. This may be seen from the difference in the breeding periods noted in the same species *Teredo furcifer* at Cochin and at Visakhapatnam. Each species has its own characteristic preferences, life history and season of attachment, and therefore, generalisations should be made with great caution. A scheme evolved after elaborate study and experimentation for one locality may prove uneffective for another. So it is evident that the problem varies with the species occurring in a locality and

TABLE III

3-SERIES, LONG-TERM BLOCKS SHOWING THE PROGRESS OF SETTLEMENT OF MARINE WOOD BORERS AT THE TREE LEVELS NAMELY INTERTITAL (IT), BELOW LOW WATER (T) AND ABOVE MUD-LINE (B) DURING THE PRE-MONSOON, MONSOON AND POST-MONSOON PERIODS. THE NUMBERS REPRESENT THE TOTAL NUMBER OF ENTRANCE HOLES COUNTED ON TEST BLOCKS.

Block number and period of immersion	<i>Martesia striata</i>			<i>Teredo furcifera</i>			<i>Nausitora hedleyi</i>			<i>Sphaeroma terebrans</i>		
	IT	T	B	IT	T	B	IT	T	B	IT	T	B
<b>PRE-MONSOON</b>												
B1 - 14 Feb. - 14 March	5	52	327	28	141	1080	0	0	0	0	0	0
B2 - 14 Feb. - 14 April	28	159	342	27	141	1070	0	0	0	0	0	0
B3 - 14 Feb. - 14 May	12	198	201	19	251	571	0	0	0	0	0	0
B4 - 14 Feb. - 14 June	146	90	358	55	185	221	0	0	0	0	0	0
Total for pre-monsoon	191	499	1228	129	718	2942	0	0	0	0	0	0
<b>MONSOON</b>												
B1 - 1 June - 1 July	0	0	5	0	0	104	0	0	0	0	0	0
B2 - 1 June - 1 August	0	0	0	0	53	65	0	41	62	0	4	2
B3 - 1 June - 1 Sept.	0	0	0	0	0	123	23	42	32	7	6	1
B4 - 1 June - 1 October	0	0	0	5	5	95	41	39	39	52	5	0
Total for monsoon	0	0	5	5	58	387	64	122	133	59	15	3
<b>POST-MONSOON</b>												
B1 - 1 Oct. - 1 Nov.	0	0	0	0	0	0	0	54	54	1	0	0
B2 - 1 Oct. A 1 Dec.	0	0	0	0	0	0	24	114	218	2	0	0
B3 - 1 Oct. - 1 Jan.	0	0	0	0	0	0	342	200	650	166	18	3
B4 - 1 Oct. - 1 Feb.	0	12	36	0	0	15	238	185	234	16	1	0
Total for post-monsoon	0	12	36	0	0	15	604	553	1156	185	19	3
Total for the year	191	511	1269	134	776	3344	668	675	1289	244	34	6

also with climatic and hydrographic conditions. The vagaries and discriminations of these pests are such, that most of the conclusions drawn from any investigation must, for the present, be considered as purely of local application. This may be seen from the fact that the dominant species reported from Visakhapatnam are *B. campanellata*, *T. furcifera* and *Martesia striata* (Nagabhushanam, 1962). Data from test panels reveal that the incidence of *B. campanellata* in that locality is during August to February with peak activity during the period November-January. The other two species show a different type of cycle with settlement throughout the year, with maximum intensity in summer months, March-June, and the peak in May.

For *Bankia carinata* in Madras, Nair (1957) noticed that the period July-August is the most conducive for larval development and settling even though there is evidence to show that the settlement of this species takes place throughout the year.

Information regarding the pattern of vertical distribution of borers is also needed, and is of considerable value, since the degree of deterioration at different levels along a pile is based on the intensity of settlement and growth of these pests at these levels.

Similar data from selected localities will be very beneficial for a comparative study of the activity of marine wood-boring organisms along the Indian coasts.

#### COMMENSALS, PREDATORS AND PARASITES OF TIMBER-BORING ORGANISMS

An interesting fauna of commensals, parasites, predators,

and similar organisms which are close associates of these timber-borers, have also been brought to light as a result of the observations in the Oceanographic Laboratory, Ernakulam. Ciliates belonging to the following families have so far been collected in large numbers. (1) Boveridae, (2) Urceolariidae, (3) Thigmophryidae, (4) Spirostomidae, (5) Licnophoridae, (6) Hysteroconetidae, (7) Stentoridae. Besides these, *Zoothamnium* sp., *Lagenophrys* sp., *Trochilioides* sp., have also been noticed. Detailed taxonomical and ecological work are in progress. According to Dr. Fenchel of Denmark many of these forms are new to science and are extremely interesting protozoan associates. Similarly, a hitherto undescribed hydroid assignable to the genus *Eugymnanthea* has been collected from the ctenidia of *Martesia striata*, *Teredo furcifera* as well as *Nausitora hedleyi*. However, the present form differs from all other species described under the genus *Eugymnanthea* in the nature of the polyps which are not solitary but branched. This form is further different from the other described species of the genus in that it is seen attached only to the ctenidia and not to any other part of the body. Further, the attachment itself is not temporary but apparently permanent being effectively secured to the substratum with the aid of a basal disc which in sections reveals to be implanted entirely within the tissue of the ctenidium. The attachment is further augmented with the aid of protrusions or hold-fasts which could be seen projecting from the basal disc in the fissure of the ctenidium. These features clearly distinguish the present hydroid from all others known under this genus. In other *Eugymnanthea* the attachment by the basal disc is effected with the aid of suction achieved through the muscular activity

TABLE IV

MONTHLY AVERAGE OF MAXIMUM AND MINIMUM TEMPERATURE (ATMOSPHERIC) RELATIVE HUMIDITY MONTHLY RAINFALL, TEMPERATURE AND SALINITY OF THE SURFACE WATER AT THE ERNAKULAM CHANNEL AND AT THE FOURTH BUOY BEYOND THE BARMOUTH IN THE ARABIAN SEA FOR THE PERIOD JANUARY, 1963 TO JANUARY, 1964.

Month	Atmospheric Temp. °C		Rainfall in mm	Relative humidity percentage	Ernakulam Channel		Fourth Buoy	
	Maximum	Minimum			Temp. °C	Salinity ‰	Temp. °C	Salinity ‰
January, 1963	31.5	22.4	25.0	66	28.10	32.56	27.93	32.92
February	32.1	22.6	5.3	73	28.50	32.97	28.00	33.32
March	32.5	25.0	45.8	73	30.92	33.23	31.25	33.76
April	33.0	24.5	63.4	72	32.33	33.47	32.35	33.77
May	32.9	25.7	120.8	79	32.35	33.48	31.50	32.50
June	30.5	24.0	440.9	80	28.70	11.30	28.60	15.96
July	29.4	23.7	525.5	87	28.40	2.46	27.55	11.94
August	25.9	23.8	539.8	86	28.85	1.43	27.50	15.21
September	30.1	23.8	405.3	82	29.70	3.33	28.32	14.38
October	30.4	23.9	269.3	76	30.60	5.58	29.00	22.97
November	31.7	24.3	153.1	73	29.23	16.97	29.33	22.88
December	31.4	22.4	53.3	73	29.85	12.75	29.50	29.47
January, 1964	31.7	21.0	Trace	64	28.00	31.12	27.95	32.00

of the cell layers, thereby enabling the commensal to get detached from one site and get re-attached to another part of the host's body. The present form, however, seems to have lost such abilities owing to the more intimate relationship with the host, leading to an almost permanent and firm attachment involving the tissue of the host. Here removal of the hydroid invariably leads to the damage of the ctenidium of the host. Thus this species presents one more step in the evolution of *Eugymnanthea* by making the attachment to the host more intimate and almost permanent to circumvent the difficulty of holding on to its substratum in the strong current in the mantle cavity of the host. The detailed ecology of this interesting form is under investigation and a preliminary report has already gone to press (Santhakumari and Nair, 1969).

Similarly a new species of entocytherid ostracod (*Microsyssitria indica*) assignable to a new sub family Microsyssitriinae and a new genus *Microsyssitria* has been collected and described from *Sphaeroma terebrans* (Hart, Jr., Nair and Hart, 1967). We have also collected isopods and copepods from the mantle cavity of shipworms and planarians and polychaetes in close association with shipworms from the habitat of these timber-borers. Detailed ecophysiological studies on these are in progress. The conditions under which these live, the exact nature of the relationship etc., are being investigated.

#### GENERAL REMARKS

The time of settlement on fresh surfaces by these organisms is an important period from the economic point of view. It is during this period that these organisms come into intimate contact with water-front structures and experience the effects of preservatives used on timber. More information is needed regarding the behaviour of the larvae at the time of penetration into timber and their reaction to other organisms present around them. An understanding of the precise role of bacteria and fungi in the ecology of marine borers also is essential.

Fundamental research on the biology of these organisms with special emphasis on the possibility of biological control through the exploitation of parasites and predators will certainly be rewarding. Our observations have shown the presence of several species of ciliates, planarians and poly-

chaetes in close association with shipworms in this locality. An essential pre-requisite in this context is an accurate understanding of the exact nature of the relationship between the timber-boring animals and their close associates, especially those species which are suspected as predators and parasites. In the haste to obtain results of immediate practical value, there has unfortunately been a tendency to overlook these basic studies which may appear arduous and difficult. With a view to providing answers for at least some of these biological problems, we have undertaken the study of the ecology of this fascinating group of animals, in the University of Kerala.

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#### DISCUSSION

G. RODRIGUEZ (Venezuela): You mentioned that the attack by *Teredo* was very small above the intertidal zones. Do you have any data on the rate of settlement, according to sea level?

Prof. N. BALAKRISHNAN NAIR: We have been using test panels at three different levels, one set in the intertidal zone, one set just below the low water mark and the third set above the mud-line. Also we have been using test piles with a view to finding out the nature of settlement of marine timber borers. The width of the intertidal zone at Cochin is about one metre. The tidal amplitude is thus not of a high magnitude. The test panels were of two kinds one short-term panels and the other long-term panels. The short-term panels were of one month duration, the long-term panels were changed at intervals of one month, two months, three months and so on extending for one year. Thus it was possible to obtain results regarding the nature of attack for the respective period of immersion. They also furnished data on the cumulative attack for the year.

Dr. JONES (England): How intensified is your testing procedure around the Indian coasts? What is your testing procedure at each sight? work about to be published by Dr. Ruth Turnes, suggests that if you test an area at one point, you may get misleading results as to the borers present. A more accurate picture will be obtained by testing at a number of points and at different levels.

Prof. NAIR: Tests and studies on marine borers of India have been conducted not by one agency but by different unrelated enthusiasts. There has, therefore, unfortunately not been much co-ordination or co-operation in regard to collection of data. The various Universities situated along the coasts have their own programmes. The Forest Research Institute has a comprehensive scheme on marine borers. Our limited surveys along the coasts of India have shown the existence of 33 species of borers along the east coast and 17 species along the west coast. The occurrence of such a large number of species makes the whole problem very difficult because of the varied habits and reactions of the different species. Our observations have not been very

intensive either, but in all tests along the south-west coast of India the procedure has been the same as may be seen from the tabulated statements using short-term and long-term panels exposed at different positions in the column of water.

Dr. JONES: Am I right in assuming that you are just testing at one place and at one level? You are not testing intensively the area around this spot.

Prof. NAIR: Well, at each test site the short-term panels consist of 12 sets, each with three units for the three levels of exposure. Each set was put out and changed at the end of 30 days as shown in the tables. The long-term panels consisted of 12 sets each with three units as for the short-term sets exposed in three groups of 4 each, one for the pre-monsoon, second for the monsoon and the third for the post-monsoon period. For each set there were replications also.

Dr. JONES: Your tests are giving results for one spot so that they may not be indicative for the full area, say over a five miles radius.

Prof. NAIR: In the case of Cochin Harbour we had four test sites representing four ecologically different habitats. But in this paper results from only one station is included.

Dr. JONES: May I ask one more question? You say that marine fungi condition the wood before borers get in. How vital do you think marine fungi are to the penetration of *Teredo* and *Martesia*?

Prof. NAIR: I feel that there is apparently a sort of softening of the timber through a hydrolytic process as a result of the activity of the fungi. This is probably one among the several conditions necessary for the successful attack by marine borers more especially by the shipworms. The shell valves of shipworm larvae are apparently very flimsy to penetrate into fresh unconditioned timber pieces. When you expose conditioned pieces and fresh pieces of timber together the attack of shipworms is confined only to conditioned pieces i.e. those pieces showing some bacterial or fungal infestation. We have also identified nearly five species of cellulolytic fungi from timber test panels exposed at Cochin Harbour.

# PROPRIETES ANTISALISSURES DE QUELQUES ALLIAGES DE CUIVRE

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## RÉSUMÉ

Il a été procédé en immersion, sur le littoral français, à un essai, d'une durée de 46 mois, sur 9 éprouvettes métalliques en alliage à base de cuivre. Ces essais ont été réalisés en vue de tester leur pouvoir antisalissure. Les pertes de poids ont également été notées au bout de cette période d'immersion.

Il a pu être constaté que tous ces alliages possèdent un pouvoir antisalissure à un degré variable, suivant la nature de l'alliage. Il a été possible d'établir un classement dans lequel le cuivre pur et les trois alliages suivants: cuprobéryllium, cuivre au phosphore et laiton, viennent en tête.

Il faut remarquer que le pouvoir antisalissures des alliages du cuivre est beaucoup moins sensible vis-à-vis des algues que vis-à-vis de la faune.

Profitant de ces essais à caractère biologique, la corrosion de ces alliages a également été observée.

Il a été noté que la plus faible perte de poids affectait le cuivre pur et que les autres alliages avaient perdu, en 4 années d'immersion, des poids assez proches les uns des autres.

De telles études méritent d'être poursuivies pour un éventail plus large des alliages et dans des eaux de mer de caractéristiques différentes.

Dans le cadre des études poursuivies pour déterminer le pouvoir antisalissure de divers métaux purs et des alliages, nous avons déjà présentés ceux relatifs au zinc<sup>1</sup>. La présente communication rend compte des essais entrepris, sur le même radeau, sur des alliages de cuivre.

Le 18 novembre 1957, 9 éprouvettes métalliques et une éprouvette en matière inerte, furent immergées sur le radeau

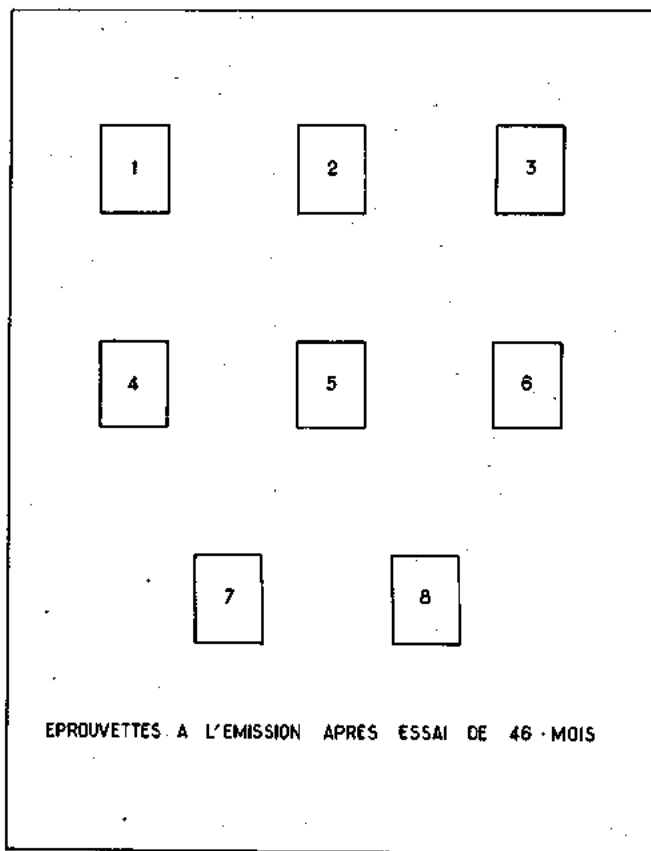
appartenant à l'Electricité de France dans l'estuaire de la Rance (côte nord de la Bretagne sur la Manche). Elles furent retirées le 25 septembre 1961, c'est-à-dire après 46 mois d'immersion. Elles sont donc restées dans l'eau pendant près de 4 ans. Pendant cette période, huit observations furent réalisées à des intervalles de temps indiqués dans le tableau I.

Les eaux de la Rance ont une salinité normale d'eau de

TABLEAU I  
RESULTATS DES ESSAIS SUR LE POUVOIR ANTISALISSURE

Date des examens	Durée d'immersion (mois)	1 Cupro-beryllium	2 Cupronickel	3 Cupro-silicium	4 Cuivre phosphore	5 Cuivre électro	6 Cuproaluminium	7 Laiton	8 Monel	9 Laiton Amiraute
5 février 1958	3									
23 octobre 1958	11								X Hydrides algues	
25 mars 1959	16						X Algues		XX Hydrides algues ascidies	
15 octobre 1959	23		X Algues				XX Hydrides-algues		XXX nombreuses espèces	
20 mars 1960	28		X Algues				XX Hydrides-algues			
8 juillet 1960	32		X Hydrides-algues	X Algues			XXX Hydrides-algues balanes	X Algues	XXXX toutes espèces	
15 mars 1961	40		X Algues	X Algues			XXX Hydrides-algues balanes		XXXX toutes espèces	X Algues
25 septembre 1961	46		XX Algues-hydrides	XX Algues hydrides		X Algues	XX Algues hydrides	X Algues	éprouvette perdue	éprouvette perdue

X très rares  
XX rares  
XXX abondants  
XXXX très abondants



mer car le débit fluvial de la Rance est négligeable par rapport au jeu des marées. Ces eaux sont très salissantes comme le prouve l'abondante faune déposée sur les éprouvettes inertes. Il faut remarquer que ces expériences furent réalisées avant la construction de l'usine marémotrice au moment où l'estuaire était encore libre.

Malgré cette abondance des salissures, le pouvoir antisalissure des métaux immergés fut remarquable.

Les alliages que nous avons utilisés étaient au nombre de 8 auxquels nous avons ajouté un cuivre électro.

Les éprouvettes se présentaient sous la forme de plaque de 200 x 300 x 3 mm. Elles étaient placées dans des cadres, ces derniers immergés sur le radeau à 50 cm sous la surface de l'eau. Les divers métaux avaient les caractéristiques suivantes :

Cuprobéryllium	Cu : 98%	Be : 2%	
Cupronickel	Cu : 75%	Ni : 25%	
Cuprosilicium CF 53	Cu : 96%	Si : 3%	Mn : 1%
Cuivre au phosphore	Cu : 99,9%	P : 0,04%	
Cuivre électro	Cu : 99,95%		
Cuproaluminium			
Mis. A 10	Cu : 89,5%	Al : 9%	Mn : 1,5%
Laiton	Cu : 70%	Zn : 30%	
Laiton Amirauté H.R.	Cu : 60%	Zn : 39%	Sn : 1%

A la fin des essais, c'est-à-dire au bout de 46 mois, le cuprobéryllium et le cuivre au phosphore ne comportaient absolument aucune salissure. Le cuivre électro, le laiton 70/30 et le laiton Amirauté ne présentaient que quelques touffes d'algues. Par contre, le cuivre au nickel vit apparaître des hydrides au bout de 32 mois, tandis que le cuproaluminium présenta des hydrides au bout de 23 mois; quant au cuprosilicium, les hydrides ne furent remarqués qu'au bout de 40 mois. Le pouvoir antisalissure du monel avait commencé

à disparaître au bout de 11 mois et au 32<sup>ème</sup> mois toutes les salissures s'y étaient fixées avec une grande abondance.

Le classement de ces alliages est donc le suivant, si l'on considère le moment de l'apparition de la première salissure (algues exclues):

Cuprobéryllium	}	plus de 46 mois
Cuivre au phosphore		
Cuivre électro		
Laiton		
Laiton Amirauté		
Cuprosilicium		40 mois
Cupronickel		28 mois
Cuproaluminium		16 mois
Monel		moins de 10 mois

Il est donc démontré que, dans les eaux où nous avons travaillé, les alliages du cuivre possèdent un bon pouvoir antisalissures, certains mêmes ont un comportement excellent. Le tableau n° 1 résume l'ensemble des observations sur cette propriété.

Pourtant, dans les essais réalisés à Miami (Floride) par A.C. Redfield<sup>2</sup>, aucun alliage n'avait tenu aux salissures plus d'un an. Cette divergence entre nos essais et ceux des Américains est-elle due à la différence des caractéristiques des eaux? On pourrait le supposer, mais dans ce domaine une recherche coopérative semble devoir être fructueuse.

Nous avons profité de cette étude pour déterminer le taux de corrosion, en pesant les éprouvettes avant et après l'immersion. Le tableau n° 2 donne les pertes de poids des diverses éprouvettes.

Du point de vue des pertes de poids les divers alliages se classent donc de la manière suivante:

Cuivre électro
Cuprosilicium
Cupronickel
Cuproaluminium
Laiton 70/30
Cuivre au phosphore
Cuprobéryllium.

Pourtant il faut remarquer que c'est le cuproaluminium qui présentait les attaques (crevasses) les plus spectaculaires, comme le montre la photographie de l'éprouvette après nettoyage. Pour tous les autres alliages la perte de poids était répartie assez uniformément sur toute la surface de l'éprouvette. Malheureusement nous n'avons pas pu déterminer la perte de poids du laiton Amirauté car l'éprouvette a été perdue quatre mois avant la fin de la durée totale d'immersion.

TABLEAU 2  
CORROSION DES ALLIAGES DE CUIVRE

Nature du métal	Durée d'immersion (mois)	Perte de poids totale (gr.)	Perte de poids en gr/m <sup>2</sup> /an
Cuprobéryllium (2 Be)	46	77	160
Cupronickel 75/25	46	61	127
Cuprosilicium (CFM 53 écroui)	46	59	124
Cuivre au phosphore	46	75	156
Cuivre électro	46	14	29
Cuproaluminium (9 al)	46	61	127
Laiton 70/30	46	73	152





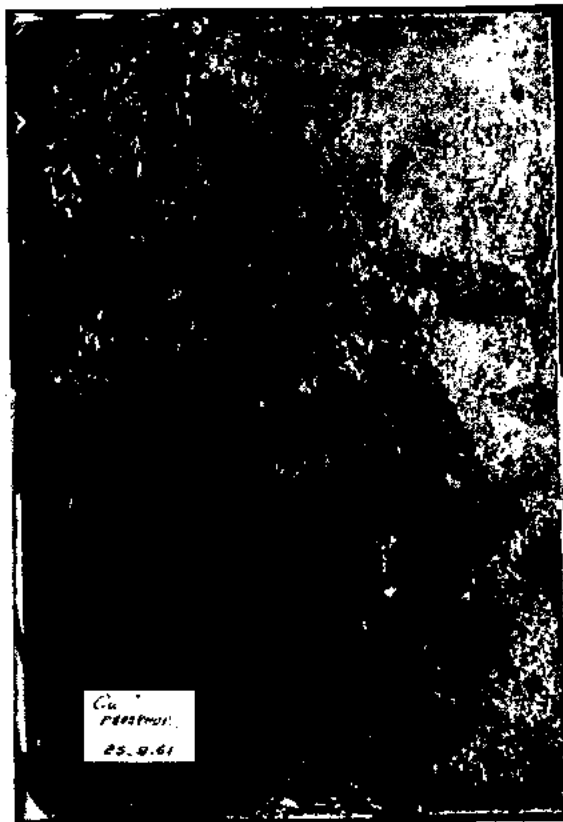
1. Cuproberyllium



2. Cupronickel



3. Cuprosilicium



4. Cuivre au Phosphore



Cu  
ELECTRO  
24.9.67

5. Cuivre Electro



Cuproal  
24.9.67

6. Cuproaluminium



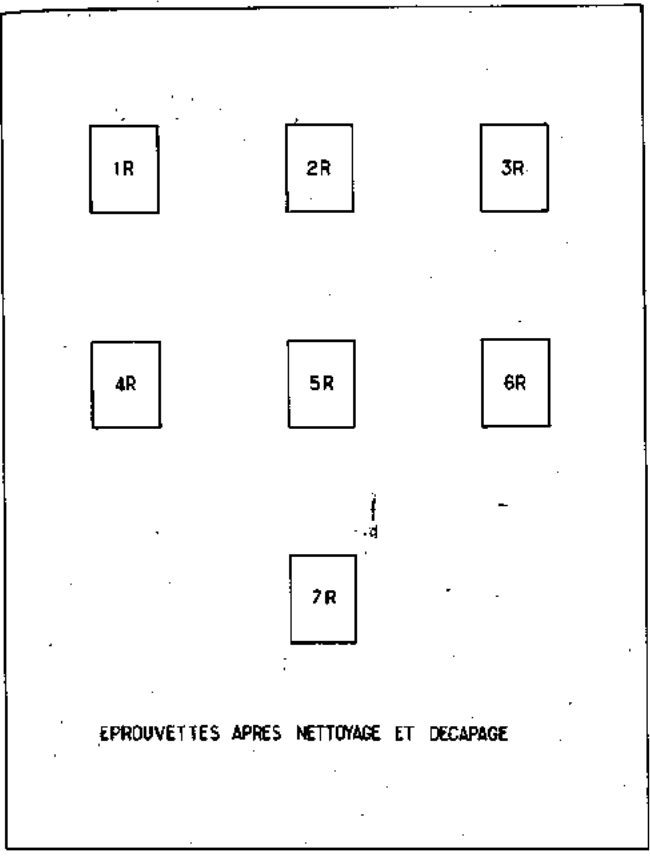
Laiton  
24.9.67

7. Laiton



Monel  
24.9.67

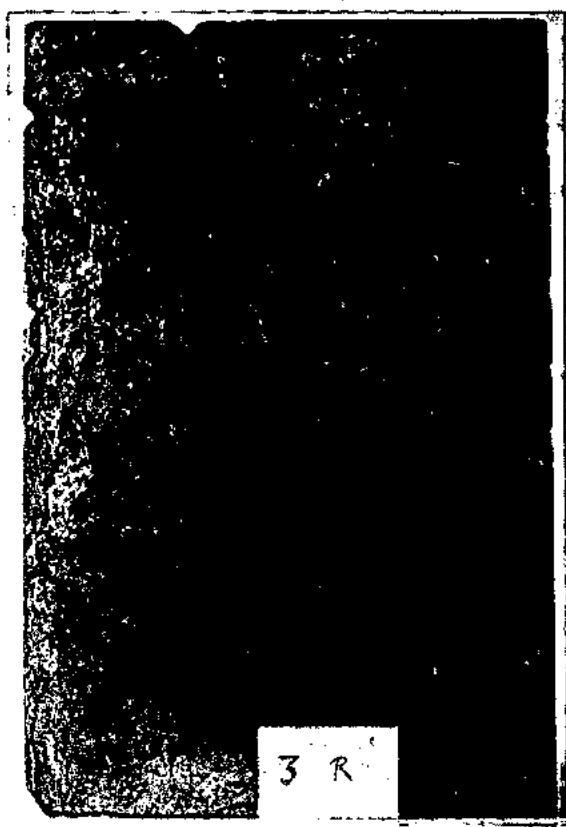
8. Monel



1R. Cuproberyllium



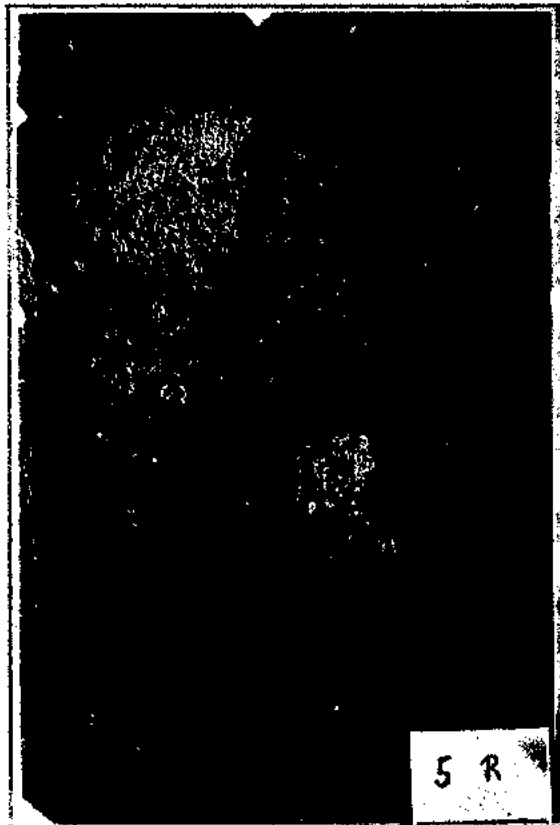
2R. Cupronickel



3R. Cuprosilicium



4R. Cuivre au Phosphore



5R. Cuivre Elektro



6R. Cuproaluminium



7R. Laiton

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**Séance - Meeting - Sitzung - Συνεδρίασις**  
**21.9.1968**

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**Dr. D.R. HOUGHTON (Great Britain).**

# DIE BEEINFLUSSUNG DER METAMORPHOSE VON *BALANUS IMPROVISUS* DARWIN DURCH GIFTSTOFFE

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## ZUSAMMENFASSUNG

Der zeitliche Ablauf der Metamorphose von *Balanus improvisus* wird beschrieben und nach äusseren Merkmalen in sieben Phasen eingeteilt, die von verschiedenen langer Dauer sind. (Charakteristische Bewegungen der Cypris, Aufrichten, Abstossen der Larvenhaut). Nach dem Schlüpfen geht die Verkalkung der Schale schnell vor sich, die Ausbildung der Cirren ist nach 3-4 Tagen beendet, danach kann Nahrung aufgenommen werden. Bis zu dieser Zeit sind die jungen Balanen sehr empfindlich, die Anfangssterblichkeit ist sehr hoch. In Cuxhaven bleiben nur etwa 5% der angehefteten Seepocken am Leben.

Antifoulings beeinflussen den Ablauf der Metamorphose von *Balanus* in sehr unterschiedlicher Weise. Bei einer starken Giftwirkung wird die Cyprislarve schon während der ersten Phasen abgetötet, die Umwandlung wird also nicht beendet. Bei schwächeren Wirkungen verläuft die Metamorphose

pathologisch, der Ablauf kann stark verzögert werden, es treten Quellungen der Antennulen oder Thorakalpartien in verschieden starkem Masse oder zu verschiedenen Zeiten auf. Sie führen meistens zum Tode, da das Abstreifen der Larvenhaut oder der Schwimmbeine usw. unmöglich wird.

Wird die Cyprislarve nach einer bestimmten Zeit dem Gifteinfluss entzogen, so können in einigen Fällen die Schädigungen zurückgehen, wenn die Einwirkungsdauer nur kurz war. In den meisten Fällen sind die Schädigungen aber nicht reversibel. Stark wirkende Antifoulings, die die Larven schnell abtöten, verhalten sich nach längerer Expositionszeit wie schwach wirkende Bewuchsschutzanstriche (pathologischer Ablauf). Länger andauernde geringere Giftwirkungen lassen sich auch bei «normal» verlaufener Metamorphose später noch durch Wachstumshemmung, ungenügende Haftfestigkeit und Missbildungen an der Basis erkennen.

Die Verhinderung der Anheftung von Bewuchsorganismen an Schiffsböden und anderen Gegenständen wird heute zumeist durch vergiftete Anstriche mit einem gewissen Erfolg erreicht. Die Frage, in welcher Weise die Vergiftung der Bewuchsorganismen vor sich geht, ist von grossem Interesse und auch des öfteren diskutiert worden (RAGG u.a.). Nachfolgend sollen einige Untersuchungen über die Beeinflussung des Seepocken-Ansatzes durch Giftstoffe mitgeteilt werden. Die Balaniden spielen bekanntlich im Schiffsbewuchs eine grosse Rolle, da etwa 70% aller bewachsenen Schiffe Balaniden als Erstansiedler haben.

Die zur Anheftung bereite Larve der Balaniden, die Cyprislarve, nimmt keine Nahrung mehr auf, sie schwimmt eine Zeit lang im Wasser. Die Cyprislarve hat nur die biologische Aufgabe, einen Siedelplatz aufzusuchen, was sie durch Schwimmen und Laufen erreichen kann. Hat die Cyprislarve den Platz ausgewählt, und ist die Umwandlung zum *Balanus* eingeleitet, so ist eine Ortsveränderung nicht mehr möglich.

Wie später noch näher ausgeführt wird, ist eine Vergiftung während oder kurz nach der Metamorphose am wirksamsten, da die jungen Balanen mit zunehmendem Alter und Wachstum widerstandsfähiger werden.

Aus der Literatur ist bekannt, und eigene Untersuchungen bestätigten das, dass eine Schädigung durch Gifte auch noch zu einem späteren Zeitpunkt möglich ist. Das Wachstum kann gehemmt sein, auch kann die Verankerung auf dem Substrat mangelhaft sein, wenn die Seepocken nicht mehr mit der ganzen Basalfläche auf der Unterlage haften, sondern nur mit pathologisch veränderten, verdickten Basalrändern dem Untergrund aufsitzen. (POMERAT & WEISS 1946). Wegen der schlechten Haftung auf dem Substrat können die Balanen dann leichter durch äussere Einwirkungen z.B. Wasserströmungen, wieder verschwinden. In den meisten

Fällen ist dies aber nur bei schwächeren Gifteinwirkungen der Fall.

Um die Wirkung von Giftstoffen auf die Besiedlung durch Seepocken verstehen zu können, ist es erforderlich, zunächst den normalen Verlauf der Metamorphose kurz zu behandeln. Die Untersuchungen wurden vorwiegend mit *Balanus improvisus* DARWIN durchgeführt, einer Art, die für derartige Versuche besonders geeignet erscheint, da die Ansprüche, die diese eurytopy Art an das Substrat stellt, sehr gering sind.

Das Aufsuchen des Siedelplatzes geschieht zunächst durch Schwimmen, (Abb. 1) wofür der Larve sechs Paar Ruderrüsse zur Verfügung stehen. Mit Hilfe der zusammengesetzten Augen, die nur die Cyprislarve besitzt, werden dunkle, sich im Wasser gegen den Hintergrund abhebende Gegenstände angesteuert, wie entsprechende Versuche zeigten (KÜHL 1952). Von einer «abschreckenden» Wirkung grüner Farbtöne (Wellenlänge 530-545m $\mu$ ) kann man aber nicht sprechen. (NEU 1923). Beim Auftreffen auf einen festen Untergrund wird die Platzsuche durch Laufen mit Hilfe der sehr beweglichen Antennulen fortgesetzt, die mit einem Saugnapf versehen sind. Die Antennulen besitzen ausserdem Sinneshaare, durch die das Substrat taktil und chemisch geprüft werden kann (Abb. 2). Es konnte gezeigt werden, dass durch adäquate Reize die Cyprislarven zur «Gruppenbildung» angeregt werden (KNIGHT-JONES & STEVENSON 1950, KÜHL 1952), d.h. dass sie möglichst nahe beieinander siedeln, wodurch später eine gegenseitige Befruchtung ermöglicht wird. Auch taktil wird der Untergrund geprüft, indem Unebenheiten im Substrat ausgenutzt werden; Vertiefungen, wie Löcher und Rillen werden bevorzugt besiedelt. Die Cyprislarve kann aber ein Substrat auch wieder verlassen und fortswimmen, sie besitzt ausreichend Reservestoffe, die «Oelkugeln», die in den letzten Naupliusstadien angelegt werden

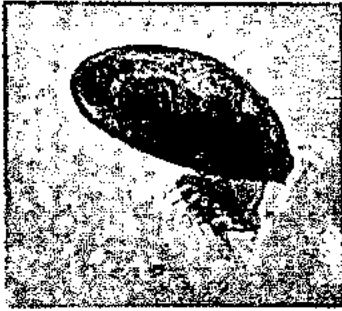


Abb. 1. — Schwimmende Cyprislarve von *Balanus improvisus*. Die Antennulen sind eingezogen. Im Larven-Vorderende (links) sind die Reservestoffe zu erkennen.



Abb. 2. — Cyprislarve mit ausgestreckten Antennulen. Am Larven-Hinterende ragen die Borsten der Ruderfüsse etwas aus der Schale heraus.

und sich im Vorder- und Hinterende der Cyprislarve befinden. Durch Versuche konnte festgestellt werden, dass die Reservestoffe für drei Wochen ausreichen, die Larve hat also für die Platzsuche genügend Zeit.

Ist der Siedelplatz gefunden und die Metamorphose eingeleitet, kann die Cyprislarve, die man nun als Cypris-puppe bezeichnet, keine Ortsveränderung mehr vornehmen. Die Metamorphose dauert bei *Balanus improvisus* etwa 24 Stunden, jedenfalls war sie nach dieser Zeit unter normalen Umständen beendet.

Zu Beginn der Metamorphose zieht die Cypris-puppe die Antennulen an, sodass sie nunmehr flach dem Substrat aufliegt (Abb. 3). Die drei Augen, das unpaare Naupliusauge und die zwei zusammengesetzten Augen sind von oben deutlich zu erkennen. Im Puppen — Vorder- und Hinterende befinden sich die Reservestoffe als gelbe «Oelkugeln», ausserdem noch kleine, doppeltbrechende weisslich-gelbe Konglomerate, die im letzten Naupliusstadium bereits angelegt sind und für die Initial-Schalenbildung verwendet werden.

Nach etwa vier Stunden wandern die Augen in die Tiefe, sodass sie von oben zunächst noch schwach, dann gar nicht mehr zu sehen sind. Die Fettkugeln verteilen sich, ebenso wandern die Kalk-Konglomerate zur Körpermitte hin. Die Cypris-puppe bleibt so für weitere vier Stunden ohne äusserlich erkennbare Beugung liegen. Im Verlauf der nächsten Stunden finden Kontraktionen des Körpers in der Schale in Längsrichtung statt, der Körper zieht sich zusammen, und die Puppe macht drehende seitliche Bewegungen um den Ansatzpunkt herum. Am Ende dieser Phase richtet sich die Puppe auf und macht für die weiteren ein bis vier Stunden drehende Bewegungen. Dann werden die beiden Komplexaugen, zusammen mit den V-förmigen Sehnen der Antennulen abgestossen, sie bleiben normalerweise an der Schale hängen. Der Körper ist zum Vorderende hin stark kontrahiert, schliesslich schlüpft die Puppe aus dem basalen Spalt der Schale heraus. Diese schwierige Endphase kann in einer halben Stunde beendet sein, sie kann aber auch Stunden oder sogar Tage dauern, wenn die Schale sich nicht vollständig vom jungen Seepocken-körper ablöst (Abb. 4).

Die junge, eben geschlüpfte Seepocke macht nun auf dem Substrat kreisende und schiebende eigenartige Bewegungen, deren Sinn es offenbar ist, den Untergrund für die weitere Anheftung zu präparieren, zu «reinigen» und mit dem Sekret der «Zementdrüsen» einzuschmieren. Inzwischen sind auch die Kalkkörperchen an bestimmte Stellen der schon vorgebildeten Primordialplatte gewandert und haben die erste Verkalkung der Mauerkrone und des Operculums eingeleitet. Der junge *Balanus improvisus* besitzt am Basalrand eine grössere Anzahl von Borsten, die später verschwinden. Die Cirren sind noch nicht ausgebildet, sie entwickeln sich erst im Verlauf der folgenden 3-4 Tage. Vom. 5. Tage ab ist dann eine Nahrungsaufnahme möglich.

In diesen ersten Tagen ist der junge *Balanus* gegenüber

äusseren Einflüssen noch sehr empfindlich, das geht aus der hohen Anfangssterblichkeit deutlich hervor. In Cuxhaven können sich in der Hauptbewuchszeit bis zu 7000 Balanen auf 100 cm<sup>2</sup> in einer Woche ansetzen, was einer Besiedlungsdichte von etwa 40% entspricht. Nach vier Wochen sind es aber nur noch 300-400 Individuen, die inzwischen auf 3-4 mm Ø herangewachsen sind, das Substrat ist dann zu 100% bewachsen.

Für die Untersuchungen ist die Tatsache sehr wichtig, dass die bereits festgeheftete Cyprislarve auch dann ihre Metamorphose normal vollenden kann, wenn sie mit einer Nadel vorsichtig vom Substrat abgelöst und in ein Blockschälchen gesetzt wird.

Auf diese Weise war es möglich, zu untersuchen, in welcher Weise sich verschiedene Giftstoffe in Anstrichen auswirken, ihre Einwirkungsdauer zu bestimmen und deren Folgen kennenzulernen.

Die Versuche, über die hier berichtet werden soll, wurden mit vier Anstrichen durchgeführt und zwar mit einem

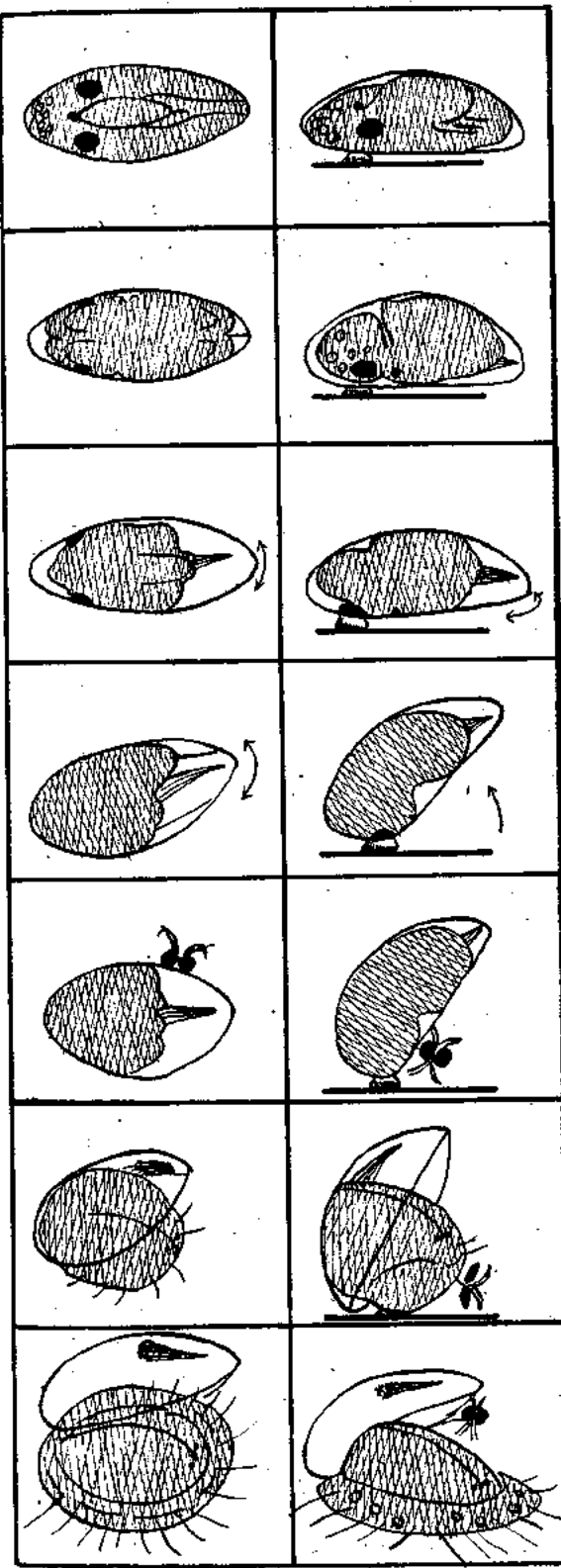
- |  |      |
|--|------|
| unvergifteten Anstrich   | : A  |
| einem schwächer vergiftetem Anstrich (Zn + ZnO)                | : B  |
| einer handelsüblichen Schiffsbodenfarbe III A                  | : C  |
| und einem stark vergifteten Anstrich (Cu <sub>2</sub> O + HgO) | : D. |

Die Anstriche wurden auf entsprechend vorbereitete Stahlplatten von den Ausmassen 250 × 250 × 3 mm aufgetragen und an der «Alten Liebe» in Cuxhaven 0,5 m unter Tiden-Niedrigwasser ausgelegt. Die Anstriche B und D wurden einmal sofort untersucht und ausserdem nach einjähriger Versuchsdauer, um ein Nachlassen der Giftwirkung zu beobachten.

Die Versuchstafeln wurden mit einem Gradnetz versehen (cm<sup>2</sup>), sodass der Besiedlungsverlauf stündlich verfolgt werden konnte. In einer Versuchsgruppe wurden die Tafeln nach zweibis vierstündiger Freiwasserlagerung mit den angehefteten Cyprislarven in das Laboratorium gebracht und in fliessendes Seewasser gelegt. Nach verschieden langer Einwirkungsdauer (5-100 Stunden) wurden die Cyprislarven vorsichtig von den Anstrichen abgelöst und in Blockschälchen unter dem Binokular weiter beobachtet. Ausserdem wurden noch Objektträger mit Anstrichen versehen und die Besiedlung mit Seepocken verfolgt. Über andere Untersuchungen, bei denen die Cyprislarven in Blockschälchen direkt den Giftlösungen ausgesetzt waren, soll hier nicht berichtet werden.

Ein erstes wichtiges Versuchsergebnis war, dass auch bei hochwirksamen Bewuchsschutzanstrichen eine Anheftung von Cyprislarven stattfinden kann, die Besiedlungsrate ist oft allerdings nur gering. Bei starker Giftwirkung wird die Cypris-puppe sehr schnell abgetötet, die Metamorphose kommt bereits in der 2.-3. Phase zum Stillstand, wird also nicht beendet. Dabei ist der Körper in der Schale stark zusammengezogen, oft auch trübe (vgl. Abb. 3, II-III). Es kann vorkommen, dass die Cypris-puppe nach kurzfristiger Einwirkung





1. Phase. — Cyprislarve nach der Anheftung. Zunächst Bewegungen. Augen und «Ölkugeln» von oben sichtbar.

2. Phase. — Dauer ca 4 Std. Die Augen sind in die Tiefe gewandert, die Fettstoffe verteilt: von oben nicht mehr sichtbar. Ruhe.

3. Phase. — Mehrere Std. Kontraktion des Cypris-Körpers. Bewegungen der Puppe um den Ansatz-Punkt und im Inneren.

4. Phase. — 1-4 Std. Die Puppe hat sich aufgerichtet, weiterhin Bewegungen wie in der 3. Phase.

5. Phase. — Ca 10 min. Abstossen der Komplexaugen und V-Sehnen. Kreisende und pendelnde Bewegungen wie vorher.

6. Phase. — ¼ Std bis mehrere Tage. Schließen der Seepocke am basalen Spalt, Abwerfen der Larvenschale.

7. Phase. — 4-5 Tage Ausbildung der Cirren, Zunehmende Verkalkung der Schalen-Platten.

Abb. 3. — Schematische Darstellung der Metamorphose von *Balanus improvisus*. Ansicht von oben und von der Seite. Die Pfeile geben die Bewegungsrichtung an. Länge der Puppe 0,6 mm.



Abb. 4. — Abgeworfene Cypris-Schalen von *Balanus improvisus*, am unteren Teil mit den abgeworfenen Komplexaugen, und den Schwimmblau-Häuten im Inneren der Schale.



Abb. 5. — Im Anfangsstadium der Metamorphose (Phase 2) abgestorbene Cypris-Puppe, stark kontrahiert und trübe.

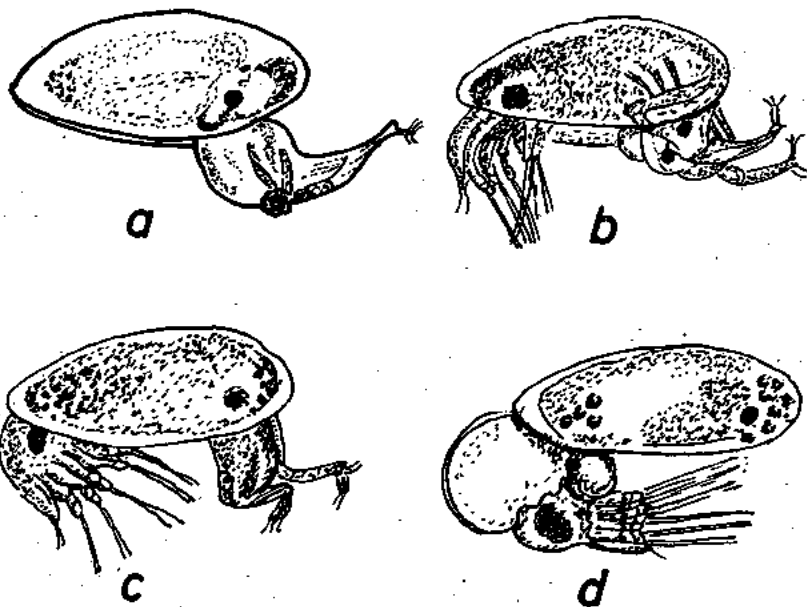


Abb. 6. — Quellungserscheinung bei Cypris-Puppen. 6 a und b: Die Antennulen-partie ist aufgequollen und mit einem (a) bzw. beiden Komplexaugen (b) aus der Schale herausgestreten. bei c sind Antennulen- und Thorakal-Parteien aufgequollen bei d ist der Thorax sehr stark aufgequollen und blasig aufgetrieben. (Metamorphosestadium 3-4).

im Blockschalchen noch einige Zeit, u.U. Tage lebt, zu einer Umwandlung kommt es aber nicht. (Abb. 5).

Nimmt die Giftwirkung ab, so verläuft die Metamorphose pathologisch, und die abartigen Erscheinungen sind sehr mannigfaltig. Dabei ist es offenbar gleichgültig, ob es sich um ein schwächer wirkendes Gift handelt, oder ob die Menge eines hochwirksamen Giftstoffes zu gering ist.

An der Cypris-Puppe sind oft Quellungen zu beobachten, die entweder am Vorderende an den Antennulen, dem späteren Anheftungsorgan, oder an den Thorakalpartien mit den Ruderfüßen, oder auch an beiden auftreten können. Einige

Beispiele hierfür sind in Abb. 6 dargestellt. Die Tiere können noch eine Zeit lang weiterleben, solange die Reservestoffe ausreichen. In den meisten Fällen sind die Quellungserscheinungen irreparabel, auch wenn die Puppen dem Gifteinfluss entzogen sind. Die Metamorphose wird also auch hier nicht vollendet. Nebenbei sei bemerkt, dass auch im Plankton Cyprislarven mit aufgequollenen Körperteilen vorkommen.

Schwächere Giftwirkungen führen zu Störungen in späteren Phasen der Metamorphose, wofür die Abb. 7. einige Beispiele bietet. So kann es bis zur Ausbildung der Primordialplatten innerhalb der Larvenhaut kommen. Die Puppe schlüpft nicht,

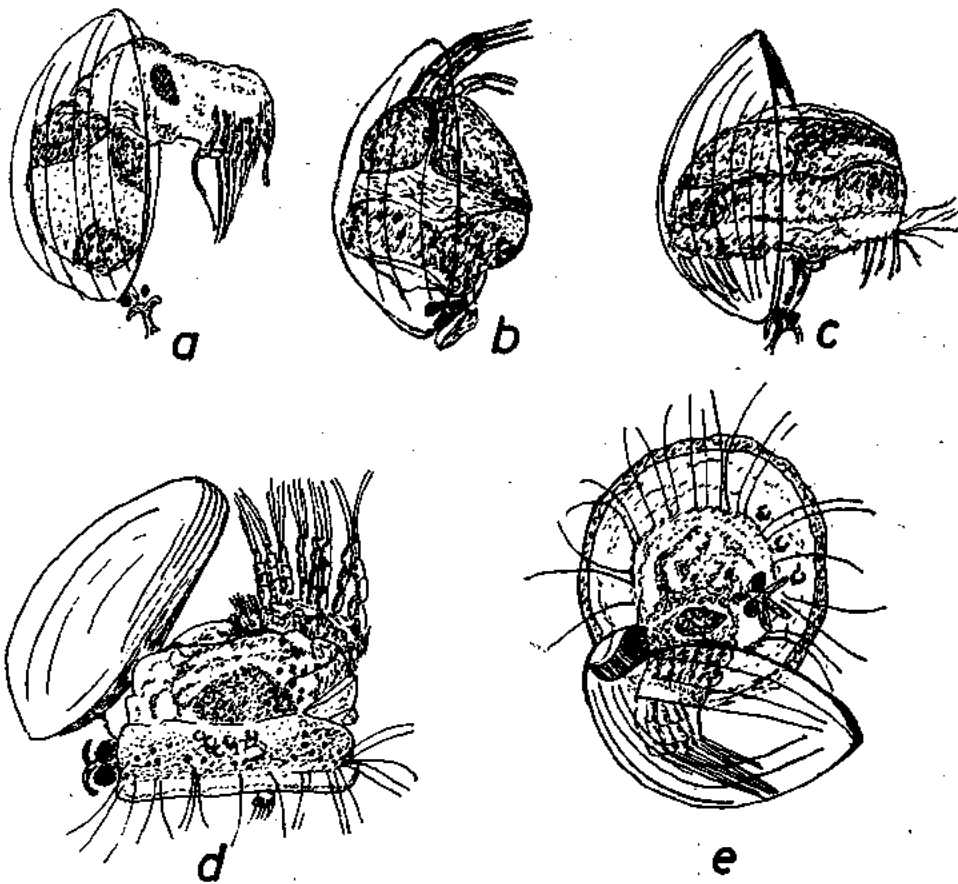


Abb. 7.— Anomale Metamorphose. a bis c Ausbildung der Primordialplatten in der Schale. Ein Schlüpfen hat nicht stattgefunden. Bei b ist die Thorakalpartie aufgequollen.  
 d: die Schwimmbeine sind nicht gehäutet (vgl. Abb. 4).  
 e: der Thorax ist zusammen mit den Schwimmbeinen in der Schale steckengeblieben.

kann aber auch eine ganze Zeit weiter leben. Auch in diesem Fall wird die Metamorphose nicht beendet (Abb. 7a,b). Schliesslich kann die Umbildung bis zur letzten Phase verlaufen, aber die Ruderfüsse, die der Cyprislarve zum Schwimmen dienten, werden nicht gehäutet; normalerweise bleiben die Ruderfuss-Häute in der abgeworfenen Larvenschale zurück (Abb. 4). Auch in diesem Falle kann die umgewandelte Seepocke noch eine Zeit lang am Leben bleiben, sie ist aber zur Nahrungsaufnahme unfähig und geht schliesslich ein, denn aus den Ruderfüssen entstehen durch Umbildung die Cirren, die der Nahrungsaufnahme dienen.

Das Gleiche ist der Fall, wenn zwar die Metamorphose bis zum Ende verläuft, auch das Abwerfen der Schale gelingt, aber die Basalpartien und der Thorax stark aufgequollen sind. Diese monströsen Balanen haben eine minimale Haftung, sie sind ebenfalls unfähig, Nahrung aufzunehmen, sie können solange am Leben bleiben, bis die Reservestoffe aufgebraucht sind (Abb. 8).

Die Schädigung durch eine schwächere Giftwirkung kann auch erst zu einem späteren Zeitpunkt in Erscheinung treten. So wurde z.B. eine Cypris-Puppe nach fünf Tagen von einer Platte abgenommen und in ein Blockschälchen gesetzt. Die Puppe zeigte äusserlich keine Missbildung (Abb. 9a). Nach neun Tagen, also einem recht langen Zeitraum, hatte sie sich zu einer monströsen Seepocke mit aufgequollener Basis entwickelt (Abb. 9 b); die Larvenschale war zwar nach weiteren fünf Tagen abgeworfen, aber die Ruderfuss-Häute waren

nicht abgestreift (Abb. 9 c). Die Seepocke ging schliesslich nach weiteren 14 Tagen ohne Veränderungen ein. Derartige Missbildungen sind auf Versuchstafeln im Freien nur sehr selten zu sehen, da sie meist vorher schon von der Oberfläche verschwinden.

Dabei können sich die Cirren innerhalb der Ruderfuss-Häute entwickeln, sie sind dann aber als Organe der Nahrungsaufnahme ungeeignet.

Es soll jedoch nicht unerwähnt bleiben, dass auch einige Fälle beobachtet werden konnten, bei denen die Quellungen — besonders an der Basis — wieder zurückgingen, die Störungen durch die Gifte wieder ausgeglichen wurden. Das war aber nur der Fall, wenn die jungen Seepocken dem weiteren Gifteinfluss entzogen worden waren.

Diese wenigen Beispiele mögen genügen, um die mannigfachen Veränderungen aufzuzeigen, die bei der Metamorphose unter dem Einfluss von Giften auftreten.

Wir können daraus ersehen, dass ein hochwirksamer Giftnstrich die Cypris-Larve bzw. Puppe in den ersten Stunden abtötet, dass beim Nachlassen der Giftwirkung die Metamorphose weiter fortschreitet, wobei allerlei Missbildungen auftreten können, die schliesslich auch zum Tode führen. Es kann auch eine Umwandlung zu einer mehr oder weniger missgestalteten Seepocke kommen, deren Lebensfähigkeit ebenfalls sehr gering ist. Ist die Giftwirkung so schwach geworden, dass die Metamorphose zur Seepocke normal verläuft, so besteht immer noch die Möglichkeit, dass, wie oben



Abb. 8. — Missgestaltete Seepocke nach vollendeter Metamorphose. Die Basis ist stark aufgequollen, auch die Cirren sind zur Nahrungsaufnahme unfähig.

bereits erwähnt, Wachstumshemmungen auftreten, oder pathologische Veränderungen im Schalenbau, Verdickungen an der Basis und verminderte Haftfestigkeit festzustellen sind.

Zur Erläuterung dieser Verhältnisse sind in Tabelle 1 zahlreiche Versuchsergebnisse zusammengestellt und zwar für einen unvergifteten Anstrich (A), einem schwach vergifteten Anstrich (B) und zwei verschieden stark vergiftete Anstriche (C und D) nach verschieden langer Einwirkungsdauer. Darin ist die normale Metamorphose zur Seepocke mit «+», die starke Giftwirkung (schnelle Abtötung der Cypris-Larve) mit «+» und die pathologische Metamorphose mit «x» gekennzeichnet.

Nach der oben angegebenen Kennzeichnung einer starken und schwächer werdenden Giftwirkung wird die Erschöpfung eines Bewuchsschutzanstriches auch biologisch verständlich, was durch über mehrere Bewuchsperioden laufende Versuche gut beobachtet werden konnte.

Ein hochwirksamer Anstrich SB III A S verhielt sich z. B. im zweiten Versuchsjahr bei Beginn der Bewuchsperiode wie ein schwächer wirkender Anstrich SB III am Anfang, aber nach Beendigung der zweiten Bewuchsperiode, also nach 16 Monaten, wie ein schwach vergifteter Anstrich SB II, wobei die Metamorphose dann vollendet wurde und die Zahl der «Normalen» Umwandlungen zur Seepocke immer mehr zunahm.

Wenn Antifoulings ungleichmäßig aufgetragen sind, bzw. Risse, Poren oder aufgeplatzte kleine Bläschen vorhanden sind, also sehr unterschiedliche Schichtdicken gemessen werden, so kann man ebenfalls alle Grade der Gifteinwirkung auf die Seepocken-Metamorphose beobachten.

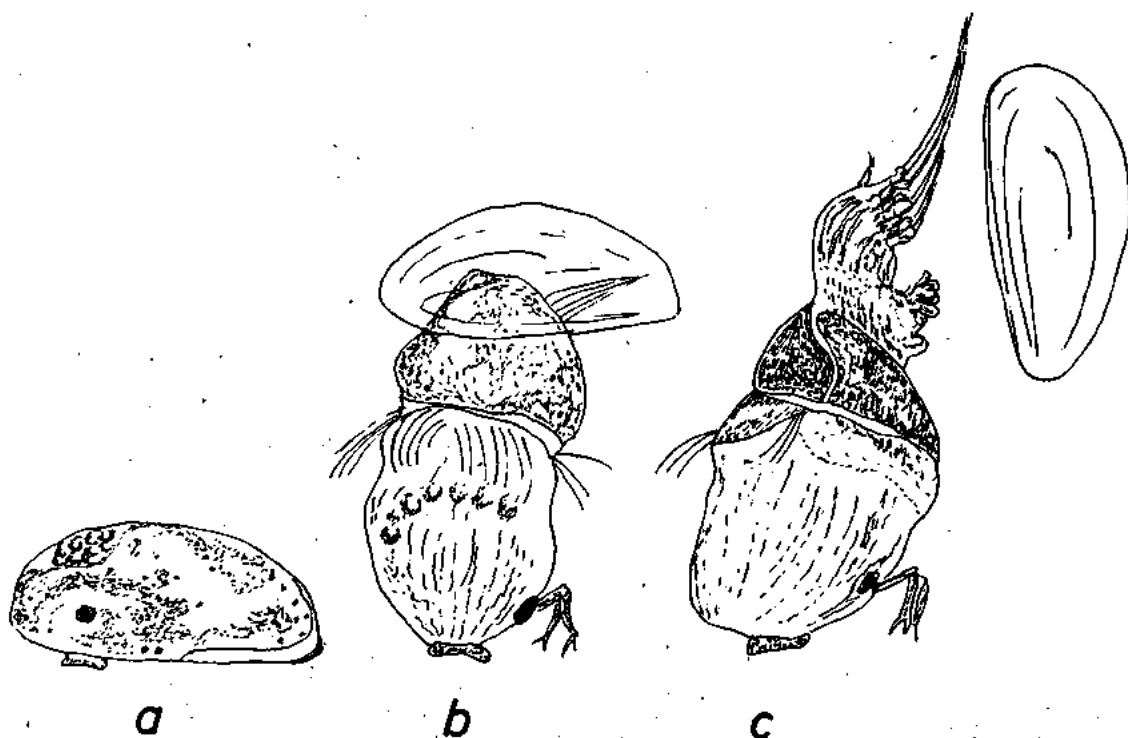


Abb. 9. — Cyprislarve am 26. X. 1945 auf SB III angeheftet (Phase 1-2, Abb. 3).

- a: am 31. X. abgenommen und in Seewassergesetzt
  - b: anomale Metamorphose bis 9. XI.
  - c: am 14. XI sind die Ruderrfüsse noch nicht gehäutet eine Nahrungsaufnahme ist nicht möglich.
- am 29. XI. nach Verbrauch der Reservestoffe tot.  
Die «Oelkugeln» sind im aufgequollenen Basisteil sichtbar.

TABELLE 1

Stunden:	5	10	20	50	75	100
Anstriche						
A	o	o	o	o	o	o
B neu	o	o x	x	x +	+	+
B alt	o	o	o x	o x	o x	o x
C	o	o x	x	x	x +	+
D neu	x +	+	+	+	+	+
D alt	o x	o x	x	x +	+	+

Wirkung von Anstrichgiften auf den Verlauf der Metamorphose von *Balanus improvisus* nach verschieden langer Einwirkungszeit.

o normale Umwandlung zur Seepocke.

x die Metamorphose wird anomal beendet.

+ die Cypris puppe stirbt schon während der 1. - 3. Phase der Umwandlung ab, die Metamorphose wird also nicht beendet.

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## DISKUSSION

Dr. HOUGHTON (England): Ihre Arbeit, Dr. Kühl, war sehr interessant. Ich möchte fragen, ob Sie wissen, wie die Vergiftung der angehefteten Larven stattfindet. Ich habe bemerkt, dass Larven von *Balanus balanoides* in einer vergifteten Umgebung überleben können; sind sie fähig, auch nach der Anheftung zu überleben?

Dr. KÜHL: Die Frage, in welcher Weise die Gifte in die Cyprislarve eindringen, lässt sich in folgender Weise beantworten. Es gibt zwei Möglichkeiten, die in der Abbildung angedeutet sind: 1. Die Giftstoffe, die aus dem Anstrich herausgetreten sind, gelangen durch die ganze Körperoberfläche der Cyprislarve in das Körperinnere, und 2. Die Giftstoffe dringen durch das Anheftungsorgan, die Antennule, und den basalen Spalt der Larvenschale in das Innere der Cyprislarve. Auf Grund zahlreicher Untersuchungen nehme ich an, dass die Vergiftung hauptsächlich über den Ansatzpunkt — Antennule — und basalen Spalt erfolgt (2. Möglichkeit, in der Abbildung unten). Diese Auffassung hat insofern eine praktische Bedeutung, als immer wieder Versuche unternommen werden, — ich selbst habe es auch jahrelang getan — die Giftresistenz von Cyprislarven und auch anderen Organismen *in vitro* zu prüfen. Man erhält hierdurch natürlich bestimmte Ergebnisse, in vielen Fällen stimmen diese Ergebnisse aber nicht mit den so aufwendigen „Plattenversuchen“ im Freien überein, besonders dann wenn es sich um organische oder metallorganische Gifte handelt. Wie gut die Cyprislarve durch ihre Schale geschützt ist, geht auch daraus hervor, dass es erhebliche Schwierigkeiten bereitet, die Cyprislarve für histologische Untersuchungen zu fixieren und zu färben, es gelingt nur bei Anwendung spezieller Verfahren. Der direkte Nachweis für die Art

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des Eindringens von Giftstoffen in die Larve dürfte mit Hilfe fluoreszenzmikroskopischer Untersuchungen möglich sein, eigene Untersuchungen wurden in dieser Richtung bisher nicht durchgeführt.

Ing. BARTHA (Sweden): Ich möchte Dr. Kühl fragen, ob Vibrationsphänomene die Ansiedlung von Cyprislarven beeinflussen. Wir haben einige Experimente gemacht und beobachtet, dass Vibrationen, die von Pumpanlagen kamen, eine Anheftung von *Balanus* völlig verhindert haben, die Plätze waren ganz frei. Die zweite Frage: kann eine primäre Bakterien-schicht, die sich auf einer Giftfarbe gebildet hat, dazu verhelfen, dass sich die Balaniden nach 2 oder 3 Monaten ansetzen können. Die dritte Frage betrifft die Strömungsgeschwindigkeit, ich denke dabei an Kühlwasserleitungen. Es ist ja schwierig für Schiffe und Kraftanlagen, wenn kleine Röhre durch Balaniden und andere Organismen bewachsen werden. Dadurch kann die Kühlung verschlechtert werden, was allerlei ökonomische und technische Folgen haben kann. Bei welchen Geschwindigkeiten nun, — im Minimum oder Maximum — können die Balanuslarven noch siedeln — oder nicht?

Dr. KÜHL: Ich fange mit der letzten Frage an. Es ist so: wenn die Larve mit der Strömung an einen Gegenstand getrieben wird, streckt sie sofort die Antennulen aus, beginnt zu laufen, und es kann dann zur endgültigen Anheftung kommen. Über die Strömungsgeschwindigkeit kann ich nur sagen, dass die natürliche Strömungsgeschwindigkeit in Cuxhaven bei Ebbe 4 sm, also etwa 7 km/h, betragen kann, wobei ein Ansetzen möglich ist; das kann sicher auch noch bei höheren Geschwindigkeiten der Fall sein; wo die Grenze liegt, kann ich nicht sagen. In einem starken Strudel ist es vielleicht nicht mehr möglich, aber in einem Rohrsystem gibt es immer auch Stellen, Ecken und Winkel, mit gerin-

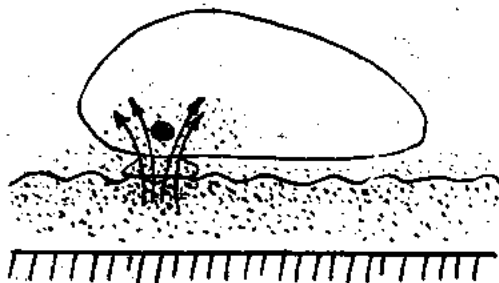
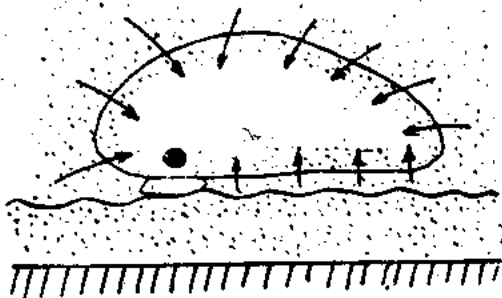


Abb.  
Das Eindringen von Giftstoffen (punktiert) aus einem Anstrich in eine angeheftete Cyprislarve (Pfeile).  
1. oben: durch die gesamte Körperoberfläche  
2. unten: über die Ansatzstelle der Antennulen.

gerer Strömungsgeschwindigkeit, und es ist durchaus möglich, dass hier eine Anheftung stattfinden kann.

Zur Frage des Primärschleims ist zu sagen, dass unter Umständen eine Anheftung erschwert ist, wenn die Schleimschicht sehr stark ausgebildet ist. Da die Cyprislarven bei der Platzsuche eine Auswahl treffen, verlassen sie einen ungeeigneten Ort. Für unsere Gewässer trifft das nur teilweise zu. Wenn während der Bewuchsperiode eine neutrale Platte ausgesetzt wird, so wird die sofort innerhalb der nächsten Stunden besiedelt, also noch bevor sich eine Primärschleimschicht bilden kann. Diese Bildung benötigt einige Zeit, oft mehrere Tage. In unserem Falle sind die Seepocken also schneller.

Über die bewuchshemmende Wirkung von Vibrationen habe ich keine Versuchsergebnisse vorliegen, die Beobachtungen von Herrn Bartha sind aber sehr interessant.

Ing. BARTHA (Sweden): Wir haben mit Chlorierung Versuche gemacht, wir haben das Wasser mit Natriumhypochlorit vergiftet, 0,005 ppm Hypochlorit (freies Chlor) im maximum, — über 1 mg ist schon gefährlich für die Korrosion — wir fanden, dass die Rohrleitung mit vergiftetem Wasser keinen Seepocken — oder anderen Bewuchs hatte. Das bedeutet, dass solche kleinen Mengen von Chlor wirksam sind. Diese Chlorierung ist jetzt vorgeschrieben, für die tropischen Regionen zweimal täglich, in unseren nördlichen Gewässern einmal täglich von Mai bis September.

Dr. KÜHL: Wenn ich vorher sagte, dass die Giftwirkung in vitro eine andere sein kann als im Anstrich, so ist es natürlich durchaus möglich, dass die Larven von Bewuchsorganismen in einem Natriumhypochlorit-Milieu getötet werden können. Ich wollte mit meinem Referat nur eine Erklärung für die Giftwirkung von Antifouling geben. Es kann z.B. vorkommen, dass in bestimmten Giftlösungen die Cyprislarven bis zu drei Wochen leben können, ohne dass es zu einer Metamorphose kommt, wenn man sie dann aus der Giftlösung herausnimmt können sie sich durchaus noch umwandeln. Natürlich können auch andere chemische Faktoren, wie Sauerstoffarmut, Stickstoffverbindungen zum Tode führen.

Dr. WICHERS (Holland): Haben Sie die Vorstellung, dass im Körper das Gift gleichmäßig verteilt ist, oder gibt es Stellen mit mehr oder weniger Gift?

Dr. KÜHL: Diese Frage kann ich nicht beantworten. Vor vielen Jahren wollte ich schon Untersuchungen mit Hilfe der Fluoreszenz-Mikroskopie durchführen, um den Weg der Giftstoffe im Larvenkörper zu verfolgen, — leider ist es nicht dazu gekommen. Es ist dies ein Problem, das mich immer sehr interessiert hat, — ich glaube aber doch, dass die Vergiftung, wie ich schon oben sagte, über die Antennulen und den basalen Spalt erfolgt, aber wie der Weg im einzelnen verläuft, kann ich nicht sagen, ich nehme an über den Zementdrüsensegang.

Dr. LITTAUER (USA): Sind Sie der Meinung, dass das Absterben noch nach der Anheftung stattfindet. Ist die Sache ähnlich auch bei anderen Organismen, die hier nicht erwähnt sind?

Dr. KÜHL: Wie ich schon sagte, findet die Vergiftung auch nach der Festheftung noch statt. Meine hauptsächlichsten Untersuchungen befassten sich mit Balaniden, die mir in Cuxhaven reichlich zur Verfügung stehen. Ausserdem habe ich noch einige Untersuchungen mit Sponiden, also sedentären Würmern gemacht, Verwandten der kalkröhrenbauenden Serpoliden. Die Vergiftung erfolgt hier ähnlich. Erfahrungen mit anderen Bewuchsorganismen habe ich nicht.

# THE PHENOLOGY OF FOULING ORGANISMS IN THE SOUTHERN BALTIC

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## SUMMARY

This paper aims to give the description of biological aspects of fouling organisms occurring in the Southern Baltic.

The aim of the present study was to obtain the knowledge of this biotope in respect of:

1. explanation of the phenology of such organisms as Hydrozoa, barnacles, edible mussels and Bryozoa;
2. determination of the struggle for space among individuals and among species;
3. the knowledge of the rate of growth of particular species;
4. computation of the total biomass for a definite surface area.

The investigations cover the period from June, 1964 till December, 1965. The observations, carried out with monthly intervals consisted in immersion of plates of the dimensions 35 × 25 cm, (made of polyvinyl chloride «Winidur») on which there were determined quantitative and qualitative differences of the overgrowth.

To the most common fouling organisms in the Baltic Sea belongs the barnacle *Balanus improvisus*. As it has been shown by the investigations there exists close relation between high temperature of the water and the intensity of spawning. Moreover both the factors should coincide, otherwise the intensity of spawning drops by nearly 40%.

Also the relation between the number of attached larvae, metamorphosis and growth was subject to investigations. On their basis it may be assumed that in the competition for the space the number of individuals decreases four times from the moment of metamorphosis till sexual maturity.

In the spawning cycle of edible mussel there has been also established close relation between water temperature and sexual maturity. On the basis of the present observations it was possible to ascertain that the beginning of spawning of edible mussel in the Baltic Sea takes place at the end of May and its intensity in June and July.

The third species to which belongs the role of fouling or-

ganism in the Baltic Sea is the bryozoid *Membranipora crustulenta*. Its distribution in the Baltic reaches the 3‰ isohaline. The surface of a single colony may attain 6 cm<sup>2</sup> and it occurs in the depth even down to 300 m. The first colonies settle already in July which shows that the spawning has began a few days earlier. It was found that the colony covered the area of abt. 4 cm<sup>2</sup> within two month. The colonies are characterized by even growth all year through.

The weight of the biomass, tabulated and calculated per 1 m<sup>2</sup>, is as follows:

for June 1964 (the period of 12 months, VI-V)  
barnacles — 86% — 14.62 kg  
edible mussels — 12% — 2.04 kg  
other species — 2% — 0.34 kg

for July 1964 (the period of 11 months, VII-V)  
barnacles — 77% — 9.24 kg  
edible mussels — 14% — 1.68 kg  
other species — 9% — 1.08 kg

for August 1964 (the period of 10 months, VIII-V)  
barnacles — 74% — 1.18 kg  
edible mussels — 17% — 0.27 kg  
other species — 9% — 0.15 kg

for September 1964 (the period of 9 months, IX-V)  
barnacles — 33% — 0.26 kg  
edible mussels — 53% — 0.17 kg  
other species — 14% — 0.07 kg

As it appears from above data along with passing towards winter months the biomass of barnacles decreases and the proportion becomes more favourable for edible mussels. For this reason it is to be assumed that the most favourable period for development of fouling animals in the Baltic extends from May till August. This period therefore is of practical consequences for launching new ships.

This paper aims to give the description of biological aspects of fouling organisms occurring in the Southern Baltic. The knowledge of development cycles of fouling animal species has been taken as a basis for establishing suitable methods of protection of ship's hulls and harbour facilities against fouling.

In view of the fact that the most intensive fouling occurs during ship's laytime in the ports the experimental station was localized in the port of Władysławowo, which was justified by:

- a) the choice of region — South-eastern part of the Baltic Sea, being the most representative for this kind of

investigations;

- b) the choice of localization — port.

The aim of the present study was to obtain the knowledge of this biotope in respect of:

- 1 - explanation of the phenology of such organisms as Hydrozoa, barnacles, edible mussels and Bryozoa;
- 2 - determination of the struggle for space among individuals and among species;
- 3 - the knowledge of the rate of growth of particular species;
- 4 - computation of the total biomass for a definite surface area.

The plants were excluded from the subject of investigations since their development depends solely on the year's season, and for another reason, namely because their greatest number — this having the influence upon the biomass — attaches directly under water surface (green algae). The investigations cover the period from June, 1964 till December, 1965.

The observations, carried out with monthly intervals, consisted in immersion of plates of the dimensions 35 × 25 cm (made of polyvinyl chloride «WiniDur») on which there were determined quantitative and qualitative differences of the overgrowth Fig. 1. The fundamental test device for calculation of quantity and determination of species was a cardboard stencil (of the size of the plate) in which there were cut out five squares with the length of 2 cm. of each side (4 cm<sup>2</sup>). Each time the stencil was put upon the overgrown plate and the number of individuals in each square was established. Moreover, after one year's immersion in the water the plates were taken out and cleaned up, which permitted to determine total biomass of fouling animals. There were also taken the samples of attached organisms, which made basis for determination of the rate of growth of particular fouling species.

On the basis of the collected material it was found that the spring-summer period of the year 1964 was considerably warmer than analogical period of the year 1965. This was particularly evident in the months May - June and as the result of it the highest water temperature in 1965 was noted with the delay of one month. Fig. 2. This delay was very essential for the months of April, May and June when intensive spawning and development of the majority of Baltic species starts.

To the most common fouling organisms in the Baltic Sea belongs the barnacle *Balanus improvisus*. As it has been shown by the investigations there exists close relation between high temperature of the water and the intensity of spawning. Moreover, both the factors should coincide, otherwise the intensity of spawning drops by nearly 40%. Fig. 3.

Also the relation between the number of attached larvae, metamorphosis and growth was subject to investigations. On their basis it may be assumed that in the competition for the space the number of individuals decreases four times from the moment of metamorphosis till sexual maturity. Fig. 4.

Another important species for the problem of fouling is edible mussel (*Mytilus edulis*). According to the investigations it has been found that over 20,000 individuals may occur in 1 m<sup>2</sup> (within 12 months).

In the spawning cycle of edible mussel there has been also established close relation between water temperature and sexual maturity. On the basis of the present observations it was possible to ascertain that the beginning of spawning of edible mussel in the Baltic Sea place at the end of May and its intensity in June and July. Fig. 5.

This is not a rule, however, since if the temperature of the water in May will remain below 10°C the sexual maturation becomes retarded and though the water temperature in June may rise again above the minimum the intensity of spawning will be considerably limited.

A new and unknown problem in the investigations on Baltic edible mussels is their rate of growth and consequently the possibility of determination of the biomass increase in a given time period.

Within two weeks from the moment edible mussel attaches to an object it reaches 1.7 mm. length. According to the observations its size increase is not even in the year's period. The greatest size is attained by those individuals which get first attached. This is shown in the diagrams 6 and 7. Besides, it was found that there is a distinct retardation of the rate of growth of edible mussel, noted in the months November - March (Fig. 8), whereas rapid increase of the rate of growth of this species is observed in the period from March till April, when the size of edible mussel increases by abt. 100 - 120%.

Very typical is the correlation of both retardation and increase of the rate of growth along with the changes of the temperature of water. It may be thus concluded that the

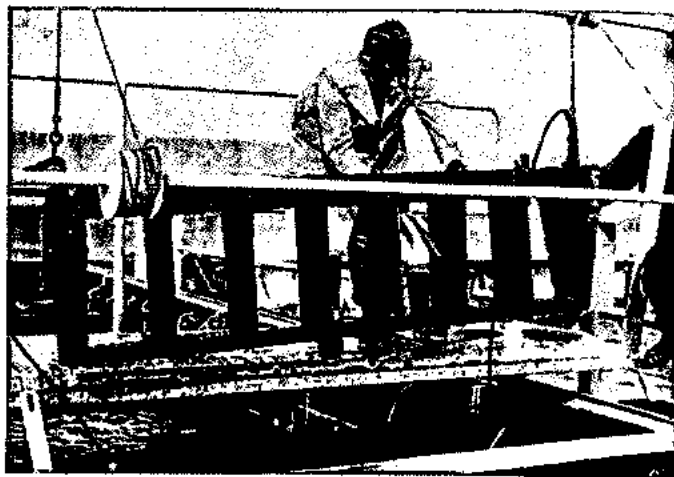


Fig. 1. — The frame with experimental plates.

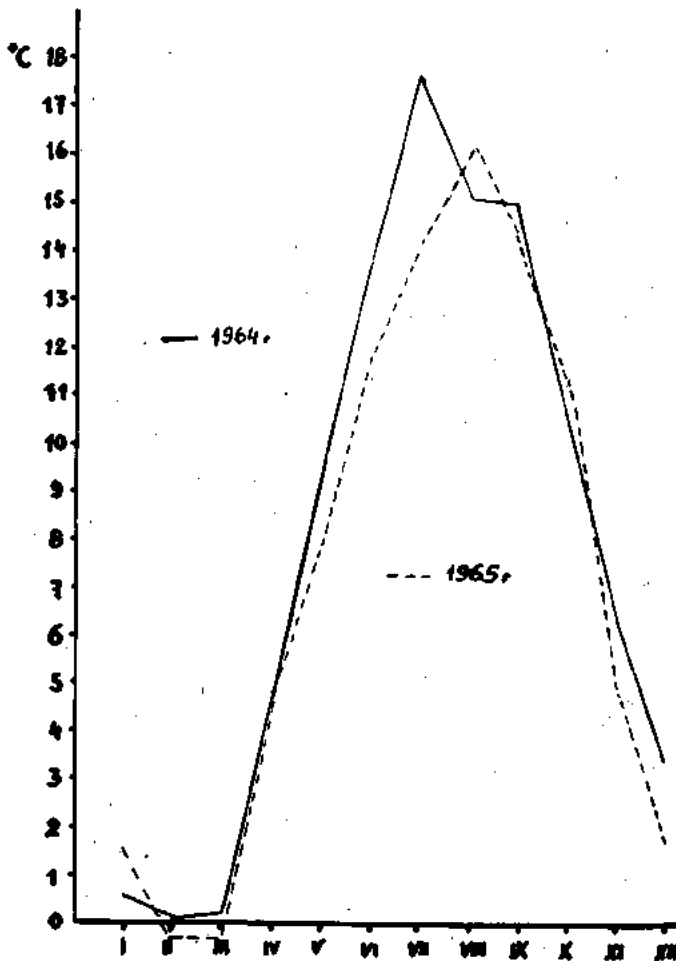


Fig. 2. — The range of oscillations of water temperature in the port of Władystawowo.



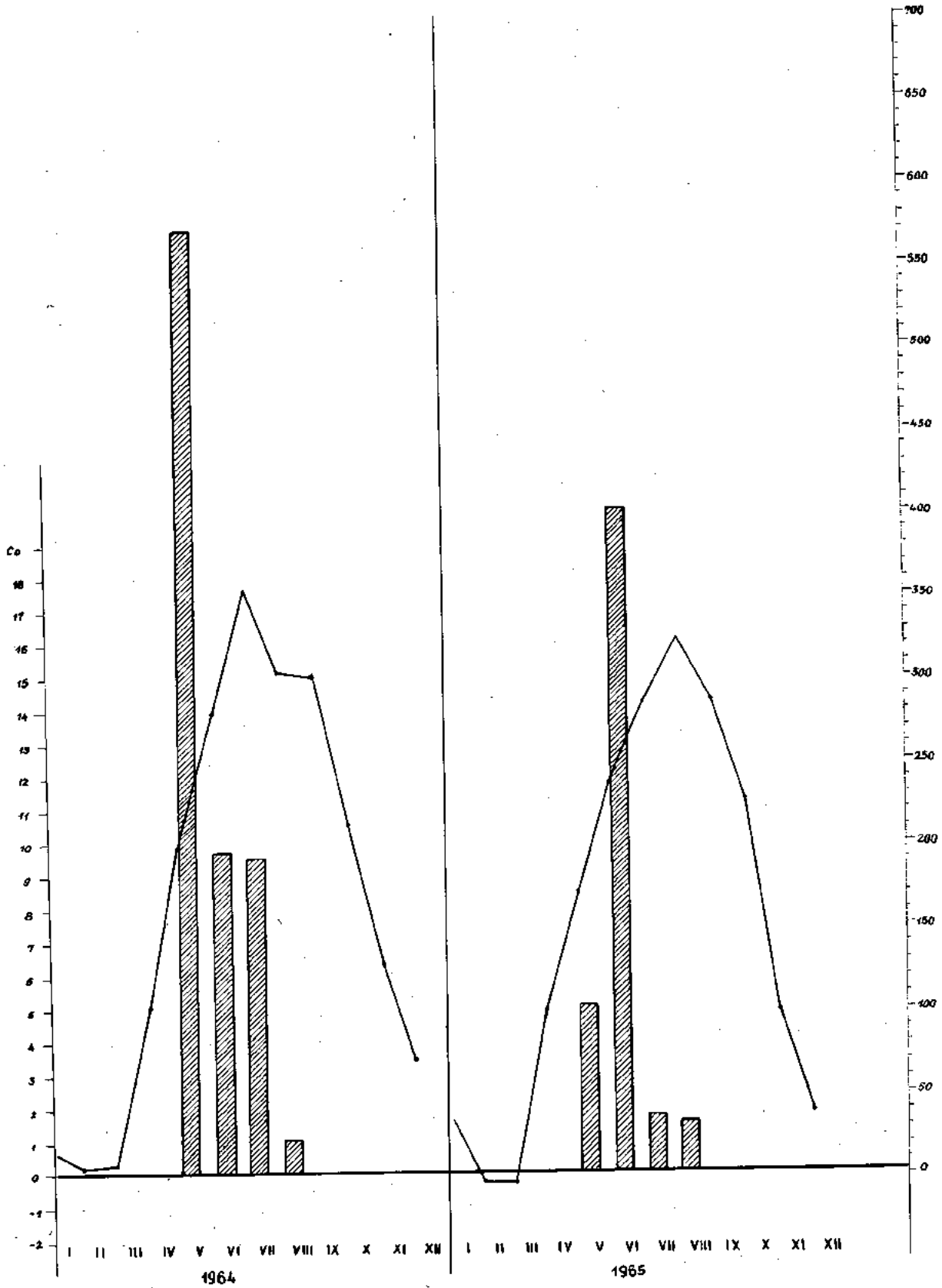


FIG. 3. —

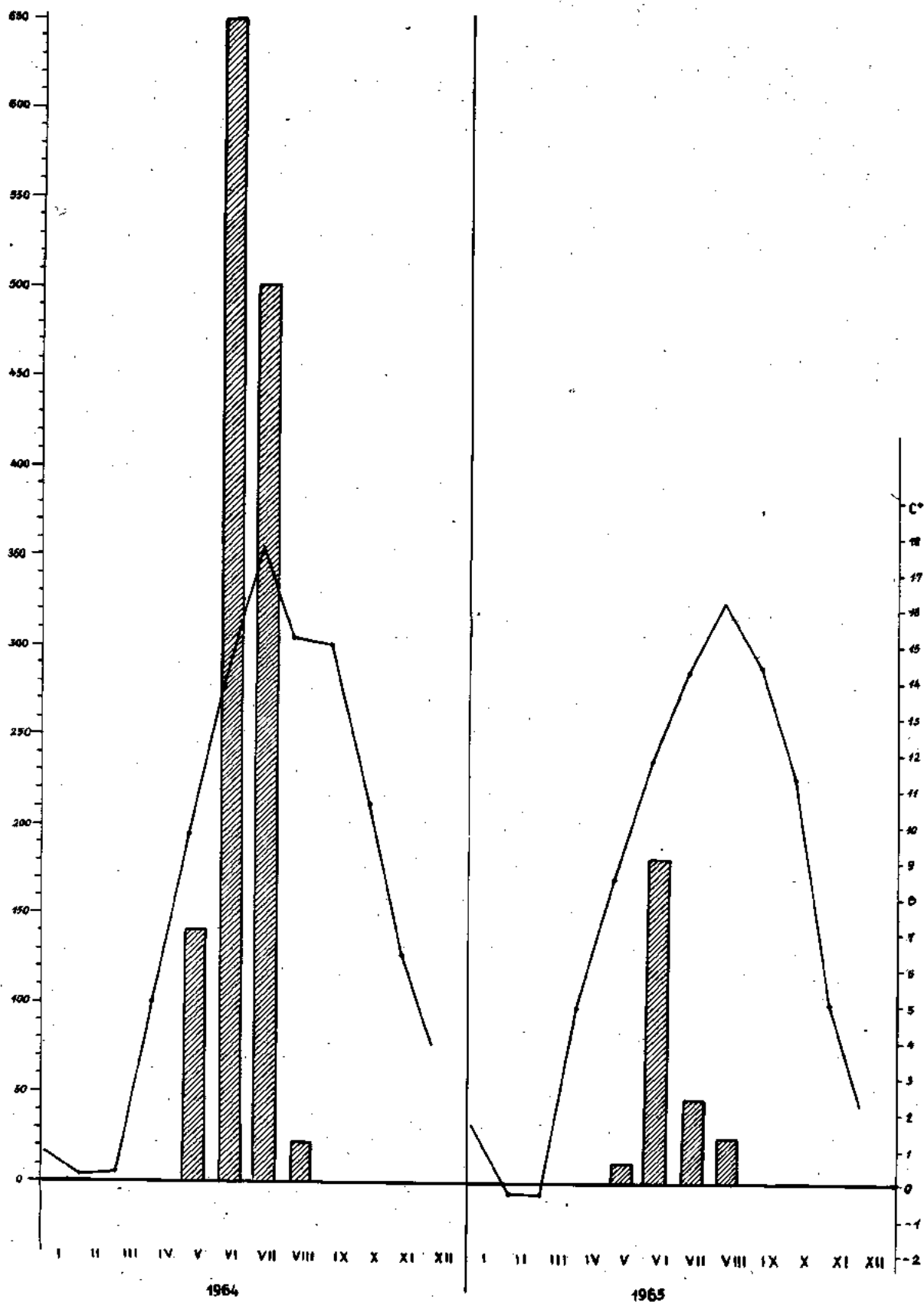


Fig. 5. —

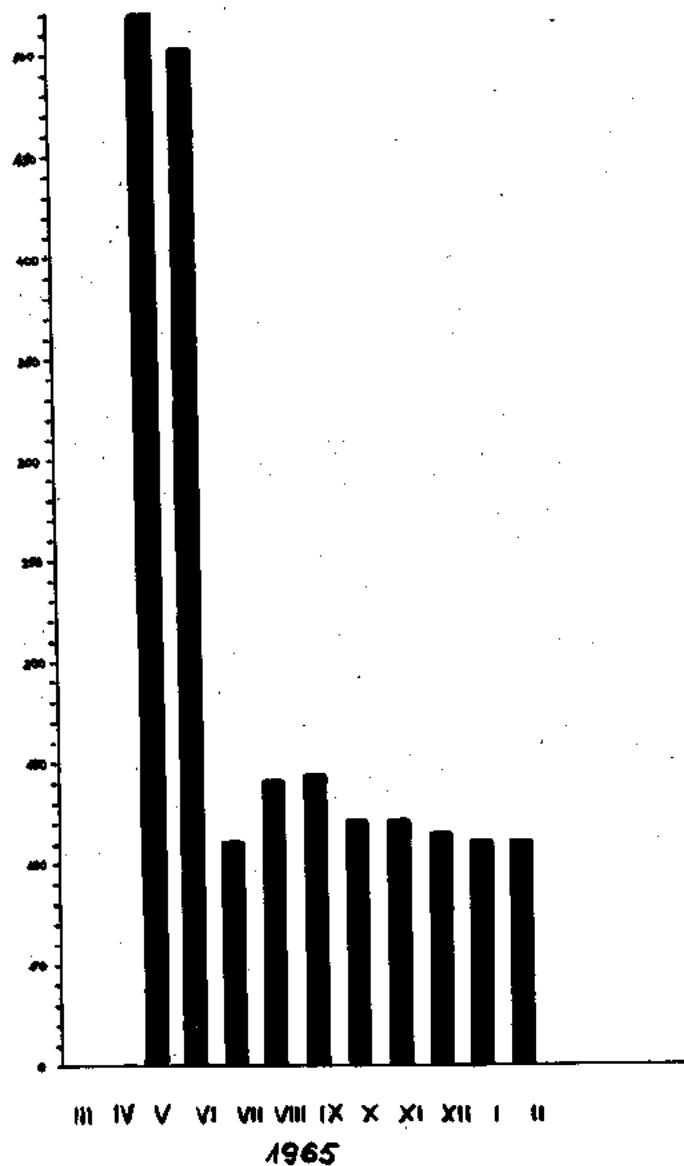


Fig. 4. — The number of attached barnacles per 20 cm<sup>2</sup>, perishing in the competition for space.

growth of edible mussel in the Baltic Sea is subject to the temperature of the water and probably the minimum water temperature for normal development of edible mussel is 6°C, while for the beginning of spawning it must remain within the temperature of abt. 10°C.

The third species to which belongs the role of fouling organism in the Baltic Sea is the bryozoid *Membranipora crustulenta*. Its distribution in the Baltic reaches the 3‰ isohaline. The surface of a single colony may attain 6 cm<sup>2</sup>, and it occurs in the depth even down to 300 m. The first colonies settle already in July which shows that the spawning has begun a few days earlier. It was found that the colony covered the area of abt. 4 cm<sup>2</sup> within two months. The colonies are characterized by even growth all year through. Fig. 9.

Among other fouling organisms, occurring in the Baltic Sea, we find the Hydrozoid *Leomedea flexuosa*. Though it does not gather into large concentrations its role is to create very favourable conditions for the settlement of other fouling animals. This is through covering the surface of an object

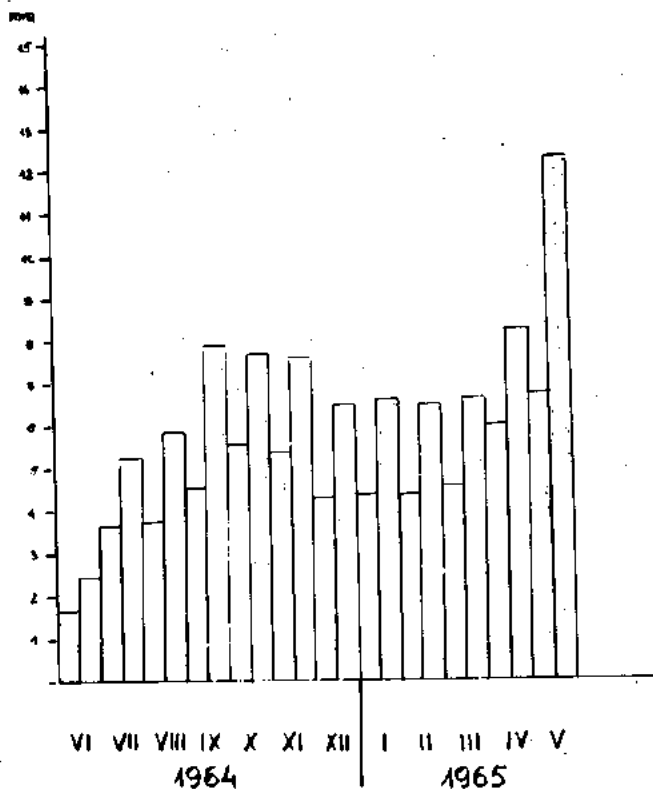


Fig. 6. — Average monthly size increase of edible mussels.

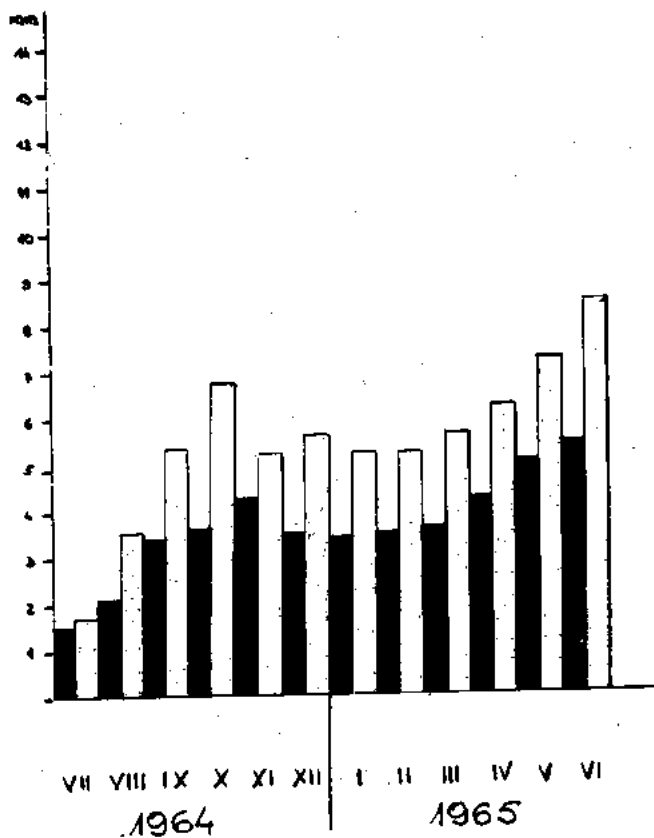


Fig. 7. — Average monthly size increase of edible mussels.

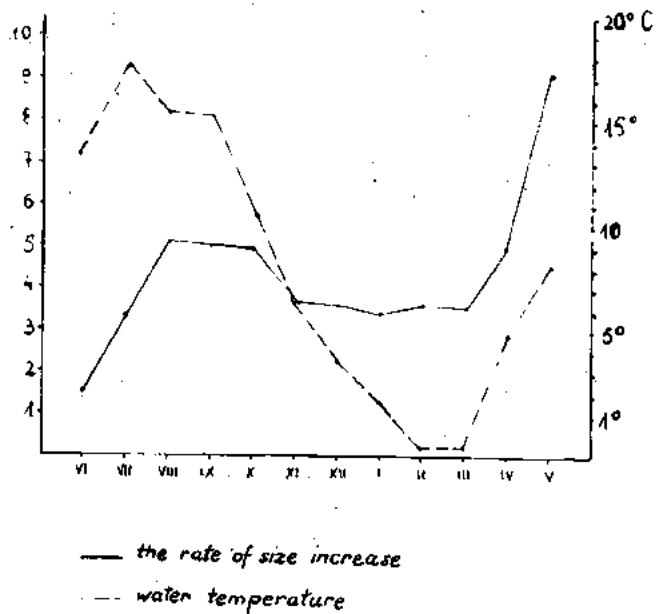


Fig. 8. — Mean monthly rate of growth of edible mussels.

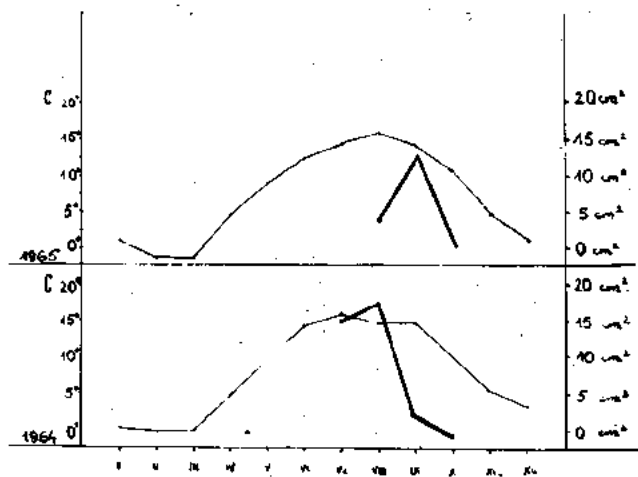


Fig. 9. — Spawning intensity and the area occupied by Bryosoa per 20 cm<sup>2</sup>.

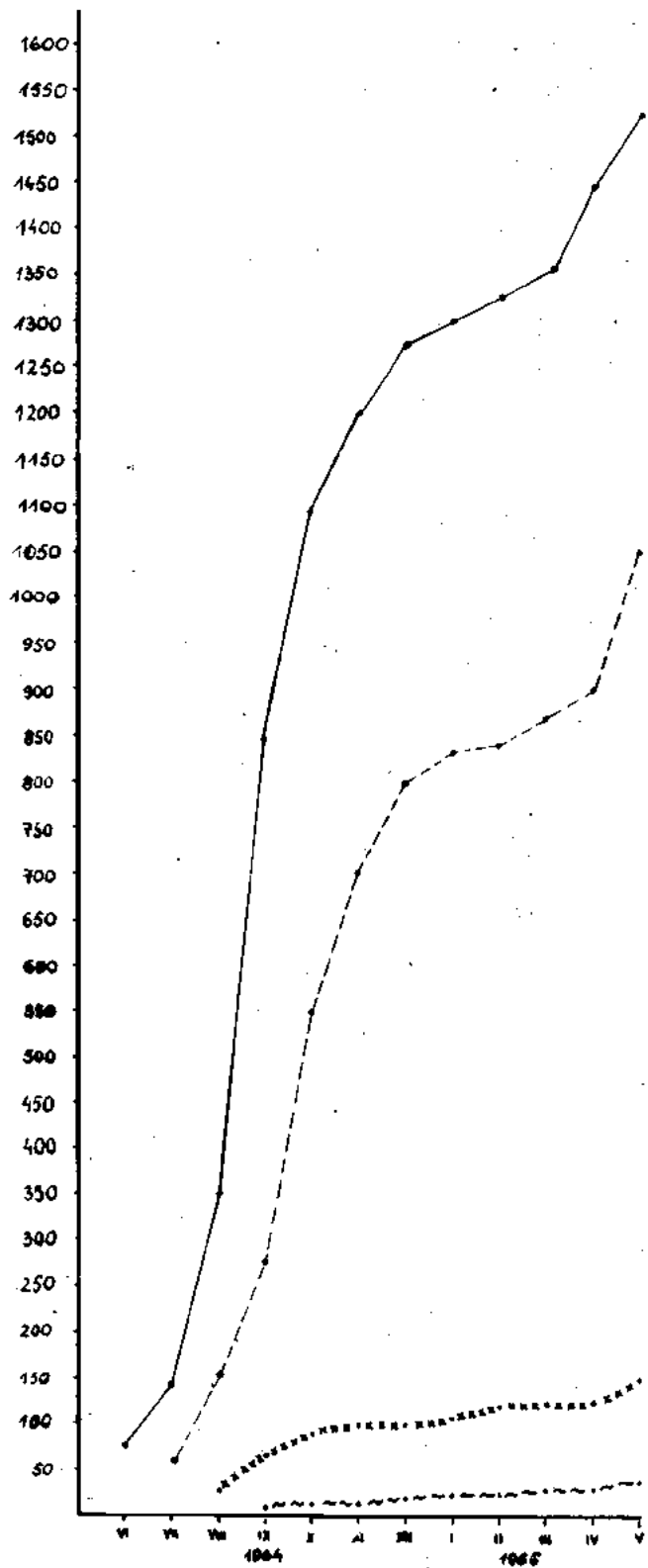


Fig. 10. — The relation between the period of growth and the biomass (wet) on the area of 875 cm<sup>2</sup>.

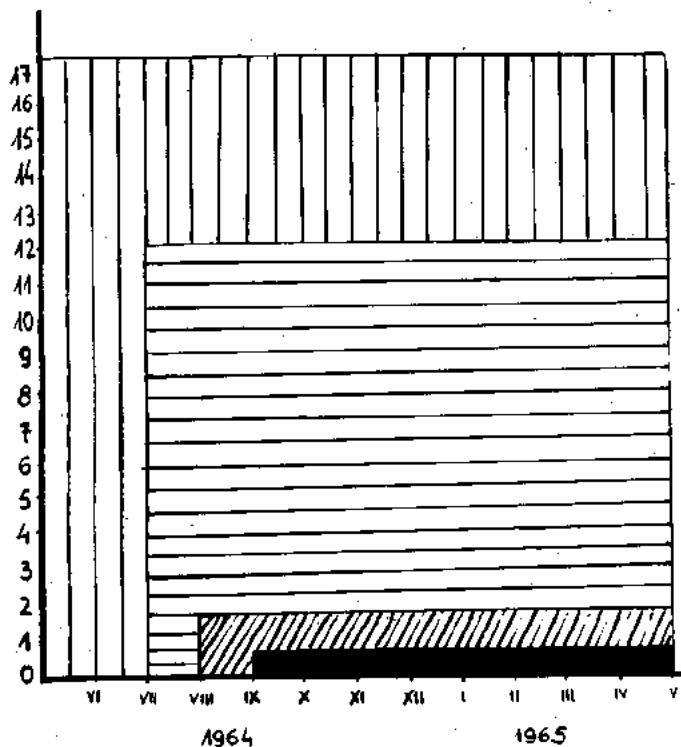


Fig. 11. — The biomass in Kg per 1 cm<sup>2</sup> in relation to the months of growth.

with hydrorhiza and thus capturing larvae of edible mussel or barnacles. Some confirmation of this fact was found on those plates which were covered with *Laomedea flexuosa* and upon which much richer life was noted. The first occurrence of *Laomedea flexuosa* takes place in August (1964) and September (1965). In the period of one month the colony increases and covers nearly 10 cm<sup>2</sup>. As appears from the analysis of particular plates the rate of growth of the colonies does not cease in wintertime.

#### ECONOMIC IMPORTANCE

It is an interesting problem to determine the total biomass of fouling animals. It is evident that in the Baltic Sea the

amount of biomass will change and will depend upon the year's season in which the settlement of larvae of particular group of animals takes place. Of course, the biomass will differ from year to year, which does not mean, however, that the results of fouling will be different.

The changes are depicted in the Fig. 10. As it appears from this Figure the largest biomass is noted in the months of June and July, while the growth increase is noted between June and September and in the period from July till August the weight of biomass is doubled. A considerable decrease of the biomass in wintertime (November-March) is caused both by too low temperature of water and the limited amount of available food. The least amount of biomass is noted in the month of autumn and winter, which is quite obvious — the absence of larval forms of fouling animals. Fig. 11.

The weight of the biomass, tabulated and calculated per 1 m<sup>2</sup> is as follows:

VI	— 17.0 kg.	— the period of 12 months (VI-V)
VII	— 12.0 kg.	— " " " 11 " (VII-V)
VIII	— 1.6 kg.	— " " " 10 " (VIII-V)
IX	— 0.5 kg.	— " " " 9 " (IX-V)

It is obvious that the number of months does not matter in the case, whereas only the period of mass spawning and development of all fouling organisms is decisive.

The total biomass, given as weight percent for particular species, was as follows:

for June 1964

barnacles	— 86%	— 14.62 kg.
edible mussels	— 12%	— 2.04 kg.
other species	— 2%	— 0.34 kg.

for July 1964

barnacles	— 77%	— 9.24 kg.
edible mussels	— 14%	— 1.68 kg.
other species	— 9%	— 1.08 kg.

for August 1964

barnacles	— 74%	— 1.18 kg.
edible mussels	— 17%	— 0.27 kg.
other species	— 9%	— 0.15 kg.

for September 1964

barnacles	— 33%	— 0.26 kg.
edible mussels	— 53%	— 0.17 kg.
other species	— 14%	— 0.07 kg.

As it appears from above data along with passing towards winter months the biomass of barnacles decreases and the proportion becomes more favourable for edible mussels. For this reason it is to be assumed that the most favourable period for development of fouling animals in the Baltic Sea extends from May till August. This period therefore is of practical consequences for launching new ships.

# A THEORETICAL CONSIDERATION OF CROWDING AND ITS EFFECTS ON THE BIOLOGY OF THE ROCK-BORING CLAM, *PENITELLA PENITA*

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## SUMMARY

*Penitella penita*, in common with most other mechanically boring bivalves, avoids burrowing into neighboring burrows. Upon approaching another burrow, the clam can sense its presence and turns to avoid it. If conditions are crowded so that there is no free rock to bore, the animal will cease to bore altogether and metamorphose to a stunted adult or «stenomorph».

The sensory mechanism is not known but it is hypothesized to be of a vibratory nature. The vibrations set up by the rasping movements of the valves on the rock are monitored by the pholad. The vibrations would be louder as another burrow is approached. Vibrations are probably only received from the anterior ventral aspect through the pedal gape.

The theoretical maximum number of animals/m<sup>2</sup> at any given depth in the rock is the «carrying capacity». It can be calculated if the average shape of conical burrow is known. Data is presented for three different rock types, giving relative rock hardness, burrow shape (ratio: burrow length to valve depth) and carrying capacity at selected depths. The results show that carrying capacity is reduced with increased depth and at any given depth reduced with increased rock hardness.

An area of an intertidal platform was cleared of all animals in August, 1963; and after 12, 16, 21, and 34 months

exposure, samples of rock were collected. The utilization efficiency was calculated by comparing the actual number of animals living at or deeper than a given depth with the carrying capacity at this depth. The results show that: a) at any given depth utilization efficiency increases with time; b) the depth of greatest utilization increases with time; c) near the surface, the increases in utilization are relatively slight and are due to settlement of additional animals. The more dramatic increases deeper in the rock are due to larger, older animals growing into these areas.

With knowledge of the growth rate of active animals, the future utilization efficiency can be extrapolated from the available data. Two 13 month extrapolations were performed (21 to 34 months, and 34 to 47 months); the first was merely to check the accuracy of the method. The results of the latter extrapolation indicate that these rock surfaces would be nearly saturated after 4 years exposure at a depth of 8.5 cm.

It was concluded that soon after four years the rock would not be able to hold any more adult animals and that complete saturation would occur at progressively lesser depths. This would lead to eventual extinction of the population were it not for erosion which removes surface rock and constantly exposes fresh rock for further settlement.

## INTRODUCTION

In previous studies the morphology of the valves (Evans 1968a) and the form of the burrows (Evans 1968b) of the rock boring clam *Penitella penita* were described.

The burrows are conical in shape with a narrow entrance and large rounded bottom, in cross section they are round. Crowding is very commonly encountered in pholad infested rock because more animals can settle at the surface than can live at depth (Fig. 1).

*Penitella penita* and other members of the Martesiinae pass through two clearly defined stages while in the rock. First an actively boring stage and then a non-boring, non-growing adult stage. In uncrowded conditions this metamorphosis takes place at a specified size which depends on rock hardness (Evans 1968a).

Actively boring *Penitella penita* very rarely break into neighboring burrows regardless of whether the latter are occupied, empty, or mud-filled. On approaching to within 1 mm of another burrow, the pholad will either turn to avoid it, or if it is surrounded on all sides will stop burrowing and metamorphose to a non-boring adult of substandard size. This form is called a «stenomorph» (Bartsch 1923).

The ability to avoid neighboring burrows is a behavioural characteristic shared by many of the mechanically boring bivalves, including the Teredinidae, Pholadidae, and *Hiatella*.

## THEORETICAL CONSIDERATION OF THE CROWDING EFFECT

While crowding in pholads has been observed many times, no attempt has ever been made to quantify the observations. In order to do this, it is necessary to know, A) the «carrying capacity» which is a measure of the maximum possible number of pholads that can be accommodated in a square meter of a specified type of rock at a given depth in the rock, and B) the utilization efficiency which is determined by comparing the carrying capacity at a given depth with the actual number of animals that have reached or passed that depth.

## CARRYING CAPACITY

Carrying capacity is a theoretical figure, the calculation of which is dependant on a knowledge of the shape of the burrow, this can be described by a ratio: burrow length (measured from entrance to point of maximum diameter)/valve depth of active animals (measured from dorsal to ventral extremity of the umbral sulcus). Valve depth is equivalent (with a small correction factor) to maximum burrow diameter, it is used because this information is considerably easier to gather. This ratio varies in rock of different hardness (Evans 1968b), therefore it is necessary to calculate it for each substrate.

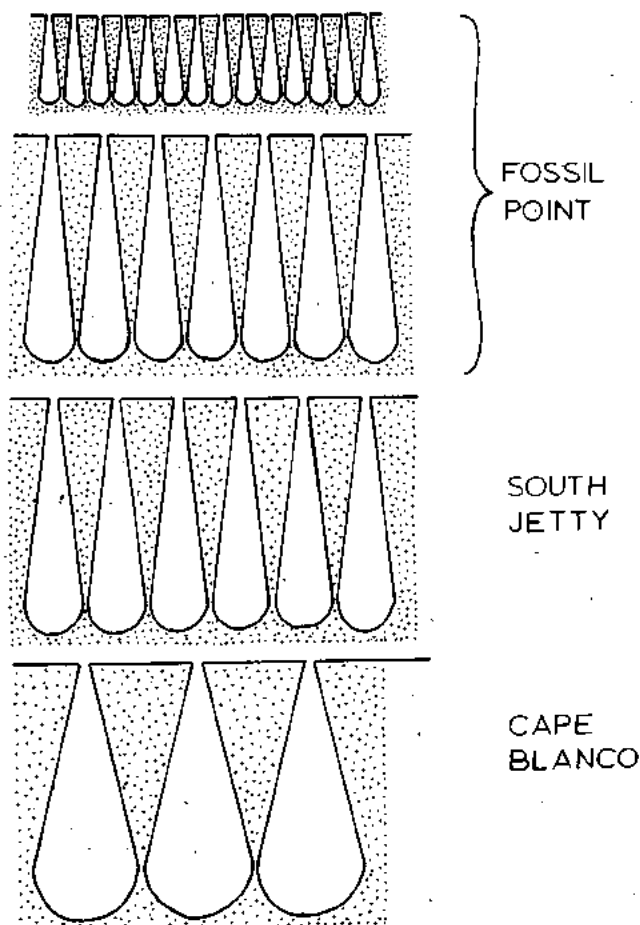


Fig. 1. Average burrow shapes in uncrowded conditions. Relative rock hardness:

Fossil Point = 1  
 South Jetty = 2  
 Cape Blanco = 4

The ratios for three different rock types from the Oregon Coast were measured (Table 1); it can be seen that the ratio decreases as the rock hardness increases. As a result, the carrying capacity at any given depth decreases as rock hardness increases because of the squatter shape of the burrow. The ratio for the softest (Fossil Point) rock was calculated from animals approximately 19 months old taken from uncrowded

conditions. Under crowded conditions, the burrows tend to be longer for any given size of animal ( $\bar{X}$  ratio = 5.3; SE = 0.15; N = 74). Because of the low density at South Jetty and Cape Blanco, animals from these areas were usually growing under uncrowded conditions.

#### CALCULATION OF CARRYING CAPACITY

Under conditions of maximum utilization, the burrows (all of one size) would have to be arranged in a honeycomb pattern. Each animal occupies a hexagonal area.

The hexagonal area occupied by an animal at a given depth in the rock is measured as follows: a) Valve depth is calculated by dividing the burrow length (= depth in rock) by the appropriate burrow length/valve depth ratio, b) Since the animal is somewhat loose in its burrow, valve depth is not a true measure of the diameter of the burrow. The valve depths of 17 active Fossil Point animals were compared with the maximum diameters of their burrows. The burrows averaged 0.9 mm larger than the depth of the valves (maximum 1.4 mm, minimum 0.4 mm). Also when calculating the area occupied by the animal, one must take into account the fact that *P. penita* usually does not approach closer than 1 mm to a neighboring burrow. The area required by an animal at any particular depth in the rock is, therefore, equal to a hexagon with an inscribed circle, the diameter of which equals the valve depth plus 1.9 mm to correct for space in the burrow and wall thickness.

The carrying capacity is obtained by dividing the area of the hexagon into one sq. meter. The theoretical carrying capacity of different areas and depths is shown in Table 2.

The results show that carrying capacity decreases as rock hardness increases and as depth in the rock increases.

TABLE 2

#### THEORETICAL CARRYING CAPACITY IN 1 SQ. METER

Rock Depth cm.	Fossil Point	ROCK TYPE South Jetty	Cape Blanco
X	19,400,857 $(\bar{X} + 7.79)^2$	14,949,974 $(\bar{X} + 6.84)^2$	4,171,260 $(\bar{X} + 3.61)^2$
1.0	61,302	52,715	22,523
2.0	25,121	20,753	7,483
4.0	8,495	6,814	2,193
6.0	4,222	3,346	1,031
8.0	2,517	1,982	597
10.0	1,670	1,310	389
12.0	1,186	929	273*
14.0	888	693*	202
16.0	689*	537	156

\* Maximum observed burrow length.

TABLE 1  
 BURROW SHAPE OF ACTIVE ANIMALS IN ROCKS OF DIFFERENT HARDNESS

	Fossil Point	South Jetty	Cape Blanco
Relative rock hardness	1	2	4
Mean ratio: Burrow length/valve depth	4.1	3.6	1.9
Standard Error	0.15	0.21	0.09
Number	17	7	6

#### UTILIZATION EFFICIENCY

The efficiency with which the rock space is being utilized is determined by comparing the carrying capacity at a given depth with the actual number of animals that have reached or passed that depth. This is theoretically quite straight forward but somewhat more complicated to calculate in practice. Samples of rock, exposed for known lengths of time are collected; the surface area is measured, then all the animals are dissected out, measured, counted, and arranged in size classes. The length of the burrow of each size class can then be calculated by multiplying the valve depth by the burrow length/valve depth ratio (4.1 for uncrowded Fossil Point rock). From the burrow length, the carrying capacity can be calculated. This can then be compared with the actual number of animals that have reached or exceeded that depth, and from this the percent utilization is directly obtainable.

TABLE 3

UTILIZATION EFFICIENCY USING BURROW SHAPE OF 19-MONTH-OLD FOSSIL POINT ANIMALS AS STANDARD (Ratio: burrow length to valve depth = 4.1).

A = Calculated burrow length cm = (Valve depth x 4.1).

B = Carrying capacity at this depth in Fossil Point rock exposed 19 months.

C = Number animals/m<sup>2</sup> at or larger than given valve depth 12 month exposure (Area collected = 1350 cm<sup>2</sup>)

D = " " " " " " " " " " " " " " ( " " " = 1670 cm<sup>2</sup>)

E = " " " " " " " " " " " " " " ( " " " = 1460 cm<sup>2</sup>)

F = " " " " " " " " " " " " " " ( " " " = 620 cm<sup>2</sup>)

% = Utilization efficiency

Valve depth cm	A	B	C	%	D	%	E	%	F	%
.4	1.64	33,155	2,244	6.8			3,603	10.9	3,823	11.5
.6	2.46	18,493	1,333	7.2	2,719	14.7	2,897	15.7	3,677	19.9
.8	3.28	11,776	815	6.9	1,820	15.5	2,164	18.4	3,419	29.0
1.0	4.10	8,150	370	4.5	1,180	14.5	1,438	17.6	3,065	37.6
1.2	4.92	5,973	133	2.2	683	11.4	890	14.9	2,783	46.6
1.4	5.74	4,565	22	0.5	401	8.9	432	9.5	2,306	50.5
1.6	6.56	3,602			168	4.7	178	4.9	1,935	53.7
1.8	7.38	2,914			53	1.8	41	1.4	1,419	48.7
2.0	8.20	2,406			18	0.7			1,032	42.9
2.2	9.02	2,020							710	35.1
2.4	9.84	1,720							565	32.8
2.6	10.66	1,483							290	19.6
2.8	11.48	1,291							81	6.3
3.0	12.30	1,134							65	5.7

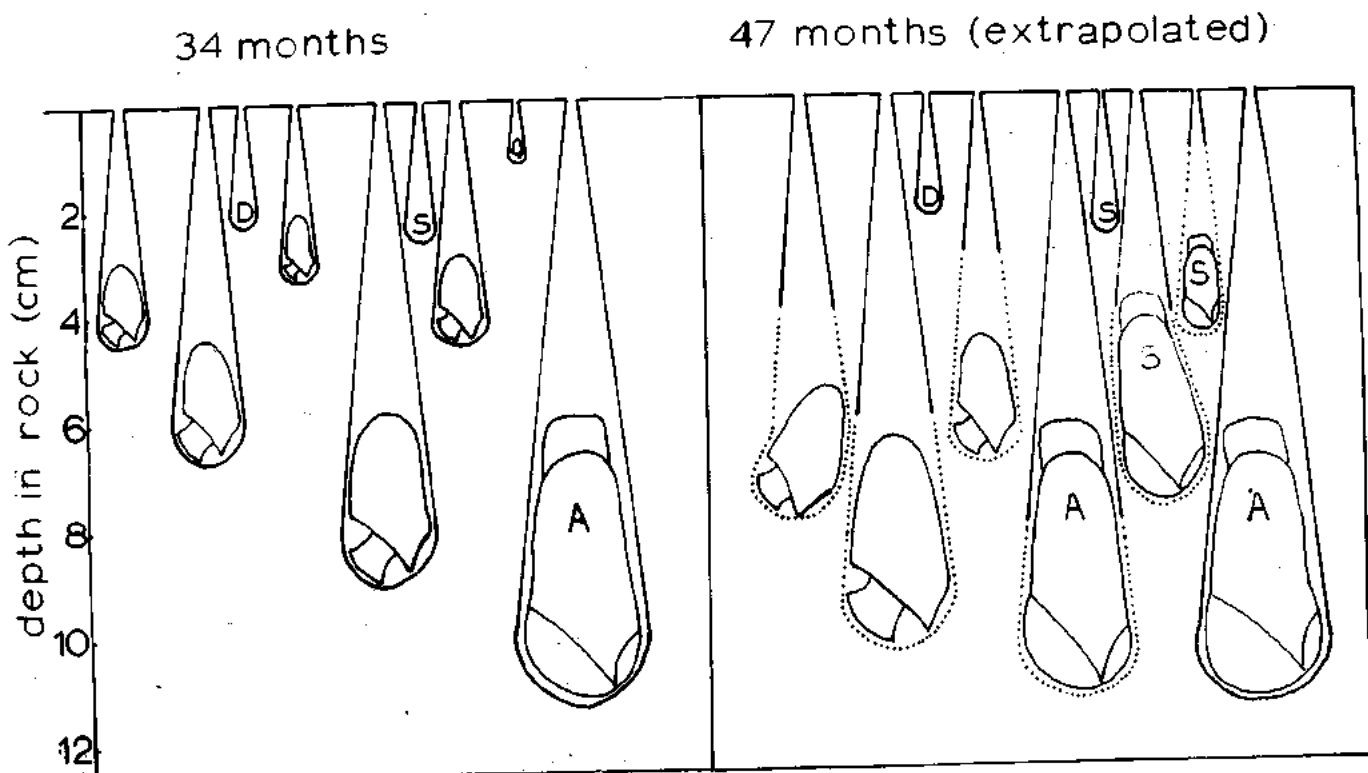


Fig. 2. Diagram to show possible changes that will take place in a rock between the 34th month and the 47th month of exposure following clearing.

D = dead  
S = Stenomorph  
A = Adult  
Unmarked = Actively boring



This can only be done with young animals boring into freshly exposed rock because only under such conditions can the length and shape of the burrow be estimated with confidence.

The utilization efficiency of rock exposed for 12, 16, 21, and 34 months at Fossil Point was calculated (Table 3, Fig. 2, 3). A number of observations on this data can be made. 1) At most depths the utilization efficiency increased with increased duration of rock exposure. 2) The depth of greatest utilization increased with time. 3) The increases in utilization near the surface are relatively slight and are due to settlement of additional animals. The more dramatic increases deeper in the rock are due to larger, older animals growing into these areas.

#### EXTRAPOLATION OF UTILIZATION EFFICIENCY

Knowledge of the average growth rate of young active *P. penita* at Fossil Point makes it possible to predict utilization efficiency in older rock. It is assumed: a) that rock exposed for 21 or 34 months was left in the sea for an additional 13 months; b) that no new settlement took place during this period (this would underestimate the utilization efficiency as deep as the first 5 cm but would not effect the extrapolation below that level); c) that all animals alive and active at 21 or 34 months will continue to live and that valves will increase in depth 8 mm during the 13 month period, or until they reach 26 mm in depth at which time they would metamorphose to adults. The average growth rate of *P. penita* at Fossil Point over a period of 13 months is actually closer to 10 mm than to 8 mm (Evans 1968c); however, the latter rate was chosen because, using this rate, a closer correspondence was obtained between the predicted utilization at 34 months (extrapolated from 21 month data) and the actual utilization

at 34 months (Table 4, row F, G, Fig. 4). By using a somewhat low rate of growth for extrapolations, more realistic estimates can be expected because arrest of growth, due to crowding or death of a few of the alive active animals, would be compensated for.

The results of extrapolation to 47 months are probably somewhat high, (Table 4, row K, Fig. 4) since the animals are not arranged in a neat geometric pattern throughout the rock. Stenomorph formation will become progressively more prevalent as the saturation level is approached.

The extrapolation does serve to demonstrate that after four years exposure, this rock will be almost completely saturated at a depth of about 8.5 cm in the rock. Further growth of the remaining alive active animals will result in saturation of the rock below this level, down to about 12 to 13 cm, and above it to about 6 cm level. Subsequent settlement will continue to saturate the rock at progressively lesser depths.

This reduction of settling and growing space would eventually cause extinction of the population were it not for erosion which removes the heavily bored surface rock, thus exposing new rock for colonization (Hunter, 1949; Evans, 1968d). Since saturation first occurs deep in the rock and because the percent of rock removed is larger at greater depth (Table 5), it is unlikely that erosion will take place by even surface wear. It is more likely to proceed in a piecemeal fashion with large chunks of surface rocks breaking away.

#### PRACTICAL CONSIDERATIONS

This study is not directly applicable to practical problems as are most of the papers in this collection. However, it has often been demonstrated that basic research can, in unexpected ways, aid the practically oriented investigator.

TABLE 4  
EXTRAPOLATION OF UTILIZATION EFFICIENCY (21 - 34 MONTHS) (34 - 47 MONTHS)

- Assumptions. 1) Rock exposed for 21 or 34 months was left in place for an additional 13 months.  
2) No additional settlement takes place.  
3) Animals alive and active at the 21 or 34 month stage increase in depth 0.8 cm or until they reach 2.6 cm in depth.

- Note: rows C - F = 21 - 34 month extrapolation; rows H - K = 34 - 47 month extrapolation.  
A) Calculated burrow length cm = (Valve depth x 4.1).  
B) Carrying capacity at this depth in Fossil Point rock.  
C & H) Number non-boring animals/m<sup>2</sup> at or larger than given depth.  
D & I) Number alive, active animals/m<sup>2</sup> at or larger than given depth (assuming that those animals have grown 0.8cm during 13 months additional exposure).  
E) D + C  
F) Extrapolated utilization efficiency 34 months (%).  
G) Actual utilization efficiency 34 months (%).  
J) H + I  
K) Extrapolated utilization efficiency 47 months (%).

Valve depth cm	A	B	C	D	E	F	G	H	I	J	K
.4	1.64	33,155	432	3171	3603	10.9	11.5	1210	2613	3823	11.5
.6	2.46	18,493	370	3171	3541	19.1	19.9	1210	2613	3823	20.7
.8	3.28	11,776	267	3171	3438	29.2	29.0	1129	2613	3742	31.8
1.0	4.10	8,150	151	3171	3322	40.8	37.6	1032	2613	3645	44.7
1.2	4.92	5,973	75	3171	3246	54.3	46.6	903	2613	3516	58.9
1.4	5.74	4,565	21	2527	2548	55.8	50.5	790	2467	3257	71.3
1.6	6.56	3,602	7	1897	1904	52.9	53.7	710	2290	3000	83.3
1.8	7.38	2,914	0	1287	1287	44.2	48.7	532	2033	2565	88.0
2.0	8.20	2,406	0	815	815	33.9	42.9	435	1880	2315	96.2
2.2	9.02	2,020	0	411	411	20.3	35.1	339	1516	1855	91.8
2.4	9.84	1,720	0	171	171	9.9	32.8	274	1225	1499	87.2
2.6	10.66	1,483	0	41	41	2.8	19.6	145	887	1032	69.6
2.8	11.48	1,291	0	0	0	0	6.3	32	49	81	6.3
3.0	12.30	1,134	0	0	0	0	5.7	32	33	65	5.7

# UTILIZATION EFFICIENCY

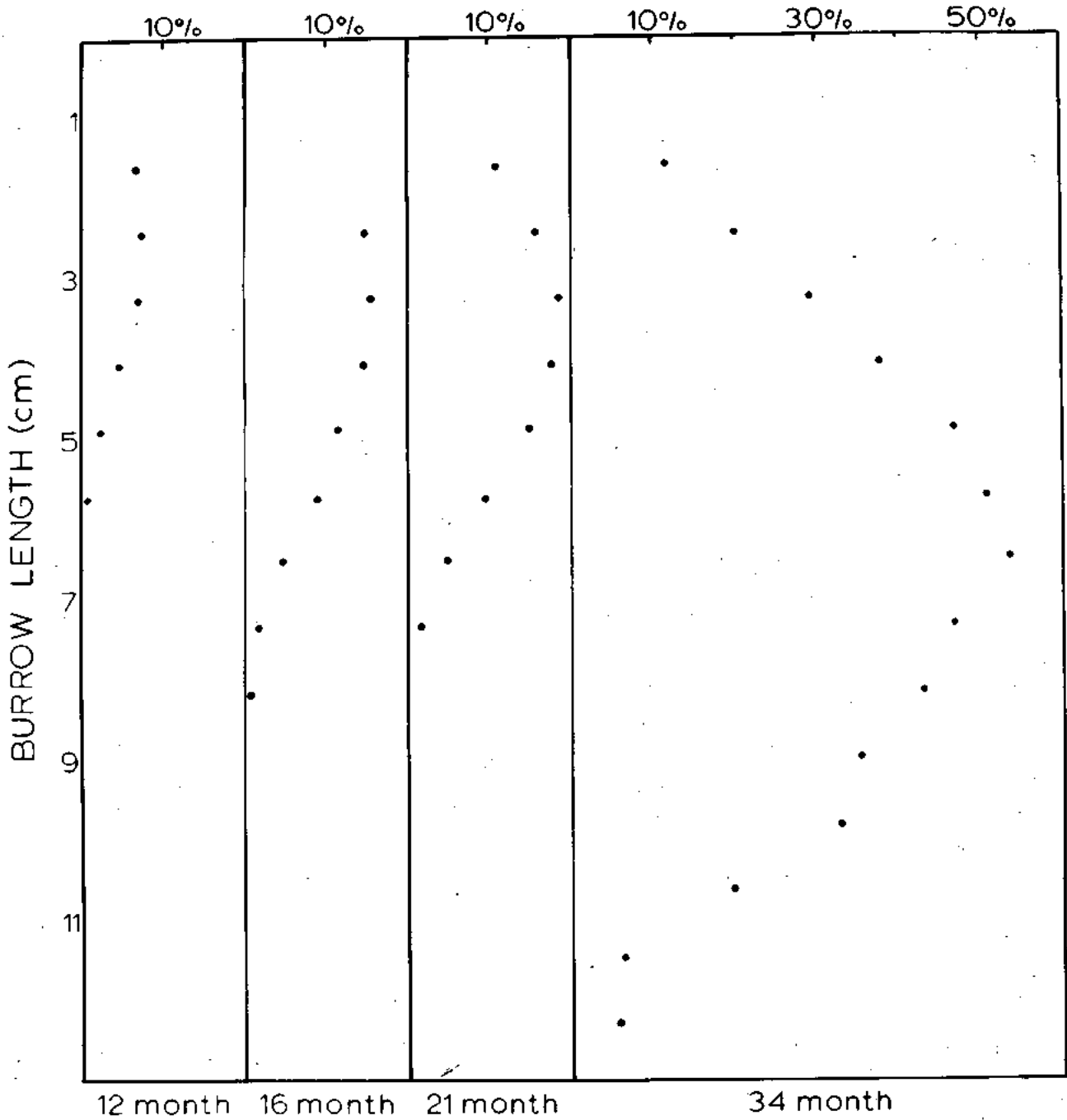


Fig. 3. Shows actual utilization efficiency.

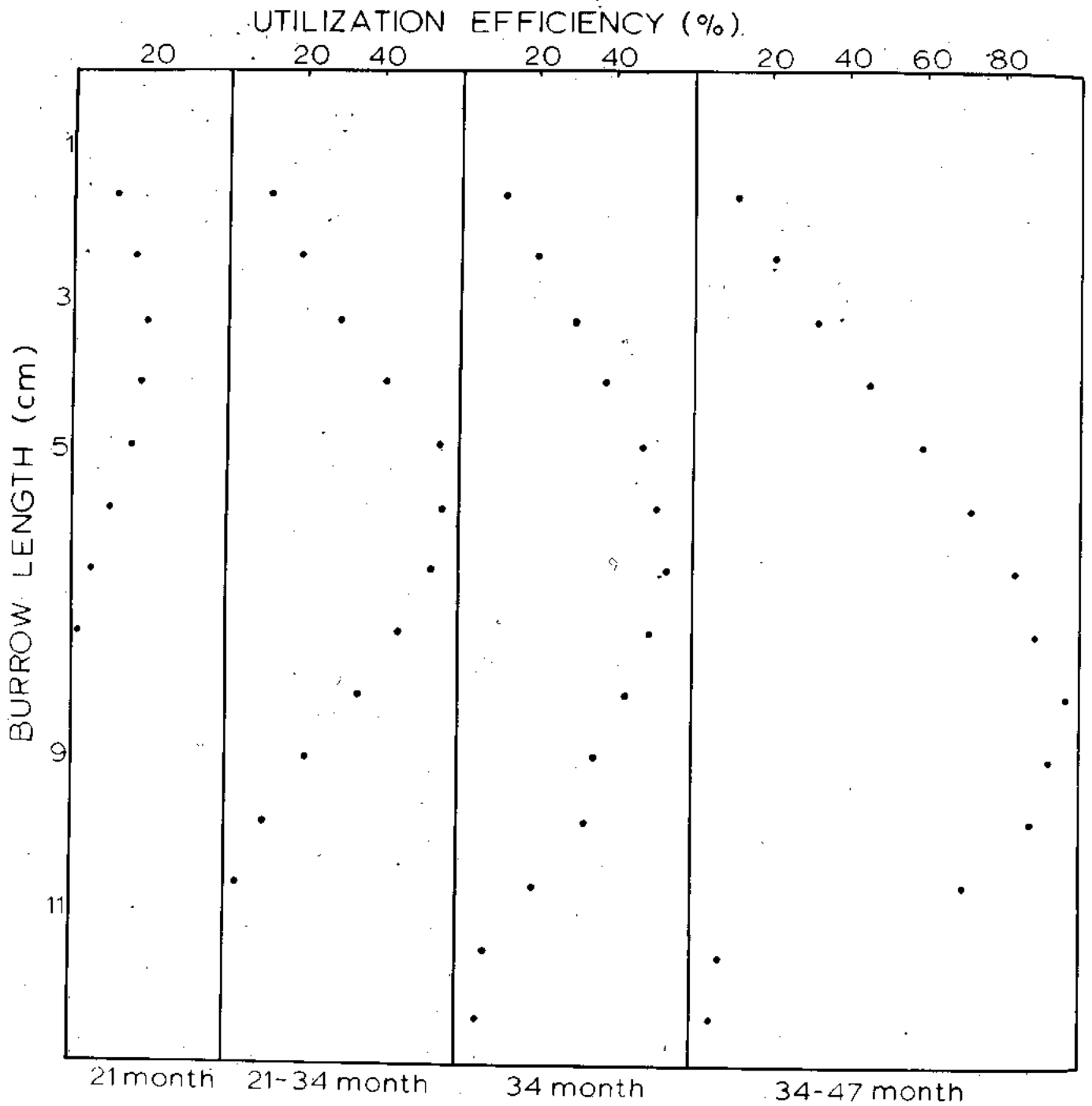


Fig. 4. Shows extrapolated utilization efficiencies. The 21-34 month extrapolation shows the accuracy of the method when it is compared with the actual 34 month utilization efficiency. The 34 - 47 month extrapolation indicates the predicted condition of the rock after 47 months exposure.

TABLE 5

## AMOUNT OF ROCK REMOVED UNDER CONDITIONS OF 100% UTILIZATION

Assumptions: (A) Carrying capacity values of Fossil Point uncrowded rock are used. (B) Wall thickness between neighboring burrows is 1 mm.

Rock Depth cm	% of Rock Removed
1.0	53.7
2.0	65.9
4.0	75.8
6.0	80.0
8.0	82.4
10.0	84.0
12.0	84.8
14.0	85.7
16.0	86.3

*Penitella penita* is closely related to the tropical wood borer *Martesia striata*. The morphology and biology of these two forms are very similar. The information presented in this paper will probably be most useful to workers in tropical regions who are concerned with the control of this important timber borer.

B. CALLAME (France): What is the geographical distribution of the studied species?  
 Prof. J. EVANS: They extend from Alaska down to Southern

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## DISCUSSION

California, the west coast of North America in other words. Similar related species are found in many other areas. There is an economically important timber borer of tropical waters, *Martesia striata*.

# QUELQUES CAS DE MACROBIODETERIORATION PAR LES MOLLUSQUES EN MILIEU MARIN

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## RÉSUMÉ

Nous avons cherché à préciser dans quelques cas les limites du rôle de certains facteurs écologiques pour certains agents biodestructeurs des structures immergées, en particu-

lier des mollusques perforants, par des observations ou des méthodes expérimentales.

Parmi ces facteurs citons la profondeur et le courant.

## INTRODUCTION

Une connaissance précise des conditions géographiques, physicochimiques entre lesquelles peut s'effectuer la reproduction, l'installation et le développement des organismes marins biodestructeurs est nécessaire pour localiser les zones les plus dangereuses et les périodes dangereuses d'infestation.

On pourra alors déterminer, en connaissance de cause le rythme et la nature de l'application des méthodes de protection. Cela permet aussi d'expliquer certaines «épidémies», certains cycles. La Hollande aurait subi un cycle de trente ans qui s'expliquerait par le retour d'années chaudes qui augmentent la salinité.

Les caractéristiques du milieu (température, salinité, taux d'oxygène, pH, vitesse du courant, etc., également encombrement des surfaces par les salissures sont des facteurs qui régissent la dispersion et la répartition des espèces, en permettant, restreignant ou interdisant leur développement; mais il en est d'autres qui tiennent aux conditions géographiques (éloignement des côtes, profondeur d'immersion) et enfin d'autres à la nature du substrat qui sert d'habitat. Notamment il serait nécessaire de connaître quand et pourquoi les organismes pourraient pénétrer dans les matériaux autres que le bois, d'une manière plus complète.

## SALINITÉ

Roch signale que les possibilités d'adaptation à la salinité varient entre *Teredo Norvegica*, *Teredo pedicellata* et *Teredo navalis* qui sont les espèces que l'on trouve sur la Côte atlantique. Mais, certaines espèces australiennes ou de la Guyanne (*Teredo miraflores*, *Nausitora messelli*), d'autres espèces de la Côte d'Ivoire survivent ou vivent dans des eaux presque douces. Il y a là, on le voit, une possibilité de sélection entre les espèces.

Il faut évenement distinguer entre la salinité létale et celle qui autorise le développement complet (reproduction et ponte).

## TEMPÉRATURE

Sur la côte atlantique, *Teredo pedicellata* Quatrefages est plus méridional. Cependant, cette espèce est apparue en 1957 notamment à notre radeau d'essai de La Pallice et aussi certaines années des exemplaires de *Teredo Norvegica*. On

peut penser qu'il n'y a pas eu d'infestation fortuite par les bateaux de pêche qui fréquentent chaque année les mêmes zones.

Les espèces de *Limnoria* peuvent être également plus ou moins méridionales.

## PROFONDEUR

Grâce à la collaboration du CREO, de quelques chalutiers et navires de recherches océanographiques, nous avons pu recueillir des échantillons de bois flotté (par draguage) ou fixés à des cables. Certains perforants de ces bois ont le plus grand diamètre connu pour leurs espèces. Ces observations présentent un grand intérêt pour déterminer éventuellement les conditions d'attaque des cables sous marins et tout matériel. Il s'agit de *Xylophagas*, mollusques toujours pélagiques. Il peut d'ailleurs exister dans ces bois plusieurs espèces de perforants.

Grâce à la bonne volonté des marins du Pelago, nous avons également pu recueillir des roches perforées, en profondeur.

On peut se demander comment une infestation est possible, si loin des côtes. La durée de vie nageuse des larves est un facteur déterminant, mais il ne nous semble guère que le phénomène soit éclairci.

On a même parlé pour les *Xylophagas* de la possibilité d'une autofécondation (ce qui demeure un phénomène biologiquement exceptionnel) et qui expliquerait une possibilité d'infestation à partir d'un seul individu.

Nous ne pouvons pas toujours nous prononcer pour les tarets au grand large: l'installation de quelques individus étant possible dans le bois flotté, avant qu'il ne sombre. (Un badigeon au coaltar qui assure une protection temporaire pourrait s'utiliser avant l'immersion des éprouvettes pour empêcher l'infestation durant l'immersion des éprouvettes).

Pour les petits crustacés (*limnoria*) il semble que nous avons une limite au large d'Antibes (profondeur 100 m.). Il n'y en a pas dans les autres échantillons que nous avons pu obtenir. Egalement, il y a bien des *Bankias* dans les éprouvettes immergées au large d'Antibes. La limite semble s'établir vers 130 mètres.

Les débris de coquilles sont difficiles à analyser: nous avons cherché à prendre des photographies au moyen des méthodes de moulages décrite.

Ces photographies permettent d'identifier l'agent destructeur.

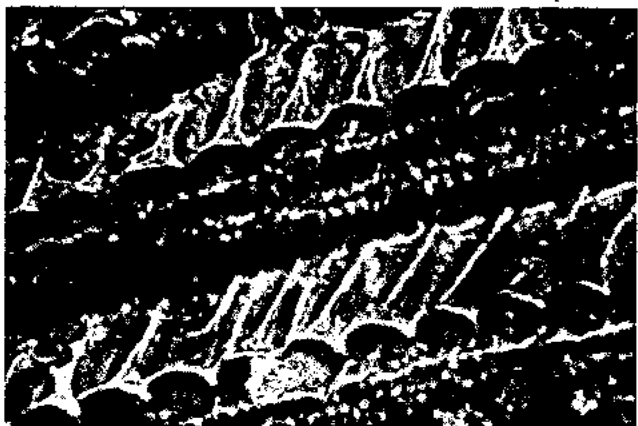


Fig. 1. Réplique : Dents des xylophagas sur les stries d'accroissement

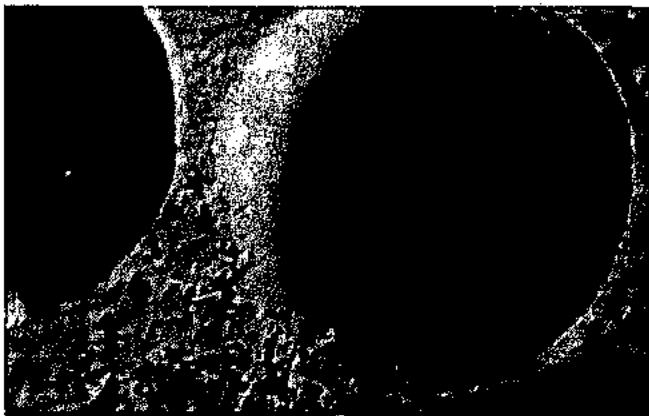


Fig. 2. Biocénose de tarets et de xylophagas. Les galeries de tarets sont tapinés de manchon calcaire.

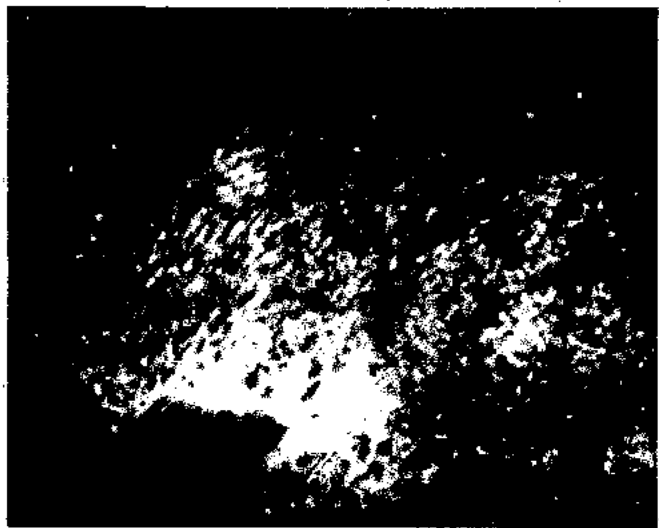


Fig. 3. Stries de peyoración de taret dans le chloroformyl



Fig. 4. Lithodoma dans le béton.

teur pour les attaques de câbles sous-marins, mais nous ne pouvons pas séparer une attaque de tarets d'une attaque de Xylophagas.

Cette méthode, des répliques de surface est également applicable pour déceler une attaque de mollusques lithophiles.

En conclusion, des profondeurs même assez considérables et l'éloignement des côtes ne paraissent pas mettre à l'abri les structures des dégradations par les Xylophagas. L'attaque par les tarets peut être au contraire réduite ou nulle.

Voici à cet égard un tableau qui résume les observations que nous avons pu faire :

Organismes	Substrat	Epreuves et câbles	Observations
Teredo (Norvegica) Xylophaga prestans	Bois flotté		
Xylophaga (?)	Câble-jute	câble 1 100 m	la gutta et le jute sont attaqués
Bankia Limnoria Xylophaga	pin	épreuves (100 m Antibes)	peu de Bankias et de crustacés

Deux faits nous paraissent intéressants à noter: c'est la présence constante des Xylophagas en profondeur et la tendance à attaquer d'autres substrats, par exemple enveloppe de jute recouverte d'un coumpound, des câbles sous-marins. Nous en avons obtenu grâce à M. Chabot, Ingénieur au C.R.E.O., un échantillon très remarquable, situé à une profondeur d'environ 1.100 mètres au large des Açores.

La méthode de superposition que nous avons utilisée depuis 1965, permet de tester non seulement la résistance aux attaques, des couches de colle intercalaires, mais aussi la résistance naturelle de l'essence dont le déroulé (de 6/10<sup>e</sup> de mm d'épaisseur) par exemple, constitue la couche extérieure. Il apparaît que dans le cas des contreplaqués marins, il est très important de choisir judicieusement la première couche, celle-ci pourrait aussi bien que la couche de colle servir de barrière aux organismes.

Rappelons que certaines essences se montrent apparemment répulsives, vis-à-vis des petits crustacés, alors qu'elles sont attaquées par les tarets. Nous avons également fait des agglomérés qui peuvent donner de grandes possibilités d'études.

D'après Tamblin N. and Gordon A. il est possible d'incorporer des éléments toxiques dans la colle qui sert d'adhésif au feuillet. Il faut pour des essais valables que la colle ne s'oppose pas par sa dureté à l'installation des tarets. Il y a donc nécessité de choisir les adhésifs qui doivent être employés; ils doivent être non toxiques et avoir certaines caractéristiques mécaniques de dureté pour ne pas intervenir dans les essais de toxicité.

Des essais ont d'ailleurs été pratiqués sur des morceaux de contreplaqués marins dans les conditions normales d'utilisation et de fabrication de ces produits. Les «déroulés» peuvent également être utilisés sans colle intermédiaire, d'après les essais que nous avons pu faire au laboratoire à condition d'avoir une possibilité de serrage des feuillets, au moyen de vis de laiton ou de nylon. Nous avons fait à cet égard des essais concluants avec des feuillets de hêtre et des feuillets de papier provenant d'un livre, avec une plaquette de bois plus épaisse comme «piège» qui est également utilisée pour placer les vis de serrages qui maintiennent les feuillets de bois déroulés entre eux.

Ces essais montrent d'une part que les organismes peuvent se contenter de matériaux ligneux, très dégradés et permettent d'obtenir d'une manière très aisée des spécimens complets hors du bois. Ces essais paraissent également valables pour les crustacés.

Nous avions conseillé à cet égard l'emploi du bois de balsa, et montré que les tarets peuvent s'installer dans des branches de sureau, et vivent très bien dans la cellulose régénérée. Ils peuvent également creuser des sillons dans certaines matières plastiques. Si un jour nous voulions expérimenter les anciennes habitudes des Vénitiens et des indigènes de quelques îles qui estimaient leur chair on aurait là des méthodes pour se procurer plus facilement des spé-

cimens entiers sans avoir à découper le bois. Ces spécimens sont indispensables pour des études systématiques.

#### ACTION DU COURANT

Les observations que nous avons pu faire en Bretagne ont une analogie avec celles de Greenfield pour les tarets des bords de rivière. Chaque espèce a des exigences très différentes sur la salinité, mais en Bretagne l'eau salée à cause de la profondeur et de la conformation des estuaires (comme dans des fjords de Norvège) remonte fort loin. D'autre part, il existe des courants de marée très violents, qui s'opposent à la fixation des organismes. Citons à cet égard, la Baie de la Fresnaye où existent pourtant des pieux pour la mytiliculture. Mais dans la «rivière de Tréguier» par exemple, sur les bords de la rivière et près du fond, nous avons constaté la présence de *Teredo pedicellata* (vraisemblablement) et des *Limnorias*. *Teredo* existe aussi dans l'estuaire de la Rance en face de Dinard, mais sans doute pas dans tout le golfe du Morbihan.

Des remarques analogues peuvent être faites pour la région de Cancale, ou de la Baie de la Fresnaye.

Les mytiliculteurs de la région paraissent moins soucieux des déprédations commises par les tarets que de celles des crabes. La base des pieux est entourée d'un manchon de toile de nylon: ce qui constitue d'ailleurs également une protection contre les tarets. Dans la Baie de l'Aiguillon autour de La Rochelle, les mytiliculteurs affirment que certaines zones à petits tourbillons sont plus infestées de tarets que les chenaux à courants de marée. Des observations analogues s'appliquent aux *Limnorias*.

Dans des régions où l'amplitude de la marée moyenne est très forte (six mètres pour la région de La Rochelle) l'infestation peut n'être possible qu'en morte eau c'est-à-dire au moment où les courants de marée sont moins forts.

Nous avons pu faire grâce à des échantillons amenés par les marins du Pelago, des observations analogues sur des mollusques perforants les roches. Nous avons pu observer, dans un morceau de roche qui serait un gneiss très dégradé et friable, ramené par dragage au chalut (du banc des Smalls) la présence de coquilles de *Pholadidea loscumbrina*.

Sur la plage du Lido, nous avons recueilli un échantillon de *Lithodome*, dans un mortier artificiel. Il y a une analogie avec les observations que nous avons pu faire dans des agglomérés, pour les tarets, mais dans le cas des organismes lithophiles nous n'avons fait jusqu'ici que des observations.

Signalons d'ailleurs que le substrat «bois» réagit sur la morphologie des coquilles et des galeries et peut dans certains cas s'opposer à l'installation: ces cas de sténomorphose sont connus chez les *Pholades* et les *Pénitella*.

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## DISCUSSION

D. KALLAS (USA): Votre proposition pour une expérimentation et des possibilités futures me rappelle une expérimentation que nous avons exécuté et dont je voudrais vous informer, bien que pour le moment mon information soit encore incomplète.

Nous avons exposé une grande variété de bois de différentes essences à une profondeur de 4200 pieds aux Bahamas; nous avons été étonné de constater que plusieurs organismes xylophages ont attaqué ces bois — je ne suis pas sûr — qu'il y ait parmi eux des Tereos. Comme je l'ai déjà dit mon information est incomplète: on est toujours en train de déterminer la nature des espèces qui ont attaqué ces bois et il doit y avoir d'autres informations statistiques.

Naturellement tout cela est en corrélation avec la note que vous avez fait en vous référant à l'attaque des cables sous marins et des revêtements analogues à des chlorures de polyvinyl.

Il est possible et l'on s'attend à des attaques aux grandes profondeurs. Il ne s'agit pas d'une question posée mais je pense, Monsieur le Président, que cette information est utile.

P. DESCHAMPS: Nous avons également en cours des essais en profondeur notamment sur le plateau de Rochebonne et nous allons tâcher de profiter de toutes les possibilités, il y a intérêt à pouvoir retirer les éprouvettes au bout d'un certain temps pour pouvoir déterminer le taux d'investigation.

Prof. BALAKRISHNAN NAIR (India): Pourriez vous, s'il vous plaît, m'informer de la nature du milieu où vous avez recueilli des espèces de Tereidines de l'eau douce?

P. DESCHAMPS: Je dirai au Docteur Balakrishnan Nair que je n'ai pas d'expérience personnelle sur ce sujet. Dans nos régions il n'existe pas d'espèces d'eau douce. Je vous ai simplement donné des renseignements bibliographiques.

Prof. BALAKRISHNAN NAIR: J'ai posé cette question parce que

vous savez aux Indes on a observé une espèce dans une rivière à peu près 150 miles loin des embouchures. On croit qu'il s'agit de l'eau douce mais je suis sûr qu'il y a une salinité quelconque, dû à l'influence de la marée. Je sais personnellement qu'il y a en Indes des espèces vivants dans de l'eau presque douce, sa salinité doit être à peu près 0,5‰ ou 0,8‰, c'est-à-dire pas justement de l'eau douce.

P. DESCHAMPS: Il faut dire que certaines espèces que nous avons sur les Côtes Françaises surtout *Teredo navalis* résistent plusieurs semaines à un séjour dans l'eau douce; s'il y a des courants de marée qui modifient périodiquement la salinité l'animal en rétractant ses siphons et en rapprochant ses pallettes peut s'isoler pendant la période douce. Ce ne sont pas là des espèces d'eau douce. Il faut faire une série de mesures de salinité.

Dr. KÜHL (Allemagne): Quant aux dernières questions on sait que les épidémies se rencontrent aux sites (pays) où il y a des variations de la salinité et de la température. Quand la salinité est assez haute et simultanément aussi la température on peut avoir une multiplication des organismes; aux embouchures de nos rivières ainsi qu'en Hollande où la salinité s'abaisse pendant toute l'année à cause des affluences d'eau douce quand la température est haute, nous observons une grande multiplication des organismes. Nous devons séparer la température végétative et la température propagative, c'est pareil pour la salinité. La *Teredo navalis* est pour trois ou quatre semaines compatible avec l'eau douce mais elle ne peut pas se reproduire. C'est pour cela qu'une salinité de 7 jusqu'à 10 pro mil est indispensable. Aux pays tropicaux où la température reste presque constante pendant toute l'année on observe une montée des organismes de mer le long de la rivière. Et dès que la température est, comme déjà mentionnée, constante pendant toute l'année les activités physiques de ces organismes ne varient pas



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**Prof. K. KRIMBAS (Grèce),**

**Dr. V. ROMANOVSKY, President**

**COIPM, Directeur C.R.E.O. (France).**

# CHLORINE TOLERANCE OF MYTILUS EDULIS L.

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## SUMMARY

In this paper, the nature of chlorine tolerance of a common sea-mussel, *Mytilus edulis* L. which brings most harmful fouling in cooling condenser systems were studied with experimental chlorination in laboratory.

Two kinds of responses to free available chlorine: the death and the shell-closing were observed throughout the development of the mussel using laboratory-reared larvae

of each stages. These responses are the straight lines of regression when free chlorine concentrations are plotted against contact times on logarithmic paper.

The modes of the responses shown as the regression lines were examined with the testings of «differences in slope» and «differences in position» by covariance analysis.

## INTRODUCTION

Chlorination is the most economical and widely used means of controlling fouling organisms in condenser cooling systems. Nowadays, huge volume of chlorine is being consumed in many littoral industrial plants such as thermal power station, iron and steel work, and petroleum chemical factory. A purpose of these sea-water chlorination is to prevent and control a common mussel, *Mytilus edulis* L. which is the most dominant and important fouler of cooling water conduit in Japan (NISHIMURA, 1959; KUBO and MASUZAWA, 1960; MIYAZI and YAMAJI, 1960; OSHIMA et al., 1960; TOBE, 1960; MAWATARI et al., 1962; YAMAZAKI, 1964), or in other country (DOBSON, 1946; TURNER et al., 1948; CLAPP, 1950).

On the basis of evaluation and management of the chlorination, it is considered very useful to know the nature of chlorine tolerance in larval stages and adult of the mussel. However, no systematic studies have been made on this problem. Therefore, the modes of responses to chlorine in each stage and its intergradation were studied in this paper, by using of artificially cultured larvae, and results of the experiments were statistically discussed with covariance analysis.

In the case of short contact time of chlorine to sea water, as such the cooling water chlorination, combined available chlorine (chloramines and other chloro derivatives) has almost not been produced. The author found that majority of available chlorine detected from cooling sea-water was free chlorine (unpublished). This studies, therefore, are dealing with the tolerance to free chlorine. The data for the death response of adult were referred to and arranged from the results of practical chlorination by DOBSON (1946) and TURNER et al. (1948), because the experiment was hard to conduct with laboratorial scale.

The results of setting stage in this paper has briefly presented at the 2nd International Conference on Water Pollution Research by YAMAZAKI (1964).

## MATERIALS

Records indicate the spawning season of *Mytilus edulis* in Japan from December to April with peaks between January and March (MIYAZAKI, 1935; UCHIHASHI, 1951; WADA,

1955; SUMJKAWA, 1963; KAZIHARA, 1964). In order to obtain the larvae of each stage by cultivation, the mussels were collected in December at Kurihama which is located near Misaki and at the mouth of Tokyo Bay.

Matured mussels spawn easily by stimulations such as rough handling or sharp changes in temperature. The spawning was induced by the soaking of 10-20 mussels in 10 l of sea water and keeping them at about 20°C for an hour or so. Both sexes spawned in same vessel. The fertilized eggs settled on the bottom were transferred to culture vessel after rinsing several times with clean sea water.

Trochophora larvae, 60-70  $\mu$  in diameter, were obtained within 24 hours after fertilization. They developed into D-shaped (straight hinge) larvae measured  $110 \pm 6.9 \mu$  in length within 1 or 2 days. The following stages were obtained by feeding the larvae with cultured green flagellate, *Chlamydomonas* sp. The umbo began to appear when the larvae were about 20 days old and  $143 \pm 7.4 \mu$  in length. This stage might be called the early umbo stage. On the 30th day, they were of  $162 \pm 11.9 \mu$  in length and attained to the benthonic stage by metamorphosis. The setting of fully-metamorphosed larvae started on the 40th day after fertilization. Their length at that time was  $226 \pm 22.9 \mu$ .

To feed the veliger larvae of the above mentioned stages, *Chlamydomonas* sp. (8-15  $\mu$  in diameter) was continuously cultured in culture solution of MATSUE (1954). It was added into the culture vessel in concentration of approximately  $10^8$  cells per ml. The 6.5 l culture vessel containing about 3000 individuals of veliger larvae and *Chlamydomonas*-suspension was placed in an incubator at 20°C and kept in dark so as to prevent increasing of pH by blooming.

In addition to these larvae of different stages, young mussel and adult collected at same locality were used for the experiments.

## METHODS

As regards the tolerance of mussel to available chlorine, two kinds of responses were observed in the experiments: the death and the shell-closing. These responses might be used as fundamental knowledge for judgement and design of effective chlorination. Data were checked as the relation between chlorine concentration and contact time.

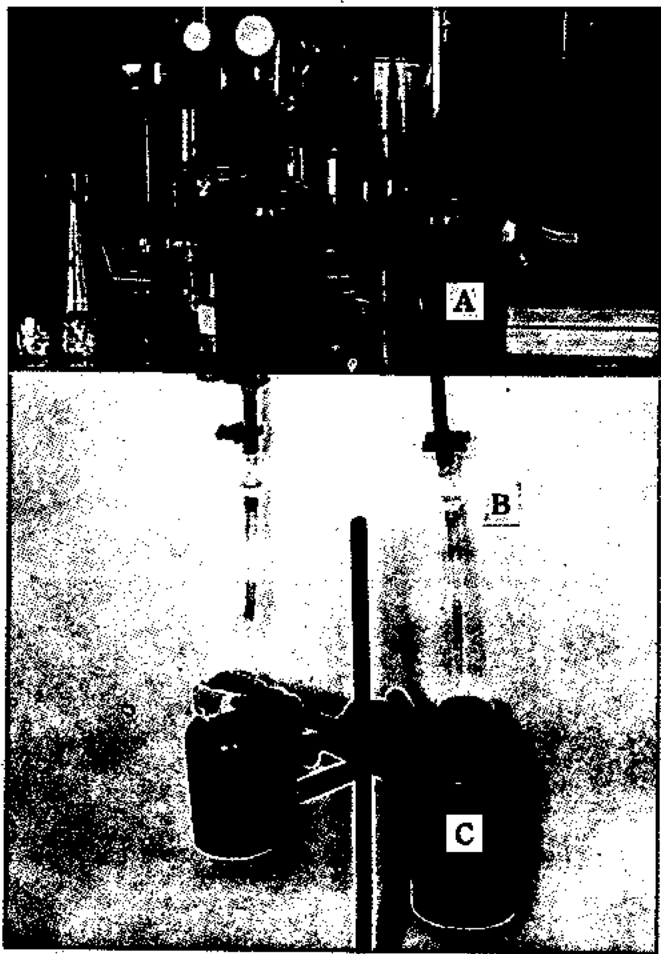


Fig. 1. Two sets of apparatus for checking responses of veliger larvae to experimental chlorinations.  
 A: Diluted chlorine solution vessel.  
 B: Chamber for larvae.  
 C: Vessel for waste.

Stock chlorine solution was prepared by passing chlorine gas through aged sea water. Dilutions were made with chlorine «demand free» sea water, prepared after the method of MOORE et al. (1943). The pH of the chlorinated sea water was not controlled. The initial pH was 8.2 or so.

The determination of free available chlorine was made with the acid starch-iodide procedure as described in «Standard Methods» (1960). The standard orthotolidine procedure is not applicable to high concentration which is able to kill the mussel or is higher than 10 ppm.

The suspension of free-swimming larvae was diluted in demand free sea water chlorinated to desired concentration. At desired time intervals, a small sample of the diluted suspension was collected after stirring and observed with microscope. The percentage of response to a chlorine concentration, average of initial and final determination, was obtained in each time of observation. When the chlorine concentration fell too far under to average, the experiment was closed.

As for the death response, each survival was measured at about 24 hours, after the experimental chlorination was over and the materials were transferred to fresh sea water by means of filtering. Experimental procedures for young and adult were not so different as that for the larval stages except handling of the materials.

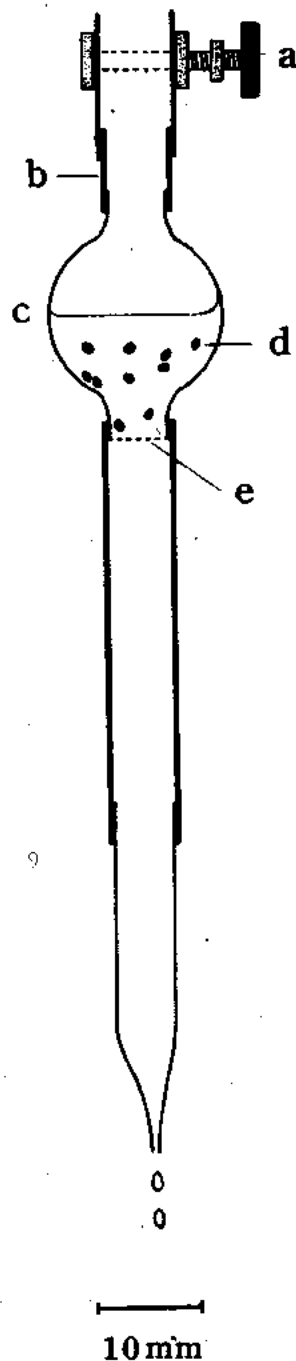


Fig. 2. The scheme of the chamber.  
 a: Screw-cock for flow control.  
 b: Separating portion.  
 c: Cage for larvae.  
 d: Veliger larva.  
 e: Müller-gauze.

Even under the best conditions of the culture, there have been delay of the growth and occasional mortalities of feeding stages; in particular, of the setting stage. These circumstances forced to spend the larvae sparingly for the experiments.

For that purpose, an apparatus in which the response of materials can be examined continuously was designed as shown in Fig. (1, 2). The vessel A supplies diluted chlorine sea water at a constant rate into the chamber B where materials

are exposed. Waste is reserved temporarily in vessel *C* for the check of chlorine concentration. The chamber (Fig. 2) was made of glass, gum tube, and vinyl tube. The rate of flow can be controlled by screw-cock *a*. Materials, i.e. the larvae are caged in *c* enclosed with Müller-gauze, and taken in and out through separating of portion *b*. At desired time of experiment, the materials were taken out and survival or shell-closing were counted. They were taken back to the apparatus soon after the observation and chlorinated until next counting. It was previously understood that the death of veliger larva is known from the ceasing of cardiac beating and ciliary movement in digestive tract, or disintegration of tissue. These symptoms were used for the continuous measuring of survivals.

From a series of responses to a chlorine concentration in desired time intervals, response time of half number of individuals to the concentration was interpolated by DOUDOROFF's straight-line graphical method using semi-log paper (DOUDOROFF et al., 1951). The values obtained in this way were graphed on a log-log grid. Thus, two kinds of responses, i.e. the death and the shell-closing for each stage were shown as the scattergrams and the regression lines. Experiments on effects of temperature on the responses were carried out using D-shaped stage at some constant temperatures ranging from 9° to 25°C.

## RESULTS

The scattergrams of the responses in each stage showing the relation between free chlorine concentration and contact time are given in Figure 3 to 7. Straight lines on this type of plot follow the general equation

$$C^n T = k$$

$$\text{or } n \log C + \log T = \log k$$

where *C* is concentration of free available chlorine (ppm), *T* is time of contact (hour), *n* and *k* are constants; *n* is positive number and  $-n$  shows the slope of the straight lines. Applying the method of least squares, the most probable values of the constants *n* and  $\log k$  in the equation were obtained as shown in Table 1 and 2.

As mentioned above, since experiment on the survival of adult was hard to carry out in the laboratory, the values for them were calculated from the results of DOBSON (1946) and TURNER et al. (1948).

Two tables indicate that there are wide differences in values of *n*, while  $\log k$  tend to become higher in accordance with the development. However, these differences are uncertain because of their considerable variation of plot. Therefore, differences in the two constants during stages and between two type of responses in a stage should be tested statistically. As to know the significant differences in *n* and  $\log k$ , testings of «differences in slope» and «differences in position» in the regression lines by covariance analysis which were used in morphological studies of REEVE (1940) and ITO (1953) were applied. The results are shown from Table 3 to Table 14.

### 1) Trochophora stage (Figure 3, Table 3).

An exception of experiment on this stage is that the developmental rate to D-shaped stage was checked as a substitute for survival. While, the percentage of individuals which ceased ciliary movement was used in stead of shell-closing in later stages, because shell-closing always accompanied with the ceasing in velum. The regression lines of these responses have steep slopes as seen in Figure 3. There is no significant difference in *n*, while difference in  $\log k$ , between two regression lines as shown in Table 3.

### 2) D-shaped stage (Figure 4, Table 4 to 6).

The effect of temperature to the responses were examined in this stage. Three different temperatures namely 9°, 16° and 25°C and two different temperatures namely 14° and 19°C were arranged for the experiments on survival and the experiments on shell-closing respectively. Difference of values of

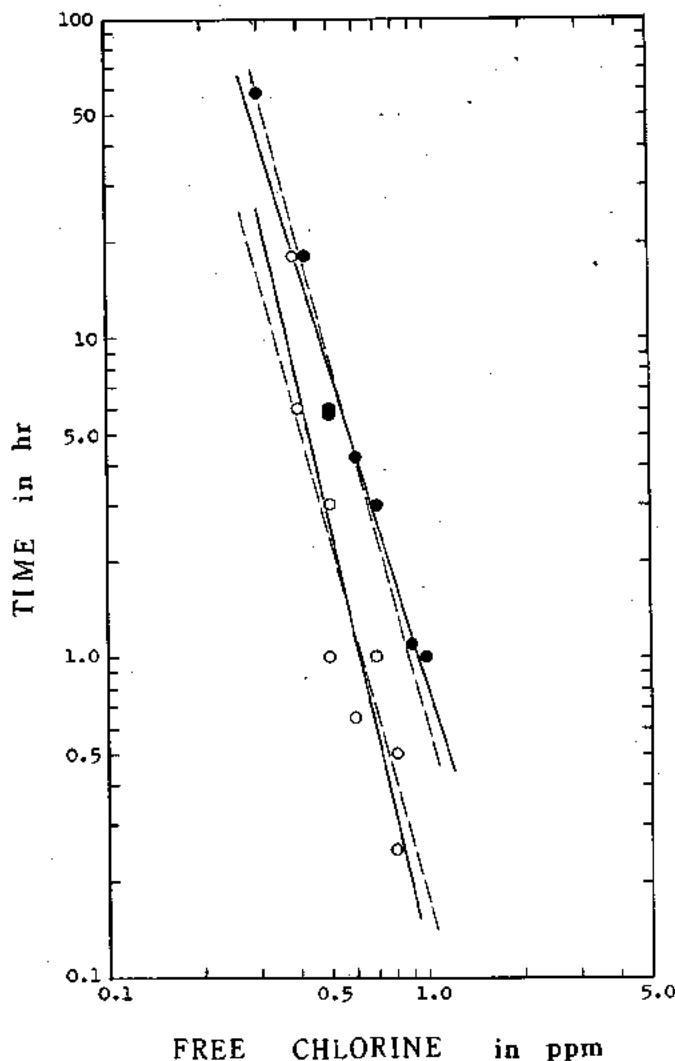


Fig. 3. The responses of trochophora larva to free chlorine, as shown by relation between free available chlorine and contact time. ●: 50% development, ○: 50% ceasing to swim. Solid lines are regression lines. Dotted lines are revised lines.

*n* among survival lines in different temperature is not significant as values of  $\log k$  as shown in Table 4. Shell-closing lines of two temperatures are significantly different in *n* and  $\log k$  (Table 5).

As for the comparison of two kinds of responses, there is no difference in *n* between survival line *b* and shell-closing line *a* at the middle temperature (Table 6). As for  $\log k$ , the difference can be seen in Figure 4, without the test.

### 3) Early umbo stage (Table 7).

There is a wide difference in  $\log k$  between the survival line and the shell-closing line, therefore, no further test was needed. The two lines show no difference in *n* (Table 7).

### 4) Setting stage (Figure 5, Table 8).

The difference in  $\log k$  between the survival line and the shell-closing line is obvious in Figure 5. The test shows no significant difference in *n* between the two lines (Table 8).

### 5) Young shell (Figure 6 and 7, Table 9).

As seen in Figure 6 and Figure 7, the survival line has gentle slope against the shell-closing line. The test also in-

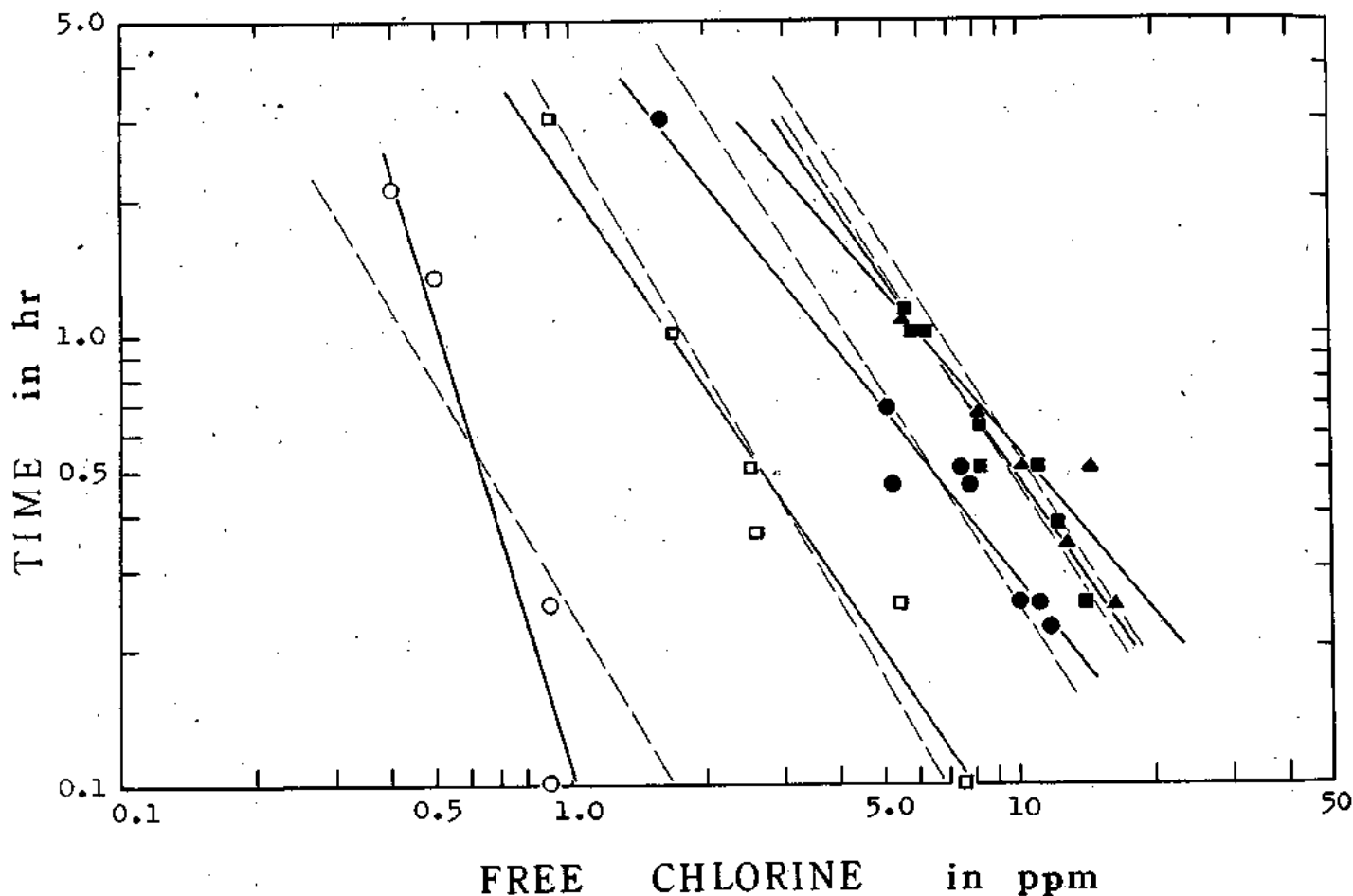


Fig. 6. The responses of D-shaped larva to free chlorine, as shown by relation between free available chlorine and contact time.  $\blacktriangle$ : 50% survival at  $8.9 \pm 0.2^\circ\text{C}$  (a).  $\blacksquare$ : 50% survival at  $16.0 \pm 0.3^\circ\text{C}$  (b).  $\bullet$ : 50% survival at  $25.0 \pm 0.9^\circ\text{C}$  (c).  $\blacklozenge$ : 50% shell-closing at  $14.3 \pm 1.0^\circ\text{C}$  (a).  $\circ$ : 50% shell-closing at  $19.0 \pm 0.9^\circ\text{C}$  (b). Solid lines are regression lines. Dotted lines are revised lines.

TABLE 1.

VALUES OF CONSTANTS IN THE EQUATION:  $n \log C + \log T = \log k$  FOR 50% SURVIVAL OF EACH STAGE

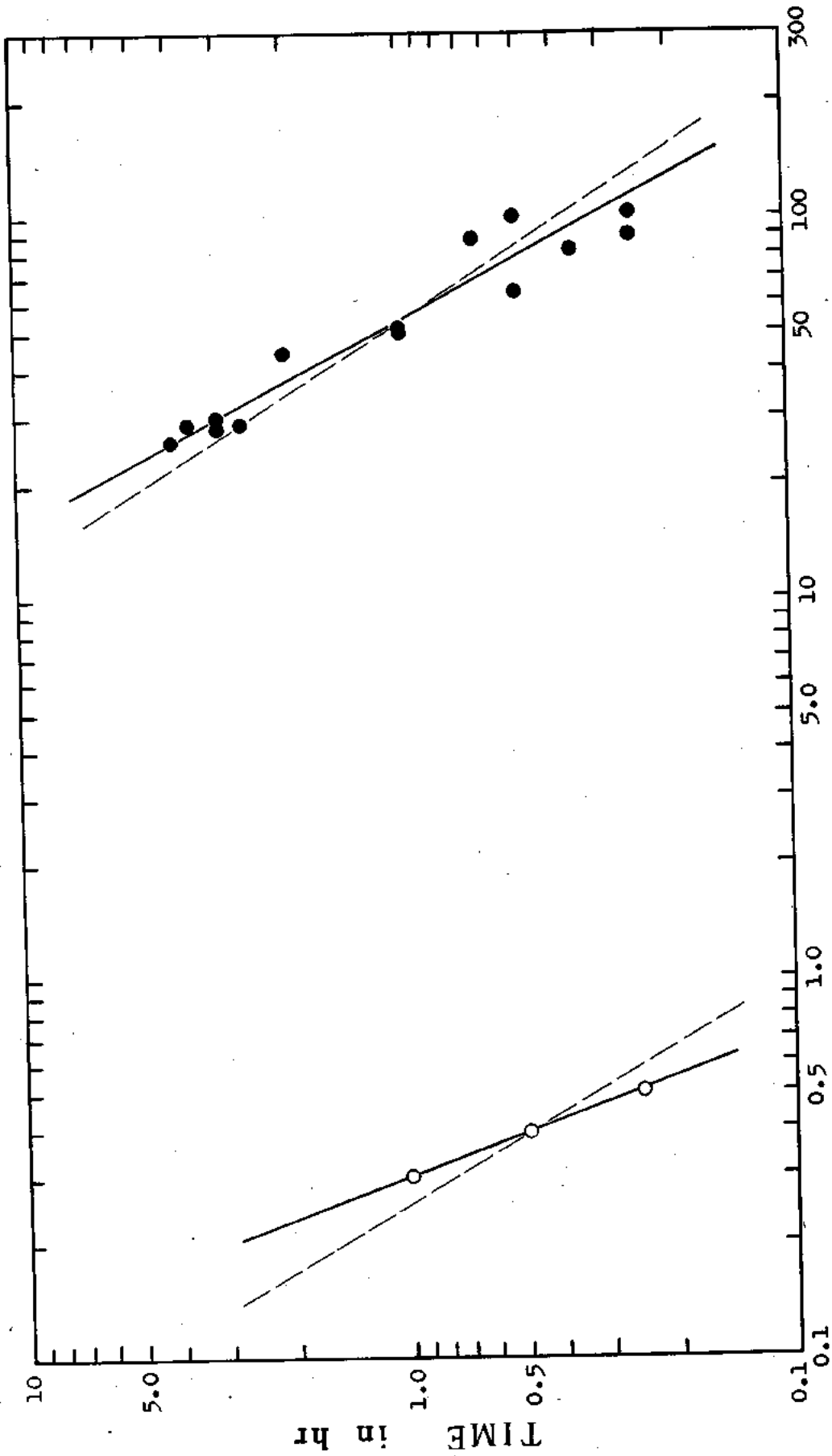
Stage	$n$	$\log k$	Size *	Temperature
Trochophora stage **	3.3134	-0.0929	60-70 $\mu$	$16.6 \pm 1.0^\circ\text{C}$
D-shaped stage, (a)	1.1926	0.9208	$110 \pm 6.9 \mu$	$8.9 \pm 0.2$
D-shaped stage, (b)	1.4609	1.1305	$110 \pm 6.9$	$16.0 \pm 0.3$
D-shaped stage, (c)	1.2699	0.7162	$110 \pm 6.9$	$25.0 \pm 0.9$
Early umbo stage	1.2622	1.4201	$143 \pm 7.4$	$17.8 \pm 0.9$
Benthonic umbo stage	1.7499	2.7196	$162 \pm 11.9$	$16.1 \pm 0.2$
Setting stage	1.8662	3.2264	$226 \pm 22.9$	$18.8 \pm 0.8$
Young	0.2334	2.0298	$10.3 \pm 1.50 \text{ mm}$	$21.8 \pm 0.9$
Adult, (a) ***	0.2388	1.9779		
Adult, (b) ****	0.2074	2.3611.		$21.7 \pm 0.8$

\* Diameter in trochophora and shell length in others.

\*\* 50% development was used in stead of survival.

\*\*\* Calculated from the result of TURNER et al (1948).

\*\*\*\* Calculated from the result of DOBSON (1946)



### FREE CHLORINE in ppm

Fig. 5. The responses of larva of setting stage to free chlorine, as shown by relation between free available chlorine and contact time. ●: 50% survival. ○: 50% shell-closing. Solid lines are regression lines. Dotted lines are revised lines.

TABLE 2

VALUES OF CONSTANTS IN THE EQUATION:  $n \log C + \log T = \log k$  FOR 50% SHELL-CLOSING OF EACH STAGE

Stage	$n$	$\log k$	Size *	Temperature
Trochophora stage **	4.4934	-0.9280	60-70 $\mu$	16.6 $\pm$ 1.0°C
D-shaped stage, (a)	1.4776	0.3327	110 $\pm$ 6.9	14.3 $\pm$ 1.0
D-shaped stage, (b)	3.3084	-0.9428	110 $\pm$ 6.9	19.0 $\pm$ 0.9
Early umbo stage	1.9801	-1.3942	143 $\pm$ 7.4	18.5 $\pm$ 1.1
Setting stage	2.6989	-1.4002	226 $\pm$ 22.9	20.7 $\pm$ 1.6
Young	1.4329	-0.5902	9.0 $\pm$ 1.39 mm	22.1 $\pm$ 0.9
Adult	1.5026	0.1652	34.7 $\pm$ 1.74	21.0 $\pm$ 1.3

\* Diameter in trochophora and shell length in others.

\*\* 50% of number of individuals ceasing ciliary movement was used in stead of shell-closing.

TABLE 3.

TEST FOR DIFFERENCES IN  $n$  AND  $\log k$  BETWEEN UNDEVELOPED AND CILIARY MOVEMENT CEASING LINES OF TROCHOPHORA STAGE.

Residue from:	Sum of squares	d.f.	Mean square	$F_0$
Two separate lines	0.578420	12	0.0482017	2.046
Slope differences	0.098604	1	0.0986040	
Two parallel lines	0.677024	13		
Two parallel lines	0.677024	13	0.0520788	22.882**
Positional differences	1.191653	1	1.1916530	
Single line	1.868677	14		

\* Significance at 5% level.

\*\* Significance at 1% level

TABLE 4.

TEST FOR DIFFERENCES IN  $n$  AND  $\log k$  AMONG SURVIVAL LINES OF D-SHAPED STAGE  $a$ ,  $b$ , AND  $c$ . (EFFECT OF TEMPERATURE)

Residue from:	S.S.	d.f.	M.S.	$F_0$
Three separate lines	0.100009	17	0.0058829	0.589
Slope differences	0.006925	2	0.0034625	
Three parallel lines	0.106934	19		
Three parallel lines	0.106934	19	0.0056281	28.502**
Positional differences	0.320821	2	0.1604105	
Single line	0.427755	21		

TABLE 5.

TEST FOR DIFFERENCES IN  $n$  AND  $\log k$  BETWEEN SHELL-CLOSING LINES OF D-SHAPED STAGE  $a$  AND  $b$ . (EFFECT OF TEMPERATURE)

Residue from:	S.S.	d.f.	M.S.	$F_0$
Two separate lines	0.143939	6	0.0239898	11.563*
Slope differences	0.277396	1	0.2773960	
Two parallel lines	0.421335	7		
Two parallel lines	0.421335	7	0.0601907	19.077**
Positional differences	1.148282	1	1.1482820	
Single line	1.569617	8		

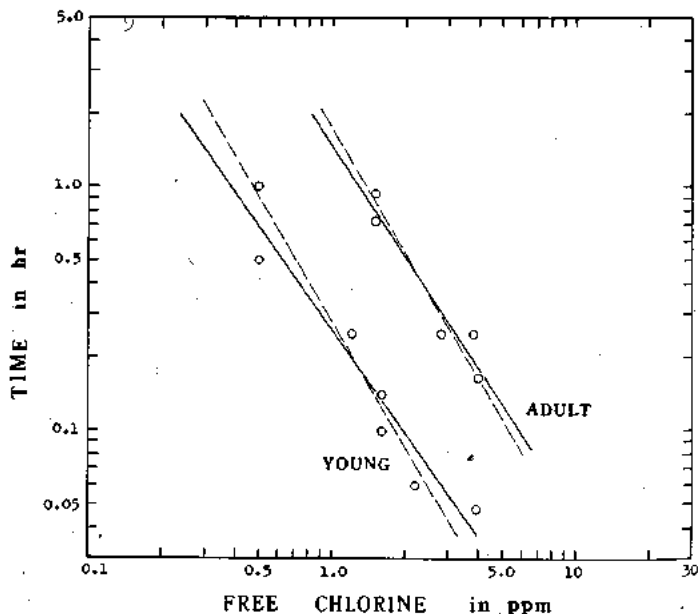


Fig. 6. 50% shell-closing of young and adult to free chlorine, as shown by relation between free available chlorine and contact time. Solid lines are regression lines. Dotted lines are revised lines.

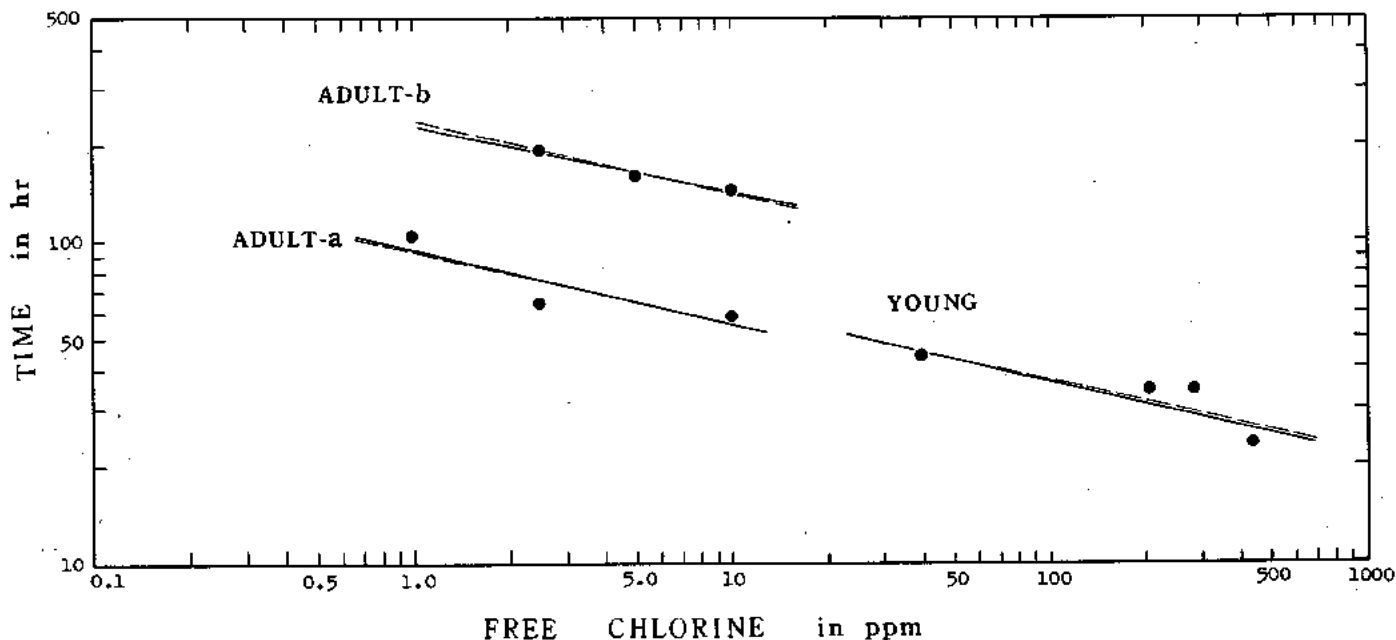


Fig. 7. 50% survival of young and adult to free chlorine, as shown by relation between free available chlorine and contact time. Solid lines are regression lines. Dotted lines are revised lines.

indicates that these values of  $n$  are significantly different as shown in Table 9. The values of  $\log k$  are widely different as seen in Figure 6 and Figure 7.

#### 6) Adult (Figure 6 and 7, Table 10).

Both survival lines obtained from the results of experiments by DOBSON (1946) and TURNER et al. (1948) are bearing the similar gentle slopes as seen in Figure 7, though these are different in position. And the covariance test indicates that significant difference between them is present

in  $\log k$  and not in  $n$  (Table 10). The shell-closing line of adult examined with the same procedure as the young is far apart from the survival lines. Its slope resembles to that of the young (Figure 6).

All of these response-lines from trochophora to adult are collectively illustrated in Figure 8. From this figure, it seemed that there is no significant difference in  $n$ , the value of slope, among all of survival lines and shell-closing lines from D-shaped stage to adult except the survival lines of young and adult. However, the test indicated the significant difference

TABLE 6

TEST FOR DIFFERENCES IN  $n$  BETWEEN SURVIVAL LINE *b* AND SHELL HYPHEN CLOSING LINE *a* OF D-SHAPED STAGE (AT MIDDLE TEMPERATURE)

Residue from:	S.S.	d.f.	M.S.	F <sub>0</sub>
Two separate lines	0.080393	10	0.0080393	0.004
Slope differences	0.000035	1	0.0000350	
Two parallel lines	0.080428	11		

TABLE 7

TEST FOR DIFFERENCES IN  $n$  BETWEEN SURVIVAL LINE AND SHELL HYPHEN CLOSING LINE OF EARLY UMBO STAGE

Residue from:	S.S.	d.f.	M.S.	F <sub>0</sub>
Two separate lines	0.213114	11	0.0193740	4.805
Slope differences	0.093092	1	0.0930920	
Two parallel lines	0.306206	12		

TABLE 8

TEST FOR DIFFERENCES IN  $n$  BETWEEN SURVIVAL LINE AND SHELL HYPHEN CLOSING LINE OF SETTING STAGE

Residue from:	S.S.	d.f.	M.S.	F <sub>0</sub>
Two separate lines	0.217357	13	0.0167198	0.987
Slope differences	0.016509	1	0.0165090	
Two parallel lines	0.233866	14		

TABLE 9

TEST FOR DIFFERENCES IN  $n$  BETWEEN SURVIVAL LINE AND SHELL HYPHEN CLOSING LINE OF YOUNG SHELL

Residue from:	S.S.	d.f.	M.S.	F <sub>0</sub>
Two separate lines	0.409866	7	0.0156951	28.252**
Slope differences	0.443422	1	0.4434220	
Two parallel lines	0.553288			



TABLE 10.

TEST FOR DIFFERENCES IN  $n$  AND  $\log k$  BETWEEN SURVIVAL LINES OF ADULT  $a$  (TURNER'S EXP.) AND  $b$  (DOBSON'S EXP.)

Residue from:	S.S.	d.f.	M.S.	F <sub>0</sub>
Two separate lines	0.008920	2	0.0044602	0.029
Slope differences	0.000131	1	0.0001310	
Two parallel lines	0.009051	3		
Two parallel lines	0.009051	3	0.0030170	72.279**
Positional differences	0.218067	1	0.2180670	
Single line	0.227118	4		

TABLE 11.

TEST FOR DIFFERENCES IN  $n$  AND  $\log k$  AMONG ALL OF SURVIVAL LINES AND SHELL-CLOSING LINES FROM D-SHAPED STAGE TO ADULT EXCEPT THE SURVIVAL LINES OF YOUNG AND ADULT

Residue from:	S.S.	d.f.	M.S.	F <sub>0</sub>
Twelve separate lines	0.987436	66	0.0149612	3.733**
Slope differences	0.614314	11	0.0558467	
Twelve parallel lines	1.601750	77		

among them (Table 11).

In case of the grouping of survival lines which includes D-shaped stage  $a$ ,  $b$ ,  $c$ , early umbo stage, benthonic umbo stage and setting stage, the difference in  $n$  is significant at 5% level but insignificant at 1% level (Table 12). Similarly, the grouping of shell-closing lines which includes D-shaped stage  $a$ ,  $b$ , early umbo stage, setting stage, young and adult has no significant difference in  $n$  at 1% level (Table 13). In addition, there is no significant difference in  $n$  among survival lines of young, adult  $a$  (TURNER'S exp.) and adult  $b$  (DOBSON'S exp.) as seen in Table 14. Therefore, each group would have a best-fitting slope calculated from their sum of squares as follows:

$$n_1 = \frac{S_E(xy)}{S_E(xx)} = \frac{S_1(xy) + S_2(xy) + \dots + S_k(xy)}{S_1(xx) + S_2(xx) + \dots + S_k(xx)}$$

The revised constants of all the lines are listed in Table 15 and Table 16 with the standard errors of  $\log k$ . Namely, survival line and shell-closing line of trochophora, survival lines including from D-shaped stage to setting stage, shell-closing lines from D-shaped stage to adult, and survival lines of young and adult may possess their common constant  $n$ . On the other hand, there are also facts which support that  $n$  of two responses in each stage are not significantly different except young and adult. This needs a further investigation.

Practical informations can be derived from the figures and tables. For example, the half mortality by 10 ppm of free available chlorine would be reached instantly in trochophora, in half an hour in D-shaped stage, in 15 hours in setting stage, and in 70-150 hours in young and adult; while 1.0 ppm of free available chlorine and about 10 to above 100 hours would be required for stages over the D-shaped to have the same effect except trochophora in which one hour is enough. In 0.1 ppm of free chlorine, it may need the contact of above 100 hours to kill 50% of every stages. And free chlorine dose of 100 ppm would be able to kill half of number of individuals of all stages within 30 minutes except adult which is tolerant

TABLE 12.

TEST FOR DIFFERENCES IN  $n$  AMONG SURVIVAL LINES OF D-SHAPED STAGE  $a$ ,  $b$ ,  $c$ , EARLY UMBO STAGE, BENTHONIC UMBO STAGE AND SETTING STAGE.

Residue from:	S.S.	d.f.	M.S.	F <sub>0</sub>
Six separate lines	0.527009	45	0.0117113	3.136*
Slope differences	0.183622	5	0.0367244	
Six parallel lines	0.710631	50		

TABLE 13.

TEST FOR DIFFERENCES IN  $n$  AMONG SHELL-CLOSING LINES OF D-SHAPED STAGE  $a$ ,  $b$ , EARLY UMBO STAGE, SETTING STAGE, YOUNG AND ADULT

Residue from:	S.S.	d.f.	M.S.	F <sub>0</sub>
Six separate lines	0.460427	21	0.0219251	3.708*
Slope differences	0.406487	5	0.0812974	
Six parallel lines	0.866914	26		

TABLE 14.

TEST FOR DIFFERENCES IN  $n$  AMONG SURVIVAL LINES OF YOUNG, ADULT  $a$  (TURNER'S EXP.) AND  $b$  (DOBSON'S EXP.)

Residue from:	S.S.	d.f.	M.S.	F <sub>0</sub>
Three separate lines	0.014598	4	0.0036495	0.018
Slope differences	0.000134	2	0.0000670	
Three parallel lines	0.014732	6		

for several hours.

The shell-closing response of half numbers would be expected in 10 minutes or so by 1.0 ppm of free chlorine in every stages except adult which responds in about an hour. It delays from several hours to several tens hours when 0.1 ppm is dosed.

These graphical derivations are restricted in the middle temperature ranging from 16° to 22°C.

## DISCUSSION

The mode of two responses to free available chlorine: the death and the shell-closing, and their intergradation with the development have been shown in Figure 3 or Table 15 and 16.

Increasing of free chlorine tolerance in accordance with the development can be seen from the fact that values of  $\log k$  is becoming higher, while  $n$ , the slope, becomes gentle.

The nature of constant  $n$  resembles chemical reaction velocity. It has been suggested that the toxic velocity has relations to dispersion of toxic substance in body tissue, permeation velocity to cells and its excretion (YAGI and KOIZUMI, 1929). These functions would be subject to body structure. Then, the three groupings of survival lines in  $n$  of 1) Trochophora, 2) D-shaped to setting stage, 3) Young and adult, might be attributed to their structural identity. While, it is supposed that the constant  $\log k$  is preferably affected by size, condition, and environmental factors such as temperature, water quality and etc.

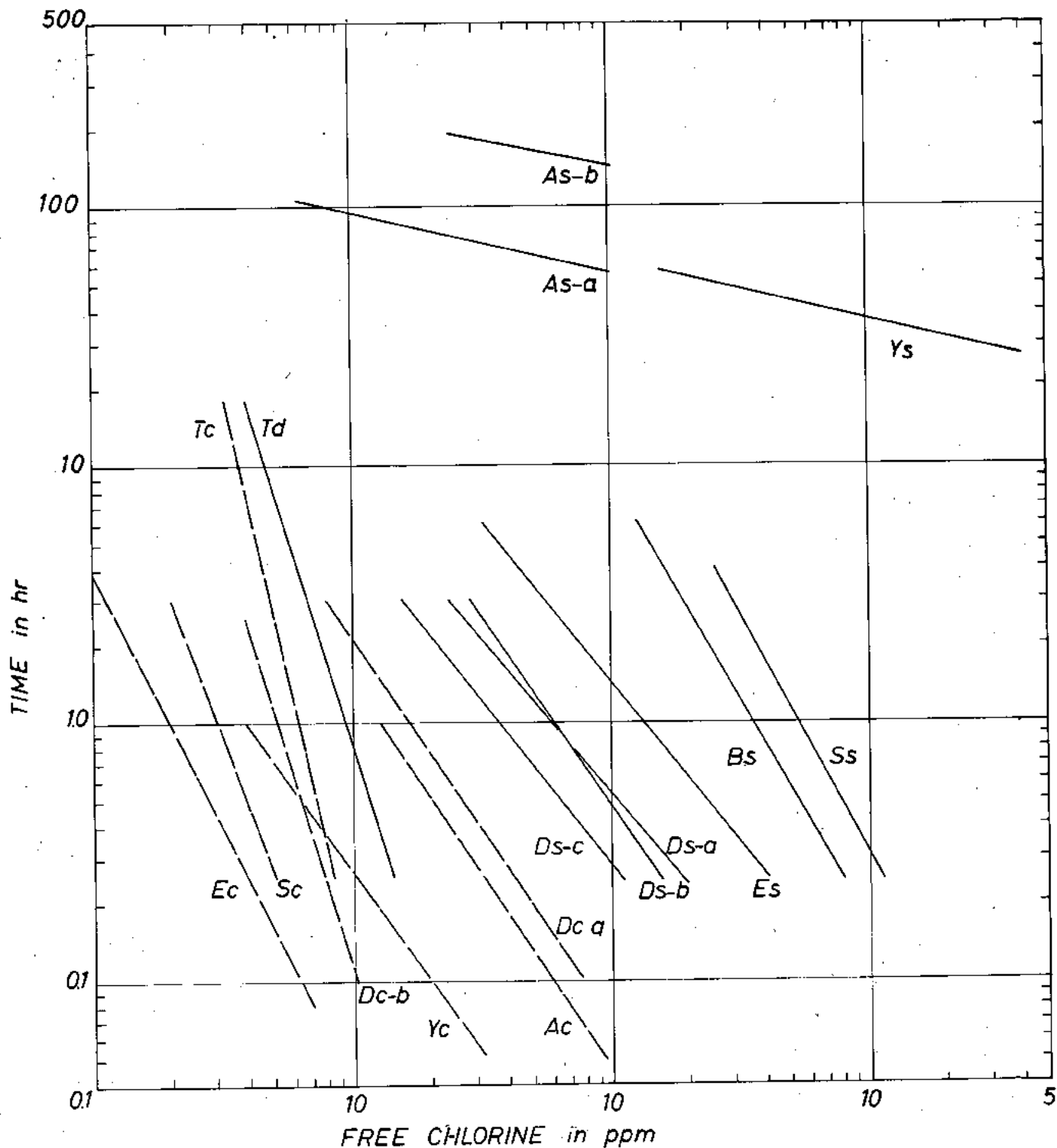


Fig. 8. The responses of *Mytilus edulis* in each stage to free chlorine, as shown by relation between free available chlorine and contact time.  
 Solid lines indicate 50% survival. Dotted lines indicate 50% shell Hyphen closing.

Td: Trochophora, development (instead of survival),  
 Ds-a: D-shaped stage, survival (a),  
 Ds-b: D-shaped stage, survival (b),  
 Ds-c: D-shaped stage, survival (c),  
 Bs: Benthonic stage, survival,  
 Te: Trochophora, ceasing to swim (instead of shell-closing),  
 Dc-a: D-shaped stage, shell-closing (a),  
 Dc-b: D-shaped stage, shell-closing (b),  
 Ec: Early umbo stage, shell-closing,

Es: Early umbo stage, survival,  
 Ss: Setting stage, survival,  
 Ys: Young, survival,  
 As-a: Adult, survival (a),  
 As-b: Adult, survival (b),  
 Sc: Setting stage, shell-closing,  
 Yc: Young, shell-closing,  
 Ac: Adult, shell-closing.

TABLE 15

REVISED VALUES OF CONSTANTS IN THE EQUATION:  
 $n \log C + \log T = \log k' * \text{ FOR } 50\% \text{ SURVIVAL OF EACH STAGE}$

Stage	$n'$	$\log k'$ (with S.F.)
Trochophora stage**	3.7017	-0.1874 ± 0.1177
D-shaped stage, (a)	1.5606	1.2730 ± 0.1175
D-shaped stage, (b)	1.5606	1.2156 ± 0.0629
D-shaped stage, (c)	1.5606	0.9525 ± 0.1099
Early umbo stage	1.5606	1.8267 ± 0.0942
Benthonic umbo stage	1.5606	2.4329 ± 0.1312
Setting stage	1.5606	2.7005 ± 0.1453
young	0.2319	2.0265 ± 0.0435
Adult, (a) ***	0.2319	1.9747 ± 0.0664
Adult, (b) ****	0.2319	2.3783 ± 0.0109

- \* C: Free chlorine concentration in ppm, T: Contact time in hr.  
 \*\* 50% development was used instead of survival.  
 \*\*\* Calculated from the result of TURNER et al. (1948).  
 \*\*\*\* Calculated from the result of DOBSON (1946).

TABLE 16

REVISED VALUES OF CONSTANTS IN THE EQUATION:  
 $n \log C + \log T = \log k' * \text{ FOR } 50\% \text{ SHELL-CLOSING OF EACH STAGE}$

Stage	$n'$	$\log k'$ (with S.E.)
Trochophora stage **	3.7017	-0.7332 ± 0.2879
D-shaped stage, (a)	1.7056	0.4322 ± 0.2940
D-shaped stage, (b)	1.7056	-0.6253 ± 0.5283
Early umbo stage	1.7056	-1.2525 ± 0.1806
Setting stage	1.7056	-0.9957 ± 0.4127
Young	1.7056	-0.5573 ± 0.1608
Adult	1.7056	0.2456 ± 0.0945

- \* C: Free chlorine concentration in ppm, T: Contact time in hr.  
 \*\* 50% of number of individuals ceasing ciliary movement was used instead of shell-closing.

The effect of temperature on the  $\log k$  was remarkable and it varied 0.0087 per 1°C between 9° and 16°C, and 0.0300 per 1°C between 16° and 25°C, in D-shaped stage.

It is not easy to explain what internal factors make the slope becoming gentle with the progress of the development. But, next hypothesis may lead to a solution of this question in future. In trochophora, having the steepest slope, concentration is rather critical than contact time, and on this occasion a certain strength of chlorine dispersion to body tissue might be lethal. On the contrary, in young and adult having gentle slopes, contact time is rather critical than concentration which is very high. Being contacted to high chlorine concentration, they are wont to keep their shells closed till the time limit of anaerobic respiration. This lethal time would have less relation to chlorine concentration. The slopes of larvae from D-shaped stage to setting stage are just intermediate, and the mechanism of their tolerance might be transitive.

There is no significant difference in  $n$ , the slope of shell-closing lines from D-shaped stage to adult. The effect of temperature on  $\log k$  of shell-closing response was more remarkable than that of survivals; it varied 0.2251 per 1°C

between 14° and 19°C, in D-shaped stage. If the shell-closing can be kept till the time limit of anaerobic respiration, it may also become to lethal after that. Otherwise, mussel can not to spin byssus strands for attachment while they closed shells. This response is worth notice for the controlling thereby.

In general, chlorine tolerances indicated with survival and shell-closing lines were steadily rising according to the development. And the period weakening the tolerance was not observed. Therefore, practical chlorination should aim at the larvae of setting stage which are introduced by cooling-water conduit from outside and cause new fouling growth.

## ACKNOWLEDGMENTS

The author expresses his grateful thanks to Emeritus Professor Y. MATSUE, for his guidance and encouragement for this study, to Professor S. ARASAKI and Associate Professor A. SAEKI for their helpful suggestions, and to Associate Professor R. HIRANO for his technical assistance. The professors and associate professors mentioned above are of the University of Tokyo. The author also expresses his thanks to the Engineering Research Institute of the Tokyo Electric Power Company, Inc., for its financial support of a part of this study.

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#### DISCUSSION

Dr. WISHERS (Holland): Wasn't there an effect of overcrowding with your larvae in the test-tubes (because the tubes were very small).

Prof. KUWABARA: About 20 to 40 veliger larvae were taken in the chamber (test-tube) of the experimental apparatus with the precaution of overcrowding.

# QUELQUES RESULTATS DE L'APPLICATION DE COMPOSÉS ORGANO-METALLIQUES DE PLOMB A DES PEINTURES ANTI-SALISSURES

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Madrid, ESPAGNE

## RÉSUMÉ

On trouvera dans ce papier les résultats obtenus, dans les eaux de la Baie de Cadix (Espagne), avec une série de peintures anti-salissures, pour lesquelles, à côté de formules classiques, on a utilisé comme pigments toxiques des composés organo-métalliques de plomb (acétate de tributyle plomb, acétate de triphényle plomb, laurate de triphényle plomb et laurate de tributyle plomb), pour éviter la fixation d'organismes. Les liants utilisés sont les vinyliques, vinyliques à haute teneur en résine et les olé-résineuses. Dans chacun de ces trois types de peintures expérimentées, il y a :

- une peinture de contrôle qui ne contient pas de composé organo-plomb et qui est à base d'oxyde cuivreux seulement,
- quatre peintures contenant des composés organo-plomb plus de l'oxyde cuivreux,
- et enfin quatre autres avec des composés organo-plomb seulement.

Les quatre composés organo-plomb essayés révèlent de claires propriétés anti-salissures, et ils sont spécialement efficaces combinés avec l'oxyde cuivreux.

Dans les systèmes «vinyliques standard» et «vinylique à haute teneur en résine», le comportement des composés organo-plomb a été excellent lorsqu'ils ont été utilisés conjointement avec l'oxyde cuivreux puisque les éprouvettes se sont maintenues pratiquement libres de salissures organiques. Quand le composé organo-plomb remplace complètement le  $Cu_2O$ , c'est l'acétate de triphényle plomb qui a donné les meilleurs résultats dans les cas des peintures «vinylique standard», et l'acétate de tributyle plomb dans celui des «vinyliques à haute teneur en résine».

Avec les peintures «olé-résineuses», au bout de les dix premiers mois d'essai, les composés organo-plomb, remplaçant en partie ou en tout le  $Cu_2O$ , montrent toujours un bon comportement, et en tous cas, ce résultat est très supérieur à celui de la peinture de contrôle basée exclusivement sur l'oxyde cuivreux, qui, fut rapidement couverte d'organismes. La seule exception a été la peinture basée sur le laurate de triphényle plomb sans  $Cu_2O$ , qui est apparue avec un grand nombre de salissures après quatre mois et demi.

## INTRODUCTION

On connaît très bien l'action fortement corrosive de l'eau de mer sur les métaux, en particulier sur le fer et l'acier, en raison des sels qu'elle contient, le chlorure de sodium spécialement<sup>1</sup>. Or la mer est un milieu vivant, peuplé de tout un monde biologique, microscopique et macroscopique, qui exerce son action sur les objets que l'on immerge artificiellement, en une symbiose complexe d'organismes végétaux et animaux<sup>2</sup>.

Dans ce milieu marin, phénomène corrosif et phénomène biologique sont d'habitude intimement liés<sup>3</sup>. Le comportement d'un revêtement anticorrosif peut être influencé par la fixation d'organismes qui le détachent, et mettent ainsi en contact direct le métal et l'eau de mer. De même, ces organismes peuvent provoquer des phénomènes d'aération différentielle. C'est dans les ports que la corrosion est le plus spécialement favorisée, à cause de la pollution de l'eau (déversement d'égoûts, déchets organiques ou minéraux de différente nature), ou de la présence de bactéries réductrices de sulfates, ou enfin à cause des produits du métabolisme des organismes salissants eux-mêmes (production d'acide sulfurique dans le cas des ascidies).

Dans la construction navale, la fixation d'organismes constitue un grave problème, non seulement du point de vue de la corrosion mais du fait que cela peut arriver à affecter la bonne marche des bateaux; en effet, le frottement de la carène augmente considérablement, et, pour maintenir la même vitesse il faut accroître la quantité de combustible. À cet accroissement des frais en combustible, il faut ajouter

ceux du piquage périodique de la carène en cale, plus les jours de navigation perdus par le bateau<sup>4</sup>.

Pour éviter la fixation et le développement de végétaux et d'animaux sur la superficie submergée de bâtiments, on a mis au point des peintures toxiques, dont les pigments sont en général des sels de cuivre ou de mercure. Malgré l'abondance de brevets existants dans tous les pays, on est loin d'avoir obtenu la peinture idéale, et c'est pourquoi on continue à expérimenter de nouvelles formulations et de nouveaux pigments toxiques, tels certains composés organo-métalliques.

L'expérimentation d'une même formule en différentes parties du monde n'est pas seulement conseillable mais nécessaire. Un bateau peut passer rapidement dans des zones marines aux caractéristiques biologiques et hydrologiques très différentes. C'est ainsi que dans les régions tropicales, en raison de la température de l'eau, la fixation d'organismes est pratiquement ininterrompue toute l'année, tandis que dans les zones tempérées elle est saisonnière et a lieu de préférence au printemps et en été<sup>5</sup>.

On trouvera dans ce papier les résultats obtenus dans les eaux de la Baie de Cadix (Espagne) avec une série de peintures anti-salissures, pour lesquelles, à côté de formules classiques, on a utilisé comme pigments toxiques des composés organo-métalliques de plomb (acétate de tributyle plomb, acétate de triphényle plomb, laurate de triphényle plomb et laurate de tributyle plomb) pour éviter la fixation d'organismes. Ces composés nous ont été procurés par l'Institut de Chimie Organique T.N.O. de Hollande. La première à les essayer systématiquement en les peintures anti-salissures fut la «International Lead Zinc Research Organisation, Inc.»

en 1964. Les expériences furent réalisées alors dans trois stations d'essais situées à Miami Beach (Floride), Sayville (Long Island), Pearl Harbour (Hawaii) aux Etats-Unis. Quelques-uns des résultats de cette recherche sont portés au Tableau I\*.

TABLEAU I

COMPORTEMENT DES  
PEINTURES ANTI-SALISSURES (6)  
(ECHELLE D'ÉVALUATION: 100 SUPERFICIE PROPRE;  
0 SUPERFICIE TOTALEMENT COUVERTE DES  
SALISSURES)

Peinture	Pearl Harbor 13 mois	Miami Beach 18 mois
<i>Vinylque Standard</i>		
Control	55	92
Cu <sub>2</sub> O/T P L A	100	100
Cu <sub>2</sub> O/P P L L	20	83
Cu <sub>2</sub> O/T B L A	75	86
Cu <sub>2</sub> O/T B L L	75	97
T P L A	96	72
T P L L	0	0
T B L A	0	0
T B L L	0	0
<i>Vinylque haute en résine</i>		
Control	100	100
Cu <sub>2</sub> O/T P L A	100	95
Cu <sub>2</sub> O/T P L L	90	92
Cu <sub>2</sub> O/T B L A	100	100
Cu <sub>2</sub> O/T B L L	100	97
T P L A	0	0
T P L L	0	0
T B L A	55	33
T B L L	0	0
<i>Oléo-résineuse</i>		
Control	0	0
Cu <sub>2</sub> O/T P L A	90	0
Cu <sub>2</sub> O/T P L L	0	0
Cu <sub>2</sub> O/T B L A	0	0
Cu <sub>2</sub> O/T B L L	0	0
T P L A	0	0
T P L L	0	0
T B L A	0	0
T B L L	0	0

T P L A = Acetate de triphényle plomb;  
T P L L = Laurate de triphényle plomb;  
T B L A = Acetate de tributyle plomb;  
T B L L = Laurate de tributyle plomb.

L'étude réalisée à présent en Espagne par le Centre Nationale de Recherches Métallurgiques, dans sa station d'essais de Corrosion à Cadix, sera complétée par celle que l'on effectue dans la Station Méditerranéenne de Barcelone, et qui a commencé récemment.

CARACTÉRISTIQUES DE LA STATION D'ESSAIS DE  
CORROSION A CADIX

Le radeau où furent exposés les éprouvettes d'essais se trouve donc situé dans la Baie de Cadix (Espagne), dans

l'Atlantique Sud, et très près de la porte de la Méditerranée. Sa situation géographique est comprise entre 36° et 37°2' de latitude N et 5°5' et 6°26' de longitude 0 du méridien de Greenwich.

Dans le radeau les éprouvettes furent suspendues à un mètre de profondeur.

Etant donné leur importance dans le développement d'organismes, nous allons examiner brièvement le rôle que jouent les caractéristiques hydrologiques de l'eau, en faisant justement appel aux données obtenues en Baie de Cadix.

Température

On peut considérer que la température est le facteur déterminant en ce qui concerne la fixation d'organismes, car elle agit comme la régulatrice de fonctions vitales fondamentales. Elle a donc une influence décisive dans la reproduction de la plupart des espèces et dans le développement larvaire. Dans quelques cas, elle peut affecter l'alimentation et le rythme respiratoire<sup>6,7</sup>.

Le graphique de la Fig. 1 montre les variations mensuelles de la température dans la Baie de Cadix pendant 1967. On peut observer que la différence maximale est d'environ 12°C, ce qui nous indique que biogéographiquement cette zone peut être placée dans les régions tempérées<sup>8</sup>.

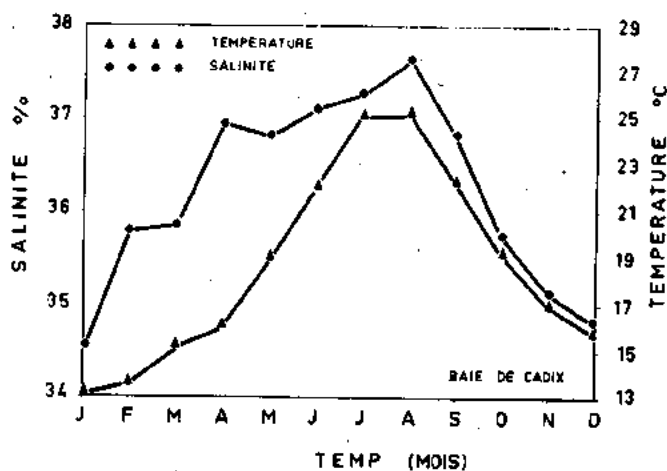


Fig. 1. Variations mensuelles de la température et de la salinité dans la Baie de Cadix en 1967.

Salinité

Bien qu'importante, la salinité a un rôle moins décisive que la température. Les valeurs normales pour ce facteur sont en général du 35‰. La variation de la salinité affecte les organismes, dans leur gravité spécifique et dans la pression osmotique de leurs cellules. Une baisse de la salinité affecte aussi le rythme respiratoire des végétaux marins<sup>9,10,11</sup>.

Dans les eaux de la Baie de Cadix, la salinité peut être considéré comme normale, de même que les variations qu'elle subit au cours des mois de l'année, Fig. 1.

Oxygène

Cet élément est indispensable pour le développement des êtres vivants. Dans la mer, dans des zones propres, la teneur en oxygène ne varie pas sensiblement, car les mouvements de l'eau produisent une aération qui maintient les valeurs normales. L'oxygène baisse logiquement en fonction de la profondeur, ainsi que par pollution et par un mauvais renouvellement.

ment de l'eau, dans les zones portuaires en particulier<sup>12</sup>.

Le radeau où ont été réalisées les expériences est situé dans une eau propre, soumise à des marées, et par conséquent, renouvelée. Les analyses de l'oxygène n'ont pas pu être réalisées périodiquement, mais les résultats des déterminations éloignées, à différentes époques de l'année, ont été compris entre 6 et 8 mg/l<sup>13</sup>.

pH

L'eau de mer est un milieu tamponné, et son pH normal est légèrement alcalin (pH = 8,1 - 8,3). En milieu marin de légères variations du pH peuvent produire de grandes modifications dans les réactions physiologiques de divers tissus, de la même manière que dans les processus où interviennent les enzymes<sup>14</sup>.

Les déterminations réalisées à Cadix ont donné une valeur de pH = 8,0.

#### PRÉPARATION DES ÉPROUVETTES ET COMPOSITION DES PEINTURES ANTI-SALISSURES MISES A L'ESSAI

Les éprouvettes métalliques, de 200 × 300 mm de dimension, furent découpées d'une plaque d'acier de construction de 3 mm d'épaisseur, laminée à chaud, et dont la composition chimique est : C = 0,030% ; Mn = 0,38% ; Si < 0,025% ; P < 0,008% et S < 0,01%.

Après les avoir immatriculées, on les a soumises à un grenaillage avec de la grenaille d'acier anguleuse d'une granulométrie de 0 - 0,2 mm., et sous 5,5 kg/cm<sup>2</sup> de pression d'air ; ensuite on donne à toutes les éprouvettes une couche de «Wash-primer» (MIL-P-15328 B : Formule 117).

Postérieurement, et en tenant compte de la peinture anti-salissures qui allait leur être appliquée, on donne aux unes une peinture anticorrosive vinylique (MIL-P-15929 B : Formule 119) et à d'autres une peinture anticorrosive oléorésineuse (MIL-P-19453 : Formule 14 N). Lorsque la couche de peinture anticorrosive fut bien sèche, on applique le premier feuillet de peinture anti-salissures, et le second trois heures avant l'immersion.

Le Tableau II rassemble les compositions des peintures anti-salissures essayées. Les «vinyliques standard» et les «vinyliques à haute teneur en résine» sont semblables, et les «oléorésineuses» identiques, à les utilisées dans le travail<sup>15</sup>. Dans chacun de ces trois types de peintures expérimentées, il y a :

- une peinture de contrôle qui ne contient pas de composé organo-plomb et qui est à base d'oxyde cuivreux seulement,
- quatre peintures contenant des composés organo-plomb plus de l'oxyde cuivreux, et enfin quatre autres avec des composés organo-plomb seulement.

Les composés organo-plomb expérimentés sont l'acétate de triphényle plomb, le laurate de triphényle plomb, l'acétate de tributyle plomb et le laurate de tributyle plomb, que l'on désignera (en utilisant les mêmes symboles qu'<sup>16</sup>) par TPLA, TPLL, TBLA et TBLL, ) respectivement.

L'immersion des éprouvettes à Cadix fut effectuée en Avril 1967, c'est-à-dire à une excellente époque pour la fixation et le développement d'organismes. Les révisions ont été réalisées tous les deux mois périodiquement.

Les résultats que nous donnons ci-dessous correspondent à dix mois de séjour en eau de mer.

#### RÉSULTATS

La quantité totale d'organismes sur une éprouvette est indiquée par le numéro 100 si la surface est parfaitement propre, par 0 si elle est complètement couverte de salissures, et de même, par les chiffres intermédiaires suivant la proportion de surface intacte existant dans chaque cas.

Les intensités de fixation de chaque espèce, sur les différentes éprouvettes, sont portées (au Tableau IV) à l'échelle O.C.D.E.<sup>15</sup>, selon laquelle :

Intensité	No. d'organismes par dm <sup>2</sup>
(0)	moins de 5
(1)	5 - 10
(2)	11 - 25
(3)	26 - 50
(4)	plus de 50

Le Tableau III groupe les résultats obtenus avec les différentes peintures essayées après dix mois d'exposition. Au tableau IV on spécifie les salissures adhérentes à chaque plaque.

#### DISCUSSION DES RÉSULTATS

Avant de discuter brièvement les résultats obtenus, il faut signaler qu'une éprouvette témoin d'acier nu était, au bout d'un mois d'immersion, totalement recouverte d'organismes (Fig. 2).



Fig. 2. Eprouvette-control sans peinture, après 10 mois d'immersion.

#### Peinture vinylique standard

Avec ce liant, toutes les combinaisons de composés organo-plomb + Cu<sub>2</sub>O ont donné des résultats tout-à-fait satisfaisants (Tableau III), puisque toutes les éprouvettes étaient encore propres après les dix mois d'essai (Fig. 3).

Par contre, dans les formulations sans Cu<sub>2</sub>O, il n'y a que l'acétate de triphényle plomb qui ait aussi donné de bons résultats dans le même laps de temps. Avec l'acétate de tributyle plomb les résultats ont été un peu moins bons et ils ont été mauvais avec les peintures basées exclusivement sur les laurates de triphényle et tributyle plomb ; en effet, la première apparut couverte de salissures au bout de deux mois et demi et la seconde au bout de sept mois et demi (Fig. 4).

On observe une tendance assez accusée à la formation de petites cloques sur la couche de peinture anti-salissures, aussi bien sur l'éprouvette de contrôle (No. 1), que sur celles où le composé organo-plomb a remplacé en partie le Cu<sub>2</sub>O (Fig. 3). La substitution totale du Cu<sub>2</sub>O ne supprime pas non plus cette tendance au cloquage (Fig. 4), qu'on doit peut-être attribuer à un défaut possible dans la préparation ou la formulation exacte des peintures utilisées dans ce travail.

TABLEAU II (a)  
COMPOSITIONS DES PEINTURES ANTI-SALISSURES (gr.)

Composantes	P E I N T U R E S													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
OXYDE CUIVREUX	80	40	40	40	40					144	72	72	72	72
T P L A	—	20				20					20			
T P L L	—		20				20					20		
T B L A	—			20				20					20	
T B L L	—				20				20					20
VINILITE- VACH 30%	26,7	26,7	26,7	26,7	26,7	26,7	26,7	26,7	26,7	18,4	18,4	18,4	18,4	18,4
COLOPHANE 60% XILENE	13,35	13,35	13,35	13,35	13,35	13,35	13,35	13,35	13,35	35,85	35,85	35,85	35,85	35,85
TRICRESYL- PHOSPHATE	3	3	3	3	3	3	3	3	3	5	5	5	5	5
ACETATE DE CELLOSOLVE	8,8	8,8	8,8	8,8	8,8	8,8	8,8	8,8	8,8	1,1	1,1	1,1	1,1	1,1
XYLENE	13,15	13,15	13,15	13,15	13,15	13,15	13,15	13,15	13,15	—	—	—	—	—
BARYTE MOULUE	—	40	40	40	40	40	40	40	40	—	85	85	85	85
OXYDE DE FER ROUGE	—	20	20	20	20	20	20	20	20	—	20	20	20	20
BENTONE 38										0,7	0,7	0,7	0,7	0,7
ALCOOL ETHYLIQUE										0,3	0,3	0,3	0,3	0,3

TABLEAU II (b)  
COMPOSITION DES PEINTURES ANTI-SALISSURES (gr.)

Composantes	P E I N T U R E S													
	15	16	17	18	19	20	21	22	23	24	25	26	27	
OXYDE CUIVREUX	—	—	—	—	58,9	29,5	29,5	29,5	29,5					
T P L A	20					20				20				
T P L L		20					20				20			
T B L A			20					20				20		
T B L L				20					20				20	
VINILITE-VACH 30%	18,4	18,4	18,4	18,4					20					
COLOPHANE 60% XILENE	38,85	38,85	38,85	38,85	46,2	46,2	46,2	46,2	46,2	46,2	46,2	46,2	46,2	
TRICRESYL-PHOSPHATE	5	5	5	5										
ACETATE DE CELLOSOLVE	1,1	1,1	1,1	1,1										
XYLENE	—	—	—	—	5,6	5,6	5,6	5,6	5,6	5,6	5,6	5,6	5,6	
BARYTE MOULUE	85	85	85	85	23,5	23,5	23,5	23,5	23,5	23,5	23,5	23,5	23,5	
OXYDE DE FER ROUGE	20	20	20	20		20	20	20	20	20	20	20	20	
BENTONE 38	0,7	0,7	0,7	0,7										
ALCOOL ETHYLIQUE	0,3	0,3	0,3	0,3										
OXYDE DE ZINC					16,1	16,1	16,1	16,1	16,1	16,1	16,1	16,1	16,1	
STEARATE DE ZINC					1,8	1,8	1,8	1,8	1,8	1,8	1,8	1,8	1,8	
TALC					5,6	5,6	5,6	5,6	5,6	5,6	5,6	5,6	5,6	
HUILE DE POISSON POLYMERISE					11,8	11,8	11,8	11,8	11,8	11,8	11,8	11,8	11,8	





Fig. 3. Peintures vinyliques standard, après 10 mois d'immersion.  
 No. 2: Peinture renferment du  $Cu_2O$  + TPPLA  
 No. 3: " " " " TPPLA  
 No. 4: " " " "  $Cu_2O$  + TPPLA  
 No. 5: " " " "  $Cu_2O$  + TPBLA

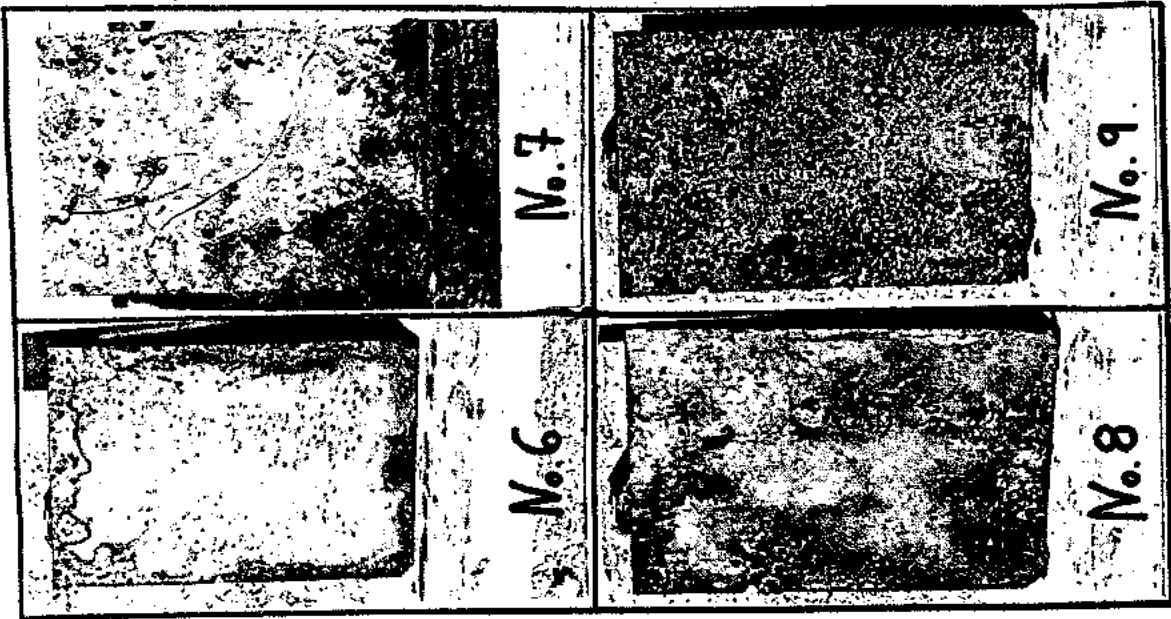


Fig. 4. Peintures vinyliques standard, après 10 mois d'immersion, excepté l'éprouvette No. 7, qui a été immergée pendant 2 mois et demi.  
 No. 6: Peinture renferment du TPBLA, sans  $Cu_2O$   
 No. 7: " " " " TPPLA  
 No. 8: " " " " TPBLA  
 No. 9: " " " " TPBLA

TABLEAU III  
COMPORTEMENT DES PEINTURES ANTI-SALISSURES  
(100 SUPERFICIE PROPRE; 0 SUPERFICIE TOTALEMENT COUVERTE DES SALISSURES)

Peinture	N° Eprouvette	Baie de Cadix 10 mois	Remarques
<i>Vinylique</i>			
Control	1	100	
Cu <sub>2</sub> O/T P L A	2	100	Cloques 25%
Cu <sub>2</sub> O/T P L L	3	100	" 30%
Cu <sub>2</sub> O/T B L A	4	100	" 30%
Cu <sub>2</sub> O/T B L L	5	100	" 25%
T P L A	6	100	" 35%
T P L L	7	30	" 25%
T B L A	8	85	Au bout de 2 mois et demi.
T B L L	9	30	Cloques 25%
			" 15%
<i>Vinylique haute en résine</i>			
Control	10	100	
Cu <sub>2</sub> O/T P L A	12	100	Cloques 15%
Cu <sub>2</sub> O/T P L L	13	100	" 5%
Cu <sub>2</sub> O/T B L A	14	100	" 5%
Cu <sub>2</sub> O/T B L L	15	100	" 20%
T P L A	16	100	" 10%
T P L L	17	30	Au bout de 2 mois et demi.
T B L A	18	40	Au bout de 4 mois et demi.
T B L L	19	100	Cloques 35%
		85	" 5%
<i>Oléo-résineuse</i>			
Control	20	20	
Cu <sub>2</sub> O/T P L A	23	100	} Au bout de deux mois et demi, peinture antisalissure détachée en quelques points.  Quelques cloques cassées. Au bout de 4 1/2 mois et demi. } Peinture anti-salissure détachée dans quelques points.
Cu <sub>2</sub> O/T P L L	24	99	
Cu <sub>2</sub> O/T B L A	25	100	
Cu <sub>2</sub> O/T B L L	26	100	
T P L A	27	100	
T P L L	28	40	
T B L A	29	100	
T B L L	30	100	

*Peinture vinylique à haute teneur en résine*

Pour ce qui est de ce liant, toutes les combinaisons de composé organo-plomb + Cu<sub>2</sub>O ont également donné des résultats entièrement satisfaisants au bout des dix mois d'essai (Fig. 5). Durant ce laps de temps, dans les formulations sans Cu<sub>2</sub>O, le comportement de l'acétate de tributyle plomb a été correct; celui du laurate de tributyle plomb assez bon, et il faut rejeter l'acétate et le laurate de triphényle plomb agissant seuls (Fig. 6). Leurs éprouvettes étaient en très mauvais état au bout de deux mois et demi et quatre mois respectivement.

Avec ces peintures à haute teneur en résine, la tendance au cloquage, mise en évidence dans la «vinylique standard», a notablement diminué.

*Peinture oléo-résineuse*

De même, les résultats ont été satisfaisants au bout des dix mois d'essais, pour les combinaisons organo-plomb + Cu<sub>2</sub>O dans ce liant, pour ce qui est d'éviter la fixation d'organismes (Fig. 7). Dans les peintures où les composés organo-plomb agissent seuls, le comportement a été correct dans le cas de l'acétate de triphényle plomb, de l'acétate de tributyle plomb et du laurate de tributyle plomb; mais il faut rejeter le laurate de triphényle plomb (Fig. 8). L'éprouvette contrôle (No. 20), basée exclusivement sur le Cu<sub>2</sub>O (sans composé organo-

plomb), fut rapidement converti d'organismes (Fig. 9).

Dans ce milieu oléo-résineux il n'y a pas eu de formation de cloques; cependant la peinture anti-salissures s'est détachée en plusieurs endroits (petits décollements longitudinaux isolés), en laissant voir l'imprimure anti-corrosive. Le Tableau V indique, dans chaque cas, le moment où l'on a observé cette détérioration de la peinture toxique. Il semble très probable que ce détachement soit principalement dû au contenu en Cu<sub>2</sub>O, puisque l'éprouvette-contrôle avec un 58,9% de Cu<sub>2</sub>O a été, dès le début, celle qui a présenté les symptômes les plus alarmants. L'addition du composé organo-plomb, remplaçant en partie le Cu<sub>2</sub>O, agit positivement pour réduire le détachement de la peinture anti-salissures. L'élimination totale du Cu<sub>2</sub>O supprime presque tout-à-fait ce défaut (Fig. 8). Cependant, même dans les zones de peinture abimée, on n'a pas remarqué une plus grande propension à la fixation d'organismes (Fig. 7).

CONCLUSIONS

Les résultats obtenus dans les eaux de Cadix (Espagne) avec des peintures anti-salissures, dans lesquelles, en partie ou totalement, l'oxyde cuivreux a été remplacé par des composés organo-plomb, confirment, en lignes générales, les résultats obtenus par Ilzro à Pearl Harbour et Miami Beach dans un travail antérieur<sup>4</sup>.



Fig. 5. Peintures vinyliques à haute teneur en résine, après 10 mois d'immersion.

No. 12 : Peinture renfermant du  $Cu_2O$  + T.P.L.L.  
 No. 13 :  $Cu_2O$  + T.P.L.L.  
 No. 14 :  $Cu_2O$  + T.B.L.L.  
 No. 15 :  $Cu_2O$  + T.B.L.L.

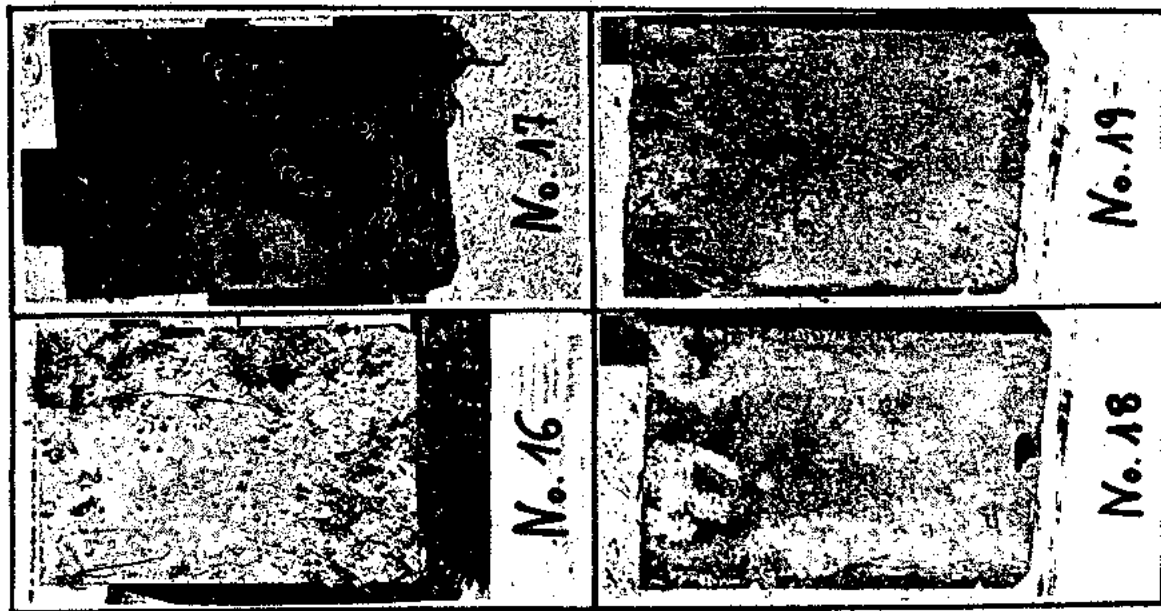


Fig. 6. Peintures vinyliques à haute teneur en résine. Eprouviettes Nos. 16 et 17 après 2 mois et demi et 4 mois et demi, respectivement; éprouviettes Nos. 18 et 19 après 10 mois d'immersion.

No. 16 : Peinture renfermant du T.P.L.L., sans  $Cu_2O$   
 No. 17 : T.P.L.L.  
 No. 18 : T.B.L.L.  
 No. 19 : T.B.L.L.

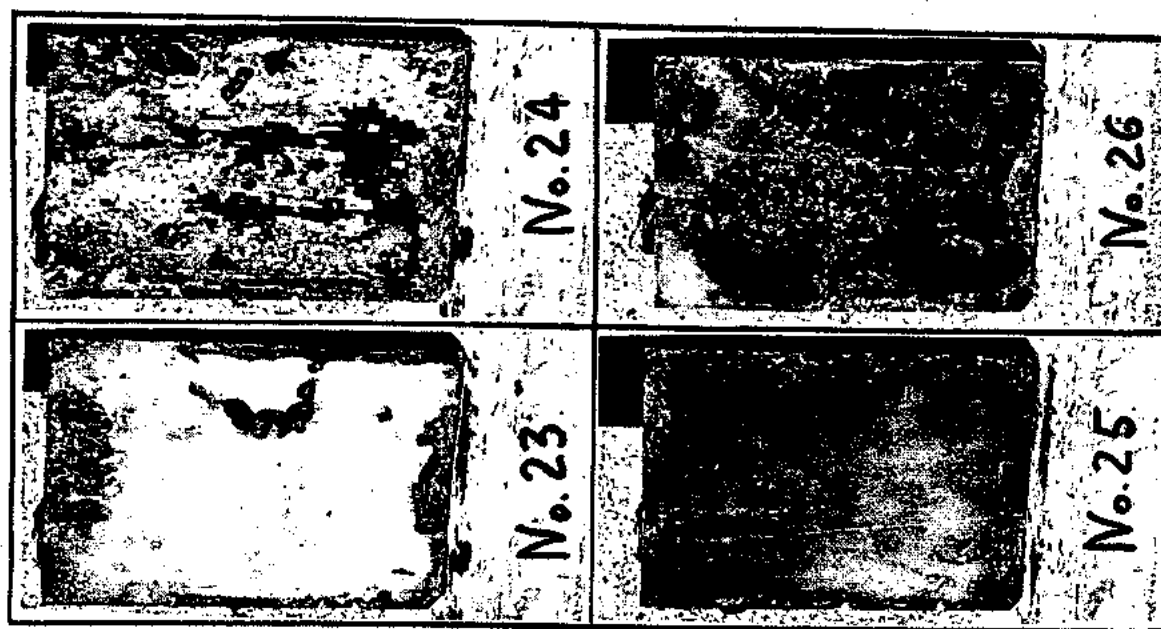


Fig. 7. Peintures époxy-résineuses, après 10 mois d'immersion.  
 No. 23 : Peinture renforcement du  $Cu_2O + TPPLLA$   
 No. 24 : " " " " " "  
 No. 25 : " " " " " "  
 No. 26 : " " " " " "



Fig. 8. Peintures époxy-résineuses, après 10 mois d'immersion, excepté l'éprouvette No. 28, qui a été immergée pendant 4 mois et défil.  
 No. 27 : Peinture renforcement du  $TPLLA$   
 No. 28 : " " " " sans  $Cu_2O$   
 No. 29 : " " " " "  
 No. 30 : " " " " "

TABLEAU IV  
ORGANISMES SALISSANTS SUR LES ÉPROUVETTES APRÈS 10 MOIS D'IMMERSION

No. Eprouvette	Organismes salissants
0 (sans peinture)	Ascidias ( <i>ciona intestinalis</i> ) (4); Serpula (4).
1	Aucune salissure.
2	" "
3	" "
4	" "
5	" "
6	" "
7	Balanus Amphitrite (4); B. Simplex (4); B. Neritina (4); (Après 2½ mois).
8	Balanus eburneus (2); Ascidias ( <i>ciona intestinalis</i> ) (0); Serpula (0); B. Simplex (1).
9	Balanus eburneus (2); Ascidias (1); Serpula (0); B. Simplex (2).
10	Aucune salissure.
12	" "
13	" "
14	" "
15	" "
16	Balanus Amphitrite (4); B. Simplex (4); B. Neritina (4); (Après 2½ mois).
17	Balanus Amphite (4); Ascidias (4); Serpula (1); B. Neritina (2); (Après 4½ mois).
18	Aucune salissure.
19	Balanus eburneus (1); Ascidias (0); B. Simplex (0); Alga enteromorfa (1).
20	Balanus eburneus (4); Ascidias (2); Serpula (4).
23	Aucune salissure.
24	Balanus eburneus (0); Ascidias (0); Serpula (0).
25	Aucune salissure.
26	" "
27	" "
28	Balanus Amphitrite (4) (Après 4½ mois).
29	" " (0)
30	" " "

Les quatre composés organo-plomb essayés révèlent de claires propriétés anti-salissures, et ils sont spécialement efficaces combinés avec l'oxyde cuivreux.

Dans les systèmes «vinyliques standard» et «vinylique à haute teneur en résine», le comportement des composés organo-plomb a été excellent lorsqu'ils ont été utilisés conjointement avec l'oxyde cuivreux; en effet, les éprouvettes se sont maintenues pratiquement libres de salissures organiques. Quand le composé organo-plomb remplace complètement le  $Cu_2O$ , c'est l'acétate de triphényle plomb qui a donné les meilleurs résultats dans les cas des peintures «vinylique standard», et l'acétate de tributyle plomb dans celui des «vinyliques à haute teneur en résine».

Les résultats obtenus à Cadix avec les peintures «oléo-résineuses» semblent être, au premier abord, plus prometteurs que ceux qui sont indiqués à<sup>6</sup>.

Au bout des dix premiers mois d'essai, les composés organo-plomb, remplaçant en partie ou en tout le  $Cu_2O$ , montrent toujours un bon comportement, et en tous cas, ce résultat est très supérieur à celui de la peinture de contrôle basée exclusivement sur l'oxyde cuivreux, qui, ainsi qu'a<sup>6</sup>, fut rapidement couverte d'organismes. La seule exception a été la peinture basée sur le laurate de triphényle plomb sans  $Cu_2O$ , qui est apparue avec un grand nombre de salissures après quatre mois et demi.

Un problème a surgi dans ce travail; c'est celui d'une certaine tendance, — mise en évidence sur part des revêtements anti-salissures essayés à Cadix —, au cloquage ou au détachement avec le temps. On en ignore les causes, dues peut-être à un défaut en rapport avec la préparation ou la formulation exacte des peintures employées. Il faut cependant



Fig. 9. Peinture oléo-résineuse. Eprouvette-contrôle avec 58,9% de  $Cu_2O$ , sans composé organo-plomb.

souligner; que ces phénomènes ont à peine été détectés avec les peintures «vinyliques à haute teneur en résine».

TABLEAU V.

TEMPS D'APPARITION DE DÉTACHEMENTS SUR LES PEINTURES ANTI-SALISSURES OLÉO-RÉSINEUSES

No. Epreuve	Temps d'apparition des détachements	Remarques
20	Aux 2 mois et demi	Depuis 7 mois et demi
23	» » » » »	couverte des salissures
24	» » » » »	
25	» 4 mois et demi	Traces de détachement
26	» » » » »	» » »
27	» » » » »	Quelques cloques isolées
28	» 2 mois et demi	Depuis 2 mois et demi
		couverte des salissures
29	» 7 mois et demi	Traces de détachement
30	» » » » »	» » »

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Nous tenons à remercier vivement l'Institut de Chimie Organique T.N.O. de Hollande qui a eu l'amabilité de nous fournir les composés organo-plomb essayés.

Nous voulons exprimer, de même, tous nos remerciements aux Drs. Rodriguez-Roda et Establier de l'Instituto de Investigaciones Pesqueras qui ont bien voulu nous communiquer les données hydrologiques de la Baie de Cadix.

Finalement, nous tenons à remercier aussi la collaboration prêtée pour la «Empresa Nacional Bazan» et pour le «Arsenal de la Carraca», qui nous ont facilité l'emplacement, l'entretien et la surveillance du radeau.

DISCUSSION

Dr. LITTAUER (U.S.A.): Je voudrais présenter des observations: Premièrement — Il est connu que les peintures basées à l'oxyde de cuivre, mercure et arsenic peuvent donner une protection pendant plusieurs années, les poisons organométalliques se sont composés pour créer une situation où la corrosion galvanique de fer et particulièrement d'aluminium n'est pas stimulée qui on trouve avec les peintures à base de cuivre. Deuxièmement — Y a-t-il des composés organiques de plomb si toxiques que les composés organiques d'étain et troisièmement — J'ai trouvé aux Etats-Unis que l'efficacité antisalissure de peintures basées à tributyl étain-oxyde et d'autres composés organiques d'étain lesquelles nous y avons examiné était à Miami assez efficaces, à Californie du Sud moins efficaces et à Hawaii ont indiqué une efficacité intermédiaire.

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Dr. GUILLEN (Espagne): Je suis d'accord avec ce qui vient de nous dire le Dr. Littauer et j'aime bien le remercier.

Dr. KÜHL (Allemagne): Vous avez parlé des salissures en général, et je voudrais demander quelles différences avez vous trouvées concernant des espèces des animaux et des algues à Cadix et à Barcelone.

Dr. GUILLEN: Vous connaissez très bien notre station d'essais à Barcelone et aussi son hydrologie et biologie. La station que nous avons à Cadix évidemment a de différences, au point de vue, des périodes de fixation, du plancton, des végétaux et des animaux, j'espère que bientôt nous pourrions faire une publication sur son hydrologie et son biologie.

# THE INFLUENCE OF CATHODIC PROTECTION ON THE ANTI - FOULING ACTION OF ANTI - FOULING PAINTS

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## SUMMARY

Theoretically cathodic protection may effect anti-fouling paints. Its effects are, however, unpredictable.

More knowledge of the possible effects is not only of general interest, but may also offer possibilities to improve the effective life of anti-fouling compositions. By means of laboratory tests and ships' trials data have been collected as to the influence of cathodic protection on the release of

copper from nine cuprous-oxide based anti-fouling paints. These tests have been carried out by copper analysis of aged paint coats and microscopical examination of cross-sections.

The conclusion of the tests is that the effect of cathodic protection on the performance of anti-fouling paints is not of practical importance.

## INTRODUCTION

Shipbottom paint systems have a double function: the protection of the steel against corrosion and the prevention of the settling of fouling. For this reason shipbottom paint systems consist of an anti-corrosive part and an antifouling part.

In practice the corrosion protection by anticorrosive paints can never be foolproof because of unavoidable damages in the paint coat. Cathodic protection offers, however, an ideal supplementary protection which is concentrated to those spots on the ship bottom where the protection by the paint coating fails.

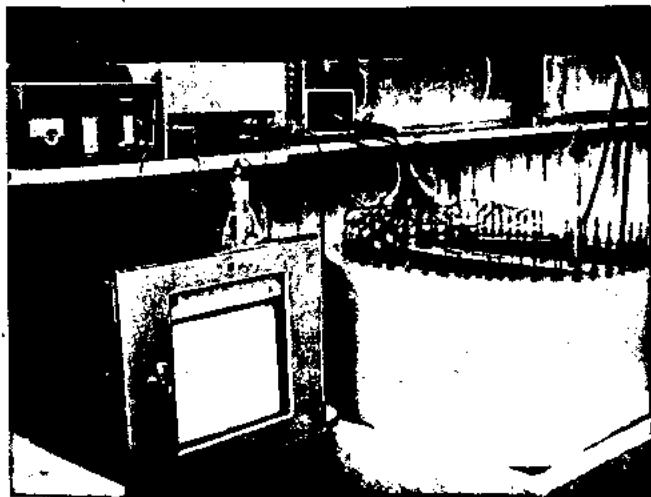
The action of anti-fouling paints is based on the active release of a toxic agent from the paint coat. The rate of loss of poison must be above a certain critical minimum value. If this leaching rate is or is getting lower than the minimum value referred to the paint has not or no longer a fouling

preventive action.

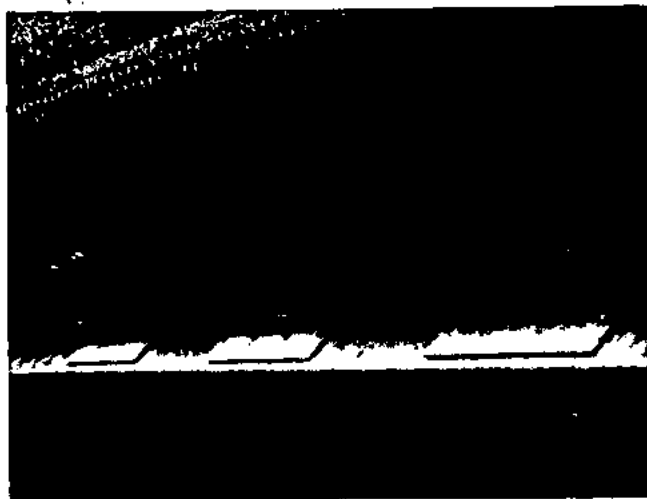
It is obvious that the toxic in the paint is being used most effectively if the leaching rate is just a little above the minimum critical value to prevent fouling at the moment fouling might occur, which means in practice during the time the ship is in dock or anchored inshore. The present-day anti-fouling paints however, loose most of their poison during the time the ship is on its way<sup>1</sup>. So the main part of the expensive poison in the anti-fouling paint is in fact being wasted (see Fig. 1).

An important improvement of the effective lifetime of anti-fouling paints would be effectuated if the leaching rate could be controlled that way that it is being suppressed when the ship sails and stimulated when the ship is in a dock, where fouling may occur.

Theoretically cathodic protection might be of influence on the leaching rate of anti-fouling paints and so it was considered worthwhile to investigate this phenomenon.



View of laboratory cathodic protection set-up.



View of practical testing using bilge-keel test panels.

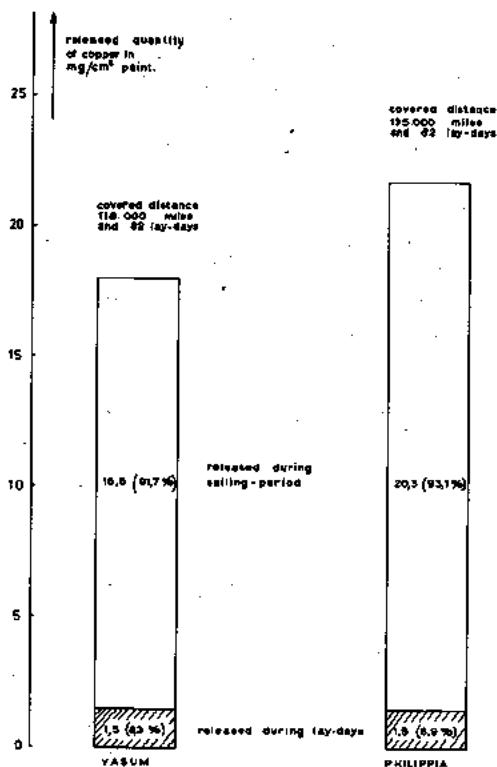


Fig. 1. Comparison of copper released during the sailing-period and the lay-days.

### THEORY

Most anti-fouling compositions contain cuprous oxide as the toxic pigment and their action is based on the release of copper. The chemical form in which copper is being released is still unknown. Probably the cuprous oxide will be transferred in a cupric-form<sup>3</sup>, but this may be a positively charged cupri-ion as well as a negatively charged cupriccomplex ion<sup>4</sup>.

The vehicle of anti-fouling paints plays an important role in the leaching process. Most anti-fouling paints contain a certain amount of rosin to obtain sufficient seawater sensitivity of the paint coat, which is necessary to enable diffusion of toxic material in the paint coat<sup>5</sup>.

Cathodic protection may have the following effects on the leaching rate of copper-containing anti-fouling paints:

- attraction, respectively repulsion of positively charged cupric-ions and negatively charged copper complex-ions by the negatively charged ship's hull,
- decrease of the solubility of cuprous oxide<sup>6</sup> and increase in rosin solubility<sup>2</sup> caused by the excess of hydroxyl ions near the cathode (= ship's hull),
- a higher concentration of positively charged ions present in seawater near the cathode (ship's hull), among which calcium- and magnesium ions.

The latter may react with rosin, leading to calcium- and magnesium resins, with a definite lower-solubility than rosin itself<sup>2</sup>.

So the effects possible are indistinct and eventually opposite to each other, so that it has no sense to predict a certain effect of cathodic protection on anti-fouling paints.

### TESTS

In order to study the effects of cathodic protection on anti-fouling paints tests have been carried out in the laboratory and on ships with three different anti-fouling paints. In a

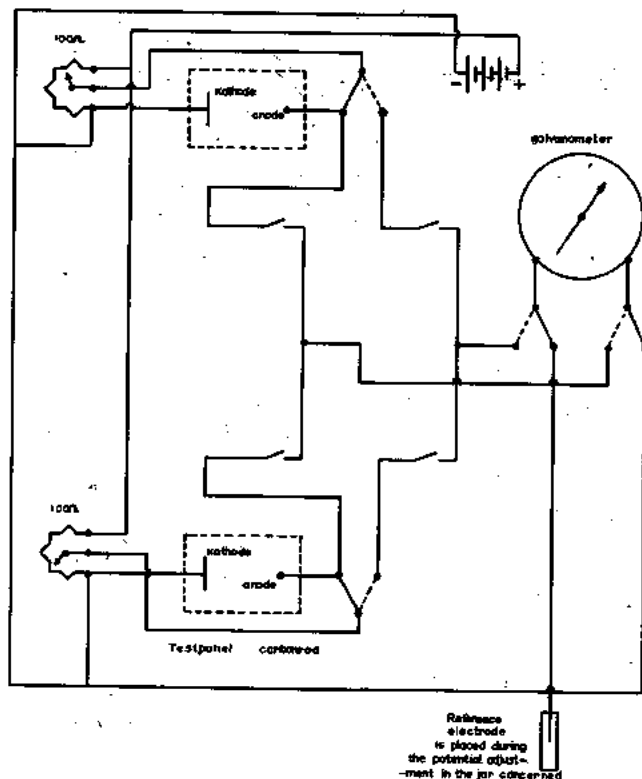


Fig. 2. Wiring diagram for the cathodic protection experiments in the laboratory.

a second test series six other paints have been examined by laboratory tests only.

### Laboratory tests

Panels covered with the paints under test have been aged in natural seawater of 30°C, the seawater being refreshed continuously and moreover stirred by bubbling air. Half the number of the test panels have been aged without, the other half with cathodic protection; (see wiring diagram in fig. 2).

During the ageing under cathodic protection the potential of the test panels was kept at -950 mV relative to a saturated calomel electrode by daily adjustment. The current density was recorded daily as well.

The test panels were made of steel and had the dimensions 10 × 8 × 0.2 cm. The paints had been applied by the spinning method. On the test panels for use under cathodic protection an area of approximately 1% of the total area had not been painted at all in order to enable adjustment of the correct potential (fig. 3).

After distinct ageing periods the leaching rate of the paints was determined according to a method described earlier<sup>1</sup>.

This determination has been carried out two times in succession, with and without using cathodic protection or just the other way about, dependent on the method of ageing. For test panels aged under cathodic protection the first leaching rate determination was carried out under this protection and the second without. For the test panels aged without cathodic protection the reverse sequence was followed. Between the two determinations the test panels were kept for 90 minutes under the conditions of the last determination.

During the determination using cathodic protection the potential was kept at -950 mV relative to a saturated calomel electrode the current density being recorded.



T A B L E 1  
COMPOSITION OF THE DRY PAINT IN PERCENTAGE BY VOLUME

Constituent	Paint								
	A	B	C	D	E	F	G	H	K
Vinylresin	25.2	43.0	—	—	—	18.0	18.0	45.0	45.0
Rosin	19.8	—	47.2	47.0	26.5	27.0	27.0	—	—
Fish oil	—	—	21.8	21.7	—	—	—	—	—
Chlorinated rubber	—	—	—	—	18.1	—	—	—	—
Chlorinated paraffine	—	6.9	—	—	6.6	—	—	8.0	—
Tricresylphosphate	8.5	—	—	—	—	8.0	8.0	—	8.0
Cuprous oxide	46.5	50.1	18.6	18.5	48.8	32.0	32.0	47.0	47.0
Zinc oxide	—	—	5.4	—	—	15.0	—	—	—
Iron oxide	—	—	—	5.9	—	—	15.0	—	—
Magnesium silicate	—	—	3.6	3.6	—	—	—	—	—
Zinc stearate	—	—	3.4	3.3	—	—	—	—	—
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

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FIG. 3: TESTPANELS USED.

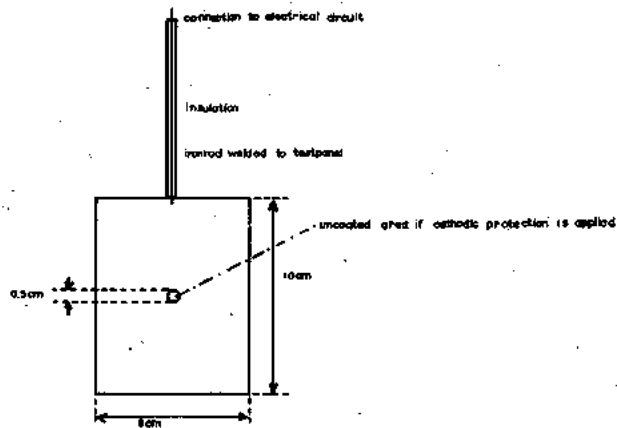


Fig 3 a: Laboratory testpanel

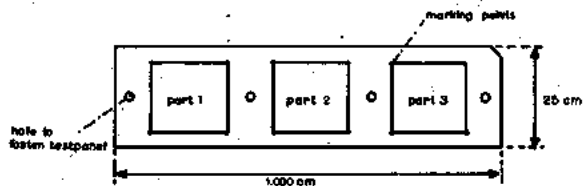


Fig 3 b: Testpanel for ships' trial.

Fig. 8. Testpanels used.

In addition to the leaching rate determination a cross section was made of the paint coat<sup>1</sup>. Moreover the amount of copper in the aged paint-coat was determined using an iodometrical method.

#### *Ships' trials*

The ships' trials have been carried out on two ships being cathodically protected by zinc anodes.

Test panels had been mounted on the bilge-keel of the ships, half the number electrically insulated (ageing without cathodic protection) and the other half welded to the hull (ageing with cathodic protection).

The test panels were divided in three parts (Fig. 3). The tests were carried out in duplicate, one panel on starboardside and one on port-side.

After ageing cross-sections have been made of the paint coat and the amount of residual copper in the paint coat was determined.

The ships concerned were tankers both operating on practically the same routes with a speed of 15-17 knots. The number of lay-days of both ships during the period of test was 82 days, the covered distance for ship 1 118,000 miles and for ship 2 135,000 miles.

#### PAINTS

The anti-fouling paints used for the tests were experimental paints except A and C which were made according to U.S. specifications.

The composition of the paints is given in table 1. The paints were of different kind, i.e. so-called soluble binder paints as well as so-called continuous-contact type paints.

As anti-corrosive paints were used red lead primers on vinyl resin or chlorinated rubber base.

#### RESULTS

The results of the experiments are compiled in the tables 2, 3 and 4. In the figures 3 and 4 the cross-sections of the paint coats are schematically given. Paint C tested on the ships and paint D tested in the laboratory were deteriorated, the preparation of cross-sections therefore not being possible.

The results show in general a reasonable to good reliability as can be seen from the duplicate tests. Only the leaching-rate determinations show big differences between du-

T A B L E 2

## RESULTS OF LABORATORY EXPERIMENTS WITH THE PAINTS A, B AND C

Paint	Test-panel	Time and method of ageing	Mean potential* and current density during ageing		Leaching-rate in $\mu\text{g}/\text{cm}^2\text{-day}$ determined after the ageing period with and without using cathodic protection	Mean potential* and current density during the leaching-rate determination using cathodic protection		Quantity of copper in $\text{mg}/\text{cm}^2$ paint		
			mV	$\mu\text{A}/\text{cm}^2$		mV	$\mu\text{A}/\text{cm}^2$	Before ageing (calculated**)	After ageing (determined)	Released during ageing
A	21	not aged	—	—	—	—	—	13.19	13.06	—
	22	not aged	—	—	—	—	—	18.47	18.26	—
	23	3 months with cathodic protection	-935	1.0	+C.P.: 40, -C.P.: 33	-950	1.7	13.36	11.35	2.01
	24	3 months without cathodic protection	-930	1.4	+C.P.: 43, -C.P.: 32	-950	2.3	13.52	11.75	1.77
	25	3 months with cathodic protection	—	—	-C.P.: 24, +C.P.: 28	-960	1.9	14.06	12.07	1.99
	26	3 months without cathodic protection	—	—	+C.P.: 22, +C.P.: 27	-950	1.7	13.03	11.25	1.78
	27	6 months with cathodic protection	-940	2.9	+C.P.: 24, -C.P.: 22	-950	3.2	13.32	7.94	5.38
	28	6 months without cathodic protection	-935	2.6	+C.P.: 27, -C.P.: 36	-950	2.9	13.73	8.86	4.87
	29	6 months with cathodic protection	—	—	-C.P.: 33, +C.P.: 37	-950	1.9	12.95	7.98	4.97
	30	6 months without cathodic protection	—	—	-C.P.: 34, +C.P.: 41	-950	1.8	13.48	8.98	4.50
B	11	not aged	—	—	—	—	—	9.08	9.00	—
	12	not aged	—	—	—	—	—	9.18	9.09	—
	13	3 months with cathodic protection	-940	1.0	+C.P.: 8, -C.P.: 6	-950	1.9	9.26	8.62	0.63
	14	3 months without cathodic protection	-935	0.7	+C.P.: 10, -C.P.: 4	-950	1.5	9.25	8.58	0.69
	15	3 months with cathodic protection	—	—	-C.P.: 8, +C.P.: 12	-950	1.8	9.67	9.09	1.09
	16	3 months without cathodic protection	—	—	+C.P.: 11, +C.P.: 9	-950	1.4	40.09	1.00	1.00
	17	6 months with cathodic protection	-935	1.3	+C.P.: 13, -C.P.: 0	-950	5.9	9.26	7.95	1.31
	18	6 months without cathodic protection	-935	1.3	+C.P.: 34, -C.P.: 0	-950	4.0	9.38	7.96	1.42
	19	6 months with cathodic protection	—	—	-C.P.: 2, +C.P.: 14	-950	1.5	9.64	7.96	1.68
	20	6 months without cathodic protection	—	—	-C.P.: 0, +C.P.: 6	-950	1.7	9.38	7.96	1.42
C	1	not aged	—	—	—	—	—	4.08	3.98	—
	2	not aged	—	—	—	—	—	4.04	3.91	—
	3	3 months with cathodic protection	-940	0.8	+C.P.: 28, -C.P.: 28	-950	2.4	4.15	2.49	1.66
	4	3 months without cathodic protection	-935	0.8	+C.P.: 37, -C.P.: 28	-950	2.9	4.19	2.02	2.17
	5	3 months with cathodic protection	—	—	-C.P.: 20, +C.P.: 35	-950	1.8	4.49	1.93	2.56
	6	3 months without cathodic protection	—	—	+C.P.: 21, +C.P.: 40	-950	1.7	4.28	2.29	2.09
	7	6 months with cathodic protection	-940	1.7	+C.P.: 20, -C.P.: 13	-950	2.8	4.33	0.39	3.94
	8	6 months without cathodic protection	-935	1.8	+C.P.: 23, -C.P.: 17	-950	3.0	4.12	0.57	3.55
	9	6 months with cathodic protection	—	—	-C.P.: 22, +C.P.: 34	-950	1.8	4.31	0.68	3.63
	10	6 months without cathodic protection	—	—	-C.P.: 24, +C.P.: 29	-950	2.0	4.54	0.78	3.76

\* relative to a saturated calomel electrode.

\*\* calculated from the quantity of paint per  $\text{cm}^2$  and the paint composition.

\*\*\* determination failed.

T A B L E 3

## RESULTS OF SHIPS' TRIALS WITH THE PAINTS A, B AND C

Paint	Test panel	Data of ships' trial					Defects in anti-fouling paint coat	Fouling of algae **	Quantity of copper in mg/cm <sup>2</sup> paint		
		Ship	Period of the test in months	Covered distance in miles	Place of the panel on the hull	Cathodic protection			Before ageing (calculated)	After ageing (determined)	Released during ageing*
A	381	1	12½	118,000	Portside	yes	none	none	19.5	3.3	16.3 (1.0)
	382	1	12½	118,000	starboardside	yes	none	none	22.3	3.5	18.8 (0.2)
	383	1	12½	118,000	portside	no	none	none	21.8	4.0	17.8 (0.5)
	384	1	12½	118,000	starboardside	no	none	none	22.9	3.8	19.1 (0.8)
A	404	2	15	135,000	portside	yes	none	none	31.7	10.8	20.9 (0.7)
	402	2	15	135,000	starboardside	yes	none	none	31.6	9.2	22.4 (1.5)
	403	2	15	135,000	portside	no	none	serious	31.7	10.0	21.7 (0.5)
	401	2	15	135,000	starboardside	no	none	none	33.6	11.3	22.3 (2.0)
B	385	1	12½	118,000	portside	yes	none	very serious	27.5	18.0	9.5 (0.8)
	386	1	12½	118,000	starboardside	yes	none	very serious	28.7	18.4	10.3 (1.2)
	387	1	12½	118,000	portside	no	none	very serious	27.4	18.8	8.6 (0.65)
	388	1	12½	118,000	starboardside	no	none	very serious	28.5	17.8	10.7 (0.4)
B	408	2	15	135,000	portside	yes	none	serious	24.4	18.6	5.8 (1.9)
	406	2	15	135,000	starboardside	yes	none	trace	24.9	19.6	5.3 (0.5)
	407	2	15	135,000	portside	no	none	very serious	25.3	18.9	6.4 (0.4)
	405	2	15	135,000	starboardside	no	none	trace	24.9	19.8	5.1 (0.3)
C	389	1	12½	118,000	portside	yes	30% dissolved?	none	16.4	***	—
	390	1	12½	118,000	starboardside	yes	15% dissolved?	none	15.7	***	—
	391	1	12½	118,000	portside	no	50% dissolved?	none	15.2	***	—
	392	1	12½	118,000	starboardside	no	50% dissolved?	none	15.1	***	—
C	412	2	15	135,000	portside	yes	20% dissolved?	none on	15.5	***	—
	410	2	15	135,000	starboardside	yes	40% dissolved?	anti-	15.2	***	—
	411	2	15	135,000	portside	no	45% dissolved?	fouling	14.3	***	—
	409	2	15	135,000	starboardside	no	70% dissolved?	coat	14.6	***	—

\* Numbers between brackets is the standard deviation of three apart determinations (part 1, 2 and 3 of a testpanel).

\*\* Arbitrary scale: trace - little - moderate - serious - very serious.

\*\*\* Determinations not possible because of dissolving of the paint coat.

plicate test panels especially when the determinations had been carried out using cathodic protection.

## DISCUSSION

The leaching rate determinations carried out under cathodic protection give in general higher values than those carried out without cathodic protection. This indicates an effect of cathodic protection. However, issue is not being confirmed by the results of the determination of the released copper and the examination of the cross-sections. These latter results are more reliable, showing a much better repeatability and being in accordance to each other. Moreover these results are based on long testing periods as compared with the duration of the leaching rate determination, which only takes 90 minutes.

The data obtained by leaching-rate determinations cannot be used to calculate the loss of toxic material during ageing; this fact has already been stated earlier<sup>1</sup>.

This does not explain, however, the discrepancy between the leaching rate determination under and without cathodic protection.

This fact requires further attention.

The results of copper release and the pictures of the cross-sections show that the effect of cathodic protection on copper

release from anti-fouling paints is neither quantitatively nor qualitatively of importance. Besides during the testing period no influence can be observed of current density on copper release.

The results of the ships' trials show also no differences with or without using cathodic protection. It is very remarkable, however, that the results of the test panels on starboardside and on port-side of one ship differ considerably. On both ships the release of copper from the paints proceeds faster on port-side than on starboardside. On ship 1 this difference is significant and on ship 2 probably significant. An explanation for this effect is not possible without more data and research work.

The results on the two ships are also different, not only quantitatively but also qualitatively. The quantitative difference between the results on ship 1 and 2 can be explained for paint A by the bigger distance covered by ship 2. Strange enough paint B has released much more copper during the test on ship 1. The qualitative differences as can be seen in the cross-sections in fig. 3 cannot be explained. These differences between tests on different ships and between tests on port-side and starboardside ask for further research.

Summarizing the available test data show that there is only a little effect of cathodic protection on anti-fouling paints (see fig. 5). This result is in accordance with other data<sup>8,9</sup>.

T A B L E 4

## RESULTS OF LABORATORY EXPERIMENTS WITH THE PAINTS D.E.F.G.H. AND K.

Paint	Test-panel	Time and method of ageing	Mean potential* and current density during ageing		Leaching-rate in $\mu\text{g}$ Cu/cm <sup>2</sup> -day determined after the ageing period with and without using cathodic protection	Mean potential* and current density during leaching-rate determination using cathodic protection		Quantity of copper in mg/cm <sup>2</sup> paint		
			mV	$\mu\text{A}/\text{cm}^2$		mV	$\mu\text{A}/\text{cm}$	Before ageing (calculated**)	After ageing (determined)	Released during ageing
D	9	19 weeks with cathodic protection	-945	3.6	+C.P.: 5, -C.P.: 5	-950	6.9	2.25	0.30	1.95
	10	19 weeks without cathodic protection	-940	4.6	+C.P.: 147, -C.P.: 34	-950	9.5	2.24	0.16	2.08
	12	19 weeks with cathodic protection	—	—	-C.P.: 5, +C.P.: 30 -C.P.: 0, +C.P.: 32	-950	3.6	2.14	0.41	1.73
E	1	19 weeks with cathodic protection	-945	10.5	+C.P.: 33, -C.P.: 10	-950	36	5.14	3.04	2.10
	2	19 weeks with cathodic protection	-935	8.6	+C.P.: 66, -C.P.: 13	-950	29	5.22	2.86	2.36
	3	19 weeks without cathodic protection	—	—	-C.P.: 11, +C.P.: 110	-950	5.4	5.62	3.69	1.93
	4	19 weeks with cathodic protection	—	—	-C.P.: 12, +C.P.: 68	-950	4.9	5.25	3.41	1.84
F	13	10 weeks with cathodic protection	-940	17.8	+C.P.: ***, -C.P.: ***	—	—	13.04	40.10	2.94
	14	19 weeks with cathodic protection	-940	8.0	+C.P.: ***, -C.P.: ***	—	—	12.61	10.50	2.41
	15	19 weeks without cathodic protection	—	—	-C.P.: 21, +C.P.: 15	-950	2.1	12.93	9.59	3.34
	16	19 weeks with cathodic protection	—	—	-C.P.: 26, +C.P.: 12	-950	2.3	12.67	9.19	3.48
G	20	19 weeks with cathodic protection	-940	2.2	+C.P.: 39, -C.P.: 20	-950	4.2	9.44	5.36	4.08
	21	19 weeks with cathodic protection	-945	2.2	+C.P.: 63, -C.P.: 23	-950	3.5	8.90	5.59	3.31
	22	19 weeks without cathodic protection	—	—	-C.P.: 22, +C.P.: 13	-950	2.9	8.43	5.49	2.94
	24	19 weeks with cathodic protection	—	—	-C.P.: 21, +C.P.: 64	-950	2.6	9.08	5.90	3.18
H	26	19 weeks with cathodic protection	-940	3.9	+C.P.: 20, -C.P.: 5	-950	12.5	9.87	8.71	1.16
	27	19 weeks with cathodic protection	-940	2.0	+C.P.: 48, -C.P.: 5	-950	5.3	9.84	8.95	0.89
	29	19 weeks without cathodic protection	—	—	-C.P.: 0, +C.P.: 28	-950	2.4	9.95	8.75	1.20
	30	19 weeks with cathodic protection	—	—	-C.P.: 0, +C.P.: 114	-950	2.5	11.65	9.07	2.58
K	31	19 weeks with cathodic protection	-925	3.7	+C.P.: 8, -C.P.: 29	-950	13.2	9.66	7.77	1.89
	33	19 weeks with cathodic protection	-935	3.2	+C.P.: 20, -C.P.: 2	-950	10.6	10.38	8.21	2.17
	35	19 weeks without cathodic protection	—	—	-C.P.: 4, +C.P.: 18	-950	2.4	10.31	9.23	1.08
	36	19 weeks with cathodic protection	—	—	-C.P.: 7, +C.P.: 143	-950	2.3	9.55	8.16	1.39

\* relative to a saturated calomel electrode.

\*\* calculated from the quantity of paint per cm<sup>2</sup> and the paint composition (corrected for solvent retention).

\*\*\* not determined because of bad condition of the paint.

Fig. 4 : Schematic picture of the cross sections of the paint coats of paint A and B

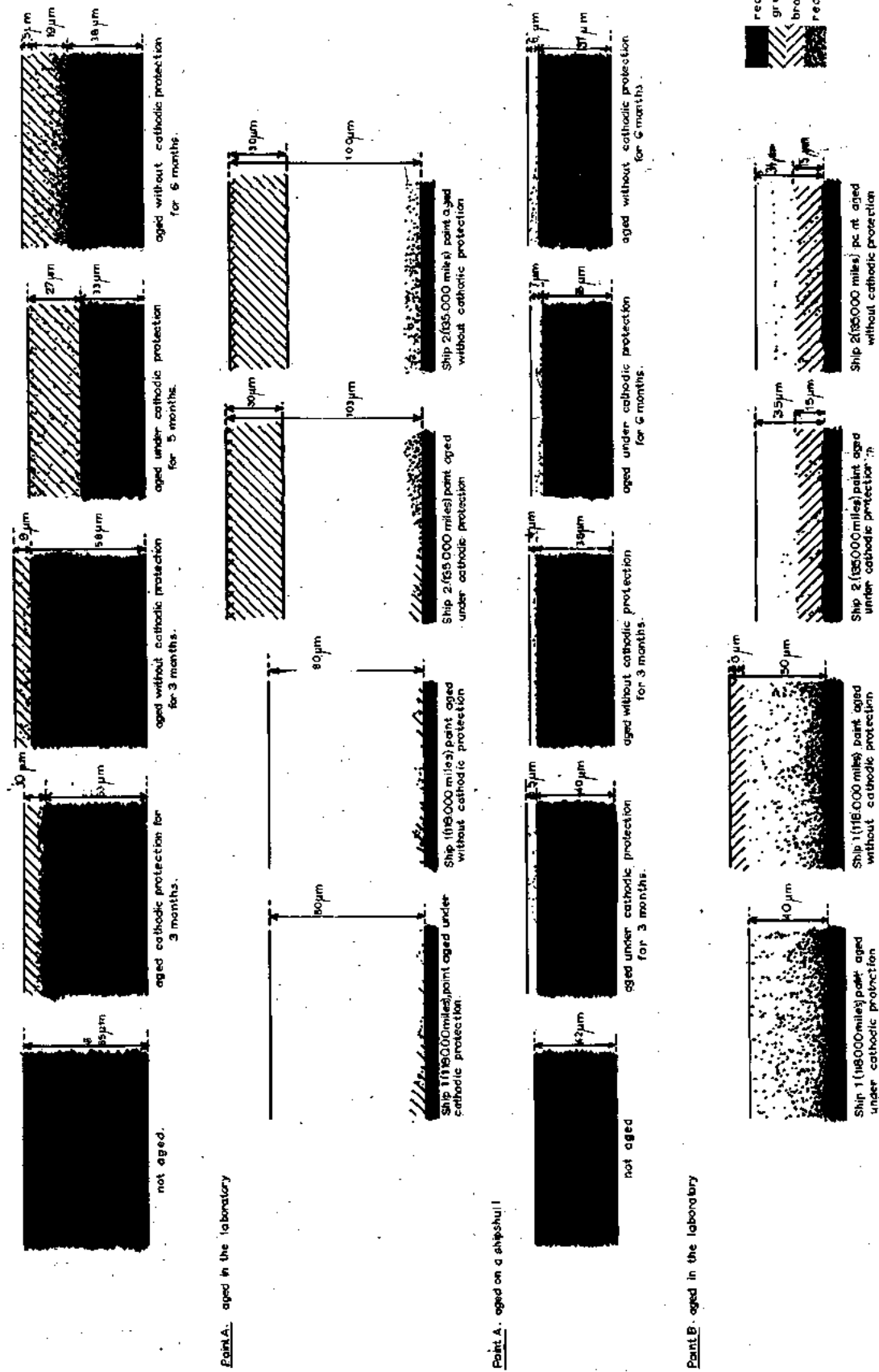
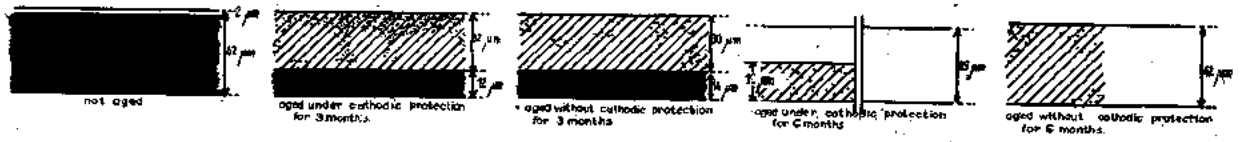
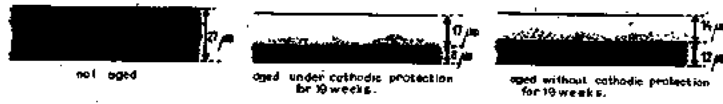


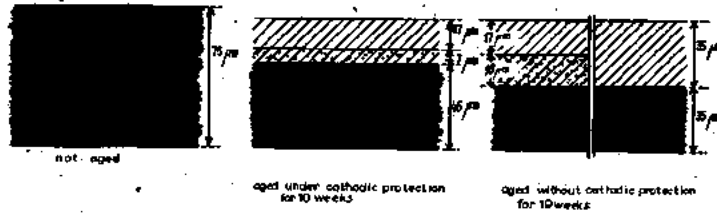
Fig. 4. Schematic picture of the cross-sections of the paint A and B.



Paint C aged in the laboratory



Paint E aged in the laboratory



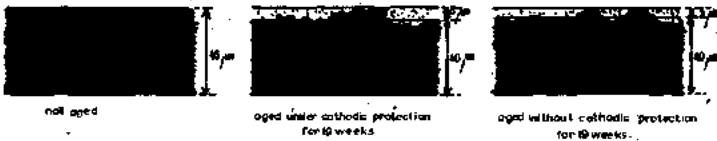
Paint F aged in the laboratory



Paint G aged in the laboratory



Paint H aged in the laboratory



Paint K aged in the laboratory



Fig. 5. Schematic picture of the cross-sections of the paints C, E, F, G, H and K.

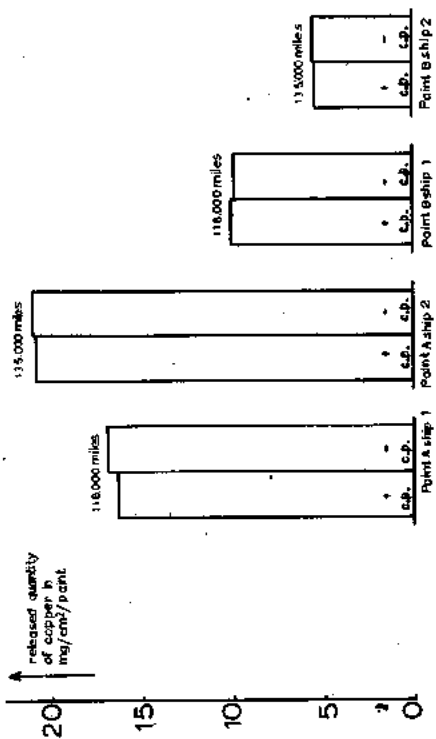


Fig. 5b: Amount of copper released during ship trials with or without cathodic protection (c.p.)

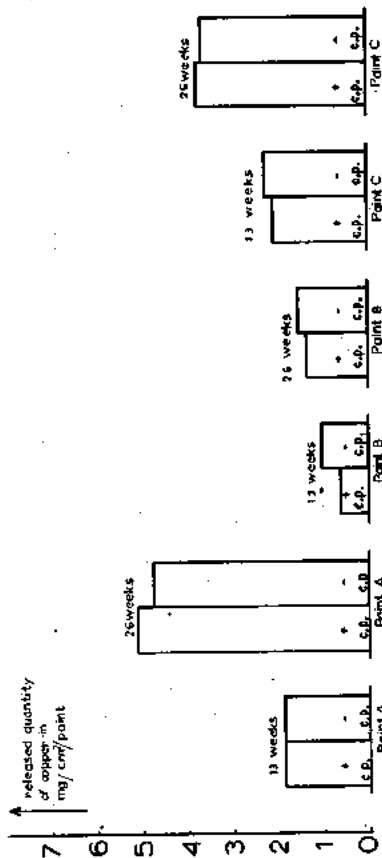


Fig. 5c: Amount of copper released during laboratory ageing with or without cathodic protection (c.p.)

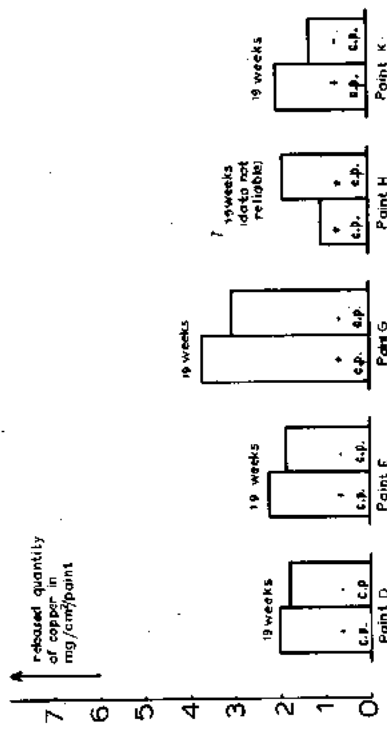


Fig. 6: Graphical picture of copper released from some anti-fouling paints aged in different ways with or without using cathodic protection.

## CONCLUSION

Cathodic protection on ships has no effect of any practical importance on the anti-fouling action of anti-fouling paints.

## ACKNOWLEDGEMENT

The author wishes to acknowledge gratefully the contributions of

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  - Koninklijke Nederlandsche Reedersvereniging (Ship-owners) and
  - Nederlandse Vereniging Voor Research op het Gebied Van Scheepshuidverven (marine paint manufacturers).
- He also desires to mention Mr. W. Mulder and Mr. R. Biersteker for their part in this work.

## LITERATURE

1. A.M. van Londen, A study of shipbottom paints, in particular pertaining to the behaviour and action of anti-

## DISCUSSION

J. SPARROW (England): Mr. van Londen says that antifouling protection is only needed when the ship is stationary because fouling only settles when the ship is still, or practically still, in relation to the surrounding sea water. There is very good experimental evidence to show that this is true with animal fouling such as barnacles and hydroids, but does he think that the evidence is as strong in the case of weed fouling? This point is particularly important at this time when weed fouling is becoming increasingly significant.

A. VAN LONDEN: I fully agree with Mr. Sparrow that the settlement of algae on a moving ship is still debatable. It is difficult to find reliable data about that phenomenon. On theoretical grounds I am quite sure that also algae are not able to settle under turbulent conditions as present along the hull of a moving ship.

J. CARSON (Canada): First I would like to compliment Mr. van Londen on his making a science of this particular study, and I think his work has contributed a great deal to the understanding of the behaviour of antifouling paints. With regard to the effect of cathodic protection on antifouling paints, we have found that there can be an effect on the cuprous oxide pigmented vinyl type. At what appear to be flaws in the

fouling paints. Netherlands Research Centre TNO for Shipbuilding and Navigation, Report 54 C (September 1963).

2. Woods Hole Oceanographic Institution, Marine Fouling and its Prevention. U.S. Naval Institute, Annapolis, Maryland, 1952.
3. J.P. Crennell, Cathodic Protection. Chem. and Ind. (Febr. 1954).
4. E. de Barry Barnett and C.L. Wilson, Inorganic Chemistry, London 1955, pag. 227.
5. A.M. van Londen, The mode of action of anti-fouling paints: Interaction between anti-fouling paints and seawater. VIIIth FATIPEC Congress 1964.
6. J.D. Ferry and D.E. Carritt, Action of Antifouling Paints Solubility and Rate of Solution of Cuprous Oxide in Sea Water. Ind. and Eng. Chem. 38, nr. 6 (June 1946).
7. H.W. van der Hoeven, Cathodic Protection in Relation to Ships Bottom Paints, J.O.C.C.A. 40, no. 8 (Aug. 1957).
8. Z. Ogusi, O. Kawada and T. Myasita, Study of the effect of Cathodic Electric Current on Fouling Resistance of Shipbottom Paint. J. Jap. Soc. Col. Mat. 32, no. 4 (1959).

anti-corrosive, «plugs» of metallic copper build up and when the plug gets to the antifouling layer it spreads out in concentric rings. The metallic copper replaces the cuprous oxide pigment in the antifouling. Because it is connected to the hull and cathodic, the copper patch becomes coated with calcareous cathodic salts. Fouling can and does settle on these patches. Although the percent of underwater hull area so affected is normally small, it is a definite effect of cathodic protection.

A. VAN LONDEN: As my informations are correct this effect will only occur using a high potential and especially near flows in the coating system, so that an electrical contact exist between antifouling coat and the metal substrate.

Dr. GUILLEN (Spain): I would like to ask Mr. van Londen what was the anticorrosive paint used and if the anticorrosive system used was in relation with the applied current.

A. VAN LONDEN: You will find these data in my paper. For the laboratory tests an impressed current system is used, with carbon rod anodes and a controlled potential of 350 mV relative to a saturated calomel electrode. For the ships' trials we had only the possibility to see ships protected with zinc anodes.



# INFLUENCE DU pH DU SUBSTRATUM SUR LA FIXATION DES ORGANISMES DU FOULING

Par Prof. E. MOR

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Gênes, ITALIE

## RÉSUMÉ

On étudie la fixation et l'accroissement des organismes du fouling en modifiant la valeur du pH du substratum.

A ce but on a utilisé des particuliers dispositifs alimentés par l'eau de mer à pH modifié.

La recherche nous a permis de vérifier les limites de fixation soit pour les pH acides que pour les pH alcalins et de constater une sélection parmi les diverses espèces.

## INTRODUCTION

L'eau de mer est un système complexe d'électrolytes bien tamponné dans la valeur de la concentration en ions hydrogène, de façon à ce que les valeurs du pH varient entre des limites assez étroites par rapport aux autres caractéristiques hydrologiques.

A la Station Expérimentale que nous avons en fonction depuis dix ans à proximité de l'entrée Est du Port de Gênes : long. 8°55'44" E — lat. 44°25'42" N (photo 1) et où nous disposons donc non seulement d'eaux côtières superficielles,

mais aussi d'eaux qui, quelque fertiles qu'elles soient en végétation, sont influées par le voisinage d'une ville de port, les valeurs du pH restent dans des limites assez étroites, c'est-à-dire entre 8,0 et 8,2. Les données, qui peuvent avoir quelques dixièmes en plus ou en moins, paraissent toujours à fait exceptionnelles et elles sont enregistrées de toute façon pour des temps très courts. Cela dit, il semblait utile de se demander quelles sont les limites du pH dans lesquelles les organismes du fouling peuvent se fixer et survivre.

Une telle idée semble pas étrangère à nos études sur les matériaux immergés en milieu marin, si on rappelle que dans la technique de la protection cathodique, on enregistre de fortes altérations dans la concentration des ions hydrogène. On sait en effet que l'attaque corrosive sur les plaques immergées se produit avec la formation de régions différenciées anodiques et cathodiques où, par des expériences convenables, on peut contrôler des valeurs du pH autour de 4 unités dans les cavités anodiques, et jusqu'à 13 dans les bulles cathodiques (9). On sait également que dans la protection cathodique absolue la valeur du pH sur les zones protégées atteint 10,9 unités pH.

Les auteurs ne sont pas d'accord au sujet de l'action antisalissure de la protection cathodique, puisque quelques-uns, admettent une action antifouling sûre et contemporaine tandis que d'autres affirment le contraire. (10,11,12,13)

Nous verrons comment le travail expérimental qui suit peut faire comprendre une telle divergence.

## PRÉPARATION DES SOLUTIONS D'EAU DE MER À pH MODIFIÉ.

Comme nous l'avons vu, l'eau de mer est une solution stablement tamponnée sur des valeurs autour de 8, la préparation des solutions ayant un pH différent et, en particulier près de cette valeur, comporte des difficultés surtout lorsqu'on veut éviter l'introduction d'ions étrangers à l'eau de mer.

Ces difficultés furent logiquement trouvées plus grandes pour les pH alcalins parce que la présence du magnésium et du calcium provoque des phénomènes de précipitation à partir des valeurs autour de 9,6.

Nos expériences démontrèrent que, au-dessous de pH 3,5 et au-dessus de pH 10,5 le fouling est totalement inhibé, d'où il résulte que la préparation des solutions, comme on le voit

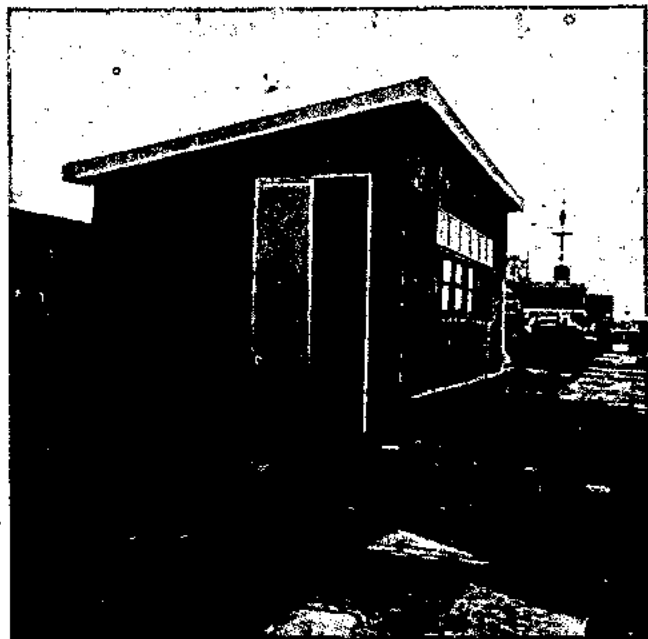


Photo 1. Station Hydrologique du Laboratoire pour l'étude de la corrosion marine des métaux, située dans l'Avant-port de Gênes (Italie).

TABLEAU I

EAU DE MER TAMPONNÉE A DIFFÉRENTS pH

pH obtenu	Agents employés
pH = 0	20,251 HCl gas (n.c.) /litre de même que : 75 ml HCl 37% /litre (*)
pH = 1	12,50ml HCl 37% /litre
pH = 2	1,75 ml HCl 37% /litre
pH = 3	3,90 ml HCl N /litre
pH = 4	2,70 ml HCl N /litre
pH = 5	2,58 ml HCl N /litre
pH = 6	1,41 ml HCl N /litre
pH = 7	0,42 ml HCl N /litre
pH = 8,2	eau de mer naturelle (v. tableau II)
pH = 9	1,51 ml NaOH N /litre
pH = 10	21 g ac. citrique + 14,35 g NaOH /litre
pH = 11	28 g ac. citrique + 18,7 g NaOH /litre
pH = 12	56 g ac. citrique + 35,7 g NaOH /litre
pH = 13	20,62 g NaOH (**)
pH = 14	51,6 g NaOH (**)

(\*) Il est indiqué d'employer du HCl gazeux pour éviter la dilution de l'eau de mer.

(\*\*) Dans le but de ne pas modifier de façon excessive la composition de l'eau de mer, on a préféré, au lieu d'ajouter une grande quantité d'agent chélateur, ajouter seulement du NaOH, laissant Mg et Ca se précipiter et décantant ensuite la solution limpide. Cette solution n'a pas été employée pour le contrôle du fouling.

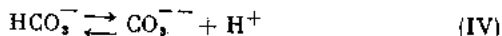
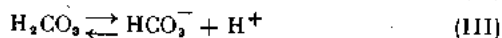
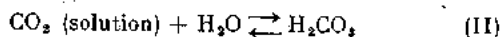
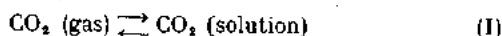
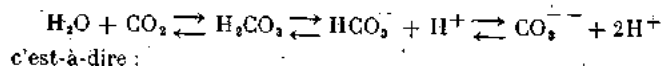
NOTE: L'acide chlorhydrique, la soude caustique et l'acide citrique employés correspondent aux produits CARLO ERBA RP.

TABLEAU II

CARACTÉRISTIQUES PHYSICO-CHIMIQUES DE L'EAU DE MER

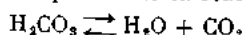
Salinité (‰)	= 37,76
Oxygène dissous (q)	= 6,64 ml /litre
Poids spécifique ( $\sigma_{20}$ )	= 28,95
Conductibilité électrique	= $5,33 \cdot 10^{-4} \mu S/cm$
Concentration ions	
hydrogène (pH)	= 8,2
Alcalinité	= 2,604 milliéquivalent g /litre
Anhydride carbonique totale	= 2,297 m Mol /litre

sur le tableau ci-joint, (v. Tableau II), peut être obtenue en ajoutant de l'acide chlorhydrique (HCl), pour les pH acides, et de la soude caustique (NaOH) jusqu'à pH 9,5, et de la soude caustique avec en plus un agent complexant, de pH 9,5 à pH 10,5. Une explication des difficultés rencontrées pour maintenir les valeurs du pH stables autour de 8 est fournie par les suivantes équations d'équilibre du gaz carbonique dans l'eau de mer.



Il y a une constante d'équilibre associée à chaque passage. La (III) et la (IV) sont extrêmement rapides comme toutes les réactions ioniques, de telle façon que nous pouvons les considérer comme instantanées, mais l'hydratation du  $CO_2$  dissous et la déhydratation de l'acide carbonique sont des réactions relativement lentes.

En particulier la réaction de déhydratation :



est de premier ordre et a une constante de vitesse d'environ  $20 \text{ sec}^{-1}$  à  $25^\circ C$ .

En ajoutant un acide fort (HCl), tous les équilibres du système mentionnés plus haut doivent se déplacer vers la gauche conformément à la loi d'action de masse.

Les deux processus (IV) et (III) seront pratiquement instantanés, mais la réaction (II) étant de beaucoup plus lente, on obtiendra tout de suite la formation de  $H_2CO_3$  et son accumulation en solution. En outre, le  $CO_2$  qui se forme par le processus (II) devrait se perdre dans l'atmosphère selon le (I) à une vitesse proportionnelle à la différence entre les pressions partielles dans les deux phases :

$$\frac{dQ}{dt} = K_a (P_{CO_2} - P'_{CO_2})$$

où :  $K_a$  est une constante de vitesse ;

$P_{CO_2}$ , la pression partielle du  $CO_2$  dans l'eau ;

$P'_{CO_2}$ , la pression partielle du  $CO_2$  dans l'air.

Cette vitesse a une valeur assez petite et dépend de façon évidente de beaucoup de paramètres, parmi lesquelles, précisément, l'agitation, la concentration, etc.

Il faut se rappeler, en outre, de la vitesse de diffusion moléculaire du  $CO_2$  à travers les couches acquises.

Tout ceci contribue à faire de sorte que le  $H_2CO_3$  reste comme tel dans la solution.

On comprend donc que, au-dessus de pH 4, l'influence du  $H_2CO_3$  augmente progressivement et, par conséquent, le déplacement de ces pH.

Le problème pour les pH alcalins présente, en dehors de cette influence, les difficultés mentionnées plus haut relatives à la précipitation du magnésium et du calcium (comme carbonate).

En effet, l'eau de mer — de laquelle on élimine par filtration ces éléments, ainsi que tous les autres qui peuvent être coprecipités avec eux — pourrait être chimiquement indiquée pour de spéciales expériences de laboratoire, mais pas pour celles en haute mer, étant donné que cette eau venue en contact, à travers les dispositifs poreux dont on parlera plus loin, avec l'eau de mer naturelle, reformerait un nouveau précipité, ce qui modifierait les conditions de l'expérience.

D'autre part on sait, combien ces éléments, et tout particulièrement le calcium sont nécessaires du point de vue biologique. On a alors pensé d'utiliser des complexants. Le problème était attaqué sous un double aspect, c'est-à-dire du point de vue tant analytique que biologique.

Les constantes de stabilité des complexes métalliques dans l'eau, par rapport aux valeurs les plus élevées et prenant volontairement en considération les éléments dont tous les organismes vivants (ainsi que le sodium, le potassium et le calcium) ont besoin, mentionnés au Tableau III, démontrent clairement les difficultés pour maintenir le magnésium en solution.

Il semble, d'autre part, qu'il y ait, du point de vue biologique, des coordonnants spécifiques pour ces métaux (et peut-être pour le vanadium qui, dans les ascidies, a le rôle du fer dans le pigment transporteur d'oxygène du sang). Le degré de sélectivité (dans l'ascidie «Phallusia mammillata», la concentration du vanadium est de  $10^6$  fois plus grande que dans l'eau de mer dans laquelle elle vit) parmi les ions métalliques serait donc élevée par rapport à celui qu'on trouve dans les modèles conventionnels de substances chélatantes.

Il est probable aussi que les complexes à l'éthylène-diamine et à l'acide éthylène-diamine-tétracétique ne constituent pas un obstacle pour l'utilisation des ions métalliques de la part du benthos sessile.

**TABEAU III**  
**CONSTANTES DE STABILITÉ DE COMPLEXES MÉTALLIQUES**

(valeurs logarithmiques ( $\log_{10}$ ) dans l'eau à 20°C)

Agent complexant	Métaux pris en considération						
	Fe <sup>3+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Co <sup>2+</sup>	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Mg <sup>2+</sup>
Glycocolle	10	15	9	9	8	5,5	4
Cystéine	—	—	18	16	6	4	4
Histidine	—	19	12	13	9	4	4
Ethylène-diamine	—	20	12	14	9,5	5	0,4
Acide éthylène-diaminotétracétique (ETDA)	24	19	16	16	14	13,5	9
8-Oxyquinoléine	36	23	8,5	17	15	12	4,5
Acide oxalique	10	6	5	4,5	4,5	4	3
Tétracycline	25	13	9	10	9	8	4
Acide citrique	—	14,21	—	—	—	—	—

On sait, en effet (Hill-Cottingham et Lloyd-Jones, 1964) que l'EDTA, complexe ferrique, est, par exemple, absorbé tel quel par certaines plantes et par la suite séparé métaboliquement pour l'utilisation du fer.

D'autre part, étant donné qu'il est absolument nécessaire, pour nos recherches, de réduire le plus possible les doutes en ce qui regarde l'éventuelle sélectivité du «fouling» en fonction du pH, nous avons pensé de limiter au maximum les actions extérieures en employant l'acide citrique qui, ainsi qu'on le sait, fait partie, avec les acides de ce cycle, des agents liants de la cellule.

Cet acide, parmi les nombreuses substances expérimentées, nous a permis de préparer des solutions limpides et assez stables d'eau de mer (voir Tableau II) aux pH 10, 11, 12. Le pH 9 fut trouvé assez stable en ajoutant seulement NaOH N.

Dans le Tableau IV on a mentionné certains pH alcalins bien tamponnés en employant en même temps de l'éthylène-diamine et de l'acide citrique. Cette combinaison a permis de préparer des solutions limpides et stables jusqu'à des valeurs de concentration alcaline élevée, mieux que ce que l'on obtient par le sel tétrasodique de l'acide éthylène-diamine-tétracétique (EDTA-Na<sub>4</sub>). Ces solutions n'ont d'ailleurs pas été employées pour le contrôle de la fixation du «fouling».

On a préparé, enfin, par la même méthode mentionnée plus haut, et là où les expériences le demandaient, toutes les valeurs du pH intermédiaires entre celles mentionnées au Tableau I.

**TABEAU IV**

**EAU DE MER A  
pH ALCALIN TAMPONNÉE DE FAÇON STABLE**

pH obtenu	Agents employés
pH = 10	14 g acide citrique + 6 g éthylène-diamine + 7,6 g NaOH /litre
pH = 11	56 g acide citrique + 51,5 g éthylène-diamine + 5,58 g NaOH /litre
pH = 12	50 g acide citrique + 102 g éthylène-diamine + 28,1 g NaOH /litre

**MISE AU POINT DES DISPOSITIF POREUX POUR  
L'ÉTUDE DE L'EAU DE MER À pH MODIFIÉ.**

Le système le plus rationnel pour assurer la présence des solutions à pH modifié sur le substratum de fixation des organismes du «fouling», semble être celui de recourir à des vases poreux.

En effet, cette question avait déjà été l'objet d'une attention spéciale de notre part, et nous avait menés à la réalisation d'un dispositif (1, 2) qui permet l'étude du phénomène corrosif en haute mer, en excluant précisément le phénomène microbiologique (fouling) par l'emploi de parois poreuses appropriées. Les solutions à pH modifié devaient cependant maintenir mouillé le vase poreux de façon continue, en assurant, donc, pour une «couche limite» suffisante, où les larves et les spores pouvaient se fixer, une modification précise et constante pour toute la durée de l'expérience.

On pouvait penser que la valeur de la porosité n'avait pratiquement pas de sens, dans des limites raisonnables, tandis que la valeur du flux était d'extrême importance.

En effet, des valeurs élevées non seulement auraient pu influencer la fixation, mais, en «polluant» un certain volume d'eau de mer à proximité de la surface où se fait l'expérience elles auraient pu créer des conditions de milieu pré-sélectives.

Des valeurs d'écoulement insuffisantes auraient, d'autre part, certainement annulé la valeur de l'expérience en créant sur le substratum un gradient de pH et facilitant les phénomènes d'osmose.

L'étude de la vitesse d'écoulement a été effectuée également en laboratoire en reliant l'ouverture cylindrique, au moyen d'un petit tube de polythène, à un récipient à niveau constant.

Il a été ainsi possible de trouver la différence de niveau hydrostatique juste, en éliminant les porosités defectueuses.

Après divers essais sur différentes substances poreuses, on a choisi des vases poreux en kaolin, de la capacité utile d'environ 900 c.c.

Cinq vases ont été choisis pour chaque valeur de pH ou de fraction de pH, et par des épreuves en haute mer on est arrivé à établir que les meilleures résultats étaient obtenus par des vitesses d'écoulement d'un litre par 24 heures.

Les suivantes conditions étaient satisfaites de cette façon :

- La valeur du pH sur la paroi poreuse externe restait, pendant toute la durée de l'essai, égale à celle de la solution expérimentée.
- Le découlement n'influait pas les caractéristiques

TABLEAU V  
ESPÈCES SESSILES DOMINANTES  
DANS LE «FOULING» DU PORT DE GÈNES

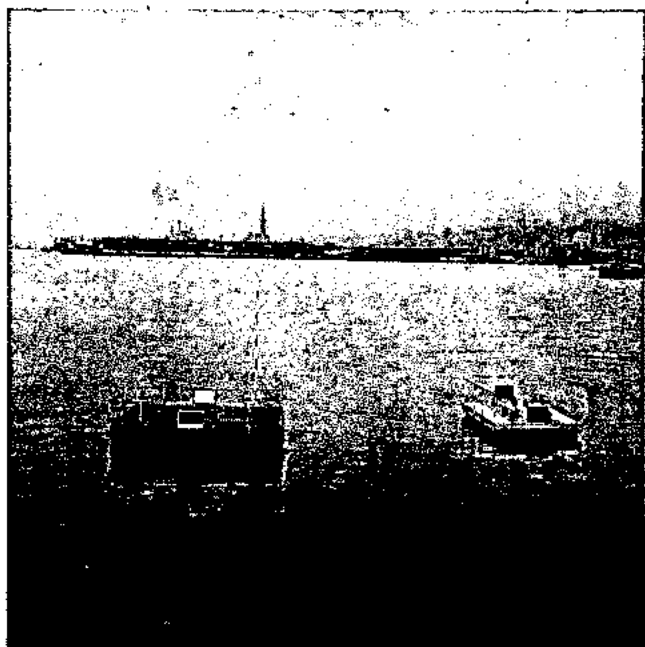


Photo 2. Les radeaux d'essai situés tout près de la Station Hydrologique.

hydrologiques de l'eau de mer dans le voisinage du vase.  
c) Le renouvellement du volume entier en 24 heures garantissait la constance du pH même pour les valeurs les plus critiques.

#### INFLUENCE DE L'EAU DE MER À pH MODIFIÉ SUR LE BENTHOS SESSILE

La surface d'eau située à l'extrémité du Môle Cagni, près de la sortie Est du Port de Gènes, à proximité de la Station Hydrologique du Centre — milieu désormais contrôlé depuis une dizaine d'années dans toutes ses caractéristiques hydrologiques et biologiques — a été choisi comme milieu pour les expériences.

Deux radeaux d'essai (photo 2) qui y avaient été amarrés, ont permis d'installer des récipients à niveau constant et des raccords en polythène aux vases poreux immergés à environ 60 cm sous le niveau de la mer.

Chaque expérience a été répétée pour chaque groupe de 5 vases au moins deux fois pendant deux années consécutives dans la même période saisonnière.

Les épreuves en blanc étaient faites des dits vases où le liquide effluent était l'eau de mer naturelle, ou de vases à vitesse de flux = 0.

Du contrôle biologique des organismes du fouling présents dans le milieu d'expérience, et mentionnés dans le Tableau V, on a trouvé que les périodes les plus indiquées pour les épreuves étaient comprises entre les mois de mai-août correspondant à la densité maximum d'espèces tant animales que végétales. La durée de chaque expérience variait de 12 à 25 jours, mais elle était toujours interrompue quand la vitesse d'écoulement sur l'épreuve en blanc tombait à moitié.

Certains auteurs, et tout spécialement Pomerat et Weiss (1946), ont constaté une influence du substratum sur la fixation des organismes du fouling, mais toujours par rapport aux caractéristiques physiques superficielles (lisse, rugueux, poreux, imperméable, etc.) ou chimiques reliées au taux de lixiviation (métaux ou compositions capables de donner naissance à des ions toxiques).

Nous n'avons pas trouvé, par contre, qu'on ait jamais pensé faire des recherches comparatives à l'échelle des pH.

Spongiaires :	<i>Sycon raphanus</i> (O. Sch. m.) <i>Lewconia crambessa</i> (Heck.)
Hydriaires :	<i>Tubularia mesembrianthemum</i> (Allman) <i>Eudendrium racemosum</i> (L.) <i>Ventroma halecioides</i> (Ald.)
Plathelminthes :	<i>Thysanozoon brocchii</i> (Grube)
Bryozoaires :	<i>Bugula avicularia</i> (L.) <i>Zoobothryon verticillatum</i> (D. Ch.) <i>Pedicellina cernua</i> (Pall.) <i>Membranipora</i> sp.
Polichètes :	<i>Hydroides norvegica</i> (Gunn.) <i>Spirorbis laevis</i> (Quatr.) <i>Sabella pavonina</i> (Savigny) <i>Polydora ciliata</i> (Johnst.) <i>Spirographis spallanzanii</i> (Viviani)
Mollusques :	<i>Mytilus galloprovincialis</i> (Lam.) <i>Ostrea edulis</i> (L.)
Cirripèdes :	<i>Balanus trigonus</i> (Darw.) <i>Balanus amphitrite</i> (Darw.) <i>Balanus eburneus</i> (Gould.) <i>Balanus perforatus</i> (Brug.)
Tuniciers :	<i>Ciona intestinalis</i> (L.) <i>Styela plicata</i> (Les.) <i>Didemnum maculosum</i> (M. Edw.) <i>Botryllus schlosseri</i> (Pall.)

Les résultats biologiques détaillés seront évidemment publiés séparément. Ici nous voulons seulement affirmer que nos recherches ont mis en évidence tant les limites de survivance qu'une sélection des organismes du fouling en fonction de la concentration des ions hydrogène.

Et précisément :

1) Les limites, au-delà desquelles la fixation n'a pas lieu, sont, pour les pH acides 3,5-4 et, pour les pH alcalins 10-10,5. Pour les pH 3,5 et 10,5 la surface des vases poreux reste propre (photo 3 et 14).

2) Les organismes qui résistent aux pH les plus bas sont des algues trouvées à pH 4 (photo 4) limitées aux zones exposées à la lumière. A des pH à peine supérieurs 4,5 (photo 5) les Balanes (limités à *B. amphitrite*) réussissent à se fixer, et par la suite *Ciona*, *Botryllus*, *Bugula*, *Hydroides*, *Serpules*, mais à une densité toujours inférieure à l'épreuve témoin (photo 9), et avec une très faible adhérence au support jusqu'à pH 5-5,5 (photo 6 et 7). Seulement à partir de pH 6 (photo 8) on constate une plus grande adhérence, une augmentation de densité et l'apparition nette des *Serpules* des *Bryozoaires* et des *Tubularia*.

3) Les organismes qui résistent aux pH les plus hauts sont encore les Balanes (*B. amphitrite*).

Mais leur dernière apparition, constatée à pH 10 (photo 13) est représentée par des rares individus. Également à pH 9,5 (photo 12) les Balanes sont peu nombreuses et peu développées.

Les *Serpules* semblent assez sensibles aux pH basiques : on ne les trouve que sur la coquille des Balanes et lorsque le pH descend à 9 (photo 11). Seulement à cette valeur on commence à noter la présence de quelques *Bugula*. Pour les valeurs de pH comprises entre 8,5 (photo 10) et 9 on a finalement constaté un fait intéressant, c'est-à-dire un plus grand



Photo 3. pH = 3,5: la surface du vase est absolument dépourvue de fouling.



Photo 4. pH = 4: il n'y a pas de fixation animale mais seulement de la boue bactérienne (slime) et des algues vertes (enteromorpha) du côté exposé à la lumière.



Photo 5. pH = 4,5: il y a un début de fixation animale avec quelques balanes amphitriles et quelques hydroides (tubularia). Du côté exposé à la lumière on note encore des algues vertes.



Photo 6. pH = 5: on voit beaucoup plus de boue bactérienne, d'algues vertes, de balanes amphitriles, d'hydroides, mais la densité du fouling est encore inférieure à celle du témoin. Il n'y a pas encore de serpules et de bryozoa.



Photo 7. pH = 5,5: on note que toutes les espèces du fouling sont en hausse, en comparaison du pH = 5, mais leur densité est encore inférieure au pH = 8 et au témoin.



Photo 8. pH = 6: les espèces du fouling sont presque égales à celles du témoin, seulement leur densité est légèrement inférieure et les espèces à coquille calcaire montrent un pouvoir de fixation plus fort.

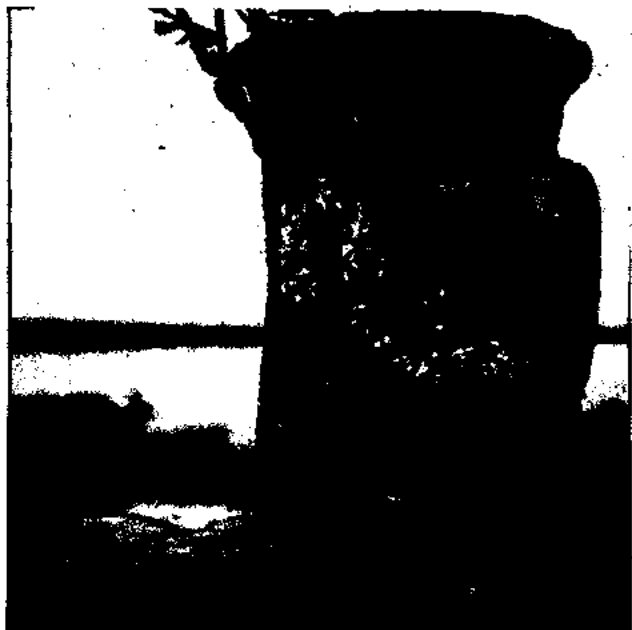


Photo 9. pH = 8,2 ou témoin: toutes les espèces du fouling susdites sont présentes en forte densité. On note, en plus, des serpulides. (Hydroides norvegica) et des briozoa.



Photo 10. pH = 8,5: la densité du fouling est presque égale à celle du témoin, mais les espèces à coquille montrent une croissance plus grande.



Photo 11. pH = 9: on note un début d'inhibition et de sélection du fouling, les balanes sont peu nombreuses et dispersées. On voit encore de la boue bactérienne, des algues vertes, quelques hydroides et quelques bugula.



Photo 12. pH = 9,5: il y a seulement de la boue bactérienne avec peu d'algues vertes et de balanes.



Photo 13. pH = 10: on note encore sur la boue bactérienne quelques algues vertes et quelques balanes, mais en densité graduellement inférieure.



Photo 14. pH = 10,5: surface dépourvue de fouling. A ce pH il semble que la fixation de la vie animale et végétale ne soit pas possible.

développement, par rapport aux contrôles à pH 8,2 (photo 9), des espèces à coquille calcaire. Comme il est toujours de règle dans les phénomènes biologiques, de telles expériences — et spécialement l'usage de l'acide citrique comme agent complexant — seront confirmées ultérieurement. Certes, ce dernier aspect du plus grand développement des espèces à coquille calcaire pour des pH légèrement alcalins semble susceptible d'être considéré ensemble avec les mêmes équations d'équilibre du système gaz carbonique que nous avons mentionné plus haut.

En effet, il n'y pas de doute qu'une légère augmentation d'alcalinité doit faciliter la formation de la coquille calcaire.

Les résultats si souvent contradictoires et opposés sur le pouvoir anti-salissure de la protection cathodique trouverait une explication, étant facile de rester en deça ou de tomber au-delà des valeurs de survivance, suivant le milieu, le mouvement, la porosité du revêtement, etc.

Mais les rapports entre la survivance du fouling et notre système carbonique ne s'arrête pas ici. Nous pouvons observer, en effet, qu'aussi la limite de la fixation vers les pH acides coïncide justement avec les valeurs au dessous desquelles l'influence de l'acide carbonique cesse.

Ce n'est pas par hasard que le minimum pH, qu'on peut obtenir avec du CO<sub>2</sub> au 100% à la pression atmosphérique, est égal à 3,95 (limite des algues vertes constatée par nous).

La survivance du benthos sessile serait donc comprise entre les limites du système carbonique, grosso modo entre pH 4 et pH 10, avec une capacité de réaction et d'adaptation au milieu extérieur, c'est-à-dire qu'il présente, par rapport aux valeurs acides, des variations de la concentration des ions hydrogène jusqu'à plus de 10.000 fois, contre des variations de moins de 100 fois, par rapport aux valeurs basiques.

Il semblerait, par conséquent, que dans cette direction où il faut prendre en considération la valeur de la réserve alcaline et du coefficient d'activité des ions OH<sup>-</sup> de l'eau de mer (f<sub>OH</sub> = 0,45), il pourrait être intéressant, par des complexants appropriés, mener des recherches pour l'inhibition du fouling.

Prof. KUWABARA (Japan): Je demandé pour quelle raison dans pH bas y - a - t - il une attaque sur la coquille du base calcaire.

Prof. MOR: Je pense qu'on peut trouver la réponse dans une réaction à l'ambiance de la part de l'organisme vivant, ce qui exige évidemment une résistance accrue du ciment de la base, qui facilement vient à obliterer, avec une composante organique, la structure poreuse du vase, en favorisant la formation d'un gradient local de pH.

Le ciment de base d'autre part n'est pas seulement du calcaire. Il présente une composition bien plus complexe et résistante aux variations du pH.

Dr. LITTAUER (U.S.A.): Il faut dire que j'ai trouvé cette communication très intéressante car dès demain je vais parler d'une étude relative à la vôtre. Je ferai demain une description des problèmes que nous rencontrons quand on travaille à hautes pH (nous l'étudions encore) et que nous les attribuons au précipitation. C'est pour cela que nous avons utilisé des agents complexes de ce type que Dr. MOR nous a parlé. Par conséquence nous avons décidé d'examiner si ces complexes

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## DISCUSSION

exercer un effet antisalissure et en effet nous avons trouvé que le citrate de fer amène à un effet antisalissure et c'est pour cela que je proposerais que les résultats obtenus ne sont pas seulement dus à la haute concentration d'OH.

Prof. MOR: Je remercie le Dr. Littauer et j'écouterai avec beaucoup d'intérêt sa communication.

Toutefois je ne suis pas d'accord sur une action antisalissure des citrates comme tels, car il est bien connu que l'acide citrique fait partie des agents liants de la cellule. Les sels de fer plutôt peuvent exercer des actions inhibitoires sur le fouling.

Dr. GUILLEN (Espagne): J'aime bien d'abord féliciter Monsieur le Professeur MOR pour son exposé très intéressant et au même temps poser la question suivant: quel est l'influence du pH sur l'apparition des hydroides?

Prof. MOR: Je remercie avant tout le Dr. Guillen pour ses expression. Les serpulides commencent à paraître à valeurs de pH autour de 4,5 pour les pH acides, et de 9 pour les pH basiques.



# CONTRIBUTIONS À L'ÉTUDE DES PEINTURES ANTISALISSURES POUR NAVIRES MARITIMES. ESSAIS DANS L'EAU DU PORT DE CONSTANTZA (MER NOIRE)

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## RÉSUMÉ

A la suite du développement du port roumain de Constantza, situé sur la côte occidentale de la Mer Noire et de l'essor des chantiers navals et de la flotte maritime commerciale roumaine, on a dû faire des recherches concernant la protection antisalissure des navires maritimes.

Les essais ont été effectués comme suit :

a) Sur une station flottante construite en vue d'exposer dans les conditions naturelles des eaux du port de Constantza les systèmes de peinture vinylique avec plusieurs variantes des toxiques antisalissures ainsi que : l'oxyde cuivreux, l'oxyde de mercure, le pentachlorophénole, le tributylxyde d'étain, le Phelam.

b) Sur des embracations portuaires sur lesquelles on a exposé les systèmes vyniliques en parallèle avec les toxiques antisalissures mentionnés ci-dessus. La peinture antisalissure à Phelam et oxyde cuivreux a résisté dans les essais effectués tant sur la station flottante que sur les embarcations portuaires. Du point de vue qualitatif, on a utilisé la peinture Antifouling 2 — un produit de la Société International (Angleterre).

c) Les peintures antisalissures ont été appliquées en vue d'expérimentation aussi sur un nombre de 4 navires maritimes de 4500 t.d.w. Les observations concernant le comportement de la peinture antisalissure ont été effectuées seulement à l'occasion de leur mise en cale, c'est-à-dire après une navigation de 12 à 15 mois. Les peintures vyniliques essayées ont assuré seulement partiellement la protection antisalissure (une période de plus d'une année). Du point de vue qualitatif, on a utilisé le système de peinture bitumineux-aluminium — un produit de l'Imperial Chemical Industries Ltd (Angleterre).

En vue de l'interprétation des observations concernant le comportement des peintures antisalissures, on a suivi le développement du fouling dans la station flottante du port de

Constantza, en établissant les périodes de fixation des principaux organismes (Balanes, Mercierella, Tunicata, algues vertes). On mentionne la présence des vers polychètes de l'espèce Mercierella enigmatica, espèce invadante observée au début du 1963 dans les eaux du port de Constantza.

Les observations effectuées sur la station flottante du port de Constantza et sur les embarcations portuaires, ont démontré que malgré le fait que la salinité de l'eau de la Mer Noire est plus réduite que celle de la Méditerranée ou de l'Océan, l'agressivité biologique de l'eau du port de Constantza est semblable à celle d'autres mers et océans. Pour ce motif, la question de la protection anticorrosive et antisalissure se pose même pour les navires qui naviguent exclusivement dans la Mer Noire ou même dans la baie du port de Constantza, ainsi que pour les remorqueurs, pontons, docks, etc.

L'étude de l'agressivité biologique de l'eau des ports maritimes a une importance exceptionnelle en ce qui concerne l'application des protections anticorrosives et surtout antisalissures. De même, la pollution de l'eau dans les ports doit être bien connue dans le but de choisir les meilleures méthodes de protection. L'apport du biologiste est essentiel pour une juste corrélation et interprétation des résultats.

Il est à souhaiter une collaboration active entre différentes institutions et hommes de science qui s'occupent du problème de l'agressivité de l'eau dans les ports de la Mer Noire et de la Méditerranée en ce qui concerne le fouling et les méthodes de protection antisalissure, aussi bien que pour l'unité des méthodes d'essais de peintures antisalissures, pour la notation du développement du fouling et pour établir le tabel des organismes représentatifs dans ces eaux.

On pourrait ainsi trouver des solutions aux problèmes dans un délai de temps beaucoup plus court.

## INTRODUCTION

A la suite du développement du port roumain de Constantza, situé sur la côte occidentale de la Mer Noire et de l'essor des chantiers navals et de la flotte maritime commerciale roumaine, on a dû faire des recherches concernant la protection antisalissure des navires maritimes.

Les essais ont été effectués par le laboratoire de recherche biologique pour protection climatique, qui fait partie de l'Institut pour recherches électrotechniques de Bucarest.

### MÉTHODE POUR VÉRIFIER LES PEINTURES ANTISALISSURES

La vérification des peintures, surtout celles antisalissures

a été effectuée dans des conditions naturelles appropriées aux conditions existantes en exploitation.

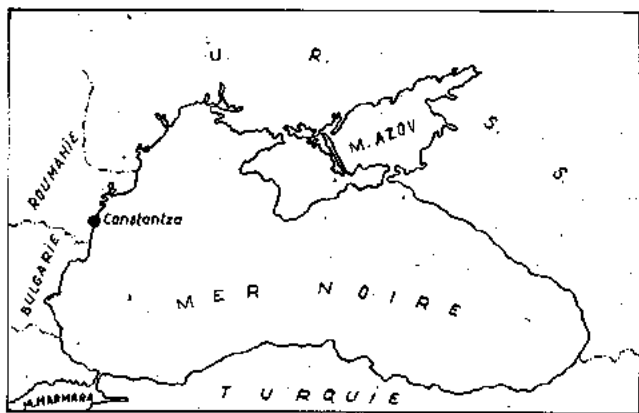
Il est établi que le contrôle de la qualité des peintures en laboratoire ne peut pas servir que pour éliminer d'avance les peintures insatisfaisantes<sup>1</sup>. Seulement les essais « in situ » peuvent être décisifs pour le choix et l'application effective d'une peinture antisalissure<sup>2</sup>.

Les essais ont été effectués comme suit :

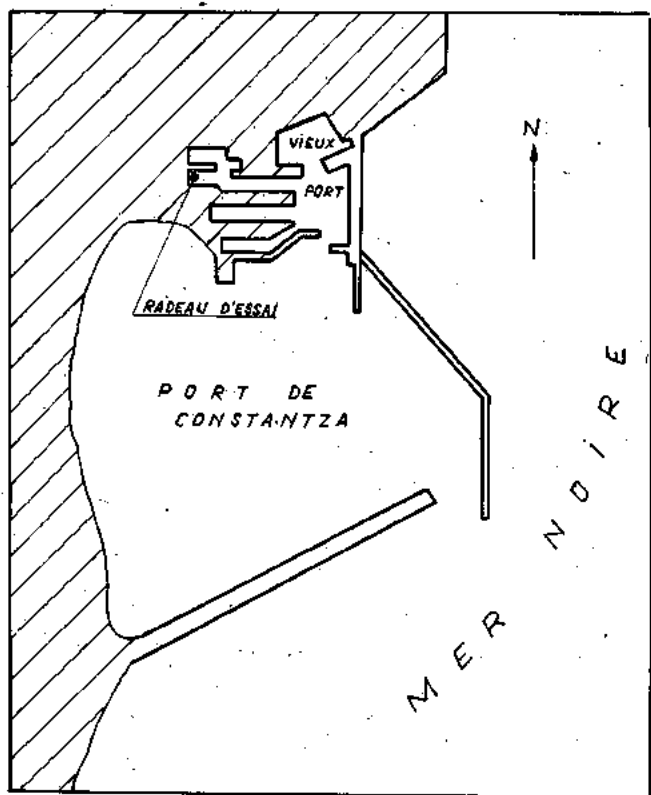
a) sur des radeaux, situés dans la baie du port de Constantza ; les peintures antisalissures ont été appliquées sur des éprouvettes (plaques métalliques) immergées dans l'eau de mer<sup>3, 4, 5</sup> ;

b) sur des embarcations portuaires ;

c) sur des navires, la peinture étant appliquée soit sur toute la surface de la coque, soit sur des portions limitées<sup>6</sup>.



a



b

Fig. 1. L'emplacement de la station flottante pour les essais de peinture, dans le port de Constantza.

### EXPÉRIMENTATIONS EFFECTUÉES

#### a) Sur le radeau

La station flottante a été construite pour mettre en contact direct avec l'eau de la mer les matériaux et les peintures antisalissures appliquées sur des plaques métalliques (tôle de navire) afin de pouvoir suivre le développement du fouling.

La station flottante se trouve dans le port de Constantza (Fig. 1a et 1b). La profondeur de l'eau à l'endroit où se trouve la station est de 8 m., le fond de la mer étant sablonneux-limoneux; l'eau est stagnante (sans courant), en général tranquille, sans vagues.

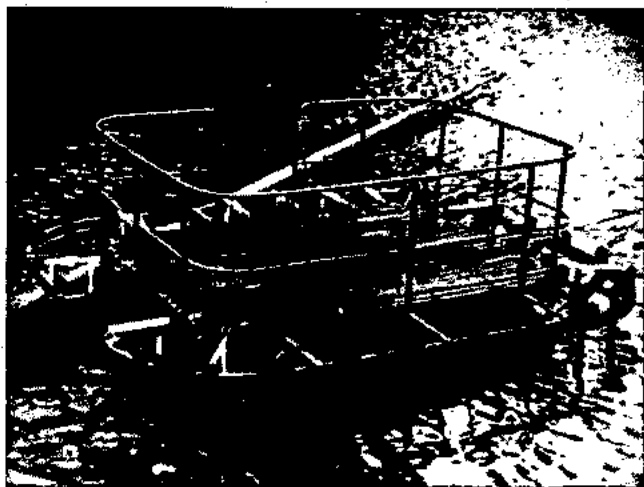


Fig. 2. Vue d'ensemble du radeau pour les essais de peintures.

La station flottante (Fig. 2) est un radeau métallique de 4,5 m × 4,5 m. La flottaison est assurée par deux flotteurs métalliques. Le pont est à 0,4 m au dessus de l'eau.

Les plaques métalliques mises à l'épreuve sont fixées dans des cadres métalliques, avec des supports en PVC. Les plaques encadrées sont disposées sur un cadre circulaire placé à l'extérieur du radeau. Cet emplacement assure les meilleures conditions pour le développement des organismes du fouling, y compris lumière, oxygène, circulation d'eau entre plaques. Entre les cadres (plaques) il y a une distance — mesurée à l'horizontale — de minimum 30 cm. En total il y a 32 cadres. L'hauteur d'un cadre est de 2,4 m., dont 0,4 m. se trouve au dessus de la mer. Dans chaque cadre on peut mettre trois plaques à trois niveaux différents, en commençant de 0,50 m. jusqu'à 1,80 m. de profondeur mesurée du niveau de l'eau.

Les plaques métalliques ont une surface de 200 × 300 mm. et une épaisseur de 1 mm. Ces dimensions ont été considérées les plus favorables pour l'essai des peintures; ce sont d'ailleurs les dimensions utilisées aussi dans les stations flottantes (La Rochelle, Toulon, Cherbourg, etc.) d'autres pays<sup>2</sup>. Les plaques métalliques sont en tôle de navire. Pour pouvoir identifier les plaques, on a pratiqué des encoches sur l'un des bords de la plaque.

Afin de contrôler le développement du fouling dans l'eau du port de Constantza, on a immergé dans la station flottante des éprouvettes en bakélite, en PVC, bois, verre poli, acier, sur lesquelles on a observé le fouling développé (Fig. 3).

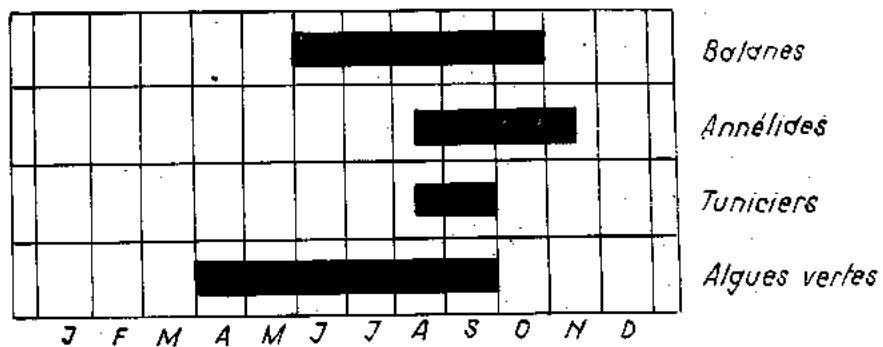
Parmi les organismes animaux observés dans le fouling développé sur les éprouvettes immergées dans la station flottante, les plus fréquents ont été: les *Balanus improvisus* (Fig. 4) qui forment avec leurs coquilles et avec les tubes calcaires de *Mercierella enigmatica* (Fig. 5) une croûte pouvant atteindre jusqu'à 20 mm. d'épaisseur. Sur la croûte des *Balanus* d'autres organismes étaient fixés: des vers marins (*Polydora ciliata*, *Nematoda*), les *Mithylus*, tout étant recouvert par des algues vertes, quelques *Tunicata*, etc.

Ce qui est intéressant c'est l'apparition dans les eaux du port de Constantza, de la *Mercierella enigmatica* Fauvel (Fig. 6), une annélide polychète sédentaire, qui s'est développée dans beaucoup de ports du monde<sup>2</sup>, étant emmenée par les côques des navires. *Mercierella* s'est introduite seulement les derniers temps dans les eaux du port de Constantza, où elle a trouvé un milieu favorable, l'eau étant calme et riche en matières organiques.

Nous avons observé le développement de *Mercierella* depuis l'été du 1963; le développement a été intense pendant certaines années, en d'autres se réduisant à quelques individus



a



b

Fig. 3. Période de fixation des principales salissures dans les eaux du port de Constantza (en 1967).



Fig. 4. Coquilles de Balanes.

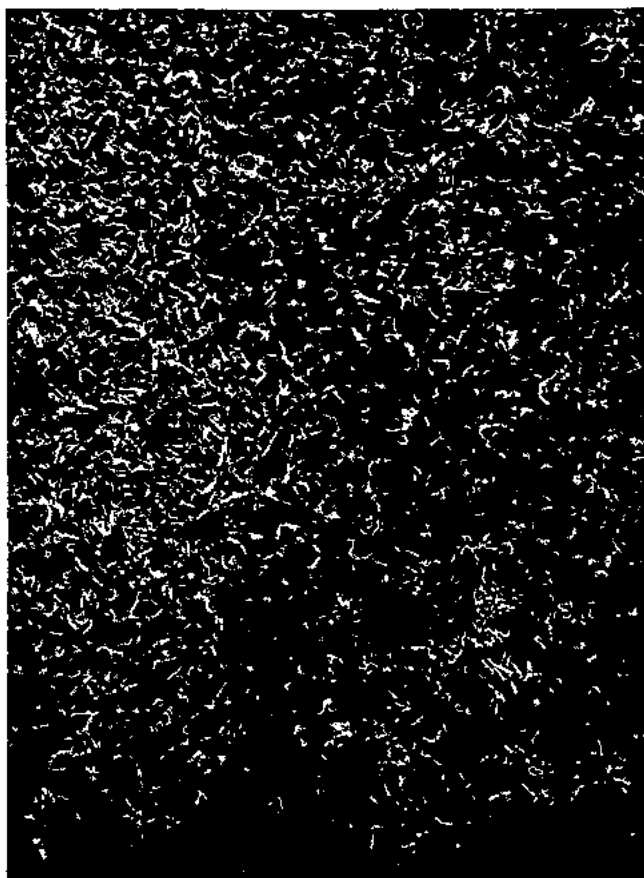


Fig. 5. Le fouling développé après une saison chaude (été) sur une plaque métallique immergée dans la station flottante de Constantza. Beaucoup de Balanes et Serpulides.



Fig. 6. Vers annélides polychètes sédentaires (les tubes calcaires).

isolés.

Le poids de l'amas de ces Serpulides observées sur la surface des éprouvettes immergées dans les eaux du port de Constantza a atteint jusqu'à  $5 \text{ kg/m}^2$ ; la longueur d'un tube calcaire a été jusqu'à 2 ou 3 cm.

Etant donné les conditions favorables pour le développement de cette espèce dans les eaux du port de Constantza, on peut craindre pour l'intégrité des installations portuaires immergées, ainsi que celles des docks, dragues, etc.

L'expérimentation des systèmes de peinture aussi bien que celle des peintures antisalissures a été effectuée en utilisant trois éprouvettes pour chaque système essayé.

Pendant une exposition ayant duré 18 mois, les peintures antisalissures ont eu le comportement présenté dans le tableau No. 1.

On constate d'après les résultats obtenus que les peintures vinyliques se comportent d'une manière satisfaisante, la pellicule restant intacte, sans que des cloques, exfoliations, rouille soient apparus.

La peinture antisalissure qui contient comme toxique le tributylxyde d'étain a prévenu le fouling pour plus d'une année, tandis que les peintures à oxyde cuivreux ou bien à oxyde cuivreux et oxyde de mercure n'ont pas résisté que six mois (été-hiver). La peinture ayant comme toxique le Phelam (diméthyl-dithiocarbamate de mercure-phenyl) a été résistante, prévenant le fouling plus d'une année.

Comme peintures comparatives on a utilisé des peintures antisalissures provenant des maisons Hempel (Danemark), Imperial Chemical Industries Ltd. (Grande Bretagne) et International (Grande Bretagne).

#### b) Expérimentations sur des embarcations portuaires

Les peintures antisalissures essayées ont été appliquées sur les coques de deux embarcations portuaires, chacune de 3 tdw, ayant une longueur de 10 m.

Sur chaque embarcation, on a appliqué cinq systèmes de peinture plus un, qui a été pris pour comparaison, ce dernier ayant été importé. Les systèmes de peinture ont été appliqués par bandeaux transversaux qui couvraient la côte des embarcations. Sur l'une des embarcations on a appliqué de dif-

TABLEAU 1

## LE COMPORTEMENT DES PEINTURES ANTISALISSURES ESSAYÉES DANS LA STATION FLOTTANTE PENDANT 18 MOIS

No.	Peinture et toxique antifouling Immersion au mois de Juin	Octobre	Février	Août	Décembre
1.	Bitumineuse à oxyde cuivreux	Fouling plus de 50% Cloques, exfoliation, rouille plus de 50% Notation : faible	Même aspect  Notation : faible	Même aspect  Notation : faible	Même aspect  Notation : faible
2.	Vynilique à oxyde cuivreux	Pellicule intacte, propre. Notation : très bon.	Presque le même aspect. Notation : bon	Petites cloques Notation : faible	20% fouling (vers Polychète) Notation : faible.
3.	Vynilique à oxyde cuivreux et oxyde de mercure.	Pellicule intacte, propre. Notation : très bon.	Même aspect. Notation : très bon	Algues vertes. Notation : faible	Fouling (vers Polychète) Notation : faible
4.	Vynilique à pentachlorophénole	Plus de 50% fouling (Balanes). Notation : faible	Même aspect. Notation : faible	Même aspect. Notation : faible	Même aspect. Notation : faible
5.	Vynilique à tributylxyde d'étain	Pellicule intacte, propre. Notation : très bon	Même aspect. Notation : très bon	Presque le même aspect. Notation : bon	Plus de 50% fouling (Balanes) Notation : faible
6.	Vynilique à Phelam et oxyde cuivreux	Pellicule intacte, propre. Notation : très bon.	Même aspect. Notation : très bon.	Même aspect. Notation : très bon.	Même aspect. Notation : très bon.

férents systèmes de peinture en commençant par la proue, tandis que sur la seconde on a commencé avec la poupe.

L'application a été faite au rouleau la première couche et au pistolet le reste.

La peinture a été mise à l'épreuve au début de la saison chaude (le mois de Juin). Les observations ont été faites à la fin de la saison chaude (après six mois de navigations des embarcations) en obtenant les résultats suivants.

TABLEAU 2

Peinture essayée	Comportement	Appréciation
1. Peinture à l'huile à oxyde cuivreux	Couverte par le fouling	Non efficace
2. Peinture à chloro-caoutchouc à oxyde cuivreux	Couverte par le fouling	Non efficace
3. Peinture vynilique à pentachlorophénole	Couverte par le fouling	Non efficace
4. Peinture à tributylxyde d'étain	Couverte par le fouling	Non efficace
5. Peinture à Phelam et oxyde cuivreux	Non couverte par le fouling	Efficace
6. Peinture «Internationale» Antifouling 2.	Non couverte par le fouling.	Efficace

Il en résulte de ces essais que la peinture vynilique antisalissure à Phelam et oxyde cuivreux a été la plus efficace, en donnant les mêmes résultats que la peinture importée prise pour comparaison.

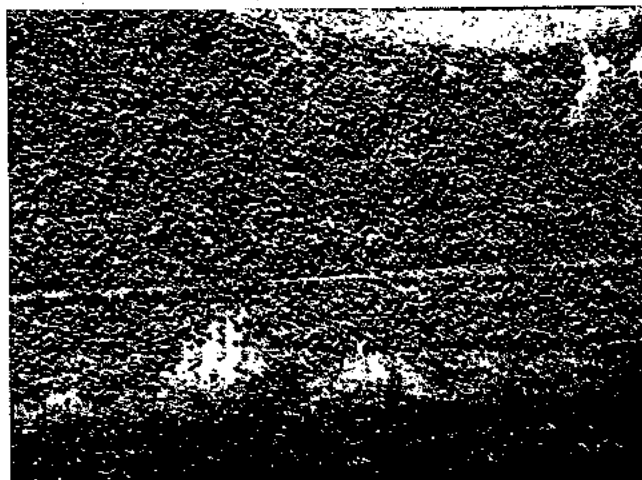


Fig. 7. Fouling développé sur la coque d'un navire, représenté spécialement par les coquilles de Balanes.

c) *Expérimentations sur navires*

Afin d'établir le comportement des peintures vynilliques et antisalissures, on a appliqué, à titre d'expérimentation, ces systèmes de peinture sur des navires maritimes commerciaux.

Les peintures ont été appliquées sur la coque de chaque navire (sur une surface de 1400 m<sup>2</sup>) d'après le système suivant:

- 1 couche primaire à réaction;
- 3 couches primaires anticorrosives;
- 2 couches peinture antisalissure.

Avant la peinture, la tôle a été débarrassée de la peinture ancienne et de la rouille par grattage et brossage métallique et dégraissage.

On a fait des observations (Fig. 7) concernant le comportement de la peinture après 12 à 15 mois de navigation; elles sont présentées en ce qui suit:

TABLEAU 3

Nom du navire	Tonnage	Durée entre deux peintures appliquées -mois-	Mer où on a navigué	Durée de Stationnement dans les mers chaudes -mois-	Comportement de la peinture antisalissure
Cluj	4500	15	Méditerranée, Oc. Atlantique	1	Partiellement couverte par le fouling
Brasov	»	13	Méditerranée, Oc. Atlantique, M. Rouge	1	»
Braila	»	12	Méditerranée, Oc. Atlantique	1	»
Suceava	»	12	»	1,5	»

A la suite des observations faites, on a conclu que les peintures antisalissures essayées ne peuvent pas assurer qu'en partie la protection contre le fouling, quand la durée dépasse une année (Fig. 8).

Comme échantillon de comparaison, on a pris les peintures bitumineuses, à l'aluminium, fabriquées par Imperial Chemical Industries Ltd., qui a assuré une parfaite protection sur la coque du cargo «Bucuresti». La peinture est restée propre et sans fouling, plus de 14 mois, jusqu'à la mise en cale sèche du cargo.

DISCUSSIONS CONCERNANT LES METHODES D'ESSAIS ET D'INTERPRETATION DES RESULTATS.

Basés sur les résultats des expérimentations présentées par la littérature technique aussi bien que sur les résultats obtenus dans nos essais, nous pouvons tirer des conclusions concernant: la manière dont on doit faire les essais, l'interprétation des résultats obtenus et la manière dont ces derniers doivent être interprétés.

a) Les peintures antisalissures peuvent être essayées sur les radeaux placés dans les ports<sup>9</sup>.

Grâce à son emplacement, le matériel est exposé à des facteurs qui peuvent être déterminés et enregistrés en permanence, comme: température, salinité, fouling, etc.<sup>10</sup>.

La différence existant entre les résultats obtenus par l'ap-

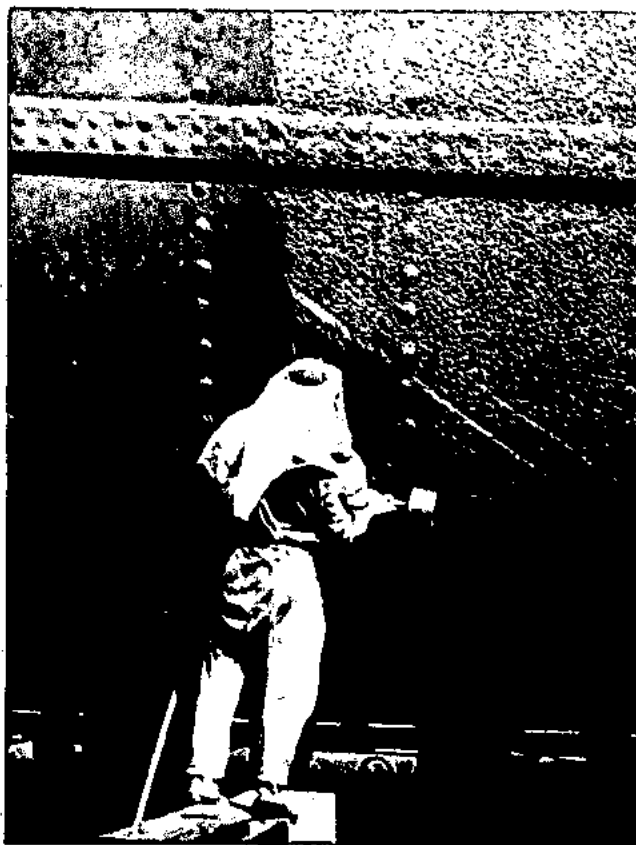


Fig. 8. L'enlèvement du fouling sur la coque d'un navire.

plication des peintures sur radeaux et ceux obtenus par l'application des peintures sur navires, réside dans le fait que sur le radeau les éprouvettes sont exposées aux facteurs environnants dans des conditions statiques, tandis que pendant l'exposition dans différents mers et océans, sur les navires existent des conditions dynamiques, les peintures subissant en même temps les conséquences dues au changement des mers et des ports.

Quant au développement du fouling, les essais sur les radeaux peuvent être considérés des essais accélérés, étant donné que — chose connue — la fixation des organismes animaux et végétaux sur la coque des navires se produit seulement s'ils restent sur la place ou avancent très lentement (vitesse maximum deux milles à l'heure) et non pendant la course qui a lieu d'habitude à une vitesse de 10 milles à l'heure. En plus; l'eau portuaire est souvent chargée et polluée avec des résidus organiques, pétroliers, etc., ce qui provoque, à une température favorable, un développement optimum du fouling.

Pour les motifs ci-dessus mentionnés, nous considérons que les essais sur radeaux doivent se faire obligatoirement pour vérifier les peintures nouvellement élaborées, aussi bien que pour le choix des meilleures d'entre elles<sup>11</sup>.

Le désavantage de l'exposition des peintures sur les radeaux, qui se trouvent dans les mers tempérées, comme celle du port de Constantza, réside dans le fait qu'en saison chaude le fouling se développe dans des conditions optima, presque d'une manière explosive, tandis qu'en saison froide, le développement du fouling et surtout des organismes qui forment la croûte calcaire sur les navires, cesse presque totalement.

Dans de pareilles conditions, les peintures exposées pendant l'été seront soumises presque tout de suite à l'attaque du fouling, tandis que celles exposées pendant l'hiver subiront

en premier lieu l'attaque agressive de l'eau de mer ; pendant ce délai il se peut produire l'épuisement du toxique antifouling, dont l'efficacité sera vérifiée seulement l'été suivant.

Il s'en suit qu'il faut tenir compte quand on procède à l'interprétation des résultats, de la saison de l'exposition et de la durée de celle-ci, qui doit contenir en tout cas une saison chaude, favorable au développement du fouling.

Sans avoir égard à ces conditions, on ne peut pas obtenir des conclusions fermes en ce qui concerne le comportement des peintures antifouling essayées sur des radeaux.

b) Les essais sur embarcations portuaires ont l'avantage qu'on peut sortir de l'eau facilement les embarcations à cause de leur tonnage réduit (sous 5 tdw) et on peut examiner périodiquement le comportement des peintures.

Vu les conditions caractéristiques des eaux portuaires, il s'en suit que ces essais peuvent être considérés, à leur tour, des essais accélérés.

Quand on applique sur la même embarcation parallèlement plusieurs systèmes de peinture, on peut établir comparativement leur comportement, de sorte qu'on puisse choisir la meilleure peinture.

L'expérimentation sur des embarcations portuaires a, à son tour, des inconvénients dus au fait que l'essai est réalisé dans des conditions locales (le périmètre du port), que la durée de la navigation est réduite par rapport au temps de stationnement et que la surface sur laquelle on applique la peinture est limitée.

Les résultats ont quand même de la valeur, puisque le comportement de la peinture et la fixation du fouling peuvent être suivis en permanence, en pouvant comparer ces résultats avec ceux obtenus sur des radeaux ou sur des navires, ce qui conduit à une évaluation plus correcte du comportement des peintures.

c) Les expérimentations sur navires, quoique réalisées en conditions réelles, ont le grand inconvénient de ne pas permettre d'effectuer des observations si le navire n'est pas sorti de l'eau, c'est-à-dire à la fin d'une course dont la durée peut se prolonger actuellement jusqu'à 12 à 16 mois. Dans de pareilles conditions d'essais, une peinture qui pourrait assurer la protection antisalissure pour une période moins longue que la durée de la course (par exemple 12 mois) pourrait être considérée non-satisfaisante, malgré qu'elle aurait été efficace mais pour une durée plus courte que celle écoulée entre les deux mises en cale.

Le comportement de la peinture étant conditionné par la saison, par les mers parcourues (chaudes, tempérées, froides) ainsi que par la durée de la course et du stationnement du navire dans les ports, il en résulte que les résultats obtenus n'ont de la valeur que rapportés aux conditions dans lesquelles certain navire s'est réellement trouvé. Pour cette raison, la comparaison entre les peintures appliquées sur différents navires n'est pas concluante.

Les expérimentations sur navires — afin d'aboutir à des résultats valables — doivent être faites sur un grand nombre de navires, pour que l'on puisse avoir des conclusions basées sur des données statistiques. Pratiquement, cette chose n'est pas possible, puisqu'une peinture expérimentale ne peut pas être appliquée sur de dizaines de navires.

La vérification des peintures expérimentales sur des navires en navigation peut être faite, avec une légère dépense, par application de peintures par bandeaux, afin qu'elles soient exposées sur le même navire, aux mêmes conditions environnantes.

Cette méthode peut fournir des données comparatives, ce qui permet de se faire une idée orientative, quand à l'efficacité de la peinture. L'interprétation des résultats et des conclusions sera plus difficile quand l'application a été faite sur un seul navire ou bien sur un nombre réduit de navires.

En faisant les expérimentations en conditions naturelles, par les trois méthodes énoncées, on peut arriver à une juste idée sur l'efficacité des peintures antisalissures, avant de les employer pour la protection définitive des navires. L'apport du biologiste est essentiel pour une juste corrélation et interprétation des résultats.

1. Les observations effectuées sur les radeaux et sur les embarcations portuaires ont démontré que la peinture vinylique, appliquée sur une surface bien nettoyée, peut assurer une protection adéquate de la coque du navire.

2. L'intervalle entre deux mises en cale sèche des navires (durée de l'exploitation d'une peinture) s'est prolongé ces dernières années à plus d'une année (12 à 18 mois); cela nécessite une peinture antisalissure qui assure la protection pour une durée plus longue.

3. Quand la durée entre deux mises en cale sèche a dépassé une année, le système vinylique essayé sur des navires n'a assuré qu'une protection partielle contre le fouling.

4. Les observations effectuées sur la station flottante du port de Constantza et sur les embarcations portuaires, ont démontré que malgré le fait que la salinité de l'eau de la Mer Noire est plus réduite que celle de la Méditerranée ou de l'Océan, l'agressivité biologique de l'eau du port de Constantza est semblable à celle d'autres mers et océans. Pour ce motif, la question de la protection anticorrosive et antisalissure se pose même pour les navires qui naviguent exclusivement dans la Mer Noire ou même dans la baie du port de Constantza, ainsi que pour les remorqueurs, pontons, docks, etc.

5. L'étude de l'agressivité biologique de l'eau des ports maritimes a une importance excessive en ce qui concerne l'application des protections anticorrosives et surtout antisalissures. De même, la pollution de l'eau dans les ports doit être bien connue dans le but de choisir les meilleures méthodes de protection.

6. Il est à souhaiter une collaboration active entre différentes institutions et hommes de sciences qui s'occupent du problème de l'agressivité de l'eau dans les ports de la Mer Noire et de la Méditerranée, en ce qui concerne le fouling et les méthodes de protection antisalissure, aussi bien que pour l'unité des méthodes d'essais de peintures antisalissures, pour la notation du développement du fouling et pour établir le label des organismes représentatifs dans ces eaux.

On pourrait ainsi trouver des solutions aux problèmes dans un délai de temps beaucoup plus court.

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# SOME RADIOECOLOGICAL ASPECTS OF INVESTIGATION OF THE FOULING ORGANISMS

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## SUMMARY

The concentration factors of Strontium - 90 and stable strontium for ten species of the Black Sea foulings were experimentally estimated.

The fouling study in the radioecological aspect has some grounds. First for to estimate radioecological situations it is useful to determine concentration factors. (Polikarpov, 1966) and to do searchings among the organisms as indicators of foulings these or those radionuclides. Second knowing the radioactive elements content in the foulings of separate marine buildings it is possible to calculate the radiation dose formed by the foulers. In other words, the fouling organisms enforce the radioecological factor of marine surrounding and create the field of its higher intensity.

Taking into consideration the all above mentioned we researched some species of the Black Sea foulings: sponges, sedentary polychaetas, molluscs and algae.

There were found the concentration factors of strontium-90 and stable strontium for 10 species of the foulings. Water and organisms samples were taken at the same time. Concentration of strontium-90 was defined by the carbonate precipitation method in the presence of  $NH_4Cl$  (Popov, Orlov and alth..., 1964). The determination of  $^{90}Sr$  content was

based on the oxalate precipitation of the 2nd group of elements from HCl solution of ash. The content of strontium-90 was calculated through its daughter product yttrium-90. The obtained data were treated statistically. (Mitropolshy, 1961).

The data of strontium-90 concentration factors and its statistic characteristics are shown in the Table enclosed.

Spirorbis and molluscs (440-125) possess the highest concentration factors in comparison with algae and sponges (31-5.2). Excepting the calciphil red alga *Corallina officinalis* with its concentration factor equalled to 264. This is quite understandable since Sr (analog of Ca) accumulates mostly in carbonate formation in algae, in the shells of *Mytilus* and in the «tubes» of Polychaetas. The concentration factors for the *Mytilus* shells are approximately 1.5 more than for the whole mollusc is and 63 times more than for the mollusc body (315, 211 and 5 respectively).

The obtained concentration factors of stable strontium are complete close to the  $^{90}Sr$  concentration factors in the same organisms; for the shells of *Mytilus*-373-283; bodies of

T A B L E  
CONCENTRATION FACTORS OF STRONTIUM-90 IN SOME FOULING ORGANISMS

Blacksea hydrobionts	n	$\bar{X} \pm t_{0.10} \frac{S}{\sqrt{n}}$	S	$O_{\bar{x}}$	$O_s$	V, %	P, %	$O_v$
<i>Mytilus galloprovincialis</i>	3	211 ± 79	47	27.1	19.1	22.2	13.0	9.4
<i>M. galloprovincialis</i> , shell	5	315 ± 77	81	36.1	25.6	25.7	11.4	8.5
<i>M. galloprovincialis</i> , body	1	5.0	—	—	—	—	—	—
<i>Mytilaster lineatus</i>	5	125 ± 19	30	14	9.5	24.0	11.2	8.2
<i>Ulva rigida</i>	3	11.1 ± 6.1	3.06	1.77	1.25	27.6	15.9	12.0
<i>Corallina officinalis</i>	4	264 ± 118	101	50	36	38.2	18.7	15.3
<i>Laurencia obtusa</i>	2	31.1 ± 11.4	2.5	1.8	1.3	8.1	5.8	4.2
<i>Ceramium rubrum</i>	1	12.2	—	—	—	—	—	—

n — number of samples  
 $\bar{X}$  — arithmetic mean  
 S — standard deviation  
 V, % — factor of variability  
 P, % — indicator of exactness

$O_{\bar{x}}$  — error of  $\bar{X}$   
 $O_s$  — error of S  
 $O_v$  — error of V  
 $t_{0.10} \cdot \frac{S}{\sqrt{n}}$  — interval of confidence



Mytilus-1.6-5; Mytilaster-198-125; Ulva-8.5-14.8; Corallina-209-339; Laurencia-14.8-29.3. There were found the concentration factors only for stable strontium-5 and 440 in Sponges and Spirorbises. As it's seen from this comparison and other our figures (Batchurin, Kulebakina, Polikarpov, 1967) the concentration factors of radioactive and stable strontium are very close. It indicates that practically the complete isotopic exchange have been occurred between radioactive and stable Sr in the shelf zone.

As it is so one may use concentration factors of radioactive and/or stable Sr both to estimate the radioecological situation.

Molluscs, namely-Mytilus (Marine Fouling and its Prevention, 1952) contain the main portion of biomass in the foulings. From the radioecological point of view molluscs and Spirorbises are the most sensitive bioindicators of the presence of strontium-90 in the environment.

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# PROPRIÉTÉS PHYSICOCHIMIQUES DES SÉDIMENTS ET CORROSION MARINE

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## RÉSUMÉ

Le milieu marin corrosif est constitué par deux éléments essentiels : l'eau de mer et les sédiments imbibés d'une eau interstitielle dont la composition est différente de celle de l'eau de mer.

La corrosion des matériaux immergés ne sera pas identique selon qu'ils seront plongés dans l'un ou l'autre de ces milieux, ou, ce qui est fréquent, partiellement dans l'un et partiellement dans l'autre.

De plus, il existe une zone de passage où les gradients (oxygène, hydrogène sulfuré) sont importants.

On apporte quelques observations sur les différences existant entre l'eau de mer et l'eau interstitielle des sédiments, ainsi que sur les propriétés physicochimiques de ceux-ci. Le rôle des actions biologiques est examiné.

## INTRODUCTION

Le milieu marin n'est pas seulement constitué par l'eau de mer, solution saline dans laquelle interviennent de nombreux processus biologiques dus aux bactéries, aux végétaux et aux animaux qui s'y développent. Le fond marin constitué dans sa plus grande partie par des dépôts sédimentaires (sables, vases) participe aux propriétés générales de ce milieu complexe. Des échanges entre l'eau de mer surnageante et le sédiment ont lieu : échanges de sels, de gaz dissous. L'eau interstitielle, ou d'imbibition, des sédiments meubles n'a pas une composition identique à celle de l'eau de mer. La diagénèse des dépôts résulte de l'interaction entre les processus physiques et chimiques qui prennent place entre les substances en solution dans l'eau (sels, gaz dissous) et les composants solides du sédiment : corps minéraux ou organiques (protéiques, glucidiques, etc.). Il en résulte que l'eau de mer piégée dans un sédiment voit sa composition modifiée dans une mesure qui dépend de la nature et de l'intensité de telles actions ; on constate pour plusieurs de ces caractéristiques, (gaz, oxygène dissous, sulfates, etc.) des modifications qui se produisent avec le temps, et par conséquent avec la profondeur des dépôts. Des gradients s'établissent de la surface des sédiments vers le fond. Le sédiment, d'autre part n'est pas entièrement confiné sur lui-même ; des échanges ont lieu avec l'eau surnageante, (par diffusion, parfois convection) et la surface du sédiment constitue un seuil de part et d'autre duquel l'eau de mer et l'eau interstitielle présentent des compositions différentes ; un tel seuil est le siège de variations rapides de certains caractères physiques ou chimiques du milieu ; il est lui-même le siège d'actions biologiques particulières dans ce que l'on appelle la *pellicule superficielle*. Il est donc bien évident qu'un matériau métallique ne sera pas exposé à la même agression selon qu'il se trouvera immergé dans l'eau de mer ou enfoui dans un sédiment. De plus, s'il se trouve partiellement immergé et partiellement enfoui dans le sédiment il sera exposé à des gradients de concentration de l'oxygène dissous ou de l'hydrogène sulfuré, par exemple ; ceci pourra être la cause d'une accélération relative des processus de corrosion (formation de piles de concentration).

## PROPRIÉTÉS DU MILIEU INTERSTITIEL DES SÉDIMENTS MARINS

Le milieu interstitiel est constitué par l'eau d'imbibition qui contient des sels, des gaz et des substances organiques dissous. Ce milieu interstitiel occupe les pores laissés entre eux par les particules solides insolubles : grains de sable (quartz, carbonate de calcium, débris coquilliers, particules organiques). Des particules colloïdales sont en outre en suspension dans l'eau interstitielle, participant à ses mouvements et susceptibles d'échanges. Le volume de l'espace poreux par rapport au volume total du sédiment exprime la porosité du sédiment ; la teneur en eau est donc proportionnelle à la porosité ; sa mesure (dans un sédiment entièrement imbibé d'eau) permet de déterminer approximativement cette porosité. Celle-ci est sous la dépendance des caractéristiques dimensionnelles, de l'arrangement et de la forme des particules constituant le sédiment. Dans un assemblage unidimensionnel de sphères, la géométrie permet de calculer que le volume de l'espace poreux peut aller de 30,2% à 47,6% de l'espace total, en fonction de l'arrangement (cubique, rhomboédrique) des sphères auquel correspondraient (Callame, 1963) des teneurs en eau de 11,3 à 36,1%. Du fait des irrégularités de tassement, l'arrangement le plus stable (cubique) n'est jamais réalisé dans la pratique. Les sédiments naturels étant hétérogènes et pluridimensionnels, il est apparu impossible de prévoir leur porosité par le calcul, en fonction de leur granulométrie. On a pu constater, expérimentalement, d'autre part, que les sédiments naturels ont une teneur en eau d'autant plus élevée que la dimension des particules est plus faible. Ce fait semble dû en particulier, aux différents états de l'eau qu'ils renferment et qui sont les suivants :

1° *Eau libre* : C'est l'eau qui n'est pas retenue par capillarité entre les grains ; cette eau peut s'écouler par gravité lorsque les forces de rétention capillaires, sont inférieures aux forces hydrostatiques d'écoulement. L'eau libre peut circuler à l'intérieur des sédiments.

2° *L'eau capillaire* retenue dans l'espace interstitiel et à la surface des grains par capillarité en fonction des dimensions des pores.

3° L'eau liée retenue énergiquement à la surface des grains par adsorption.

L'eau libre et l'eau capillaire peuvent être séparées du sédiment aisément (chauffage, centrifugation) elles représentent le liquide interstitiel sur lequel après extraction, on effectue les dosages chimiques susceptibles de déterminer sa composition.

L'eau adsorbée est en proportion d'autant plus forte que les particules sont plus fines, étant proportionnelle au développement de la surface des particules. L'épaisseur de la couche d'eau liée serait de  $10^{-8}$  cm. Weiler et Mills (1965) calculent une surface de 1 à  $100 \text{ m}^2$  par gramme de sédiment; un sédiment dont les particules ont un diamètre de  $8\mu$  aurait un développement de  $3 \text{ m}^2$  par gramme (Shumway et Igelman, 1960). Dans ces conditions, la proportion d'eau liée est importante par rapport à l'eau totale, et les actions de surface sont prépondérantes. De ce fait, la composition de l'eau liée est différente de celle de l'eau libre, les ions et certains corps organiques se trouvent concentrés aux interfaces liquide-solide par les phénomènes d'adsorption. Cette eau ne peut être extraite que par chauffage énergique; par lavages répétés seulement il est possible de déplacer une partie des ions adsorbés par les solides; la composition de cette eau est différente de celle de l'eau libre. Retenons que les actions de surface jouent dans les sédiments, un rôle d'autant plus important que ceux-ci sont plus fins, et que tout matériau solide qui s'y trouve enfoui y est sujet.

### PERMÉABILITÉ DES SÉDIMENTS

La perméabilité obéit à la loi de Darcy par la formule  $K = \frac{Q \cdot H}{p \cdot S}$  où K est la perméabilité en *millidarcy*, Q le débit mesuré en  $\text{cm}^3/\text{sec.}$ , H la hauteur de la colonne de sédiment percolé en cm., S sa section en  $\text{cm}^2$  et p la pression hydrostatique sous laquelle l'écoulement s'est effectué en cm.

Fraser (1935) admet que le taux d'écoulement à travers une colonne de sphère est directement proportionnel au carré de leur diamètre. Dans les dépôts naturels toutefois l'uniformité des grains n'est qu'exceptionnelle et l'écoulement est régi par leur classement, leur forme et leur tassement. En pratique, nous avons pu observer des perméabilités quasi nulles dans des vases, alors qu'elles sont fortes dans des sables grossiers, décroissant rapidement avec la diminution de la taille des grains.

La figure 1 donne l'image d'une courbe de perméabilité obtenue expérimentalement (Callame, 1961). Au-dessous d'une certaine limite, la perméabilité apparaît comme pratiquement nulle; on parle alors d'une *imperméabilité hydraulique* (par rapport à une pression hydrostatique déterminée et un taux d'écoulement déterminé). Nous n'avons insisté sur la perméabilité des sédiments que pour montrer que certains d'entre eux sont perméables (l'écoulement et donc le renouvellement du milieu interstitiel peut s'y produire) (sables) et que d'autres sont pratiquement imperméables; aucun renouvellement ne s'y opère que par diffusion moléculaire. Ils sont *confinés* (vases). Des sables perméables mais où la circulation de l'eau est nulle sont également *confinés*.

### DIFFUSION DANS LES SÉDIMENTS

Les gaz et les sels dissous diffusent dans le milieu interstitiel des sédiments en fonction des gradients de concentration qui peuvent s'y rencontrer. L'oxygène par exemple, qui est consommé à l'intérieur des sédiments par les actions biologiques, diffuse à partir de l'eau surnageante vers l'intérieur du sédiment qui en est dépourvu. La vitesse de cette diffusion est proportionnelle au volume de l'espace interstitiel. Si  $D_0$  est le coefficient de diffusion dans l'eau, D le coefficient de diffusion réduit dans le milieu considéré, p la porosité, on a  $\frac{D}{D_0} = a.p.$ , ou a est un facteur dépendant de la nature du

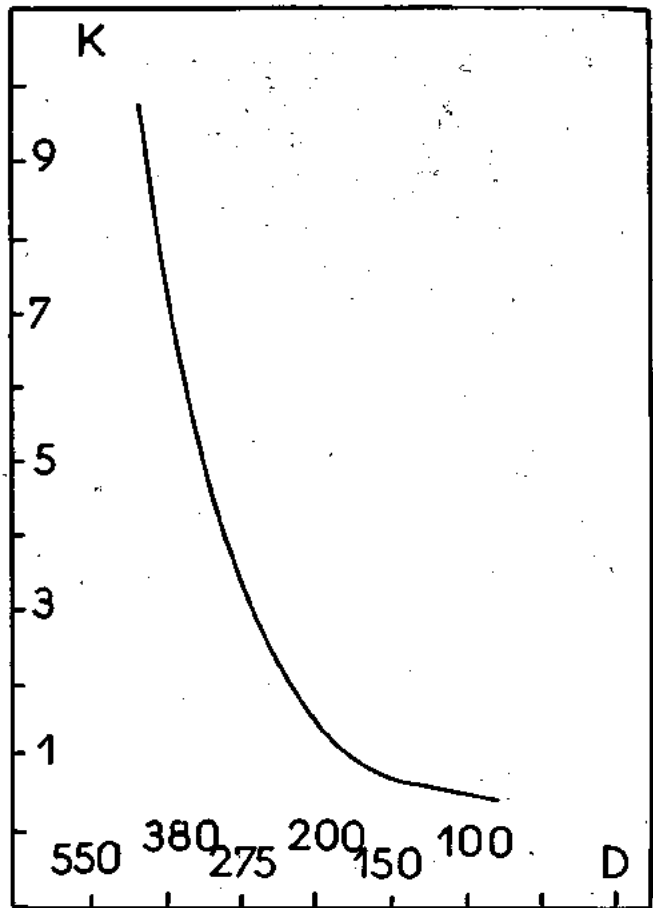


Fig. 1. Perméabilité K de sables naturels en fonction de leur diamètre moyen D, en microns.

milieu (0,6 environ pour un sol naturel). Currie (1960) a trouvé pour différents matériaux les valeurs de p suivantes :

Sphères $\phi$ 0,38	= 0,395
Sable 0,25 - 0,50	= 0,400
Sols	= 0,50 à 0,65
Talc	= 0,70 à 0,75
Kaolin	= 0,75 à 0,81
Mica	= 0,86 à 0,91

Nous retiendrons que les matériaux les plus fins sont également ceux qui permettent une meilleure diffusion moléculaire ce qui est d'ailleurs en conformité avec leurs teneurs élevées en eau.

### COMPOSITION DE L'EAU INTERSTITIELLE DES SÉDIMENTS

Au cours de la formation des dépôts, de l'eau de mer se trouve emprisonnée dans les mailles du sédiment. Si l'eau superficielle a une composition qui ne varie pas dans le temps, et si l'on supposait que d'une part les particules solides n'échangent rien avec l'eau qui les baigne, d'autre part, qu'aucune action biologique ne se manifeste, la composition de l'eau interstitielle resterait celle de l'eau surnageante. Il n'en est rien évidemment et les actions suivantes peuvent se manifester :

1° La composition des eaux surnageantes peut varier dans le temps; avec la marée dans les zones côtières, où dans les estuaires une alternance d'eau douce et d'eau de mer peut à la limite se produire deux fois par 24 heures; et également avec les saisons (saisons sèches et saisons pluvieuses). Des

variations lentes peuvent enfin se produire sur des périodes prolongées.

2° Des échanges ont lieu entre la phase solide et la phase liquide, par exemple dissolution, ou cristallisation des carbonates; le fort développement des surfaces entraîne en outre des phénomènes d'échanges d'ions.

3° Des matières organiques en voie de décomposition (débris animaux, végétaux) servent de base à une activité bactérienne intense, favorisée par les surfaces solides sur lesquelles les bactéries se trouvent fixées. Si l'on ne tient pas compte de la pellicule superficielle où se développent des algues productrices d'oxygène (diatomées en particulier), deux types d'actions bactériennes trouvent place à l'intérieur du sédiment.

a) dans les couches superficielles, où l'oxygène a accès en quantité suffisante, action des bactéries *aérobies*, consommatrices d'oxygène (respiration), acidifiantes (formation de  $\text{CO}_2$ ), décomposant les matières organiques (ammonification puis nitrification) avec abaissement corrélatif du pH et modification de l'équilibre des carbonates, pour ne citer qu'un exemple.

b) A partir d'une profondeur qui dépend à la fois du confinement des sédiments et de leur richesse en matière organique (dont dépend l'activité et l'entretien des actions biologiques) la consommation d'oxygène surpasse les apports possibles par diffusion ou par convection.

On se trouve alors en présence d'un milieu propre à l'activité des bactéries anaérobies. Les bactéries réductrices de sulfates sont les plus souvent citées de celle-ci. (*Sulfobrio desulfuricans*). Elles ont pour effet à partir des sulfates de l'eau de mer (2,6 g/l) de former de l'hydrogène sulfuré. En présence d'ions ferreux se forme alors du sulfure de fer noir  $\text{FeS}$ , qui à l'état colloïdal colore en noir les particules du sédiment. Dans les vases lacustres, pauvres en sulfates, les actions réductrices peuvent au contraire amener la formation de méthane par réduction du carbone organique. De l'ammoniaque résulte également, en milieu anaérobie, des actions bactériennes mais par contre, il ne peut être réoxydé en nitrites et nitrates comme cela se produit en présence d'oxygène. La composition de l'eau interstitielle se trouve par conséquent modifiée par cet ensemble d'actions, dont nous n'avons évoqué que les plus importantes. En effet, lorsque l'on fait l'examen des différents niveaux du sédiment on constate les caractéristiques suivantes :

1° Aspect du sédiment: les couches superficielles où l'oxygène a accès sont colorées en jaune clair, en ocre; la plus grande partie des sels de fer se trouvent à l'état ferrique ( $\text{Fe}^{+++}$ ). Les couches profondes où l'apport d'oxygène est insuffisant sont de coloration gris-noir ( $\text{Fe}$  réduit, présence de sulfure de fer).

2° La quantité d'oxygène dissous diminue avec la profondeur pour s'annuler au niveau où les actions consommatrices d'oxygène surpassent l'apport.

3° Cette limite se confond approximativement avec celle à partir de laquelle les actions anaérobies produisent de l'hydrogène sulfuré, qui se fixe à l'état de sulfure de fer. Le rapport  $\frac{\text{Fer ferrique}}{\text{Fer ferreux}}$  diminue donc avec la profondeur, ce qui se vérifie par dosage.

4° Du fait de l'utilisation des sulfates par les bactéries réductrices le rapport  $\frac{\text{chlorures}}{\text{sulfates}}$ , qui est constant et de l'ordre de 0,139 dans l'eau de mer, diminue sensiblement avec la profondeur; on a trouvé des valeurs égales à 0,100.

5° Le pH de l'eau de mer, qui est légèrement abaissé au proche voisinage du sédiment (de 8,2 à 7,5), subit une légère remontée dans les couches les plus superficielles puis profondes où il peut remonter à 8,5 (Emery, 1960).

6° Les nitrates et les phosphates, du fait des actions que nous avons citées sont plus abondants dans les eaux interstitielles.

7° Le potentiel d'oxydo-réduction est sous le contrôle

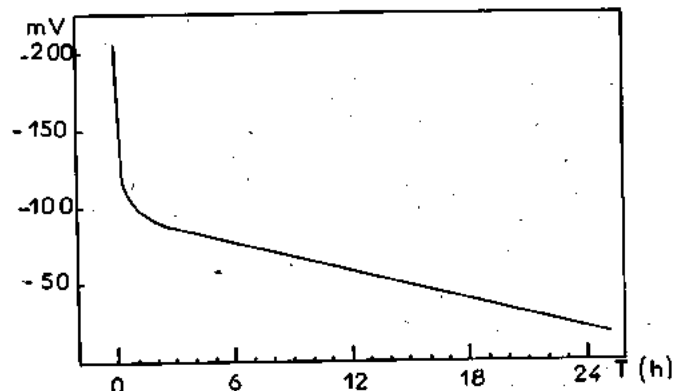


Fig. 2. Différences de potentiel entre deux éprouvettes d'acier dont l'une est immergée dans l'eau de mer et l'autre dans la vase sous-jacente. La première est positive par rapport à la seconde.

des équilibres oxydo-réducteurs principalement celui du fer ( $\frac{\text{Fe}^{+++}}{\text{Fe}^{++}}$ ). Les potentiels d'oxydo-réduction qui sont d'environ 0,420 V dans l'eau de mer sont abaissés; on constate (Emery, 1960) que les niveaux où le  $\text{Eh} = 0$  V se confondent sensiblement avec ceux où apparaît de l'hydrogène sulfuré et où l'oxygène disparaît.

8° La matière organique partiellement dégradée par les actions bactériennes jusqu'à des termes tels que  $\text{CO}_2$ ,  $\text{NH}_3$ , diminue en quantité dans les couches profondes, avec une variation caractéristique du rapport:  $\frac{\text{carbone}}{\text{azote}}$ .

Des potentiels inférieurs à -0,030 V seraient nécessaires pour le développement des bactéries réductrices des sulfates; dans des conditions où la matière organique utilisable est abondante, on peut noter des potentiels inférieurs à -0,300 V.

Dans quelle mesure les différents facteurs que nous venons de passer en revue interviennent-ils vis-à-vis du processus de corrosion des métaux immergés? Si les sédiments constituaient un milieu homogène et constamment renouvelé comme l'eau de mer libre, il serait possible connaissant la composition ionique de l'eau interstitielle, de prévoir les réactions susceptibles de prendre place, notamment celles qui résultent des piles de concentration dues au couple eau de mer-eau interstitielle.

Mais nous l'avons vu, les couches superficielles des sédiments, ou existent des gradients importants de gaz dissous ( $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ) ne sont pas homogènes. L'eau surnageante elle-même, si elle n'est pas suffisamment renouvelée voit sa composition modifiée dans les quelques centimètres qui surmontent le sédiment. Les actions de surface qui jouent probablement un rôle important dans la physico-chimie des échanges entre le milieu corrosif et le matériau corrodable, nous échappent, à notre connaissance, entièrement. Le confinement enfin du liquide interstitiel qu'on peut apprécier par des mesures de perméabilité et de diffusion est apparemment toujours important, et les produits de corrosion modifient le milieu réel auquel sont exposés les matériaux enfouis. La compacité du milieu est évidemment un obstacle à la dépolarisation des électrodes ainsi constituées.

Les expériences suivantes montrent les différences que l'on peut observer entre la corrosion d'un acier dans l'eau de mer, et la corrosion du même acier partiellement et totalement enfoui dans la vase sous-jacente. Les résultats sont exprimés en perte de poids (mg par  $\text{cm}^2$  par 24 heures).

	Durée: 4 jours	Durée: 96 jours
Eau de mer courante	0,24	0,07
1/2 eau de mer 1/2 sédiment	0,23	0,05
Sédiment	0,02	0,12

Le sédiment est une vase compacte, renfermant environ 90% d'eau. Le potentiel d'oxydo-réduction est en surface de + 0,440 V, au fond de + 0,050 V. L'accumulation des produits de corrosion est évident sur l'acier immergé dans l'eau (rouille, oxydes et sulfures noirs sous la rouille), et sur l'acier enfoui (dépôt noir, sulfure de fer).

Si nous mesurons la différence de potentiel (sans débit) existant entre deux éprouvettes d'acier non court-circuitées, identiques, dont l'une est immergée, dans de l'eau de mer et l'autre enfouie dans une vase sous-jacente, nous constatons, au départ, que l'éprouvette enfouie prend un potentiel négatif par rapport à l'autre. Cette différence s'atténue par la suite comme le montre la figure 2 pour devenir presque nulle après 48 heures. Elle s'annule en quelques heures si l'on court-circuite les deux électrodes. L'éprouvette originellement cathodique n'est plus protégée, et de la rouille s'y forme rapidement. Cet exemple montre que nous sommes en face de résultats globaux insuffisants pour avoir une idée du rôle joué par les différents facteurs que nous avons énumérés.

Dans quelle mesure pouvons nous donner une idée de l'agressivité des sédiments marins, en tenant compte du fait que le milieu qu'ils constituent n'est pas homogène, et qu'il n'intervient que rarement sans contact avec l'eau de mer. Dans des sols terrestres Booth et al. (1967) ont pu établir les rapports qui existent entre l'agressivité des terrains et certaines de leurs caractéristiques physiques : résistivité, teneur en eau, pH, potentiel d'oxydo-réduction. Les études concernant le milieu marin, qui sont de plus en plus à l'ordre du jour en raison du développement des installations maritimes, ne sont guère avancées qu'en ce qui concerne la seule eau de mer. Nous avons voulu montrer ici, les bases sur

lesquelles pourrait s'appuyer un tel travail, et qui tiennent pour une grande part aux échanges intervenant entre l'eau et les sols marins, ainsi qu'aux propriétés particulières de ceux-ci.

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#### DISCUSSION

Dr. ROMANOVSKY (France): Je vais simplement dire quelques mots à Monsieur Callame, en ce qui concerne l'intérêt de cette sorte d'étude dans les installations off shore. Vous me direz qu'actuellement la tendance est peut être à faire des plateformes semi-submersibles, puisque les forages vont se faire à des profondeurs de plus en plus importantes, mais néanmoins, il existe encore, et il existera probablement encore longtemps, des plateformes qui reposent sur leurs pieds.

Or, ces pieds sont formés de tubes qui s'enfoncent plus ou moins dans des sédiments de nature différente. Par conséquent, une étude de la corrosion à l'interface est une chose qui est susceptible d'intéresser les pétroliers et tous ceux qui s'occupent de la bonne tenue des plateformes des installations off shore. Je vous remercie Monsieur Callame.

Dr. GUILLEN: J'aimerais bien poser une question Mr. Callame, à propos des résultats des recherches de corrosion depuis 86 jours, que vous avez montré; quel est l'explication pour les différences de corrosion trouvées entre une éprouvette moitié enfouie dans les sédiments

et une éprouvette hors des sédiments.

B. CALLAME: Je dois reconnaître qu'il est difficile d'expliquer la différence de corrosion qu'il y a entre une éprouvette à moitié enfouie dans le sédiment et une éprouvette qui se trouve en dehors du sédiment.

Dans le cas des éprouvettes qui sont à moitié enfouies dans le sédiment, les phénomènes d'aération différentielle sont prépondérants, mais les produits de la corrosion ne peuvent être éliminés sur la partie de l'éprouvette enfouie dans la vase et s'accumulent. Par contre, la rouille s'élimine progressivement sur la partie immergée dans l'eau de mer.

Dr. GUILLEN: Alors, l'oxyde formé dans l'éprouvette d'acier immergée dans le sédiment, vous croyez que c'est un oxyde très protecteur.

B. CALLAME: Je pense que le dépôt est constitué d'oxyde de fer noir et de sulfure de fer, formant une couche épaisse d'opposant au renouvellement du contact entre l'eau interstitielle du sédiment et l'acier.

Séance - Meeting - Sitzung - Συνεδρίασις  
23.9.1968

Présidence - Presidency  
Präsidium - Προεδρείον

Prof. B. KIORTSIS (Grèce),  
Prof. N. CHORAFAS (Grèce),  
Dr. H. KÜHL (Deutschland).

# COUNTDOWN FOR ANTIFOULING PAINTS

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## SUMMARY

1. Fouling attachments interfere with man's endeavors to use the ocean more effectively. Fouling causes:
  - a. Loss of speed of ships.
  - b. Over-consumption of fuel due to increased friction.
  - c. Corrosion.
  - d. Mechanical damage to coatings and encapsulants.
  - e. Increase in weight of buoys and navigational equipment.
  - f. Moving parts of equipment to be inoperative.
  - g. Reduction in size of opening of conduits.
  - h. Noise which interferes with sonar operations.
2. Fouling or sessile organisms include the following:  
With hard shells: Annelids, barnacles, bryozoa, molluscs.  
Without shells: Algae, hydroids, bryozoa, tunicates, sponges.
3. Factors affecting fouling include:
  - a. The slime film which seems to favor attachments.
  - b. Texture of the surface. Some growths prefer a clean rough surface. Some observers found more growth on concrete than on wood panels. Other information concerning barnacle attachments on various surfaces: Asbestos board - 980 barnacles, wood - 748, celluloid - 11, methacrylate - 11, smooth glass - 16.
  - c. Movement of water relative to a surface. Ships underway 90% of the time apparently do not need antifouling paints since they gather very little growth. The initial cyprid barnacle attachment can withstand speeds up to 3.6 knots. Other data shows barnacles can attach on surfaces moving at speeds of 0.5 knot; tubeworms can attach at 1 knot surface speed.
  - d. Light and illumination influence fouling attachments. Barnacles prefer the dark. Algae, which survive on photosynthesis, seek light.
4. First generation antifouling paints utilize heavy metal toxic compounds which are incorporated in a matrix that must promote a steady-state leaching. This provides the lethal environment necessary to repel fouling attachments. These toxics include inorganic compounds of copper, arsenic and mercury. Metal-organic compounds of tin, lead and arsenic also have been used in the last few years. These include antifoulants such as tributyltin fluoride, triphenyllead acetate and 10, 10' *oxybisphenoarsine*.
5. To maintain a steady-state leaching of toxic various matrix-toxic formulations have been developed. These function as:
  - a. A permanent matrix which permits toxic to diffuse through minute paths in the coating.
  - b. A permanent matrix in which excess toxic has been incorporated to establish contact between particles. A volume percent of about 74 is necessary for rhombohedral packing. Cubic packing requires about 52%.
  - c. A soluble matrix in which the matrix and toxic diminish simultaneously. The acid resinous portion of

the matrix saponifies in the alkaline sea water, pH 8.1-8.3. The toxic (i.e. cuprous oxide) dissolves in sea water and is expended by a diffusion mechanism which is a concentration equilibrium-effect.

- d. A matrix which has biodegradable properties.
  - e. A coating which erodes mechanically.
6. First generation antifouling paints are depleted of toxic when the surface is in motion or there is a flow of water past the surface. In the soluble matrix type the film is reduced in thickness. The saponification products are washed away while the cuprous oxide particles dissolve and diffuse out toward the water flow. If the erosion rate of the matrix is less than the solubility of the cuprous oxide, considerable surface cuprous oxide is diffused away leaving a non-toxic surface which will be attacked by attaching larvae. In the insoluble matrix type of A.F., the thickness usually does not change much, but the cuprous oxide is wasted away through the same diffusion process.
  7. Matrix solubility or dissolution is an important property in antifouling paints. For example, rosin and abietic acid have a dissolution rate in the order of about 100  $\mu\text{g}/\text{cm}^2/\text{day}$ . This value can vary depending on the age of the rosin or abietic acid. Usually resinous acid dissolution depends upon the hydroxyl ion concentration. Neutral materials have a very low dissolution rate. These include materials like the glycerol ester of rosin, hydrogenated methyl ester of rosin, copper compound of rosin and modified pentaerythritol ester of rosin.
  8. Biodegradable action or bacterial attack on matrix materials for antifouling paints is another mechanism that can help to maintain steady-state toxic leaching necessary to prevent fouling. Biodegradable materials include: Rosin, paraffin wax, alkyd resin, phenolic resin, linseed oil, polyvinylchloride, natural and synthetic rubbers. Resistant to attack are: Vinyl resin, halowax, micro crystalline wax, coal tar pitch, chlorinated styrene and polyethylene. Chlorinated rubber is slowly attacked.
  9. Effective first generation antifouling paints that last from 2-3 years on ships have been in use for quite some time. The heavy metal toxics used leach out of a soluble matrix or an insoluble matrix at a required steady-state rate (at least 10  $\mu\text{g}/\text{cm}^2/\text{day}$ ). The two types of antifouling compositions are illustrated by formulations based on rosin-vinyl-cuprous oxide. The insoluble matrix formulation consists of cuprous oxide - 90 parts by weight (67% by vol.) and rosin - 10 parts by weight (33% by vol.). The soluble matrix formulation consists of various formulations as follows:
    - a. Cuprous oxide - 90 parts by wt. (62% by vol.)  
Rosin - 10 parts by wt. (38% by vol.)
    - b. Cuprous oxide - 85 parts by wt. (51% by vol.)  
Rosin - 15 parts by wt. (49% by vol.)
    - c. Cuprous oxide - 80 parts by wt. (42% by vol.)  
Rosin - 20 parts by wt. (58% by vol.)Effective antifouling paints used by the Navy and pres-

ently being used include the following two vinyls :

- a. Formula 121 (MIL-P-15931). Cuprous oxide volume is 45%. Rosin to vinyl weight ratio is 1 : 1.
  - b. Formula 121/63 (MIL-P-15931B). Cuprous oxide volume is 45%. Rosin to vinyl weight ratio is 4 : 1.
10. Effective second generation antifouling paint systems can be developed which modify the present methods for repairs or renewing shipbottom paints. Present touchups involve abrasive blasting which extends a 10% deficiency to a 30-40% repair. Complete renewals which are presently practiced if

there is extensive fouling, could be reduced to a cleaning operation and a rejuvenating of the antifouling paint, with no damage to the undercoat anticorrosives. This new system will utilize antifouling paints, applied over permanent anticorrosives, that can be washed off in increments or totally with hot water or an aqueous chemical solution. This removable antifouling paint could be based on the first generation formulations which utilize toxics or the new second generation compositions which prevent fouling by destroying the attaching mechanism of the larva marine organism.

## PREFACE

«Let us know more of life, and meanwhile serve the King». So in the 4th Century B.C., Aristotle set the scene for today's scientists. He gathered information, classified and compiled this information into orderly branches of human knowledge. Here in Athens also, was born the right to speak up and the courage to disagree.

## INTRODUCTION

The countdown for antifouling paints could have started with Aristotle. He referred to the barnacle or «small fish» as the «ship-stopper» capable of slowing down ships. Even at this early date, efforts were made to solve the shipbottom fouling problem. Tar or wax was applied to shipbottoms with the intent of making the hulls watertight, protecting against shipworms and preventing fouling.

The arrival at copper sheathing as a efficient antifouling surface was a solution for wooden ships. However, the age of iron and steel changed this picture because of the destructive galvanic action of copper on steel. The need for a non-corrosive antifouling composition to apply on steel shipbottoms was realized. Sir Humphrey Davy in his work with copper sheathing set forth the present basis for copper leaching. He established the antifouling action of copper in relation to its rate of solution in sea water.

## TYPES OF FOULING ORGANISMS

Certain marine growth tries to accumulate on all floating or immersed structures since the life cycles of such sea animals and plants, sessile organisms<sup>1</sup>, depend upon permanent anchorage. Some of the common organisms of the fouling family are listed in Table 1 :

Table 1

### MACROSCOPIC FOULING ORGANISMS

<i>With Hard Shells</i>	<i>Without Shells</i>
Annelids	Algae
Barnacles	Hydroids
Bryozoa	Bryozoa
Molluscs	Tunicates
	Sponges

Figure 1 photograph shows a three-inch grandfather barnacle (*Balanus Nubilus*), five to seven years old, when alive responsible for rearing thousands of young barnacles. Figure 2 photograph shows a cluster of goosebarnacles (*Pollicipes Polimerus*).

## THE EFFECTS OF FOULING GROWTH

Unless measures are taken to prevent fouling attachments, man's endeavors in the ocean cease to be useful. Fouling interferes with the use or function of the structure on which it grows. If fouled, ships move slowly and cannot reach maximum speed because of the frictional drag. There is over-consumption of fuel if efforts are made to maintain speed. Other destructive effects of fouling are summarized in Table 2.

Table 2

### EFFECTS OF AGGRESSIVE ENVIRONMENTS OF THE SEA. FOULING GROWTH

- ENVIRONMENT : Macromarine Growth Attachment (Sessile Organisms)
- DETERIORATION : Fouling Growth :
- a. Causes loss of speed of ships.
  - b. Causes over-consumption of fuel due to increased friction.
  - c. Promotes corrosion.
  - d. Causes mechanical damage of coatings and encapsulants.
  - e. Causes increase in weight of buoys and navigational equipment.
  - f. Renders moving parts of equipment inoperative.
  - g. Reduces sizes of openings in conduits.
  - h. Promotes noise which interferes with sonar operations.

The effect of fouling on speed and over-consumption of fuel is shown in Table 3 :

Table 3

### EFFECT OF FOULING AFTER SIX MONTHS OUT OF DOCK IN TEMPERATE WATERS\* (Frictional resistance is assumed to increase .25% per day)

Type of Ship	Standard Displacement (Tons)	Loss of Maximum Speed (Knots)	Percentage Increase in Fuel Consumption to Maintain Speed of:	
			10 Knots	20 Knots
Battleship	35,000	1-1/2	45	40
Aircraft Carrier	23,000	1-1/4	45	40
Cruiser	10,000	1-1/4	50	45
Destroyer	1,850	2	50	35

The values of Table 3 are further explained by the fact that at higher speeds the frictional resistance is a smaller part of the total resistance according to Table 4\*. These values were from the trial runs made on the United States Destroyer HAMILTON.

Table 4

### RELATION OF SPEED AND PERCENTAGE OF TOTAL RESISTANCE ATTRIBUTED TO FRICTION

<i>Speed</i>	<i>Frictional Resistance</i>
10 knots	67 percent
20 knots	60 percent
30 knots	41 percent

The fouling of ships may be used to illustrate the critical nature of marine problems. For example, the reduction of speed and the over-consumption of fuel (even nuclear fuel does not last forever) is very costly. The ingenious efforts of engineers to design ships to gain one knot of speed are nullified



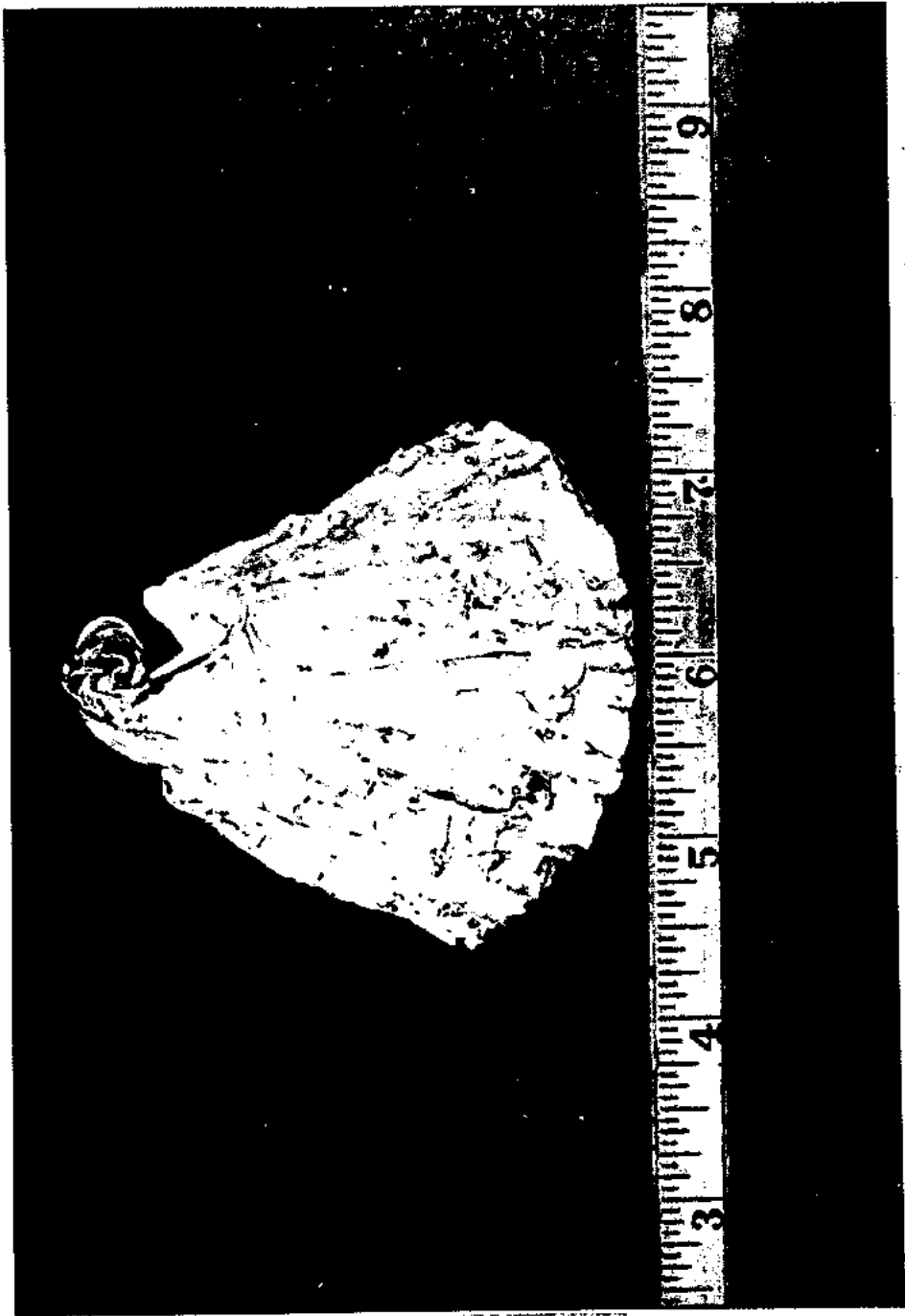


Fig. 1. A 3-inch grandfather's barnacle (*Balanus Nubilus*), 5-7 years old, when alive responsible for rearing thousands of young barnacles.



Fig. 2. Routing attachment - Pollicipes Pollimerus (Goose Barnacle).

**FIGURE A**  
**ANTIFOULING PAINTS USED BY U.S. NAVY**  
 (1929 - 1954)

<u>15a SHELLAC (1929)</u>		<u>15RC COAL TAR ROSIN (1935)</u>	
Alcohol	76 gal.	Zinc Oxide	238 lbs
Gum Shellac	82 lbs	Silica	.78 lbs
Red Gum (Yacca)	95 lbs	Magnesium Silicate	72 lbs
Pine Oil	12.5 gal.	Cuprous Oxide	145 lbs
Zinc Oxide	165 lbs	Mercuric Oxide	45 lbs
Indian Red	165 lbs	Rosin (WW)	248 lbs
Mercuric Oxide	75 lbs	Coal Tar Naphtha	47 gal.
		Coal Tar	6.4 gal.
		Pine Oil	5.2 gal.
 <u>42 HOT PLASTIC (1940)</u>		 <u>15HP HOT PLASTIC (1942)</u>	
<i>Parts by Wt.</i>		<i>(Navy Standard for World War II)</i>	
		<u>15HP-54(1954)-MIL-P-18994</u>	
Formalin Resin No. 4*	38	WW Gum Rosin	525 lbs
Paraffin	23	Phenolic Condensate*	
Cuprous Oxide	23	157 lbs	
Mercuric Oxide	8	Paraffin Wax	374 lbs
Paris Green	8	Cuprous Oxide	437 lbs
		Magnesium Silicate	113 lbs
 <u>*Formalin Resin NO. 4</u>		 <u>* Phenolic Condensate</u>	
Phenol	15	Phenol	600 lbs
Lead Acetate	9	Lead Acetate	67.5 lbs
Formalin Sol. (40%)	18	Formaldehyde Sol. (40%)	414 lbs
Water	15		
Rosin (WW)	120		

143E COLD PLASTIC (1943)<sup>1</sup>  
*(Navy Standard for World War II)*

Phenolic Vehicle*	714 lbs
Cuprous Oxide	475 lbs
Tricresylphosphate	80 lbs
Chlorinated Rubber	10.6 lbs
Coal Tar Naphtha	5.8 lbs

\*Phenolic Vehicle

WW Gum Rosin	492 lbs
**Phenolic Condensate	246 lbs
Coal Tar Naphtha	20.5 gal.

\*\*Phenolic Condensate

Phenol	284 lbs
Lead Acetate	169 lbs
Formaldehyde Sol. (40%)	258 lbs

<sup>1</sup> Patented 25 December 1961 (No. 2,579,610); commercial rights reserved to inventors.

by a lowly order of life such as the barnacle—the «ship-stopper».

Before the advent of effective antifouling paints, ship operators would allow from one-fourth to one-half percent\* increase in drag or friction per day out of dock because of the expected accumulation of fouling. Hence, lower speeds and over-consumption of fuel were planned for. It was a well-

**FIGURE B**  
**ANTIFOULING PAINTS**  
**CURRENTLY USED BY U.S. NAVY**

<u>FORMULA 134 (1960)<sup>1</sup></u> <u>MIL-P-22299</u>		<u>FORMULA 121/63 (1963)<sup>2</sup></u> <u>MIL-P-45931B</u>	
(Current Navy standard for rubber surfaces and metal sonar domes)			
	<i>Pounds</i>		<i>Pounds</i>
Cuprous Oxide	700	Cuprous Oxide	1440
Rosin	32	Vinyl Resin VYHH	55
Polyisobutylene Resin		Rosin	215
Polymer	45	Tricresylphosphate	50
Xylene	564	Methyl isobutyl ketone	165
Inhibitor (Deenax or equal)	0.05	Xylene	115
		Antisettling Agent	5 - 9
 <u>FORMULA 15HPN (PATENTED)</u> <u>MIL-P-19452</u>		 <u>FORMULA 105<sup>3</sup> (PATENTED)</u> <u>MIL-P-19451</u>	
	<i>Pounds</i>		<i>Pounds</i>
Gum Rosin (WW, 1)	420	Gum Rosin (WW, 1)	277
Paraffin Wax (143/150°F m.p.)	71	Blown Fish Oil	118
Ceresin Wax (170/175°F m.p.)	38	Zinc Stearate	18
Copper Linoleate	94	Cuprous Oxide	589
Copper Pigment or Cuprous Oxide	325	Zinc Oxide	161
Magnesium Silicate	54	Magnesium Silicate	56
		Solvent Naphtha	241

<sup>1</sup> Patent No. 3,033,809 (8 May 1962); commercial rights reserved to inventors.

<sup>2</sup> Black version, Formula 129/63 (MIL-P-16189B).

<sup>3</sup> Black version, Formula 146/50 (MIL-P-1944B).

established fact in marine circles that after nine months out of drydock a ship should again be docked for removal of fouling and for repainting. At the end of this waterborne period, there would be a substantial drop in normal speed and increased fuel consumption. Ship operators had to bear the expense of such frequent dockings at a rate of \$4,000 to \$5,000 per day in dock. An expense of \$100,000<sup>4</sup> for a large ship for docking and painting was the usual bill.

However, with research and development programs initiated by the United States Navy in cooperation with industry, improved shipbottom coatings were developed and are available today. Such coatings as the famous Mare Island 15HP Hot Antifouling Plastic and 143E Cold Plastic were used on all U.S. Navy ships. Figure A table shows a summary of antifouling paints used by the U.S. Navy between 1929 and 1954. Figure B shows the antifouling paints currently used by the U.S. Navy.

Figure 3 photograph shows three years' performance of the hot plastic antifouling coating on a carrier shipbottom.

Figure 4 photograph shows 16 months' performance of the vinyl shipbottom paint system on a submarine.

Besides the fouling of shipbottoms, buoys and other navigational devices become overlaid—the excess weight-causing them to shift. Certain sound devices become inoperative. Pipes or conduits are «choked-up» with marine growth, causing the flow of water through them to diminish or stop.

Fouling can promote and accelerate corrosion of metals. The classical example is the completely «tarred» barnacle that has plowed through a soft bituminous coating in its growth process. Once the barnacle shears open the film, water penetration to the metal is easy, permitting the corrosion action to start. Also, when the barnacle settles down near the metal surface, uneven areas between the metal and the base of the



Fig. 3. Three years performance of hot plastic anti-fouling coating on a carrier.

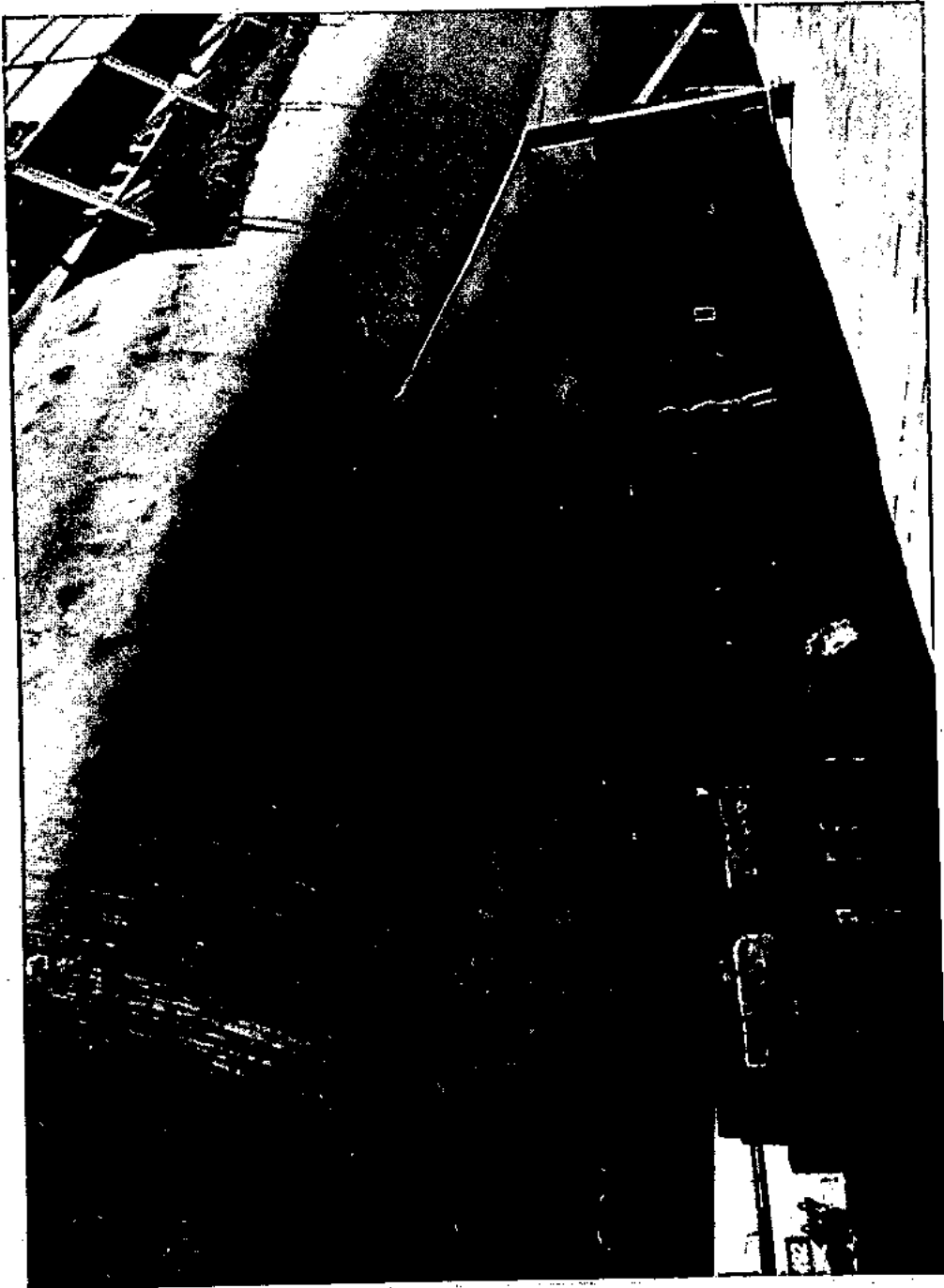


Fig. 4. Sixteen months performance of vinyl shipbottom paint system on a submarine.

barnacle may provide oxygen concentration cells which promote galvanic corrosion. Early experiments in the Navy with bare stainless steel sonar domes resulted in perforations under attached barnacles due to this formation of oxygen concentration cells. Accelerated corrosion of metal can also be promoted by the decomposition products of dead barnacles or other growths that give off hydrogen sulfide. Certain heavy-shelled marine growth may attach so firmly to a painted surface that when sufficient mechanical leverage results after growth, part of the paint can be stripped off exposing bare metal. Also, where there is fouling (dead or alive), there will be an abundance of micro-organisms of the sulfate-reducing type which can promote corrosion.<sup>5</sup>

## FACTORS AFFECTING FOULING

Marine growth accumulation on a surface exposed to normal sea environments can vary as to type and amount. Many factors enter into this race to attach. The extent of attachment depends on factors which determine the number of larvae coming in contact with a surface and those factors which limit the ability of these larvae to attach to the surface and grow.

The number of larvae coming in contact with an immersed surface depends on the type of service which the surface will experience — a moving ship, a static buoy — and the texture, color, etc. The tendency of slime to form on the surface and wetting characteristics of the surface may have significant influences on attachments.

The slime film which is usually the first type of attachment goes through a sort of biotic sequence consisting of bacteria, algae and protozoa. Many investigators have placed considerable importance on the slime film in its role in the fouling mechanism. The presence of the slime film is believed to influence subsequent attachments of larger fouling forms.

From the results of immersed glass panels in the study of the attachment of barnacle cyprids, ZoBell<sup>6</sup> concluded that the slime or gelatinous film that forms in a few days is beneficial to attachment. He enumerated the possible ways the slime film might favor fouling attachment:

- a. By engulfing or enveloping the larvae.
- b. By changing the color or reflection of surfaces.
- c. By serving as food.
- d. By acting as a barrier between the larvae and the toxics in the paint.
- e. By increasing the pH or alkalinity which would favor the deposition of calcareous cements.
- f. By influencing the electrical potential of the surface.

Adamson<sup>7</sup> has concluded that there are various types of slimes that form on different paints. The gelatinous slimes seem to discourage attachment whereas the silty or granular slimes encourage attachments. One other observer, Bray<sup>8</sup>, concluded that surfaces which accumulated the heaviest slimes finally became the most fouled.

Although there has been extensive work done in the study of slime films, there does not seem to be any real correlation between the amount or physical properties of the slime and the ability of the surface to prevent fouling. However, the slime film is quite important from the view of its toxic content which it derives from the paint film, and the effect the slime may have on the leaching rate of the paint.

Another factor that can influence fouling attachments is the type of surface and surface texture. Brooks<sup>9</sup>, for example, states that young oysters attach best to a clean, rough surface. Barnacle attachments appear to increase on monthly-collecting concrete or glass panels after the initial month's exposure. After scraping off the first month's growth, a residue usually remains on the panel which offers a rough surface conducive to more aggressive attachments.

Although surface smoothness cannot be used as a method to retard fouling, it certainly is true that the type of surface and the texture do affect the amount of fouling which may attach under comparable conditions. Coe and Allen<sup>10</sup> found more fouling, generally, on concrete blocks than on wood

panels. Further, Pomerat and Weiss<sup>11</sup> found that smooth, nonporous, nonfibrous and hard surfaces were poor selections for collecting marine growth. In one experiment, they recorded the following growth on one square foot of various surfaces over a three-month period:

Asbestos board	980 barnacles
Wood	748 barnacles
Celluloid	11 barnacles
Methacrylate	11 barnacles
Smooth glass	16 barnacles

Movement of water relative to a surface is another factor that influences fouling. It is well known that ships inadequately protected with a shipbottom system and moving 90 percent of the time gather very little marine growth whereas such ships that are underway only 30 percent of the time are usually heavily fouled. Attachment efforts of barnacles were noted by Smith<sup>12</sup> under water velocities of 0.2 to 3.8 knots. Attachments were made up to a maximum water flow of 0.5 knot. Certain tubeworms can successfully attach up to water speeds of 1.0 knot. Since the initial attachment of barnacle cyprids is through a pair of antennal suction cups (10 microns in diameter), the two small areas which provide anchorage can be pulled away by forces greater than water moving in excess of 0.5 knot. It has been calculated that the pressure developed by the antennal vacuum cup is in the order of one dyne<sup>13</sup>. Other calculations<sup>14</sup> show that the suction cups can withstand 3.6 knots, 186.4 cm/sec, and exert a force of adhesion equal to 7.5 dynes.

Various studies have been made on disks<sup>12</sup> on which various aged attached barnacles were collected. The disk was covered by sections of membrane and sectors made bare for attachment at intervals of 6 hours and 1, 2, 5 and 16 days. In one particular case, a disk was prepared on which the fouling consisted of barnacles, bryozoa and hydroids. The disk was rotated for 19 days at 60 rpm. Fouling near the periphery of the disk was removed, growth in intermediate areas was stunted, while near the center fouling continued to grow. The test also showed that the older barnacles were more resistant since they withstood higher velocities. It required velocities of over 4 knots to remove barnacles that had been attached more than 16 days.

Another factor that may influence fouling attachments is gravity. It is not too convincing, but experiments have been conducted which seem to indicate that fouling reacts a certain way to the force of gravity. In general, more attachments are present on the underside of a horizontal surface than on any other angle at which a surface may be exposed. Usually, the topside of a horizontal surface is covered with a layer of sediment which can discourage certain sessile growth attachments.

Light and illumination have a certain influence on attachment of fouling larvae which is quite similar to what occurs with gravity. Because it is darker, most larvae will attach to the underside of a horizontal surface which also results in the case of gravity. Most fouling organisms are light sensitive; barnacles seek the darkness whereas algae seek light — the algae requiring light for photosynthesis. It is known that silt in the water reduces the amount of algae growing on a vertical surface because light penetration is greatly reduced. Some larvae are negatively phototropic when attaching; in other instances, some larvae are positively phototropic when released but at the time of attaching they are negative. The cyprid larvae of barnacles are of this latter type. At the time of attachment, the cyprid seeks darkness and attaches with its head away from the light source<sup>15, 16</sup>.

Experiments with unglazed colored tiles showed about one-third the fouling on light-colored tiles as on the darker tiles<sup>17</sup>. Other exposures made by Pomerat and Reiner<sup>18</sup> at Pensacola (Florida) utilized black, clear and opal glass panels. About twice as many barnacles settled on the black plates as on the opal or clear plates. These experiments were extended to include moonless, dark nights. Attachments between 9 PM and 3 AM on all three types of panels were re-

markedly similar in number. Totalling the attachments on four of each type of plate, the fouling was 341 on the black panels, 393 on the opal, and 394 on the clear.

Another factor which has been observed as to its effect on fouling is an exfoliating surface. Such a surface disintegrates by loss of particles which are much larger than molecular size (not by solution). Since such a surface is physically weak, it offers no substantial footing for attaching organisms. It has been suggested that any amount of fouling would increase the pull on the surface and break it loose, thus fouling would not accumulate on such a sloughing surface.

Unfortunately, it has been quite difficult to prove the worth of exfoliating surfaces (A.F. paints). Most such compositions contain toxics which may be directly responsible for the antifouling property rather than the exfoliation characteristics which the material may also possess.

#### DESIGN OF FIRST GENERATION ANTIFOULING PAINTS

In designing an antifouling paint based on a toxic such as cuprous oxide several factors must be taken into consideration. First of all, there must be sufficient toxic in the applied coating film to last at least from the undocking date to the next scheduled docking. Assuming coatings of good durability, the reservoir of cuprous oxide required can be furnished by applying a relatively thin film of a highly loaded antifouling paint, or a thick film of a coating with relatively low antifoulant loading. In an average situation, it has been determined that most attachments would be prevented if a minimum toxic equal to 10 mg of copper metal was leached from 1000 sq. cm. of surface in 24 hours<sup>19</sup>. In the first type formulation, an insoluble matrix or binder, such as vinyl resin, could be used and sufficient cuprous oxide to produce continuous contact of the toxic particles. However, using only the vinyl resin, excessive amounts of cuprous oxide would be required to result in continuous contact of the toxic particles.

The practical approach is to blend a less inert binder material like rosin with the vinyl and use a combination of soluble matrix and toxic contact-type formulations. Usually, a 50:50 to 80:20 rosin:vinyl ratio by weight produces a satisfactory antifouling composition at 45 percent toxic volume in the dry film.

Besides antifouling characteristics, an antifouling paint must have durability and good adhesion to the undercoat system. Too often an antifouling paint will peel off and expose the anticorrosive coating. This «bare» area will then foul. Erroneously, the fouling resistance of such a paint is rated as poor, whereas perhaps some improvement in the adhesion may result in an excellent antifouling coating.

In the design of an antifouling paint, then, there must be a delicate balance between the physical and chemical properties of the coating. If it is desired that the coating be tough and durable, it must still possess good adhesion. Normally, there has to be some compromise for toughness to gain adhesion. Also, a tough paint would require excess toxic. Again, too much toxic would weaken the physical film, so a modification is made and some film modifier like rosin is used and a less tough but quite satisfactory coating is obtained.

For an antifouling paint based on cuprous oxide toxic to be effective, a steady state leaching rate of copper equal to at least 10 mg/1000 cm<sup>2</sup>/24 hours must be maintained. There are several ways this leaching of copper is attained. Considering essentially two classes of antifouling paints — the insoluble and soluble matrix types — the steady state leaching rate is acquired as follows:

- a. *Insoluble Matrix Type* — Toxic alone is removed by:
  - (1) Diffusion through a permeable paint
  - (2) By continuous contact of toxic particles
- b. *Soluble Matrix Type* — Toxic and matrix are removed simultaneously by:
  - (1) Dissolution of the matrix
  - (2) Bacterial or biodegradable action of the matrix
  - (3) By mechanical erosion of the matrix.

FIGURE C

#### PERMEABILITY OF MOISTURE THROUGH ORGANIC COATINGS — Burns (1939)

Coating	Milligrams of H <sub>2</sub> O/0.001 inch film/sq. inch/24 hours
1. Cellophane (not moisture proof)	300
2. Cellulose acetate	300
3. Vinyl acetate	115
4. Vinyl chloroacetate	27
5. Linseed oil	80
6. Long oil varnishes	36 - 48
7. Long oil varnishes plus aluminum powder	14
8. Short oil varnishes	17 - 24
9. Single pigment paints	29 - 56
10. Nitrocellulose lacquers	15 - 87
11. Orange shellac	16
12. Asphalt coatings	5
13. Polyamide-epoxy	1 or less
14. Vinyl copolymers	1 or less
15. Vinyl-alkyds	1 or less
16. Polyurethanes	1 or less

These values of permeability are applicable to normal conditions near the sea water surface.

In the case of the *insoluble matrix type of formulation*, the toxic is released by diffusion through a permeable paint or by continuous contact of toxic particles. It must be pointed out that the classical permeability of water through a permeable membrane or paint film (see Figure C, table of Permeability Values for Films) is not similar to the diffusion of a salt through a permeable paint. In the first case, water passes through molecular spaces in the film-forming material; in the second case, salt ions like copper pass through the paths and voids inherent in the applied paint. Also, the diffusion of copper ion is unlike the classical diffusion of one molecular species within another (one gas mixed with another or one liquid in another). The diffusion that takes place is a concentration factor. When salt water reaches a particle of cuprous oxide, a concentrated interface of copper salt is created. In an effort to reach equilibrium, the copper ions move or diffuse toward the less concentrated liquid. Stirring or motion, such as a ship moving, can promote this rate of solution or diffusion so that quantities of cuprous oxide are wasted in the surrounding water<sup>20</sup>. The biological slime film that can concentrate copper during static conditions, thus conserving the total copper in the paint film by regulation of the diffusion rate, can be washed away at high speeds and lay the paint film open to fast «solution» or diffusion of cuprous oxide. The result of expended paint is a skeleton of the insoluble matrix with a deposit of copper compounds such as basic carbonate and copper resinate.

The simplest mechanism for steady state leaching of copper takes place with the *soluble matrix type of antifouling composition*. In this case, the matrix and cuprous oxide are wasted or removed simultaneously. The result is that there is a gradual wear or recession of the paint surface. Rosin, which is the preferred soluble matrix material being a mixture of isomeric resin acids (one of which is abietic acid), dissolves in alkali such as sea water at a pH varying from 8.1 to 8.3. Darsie<sup>21</sup> showed that small rosin fibers wore or «dissolved» in sterile sea water at a rate of about 100 micrograms per square centimeter per day (or 100 mg/1000 cm<sup>2</sup>/24 hours) — see Figure D, table of Dissolution Values of Rosin in Sea Water. Significant solubilities of several hundred micrograms per cubic centimeter at the pH of sea water have been measured<sup>22</sup> for W.W. and W.G. Rosins. (See Figure E for table of dissolution of various antifouling paint matrix materials in normal sea

FIGURE D

DISSOLUTION OF ROSIN IN RUNNING SEA WATER FROM A PANEL 155 cm<sup>2</sup> IN AREA STIRRED AT 85 R.P.M. FOR 24 HOURS. THE EFFLUENT SEA WATER WAS CONTINUOUSLY EXTRACTED WITH CHLOROFORM<sup>2</sup>

Drying Time of Panel Days	Volume of Sea Water Used Liters	Total Rosin Dissolved mg	Rosin Dissolved $\mu\text{g}/\text{cm}^2$
1	24.5	19	123
2	29.5	21	135
6	12.0	37	239
7	13.0	49	316
14	14.0	62	400
93	20.0	173	1117
99	17.0	177	1140
102	20.7	226	1460

a. The amount of rosin dissolved and recovered from solution varies considerably depending on its aging time. These values range from 123  $\mu\text{g}/\text{cm}^2$  for one day old rosin to 1460  $\mu\text{g}/\text{cm}^2$  for 102 days old rosin. During the aging period the rosin oxidizes and presumably forms more soluble products or particles that can be carried away by erosion and not dissolved by dissolution or saponification.

b. Darsie<sup>21</sup> shows about the same dissolution rate for fresh rosin. He subjected thin rosin fibers to moving sterile sea water and measured the reduction in diameter of the fiber. From calculations he determined the dissolution rate to be in the order of 100  $\mu\text{g}/\text{cm}^2/\text{day}$ .

water, pH 8.1-8.3). For crude grades like K Rosin, FF Wood, Belro and Vinsol, the solubilities are lower. Also, somewhat lower values have been found for Stabelite (hydrogenated rosin). Where the carboxyl group is unmodified (W.W. Gum Rosin or Abietic Acid), the solubility or dissolution rate is proportional to the hydroxyl ion concentration.

The following neutral materials have low dissolution rates and ordinarily are not used as the major or prime matrix material:

- Ester Gum — glycerol ester of rosin
- Hercolyn — hydrogenated methyl ester of rosin
- Copper Resinate — copper compound of rosin
- Pentalyns M and G — modified pentaerythritol ester of rosin.

#### BACTERIAL ATTACK OR BIODEGRADABLE ACTION ON MATRICES

Bacterial attack or biodegradable action is another mechanism for the gradual removal of matrix in order to attain steady state leaching of toxic. When a surface is first subjected to sea water, a slime film forms which is essentially made up of bacteria and diatoms. The property of the slime which seems to be important is its toxic content. Copper removed from the paint film combines with the slime<sup>23,24</sup> and can also form slightly soluble basic carbonate. This slime-copper medium serves as a regulator for the diffusion action of cuprous oxide in the film. Also, the bacteria in the slime can help maintain the steady state copper leaching by decomposing such matrix components as rosin, paraffin and copper resinate<sup>21,25</sup>.

To further establish the role of biodegradable action of bacteria in the slime film, Renn and Johnson<sup>26</sup> partially inhibited the growth of bacterial film on antifouling paints by periodically immersing test panels in a bactericidal solution of sodium pentachlorophenate. Table 5 shows the effect of this on the leaching rates:

Table 5

#### EFFECT OF PERIODIC DISINFECTION ON LEACHING RATES OF VARIOUS ANTIFOULING PAINTS

Paint	(Weeks) Time of Immersion	Copper Leaching Rates ( $\mu\text{g}/\text{cm}^2/\text{day}$ )	
		Un-treated	Treated (Disinfected)
*142C (U.S. Navy)	4	7.4	4.1
*142C (U.S. Navy)	7	7.3	4.7
**143E (U.S. Navy)	4	14.4	8.4
***1B8 (Ester Gum)	4	2.9	2.2
*142C - Rosin, paraffin (120-125°F m.p.) and cuprous oxide			
**143E - Rosin/phenolic solution with cuprous oxide			
***1B8 - Ester Gum solution with cuprous oxide			

Where biodegradable materials were present such as rosin and

FIGURE E

#### DISSOLUTION OF VARIOUS ANTIFOULING PAINT MATRIX MATERIALS IN NORMAL SEA WATER AT pH 8.1-8.3

MATERIAL	DISSOLUTION ACTION	REFERENCE
Rosin	In the order of 100 $\mu\text{g}/\text{cm}^2/\text{day}$	Darsie <sup>21</sup>
Rosin (WW, WG; K, Belro and Vinsol)	a. Several hundred micrograms per c.c. per day for WW and WG pure rosins. For K, Belro and Vinsol the values would be the lower ones. Vinsol would be the lowest since it is a residue product of rosin. FF wood rosin would be low also.	Todd <sup>22</sup> Saroyan <sup>29</sup> (Vinsol, F.F. Wood, Rosin)
	b. Staybelite (hydrogenated rosin) Somewhat smaller solubility. Polypale (dimerized rosin). Somewhat smaller solubilities.	Todd <sup>22</sup>
	c. For WW rosin and abietic acid Solubilities are proportional to hydroxyl ion concentration.	Todd <sup>22</sup>
Neutral Resins	Negligible Solubilities	Ref. <sup>2</sup> page 289
Such as ester gum (glycerol ester of rosin), Hercolyn (hydrogenated methyl ester of rosin), copper resinate (copper reacted with rosin), and Pentalyns M and G (modified pentaerythritol ester of rosin)		
143E Matrix (Rosin-phenolic Resin)	About 100 $\mu\text{g}/\text{cm}^2/\text{day}$	Ferry <sup>23</sup>



paraffin (142C and 143E) bacterial activity was contributing to the release of the toxic. With Ester Gum the bacterial attack was limited.

### MECHANICAL EROSION OF MATRICES

Mechanical erosion is another mechanism for maintaining steady state toxic leaching through gradual removal of interfacial paint surface. This type action is unlike dissolution since the particles that are detached are of a greater size than the molecules set free in dissolution. Chemical action (dissolution or saponification) subsequent to friction and mechanical type forces promote erosion action by disintegrating the structure of the paint surface. Actual mechanical wear of antifouling paints is insignificant unless preceded by chemical action. This is illustrated by experiments related to leaching of toxic.

Hot and cold plastic antifouling paints were exhausted of the surface cuprous oxide by an acid bath. The point of exhaustion was determined by low copper content of subsequent acid baths. Disk panels so prepared were spun at 1500 rpm in sea water for several hours during which time wear should have resulted. Such disks showed no recovery of copper leaching rate<sup>26</sup>. Erosion as a mechanical mechanism for maintaining steady state leaching is not a main factor. Such wear needs to be associated with chemical dissolution.

Tests conducted at Miami, Florida, with disks coated with 143E (Cold Plastic: rosin-phenolic vehicle) and spun in the ocean at 750 rpm for 21 days showed a thickness change of 1-3 mils<sup>27</sup> on the basis of 15 µg/cm<sup>2</sup>/day normal dissolution of the 143E. This would account for only 0.5 mil of coating; so in this case a considerable acceleration of paint loss was obtained due to the erosion or wear action induced by spinning the disk. Friction induced by motion, along with the dissolution chemical action which produced rosin decomposition products as well as copper reaction products, resulted in measurable film loss:

Van Londen<sup>20,28</sup> demonstrated erosion under motion by measuring dimension changes and total copper in antifouling films when subjected to a cylinder rotating in sea water. Traveling equivalent distances of 5,000 to 50,000 miles, laboratory exposed antifouling paint films appeared similar to films observed on ships that travel like distances. For soluble types of antifouling paints, 5-10 percent of the original film thickness wore away in traveling 5,000 to 50,000 miles. However, the total copper per unit area decreased measurably, going down to below 10 percent of its original amount. This suggests the vast loss and waste of toxic encountered in soluble matrix type coatings on a ship underway. With the insoluble matrix type material there is a very small amount of film decrease as well as low toxic loss while the ship is underway.

Figure 5 photograph shows the condition of the vinyl shipbottom paint system after 8 months underway.

Figure 6 photograph shows a photomicrograph of the cross-section of a sample of vinyl shipbottom paint system on a submarine after 8 months of service. The initial thickness was 12 mils. From 1 to 1½ mils of antifouling paint of the original 5-6 mils was expended in 8 months.

### PERFORMANCE OF ANTIFOULING PAINTS

#### 1. SERIES «V» (See Figure F, composition triangle diagram and table of performance data)

Fifty solvent antifouling paints<sup>26</sup> were formulated using rosin, VYHH vinyl resin and cuprous oxide toxic. The antifouling paints were applied on wood panels to eliminate corrosion effects and evaluated for fouling resistance at the

U.S. Navy Paint Test Site at Point Reyes, California. These compositions covered a wide variation in ingredient amounts and provided the essential mechanisms to attain steady state copper leaching.

Represented were the following insoluble matrix type with varying amounts of cuprous oxide:

Formula	Cuprous Oxide % by Vol., Dry Film	Fouling Resistance (Months)			Total Solubles by Vol. %
		5	13	19	
V-1	67	100	100	100	67
V-7	56	100	100	75	56
V-13	47	100	0	0	47
V-19	35	0	0	0	35
V-25	25	0	0	0	25
V-31	16	0	0	0	16
V-37	9	0	0	0	9

From these results, it can be concluded that with the insoluble matrix type of antifouling paint, where there is no matrix dissolution, continuous contact or near continuous contact of cuprous oxide particles must be attained before effective leaching of at least 10 mg/1000 cm<sup>2</sup>/24 hours is obtained. The theoretical value for continuous contact for spheres is 74 percent by volume. Formula V-1, at 67 percent, is the only formulation approaching the 74 percent value and the only composition that performed for 19 months.

Stieg<sup>30</sup> shows various packing arrangements of pigments to get critical pigment volume content or continuous contact. He proposes a paint film as a bed of solid particles (pigment) into which a liquid (vehicle, binder or matrix) has been infused instead of a liquid into which solid particles have been stirred. It is well known that certain porosities or voids are formed when a pigment is mixed with a vehicle. These voids are very small and are not in the order of gross porosity developed in a paint film by air or solvent entrapment. Figure 7 photograph shows such gross porosity due to air entrapment as compared to Figure 8 photograph where special spray application technique was used which resulted in a dense, nonporous film. With the minute voids or porosities that are formed between pigment particles and vehicle, the following continuous contact volumes are derived with the particular arrangements of the pigment particles:

Packing Arrangement	Continuous Contact Pigment Volume
Rhombohedral	74 percent
Tetragonal-spheroidal	70 percent
Orthorhombic	60 percent
Cubic	52 percent

Accordingly, for an insoluble matrix type antifouling paint, the minimum pigment volume to get continuous contact is 52 percent with the particles arranged in the cubic form. Apparently, Formula V-1 at 67 percent pigment volume would have to have the cuprous oxide particles arranged other than in the rhombohedral form.

The completely soluble matrix formulations included the following:

Formula	Cuprous Oxide % by Vol. Dry Film	Film	Resistance (months)			Total Solubles % by Vol.
			Fouling 5	13	49	
V-6	63	Good	100	100	100	100
V-12	52	Some wear	100	100	100	100
V-18	43	Some wear	100	100	100	100
V-24	31	Paint wearing	100	100	80	100
V-30	22	A.F. worn thin	100	80	40	100
V-36	13	Considerable wear	90	0	0	100

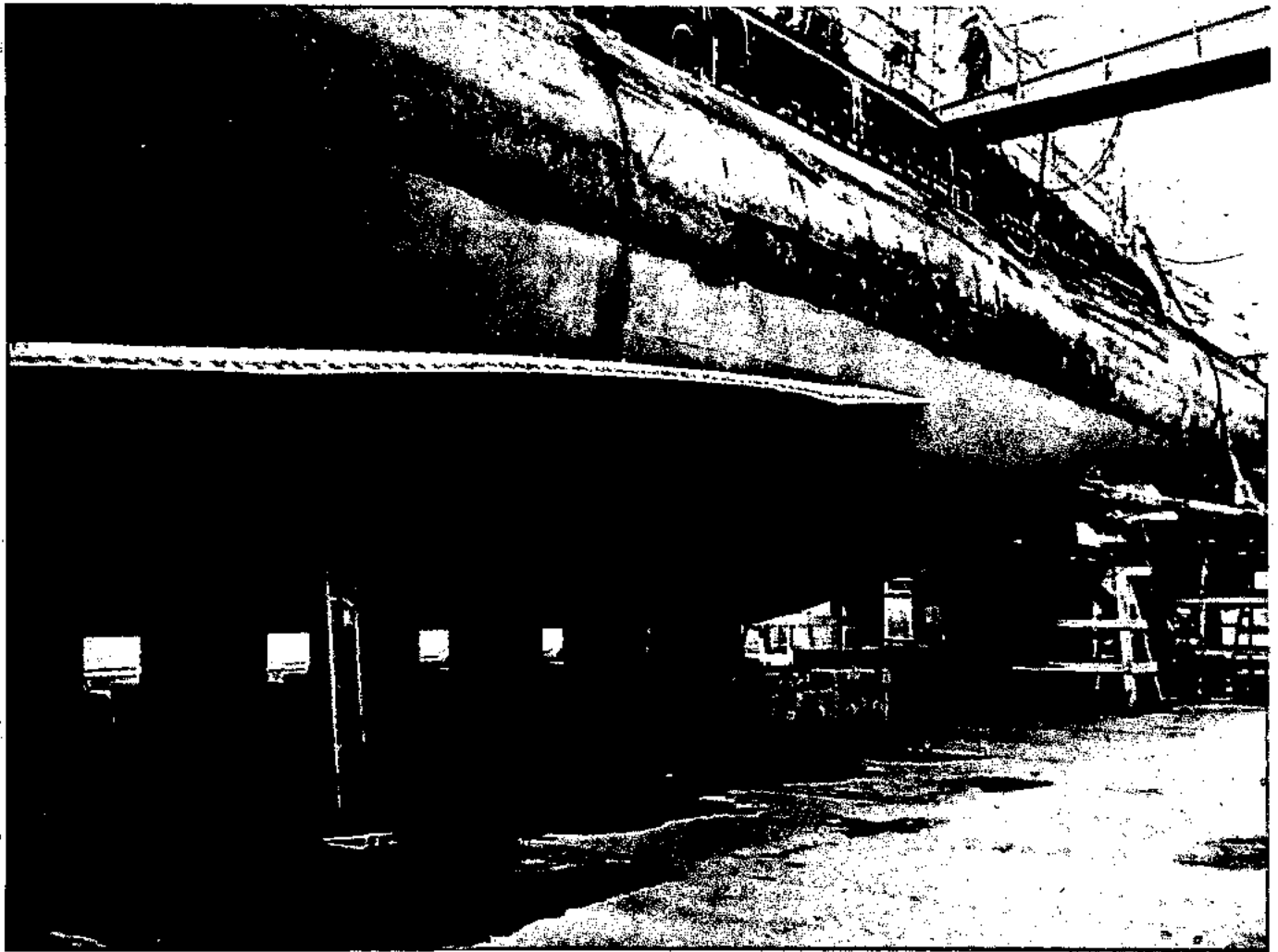


Fig. 5. Eight months performance of vinyl shipbottom paint system (i-117, 4-119 and 2 coats 121) on a submarine.)

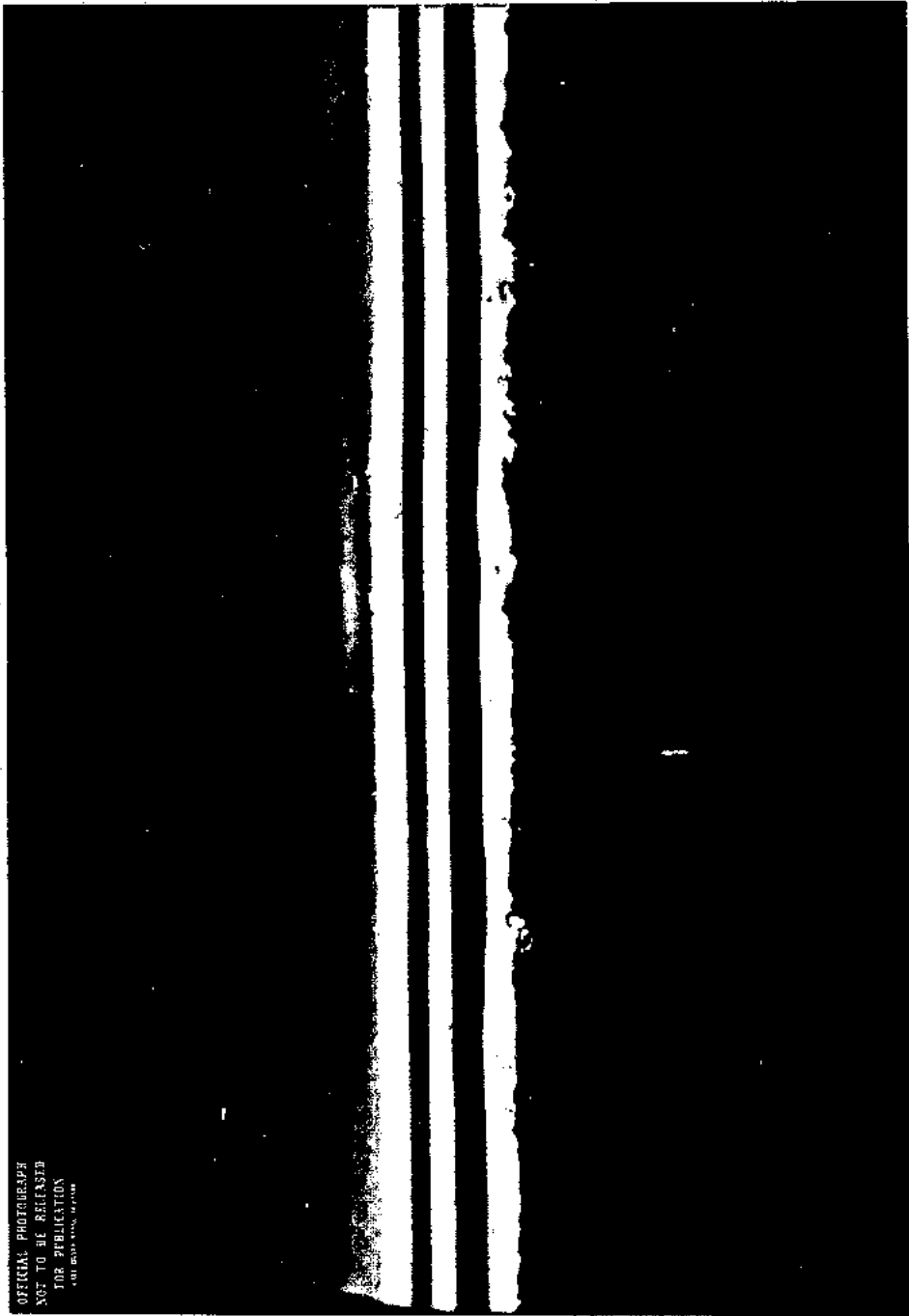


Fig. 6. Photomicrograph of the cross-section of a sample of vinyl shipbottom paint system on a submarine after eight months service. Initial thickness — 12 mils. 1-1 1/2 mils of 121 AF utilized in eight months. About 4 mils of 121 still remaining. (Mylar strip, A, is 10.2 mils; original film thickness was about 12 mils — B; the A.C. is about 6 mils-C; the remaining A.F. about 4 mil-D; and the green layer about 1-1 1/2 mils-E).

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FOR PUBLICATION  
MIL-STD-1388-1



Fig. 7. Photomicrograph of a cross-section of ordinarily, sprayed Saran, Formula # 113 (MIL-L-16389) showing gross porosity. Void spaces between pigment particles and vehicle or matrix are extremely small in comparison.



OFFICIAL PHOTOGRAPH  
NOT TO BE REPRODUCED  
FOR PUBLICATION  
GPO: 1957 O-500, 000-000

Fig. 8. Photomicrograph of a cross-section of dense non-porous Saran, Formula # 113 (MIL-J-18389) resulting from special spray technique. Void spaces between pigment particles and the vehicle or matrix may still be present but are extremely small to be seen at this magnification.

FIGURE F  
PERFORMANCE OF SOLVENT ANTIFOULING PAINTS  
CONSISTING OF  
ROSIN - CUPROUS OXIDE - VINYL RESIN  
(WOOD PANELS - STATIC EXPOSURE OFF POINT REYES BARGE)

FOR- MULA	ROSIN (9.0)			CUPROUS OXIDE (50)			VINYL RESIN (11.3)			% Total Solubles by Vol.	FOULING RESISTANCE (MONTHS)		
	Parts by Wt.	Parts by Vol.	Vol. %	Parts by Wt.	Parts by Vol.	Vol. %	Parts by Wt.	Parts by Vol.	Vol. %		5	13	19
V-1	0	0	0	90	1.8	67	10	0.89	33	67	100	100	100
V-2	2	0.22	8	90	1.8	66	8	0.71	26	74	100	100	100
V-3	4	0.44	16	90	1.8	65	6	0.53	19	81	100	100	100
V-4	6	0.66	23	90	1.8	64	4	0.35	13	87	100	100	100
V-5	8	0.88	31	90	1.8	63	2	0.18	6	94	100	100	100
V-6	10	1.11	38	90	1.8	62	0	0	0	100	100	100	100
V-7	0	0	0	85	1.7	56	15	1.33	44	56	100	100	75
V-8	3	0.33	11	85	1.7	55	12	1.06	34	66	100	100	100
V-9	6	0.66	21	85	1.7	54	9	0.80	25	75	100	100	100
V-10	9	1.00	31	85	1.7	53	6	0.53	16	84	100	100	100
V-11	12	1.33	40	85	1.7	52	3	0.27	8	92	100	100	100
V-12	15	1.66	49	85	1.7	51	0	0	0	100	100	100	100
V-13	0	0	0	80	1.6	47	20	1.77	53	47	100	0	0
V-14	4	0.44	13	80	1.6	46	16	1.42	41	59	100	100	80
V-15	8	0.88	25	80	1.6	45	12	1.06	30	70	100	100	90
V-16	12	1.33	36	80	1.6	44	8	0.71	20	80	100	100	100
V-17	16	1.77	47	80	1.6	43	4	0.35	10	90	100	100	100
V-18	20	2.22	58	80	1.6	42	0	0	0	100	100	100	100
V-19	0	0	0	70	1.4	34	30	2.66	66	34	0	0	0
V-20	6	0.66	16	70	1.4	34	24	2.13	50	50	90	0	0
V-21	12	1.33	30	70	1.4	33	18	1.60	37	63	95	85	50
V-22	18	2.00	44	70	1.4	32	12	1.06	24	76	100	90	90
V-23	24	2.66	58	70	1.4	31	6	0.53	11	89	100	90	40
V-24	30	3.33	70	70	1.4	30	0	0	0	100	100	100	80
V-25	0	0	0	60	1.2	25	40	3.54	75	25	0	0	0
V-26	8	0.88	18	60	1.2	24	32	2.83	58	42	0	0	0
V-27	16	1.77	35	60	1.2	23	24	2.13	42	58	0	0	0
V-28	24	2.66	50	60	1.2	23	16	1.42	27	73	50	0	0
V-29	32	3.55	65	60	1.2	22	8	0.71	13	87	30	0	0
V-30	40	4.44	79	60	1.2	21	0	0	0	100	100	80	40
V-31	0	0	0	45	0.9	16	55	4.86	84	16	0	0	0
V-32	11	1.22	20	45	0.9	15	44	3.89	65	35	0	0	0
V-33	22	2.44	39	45	0.9	14	33	2.92	47	53	0	0	0
V-34	33	3.66	56	45	0.9	14	22	1.94	30	70	0	0	0
V-35	44	4.88	72	45	0.9	13	11	0.97	15	85	80	0	0
V-36	55	6.11	87	45	0.9	13	0	0	0	100	90	0	0
V-37	0	0	0	30	0.6	9	70	6.19	91	9	0	0	0
V-38	14	1.55	22	30	0.6	8	56	4.96	70	30	0	0	0
V-39	28	3.11	42	30	0.6	8	42	3.71	50	50	0	0	0
V-40	42	4.66	60	30	0.6	8	28	2.48	32	68	0	0	0

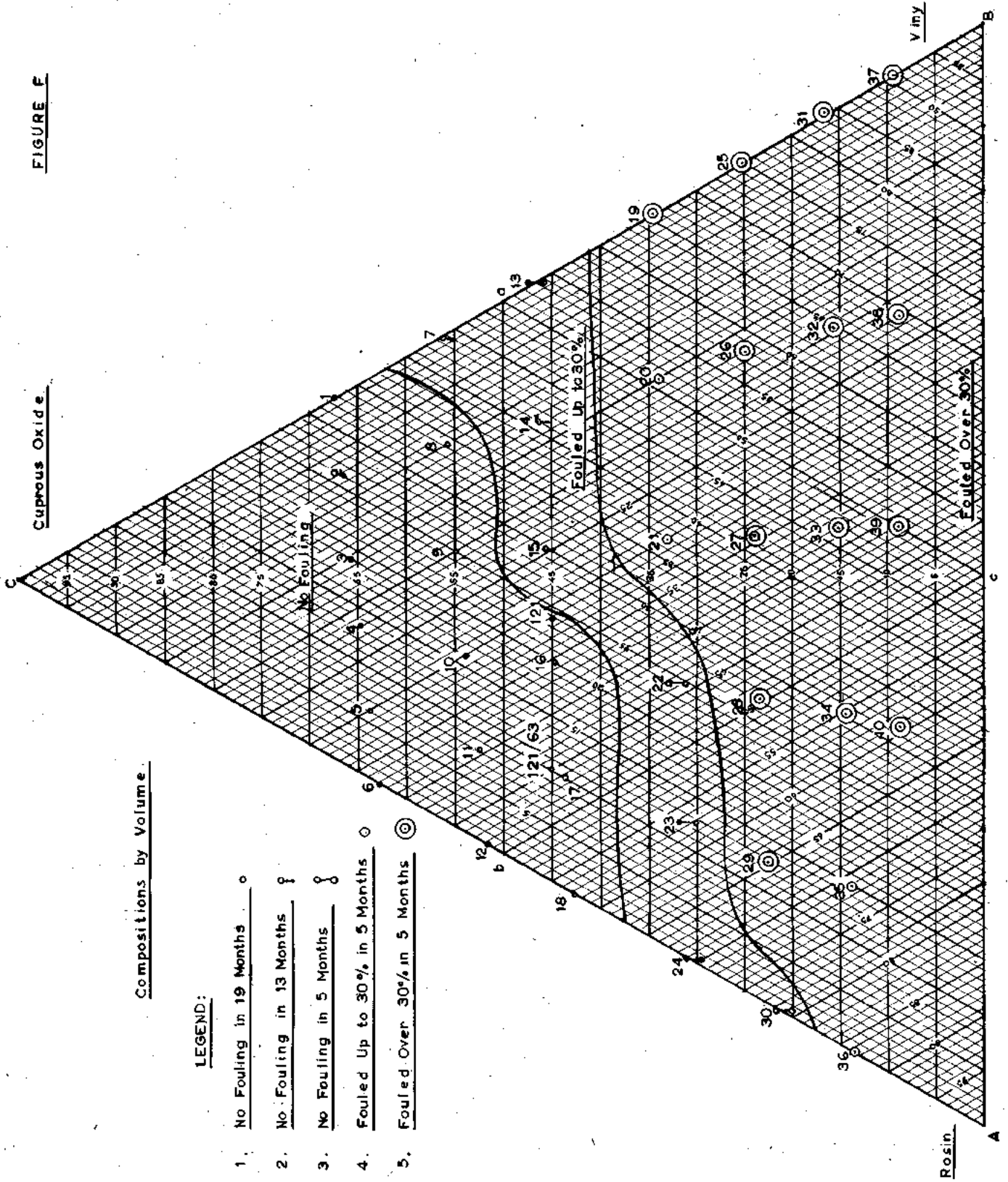
The results show that with a completely soluble matrix, like rosin, the dissolution rate is high and the paint even under static exposure is subject to excessive wear. With rosin dissolution rate about 100 mg/1000 cm<sup>2</sup>/24 hours and adequate steady state copper leaching at 10 mg/1000 cm<sup>2</sup>/24 hours, it can be seen the dissolution rate-determining material is rosin. However, if cuprous oxide is in amounts approaching continuous contact, the copper dissolution appears to take over and wear or erosion of the coating is reduced.

Formulations with variable matrix solubilities consisting of varying amounts of rosin and vinyl resin show a variety of performances, dependent upon the cuprous oxide volume content. In general, most such formulations below 45 percent

cuprous oxide content by volume are borderline or ineffective antifouling compositions. Also, compositions containing more than 25 percent vinyl resin by volume at the 45 percent toxic volume are in the inefficient area in the composition diagram (Figure F).

The Navy standard compositions, Formula No. 121 (MIL-P-15931) and Formula No. 121/63 (MIL-P-15931B) are shown in the composition diagram. It can be seen that Formula 121 is quite close to the «gray» potential fouling area. With an increase of rosin, or decrease of vinyl resin, and still maintaining 45 percent toxic pigment volume, a more effective composition was arrived at. Formula 121/63 is the current U.S. Navy standard vinyl antifouling paint.

FIGURE F



Compositions by Volume

LEGEND:

1. No Fouling in 19 Months ○
2. No Fouling in 13 Months ◐
3. No Fouling in 5 Months ◑
4. Fouled Up to 30% in 5 Months ◒
5. Fouled Over 30% in 5 Months ⊙

2. SERIES «A» (See Figure G, composition triangle diagram and table of performance data).

Fifteen hot melt antifouling compositions<sup>21</sup> were formulated with a matrix consisting of rosin, paraffin wax (melting point—126°F) and microcrystalline wax (Petrosene, melting point—165—170°F). A constant volume of cuprous oxide (6.6-6.8 percent) and inert filler (3.6 percent by volume) were used as the pigments. The compositions were applied over metal primers on 1/8-inch by 10-inch by 12-inch mild steel panels and immersed from the Paint Laboratory barge at the test site at Point Reyes, California.

The formulations were inclusive enough to demonstrate another factor affecting the steady state copper leaching and that is bacterial decomposition or biodegradable action of matrix materials. Normally, with a high total of solubles in an antifouling composition, some degree of fouling resistance is anticipated. However, a new disappointment appears when an antifouling paint that contains high total solubles fouls.

Formulations with paraffin wax (126°F melting point) and rosin as matrix performed effectively when the rosin was varied from 100 percent by volume to 66 percent by volume. However, when microcrystalline wax was used (165-170°F M.P.), there was considerable to complete fouling. Previously, with paraffin wax — increasing the volume in series by 13, 22 and 34 percent — no lowering of fouling was noted. However, substituting the microcrystalline wax for paraffin wax and utilizing a similar increase, 11.5-23-34 percent, there was fouling. This is summarized as follows:

Formula	Rosin % by Vol.	Paraffin % by Vol.	Microcrystalline Wax % by Vol.	Fouling Resistance (18 Months)
2A	87	13	—	100
3A	78	22	—	100
4A	66	34	—	100
8A	88.5	—	11.5	70
13A	77	—	23	0
15A	66	—	34	0

With formulations 2A, 3A and 4A, where paraffin wax was used, there was bacterial utilization or biodegradable action of paraffin. Certain bacteria consume straight chain hydrocarbons as food. (See Figure H for table of biodegradable action on various coating materials).

With formulations 8A, 13A and 15A, where microcrystalline wax was included; there was no biodegradable action since ocean species of bacteria cannot utilize a microcrystalline wax.

Thus, it is concluded that certain materials are attacked by bacteria and consumed as food. By this biodegradable action, matrix solubility is effected and a measure of maintenance of steady state copper leaching provided.

BARNACLE CEMENT

Current antifouling paints contain inorganic compounds of copper, arsenic and mercury. More recent toxics used are metal-organo compounds of tin, arsenic and lead. The effectiveness of these antifouling paints depends upon a mechanism that can provide a steady state leaching of the toxic. The toxic leaches out of the coating and dissolves (diffuses) in the surrounding water, creating a toxic-concentrated layer near the surface of the coating. Because of this leaching out, especially when the coated surface is in motion, the quantity of toxic emitting from the coating can fall below the critical 10 mg/1000 cm<sup>2</sup>/24 hours value (or 10 µg/cm<sup>2</sup>/day) and invite fouling attachments. Even during the period of potential effectiveness, the toxic may fail to prevent attachment of certain fouling organisms such as barnacles. The attaching form of barnacle larva, the cyprid, is believed to consume no food and therefore is less susceptible to toxics.

Figure 9 photograph shows the barnacle cyprid (Balanus Crenatus) seventh-stage from the hatched larva, about 7-14 days old, 600 microns (1/32-inch) long — a free swimming and crawling animal. The barnacle cyprid ultimately settles on a surface, attaches itself first with its antennal suction cups, and then folds in its antennal members and cements itself.

The adult forms of most of the fouling barnacles create a protective calcareous shield between their bodies and the substratum within hours after attachment. Also, the barnacle feeds at the side away from the painted surface. In addition,

FIGURE G  
PERFORMANCE OF HOT MELT ANTIFOULING COMPOSITIONS  
BASED ON ROSIN - PARAFFIN WAX - MICROCRYSTALLINE WAX -  
CUPROUS OXIDE TOXIC AND MAGNESIUM SILICATE FILLER

Formula	ROSIN (9.0)			PARAFFIN WAX (7.5)			MICROCRYSTALLINE WAX (7.7)			CUPROUS OXIDE (50)			FILLER (23.7)			Total Solubles	Fouling Resistance 18 Months
	By Wt	By Vol.	% Vol.	By Wt.	By Vol.	% Vol.	By Wt.	By Vol.	% Vol.	By Wt.	By Vol.	% Vol.	By Wt.	By Vol.	% Vol.		
1A	561	62.4	89.8	—	—	—	—	—	—	232	4.6	6.6	60	2.5	3.6	96.4	100
2A	494	54.8	78.5	59	7.9	11.3	—	—	—	232	4.6	6.6	60	2.5	3.6	85.1	100
3A	430	47.7	69.0	108	14.4	20.8	—	—	—	232	4.6	6.6	60	2.5	3.6	75.6	100
4A	369	41.0	59.3	158	21.0	30.5	—	—	—	232	4.6	6.6	60	2.5	3.6	65.9	100
5A	493	54.8	79.5	27	3.6	5.2	27	3.5	5.1	232	4.6	6.6	60	2.5	3.6	86.1	100
6A	460	51.2	74.2	54	7.2	10.4	27	3.5	5.1	232	4.6	6.7	60	2.5	3.6	80.9	92
7A	428	47.6	69.5	79	10.5	15.2	26	3.4	5.0	232	4.6	6.7	60	2.5	3.6	76.2	90
8A	491	54.6	79.5	—	—	—	55	7.1	10.3	232	4.6	6.6	60	2.5	3.6	86.1	70
9A	459	51.0	74.3	27	3.6	5.2	54	7.0	10.2	232	4.6	6.7	60	2.5	3.6	81.0	50
10A	428	47.6	69.4	54	7.2	10.4	54	7.0	10.2	232	4.6	6.7	60	2.5	3.6	75.8	50
11A	367	40.6	59.4	105	14.0	20.4	52	6.8	9.9	232	4.6	6.7	60	2.5	3.6	66.1	80
12A	427	47.5	69.2	27	3.6	5.3	80	10.4	15.2	232	4.6	6.7	60	2.5	3.6	75.9	0
13A	426	47.4	69.3	—	—	—	107	13.9	20.3	232	4.6	6.7	60	2.5	3.7	76.0	0
14A	364	40.4	59.6	52	6.9	10.2	104	13.5	19.9	232	4.6	6.7	60	2.5	3.6	66.3	0
15A	362	40.2	59.3	—	—	—	157	20.4	30.1	232	4.6	6.8	60	2.5	3.8	66.1	0



FIGURE G

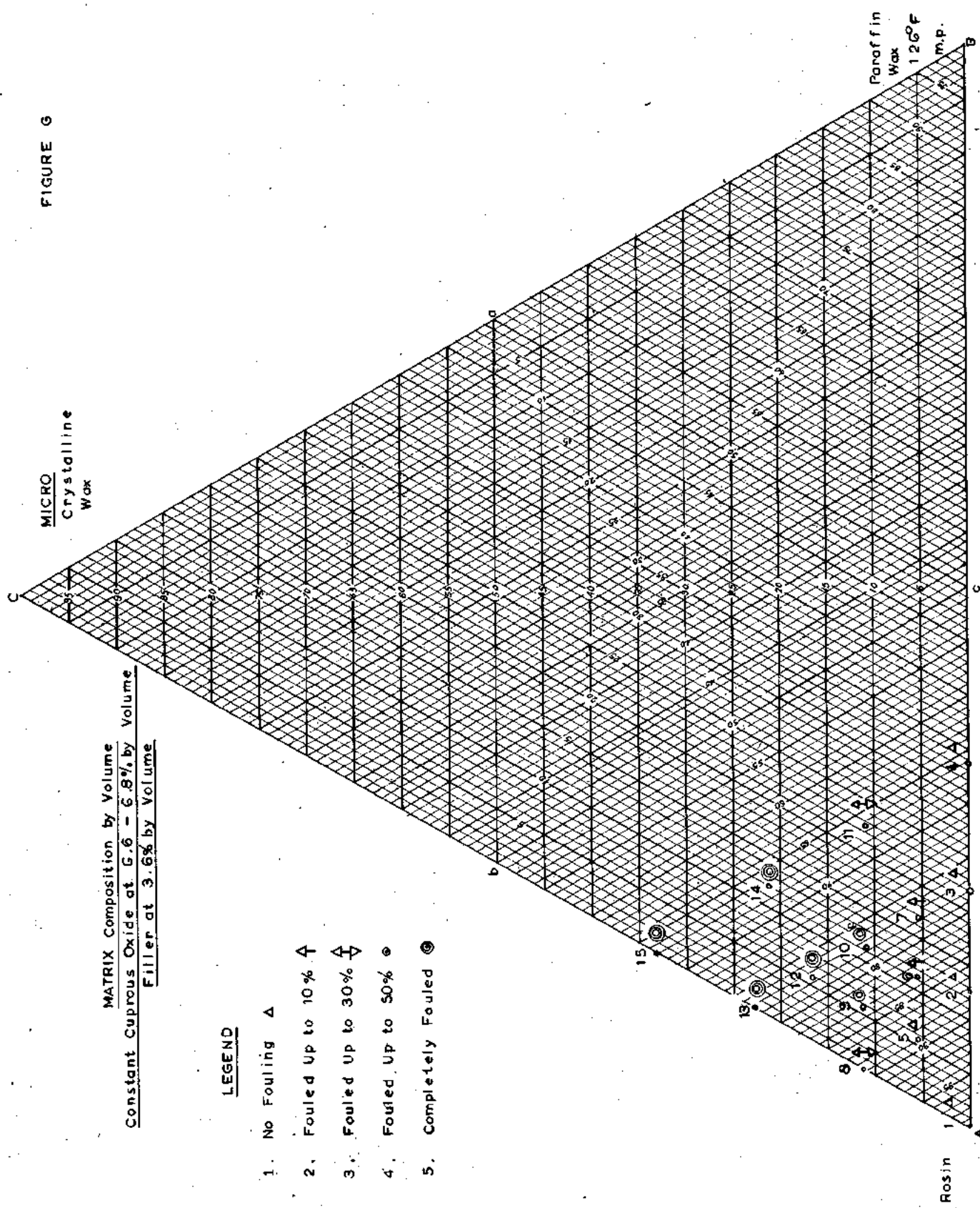




Fig. 9. The barnacle cyprid (*Balanus Crenatus*), seventieth stage from the hatched larva, about 7-14 days old, 600 microns ( $1/32''$ ) long - a free-swimming and crawling animal. The barnacle cyprid ultimately settles on a surface, attaches itself, builds a calcareous shell and becomes an attached barnacle or 'fouling'.

although the attached barnacles may eventually be killed by poisoning, the calcareous shells remain cemented to the surface. These remains become easy footholds for further fouling.

Some ten years ago, an idea was conceived in the U.S. Navy's Paint Laboratory at the Mare Island site of San Francisco Bay Naval Shipyard to attack the barnacle problem by learning what the cement is that the barnacles use to stick to waterborne surfaces. Knowing the nature or composition of the cement, certain chemical coatings could be developed that would "douse up" the sticking properties, making the cement nonadhesive and useless.

About two years ago, under the sponsorship of the U.S. Navy's Independent Research Program, the investigation of the barnacle cement was started. The objectives of the program were:

1. To develop improved antifouling coatings based on the principle of preventing the formation or hardening of the attaching cement of fouling organisms, or by reducing the adhesive strength of the attaching cement.

2. To develop a powerful adhesive which could be applied underwater or in wet conditions and which would have a hardening mechanism similar to that of the attaching cement of fouling organisms.

In the Marine and Biochemical Section of the Mare Island Paint Laboratory, significant scientific information has been revealed which suggests a breakthrough in marine science since the time of Darwin. One significant fact is that the primary antennal cement that the cyprid (young barnacle) uses for attachment has been proven to be similar or identical to subsequent or secondary cement used by the barnacle for growth and repair. Thus, instead of being forced to try to collect "micro-mini" amounts of cement from the antennal secretion, now large quantities can be "milked" in hydrospace from adult barnacles. Figure 10 photograph shows this "milking" process. The adult barnacle was detached and forced to reattach partially, about half of the baseplate area, on a microscope glass slide. The unattached baseplate area was extended over the edge of the microscope slide into the sea water medium. Efforts of the barnacle to reattach this hydrospace area resulted in the production of droplets of barnacle cement. To date, about 1-1/2 grams of this precious cement have been collected for analysis. New techniques involving surgery and dissection promise to result in providing large quantities of cement to make it possible to analyze the cement and conduct actual physical tests such as adhesion.

Other findings have to do with the anatomy and development of the attaching apparatus which includes the glands and the complicated duct network. Various concepts were reconstructed and the concepts revised. Also, it was first recognized that the attaching form of barnacle, the cyprid, uses the powerful hold of its antennal suction cups for attachment. Permanent attachment is completed when the antennae are folded. Reinforcement of this suction attachment is then completed by the secretion of a cyprid cement. Figure 11 photograph shows the initial cyprid barnacle attachments as the two suction cups and adjoining antenna segments. The suction cups are about 10 microns in diameter and the full stained area including the segments of the antenna about 20-30 microns.

Coatings which would reduce, resist or counteract the adhesion of the attaching cement of fouling organisms by a physical, physico-chemical or chemical mechanism would provide more permanent protection against fouling. The determination of the chemical composition of the barnacle cement would permit an attack on antifouling problems from a unique and previously untried direction which might well culminate in new, more effective antifouling coatings. Also, the synthetic formulation of a powerful adhesive for marine environment might be possible. Other attractive uses, such as for dentistry or bone-mending, may also materialize.

FIGURE H  
BIODEGRADABLE ACTION ON VARIOUS  
COATING MATERIALS

MATERIAL	BIODEGRADABLE ACTION	REFERENCE
1. Rosin	Attacked by bacteria	Ref. 33, 34, 35
Paraffin	" " "	"
Alkyd Resin	" " "	"
Phenolic Resin	" " "	"
Linseed Oil	" " "	"
2. Chlorinated Rubber	Slowly attacked by bacteria	"
3. Vinyl Resin	Resist Bacteria attack	"
Halowax	" " "	"
Coal Tar Pitch	" " "	"
Chlorinated Styrene	" " "	"
4. Polyethylene	Not utilized as a source of carbon by Aerobic (A) or Anaerobic (An) marine bacteria.	Reference 36
Polyvinylchloride (rigid; no plasticizer)	Utilized by (A) and (An) bacteria	"
Polyvinylchloride plasticized with Tricresylphosphate di-2-ethyl hexyl phosphate	Utilized by only (A) bacteria.	"
Polyvinylchloride plasticized with polyester	Utilized by (A) and bacteria	"
Polyvinylchloride with nitrile rubber	Utilized by (A) and (An) bacteria	"
GR-A, GR-S, Butyl, natural and neoprene rubber	Utilized by (A) and (An) bacteria. Neoprene the most resistant.	"
5. Paraffin or Mineral Oils	a. Aliphatic hydrocarbons more readily attacked than aromatic or naphthenic compounds	Reference 37
Petrolatums		
Asphalts		
Paraffin Waxes		
Natural Rubber	b. Long chain hydrocarbons are attacked more readily than similar compounds of small molecular weight.	
Synthetic Rubber		
	c. The addition of aliphatic sidechains increases the susceptibility of cyclic compounds to microbial attack.	



Fig. 10. "Milking" barnacle cement in hydrospace. The adult barnacle was detached and forced to reattach partially, about half the baseplate area, on a microscope slide. The unattached baseplate area was over the microscope slide edge into the sea water medium. Effort to reattach this area produced droplets of barnacle cement.



Fig. 11. Initial cycloid barnacle attachments showing the two suction cup areas and adjoining antenna segments. The suction cups are about 10 microns and the full stained area including the segment of antenna about 20-30 microns.



Fig. 12. Second generation antifouling paint system. Chemical removable matrix permitted to gather fouling and then half the panel washed off with chemical solution.

With the present state of coating technology, anticorrosive or barrier coatings such as epoxies, coal tar epoxies, polyurethanes, vinyls, etc., the countdown for ten years of corrosion protection against sea water has started. The aim to get ten years of fouling-free surfaces suggests second generation antifouling paint systems and a new countdown. This new countdown not only involves super-antifouling compositions but total coating systems. Techniques are required that will permit repairs and rejuvenation of antifouling paints without damage to the anticorrosive undercoat.

Present repairs or touchups, for example, of shipbottoms utilizing first generation antifouling paints involve costly abrasive blasting procedures. Even the most careful effort to remove expended or damaged coatings results in extensive repairs beyond that which were obvious. A 10-percent touchup usually ends up by being a 30-40 percent repair job. Even blasting and cleaning underwater cannot be controlled to any degree free from damaging good paint.

Research and development programs are underway now to develop second generation antifouling paints that can be removed in increment layers or totally without damage to anticorrosive undercoats. Such compositions would be susceptible to washing off with hot water or aqueous solutions. Figure 12 photograph shows a second generation antifouling paint system matrix. The matrix (without toxic or repelling agent) was permitted to gather fouling and then half the panel was washed off with chemical solution. An entire shipbottom could be rejuvenated and the intact antifouling composition given another chance to perform by chemically (or with hot water) removing fouling growth if present and the expended layer of coating material. Without resorting to abrasive blasting or scheduling a complete new shipbottom paint job, the surface of an old paint job could be renewed by chemical or hot water washing.

Such second generation antifouling coatings can be based on the first generation toxic poisoning principle or moved into orbit of a second generation effort. The attaching mechanism of fouling organisms can be attacked by chemical or other means whereby the initial attachment of the larva is impaired. This can be pursued in several ways:

a. Develop a coating that chemically will react with the cementing material used by the attaching marine organisms. For example, if the fouling is barnacle larvae, by chemical means "clouse up" the cement so it will be "leather" and not possess any adhesion. If this cement is some kind of protein, then perhaps a tannate or an oxidizing agent like hydrazine would properly "clouse up" the cement. Changing the pH of the surface would probably interfere with the adhesive properties of the cement.

b. We will learn<sup>12</sup> that the initial attachment of the barnacle larva is through two antennal suction cups which are powerful enough (7.5 dynes) to withstand 3.6 knots of flowing water. Since this grip is initially associated with muscle action, "nerve action" materials like DDT (dichlorodiphenyl-trichloroethane) could possibly "clouse up" the hold. However, when the barnacles are repelled, DDT is food for hydroids and other fouling growth.

c. Certain wetting or surface active agents could be used to alter the contact angle of the larval cement, thus interfering with proper adhesion conditions.

In conclusion, the past years have given us satisfactory first generation antifouling paints which have protected shipbottoms for periods of two to three years. Now, the countdown for second generation antifouling paints can start with the significant advances made in the new approach to fouling prevention through the study of the attachment mechanism of marine organisms. The not too distant future definitely holds promise of a Gemini BLAST-OFF for ten years of protection from marine corrosion and fouling prevention.

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#### DISCUSSION

C.P. DE (India): Our experience with the heavy duty antifouling paints is not as encouraging as reported in the literature. Vinyl based antifouling paint has given us raft life between 14 to 15 month in Bombay harbour.

J. SAROYAN: That is correct. We get about two to three years maximum (performance on ships).

C.P. DE: Is it possible to get in tropical waters with the first generation of antifouling paint a life of about three years?

J. SAROYAN: With Cuprous oxide this is a possibility but you have to have special formulations. The continuous contact type probably would be your avenue.

C.P. DE: Will hot plastic or Vinyl based formulations meet the requirement?

J. SAROYAN: Yes (Both types can be made to work. Probably the vinyl continuous contact type would give the best performance).

D.B. CAMERON (Great Britain): I would like to ask whether in your view antifouling paints in the future would be antifouling on their own or whether they would be anticorrosive paints with built in antifouling properties.

J. SAROYAN: The antifouling paint will be an entity of its own. We will probably try to build a permanent anticorrosive and put over it a renewable antifouling paint. (Such) a paint instead of being sand-

blasted off will be probably washed off with a chemical.

C.P. DE (India): Can the author give any information in respect of his experience on organolead based antifouling paints?

J. SAROYAN: I would say that they have great potentials. The U.S.A. Navy is vitally interested in this particular material especially for a black antifouling paint.

C.P. DE: What is the potentiality of pure organic toxin based antifouling paints?

J. SAROYAN: This is what we hope to do, in our second generation antifouling paint. Here we hope to have a chemical surface that will louse up or spoil the adhering cement (of attaching marine growth).

A. VAN LONDEN (Holland): Your data about the bacterial attack on some materials are related to the material as such, not the material incorporated in an antifouling paint. I think that it may well be possible that this bacterial attack only occurs on the pure material, but that this attack is decreased considerably if the material is incorporated in an antifouling paint, due to its poison content.

J. SAROYAN: This may be true, but still with the paraffin, rosin and cuprous oxide formulations in the hot plastic versus micro crystalline wax, rosin and cuprous oxide we were testing as formulated antifouling paint, with the toxic present.



# ATTACHMENT MECHANISM OF BARNACLES

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## SUMMARY

The initial attachment of the barnacle is shown to be a purely mechanical hold by the suction cups of the cyprid antennae. An adhesive cement may be secreted for reinforcement but is not essential for permanent attachment. The Balanidae have permanent, periodically functioning glands which are located in the living mantle tissue. These glands develop directly from the cyprid cement glands. The cement glands and the rest of the cementing apparatus of the Balanidae are basically identical with those of the Lepadidae. The cementing apparatus is flushed after each cement secretion. In this way, old ducts are kept open for emergency repair or reattachment. This emergency secretion is expected to be chemically identical to the cyprid and the normally secreted adult cement.

The following new concepts of the attachment mechanism of the barnacles are demonstrated, explained and proposed:

1. The initial attachment of the barnacle is only a mechanical adhesion by means of the hydraulic suction cups at the tip of the cyprid antennae. There is a rigid chamber with an elastic membrane in the second and one in the third antennal segment. These chambers are connected. The muscles attached to the elastic membrane of the second segment can increase the volume of the chamber, which will result in fluid moving from the third to the second segment. This, in turn, will pull in the elastic membrane of the third segment which acts as a suction cup if the membrane is pressed on a substratum.

2. Calculations show that the adhesive force of the suction cups is strong enough to hold the cyprid in place against currents up to 186.4 cm/sec (3.6 knots).

3. The cyprid completes the attachment by folding the antennae, resulting in sealing the passage between the two chambers. Rigid prong and socket formations of the second and third segments lock the antennae in this position; therefore, the suction of the cups can be maintained without muscle exertion and even after death.

4. The initial attachment is usually reinforced by an adhesive cement secretion, but the cement is not essential for achieving permanent attachment.

5. The pair of cyprid cement glands is retained by the adult and, in the *Balanus*, they are located in the living mantle tissue near the lateral part of the baseplate perimeter.

6. The cement glands are permanent organs throughout the life of the barnacle; they function periodically in relation with the moulting or growing period; and they do not degenerate after the secretory period.

7. During growth, as the demand for cement increases, new glands develop on each side, joining the older ones in a cluster.

8. The individual glands are connected by means of ducts. These ducts join on each side in a node from which the secretion is conducted toward the baseplate by one main channel.

9. The chemical properties of the secretion are altered in the node, probably indicating the secretion of a catalyst or crosslinking compound necessary for the cement hardening.

10. The two main channels are connected to the remnants of the second antennal segment of the cyprid at the point of initial attachment.

11. Both families of Cirripedia: the Balanidae and the Lepadidae have an anatomically identical cementing apparatus: (1) periodically functioning permanent glands on both sides in the mantle, (2) cement glands consisting of smaller units, which are connected by ducts at one point, at which the chemical properties of the secretion are altered and (3) main channels which conduct the secretion toward the initial attachment point.

12. The Balanidae develop a new duct network in each moulting period. Each network conducts the cement to the newly enlarged baseplate perimeter. After development, the duct network is moulted and becomes an integral part of the baseplate. These developments indicate that the baseplate-growing periods correspond with the moulting periods.

13. The originating points for the duct networks are the vesicles, which form around the main channel. The vesicles have no secretory function; they are only distributing chambers and in conjunction with the main channel, which goes through the vesicles as a continuous tube, the vesicles function as regulating valves.

14. A unique flushing mechanism removes the cement from the vesicles, ducts, and from the vicinity of the orifices before the cement hardens. As a result, the older portions of the duct network are kept open and ready to be used if the baseplate detaches from the substratum or is injured.

15. Barnacles are also capable of developing new ducts leading into the injured or detached areas.

16. Since the cyprid cement gland is the basis of the adult cementing apparatus, and the same apparatus is used for secondary secretion, the cyprid cement, the primary or adult cement, and the emergency or secondary cement are chemically similar or identical substances.

17. The secondary cement, which is available in larger quantities than either the cyprid or the primary cement, can be collected for chemical analysis.

18. Furthermore, now that the true cement glands in the *Balanus*, have been located, extraction of these glands makes the collection of the cement components or monomers possible for further studies.

# REPORT OF INVESTIGATION

## Introduction

An investigation of the attachment mechanism of the sessile barnacles has been pursued to aid future studies on fouling problems with an emphasis on the determination of the chemical and physical properties of the cement. The attachment apparatus of cyprids and attached adult barnacles was studied in wholmounts, partial wholmounts, and tissue sections. The anatomy and development of the attachment apparatus were reconstructed and the concepts of its function were revised. Detached adult barnacles were successfully reattached, serving as models for studies of the attachment mechanism.

## Materials and methods

Attached adult barnacles were collected on glass, Plexiglass, and rubber panels for studies of attachment. Barnacles removed from these panels served as sources of secretions for histochemical investigations and of embryos for rearing. The embryos were hatched and reared through the attaching cyprid stage by a modification of the techniques developed by Freiberger and Cologer<sup>17,18</sup>. Studies were made on the attachment organs and on the attachment mechanism of these cyprids in vivo, in wholmounts and in tissue sections.

The attaching cyprids and attached adult barnacles of the *Balanus crenatus*, *B. glandula*, and *B. improvisus* species were collected on standard glass microslides for microscopic study of the baseplate and attachment. The specimens were killed, fixed, decalcified, and stained on the original slides. Ten percent neutral buffered formalin by Lillie (1954)<sup>27</sup>, Baker's (1944) formol-calcium<sup>27</sup>, and Zenker's fluid were used for fixation. Specimens fixed in Baker's formol-calcium for 24 hours, decalcified in Jenkin's fluid<sup>28</sup> for 24 hours, and refixed in Baker's formol-calcium for 48 hours provided the most satisfactory results. For general histology, Mallory's Trichrome technique was adapted, but some special purpose stains and histochemical reactions were also employed for additional information.

For studying barnacles in microtome sections, solid paraffin blocks were exposed at the fouling sites. Barnacles attached to the paraffin were allowed to reach 3 to 6 mm in diameter before they were fixed in Baker's formol-calcium and decalcified in Jenkin's fluid, while still attached to the paraffin substratum. During the latter steps of dehydration, the substratum was dissolved to leave the specimen with all substances between its baseplate and the substratum intact for imbedding and sectioning. These sections were treated with Mallory's Trichrome for general histology, and with some additional more specific stains and reagents.

## INITIAL ATTACHMENT

### Background

In the literature, we find only a few investigations of the attachment mechanism and organs of barnacles, and the majority of these observations were made on stalked, rather than sessile Cirripedia. There are even fewer references on the initial attachment mechanism of the cyprid larva. Darwin<sup>11</sup> observed that the disc at the end of each cyprid antenna becomes cemented to the substratum and suggested that the cement is secreted at the edge of the disc. Darwin's concept is generally accepted in the literature. Scattered literature references suggest that an adhesive is secreted at the tip of the antennae and that eventually this adhesive hardens to trap the cyprid on the substratum. Recently, Crisp<sup>7</sup> stated that the first antennae are provided with suckerlike discs and that the cyprid pours cement through the sucking discs to provide the initial fixation.

The behavior of the planktonic cyprid form of the barnacle at the time of the attachment was described in detail

by several authors. As Visscher<sup>24</sup> noted, the cyprids «walk» by alternating the antennae on the substratum and «test» different areas before final attachment. The testing process can probably be explained by experiments of Pomerat and Weiss<sup>29</sup>, Weiss<sup>30</sup>, Gregg<sup>29</sup>, Crisp and Meadows<sup>30</sup>, Knight-Jones<sup>29</sup>, Crisp and Barnes<sup>8</sup>, and Smith<sup>30,31</sup> which demonstrated that cyprids exhibit definite preferences for certain physical or chemical characteristics of the substratum. Visscher also observed that the antennae adhere so firmly that the cyprid can free them only with a violent struggle. Bernard and Lane<sup>2</sup> suggest that the cyprid eventually becomes unable to detach itself, and that this completes the attachment.

## Experimental

Microscope preparations of the antenna of the *Balanus crenatus* cyprid (Fig. 1) show that the third segment is bell-shaped, having a flat, circular baseside with a thin, flexible rim. The main body of the third segment is about 30 microns in diameter and 30 microns high; the rim is about 35-40 microns in diameter. The base membrane is an average of 5 microns thick. The 5 micron thick walls of the upper two-thirds of the third segment are composed of a rigid tissue (Fig. 2), probably chitinous, which does not shrink or change shape under the influence of aging, drying, or the chemicals used during preparations. These rigid walls form a chamber of constant shape leaving only the flat, circular base flexible. A similar rigid chamber is found in the tip of the second, segment directly adjacent to the third segment. A thinner elastic membrane stretching diagonally between the rigid ribs forms the wall of this chamber inside the antenna. The inner space of these chambers appears to be lacking in solid tissues. On the outside, the rigid walls of the second and third segment form prong-like projections.



Fig. 1. Section of cyprid antenna: (A) Third segment, (B) Second segment (10 $\mu$  section, Mallory's Trichrome, 625x).



Fig. 2. *Balanus crenatus* cyprid antenna: (A) rigid shell, (B) flexible base (wholemount, Mallory's Trichrome, 625x).

Bernard and Lane<sup>2</sup> found that the antennae are folded to attain the proper position for final attachment. This is confirmed by examining the cyprid attachment and baseplates of adult *Balanus crenatus* and *B. glandula*, which always show both the third and part of the second segment touching the substratum (Fig. 3). Once this position of the antennae is assumed, the cyprid does not seem to be able to straighten the antennae. Even if the recently attached cyprid is detached by force, the antennae remain folded (Fig. 4). The folding of the antennae seems to complete the process of permanent attachment. We found no adhesive cement secretion up to this point. In fact, we found normally developed adult *B. glandula* specimens without any trace of cyprid cement (Fig. 3), which indicates that the cement secretion is not essential for achieving permanent attachment. In most cases, however, the permanent attachment is reinforced by an adhesive cement. This cement is believed to be secreted only after the antennae are folded into position, since it is shown that the third segment imbedded in the cement patch is always accompanied by part of the second segment (Fig. 5).

#### Discussion

The anatomy of the third segment of the antenna indicates that this bell-shaped segment with its elastic baseside functions as a suction cup. The rigid chambers of the second and third segment are probably connected by a passageway, and they are filled with some fluid of low viscosity. Some of the powerful muscle bands of the antennae are probably connected to the thin membrane forming the top of the chamber in the second segment and increase or decrease the volume of this chamber by their action (Fig. 6). An increase in the volume of this chamber draws in some fluid from the third antennal segment. As a result, the volume of liquid within the chamber of the third segment is reduced, which causes the flexible circular baseside to be pulled inward. If the flexible rim is pressed on a substratum and provides a tight seal, a vacuum

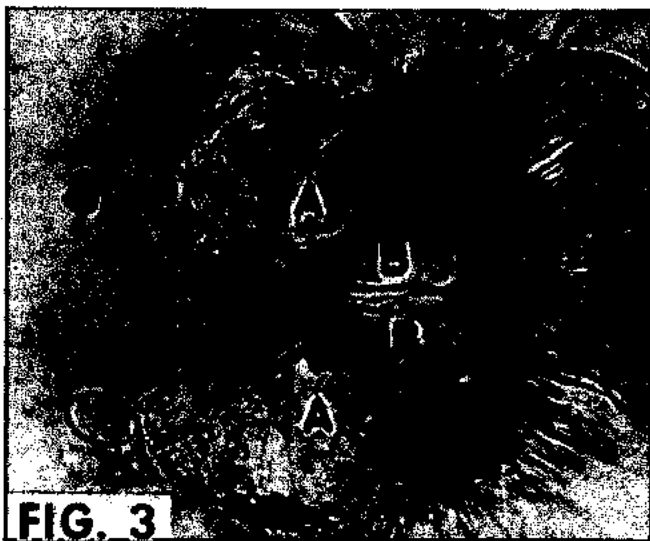


Fig. 3. *Balanus glandula* cyprid attachment in adult baseplate (A) third segment and (B) folded portion of second segment. No cement. (wholemount, TriPARS, 425x).

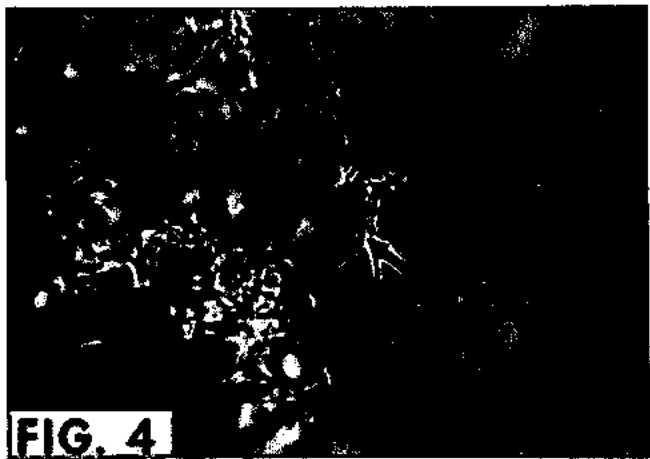


Fig. 4. Live *Balanus crenatus* cyprid was detached by force shortly after settlement. Antenna is seen locked in folded position. (440x).

is created under the base membrane as it is contracted and the baseside becomes concave. The relaxation of the muscles results in fluid flowing back into the third segment, thus releasing the vacuum under the base. By this arrangement, the third antennal segment functions as a hydraulic suction cup and the chamber of the second segment controls the operation by an action similar to that of the ampulla of the starfish suction cup.

When the antenna is folded so that the tip of the second segment also touches the substratum, the passage between the second and third segment is sealed off and permits the suction to be maintained without further muscular exertion. The folded position of the antenna is locked by the socket and prong formation on the rigid chitinous shells of the second and third segments. This locking device is somewhat similar to that of the click beetles (Elaterridae). After the antenna is locked into the folded position, the cyprid must struggle

violently to free itself again.

If the cyprid is satisfied with the settling site, the antenna is permanently locked in the suction position, which will hold the suction cups in place even after the death of the cyprid. The adhesive power of the suction cups alone is usually quite sufficient to keep the cyprid from being washed away by currents.

The atmospheric pressure and the weight of the water column above the suction cups work against the vapor pressure under it to hold the suction cups in place.

The standard atmospheric pressure

$$p_a = 1.0332 (10^3) \text{ g cm}^{-2}$$

The water pressure at six feet exposure

$$p_w = 1.88 (10^3) \text{ g cm}^{-2}$$

The vapor pressure at 14°C average temperature

$$p_v = 1.62 (10^3) \text{ g cm}^{-2}$$

Total pressure

$$P = p_a + p_w - p_v = 1.2 (10^3) \text{ g cm}^{-2} \approx 1.2 (10^3) \text{ g cm}^{-1} \text{ sec}^{-2}$$

The area within the rim of one suction cup

$$a = (10^{-2})^2 \pi = 3.14 (10^{-3}) \text{ cm}^2$$

The total adhesive force of a pair of suction cups at optimum performance

$$F = 2Pa = 7.5 \text{ g cm sec}^{-2}$$

The adhesive force must be greater than the force of the water current exerted on the elliptical profile of the body, if the cyprid is to remain in place. On the average, the cyprid of *Balanus crenatus* is 330 microns tall and 800 microns long.

The area of the elliptical profile  $A = 2.08 (10^{-2}) \text{ cm}^2$

The drag force of the current counteracts the adhesive force

$$F = \frac{1}{2} C_D \rho A v^2 = 7.5 \text{ g cm sec}^{-2}$$

$C_D$  = drag coefficient

$\rho$  = density of seawater = 1.025 g cm<sup>-3</sup>

$v$  = velocity of water current

Due to the small size of the cyprid, it is usually in the boundary layer. The current velocity inside the boundary layer is

$$v = V \left( \frac{2y}{\delta} - \frac{y^2}{\delta^2} \right)$$

$V$  = main current velocity

$y$  = mean distance of cyprid from substratum = 1.65 (10<sup>-2</sup>) cm

$\delta$  = thickness of boundary layer =  $\frac{5.2 x}{\sqrt{Re}}$

$Re$  = Reynolds number =  $V \frac{x \rho}{\mu}$

$x$  = distance of cyprid from leading edge of the substratum = arbitrarily  $\frac{1}{2}$  inch

$\mu$  = absolute viscosity of seawater of 30‰ salinity and 15°C = 1.21 (10<sup>-2</sup>) g cm<sup>-1</sup> sec<sup>-1</sup> (22)

$$v = V \left[ 2 \left( \frac{y}{5.2x} \sqrt{\frac{x\rho}{\mu}} \right) \sqrt{V} - \left( \frac{y}{5.2x} \sqrt{\frac{x\rho}{\mu}} \right)^2 V \right]$$

$$\text{if } a = \frac{1}{\left( \frac{y}{5.2x} \sqrt{\frac{x\rho}{\mu}} \right)^2} = 2.92 (10^3)$$

$$\text{then } V^4 - 4aV^3 + 2vaV^2 + a^2v^2 = 0$$

Preliminary calculations show that  $V$  current velocity will be in the order of magnitude of 10<sup>3</sup> cm sec<sup>-1</sup>, then

$$Re = V \frac{x \rho}{\mu} = 4.3 (10^4)$$

and  $C_D$  (circular disc) = 1.12 at  $Re > 10^3$  (16) and (19)

$$v = \sqrt{\frac{2F}{C_D \rho A}} = 7.94 (10^3)$$

$$V^4 - 1.188 (10^4) V^3 + 4.7 (10^3) V^2 + 5.55 (10^{10}) = 0$$

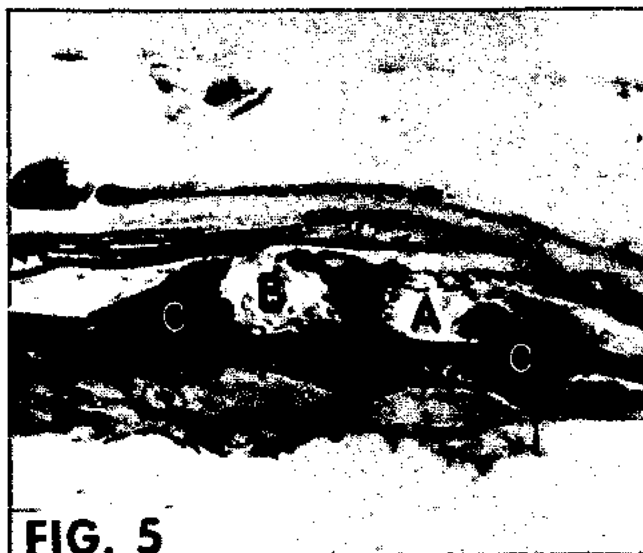


Fig. 5. Section through initial attachment of *Balanus crenatus* adult: (A) folded portion of second segment, (B) bell-shaped third segment, (C) cyprid cement patch. (10 $\mu$  section, Mallory's Trichrome, 625X).

$$\text{by approximation by Newton's method } V_2 = V_1 - \frac{f(V_1)}{f'(V_1)}$$

$$V \approx 186.4 \text{ cm/sec} \approx 3.6 \text{ knots}$$

The cyprid can, therefore, withstand currents up to 3.6 knots using only its suction cups. This value is in good agreement with experimental data<sup>20</sup>. (There is another value of about 230 knots as a solution of the fourth power equation. At this high velocity the laminar current goes through a transition into turbulent current; the drag coefficient ( $C_D$ ) drops to about 3(10<sup>-2</sup>) resulting in a drastically reduced current force).

The initial attachment, then, is only a mechanical adhesion by means of these hydraulic suction cups. The cement secretion, although usually present as a reinforcement, is not essential for permanent attachment.

## CEMENTING MECHANISM

### Background

The basic anatomy of the cementing organs of both families of adult barnacles was described by Darwin<sup>11,12</sup>. Based on studies on the Lepadidae, Darwin believed the cementing apparatus to be a modified part of the reproductive system; but Krohn<sup>24</sup> recognized the cementing apparatus as a separate organ. Pagenstecher<sup>25</sup> indicated that the cement ducts of an adult *Lepas* lead back into the remains of the cyprid antennae. Gravel's<sup>23</sup> monograph borrows mostly from Darwin's description of the cement glands and ducts, but contributes a report on the functions of the glands of the Lepadidae. Krüger<sup>26</sup> studied the histology of the cement gland of *Scalpellia* and recognized the periodic function of such glands. Based on Darwin's<sup>11,12</sup> and Gravel's<sup>22</sup> work, Thomas<sup>28</sup> speculated that the cement glands of sessile cirripedia degenerate after functioning only for one molting period, and that they are probably modified tegumental glands.

### Experimental

The mechanical attachment of the cyprid antennae is usually reinforced by a cement secretion. Both the suction cups and the tips of the second segments become imbedded

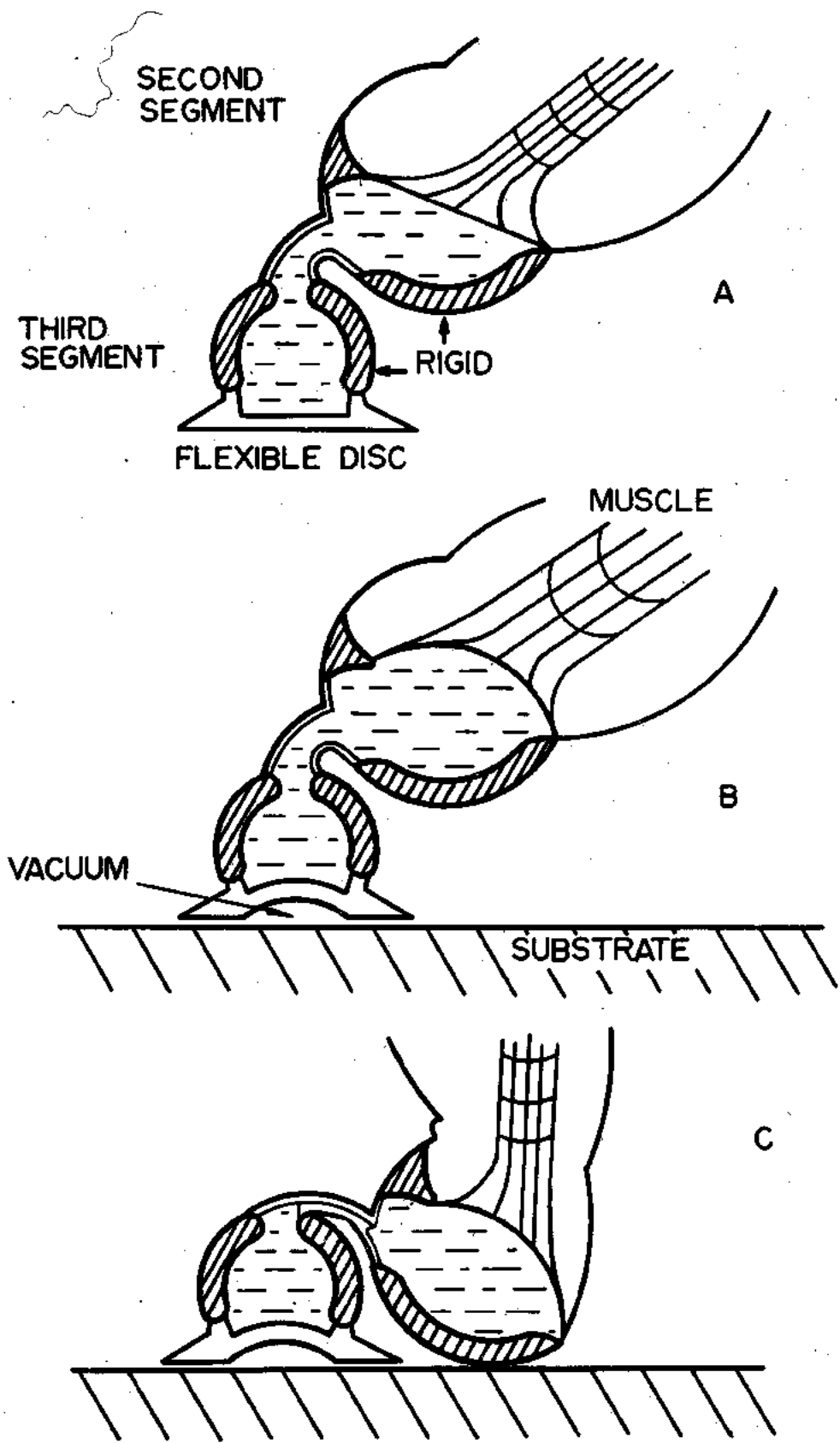


Fig. 6. (A) Antenna of cyprid prior to attachment, (B) Antenna of cyprid during attachment, (C) Antenna of cyprid after locking into position for permanent attachment.



Fig. 7. *Balanus crenatus* cyprid cement patch showing two concentric circles of cyprid cement. (wholemount, Mallory's Trichrome, 425x)



Fig. 8. Section of *Balanus crenatus* cyprid showing (A) cement gland behind (B) compound eye. (10 $\mu$  section, Mallory's Trichrome, 250x).

in one dome-shaped cement patch. This patch seems to be secreted in two steps, since two concentric irregular circles can be recognized (Fig. 7). The inner circle is about 30 microns thick and 60 to 80 microns in diameter; the outer circle is only about 5 microns thick and 150 to 200 microns in diameter. Occasionally these two circles show different staining characteristics which could be due to a number of various causes, such as difference in age, oxidation, pH, degree of polymerization, chemical, or physical composition, etc.

Darwin<sup>14</sup>, and recently Bernard and Lane<sup>2</sup>, indicate that the cement is secreted by a pair of glands located behind the cyprid's compound eyes. Our investigation of these ovoid or kidney-shaped structures shows them to be 60 to 90 microns thick and 150 microns long (Fig. 8). A pair of ducts of about 10 microns in thickness lead from the glands into the second segments of the antennae, where they are surrounded by clusters of cells, connective tissue and muscle fibers. The orifices of these ducts have not been located. The orifice is not likely to be inside the base membrane of the suction cup, because the secretion of the cement would break the vacuum and the hold before the cement could harden and become effective. Microtome sections through the patch and suction cups show little or no cement under the base membranes; the cement is mainly found piled up around and nearly covering the second and third segments. This observation seems to indicate the existence of an opening outside the suction cups.

The dissection of *Balanus glandula* cyprids, which achieved permanent attachment and secreted cement, shows that the cluster of cells surrounding the cement ducts in the second segment are connected to distinct spots in the second segment, which have staining characteristics similar to those of the cement (Fig. 9). In preparations of adult specimens we find that these same spots are the originating points for the main channels of the cementing apparatus (Fig. 10).

We know from the literature that the settled and attached cyprid moults the cyprid carapace and the exoskeleton of the body — with the exception of the embedded parts of the

antennae — and soon takes up its adult shape. In the Balanidae, the main channel begins to grow perpendicular to the rostral-carinal axis toward the perimeter of the baseplate. In each growing period, new vesicles form on the main channel and become the originating points of the separate duct networks. Darwin<sup>14</sup> and Gruvel<sup>22</sup> believed that these vesicles are the cement glands, and that the Balanidae grow a new pair of such glands in each growing period because the former ones degenerate. (They recognized, however, that the Lepididae have only two permanent cement glands). Each vesicle is larger than the former one and each duct network is more complicated than its predecessor. These networks grow on top of each other and end in numerous orifices at the corresponding baseplate perimeter. The end of the duct widens and forms a funnel to spread the cement around the perimeter under the growing baseplate in concentric circles.

The duct system develops in the epithelium of the mantle which is in contact with the calcareous baseplate. First, a number of cells concentrate around the area where the new ducts and vesicles are going to develop (Fig. 11 and Fig. 12); then, the cells elongate and pack very close together (Fig. 13) so that the outline of the duct system appears clearly (Fig. 14). In further development, most of the cells disappear, leaving only a few clinging to the outside of the completed wall (Fig. 15). The developed ducts are still in intimate contact with the epithelium layer and the ducts will break if the epithelium layer is broken. Finally, the epithelium layer recedes completely from the formed ducts and the ducts are no longer affected by any damage to the epithelium layer (Fig. 16). Microtome sections show that the completed ducts are part of a thin acellular membrane that spreads across the baseplate and piles on top of the older such layers. This membrane corresponds to the other parts of the exoskeleton of the barnacle body and mantle, which are moulted away before each growing period. Similarly, the completed new duct network and the connecting membrane is moulted away in the barnacle. Since this membrane is in contact with the calcareous shell and not



Fig. 9. (A) Cell clusters connected to (B) distinct spots on the second segment of a recently attached *Balanus glandula* cyprid. (wholemout, Mallory's Trichrome, 425x).

in open space, it cannot be expelled and, therefore, remains to become an integral part of the shell, permanently embedded in calcareous material. Despite the results of Costlow and Bookhout<sup>3, 4, 5</sup>, who were unable to show any empirical correlation between moulting and shell growth, moulting and baseplate growth have to coincide since each new duct network ends in orifices around the new baseplate perimeter and each duct network is physiologically moulted away with the rest of the exoskeleton.

The vesicles develop through identical steps and at the same time as the ducts (Fig. 13). Morphologically, the vesicles present the same appearance as the ducts (Fig. 17). No cell components, indicative of secretory functions, were ever found in the vesicles. Therefore, contrary to previous beliefs, the vesicles can not be cement glands but probably only collecting and distributing chambers for the cement.

Microscope preparations of *Balanus* indicated, that the main channel has a more important function than simply serving as a connection between the successive vesicles. Beyond the newest vesicle, the main channel continues toward the perimeter of the baseplate. This main channel extension is about 30 microns in diameter and its walls consist of tightly packed cells. The 10 to 12 micron lumen is filled with a substance with staining characteristics similar to those of the cement. Near the perimeter, the main channel extension rises through the mantle tissue from the vicinity of the baseplate to just below the epithelium of the mantle cavity (Fig. 18). Here, the channel expands into a larger node (Fig. 19) which is the originating point for numerous side-channels that lead into different directions. It is noteworthy that the staining characteristics of the contents of the main and the side channels are different. Also, the cement-staining reactions seem to diffuse into the cells of the node at the meeting place of the main and side channels.

At the end of each side channel, there is a large round organ more than 100 microns in diameter containing vacuolae and substances having various staining characteristics (Fig. 20). These organs appear to be very similar to those we find in the Lepadidae and which were reported to be giant monocellular



Fig. 10. Initial cement patch in adult *Balanus glandula* shows (A) main channel originating from (B) same spot as in Figure 9 on second segment. (wholemout, Mallory's Trichrome, 425x).

cement glands<sup>22, 25</sup> (Fig. 21). In both the Balanidae and the Lepadidae, there are usually several such glands on each side of the mantle and they form clusters.

#### Discussion

The cement gland appears first in the planktonic cyprid larva stage of the barnacles. During the settling procedure and metamorphosis to the adult form most of the cyprid organs undergo histolysis, tissue changes, reorganization, and migration. Bernard and Lane<sup>2</sup> show that, in *Balanus amphitrite niveus*, the cement glands «the post optic organs undergo considerable functional modifications during and after settling, but «they retain the same size and position». They indicate, however, that these glands disappear in the next stage of development, which they call the «decorticated settler» stage. This stage is supposed to take place between the settled cyprid and the young adult stage. It is characterized by a completely amorphous, «soft, translucent, gelatinous, cellular mass», with «no sign of appendages or of crustacean segmentation».

In *Balanus crenatus* and *B. glandula* we failed to recognize this decorticated settler stage. These species seem to moult the cyprid carapace and the body exoskeleton to reveal a fairly articulate adult form. Under the shedding exoskeleton of the cyprid thoracic appendages, the adult cirri appear, which curve into the opposite direction (Fig. 22). The internal organs also seem to be organized at this point.

We also showed that the main channel of the adult cementing apparatus originates from the same point in the second antennal segment of the cyprid to which the cyprid cementing apparatus seems to be connected (Fig. 9 and Fig. 10). These observations suggest the concept that the cyprid and the adult cementing organs are closely related and that they do not undergo much change during the metamorphosis. The morphological similarity of the cyprid and adult cement glands seems to support this concept.

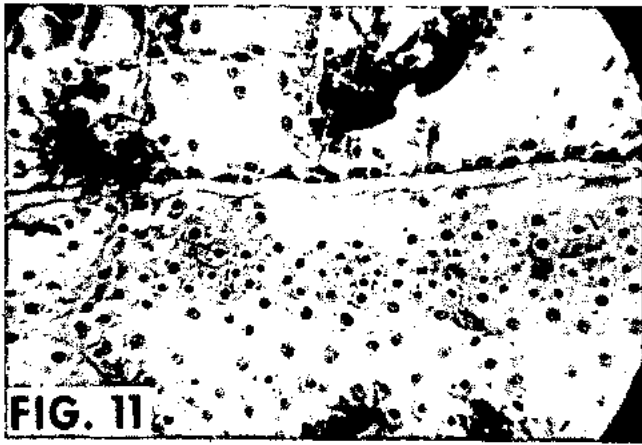


Fig. 11. Slight concentration of cells around area where new duct will be formed. (wholemout, Mallory's Trichrome, 475x).

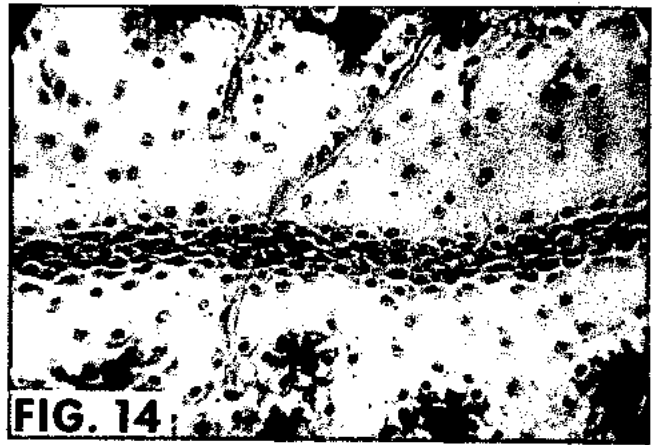


Fig. 14. Cells pack very closely, clearly showing outline of new duct. (wholemout, Mallory's Trichrome, 475x).



Fig. 12. Increased concentration of cells about new duct site (wholemout, Mallory's Trichrome, 475x).

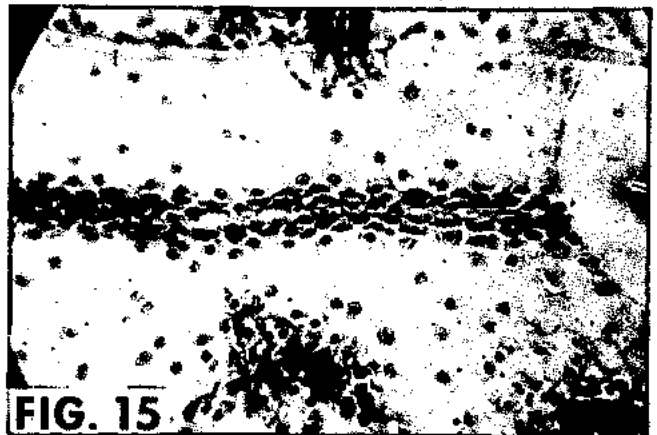


Fig. 15. Most of the cells have disappeared from the newly completed duct. The duct is still much a part of the epithelium layer in which it was formed and will break away with the epithelium. (wholemout, Mallory's Trichrome, 475x).



Fig. 13. Cells pack closely and elongate while forming (A) new duct and (B) vesicle. (wholemout, Mallory's Trichrome, 475x).

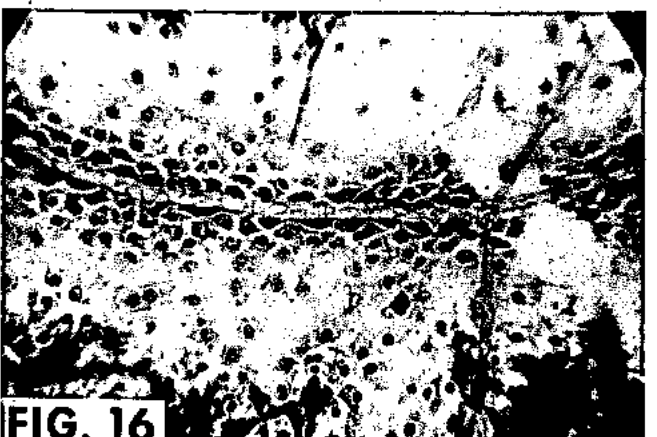
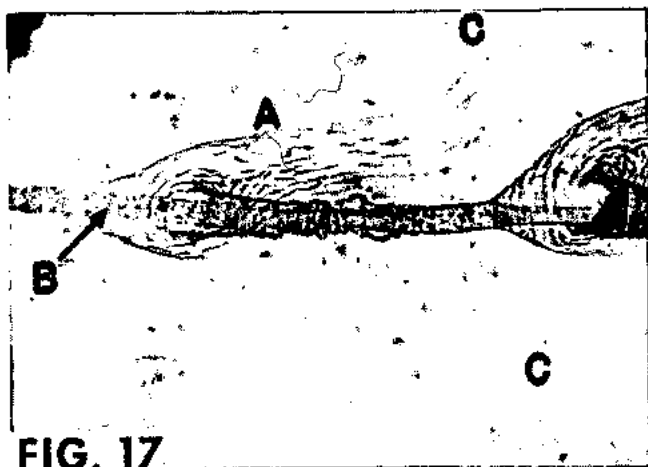


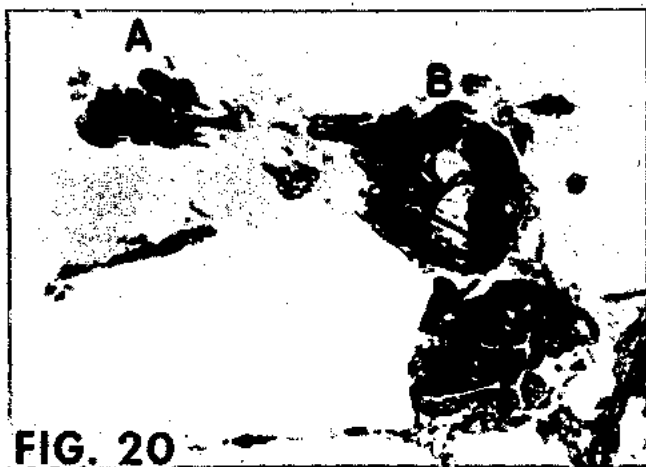
Fig. 16. Completed duct has now become separate from the epithelium. (wholemout, Mallory's Trichrome, 475x).





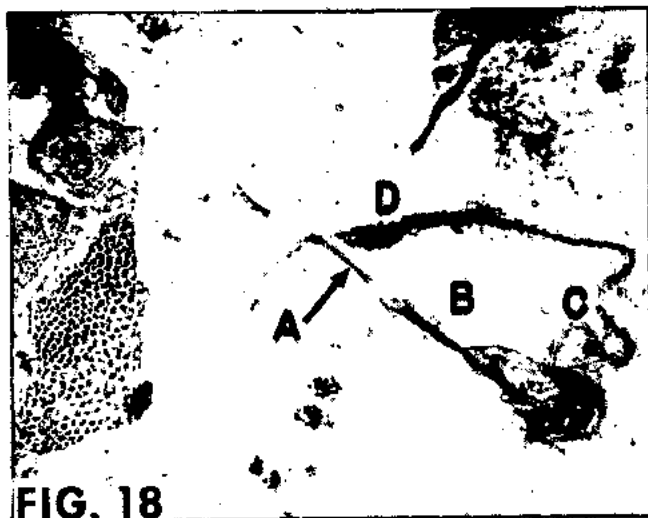
**FIG. 17**

Fig. 17. (A) Vesicles with (B) main channels passing through them, morphologically are very similar to the (C) ducts which branch from them. (wholemount, Gallego-Garcia, 375x).



**FIG. 20**

Fig. 20. (A) Node at end of main channel extension and (B) cement glands in adult *Balanus crenatus* specimen. (12 $\mu$  section, Mallory's Trichrome, 250x).



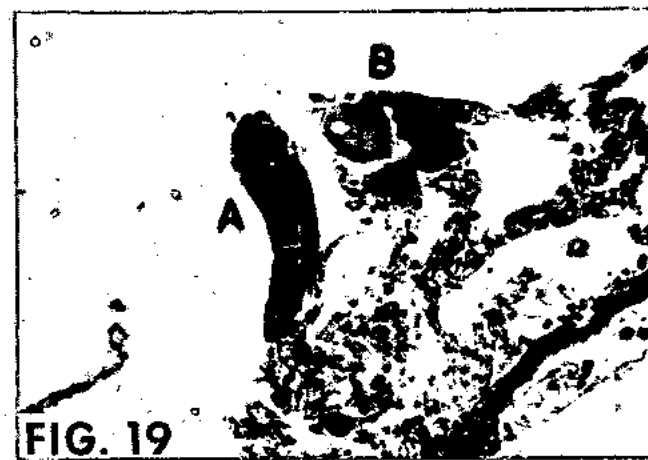
**FIG. 18**

Fig. 18. (A) Main channel connects (B) vesicles and has an (C) extension which continues beyond them and ends in a (D) node. (wholemount, Gallego-Garcia, 100x).



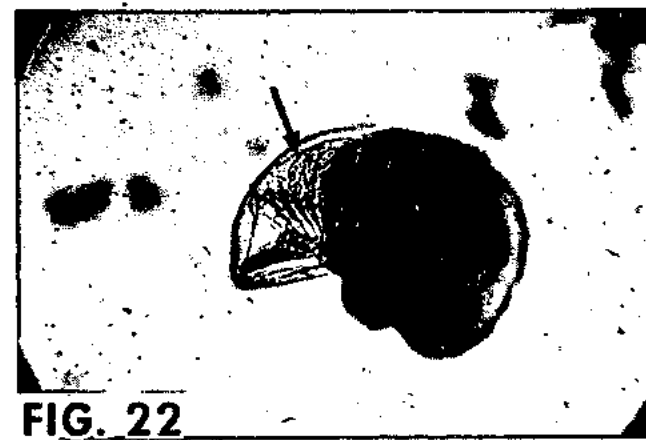
**FIG. 21**

Fig. 21. (A) Node on main channel and (B) cement glands in adult *Pollicipes polymerus*, (C) cross section of a side channel connecting main channel and gland. (10 $\mu$  section, Mallory's Trichrome, 250x).



**FIG. 19**

Fig. 19. (A) Node found at end of main channel extension, (B) cement gland (12 $\mu$  section, Mallory's Trichrome, 250x).



**FIG. 22**

Fig. 22. Adult cirri emerging from moulted cyprid exoskeleton in living *Balanus crenatus* specimen. (100x).

The cyprid cement glands are probably retained by the adult (Fig. 23). During the settlement and metamorphosis to the adult stage, these glands migrate from their position behind the compound eyes of the cyprid to the perimeter of the new baseplate of the adult perpendicular to the axis of symmetry of the body. As the adult barnacle grows, the cement glands remain in the living tissue of the mantle in the same relative position. The larger the baseplate grows, the more cement is needed for adhesion; therefore, periodically, new cement glands develop and join the existing ones, forming a cluster of glands on each side of the mantle. The individual glands of the same cluster are connected to each other by channels. These channels join in a node, from which the main channel on each side conducts the secretion toward the baseplate. The main channel connects the glands and the remains of the cyprid antennae at the point of the initial attachment.

We recognize now, that the whole cementing apparatus — the cement glands; the side channels joining in a node; and the main channels which conduct the cement toward the point of initial attachment — is anatomically identical in the two families of the sub-class Cirripedia: the Balanidae and the Lepadidae. The cement glands of both families are permanent, and they function periodically in relation to the moulting or growing periods.

In the Balanidae, in each growing period a new vesicle is formed on each main channel and becomes the starting point for each new duct network. The duct network ends at the perimeter of the baseplate in numerous orifices and spreads the cement around the edges. The vesicles and the ducts are developed by the epithelium as part of a continuous membrane on the inner side of the baseplate. This membrane is actually part of the exoskeleton and would be moulted away with the rest, but the baseplate prevents this from occurring. This membrane with the ducts and vesicles piles on top of the other membranes from earlier growth periods and becomes an integral part of the baseplate. In the Balanus species with calcareous baseplates, this layer becomes permanently embedded in the calcareous material. Once the duct network is moulted, it is no longer living tissue despite the fact that it remains in close contact with the rest of the system by means of the main channel. The moulted ducts, therefore, can not grow and reach the enlarged perimeter of the next growing period. Consequently, a new duct network must be produced to reach the newly developed areas under the enlarged baseplates.

We demonstrated that the contents of the side channels originating from the cement glands abruptly change their staining characteristics at their joining point with the main channel. This indicates a change in chemical composition of the cement at this point. Our knowledge of the chemical composition and the hardening mechanism is still limited. We can safely assume, however, that the hardening process is probably due to some sort of polymerization or cross-linking. Such a reaction mechanism can be initiated spontaneously or by catalysts. Studies are being continued to demonstrate whether different glands of the cluster produce different chemicals which are mixed at the joining point to start the reaction; or the changes in the secretion are due to pH changes at the joining point; or some small quantities of catalysts or cross-linking compounds are secreted by the cells around the joining point, to be mixed with the bulk of the secretion passing by. The fact that the cytoplasm of the surrounding cells stains similarly to the hardened cement indicates that the node possibly secretes small quantities of a chemical of low molecular weight that may be a catalyst or cross-linking compound.

In conclusion, the completed adult cementing apparatus in the Balanidae is anatomically and probably functionally identical with that of the Lepadidae. The cyprid cement gland is retained by the adult and is the basis for the adult cementing apparatus.

### Background

The walls and the baseplate of the barnacle shell are tightly connected by numerous muscle tissues around the baseplate perimeter at the inside joints of the leading edges. As a result of muscular action, the edges of the walls and the baseplate are pressed tightly on the substratum to leave only a very slight gap. The baseplate may grow into the recessions and over the protuberances of a solid substratum, faithfully duplicating its surface structure<sup>21</sup>. The forces produced by the growing barnacle enable it to plow away loose deposits, fouling organisms, and detritus and to dig beneath soft materials, such as clay or certain coatings<sup>1</sup> in order to reach an underlying solid surface. In these ways the barnacle obtains a maximum contact area for adhesion.

The baseplate is generally cemented so firmly to the substratum by an adhesive substance that the shell will usually break when an attempt is made to detach the barnacle. This adhesive substance is secreted at the perimeter of the baseplate and spreads under it to fill any gap between baseplate and substratum. Due to the pressures exerted by the barnacle, normally the gap to be filled and hence, the thickness of the cement layer, is less than 5 microns.

In crowded communities, however, the barnacles may develop abnormally. For example, in such communities, *Balanus balanoides* grows into elongated shapes, and Darwin observed that sometimes only the walls of such specimens reach the substratum, while the non-calcareous basal membrane remains suspended and deeply concave<sup>15</sup>. Darwin noticed that «thickish roots» were found hanging from the basal membrane, in the resulting gap. He believed these roots to be cement.

This development form apparently escaped the interest of later investigators since very little reference can be found on this subject in the literature. Crisp describes specimens which survived complete upward displacement by neighboring barnacles but does not mention any adhesive secretion<sup>6</sup>. Crisp also found that *Balanus balanoides* have some limited mobility under lateral pressure by neighboring barnacles and can be moved along the surface of a smooth substratum several centimeters away from their original point of attachment. Crisp speculated that the advancing edges form new adhesions as the barnacle gradually undergoes lateral displacement.

### Experimental

During the collection of large specimens of *Balanus nubilus*, one of the barnacles suffered a sizable crack in its baseplate. After 24 hours, an abundant white, opaque, rubbery exudate, or secondary secretion was found, filling and sealing this injury (Fig. 24). On numerous occasions it has been observed that barnacles sustain injury such as cracks or breaks in their baseplate as a result of the forces produced either by themselves or their neighbors. If vital organs are not seriously damaged or if the injury is not too extensive, the barnacle may survive such an accident by repairing the injuries with these secretions.

Secondary secretions were found not only in injured barnacles, but also in specimens of *Balanus crenatus* and *B. glandula* that were partially or completely separated from the substratum. Some of these separations appear to have been caused by excessive force exerted by the barnacle itself in an effort to press the growing edges of the baseplate close to the substratum. The pressures created at the perimeter may result in lifting and detaching the central portion of the baseplate. Such baseplates become concave, and the ensuing gap is usually filled with the secondary secretion (Fig. 25).

Microtome sections of these thick layers of secretions

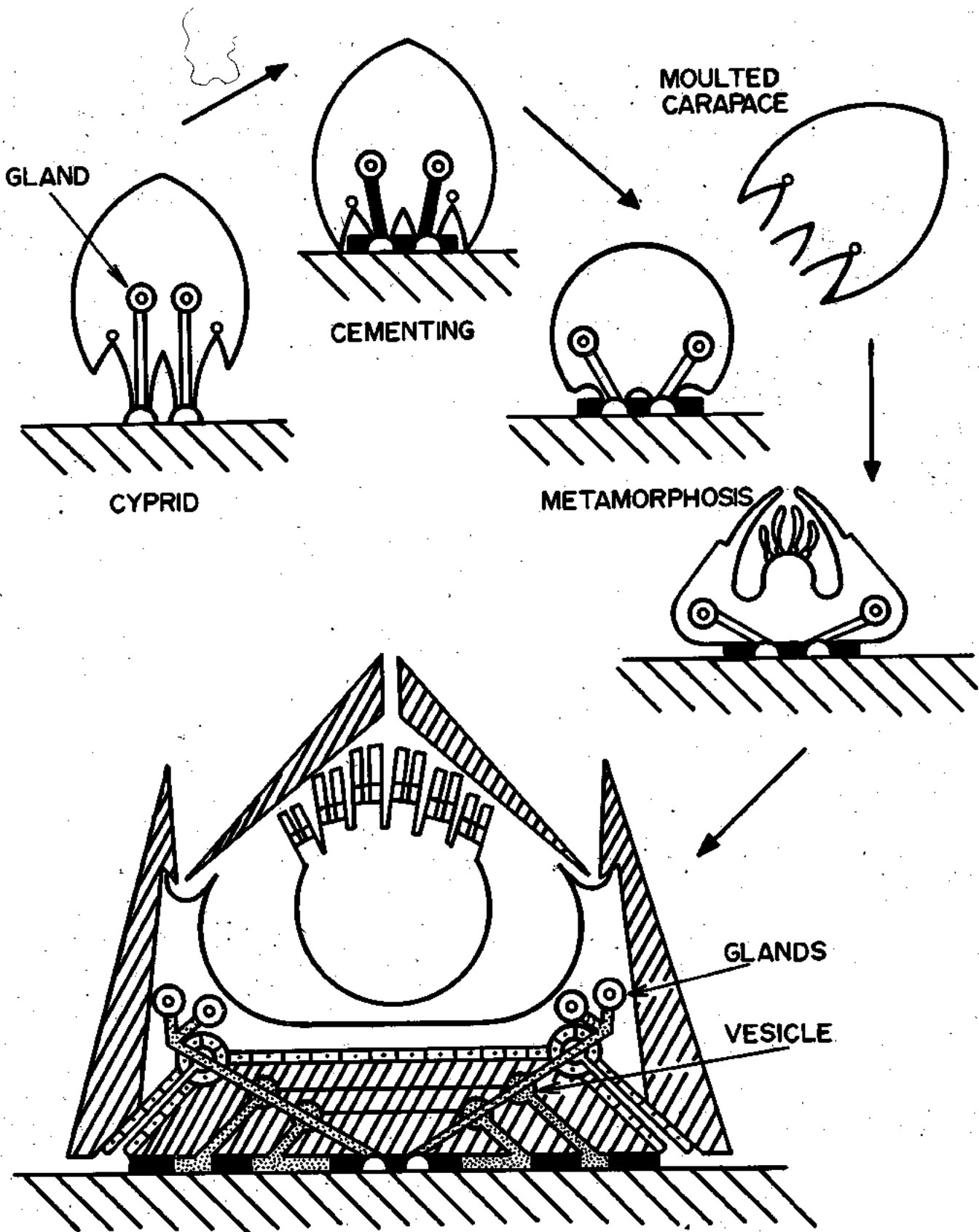


Fig. 23. Metamorphosis of cyprid to adult barnacle showing the migration of the cyprid cement glands to the position in which they are retained and function in the adult.



Fig. 24. Large specimen of *Balanus nubilus* suffered a crack in its baseplate. Within 24 hours, the secretion seen here hardened and repaired the crack.



Fig. 25. Abnormal concave baseplate on *Balanus crenatus* specimen detached from a solid substratum in the laboratory shows abundant secretions in an attempt by the barnacle to fill in the central gap.

often have a cavernous and vertically striated appearance (Fig. 26). This effect is probably caused by the continuous recession of the baseplate from the substratum. The gap created between baseplate and substratum is filled with the fluid secretion, but before hardening can take place, the baseplate continues to recede. The already viscous secretion may then pull threads of materials between the two surfaces, thus creating a loose structure. These new gaps are then filled with fresh secretions during the next period; and so the process is continued until the recession either ceases or continues at so rapid a rate that the secretory system is no longer able to supply enough material to fill the gap.

Another type of separation can occur in gregarious communities where the sidewalls of neighboring barnacles may be fused together. Since the walls grow up from their bases, a faster growing specimen may lift up and detach a slower growing one from the substratum. The space between the elevated barnacle and the substratum is usually then filled by the opaque secretion. If the gap is too large to be filled, any secretion present may be seen hanging suspended from the baseplate, indicating that an effort was made by the barnacle to reach the lost substratum and to reattach.

In the laboratory, barnacles were detached intact from smooth test panels (Fig. 27) and subsequently reattached to other smooth surfaces, such as glass microscope slides (Fig. 28). These specimens could be then kept alive indefinitely with proper care. A white, opaque substance is secreted, which spreads between baseplate and substratum if they are in close proximity. The closer the contact of the two surfaces, and hence the thinner the secretion layer, the firmer the reattachment appears to be. The reattachment can be so strong that the shell walls and body will break away before the baseplate can be detached. If the intervening space between baseplate and substratum is too large to be filled, thick droplets of secretion appear and hang from the baseplate (Fig. 29).

Assuming that the secretion is cement, it could be expected that the secretion would originate from the perimeter of the baseplate, where the newly developed cement duct orifices are located. In general, secretion does appear at the perimeter, from which it then spreads under the separated or injured area. Occasionally, however, an extensive se-

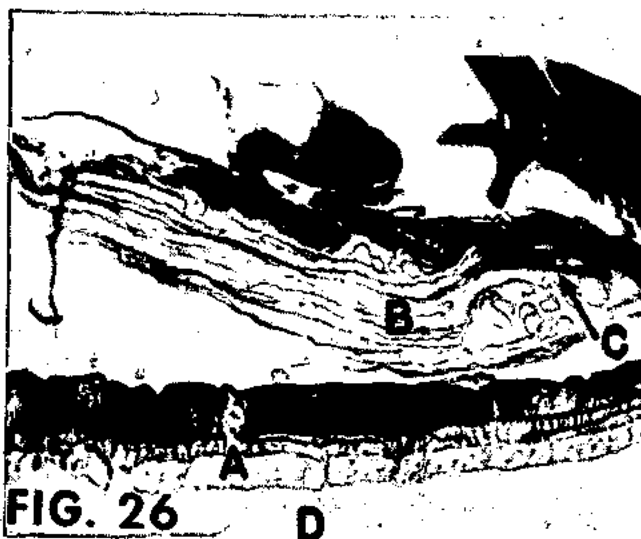
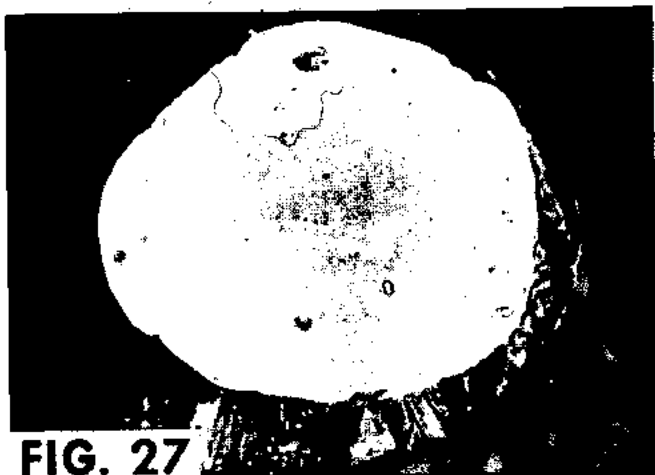
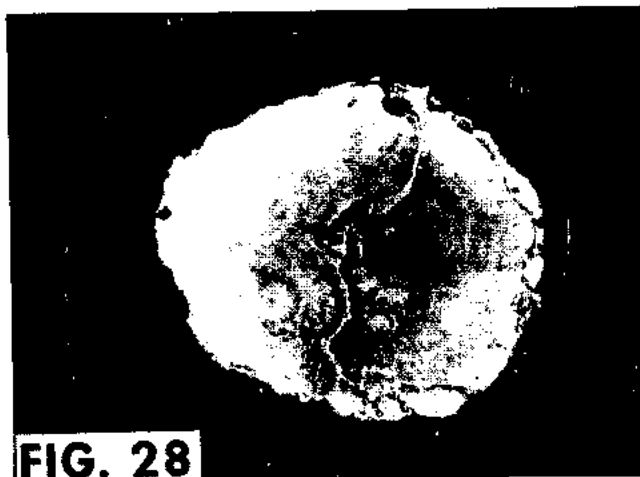


Fig. 26. Sagittal section through baseplate area of *Balanus crenatus* that was attached to paraffin shows (A) thick irregular layers of cement secretion, (B) empty ducts, (C) duct containing cement and (D) substratum. (10 $\mu$  section, Mallory's Trichrome, 250x).



**FIG. 27**

Fig. 27. Baseplate of *Balanus crenatus* specimen after detachment from test panel in the laboratory.



**FIG. 28**

Fig. 28. Baseplate of *Balanus crenatus* shown in Figure 27 after it reattached to a glass microscope slide.

paration or injury occurs isolated within the perimeter and the cement secreted at the perimeter cannot reach the effected areas in sufficient quantities. Indications are that the barnacle is able to grow new irregular ducts into such a damaged area (Fig. 30). These emergency or secondary ducts are larger in diameter than the normal ducts and have few or no bifurcations. Such a duct extends directly from the newest formed vesicle to the damaged area where it ends in an orifice. Normally only the first vesicle formed after metamorphosis would have such a duct leading from it, as

with each succeeding growth period, the duct system becomes increasingly complex in the number of branchings before the final orifices are reached.

The secondary ducts usually can be found only in those detached or injured areas where no old primary ducts and orifices can be found, as for example, near the cyprid attachment where the first available duct ends are outside the perimeter of the innermost circle. There is probably a unique mechanism that enables the barnacle to recognize the need for new ducts and to initiate the growth of these



**FIG. 29**

Fig. 29. Reattached *Balanus crenatus* specimen. Side A was reattached firmly to a glass microscope slide, while B was left suspended. Drops of secretion hang from the baseplate on the side where the barnacle was unable to reattach and adhere to the substratum.



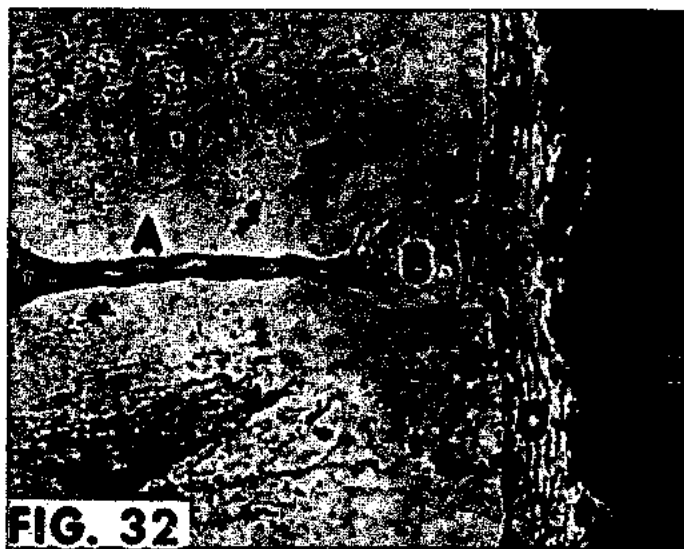
**FIG. 30**

Fig. 30. Growth of new, irregularly-shaped ducts originating from (A) vesicles into the (B) damaged initial attachment area. (wholmount, TriPARS, 100x).



**FIG. 31**

Fig. 31. Thick, circular layers of secondary cement at the orifices of old ducts. (wholemount, TriPARS, 255x).



**FIG. 32**

Fig. 32. Perimeter of an inner baseplate circle with (A) empty duct and (B) funnel-shaped orifice leading to the perimeter. The flushing process, following the cement secretion, has washed both the duct area and (C) a circular ring around the edge of the baseplate free of (D) cement before hardening took place. (wholemount, Mallory's Trichrome, 375x).

unusual ducts. Likewise, the dissolution of the calcareous matter to permit the growth of new ducts into old sites must somehow occur; similar processes are known in nature.

In the majority of cases, however, when detachment involves baseplate areas inside the baseplate perimeter, the reattaching secretion seems to originate from old primary duct ends. This reuse can be seen in wholemounts of the baseplates where several layers of additional secretion lie around the old duct ends (Fig. 31). These secretions appear in discrete layers, indicating that there was enough time for one layer to harden before the next one was laid down. Since, in the course of normal development, the edge of the growing baseplate is pressed tightly on the substratum and the cement is spread in a very thin layer, those thicker layers of secretion must have appeared at a time subsequent to the growth period during which the primary secretion took place. Therefore, we consider these thicker layers to be secondary secretions or secondary cement.

#### Discussion

It was shown that in most cases, an injured or detached barnacle uses the old duct system for repair or reattachment. This reuse is possible only if the duct system connected to these areas is still functional and the passages are still open. It would seem that since the ducts were filled with primary cement, when the cement hardens, the ducts would be plugged with solidified material and thereby rendered useless for subsequent secretion. Microscopic preparations, however, show most of the old, previously used ducts to be empty (Fig. 26).

It is believed that initially the cement is a fluid of low viscosity and solidifies within a short time after secretion from the duct system. The presence of an occasional duct filled with hardened cement suggests that the hardening process is not restricted to the hydrospace outside the duct system and that the cement is able to harden in the ducts, but is somehow removed before it can set. This removal may be due to a flushing process.

The flushing of the ducts after cement secretion and the recementing capabilities of the barnacle, as we now theorize, can be explained only if the cement is produced somewhere outside the duct and vesicle system, and not in the vesicles as previous investigators believed<sup>11, 16, 22</sup>. We showed that

the true glands are located in the living mantle tissue at the end of the main channel. The freshly produced liquid cement flows through the main channel from its origin, the peripherally located glands, toward the centrally located initial attachment. At the site of the outermost and newest vesicle or distributing chamber, the cement enters the adjoining duct network to be secreted through the duct ends at the perimeter (Fig. 34A). The cementing period ends when the flushing fluid, which is probably water-soluble, displaces the still liquid cement from the ducts (Fig. 34B). In the course of normal development, this flushing substance forces the cement out beyond the duct orifices and away from the edges of the baseplate. The cement hardens in this position under the cuticle of the joint connecting baseplate and walls. In this manner, a ten to forty micron wide circular channel is formed between the edge of the baseplate and the hardened cement, leaving the flushing fluid contained within this seal (Fig. 32). This flushing fluid may be modified cement, consisting of its monomers or of derivatives that may lack catalysts or contain polymerization inhibitors.

Although the vesicles as well as the rest of the duct network, are embedded in calcareous material in those species which possess calcareous baseplates, the vesicles are not functionless structures. The vesicles, in conjunction with the main channel, represent a unique system that is still able to function efficiently to prevent the flushing fluid from backing up and mixing with the new cement and to direct the cement to where it is needed.

The main channel goes through the vesicles as what appears to be a continuous tube rather than as a simple connection. (Fig. 33). On the basis of staining characteristics, the main channel appears to be composed of tissue different from that constituting the vesicles and ducts. The main channel develops previous to the vesicles; its walls are smooth and not scaly like the walls of vesicles and ducts. The vesicles and ducts are probably composed of chitinous material and are resistant to deterioration long after the death of the animal, while the portion of the main channel inside the vesicle soon deteriorates. This portion of the main channel is probably permeable, permitting transflux into the vesicle only. As long as the flushing fluid fills the ducts and vesicles, the system remains in balance

and no liquid passes through the permeable walls. In the course of normal development, therefore, the new cement does not go beyond the outermost and newest vesicle because the rest of the main channel and duct network is filled with the flushing fluid and no room is available for the cement (Fig. 34A). The new cement simply enters the new vesicle and duct network to be secreted at the perimeter.

However, if the baseplate separates from the substratum, the cement seal of some duct-ends breaks and the flushing fluid drains out of the corresponding ducts and vesicles. In the same fashion, a fracture in the baseplate would sever some ducts and the flushing fluid would also leak out at the injury site, followed by the cement (Fig. 34A,B,C). Since the duct networks of different growing periods are completely isolated from each other except at the vesicles, which are connected only by the main channel, the flushing fluid drains only from duct ends which are effected by the injury and only from those ducts which represent the shortest route from injury to the corresponding vesicle. The pressure inside this vesicle decreases due to fluid loss and the liquid from the main channel passes through the permeable walls into the vesicle cavity where it is also lost to the injured site. This loss of fluid is followed by the fresh cement out to the injury. Other ducts, unconnected with the injured area, remain filled with the flushing fluid and, hence, the cement bypasses those vesicles which serve the unaffected duct network.

Thus, the vesicles serve as distributing chambers and that portion of the main channel within the vesicles controls and regulates the flow of cement and flushing fluid, as would a valve. The vesicles of different age are situated near each other and are connected by the main channel. This arrangement puts all the vesicles, the corresponding duct network, and especially the duct ends, regardless of the network to which they belong, almost equidistant from the cement glands at the end of the main channel. Thus, it is practically as easy to secrete cement through older ducts as through the newest, peripheral duct system. After emergency use, the system is again flushed out and ready for further reuse. In repeated use, however, the flushing process is not always complete because usually larger and irregular amounts of cement are secreted at the emergency locations, thus plugging the orifices. Hence, those reused ducts and vesicles could contain hardened cement.

Since this secondary cement is secreted at the same time as the primary cement and is a product of the same cementing apparatus, it can be inferred that the two substances are chemically identical.

### CONCLUSIONS

1. The initial attachment of the barnacle is only a mechanical adhesion by means of the hydraulic suction cups at the tip of the cyprid antennae. The initial attachment is usually reinforced by an adhesive cement, but the cement is not essential for achieving permanent attachment.

2. Both families of Cirripedia, the Balanidae and the Lepadidae, have an anatomically identical cementing apparatus: (1) periodically functioning permanent glands on both sides in the mantle; (2) cement glands consisting of smaller units, connected at one point at which the chemical properties of the secretion are altered; and (3) main channels which conduct the secretion toward the initial attachment point.

3. The cyprid cement glands are retained in the adult, where they are found in the living mantle tissue perpendicular to the axis of symmetry of the barnacle. These glands become the basis of the adult cementing apparatus.

4. The development steps of the duct network in the Balanidae indicate that the growth periods of the baseplate correspond with the moulting periods.

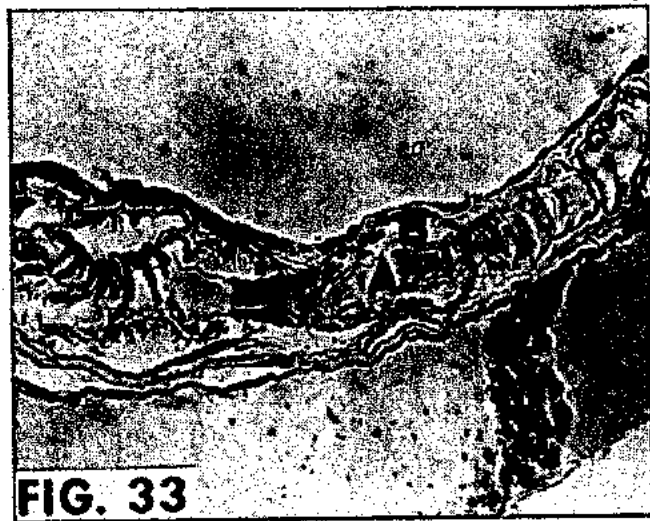


Fig. 33. Section through baseplate of an adult *Balanus crenatus* showing (A) the main channel and (B) the vesicles through which it passes. (12 $\mu$  section, Mallory's Trichrome, 325x).

5. A flushing mechanism removes the cement from the cementing apparatus before hardening can take place. Therefore, the duct network is kept open and ready for emergency reuse. The vesicles, formerly thought to be the cement glands, function as regulating valves for both the cement secretion and the flushing process.

6. We demonstrated that the primary cement secreted by the adult barnacle during normal development and the emergency secondary cement are products of the same cementing apparatus and are secreted simultaneously. It is expected, therefore, that the primary cement and the secondary cement are chemically identical substances. As it was shown that the cyprid cement is retained and becomes the basis of the adult cementing apparatus, the cyprid cement should also be a similar chemical substance.

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### ADMINISTRATIVE INFORMATION

The study of the attachment mechanism of barnacles is the biological phase of the Mare Island Paint Laboratory project: Fouling Prevention, The Study of the Adhesion Mechanism of Calcareous Types of Attaching Marine Organisms. This project is part of the In-House Research/Independent Exploratory Development Program, NAVSHIPS Project No. SFO20-99-02, Task 11906, authorized by NAVSHIPS letter 3900 Serial 03421-92 of 30 September 1966.

The work was initiated by Mr. John R. Saroyan, Head of the Mare Island Paint Laboratory, and was accomplished by Mr. Elek Lindner, Research Chemist, and Mrs. Carol A. Dooley, Chemist.

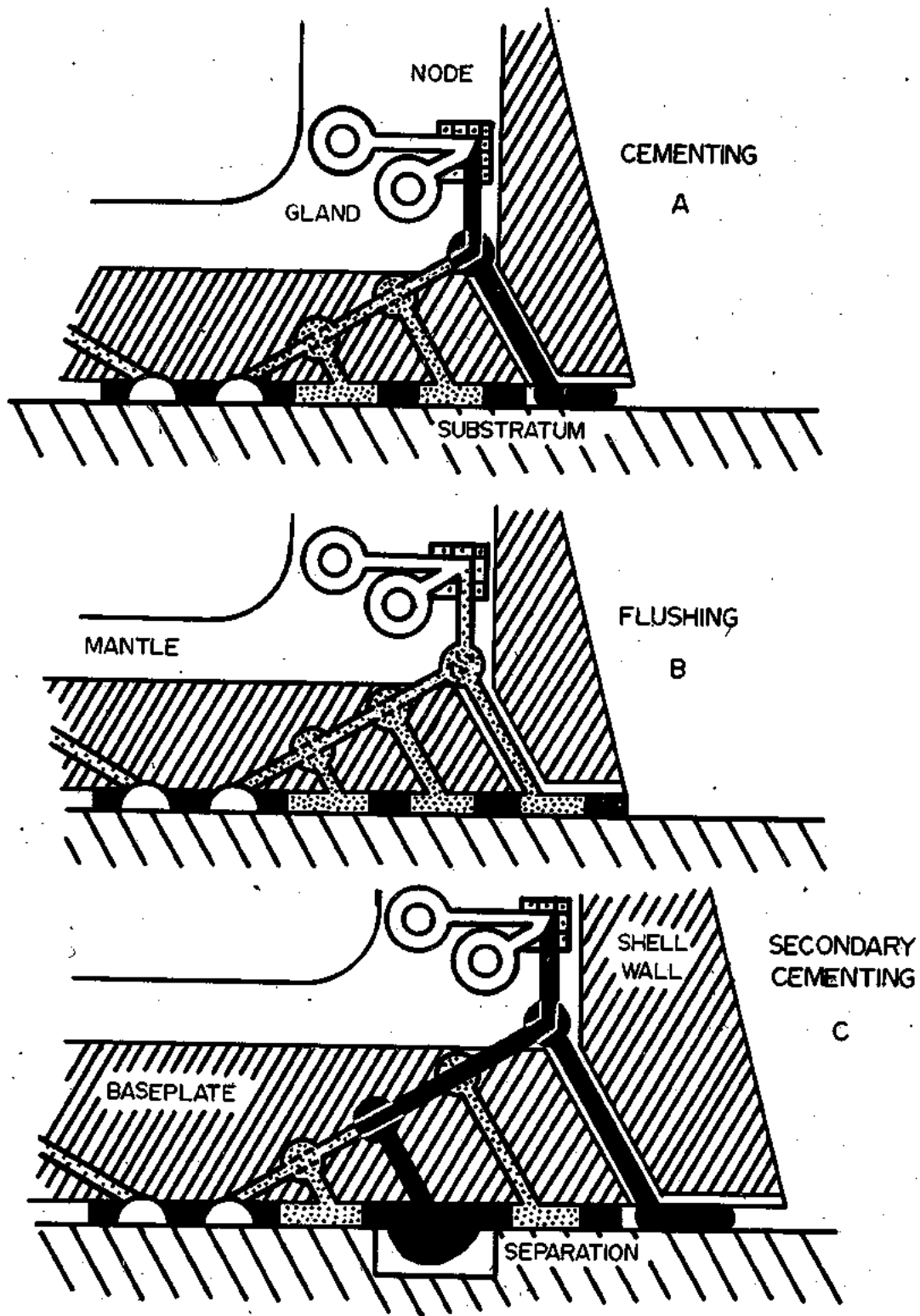


Fig. 34. (A) Secretion of cement from cement gland to newest vesicle and duct network during normal development, (B) flushing of duct network following cement secretion and (C) secretion of cement when a separation from substratum has occurred in the region of an old duct.



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## DISCUSSION

J. SPARROW (England): I have found this a most interesting talk and would like to ask which species of barnacles you were principally working with, and whether the mechanism of attachment you have described applies both to barnacles with a solid calcareous basis and to those with a membranous basis?

E. LINDNER: Unfortunately, we worked mainly with those species which have calcareous basis, namely *Balanus crenatus*, *B. glandulus*, *B. nubilus*, *B. amphitrite* and *B. improvisus*. We have another species under examination at the present time, namely *B. cariosus*, which does not have calcareous basis, but we have no data on that yet to present.

P. ROCOTAS (Greece): Can I ask, whether you have investigated the chemical composition of the cement?

E. LINDNER: The main purpose of our research was to identify the chemical composition of the cement. This work is underway at the present time, but I do not have any data on hand to present.

However, let us discuss this problem a little bit. What can the cement be? And what can the cement hardening mechanism be? We might assume that the cement is a liquid of very low viscosity when it is secreted to be able to go through the narrow ducts. Also, we might assume that the hardening mechanism of the cement is probably due to some kind of polymerization or crosslinking process. The polymerization can be triggered spontaneously or by pH changes or by catalysts or by some highly active low molecular weight substances capable of crosslinking the bulk of the secretion.

Permit me to demonstrate some very interesting observations on a few slides.

These pictures deal with that area of the cementing apparatus, where the side channels leading from the cement glands join and enter into the main channel, which in turn conducts the cement toward the vesicles and the rest of the duct network. As I pointed out, we find a node consisting of numerous cells around the area, where the side channels join the main channel. We found it quite remarkable that the chemical characteristics or staining characteristics of the secretion abruptly change at this joining point.



FIG. 35. Side channels collect secretions from the cement glands. The content of the side channel does not stain. (10 $\mu$  section, Mallory's Trichrome, 250 $\times$ ).

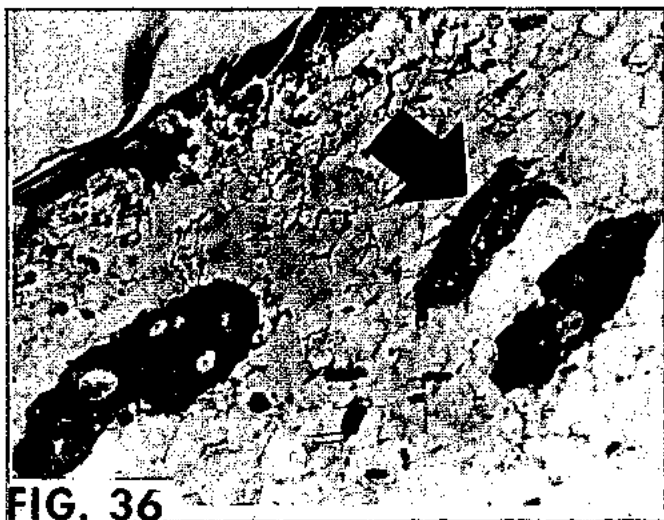


FIG. 36  
 Figure 36. The node where the side channels merge into the main channel. The content of the main channel stains red and the stained substance seems to diffuse from the cytoplasm of the surrounding cells of the node. (10 $\mu$  section, Mallory's Trichrome, 250 $\times$ ).

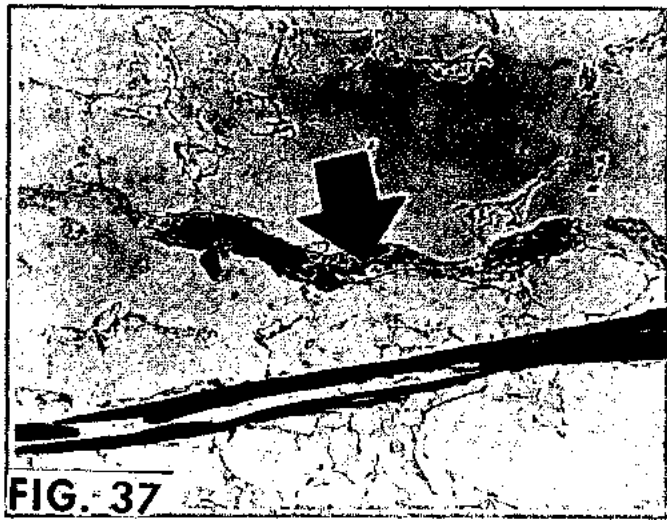


FIG. 37  
 Figure 37. The content of the main channel further away from the node stains red. Its edges are sharp, no indication of material diffusing from the surrounding cells of the main channel. (10 $\mu$  section, Mallory's Trichrome, 250 $\times$ ).

The first picture (Fig. 35) shows the cement glands and the side channels. The contents of the side channel are clear; they did not stain.

The second picture (Fig. 36) shows the joining point of the side and main channels. The secretion at this point takes up the stain. The substance, which stains, seems to diffuse from the cytoplasm of the surrounding cells of the node.

The third picture (Fig. 37) shows the main channel. The content of the main channel also stains, but no diffusion from the surrounding cells can be seen, the edges of the stained secretion are in sharp contrast to the surrounding tissues.

These pictures indicate, that a chemical change takes place at the joining point, at the node. The cells of the node could act as a second gland secreting some highly active small molecular weight compound which can trigger the polymerization through catalysis or crosslinking with the bulk material secreted by the cement glands or some other mechanism initiating the cement hardening. At this time we can only speculate on these possibilities since our study of this phase of the hardening process is still underway as well as the instrumental analysis of the barnacle cement. I hope that in the next Congress I will be in the position to report more in detail about the chemistry of the barnacle cement and its hardening mechanism.

Prof. EVANS (Canada): Have you speculated about the possibilities that this material from the cement gland is in any way related to the arthropod attraction material described by Crisp?

E. LINDNER: I am quite familiar with Professor Crisp's work and I think his main interest is in the chemoreception of the barnacles. The chemoreception aids the barnacles to settle in a gregarious manner because they are capable of identifying chemically some exposed tissue or material of their own species. Since the cement is not exposed under

normal circumstances, I do not think that it would act as an attractant. This is only my personal opinion. I do not have any evidence on this matter.

Talking about Professor Crisp, I had the honor of visiting his laboratory a week ago. They are doing remarkable work on the chemoreception or chemical sensitivity of the barnacle. In connection with this work Dr. Knott and Dr. Foster showed me their extraordinarily beautiful scanning electron micrographs of the cyprid antennae and also electron micrographs of sections of the antennal attaching disc area, the same area I discussed in the first part of my paper. My photomicrographs, which I presented to you, do not show those details, which are marvelously resolved on their electron micrographs. They demonstrated that the attachment disc resembles a brush, in that it is densely covered with very flexible, thin, hairlike projections. They also recognized some glands near the disc. As they describe it, these are not cement glands, but some mucous types of glands. I hope I do not commit any indiscretion, since I understand the paper of Dr. Foster and Dr. Knott on this subject is already under publication. Their theory about the attachment mechanism of the cyprid barnacle seems to be somewhat different from that one I presented in this paper. They found that the sticky secretion of the mucous glands saturates the brush area, which acts like a sponge saturated with sticky substance and makes the temporary attachment possible. While they postulate that the temporary attachment is simply due to the adhesion of the 'sticky sponge', I would like to add that it also can improve the seal for a suction cup mechanism to provide a better suction, and thus these newer findings do not necessarily contradict our theory. I hope that further research will give us better understanding of the cyprid attachment.

# BIOLOGICAL INVESTIGATION ON THE MOLLUSCAN WOOD BORER, *MARTESIA STRIATA* IN VISAKHAPATNAM

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## SUMMARY

Results of the investigations on some aspects of the biology of the molluscan wood borer, *Martesia striata*, were reported. *Martesia* breeds throughout the year in Visakhapatnam harbour which may be due to the favourable hydrographical conditions. The animal is oviparous and development is rather rapid, within about 24½ hours the egg reaches the stage of veliger after fertilization. A study of

the digestive enzymes of the crystalline style and digestive diverticula revealed that the enzyme, cellulase, is absent and *Martesia* appears to bore for the sake of shelter only. The distribution of *Martesia* in Visakhapatnam harbour is related with temperature and salinity. When the salinity dropped to about 5.09‰, all larvae of the borers disappeared from the test panels.

## INTRODUCTION

*Martesia striata* resembles members of the Terebinidae in its habit of boring into timber though occasionally it is also known to bore into stone. Unlike *Xylophaga dorsalis*, it is typically found in fixed structures such as timber jetties, dock gates and other structural materials of wood used in harbour installations. The shell of a fully grown *Martesia* measures about 25 mm in length. As in shipworms, the boring is accomplished with the shells. *Martesia* does not line its burrow with a calcareous deposition as do *Teredo* or *Bankia* nor does it possess pallets. As a constant communication has to be maintained with the outside water, the depth of the bore is determined approximately by the length of the shells enclosing the animals.

## BREEDING HABITS

The breeding period of *Martesia* in Visakhapatnam harbour extends throughout the year as the animals collected during the different months of the year (1956) showed ripe eggs and sperms. Monthly test panels also showed very young forms which are just settled, throughout the year. In Sydney harbour, Moore (1947) observed that *Martesia* breeds only during the warmest months of the year. Turner (1955), however, says that test board records at Guantanamo, Cuba and San Juan, Puerto Rico, indicate that this species probably breeds throughout the year and adds that this is perhaps one explanation for its wide distribution in tropics. An examination of salinity and temperature data of the Visakhapatnam harbour waters reveals that both salinity (range: 22.8 to 34.6‰) and temperature (range: 26.5 to 31.1°C.) are favourable for the continuous breeding of *Martesia*.

## EARLY DEVELOPMENT

*M. striata* is oviparous and development takes place completely outside the parent, in the sea. Developmental stages were obtained both by natural spawning and artificial fertilization. A chronological order of events in early development is given below.

3rd December 1955 8-30 A.M. Mixed eggs and sperms  
10-00 A.M. 2 cell stage  
10-15 A.M. 4 cell stage  
10-30 A.M. 8 cell stage  
10-50 A.M. 16 cell stage  
11-05 A.M. 32 cell stage  
12-05 P.M. Blastula  
2-00 P.M. Gastrulation commences  
8-30 P.M. Trochophore stage  
4th December 1955 9-00 A.M. Veliger stage

The veliger of *M. striata* has got a characteristic shape, the shell outline being semicircular or more or less D-shaped. It measures about 0.08 mm in length. The velum is the sole swimming organ and possesses a long central flagellum. The foot, which first appears as a broad median protuberance beneath the stomodaeal region, soon becomes long, broad and mobile.

The duration of the free swimming larval period is not exactly known since no further development took place in experimental bowls and all the larvae died in seven days.

## FEEDING AND DIGESTION

Samples of stomach contents from nearly 200 *Martesia* gave a fair indication as to the nature of its food. No chips of wood were encountered in the digestive tract: on the other hand, a good number of planktonic animals (diatoms, flagellates, cypris larvae, molluscan veligers and copepods) are noticed. Feeding experiments carried out with the suspensions of iron saccharate on starved *Martesia*, revealed that the iron saccharate is ingested and digested intracellularly only in the tubules of the digestive diverticula.

A detailed investigation into the digestive enzymes of the crystalline style and digestive diverticula were made (Nagabhushanam, 1966). The style extract contains amylase, maltase, lactase, invertase and glycogenase. Sacroclastic enzymes in the digestive diverticula act on starch, sucrose, glycogen, raffinose, maltose, lactose but not on inuline and cellulose. The lipase and protease of the digestive diverticula are rather weak. The absence of cellulase

both in the crystalline style and the digestive diverticula is significant as it confirms the idea that *Martesia striata* bores into the wood for the sake of shelter alone and has not the capacity to digest the wood, unlike the shipworms.

#### DISTRIBUTION OF MARTESIA IN VISAKHAPATNAM HARBOUR IN RELATION TO TEMPERATURE AND SALINITY

In Visakhapatnam harbour there appears to be a direct relationship between the relative abundance of the borer, *Martesia*, and temperature and salinity. *Martesia* was recorded in monthly test panels throughout the year, though a seasonal change in their attack rate was apparent. The borers are found in maximum numbers in summer months between March and June 1956, with a peak period in May when the highest temperature was recorded for the year at all stations in Visakhapatnam harbour (Nagabhushanam, 1961).

The influence of temperature on borer behaviour may be readily understood in temperate waters where near zero figures may be reached in the winter months. However, in tropics such wide changes in temperature are not encountered. At Visakhapatnam harbour the change from winter to summer temperature is about 6-7°C. At Miami, Florida, Greenfield (1952) recorded maximum attack of *Teredo pedicellata* in June-July period when temperature in those waters was highest for the year (31.7 - 32.9°C.), even though this organism was actively breeding and boring throughout the year. At this area the change from winter to summer temperatures is in the neighbourhood of 10°C. He (Greenfield, 1952) remarks «that observable variation in activity may be caused by small temperature changes, especially if such changes are within the active range of the organism in question, is not unlikely». Certain poikilothermic animals have been found to respond to one-half degree change in a five degree span within the active range (Prosser, et al. 1950).

In October though the temperature was favourable for the normal activity of *Martesia*, they were completely absent at stations 2 and 3, while only a few of them were recorded at station 1 (Nagabhushanam, 1961). This was probably due to the lowest salinity recorded in that month. At station 2, the salinity was 4.63‰ and at station 3, 5.09‰. These very low salinities might have killed all larvae of borers and hence the panels at those localities were free from borer attack. But at station 1, where the salinity was relatively higher i.e. 14.65‰, a few borers were collected from the test blocks.

In general in winter months (November to January) *Martesia* were found in smaller numbers in test blocks compared to the rest of the year. This was probably due to a biological competition with the shipworm, *Bankia campanulata*, whose intensity of attack was maximum during the winter months.

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# CONTRIBUTION A L'ETUDE DU COMPORTEMENT DES PEINTURES ANTISALISSURES

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## RÉSUMÉ

On a étudié des peintures antisalissures de deux types : à liant soluble et celles dites à liant insoluble. Les premières, qui agissent par solubilisation simultanée du toxique et du liant, ont été formulées avec de la colophane plastifiée comme liant. Les autres, dans lesquelles il y en a une dissolution et diffusion du toxique à travers le film, sont préparées avec des résines vinyliques.

On compare les différents toxiques minéraux ( $\text{Cu}_2\text{O}$ ,  $\text{HgO}$ ,  $\text{AsO}_4\text{Hg}_2$ ,  $\text{As}_2\text{O}_3$ ), en utilisant des mélanges avec des différents rapports entre eux. Comme toxique organique, on emploie l'oxyde de bis-tributyl-étain (TETO).

Dans ce travail on expose des résultats correspondants à un an d'immersion en radeau dans le port de Mar del Plata, dans la côte argentine. Ce port a été étudié parallèlement du point de vue biologique et hydrologique.

On a suivi mensuellement l'état des plaques peintes, en enregistrant des photos et en réalisant un relevement des

salissures fixées.

On trouve, du point de vue de l'action des différents toxiques étudiés, que dans les peintures à liant soluble les formes à base de  $\text{Cu}_2\text{O}$ - $\text{AsO}_4\text{Hg}_2$  ont un excellent pouvoir antisalissure ; dans le cas des peintures vinyliques (type contact continu), toutes les mélanges de toxiques nous ont donné des films exempts de salissures ; dans la même condition se trouve l'échantillon correspondant à l'oxyde de bis-tributyl-étain.

Par rapport aux autres variables considérées dans notre étude, on fait des considérations à propos de l'influence du rapport colophane/plastifiant ou résine vinylique/plastifiant ; de la présence de pigments inertes ou de l'oxyde de zinc dans les peintures ; et aussi du temps de broyage des toxiques, du temps de stockage des peintures et de l'épaisseur du film appliqué.

## INTRODUCTION

Les peintures antisalissures ou «antifouling», comme il est bien connu, sont des peintures toxiques, étant leur rôle principal l'empêchement de la fixation d'organismes du milieu marin sur la coque ou carène des navires<sup>1,2</sup>.

Du point de vue de leur action, elles ont été très étudiées, spécialement les compositions à base de cuivre et de mercure<sup>3,4,5</sup>. On peut considérer actuellement que le mécanisme d'action se base sur le principe de la toxicité permanente du film. Il y a une dissolution des toxiques dans l'eau de mer, sous la forme de chlorures, de carbonates basiques, etc., plus ou moins solubles, et cette solution forme une pellicule létale pour les larves des organismes marins<sup>6</sup>.

Le liant de la peinture doit être formulé pour permettre cette mise en solution. Les solubilités minimales indiquées dans la bibliographie sont, pour les peintures efficaces, de l'ordre de  $10 \mu\text{g}/\text{cm}^2/\text{jour}$  pour le cuivre et de  $2-6 \mu\text{g}/\text{cm}^2/\text{jour}$  pour le mercure. Le cuivre et le mercure sont utilisés principalement sous la forme d'oxyde cuivreux, d'oxyde mercurique, d'arséniates ou arsénites de cuivre et de mercure, de vert de Schweinfurt, etc. On emploie généralement un mélange de différentes substances. Il y en a aussi des différents toxiques organiques, comme par exemple les composés de butyl-étain.

Les valeurs indiquées ci-dessus pour le cuivre et pour le mercure sont connus sous la dénomination de *leaching rate*

ou *taux de lixiviation* de la peinture antisalissure, et il faut marquer la différence entre le *degré de lixiviation initial* (solubilisation immédiate des toxiques pour empêcher la fixation d'organismes à partir de la mise en service des peintures) et celui appelé *constant (steady state leaching rate)*. Ce dernier est le plus important du point de vue de l'efficacité des peintures pendant des longues périodes de service.

Si l'on considère la façon d'agir de ces peintures, d'accord avec les plus récentes publications de Partington<sup>7</sup> et de Van Londen<sup>8</sup>, il est possible de différencier deux types ;

- Les peintures *type contact continu* (dites à liant insoluble) portant une *dissolution* et une *diffusion* du toxique à travers le film ; et
- Les peintures à *liant soluble*, avec *solubilisation simultanée* du toxique et du liant.

Les peintures appartenant au premier cas utilisent de hauts polymères pour la préparation du milieu de suspension : résines vinyliques, caoutchoucs chlorés, résines époxydes, etc. Toutes ces peintures sont formulées avec une haute concentration de toxique, en considérant que dans leur mode d'action le contact entre les particules de pigment joue un rôle fondamental<sup>9</sup>.

Le deuxième cas est celui des peintures préparées à base d'une résine acide (colophane, 90% d'acide abiétique). Les groupes  $-\text{COOH}$  libres de sa structure, permettent la dissolution dans l'eau de mer légèrement alcaline (pH 8, environ), et la dissolution du toxique est accompagnée toujours par

celle du liant. Il faut modifier la très grande solubilité de la colophane au moyen de plastifiants ou d'un vernis, pour obtenir le taux de lixiviation le plus convenable. La substitution de la colophane par des résines ou des vernis, diminue la solubilité du liant (et par conséquent la mise en solution du toxique), améliore l'accrochage du film sur la couche de peinture anticorrosion et la tenue vis-à-vis du milieu marin qui entoure la carène du navire.

A tous ces mécanismes il faut ajouter l'action d'érosion (dans le cas des bateaux en navigation) ou une possible action bactérienne sur le film.

Il faut tenir compte aussi du voile bactérien<sup>2</sup> qui se forme sur le film antissalissure, constitué par des organismes très résistants aux toxiques (Bactéries, Diatomées), qui ne doit pas empêcher le fonctionnement de la peinture.

Vraiment, tous les facteurs déjà nommés opèrent simultanément, et l'on pense qu'il est impossible de faire une différenciation nette entre les différents types. Par exemple, les peintures vinyliques, considérées couramment à liant insoluble, modifient sa solubilité par l'addition de la colophane (c'est le cas de nos formules). C'est pour cette raison que toute la documentation moderne sur ce sujet est l'objet d'une révision continuelle.

### PROGRAMME DE RECHERCHES

Il a été préparé avec l'objet d'établir quelles sont les caractéristiques physiques et la composition chimique des peintures antissalissures les plus convenables pour remplir les exigences des normes IRAM utilisées en Argentine<sup>10</sup>. On compare aussi le comportement des peintures vinyliques, fortement étudiées aux Etats-Unis<sup>11, 12</sup> avec les peintures à liant soluble, plus couramment employées dans notre pays.

On considère l'influence des variables suivantes :

- Type de toxique : minéraux ( $\text{Cu}_2\text{O}$ ,  $\text{HgO}$ , arséniate de mercure,  $\text{As}_2\text{O}_3$ ) et organiques (TBTO, oxyde de bis-tributyl-étain).
- Type de liant : vinylique (résines VAGH et VYHH)<sup>11</sup> et à la colophane.
- Type de plastifiant et rapport colophane/liant (variation de la solubilité du film).
- Influence d'autres pigments : oxyde de zinc et oxyde de fer rouge.
- Influence de l'épaisseur du film.
- Temps de broyage des pigments et son influence sur le pouvoir antissalissure (pour quelques échantillons).
- Stabilité de la peinture pendant l'emmagasinage, et son influence sur la toxicité ; étude comparative des peintures ayant une année de stockage et immédiatement après leur préparation (1 mois).

Tous les liants ont été préparés au laboratoire, par dissolution des résines ou des vernis dans des solvants. Pour la dispersion des pigments on a utilisé une broyeuse à boulets, pendant 24 heures (sauf pour les toxiques, qui sont incorporés 4 heures avant la fin de cette opération).

### COMPOSITION DES PEINTURES. MÉLANGES DE TOXIQUES ESSAYÉS

Les possibilités de formulation des peintures antissalissures étant très grandes, on a préféré de travailler, pour les peintures vinyliques, sur la base des spécifications américaines<sup>12</sup>, en modifiant seulement les rapports entre les différents toxiques et en utilisant dans quelques cas des pigments inertes ( $\text{Fe}_2\text{O}_3$ ) et des composés organo-métalliques.

Pour les peintures antissalissures du type à liant soluble (colophane) on a appliqué notre expérience préalable sur ce sujet. On fixe une concentration de toxique et des rapports pigment/liant et résine/vernis qui nous permettra de résoudre le problème avec un minimum d'échantillons. La mise au point des formules, en considérant l'aspect commercial, sera faite dans une prochaine étape.

Les compositions préparées ont les caractéristiques générales suivantes :

	Peintures à liant soluble (colophane)	Peintures vinyliques
Pigment, % .....	58	60
Liant (résine et plastifiant) % .....	26	13,5
Solvants, % .....	16	26,5
Rapport P/V .....	1/0,45	1/0,225
Rapport colophane/liant ..	5:1 4:1 3:1	—
Rapport résine vinylique plastifiant .....	—	4:1

Toutes ces valeurs sont exprimées en poids.

Pour les peintures à liant soluble, elles ont une concentration de toxique de 30-40 pour cent sur le film sec (on emploie aussi des inertes). Dans les peintures vinyliques, les toxiques montent jusqu'à 82 pour cent excepté le cas des échantillons 220 et 221 (tableau II), dans lesquels on remplace partiellement le toxique par l'oxyde de fer rouge, afin de constater la théorie du contact continué établie pour ces peintures<sup>2, 9</sup>.

Le détail des matières premières employées est indiqué sur le tableau I.

TABLEAU I

### COMPOSITION DES PEINTURES ANTISALISSURES MATIÈRES PREMIÈRES

	Type vinylique	Type à liant soluble
Toxiques minéraux	$\text{Cu}_2\text{O}$ - $\text{HgO}$ - $\text{As}_2\text{O}_3$ -Arséniate de mercure	
Toxiques organo-métalliques ...	TBTO	
Pigments .....	$\text{Fe}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$ - $\text{ZnO}$
Liant: Résine ...	Vinylique VAGH et VYHH (copolymères de chlorure acétate de vinyle) et colophane	Colophane (rosin)
Plastifiant .....	Phosphate de tricrésile	1 <sup>re</sup> série : Vernis à résine formophénolique modifiée - standolie d'huile de lin. 2 <sup>e</sup> série : Vernis à résine formophénolique pure-huile de bois de Chine.
Solvants .....	MIBK-Toluène (1:1)	White spirit-Toluène (3:1)

Le tableau II fait référence aux rapports choisis pour les différents toxiques.

Dans le cas spécial du toxique organométallique, l'oxyde de bis-tributyl-étain (TBTO), on l'utilise afin de vérifier les expériences et les données de Zedler<sup>13</sup> et aussi comme un antécédent pour la recherche sur ses conditions de toxicité, de compatibilité avec les autres pigments et des caractéristiques de stabilité des peintures dans leurs récipients. Nous avons dans notre programme une étude approfondie sur les composés organiques de l'étain, comprenant l'oxyde, le soufre, le fluorure et le stannate.

### PROCÉDÉ EXPÉRIMENTAL

Les peintures ont été essayées dans notre radeau à Mar

TABLEAU II  
RAPPORTS DES TOXIQUES

Type de peinture	Rapport résine/plastif.			Toxiques (*)	Rapports (en poids)	Inertes
	5:1	4:1	3:1			
<i>Liant soluble:</i> 1 <sup>re</sup> série, liant colophane plastifiée avec un vernis de résine formophénolique modifiée-standolie d'huile de lin 60 P.		1 7 10 13 16 20	2 5 11 14 17	Cu <sub>2</sub> O Cu <sub>2</sub> O-HgO Cu <sub>2</sub> O-HgO-ZnO Cu <sub>2</sub> O-AsO <sub>4</sub> <sup>-3</sup> Cu <sub>2</sub> O-AsO <sub>4</sub> <sup>-3</sup> -ZnO Cu <sub>2</sub> O-HgO-TBTO TBTO	— 3,5/1 3,5/1/0,45 2,5/1 2,5/1/0,3 4/1/2 —	Fe <sub>2</sub> O <sub>3</sub> dans tous les cas
<i>Liant soluble:</i> 2 <sup>e</sup> série, liant colophane plastifiée avec un vernis de résine formophénolique pure huile de bois de Chine	100 101 104 107 110 113 116 119 122 125	102 105 108 111 114 117 120 123 126 129 132 135	103 106 109 112 115 118 121 124 127	Cu <sub>2</sub> O-HgO-AsO <sub>4</sub> <sup>-3</sup> -ZnO Cu <sub>2</sub> O Cu <sub>2</sub> O-HgO Cu <sub>2</sub> O-HgO-ZnO Cu <sub>2</sub> O-AsO <sub>4</sub> <sup>-3</sup> Cu <sub>2</sub> O-AsO <sub>4</sub> <sup>-3</sup> -ZnO Cu <sub>2</sub> O-As <sub>2</sub> O <sub>3</sub> Cu <sub>2</sub> O-As <sub>2</sub> O <sub>3</sub> -ZnO Cu <sub>2</sub> O-HgO-As <sub>2</sub> O <sub>3</sub> Cu <sub>2</sub> O-HgO-As <sub>2</sub> O <sub>3</sub> -ZnO TBTO Cu <sub>2</sub> O-TBTO Cu <sub>2</sub> O-HgO-TBTO	4/1/0,85/0,35 — 4/1 4/1/0,5 4/1 4/1/0,5 4/1 4/1/0,5 4/0,5/0,5 4/0,5/0,5/0,5 — 3/1 4/1/1	Fe <sub>2</sub> O <sub>3</sub> dans tous les cas
<i>Vinyliques:</i> résine VYHH; seulement l'échantillon 218 a été préparé avec la résine VAGH		217 218 219 220 221 222 223 224 225		Cu <sub>2</sub> O Cu <sub>2</sub> O TBTO Cu <sub>2</sub> O Cu <sub>2</sub> O-HgO Cu <sub>2</sub> O-HgO Cu <sub>2</sub> O-AsO <sub>4</sub> <sup>-3</sup> Cu <sub>2</sub> O-As <sub>2</sub> O <sub>3</sub> Cu <sub>2</sub> O-TBTO	— — — — 3/1 5/1 5/1 5/1 5/1	— — Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> — — —
	N° identif. peinture					

(\*) L'oxyde de zinc est indiquée entre les toxiques, étant vue que d'accord avec les références bibliographiques il produit une augmentation de la toxicité.

del Plata<sup>14</sup>. C'est un milieu marin dont les caractéristiques hydrologiques et biologiques sont bien connues d'après les travaux de Bastida<sup>15</sup>, et qui ont été contrôlées pendant toute la durée de nos expériences, c'est-à-dire un an (1-IX-66/67). La salinité oscille entre 31,4 et 34,1 ‰/100 et le pH entre 7,4 et 8. Le début de la fixation saisonnière d'organismes dans ce port est le mois de septembre (printemps dans l'hémisphère sud).

La variable de l'influence de la lumière sur la fixation sélective des organismes a été éliminée. Les plaques ont été immergées toutes à la même profondeur (1,70 à 2,00 m). On a utilisé de l'acier doux sablé, avec un prétraitement de «wash-primer» vinylique, et une protection à trois couches d'une peinture anticorrosion au vernis formophénolique-caoutchouc chloré ou d'une peinture vinylique, selon les cas, les deux à haut pouvoir inhibiteur. De cette façon les possibilités de corrosion dans la plaque a été écartée. Les peintures antisalissures ont été appliquées à la brosse (2 couches, d'environ 80-100 microns, épaisseur mesuré avec une gauge électromagnétique), la deuxième couche 24 heures avant leur mise en service. Le séchage a eu lieu toujours sous abri.

L'inspection mensuelle se fait directement sur le radeau,

avec le relèvement des organismes fixés sur des plaques témoin en plastique, et en enregistrant des photos du recto des plaques peintes (on photographie aussi le verso dans le cas où l'on trouve des différences). On compare avec des photos témoin correspondant à six degrés différents de salissures fixées :

- |   |  |
|---|--|
| 0 Aucune fixation   | } Peintures qui accomplissent la Norme IRAM 1185 |
| 1 Fixation très faible ou traces  |  |
| 2 Fixation faible (maximum 5 Balanus ou 0,5% de la surface)             | } Peintures de possible utilisation en service   |
| 3 Fixation modérée (maximum 10 Balanus ou 1% de la surface)             |  |
| 4 Fixation sévère (jusqu'à 50 Balanus ou surface correspondante)        | } Peintures à écarter                            |
| 5 Plaques complètement recouvertes de salissures (fixation très sévère) |  |

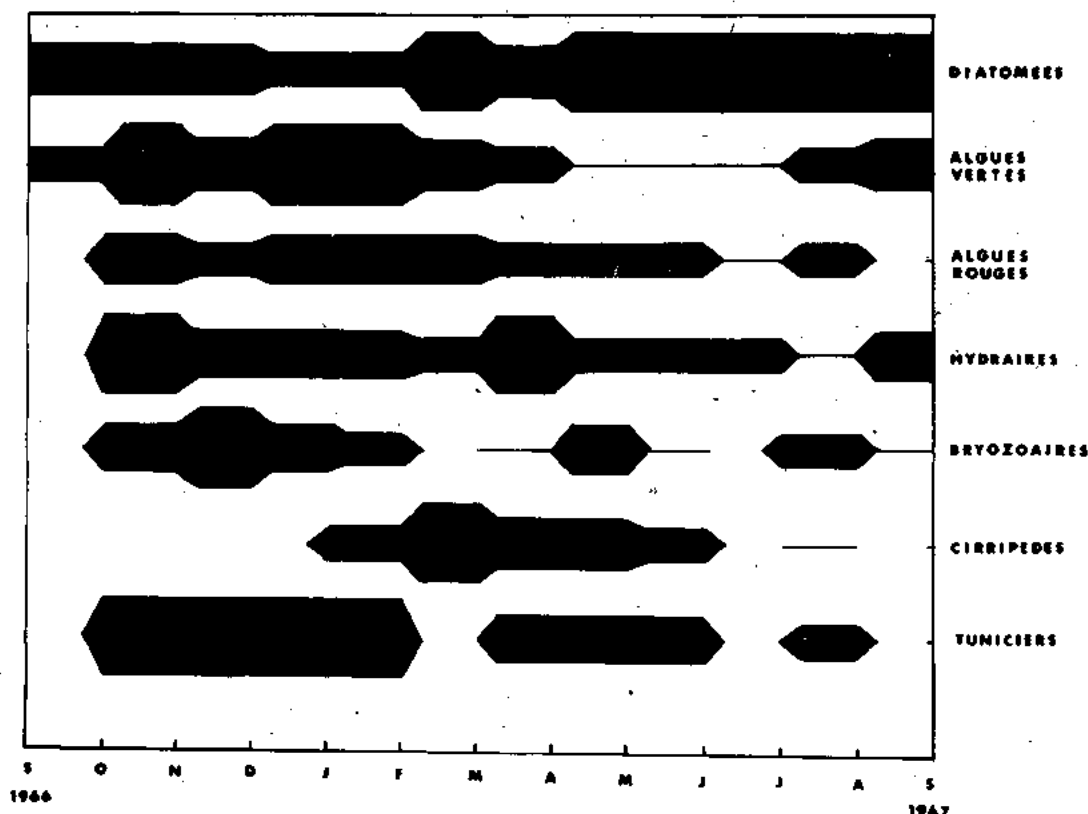


Fig. 1. Fixation saisonnière de quelques groupes de salissures sur des plaques témoin en plastiques dans le port de Mar del Plata, période 1966/67 (15)

## RÉSULTATS OBTENUS

Pendant la période d'un an, on a constaté sur les plaques témoin en plastique une fixation saisonnière normale pour les différents organismes<sup>16</sup>. Les salissures les plus importantes relevées à la profondeur indiquée (1,60 à 2,00 m) sont les suivantes (Fig. 1) :

Voile bactérien, protozoaires et diatomées.

Algues rouges et brunes.

Hydriaires (Tubularia, Obelia).

Bryozoaires (Bugula).

Mollusques (Pachysiphonaria lessoni).

Annélides (Serpules).

Crustacés cirripèdes (Balanes).

Tuniciers (Ascidia Ciona).

On trouve aussi des Algues Vertes sur les plaques témoin placées dans la ligne d'eau.

La fixation sur les plaques peintes commença dans tous les cas avec la formation du Voile Bactérien, complété par des Protozoaires et des Diatomées. Pendant les deux premiers mois (septembre-octobre) on a relevé certains crustacés ne correspondant pas à des espèces fixes ou sessiles ; en conséquence on ne les considère pas comme des salissures.

Après le deuxième mois (novembre) il commence une différenciation nette entre les peintures avec un taux de lixiviation assorti et celles qui ne solubilisent pas le toxique dans la quantité nécessaire (taux de lixiviation ou leaching rate insuffisant). Dans les peintures correspondant à ce dernier cas on trouve des colonies de Tubularia, Obelia, et aussi un grand nombre de Tuniciers (Ascidia Ciona), qui arrivent à un volume remarquable, suivi de leur détachement.

Le cinquième mois (janvier) se caractérise par une nouvelle fixation de ces espèces, qui se développent et se détachent

une deuxième fois. Après le sixième mois d'immersion, le nombre d'exemplaires de ces organismes est relativement réduit par rapport au moment du maximum de fixation. Parallèlement on a constaté la présence d'exemplaires de Bryozoaires (Bugula).

Les mois de janvier-février (commencement de l'été dans l'hémisphère sud) nous montrent la présence de Balanes et d'Annelides (Serpules) sur quelques peintures. Ce sont des espèces caractérisées par une grande résistance aux toxiques, et pour cette raison elles constituent la référence la plus importante du point de vue de l'efficacité des peintures. Dans quelques cas la fixation de Balanes s'est réduit à certains exemplaires jeunes, trouvés morts et faiblement collés. Un tiers des peintures essayées peut être écarté par la présence des organismes nommés ci-dessus. Un autre tiers doit être considéré comme de possible utilisation en service (degré de fixation 2-3).

Dans la figure 2 on a résumé les résultats correspondants à la fixation annuelle pour les différents échantillons indiqués sur le tableau II.

Dans le tableau III on a classé seulement les peintures correspondant aux degrés de fixation 0, 1 et 2. Toutes les plaques ont été contrôlées mensuellement ; par conséquent on est complètement sûr par rapport à son efficacité pendant la période indiquée, dans les conditions de notre station d'essais.

En considérant l'action des différents toxiques étudiés, dans quatre peintures à liant soluble on trouve un excellent pouvoir antisalissure, en utilisant comme toxique  $\text{Cu}_2\text{O} \cdot \text{AsO}_4^{-2}$  (peintures 10 et 11, Fig. 3) et le mélange  $\text{Cu}_2\text{O} \cdot \text{AsO}_4^{-2} - \text{ZnO}$  (peintures 13 et 14, Fig. 4), toutes avec degré de fixation 0. Le même comportement correspond à la peinture vinylique à base de TBTO (formule 219, Fig. 9).



	PEINTURE	TOXIQUE	COLOPH/ LIANT	DEGRE DE FIXATION					
				0	1	2	3	4	5
LIANT SOLUBLE (I)	1	Cu <sub>2</sub> O	4:1	[Hatched]					
	2		3:1	[Hatched]					
	5	Cu <sub>2</sub> O-HgO	3:1	[Hatched]					
	7	Cu <sub>2</sub> O-ZnO-HgO	4:1	[Hatched]					
	10		3:1	[Hatched]					
	11	Cu <sub>2</sub> O-AsO <sub>4</sub> <sup>■</sup>	4:1	[Hatched]					
	13	Cu <sub>2</sub> O-ZnO-AsO <sub>4</sub> <sup>■</sup>	3:1	[Hatched]					
	14		4:1	[Hatched]					
	16	TBTO-Cu <sub>2</sub> O-HgO	4:1	[Hatched]					
	17		3:1	[Hatched]					
20	TBTO	3:1	[Hatched]						
LIANT SOLUBLE (II)	100	Cu <sub>2</sub> O-HgO-ZnO-AsO <sub>4</sub> <sup>■</sup>	5:1	[Hatched]					
	101	Cu <sub>2</sub> O	5:1	[Hatched]					
	102		4:1	[Hatched]					
	103		3:1	[Hatched]					
	104	Cu <sub>2</sub> O-HgO	5:1	[Hatched]					
	105		4:1	[Hatched]					
	106		3:1	[Hatched]					
	107	Cu <sub>2</sub> O-HgO-ZnO	5:1	[Hatched]					
	108		4:1	[Hatched]					
	109		3:1	[Hatched]					
	110	Cu <sub>2</sub> O-AsO <sub>4</sub> <sup>■</sup>	5:1	[Hatched]					
	111		4:1	[Hatched]					
	112		3:1	[Hatched]					
	113	Cu <sub>2</sub> O-ZnO-AsO <sub>4</sub> <sup>■</sup>	5:1	[Hatched]					
	114		4:1	[Hatched]					
	115		3:1	[Hatched]					
	116	Cu <sub>2</sub> O-As <sub>2</sub> O <sub>3</sub>	5:1	[Hatched]					
	117		4:1	[Hatched]					
	118		3:1	[Hatched]					
	119	Cu <sub>2</sub> O-ZnO-As <sub>2</sub> O <sub>3</sub>	5:1	[Hatched]					
120	4:1		[Hatched]						
121	3:1		[Hatched]						
122	Cu <sub>2</sub> O-HgO-As <sub>2</sub> O <sub>3</sub>	5:1	[Hatched]						
123		4:1	[Hatched]						
124		3:1	[Hatched]						
125	Cu <sub>2</sub> O-ZnO-HgO-As <sub>2</sub> O <sub>3</sub>	5:1	[Hatched]						
126		4:1	[Hatched]						
127		3:1	[Hatched]						
129	TBTO	3:1	[Hatched]						
132	TBTO-Cu <sub>2</sub> O	3:1	[Hatched]						
135	TBTO-Cu <sub>2</sub> O-HgO	3:1	[Hatched]						
VINYLIQUES	217	Cu <sub>2</sub> O	VYHH	[Hatched]					
	218		VAGH	[Hatched]					
	220		VYHH	[Hatched]					
	219	TBTO	VYHH	[Hatched]					
	221	Cu <sub>2</sub> O-HgO	VYHH	[Hatched]					
	222		VYHH	[Hatched]					
	223	Cu <sub>2</sub> O-AsO <sub>4</sub> <sup>■</sup>	VYHH	[Hatched]					
	224	Cu <sub>2</sub> O-As <sub>2</sub> O <sub>3</sub>	VYHH	[Hatched]					
225	TBTO-Cu <sub>2</sub> O	VYHH	[Hatched]						

Fig. 2. Degré de fixation de salissures sur les plaques peintes (peintures à liant soluble et vinylique) pendant une année (1966/67).

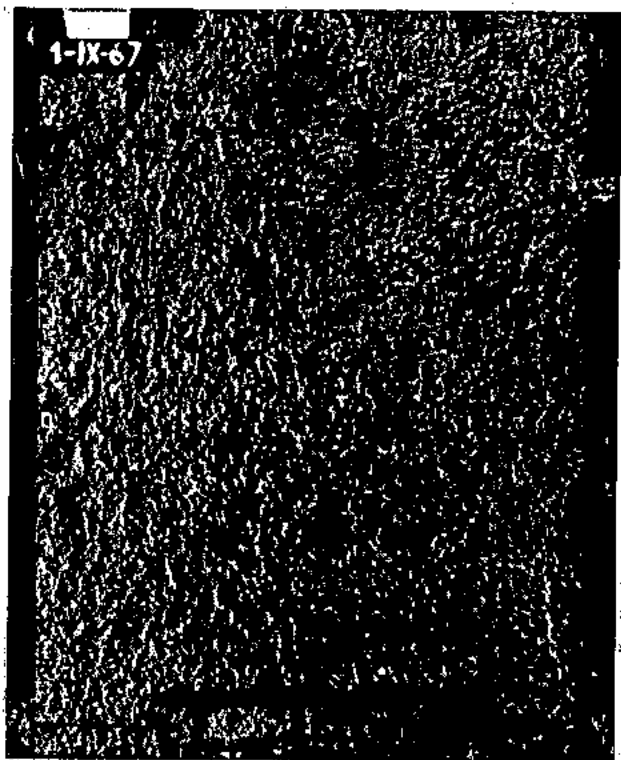


Fig. 3. Peinture 11. Toxique:  $\text{Cu}_2\text{O}-\text{AsO}_4^{3-}$

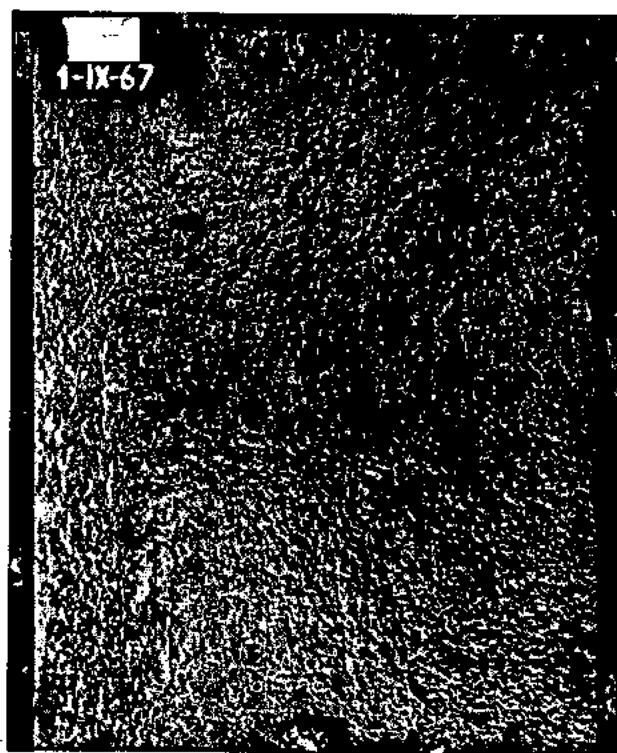


Fig. 4. Peinture 14. Toxique:  $\text{Cu}_2\text{O}-\text{AsO}_4^{3-}-\text{ZnO}$

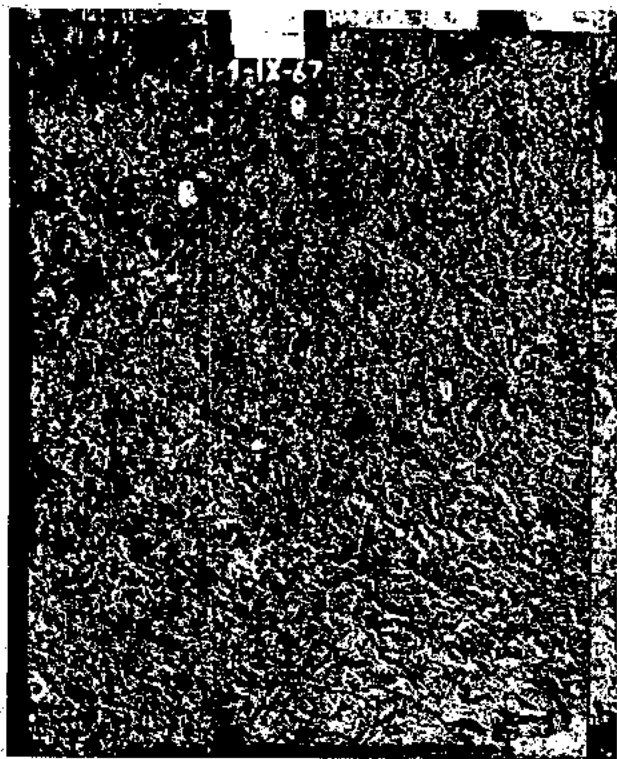


Fig. 5. Peinture 103 (liant soluble); Toxique:  $\text{Cu}_2\text{O}$

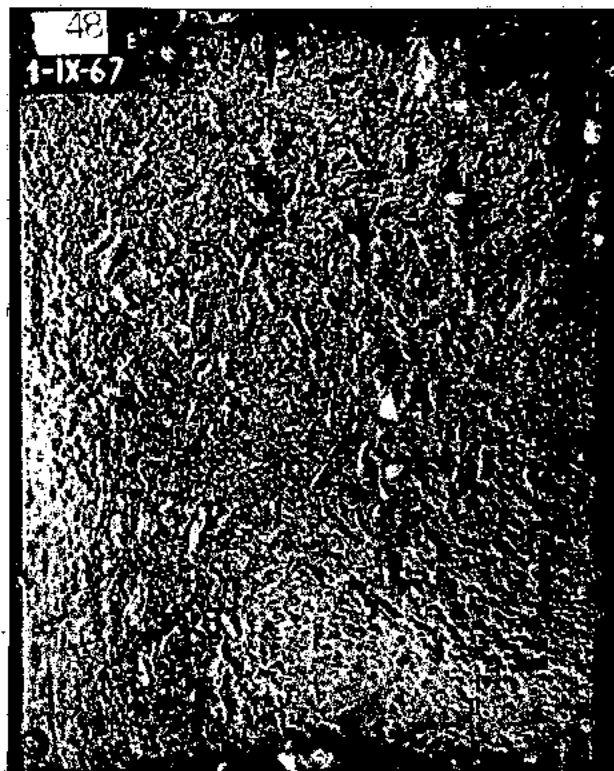


Fig. 6. Peinture 217 (vinylique); Toxique  $\text{Cu}_2\text{O}$

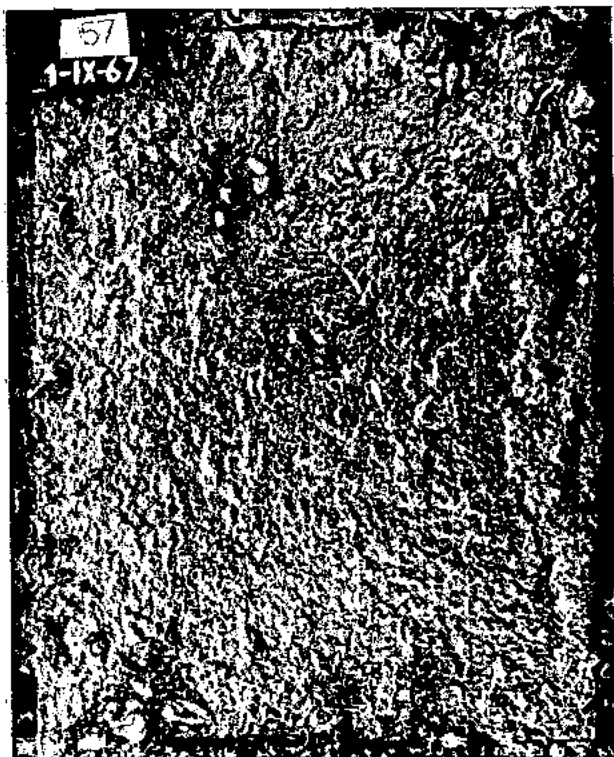


Fig. 7. Peinture 222 (vinylique); Toxique:  $\text{Cu}_2\text{O}$  —  $\text{HgO}$

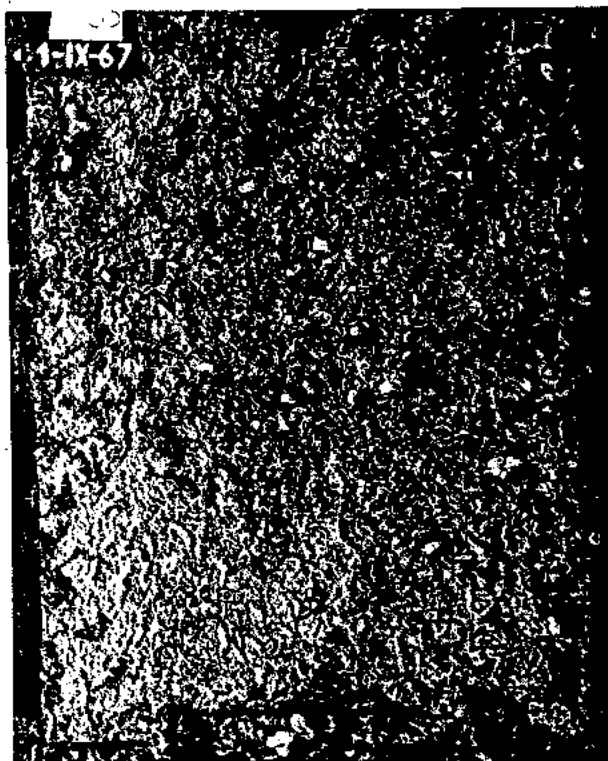


Fig. 8. Peinture 224 (vinylique); Toxique:  $\text{Cu}_2\text{O}$  —  $\text{As}_2\text{O}_3$

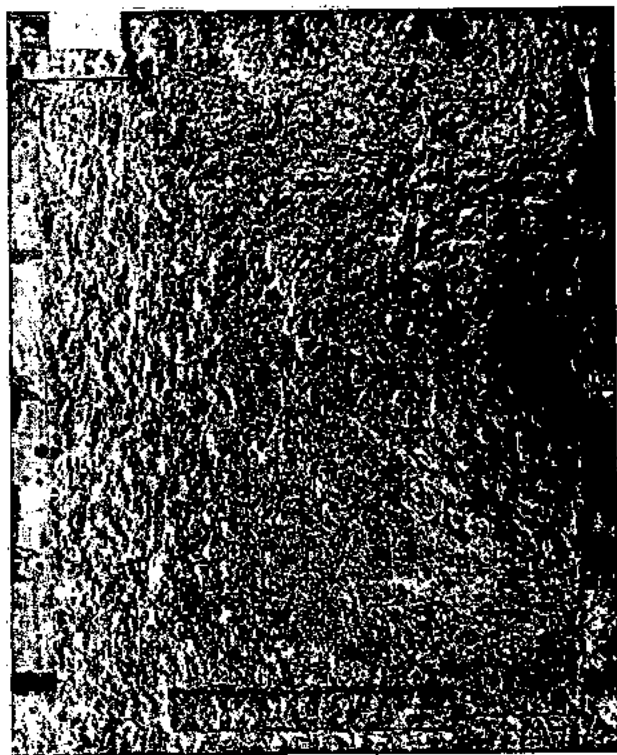


Fig. 9. Peinture 219 (vinylique); Toxique: TBTO

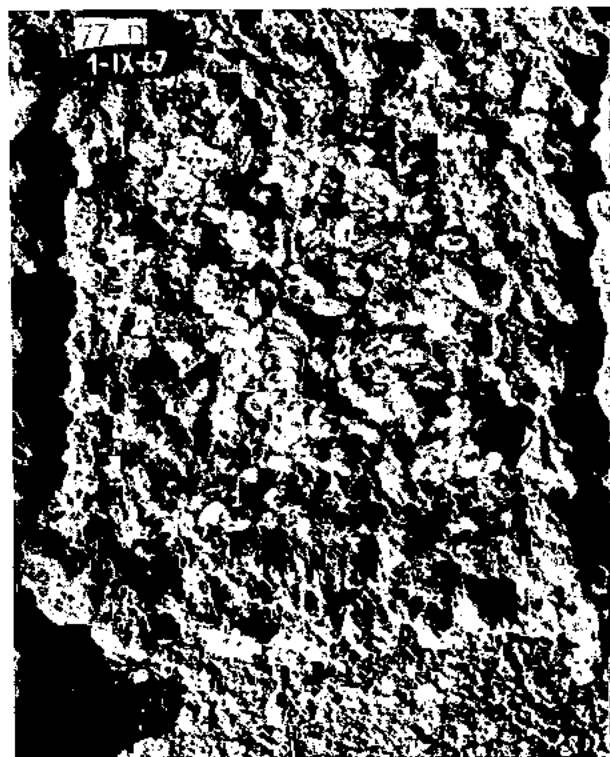


Fig. 10. Plaque témoin en plastique avec les saissures fixées au bout d'une année.

TABLEAU III  
DEGRÉ DE FIXATION POUR LES PEINTURES PLUS EFFICACES

Fixation	Type de peinture	Identification	Toxique utilisé	Degré de fixation
Aucune	Liant soluble	10	$\text{Cu}_2\text{O}-\text{AsO}_4^{3-}$	0
		11	$\text{Cu}_2\text{O}-\text{AsO}_4^{3-}$	0
13		$\text{Cu}_2\text{O}-\text{AsO}_4^{3-}-\text{ZnO}$	0	
14		$\text{Cu}_2\text{O}-\text{AsO}_4^{3-}-\text{ZnO}$	0	
	Vinylique	219	TBTO	0
Très faible ou traces	Liant soluble	103	$\text{Cu}_2\text{O}$	1
		110	$\text{Cu}_2\text{O}-\text{AsO}_4^{3-}$	0 - 1
		111	$\text{Cu}_2\text{O}-\text{AsO}_4^{3-}$	0 - 1
	Vinyliques	217	$\text{Cu}_2\text{O}$	1
		222	$\text{Cu}_2\text{O}-\text{HgO}$	1
		224	$\text{Cu}_2\text{O}-\text{As}_2\text{O}_5$	1
Faible	Liant soluble	104	$\text{Cu}_2\text{O}-\text{HgO}$	2
		112	$\text{Cu}_2\text{O}-\text{AsO}_4^{3-}$	2
		113	$\text{Cu}_2\text{O}-\text{AsO}_4^{3-}-\text{ZnO}$	1 - 2
		119	$\text{Cu}_2\text{O}-\text{As}_2\text{O}_5-\text{ZnO}$	2
		122	$\text{Cu}_2\text{O}-\text{HgO}-\text{As}_2\text{O}_5$	2
		125	$\text{Cu}_2\text{O}-\text{HgO}-\text{As}_2\text{O}_5-\text{ZnO}$	1 - 2
		126	$\text{Cu}_2\text{O}-\text{HgO}-\text{As}_2\text{O}_5-\text{ZnO}$	1 - 2
		5	$\text{Cu}_2\text{O}-\text{HgO}$	2

Dans le groupe suivant (degré de fixation 0 ou 1, c'est-à-dire très faible ou traces) on trouve des peintures à liant soluble effectives pigmentées avec de l'oxyde cuivreux (103, Fig. 5), du mélange oxyde cuivreux-arséniate (110 et 111) et vinyliques avec  $\text{Cu}_2\text{O}$  (217, Fig. 6),  $\text{Cu}_2\text{O}-\text{HgO}$  (222, Fig. 7) et  $\text{Cu}_2\text{O}-\text{As}_2\text{O}_5$  (224, Fig. 8).

Ces résultats, obtenus avec des différents mélanges, nous posent deux questions qui touchent au nœud du problème : Est-ce vraiment très important le toxique utilisé, ou son influence est secondaire en face au mécanisme de la mise en solution? (on a établi qu'une peinture avec  $\text{Cu}_2\text{O}$  présente seulement des traces de fixation). Peut-il avoir le contact continu entre les particules de toxique une influence définitive sur le taux de lixiviation des peintures, même dans les peintures à liant soluble? Il faut se rappeler que pour les peintures vinyliques, le 80% du film sec est constitué par le toxique, tandis que dans le cas des peintures à liant soluble la proportion de toxique est nettement inférieure.

Notre programme de recherches continue maintenant et les expériences en cours de réalisation nous donneront, peut-être, les réponses à ces questions.

Par rapport aux autres variables considérées dans notre étude, on peut faire les considérations suivantes :

a) *Rapport colophane/plastifiant, dans les peintures à liant soluble.* Le taux de lixiviation diminue en augmentant la quantité de vernis incorporée au liant, ce qui confirme les données de la bibliographie. Pour le cas particulier des peintures avec  $\text{Cu}_2\text{O}-\text{As}_2\text{O}_5$ , le meilleur comportement correspond à la moindre solubilité essayée (3:1). Les rapports efficaces, pour les peintures pigmentées avec oxyde cuivreux-arséniate de mercure oscillent entre 5:1 et 3:1. Le changement du vernis entre la 1<sup>re</sup> et la deuxième série (résine formophénolique

pure/huile de bois de Chine, au lieu de résine formophénolique modifiée/standolie d'huile de lin) semble être important. Toutes les peintures avec  $\text{Cu}_2\text{O}-\text{AsO}_4^{3-}$  de la deuxième série (film un peu plus dur) ont une fixation 0-1 au lieu de 0, qui caractérise les peintures 10, 11, 13 et 14. Il faudra continuer les recherches sur cet aspect.

b) *Rapport résine vinylique/plastifiant.* Le rapport 4:1 semble être correct. Il donne des films uniformes et résistants. L'utilisation de la colophane pour modifier la solubilité du film nous donne des peintures avec un taux de lixiviation assorti.

c) *Influence des pigments inertes.* L'oxyde de fer rouge ( $\text{Fe}_2\text{O}_3$ ) utilisé dans les peintures vinyliques 220 et 221, élimine l'effet du contact continu entre les particules du toxique et réduit l'efficacité des peintures vis-à-vis des échantillons sans charges. Il nous reste d'établir si dans les peintures à liant soluble, fortement chargées, il y a une inactivation pareille.

d) *Action de l'oxyde de zinc.* Dans des expériences préalables et dans celles qui sont actuellement en réalisation on constate un accroissement du pouvoir antisalissure dû à l'utilisation de l'oxyde de zinc. On observe que l'oxyde de zinc augmente la sédimentation du pigment et nous donne des dépôts difficiles à incorporer.

e) *Influence du temps de stockage des peintures.* Des échantillons de la même composition, ayant un mois et un an d'emmagasinage nous ont donné les mêmes résultats du point de vue antisalissure.

f) *Épaisseur du film.* Une épaisseur plus grande n'a pas d'influence sur le taux de lixiviation initial, mais il augmente le temps d'action de la peinture. L'accroissement de l'épaisseur du film proportionne un meilleur pouvoir protecteur du

système peinture anticorrosion-antisalissure.

g) *Temps de broyage de l'oxyde cuivreux.* On a comparé l'efficacité des peintures obtenues en broyant l'oxyde cuivreux pendant 4 et 24 heures ; pour quelques formules on a trouvé un meilleur comportement pour les premières.

h) *Influence du temps de stockage des peintures.* Des échantillons de la même composition, ayant un mois et un an d'emmagasinage, nous ont donné les mêmes résultats du point de vue antisalissure.

i) *Épaisseur du film.* Une épaisseur plus grande n'a pas d'influence sur le taux de lixiviation, mais il augmente le temps d'action des peintures à liant soluble. L'accroissement de l'épaisseur du film proportionne aussi un meilleur pouvoir protecteur du système peinture anticorrosion-antisalissure.

### CONCLUSIONS

1) Dans la préparation de peintures antisalissures efficaces, la solubilité du liant semble être une variable plus importante que le type de toxique utilisé.

2) Dans les peintures à liant soluble il est convenable l'utilisation d'un vernis à base de résine formophénolique modifiée — huile de lin — huile de bois de Chine, pour réduire la solubilité de la colophane.

3) Dans les peintures vinyliques, le rapport résine VYHH-colophane essayé (1:1) nous donne des films avec un degré de lixiviation assorti.

4) L'oxyde cuivreux est le toxique d'action générale le plus important à utiliser dans ces peintures ; dans les conditions hydrologiques et biologiques de notre station d'essais à Mar del Plata (eaux tempérées) on a obtenu des peintures efficaces avec ce seul pigment.

g) Pour des conditions plus sévères, l'arséniate de mercure est à recommander, malgré son prix de revient élevé ; il a une action plus importante que celle de l'oxyde mercurique ou de l'acide arsénieux, employés seuls ou mélangés.

6) L'oxyde de bis-tributyl-étain (TBTO) nous a permis de préparer une peinture vinylique à haut pouvoir antisalissure ; cette formule montre, par immersion dans l'eau de mer, une efficacité plus grande que celle des compositions dérivées de la formule 121, MIL-P-15931.

### DISCUSSION

L. IGNATIADIS (Grèce): Quelles sont les espèces de diatomées identifiées?

Dr. V. RASCIO: Malgré que mon spécialité ce n'est pas l'aspect biologique, je peux vous donner une copie du travail, se rapportant à l'aspect salissures, dans lequel vous trouverez la liste complète de toutes les espèces identifiées. Cette liste va être publiée aussi dans les Comptes Rendus.

P. ROCOTAS (Grèce): Est-ce que je pourrais vous demander si pour les peintures vinyliques le pigment est seulement le T.B.T.O?

Dr. RASCIO: Dans les peintures vinyliques à base de T.B.T.O. (c'est une toxique liquide) on a utilisé comme pigment couvrant un inerte, l'oxyde de fer rouge. On emploie 12 pour cent environ de T.B.T.O.

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sur la peinture, et je vous rappelle que nos peintures antisalissures vinyliques ont été formulées avec 60% de pigment au total.

P. ROCOTAS: Est-ce que vous avez essayé l'oxyde de zinc au lieu de l'oxyde de fer rouge?

Dr. RASCIO: Dans quel cas, dans les peintures vinyliques ou dans les peintures à la colophane?

P. ROCOTAS: Oui, dans les peintures vinyliques.

Dr. RASCIO: Non, dans les peintures vinyliques on n'utilise pas l'oxyde de zinc; ce pigment, comme toxique complémentaires (2 à 4 pour cent sur la peinture, environ) est employé seulement dans les formules à la colophane (peintures antisalissures oléoresineuses).

Séance - Meeting - Sitzung - Συνεδρίασις  
24.9.1968

Présidence - Presidency  
Präsidium - Προεδρείον

Prof. BONG KYUN KIM (Korea),  
Prof. K. KONOFAGOS (Greece),  
Assist. Prof. J. EVANS (Canada).

# THE PREVENTION OF MARINE FOULING BY ELECTRICAL CURRENTS

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## SUMMARY

In dealing with marine organisms one encounters many complex interrelationships not only between different organisms, but with the complexion of a given community and its physical and chemical environment. Fouling organisms have a wide range of tolerances to their surroundings due to inherent adaptation capabilities in the intertidal and estuarine environment, both of which present a hostile and fairly unstable habitat. This study has confirmed that organisms in this environment can show resistance to artificially induced modifications in their surroundings, in this case, electrical pulses. It is recognized from studies of various antifouling techniques that some organisms are affected more than others but surprisingly, very little of the published work has con-

sidered fouling on a micro-scale or considered the primary slimes of bacteria, diatoms and algae. The initiating slimes, it is believed, result from the settlement of bacteria and algae on a substrate and initiate the subsequent «breaking down» or «preparation» of the surface so that conditions become more favorable for the attachment of invertebrate larvae. We found that a measure of antifouling effectiveness was the length of time needed to establish primary slime layers, whereas the rate of development of secondary and higher organisms was of little significance. Thus, although electrical pulses could severely retard the establishment of secondary and higher communities they inexorably developed, once established, despite the hostile environment.

## INTRODUCTION

The use of electrical currents to inhibit attachment of fouling organisms to ships has been the subject of investigations dating back at least to 1863. Recently, interest in this concept has been revived due to the success of impressed current cathodic protection and the hope that an electrical system could inhibit both corrosion and fouling. This paper describes investigations performed in the laboratory and in the ocean, to determine the effect of electrical pulses at a metal/seawater interface. It has been shown that it is possible to effectively prevent fouling attachment to bare metallic substrates for up to six months under severe fouling conditions. It also has been found that the optimum condition for fouling prevention is dependent on the nature of the marine organisms existing at a certain time and location and that some marine organisms appear capable of adapting to the new environment. Once a thin layer of adapted organisms has settled on a surface, conditions can develop whereby other organisms are repelled less effectively.

Under moderate fouling conditions (during winter and spring for example) test plates remain virtually free from fouling attachment, controls placed nearby becoming well fouled, but as the fouling conditions become intense in summer, inhibition can no longer be complete, and plates foul, albeit slowly (1% - 10%) as fast as the controls.

The investigation described in this paper was concerned with discovering the effectiveness of electrical pulses and was not concerned with the use of continuous high d.c. currents. This latter aspect has been dealt with in the past<sup>1, 2, 3</sup> the theory being that by overprotecting a surface, alkaline conditions develop and a calcareous deposit will be formed. This deposit is then removed by exfoliation along with marine growths by sudden increase in current or by current reversal. Laboratory studies showed a feasibility but field experimentation has been unsuccessful due to the very high currents needed to remove the calcareous layer with concomitant hydrogen evolution or corrosion in the case of current reversal. In ad-

dition, if a calcareous layer is allowed to develop over a large surface area, the resultant drag is probably as great as serious fouling.

The authors decided to examine critically the effects of electrical currents and investigate the possibility of inhibiting fouling with pulses without formation of a calcareous deposit in which case a system effective in preventing both corrosion and fouling could result.

### *Historical Background of Electrical Antifouling*

Attempts to use electricity for fouling prevention date back to the 19th Century. A patent in 1863<sup>4</sup> claimed the use of electricity «however obtained or applied for protecting ships bottoms from corrosion, fouling, sea monsters and other evil things». Subsequent patents claimed the use of a battery<sup>5</sup>, an electrical generator<sup>6</sup>, a chain of zinc anodes<sup>7</sup>, electrolysis of hull sections to form gases which remove fouling<sup>8</sup>, alternate anodic and cathodic currents<sup>9</sup>, making the hull the armature of a large magnet<sup>10</sup> also the use of high tension a.c. current was suggested in 1911<sup>11</sup> and intermittent d.c. in 1912<sup>12</sup>. It was believed that a.c. electrical discharges would cause muscular fixation of barnacles and thus prevent their attachment. Electrically formed deposits were also proposed as an antifouling technique and a patent in 1923<sup>13</sup> claimed a device which continuously electrified the metal hull or sheathing «the resultant layer of hydrogen and sodium hydrate protecting the vessel even without paint». In 1940 Cox<sup>2</sup> patented a method for depositing calcium and magnesium salts from the sea water onto a hull. There was some antifouling effect in this process since the second and subsequent calcareous layers were less adherent to each other than the first layer was to the metal of the ship, thereby an exfoliating surface was formed which could be removed on increasing the current density appreciably.

In 1951<sup>1</sup> Castle reported that fouling developed rapidly on cathodes to which current densities of 10 - 100 mA/ft<sup>2</sup> were applied. Fouling was delayed on surfaces receiving cd's

in excess of 300 mA/ft<sup>2</sup>. The reduction of fouling was attributed to the rapid formation and sloughing off of the calcareous deposits which developed. There was no evidence that either a continuous or alternating current kept fouling larvae away from electrodes or prevented their attachment.

The use of electrical pulses applied to wire screens to induce forced migration of fish has been successful<sup>14</sup> and it was observed that certain of the screens receiving such pulses, were apparently free from fouling. Further work was performed elsewhere<sup>15</sup> but no conclusive antifouling effect was observed. Thus the history of electrical fouling prevention is protracted but virtually all work has been of an empirical nature. The investigation described below has attempted to determine the interactions between marine fouling organisms and the conditions created at a sea water/metal interface receiving pulsed electrical currents.

#### INITIAL INVESTIGATIONS

##### *Pulsing System*

Pulse generating equipment for all experimentation described consisted of a one-shot multivibrator triggered by a synchronous motor-drive cam. Multiple cams were used to allow varying repetition rates. The multivibrator's RC time constant provided current pulse duration and could be varied by adjusting the resistance in this portion of the circuit. During the period the multivibrator was on, its output provided a voltage level sufficient to gate on a silicon controlled rectifier switch, which in turn allowed high current to pass to the cathodic plates through current-limiting resistors. The limiting resistors were adjustable to provide proper current to each test plate.

##### *Biotic Progression of Marine Fouling*

In order to obtain an assessment of antifouling effectiveness, it was necessary to develop a method for the macroscopic determination of stage of fouling on a biological, rather than an empirical basis. Notations and photographic records were kept on secondary, tertiary, and quaternary fouling stages only. The conditions were plotted on a scale from 0 - 10, where 0 represented «no fouling visible», and 10 indicated that a seasonal climax existed. The stage classification, Table 1, indicates how this scale was derived.

Since no conclusive data was available concerning the electrical conditions which may be effective in preventing fouling, it was necessary to employ a wide range of pulse parameters during preliminary investigations. Cathodically protected mild steel plates (1.7 in.<sup>2</sup>) were initially pulsed using the parameters given in Table 2.

These initial studies, which were performed in two series, proceeded for one year, and clearly indicated that an inhibitory effect was being manifested. Pulse ranges showing a fouling stage progression of six or less were utilized as the commencement point for subsequent pulse optimization studies.

##### *Effects of Pulses on Zooplankton*

The most effective pulses determined in these initial field experiments were applied in laboratory tests in order that observations could be made concerning any possible behavioral characteristics of zooplankters under pulsing conditions. The apparatus shown in Figure 1 was employed in which a mild steel plate was pulsed cathodically using a stainless steel counter electrode. Additionally, a magnesium anode was used to provide a bias current for cathodic protection. In order to minimize counterelectrode reaction products building up in the bulk solution, each electrode was separated from the cathode by means of a salt bridge. An external air pump with bubbling stones was used to maintain maximum aeration

within the test cell. Pulse duration and pulse repetition rate were controlled electronically.

Zooplankter aliquots were collected prior to each run, employing the apparatus illustrated in Figure 2. This arrangement was capable of adjusting with the tides, which allowed that fresh samples could be taken continuously. New zooplankter aliquots and filtered sea water were introduced prior to each run. A long focal length microscope was used to study the behavior of organisms at the cathode/sea water interface. In every case, the illumination time of both test cell and control specimens for observation was kept constant.

TABLE 1

#### A STAGE CLASSIFICATION OF BIOTIC PROGRESSION INVOLVED IN MARINE FOULING \*

Stage **	Predominant Organisms
Primary (1, 2 & 3)	<i>Microscopic unicellular slimes</i> Bacteria, diatoms, protists, etc.
Secondary (4, 5 & 6)	<i>Microscopic organisms</i> Multicellular sessile organisms; i.e., bryozoans, barnacles, sedentary tube building polychaetes, brown and green algae, etc., with no apparent attachment or over-encrustation by other forms.
Tertiary (7, 8 & 9)	Evidence of secondary attachment of sessile species and some subsequent over-growth of the previous stage's forms although they may still remain dominant; i.e., tunicates, mussels, sponges, larger algal growths, etc. Also numerous free living organisms intimately associated with the sessile forms appear; i.e., tanaids, amphipods, isopods, errant polychaetes, etc.
Quaternary (10 = climax)	The most biologically complex, relatively stable faunal association. Depending upon the ecology of the region the community is generally dominated by one or two organisms; i.e., tunicates, mussels, sponges, bryozoans, etc., which form a broad base supporting directly or indirectly the greatest diversity of other forms.

\* It was recognized that the stage classification once established for one region or season would not necessarily be valid in another. Thus, only general groups of biota are given excluding the more aberrant forms and those which cannot be used as indicators due to their abundance throughout all stages, i.e., nematodes.

\*\* The number from 1 - 10 assigned to a fouling condition is intended to indicate the relative stage of a surface in the fouling progression and, to a lesser degree, its intensity.



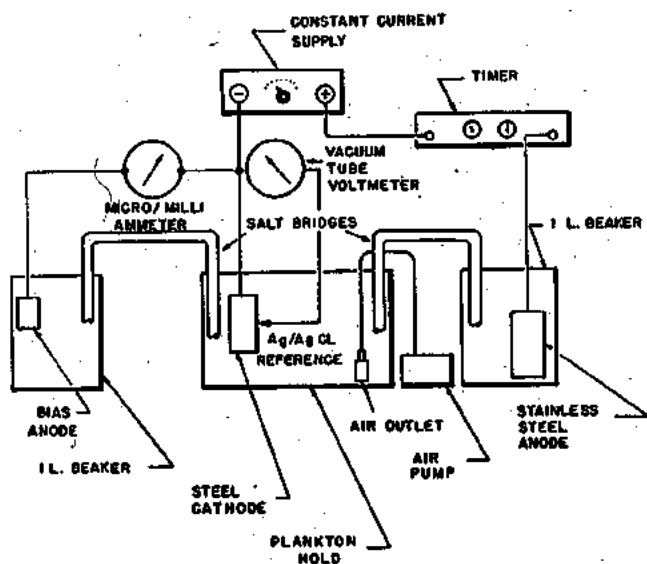


Fig. 1. Apparatus used to study effects of superimposed electrical pulses on zooplankton for cathodically protected steel plate (cathode)

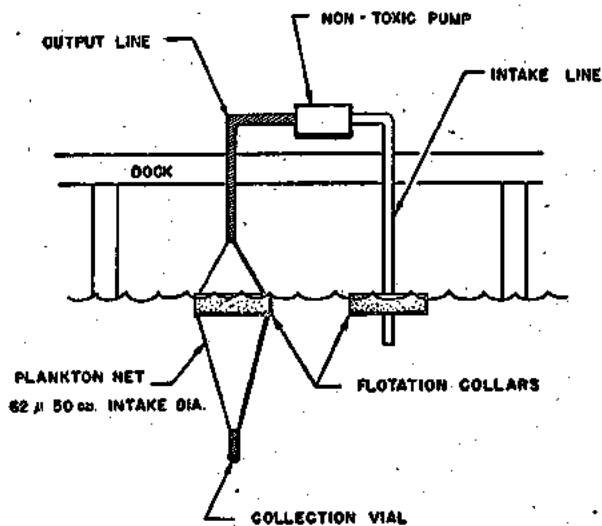


Fig. 2. Plankton sampling apparatus.

TABLE 2  
PARAMETERS AND RESULTS OF PRELIMINARY FIELD INVESTIGATIONS

	Bias Current (10 mA/ft <sup>2</sup> )	Pulse Current Density (mA/ft <sup>2</sup> )	Pulse Duration (sec.)	Pulse Repetition Interval (sec.)	Stage of Fouling
Series 1	Yes	Control			10
		Control			10
		100	1	10	8
		100	1	10	9
		10,000	1	10	6
		10,000	1	10	2
		10,000	.01	.1	(calcareous deposit)
		10,000	.01	.1	2 (heavy calcareous coating)
	No	Control			10 (Corroded)
		Control			9 (Corroded)
Series 2	Yes	Control			7
		Control			8
		100	.1	1	8
		100	.1	10	10
		100	1	10	9
		1,000	.1	1	4
		1,000	.1	10	4
		1,000	1	10	2

In no case was the response of specimens sufficiently definitive to indicate clearly whether or not zooplankters were attracted to, or repelled from, the pulsed plate. However, under those conditions where high currents were passed, a higher than normal mortality was observed vs. control aliquots. This occurred in the bulk of the solution and was ascribed to a change in the chemical nature of the sea water as a result of the alkali produced at the cathode. At lower current densities this increased mortality was not observed.

### PULSE OPTIMIZATION INVESTIGATIONS

A multiplate test apparatus (Figure 3) was constructed consisting of ten vertically mounted plates, five on each side of a float and parallel to a common mild steel anode.

The mild steel plates had an exposed surface area of 0.5

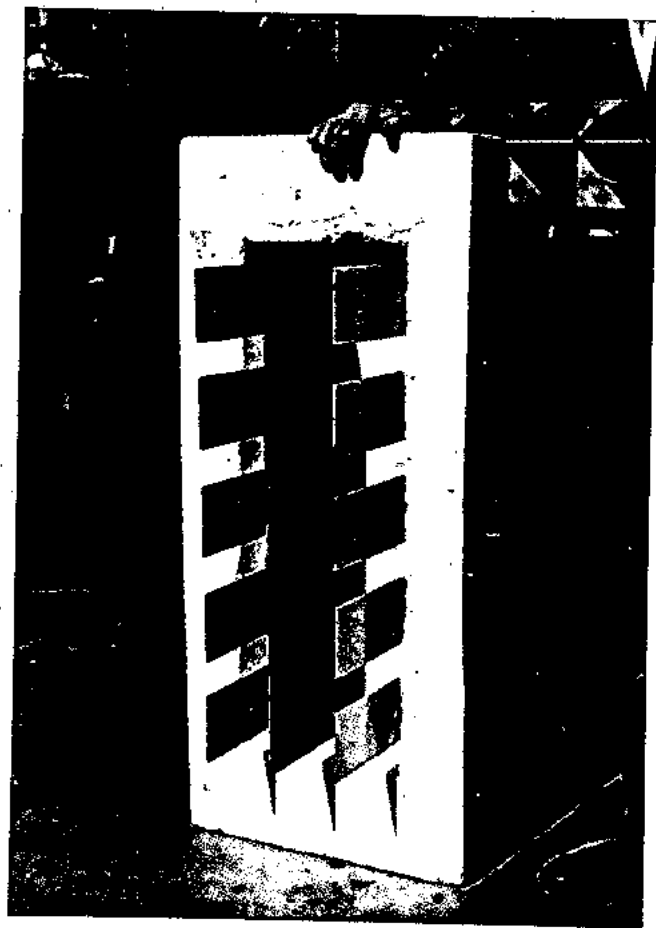


Fig. 3. 10 plate assembly.

ft.<sup>2</sup> and were mounted in an epoxy base supported by a styrofoam float. The electrical pulsing system was as described previously. The plates extended from 1"-13" below the surface water and were so positioned as to allow comparisons between high and low intensity illumination effects upon the community.

Environmental measurements were taken of water surface temperature, salinity, dissolved oxygen and biomass. Standard methods, where applicable, were used as given in

«A Manual for Processing Oceanographic Data» published by the U.S. Navy Hydrographic Office. Environmental data only reflects the conditions found in the San Diego area. (The relationship between such parameters and rate of fouling is the subject of a subsequent paper by the authors).

The observations with the ten plate system also involved microfouling and the previously described stage classification was used for assessing antifouling effectiveness. Bacterial smears were also taken, however, and comparative counts of the bacteria, algae, diatoms, larvae, and juvenile invertebrates were made. This was considered to be of principal importance, as previous observations by the authors had indicated that the appearance of primary slime groups not only gave a rough index of the time in which a given substrate would reach a seasonal climax, but also an estimate of fouling intensity. It followed that once primary slimes had formed, the surface would inevitably foul. The exception to this occurs with toxic leaching coatings, where threshold levels of toxics for the primary slimes are considerably higher than those of secondary through quaternary forms<sup>16</sup>. Thus, regular progressions subsequent to the appearance of primary forms are retarded until such time as the leach rate falls below threshold values.

The results from the optimization studies with the 10 plate system showed some dramatic differences in fouling inhibition. The varying degrees of effectiveness accomplished after four months are illustrated in Figure 4. These plates were exposed to the parameters given in Table 3.

TABLE 3

Plate	Pulse Intensity (mA/ft <sup>2</sup> )	Pulse Duration (secs.)	Pulse Repetition Rate (secs.)	Stage of Fouling
1	1000	1	10	3
2	1000	0.5	20	4
3	1000	1	30	8
4	1000	5	300	3
5	600	1	20	6
6	500	1	10	7
7	500	0.5	10	7
8	300	1	10	3
9	200	1	10	2
10	Control			10

Plates 1 and 4 showed little fouling, whereas the other plates showed varying degrees of fouling and calcareous deposit formation. Plate 3, for example, had shown excellent antifouling performance for a certain period of the year, but the parameters proved to be ineffectual during the period when the above series was taken. Even when some control was accomplished, it was never more effective than an antifouling paint.

In the analysis of results, the parameters were plotted in several ways in order to obtain the most sensitive and reliable correlation of fouling vs. pulse parameters. These included pulse width, current density, repetition rate and total charge.

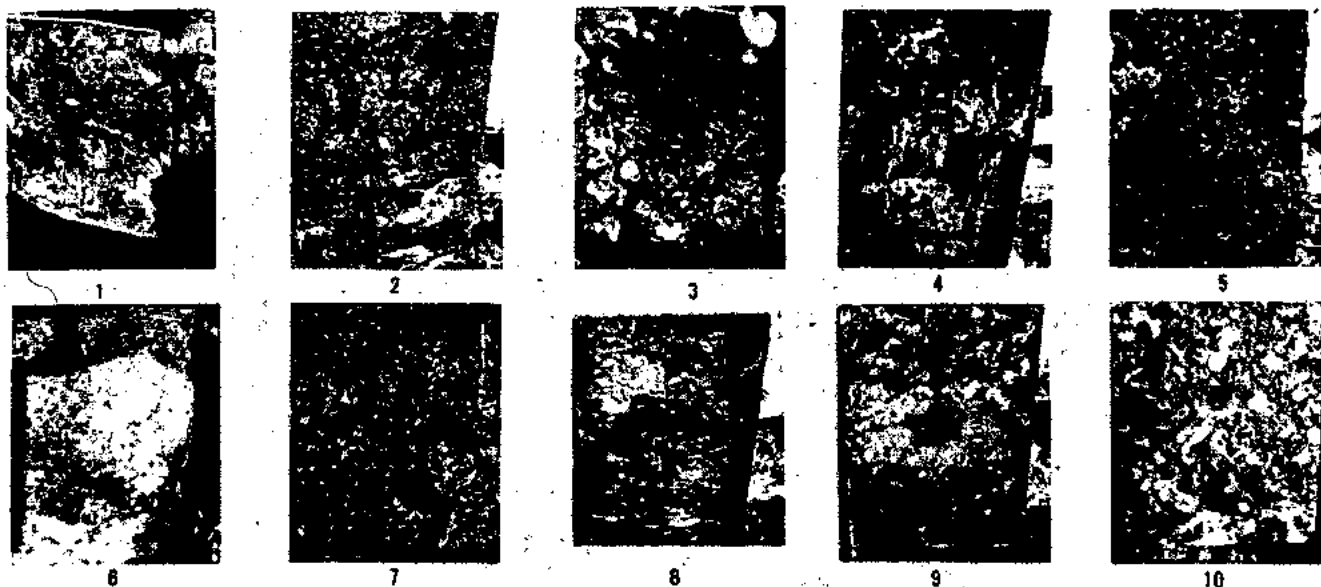
Of all these, it was found that total charge,  $eq$ , gave a good correlation,

where

$$eq = \frac{\text{pulse intensity (mA/ft}^2\text{)} \times \text{pulse duration (secs)} \times 60}{\text{pulse repetition rate (secs)}}$$

A plot of  $eq$  vs. stage of fouling is given in Figure 5, and is constructed from 214 of the pulse parameters investigated.

The parameters which gave the highest levels of inhibition were plotted and subjected to a determination of the coefficient of correlation using the formula:



### THE VARYING DEGREES OF INHIBITION ACCOMPLISHED BY CATHODIC PULSING AFTER 4 MONTHS EXPOSURE

Fig. 4.

$$r = \frac{n \cdot \sum XY - (\sum X)(\sum Y)}{\sqrt{n \cdot \sum X^2 - (\sum X)^2} \cdot \sqrt{n \cdot \sum Y^2 - (\sum Y)^2}}$$

- n = the number of pairs of observations
- X = the values on the abscissa
- Y = the values on the ordinate
- $\sum$  = the summation of n terms

With this system, if the value of r is close to 1.0, the correlation is considered valid, and predictions based upon it will also be valid. If the value of r is close to 0, there is considered to be no correlation between the data compared, and predictions based on the slope cannot be considered reliable.

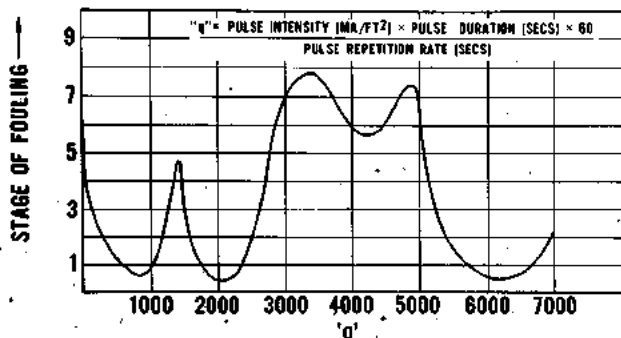
Using the coefficient calculation, the values for r ranged from 0.08 - 0.57, but at the conclusion of two years of investigations there was a consistent appearance of several levels of pulse effectiveness. The most effective parameters, with their «q» values, are given in Table 4.

TABLE 4

#### PULSE PARAMETERS MOST EFFECTIVE IN PREVENTING FOULING ON 10 PLATE SYSTEM

«q» Value	Pulse Intensity (mA/ft <sup>2</sup> )	Pulse Duration (secs)	Pulse Repetition Rate (secs)
400	200	1	30
500	1000	1	120
500	1000	5	600
600	300	1	30
1000	100	5	30
1000	1000	5	300
1000	100	5	30
1200	200	1	10
1800	300	1	10
1800	600	1	20
2000	200	5	30
2000	1000	1	30
6000	1000	1	10

Having established «q» as a convenient measurement technique, data concerning the relative percentages of biotic groups was then correlated. When each group was plotted against «q» ranges, it was expected that some correlation between the relative sensitivity of a given biotic group vs. the range of total charge would manifest itself. However,



'q' (MILLICOLUMBS/SQ FT/MINUTE) VS STAGE OF FOULING

Fig. 5.

comparison of data obtained over four periods of three months each, in which the relative abundance of algae, balanus, hydroids, diatoms, serpulids and bryozoans was observed, showed no clear correlation. Bryozoans and hydroids did clearly manifest a greater sensitivity to pulse variations than any other group but the lack of sensitivity shown by the other organisms suggests that the use of several different pulses over a period of time would not amplify any antifouling effect.

#### Testing Optimized Parameters

Subsequent experiments involved a rotating assembly which allowed for a more complete assessment of the antifouling effectiveness of given parameters and introduced the capability of observing the influence of rotational speed upon fouling attachment.

The apparatus Figure 6 consisted of four circular, coaxially and horizontally positioned, mild steel test plates of area 4.88 ft.<sup>2</sup>, mounted on a nylon shaft. Eighteen inches separated the plates which were positioned from six inches to sixty inches in depth. The plates were serviced by separate lead-platinum permanent anodes. This arrangement allowed for top-to-bottom surface high intensity vs. low intensity illumination comparisons, as well as depth declension observations. The shaft and electrical connections were so arranged that the entire plate assembly could be separated from the drive shaft for inspection. The perimeter velocity of the plates could be controlled in the range 0.8 - 7.1 knots. Each plate in the system was controlled electrically from dockside in terms of bias, current, and pulse time parameters. An assembly consisting of four duplicate control plates at corresponding depths was placed alongside the pulsed system for comparison purposes. As this was a control, no pulsing was employed, but zinc anodes were used for corrosion prevention.

In the assessment of fouling inhibition on rotating plates, the attainment of late primary or early secondary stages was sufficient reason for the termination of that particular pulse investigation. This was done for two reasons, (a) unlike toxic leaching coatings discussed previously the formation of the primary slimes on pulsed plates indicated that they would inevitably foul and (b) the velocities used were sufficiently high so as to increase the time required for secondary and later forms to appear, and this would have necessitated longer test periods resulting in a reduction in the number of pulse parameters which could have been investigated.

The authors were aware that antifouling systems which function properly in one community and fail in another are undoubtedly borderline, and will fail anywhere the intensity

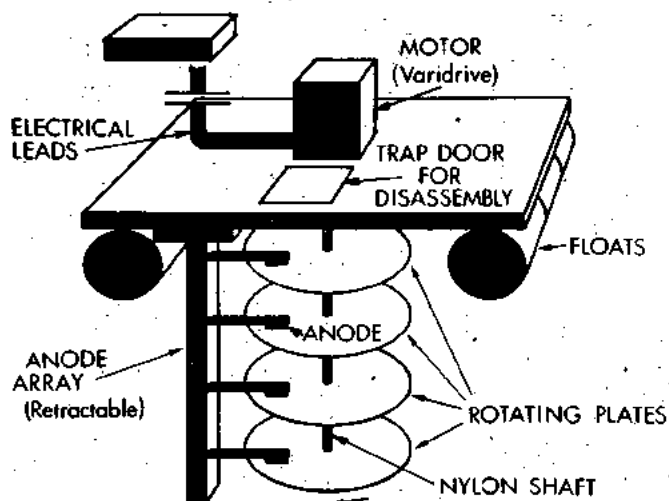


Fig. 6. Rotating plate apparatus

of fouling becomes sufficiently great. It was therefore necessary that another area of greater fouling intensity be incorporated into the program to test those parameters which were found to be most effective at the San Diego test site. This was done at Newport Beach, California, by employing a similar system to that used in San Diego.

It is relevant to note here that an extremely high correlation of results was attained between the two areas. The results of parameters tested at Newport Beach simply duplicated those from San Diego. Consequently data from the second station is not considered further.

Because of the normally seasonal nature of fouling in Southern California, both the testing and environmental parameter data were arbitrarily divided into four annual quarters, i.e., 01 November to 31 January, 01 February - 30 April, 01 May to 31 July and 01 August to 31 October. This was based on observations that June is probably the month during which maximum reproduction occurs, whereas the maximum amount of senescence and lowest reproductive rates of most species in the San Diego area occurs during December and January.

The most effective parameters found previously for static plates were employed on the dynamic plates. Data obtained from the rotating assembly (Table 5) was correlated via least squares calculations, in this case using the time required to attain only a late primary or early secondary stage of fouling for the reasons outlined above. The data covers an average of 7 per parameter investigated.

The results obtained with the rotating system were similar to those presented in Figure 5, once again showing a low coefficient of correlation. However, it was found that  $q$  values in the 100 range imparted a high degree of inhibition, which was of particular interest since this value had shown a minimal level of inhibition under static conditions.

TABLE 5

DAYS TO FOUL VS. SPEED OF ROTATION \* OF OPTIMALLY PULSED PLATES

Days to Foul	0 Knots	0.75 Knots	1.25 Knots
Nov. 1 - Control Jan. 31 Days to Foul Pulsed Plates Day to Foul	4 9	5 10	5 11
Feb. 1 - Control Apr. 30 Days to Foul Pulsed Plates Days to Foul	4 7	4 7	5 8
May 1 - Control Jul. 31 Days to Foul Pulsed Plates Days to Foul	3 7	3 7	6 8

\* Knots measured as  $\frac{1}{2}$  perimeter velocity.

Since it is known that an increase in velocity retards the initial appearance of primary slimes (above about 5 knots fouling is virtually eliminated), some obvious curiosities exist and the results show how alkaline toxic reaction products were dissipated from the water/substrate interface due to the rotation. This has been dealt with in detail in a previous report<sup>14</sup>. It was however clearly indicated that, irrespective of season or velocity (of low magnitude) there was a definite inhibitory effect manifested by the use of electrical pulses.

*Characteristics of Calcareous Deposits Formed During Electrical Pulsing*

In all previous experiments concerned with forming and spalling off of calcareous deposits, a layer of considerable thickness was involved but it is obvious that such a deposit, even if lacking adult fouling organisms, would create considerable resistance on the hull of a ship. In the studies reported here it was found that appreciable fouling prevention was accomplished with little or no appearance of a calcareous layer. This led to the thought that a situation existed whereby the calcareous film was so tenuous that it constantly dissolved or was sloughed off. Thus, it was believed that marine microorganisms settling on such a surface were carried away from the surface during the period when the current was interrupted and film dissipation was occurring. A laboratory investigation was undertaken to study the mechanism of calcareous deposit formation and to determine the conditions under which tenuous unstable films could be formed whilst maintaining cathodic protection at all times.

The glass cell, Figure 7, was used thus enabling both vertical and horizontal surfaces to be examined and accurate potential measurements to be taken. Cathode surfaces were 10 cm<sup>2</sup> each. Two constant current sources were used; one served as an adjustable bias for cathodic protection, the other was connected with a timer and could be set to give any desired pulses up to 1000 mA/cm<sup>2</sup>. A strip recorder was used to record potentials and a cathode ray oscilloscope to observe transients.

Twenty litres of aerated sea water were prepared from "Sea Salt", of composition NaCl 58.49%, MgCl<sub>2</sub>·6H<sub>2</sub>O 26.46%, Na<sub>2</sub>SO<sub>4</sub> 9.75%, CaCl<sub>2</sub>·2H<sub>2</sub>O 2.76%, KCl 1.65%, NaHCO<sub>3</sub> 0.47%, KBr 0.24%, H<sub>3</sub>BO<sub>3</sub> 0.07%, SrCl<sub>2</sub>·6H<sub>2</sub>O 0.95%, NaF 0.007%.

Solution was circulated at a rate of 500 ml/min and microscopic examination of the polished steel cathodes was made. To determine the influence of the various major salts contained in sea water on the characteristics of the calcareous deposits, some runs were made using varying quantities of CaCl<sub>2</sub>·2H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O. The concentration of NaCl was kept constant.

Microscopic examination at 250 X showed that in all cases the calcareous layers possessed pinholes whereas at low power the layers appeared impervious. No discrete ordered structure was noted in the layers which generally appeared as compressed powders.

Long term cathodic polarization of steel in sea water has been studied previously<sup>17</sup> and a relationship was found equating passivation with time. The passivation is due to the formation of an insulating layer produced from the interaction of cathodically produced hydroxyl ions with ions which form insoluble or sparingly soluble compounds, e.g., Mg<sup>++</sup>. However, the onset of passivation is not manifested by a rapid potential increase as is the case with analogous anodic processes, e.g., lead in chloride or sulphate solutions<sup>18</sup> and it is thus difficult to observe.

In the present study, cathodic currents of short duration were used and only a gradual potential increase occurred when calcareous layers formed and consolidated.

Table 6 relates the nature of the calcareous deposit with some of the pulse parameters investigated.

TABLE 6

RELATIONSHIP BETWEEN PULSE PARAMETERS AND NATURE OF CALCAREOUS DEPOSIT

Pulse Intensity mA/ft <sup>2</sup>	Pulse Duration Secs	Pulse Interval Secs	Bias (mA/ft <sup>2</sup> )	Observation
1500	1	120	9	Slight deposit
1500	2	120	12	Slight deposit
1400	2	120	12	Slight deposit
1000	1	120	24	Heavy deposit
1000	1	120	20	Moderate deposit
1000	1	120	18	Slight deposit
1000	1	120	17	No deposition
1000	1	120	15	Corrosion
1000	1	120	9	Corrosion
450	1	20	19	Heavy deposit
450	1	20	16	Moderate deposit
450	1	20	15	Slight deposit
450	1	20	13	No deposition
250	1	30	20	Heavy deposit
250	1	30	15	Slight deposit
250	1	30	13	No deposition
200	1	30	20	Heavy deposit
200	1	30	16	Moderate deposit
200	1	30	15	No deposit
200	5.5	20	9	No deposit, slight corrosion

The study of the influence of concentration of CaCl<sub>2</sub>·2H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O at varying current densities suggested that layers of a less passivating nature are formed as the concentration of the magnesium salt increases. However, no clear relationship was apparent connecting current density, solution composition and extent of passivation.

It is known that the ratio of Ca<sup>++</sup>/Mg<sup>++</sup> in solution can significantly influence the type of deposit formed when full passivation is desired. The ratio of Ca<sup>++</sup>/Mg<sup>++</sup> vs. thickness of deposit and kinetics of the deposition reaction have been examined previously<sup>19</sup> and it was shown that as pH increases, precipitation of Mg(OH)<sub>2</sub> is favored. The present investigation has shown that the influence of this ratio is far less significant when tenuous, non-passivating layers are required.

A previous study<sup>20</sup> has shown that as the current density increases, the proportion of CaCO<sub>3</sub> in the deposit decreases whilst the proportion of Mg(OH)<sub>2</sub> increases. Since the solubility of Mg(OH)<sub>2</sub> is about eight times that of CaCO<sub>3</sub>, it was clear that in order to obtain as tenuous and unstable a deposit as possible, the current density should be adjusted to cause preferential formation of Mg(OH)<sub>2</sub>. Thus, in subsequent experiments, high pulse densities of short duration were examined and it was found that highly unstable layers — constantly dissolving and forming — could be formed.

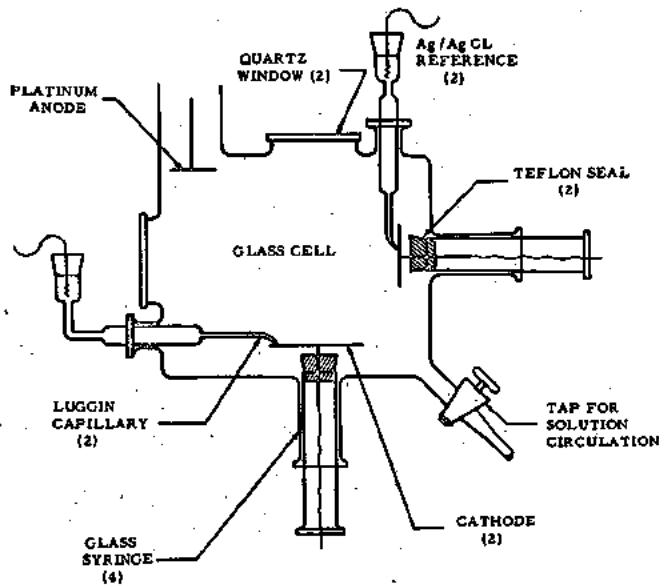


Fig. 7. Cell for study of development of calcareous deposits.

At the same time a range of pulse parameters which had shown promising antifouling effect were examined for their deposit forming characteristics. In these cases it was frequently found that calcareous layers would develop slowly and consolidate but adjustment of the bias level (cathodic protection current) leaving the pulse parameters unchanged minimized or completely prevented deposition of calcareous salts.

Subsequently runs of several days were conducted using a range of pulse parameters which had been found to give promising antifouling effect. Table 7 summarizes the condition which gave a deposit-free surface after at least 7 days exposure.

TABLE 7

CONDITIONS GIVING DEPOSIT FREE SURFACE  
AFTER AT LEAST 7 DAYS EXPOSURE

Pulse Intensity	Pulse Duration	Pulse Interval	Bias
mA/ft <sup>2</sup>	Secs	Secs	mA/ft <sup>2</sup>
200	1	30	15
250	1	30	13
450	1	20	13
1000	1	120	17

Simultaneously, pulse parameters which had previously been found in the laboratory to give a deposit free surface were examined for their antifouling effectiveness and it was found that rapid fouling occurred on a number of the plates receiving such pulses.

Whilst it was not possible to predict a particular set of parameters which would give minimal or no deposition, it was generally found that high current for short durations caused deposition of the most soluble films. It was also found that pulse parameters which showed good antifouling effect did not necessarily result in a lack of deposition of a calcareous film, but such parameters only required slight adjustment to prevent film formation. The environmental differences between the laboratory cell and the ocean would more than explain these slight variations. Most significant, however, was the fact that environmental test plates receiving pulse parameters in the laboratory to give the most tenuous deposits frequently suffered rapid and severe fouling attachment. It was concluded, therefore, that antifouling by electrical pulses is not dependent solely on the formation and dissolution of calcareous films on the surface of the metal.

## DISCUSSION

In dealing with marine organisms one encounters many complex interrelationships not only between different organisms, but with the complexion of a given community and its physical and chemical environment. Fouling organisms have a wide range of tolerances to their surroundings due to inherent adaptation capabilities in the intertidal and estuarine environment, both of which present a hostile and fairly unstable habitat. This study has confirmed that organisms in this environment can show resistance to artificially induced modifications in their surroundings, in this case, electrical pulses.

It is recognized from studies of various antifouling techniques that some organisms are affected more than others but surprisingly, very little of the published work has considered fouling on a micro-scale or considered the primary slimes of bacteria, diatoms and algae. The initiating slimes, it is believed, result from the settlement of bacteria and algae on a

substrate and initiate the subsequent «breaking down» or «preparation» of the surface so that conditions become more favorable for the attachment of invertebrate larvae. We found that a measure of antifouling effectiveness was the length of time needed to establish primary slime layers, whereas the rate of development of secondary and higher organisms was of little significance. Thus, although electrical pulses could severely retard the establishment of secondary and higher communities, they inexorably developed, once established, despite the hostile environment.

Larval forms are more sensitive to constraints than adults, but where adult forms might die subsequent to attachment to a weak antifouling paint, this behavior was not so marked with electrical pulses. There was no clear correlation evinced between the activity of a stage in the life cycle of an organism and inhibition of attachment or growth as has been observed with toxins. In the latter case, the more active stages tend to ingest more toxin during the period of maximum activity. Thus, in the case of the barnacle, the cyprid should be more vulnerable to toxic constraints than the nauplius form.

Three mechanisms have been presented as possible antifouling effects:

(1) The development and repeated sloughing off of calcareous films.

(2) The effect of fluctuating electrical fields.

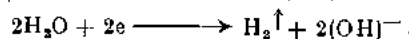
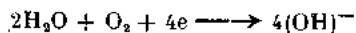
(3) Effect of alkali formed due to the cathodic reaction.

After analysis of the data accrued in this study, the following conclusions have been reached:

(1) *Calcareous Deposits*: Optimum antifouling pulse parameters were frequently — but not always — accompanied by little calcareous layer deposition. The parameters could be adjusted without forfeiting antifouling ability to cause no substantial layer. However, pulse parameters designed to cause the most tenuous deposit, i.e., one which constantly formed and dissolved, did not necessarily show good antifouling behavior. Thus, the attachment of larvae can apparently occur despite the fact that the surface is continuously forming and dissolving.

(2) *Electrical Fields*: Although certain marine and fresh water organisms are sensitive to electrical fields (notably fish, one species of which uses d.c. pulses for detection purposes), no direct reaction to electrical pulses was observed with fouling plankton when studied in the laboratory. It is assumed that the same insensitivity to electrical field polarity or current is manifested by these organisms in the marine environment. A statistical analysis of the relationship between pulse parameters and fouling rate data has also shown that there is no linear correlation between electrical charge and fouling inhibition. The coefficient of correlation of the least squares trend line was low in all cases. If electrical fields alone were an important effector of inhibition, a much closer correlation would be expected. The presence or magnitude of an electrical field has therefore been discarded as being the prime reason for inhibition.

(3) *Influence of Cathodically Produced Alkali*: The electrode reactions occurring at a steel cathode in sea water when receiving currents of the magnitude studied in this experimentation involve alkali production:



Measurements taken in the vicinity of the cathodes could give values as high as pH 13. It was, therefore, expected that the higher the current, the higher the pH, but in practice, this was not the case, since development of a calcareous deposit isolated the surface and prevented passage of charge at certain areas which thus became less alkaline. There was, therefore, a limiting situation involving:

- prevention of formation of calcareous deposit
- rate of diffusion of  $\text{OH}^-$  away from the cathode surface (this being temperature and agitation dependent).
- polarization behavior based upon the constituents contained in the sea water.

It can be shown from the data that at lower charge ( $q_p$ ) values, there was almost a linear correlation between quantity of charge  $q_p$  and days to foul. In the upper end of the range, however, increased  $q_p$  did not always have the benefit of bringing about a proportional inhibition of fouling. It was further noted that when there was a fairly strong tidal surge, the antifouling effect with equal charge values was markedly less. It was also noted that rotated plates at the same  $q_p$  values showed an increased tendency to foul. Both of the foregoing observations are ascribed to a dissipation of the alkali produced at the cathode. It was therefore concluded from our studies that the inhibition of fouling was due solely to the change in the chemical atmosphere at a plate/seawater interface and not, as has been inferred by other workers, a direct effect of electrical fields. It follows that optimum antifouling effect occurs when the maximum quantity of electricity is passed per unit time without causing any insulating calcareous layer which, by obstructing the current path, reduces overall alkali formation.

Some organisms are more affected by the alteration of the environment at the cathode than others. Those most prevalent in the winter months (hydroids, etc.) are most affected and the greatest inhibition was observed at this time. If the plates received the same pulse for any length of time, varying from 2 to 7 months, they eventually fouled. This was presumably due to the gradual build-up of algal slimes, which modified the surface sufficiently (partly by creating a slightly insulating layer), so that it was not completely inimicable to secondary invaders. This was most likely with algae since these organisms are not as chemo-sensitive as invertebrate larvae and thus, by reducing the severity of the environment by a buffering or insulating effect, subsequent growth was not completely inhibited. The lack of correlation at high  $q_p$  values was clearly due to the fact that threshold antifouling effect had been reached. Thus, at high  $q_p$  values good antifouling behavior occurred due to unrestricted formation of the maximum quantity of alkali. With slightly different pulse or environmental conditions a situation developed whereby a calcareous film formed and thus effectively reduced the alkalinity at insulated areas of the substrate/sea water interface. At lower  $q_p$  values, therefore, provided the parameters were not such as to cause a calcareous film, somewhat more regular antifouling effect was expected and found due to the generally lower sensitivity of the system to film formation. Eventual fouling occurred, however, at lower  $q_p$  values since it appears as if the maximum amount of alkali was necessary to totally inhibit fouling.

This investigation has involved an exhaustive survey of the effects of electricity on marine fouling. It has identified the causes of fouling inhibition and shown that an antifouling effect can be attained on bare metal substrates for as long as seven months. An effective antifouling system would have to give at least two seasons of antifouling action and it is not believed that this can be accomplished using quantities of electricity which are economically feasible. Six months of antifouling action on bare metallic substrates seems to be within the capabilities of the present work.

#### DISCUSSION

Dr. HOUGHTON (England): I know that you said that you are not a Biologist, but I was been interested in the figures you quoted for the speed in knots which would prevent the settlement of fouling organisms. In Smith's and other papers it would appear that something between 1.0 and 2.0 knots is sufficient to prevent settlement. Have you some further data on this subject that you could give us please?

Dr. LITTAUER: I do not have further data on the influence of speed on fouling attachment. We found that above 2.5 knots attachment of zoofoulers did not occur. In some tests with the rotating apparatus, however, the peripheral speed was 1.7 knots, and fouling was absent from the outer few inches of the plate. It would, therefore, appear as if the critical speed could be slightly less than 1.7 knots.

Prof. MOR (Italy): I want to congratulate Dr. Littauer on his interesting work and I was very pleased to learn that his results are corroborating those I myself obtained.

First of all it seems to be a question involving an inhibiting action of chemical nature strictly connected with the alkaline environment

#### CONCLUSIONS

It is suggested for the following reasons that a marketable antifouling system cannot be based solely on electrical pulses:

1. It yields only partial inhibition since some organisms are less susceptible to the conditions induced than others.
2. Even when optimum current densities and pulse parameters are used, the surface eventually becomes passivated by resistant forms. These, in turn, create a substrate for further attachment by possibly reducing the effect of cathode products.
3. The technique is sensitive to strong water currents, becoming proportionally less effective as the dissipation of toxic cathode products increases.
4. Currents high enough to provide maximum inhibition are so high as to make economic feasibility a question.
5. It would yield no better results than current low duration toxic paints even if conditions were optimum for its utilization.

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and most likely due to the probable presence of  $H_2O_2$  as a reduction product of oxygen, though a possible direct action due to the electric current pulses should not be excluded, in accordance with the tests carried out on barnacles by Dr. Köhl at Cuxhaven.

Dr. LITTAUER: Yes, this is very interesting. I was not familiar with the work you mention, but many years ago it was proposed that muscular fixation was occurring on barnacles when pulsed electrically. This is mentioned in the introductory section of my paper. There was no scientific evidence given to support the hypothesis. It is, of course, possible that the pulses which we employed do cause a muscular response of some type with barnacles, but I still feel that the major effect is a chemical one, that is, high OH at the interface, since we were able to prevent attachment of organisms which do not possess the closing mechanism of barnacles.

Dr. CALLAS (U.S.A.): Dr. Littauer has the thought that there is a possibility of gas evolution at the electrode which might also have an influence on the setting and growth of the barnacles?

Dr. LITTAUER: Yes, and this was a part of the laboratory study. At the current densities we were using, a certain amount of hydrogen evolution was occurring, and this is why we achieved the high alkalinity at the surface. However, in the electrochemistry laboratory tests we used pulsing parameters identical to those found effective in the ocean, and in the ocean we studied pulses which we found effective in the laboratory to produce high alkalinity, with little or no formation of calcareous layers. With some pulses hydrogen gas evolution was quite apparent to the naked eye; in others it was not, and we found no correlation between gas evolution and antifouling effectiveness.

Prof. H. ENGEL (Germany): May I concerning this paper and Dr.

Mor's paper of yesterday, that by applying cathodic current pulses on remark metal surface in purified sea water you produce  $H_2O_2$  as a first reduction product, also oxygen. As much as I know  $H_2O_2$  is a poison for many organisms and I think that it is not only the change in the pH value by applying the cathodic current but also the production of  $H_2O_2$  and  $O_2$ , which may influence the life of the organisms.

Dr. LITTAUER: Thank you — that is a very interesting observation that you make. Certainly  $H_2O_2$  is highly toxic, but it only exists a short period of time and, I would imagine, decomposes in sea water. We were able to make measurements of pH at the surface and obtained values as high as 13, which is a condition unstable to  $H_2O_2$ .



# THE PREVENTION OF BACTERIAL CORROSION OF MILD STEEL WITH PAINT FILMS

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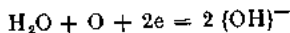
## SUMMARY

A simple laboratory method has been used to study the effect of bacterial corrosion on mild steel panels immersed in river mud. Several paint schemes applied to mild steel panels

have been studied under these conditions and complete protection of the metal was only obtained by the addition of chemical inhibitors to these paints.

## INTRODUCTION

Metallic corrosion is an electro-chemical process, the commonest form of which occurs when metal is in contact with a neutral aerobic electrolyte. The surface of the exposed metal consists of areas of varying chemical activity which variation can be due to the presence of oxide films, discontinuous paint surfaces, localised internal stresses or mechanical damage. This varying activity sets up electro-chemical cells and at the anodic areas the metal passes into solution whilst at the cathode, hydroxyl ions are formed by the reduction of dissolved oxygen.



Both these reactions occur simultaneously and for the corrosion cell to remain active it is necessary for current to pass from the anode to the cathode through the electrolyte, whilst electrons pass through the metallic circuit from the anode to the cathode. If the electrons at the cathode are not removed the cell becomes polarised and the process ceases. The formation of insoluble products indicates that corrosion is occurring. The metal goes into solution at the anode as ions and hydroxyl ions are formed at the cathode. The two ions interact forming an insoluble hydroxide which in the case of iron reacts with further dissolved oxygen to form the typical red iron rust. The foregoing typifies the normal type of corrosion which occurs on ships operating in ordinary service.

In 1951 a case of severe corrosion attack was investigated by Patterson<sup>1</sup>. This had taken place in a tidal estuary, where a vessel had been lying on a mudbank for a long period during fitting out. An inspection of the bottom at the pre-trial docking revealed areas of bottom plating that were very severely pitted where abrasion had occurred. Hundreds of rivet heads also showed this severe attack and all the corroded areas were covered with a heavy black deposit, which was found to be ferrous sulphide and not hydrated iron oxide as might have been expected. It was shown that this was not the normal type of corrosion which takes place in aerobic conditions but was anaerobic corrosion due to bacteria in the mud upon which the vessel was lying at low tide. This mud was very viscous and adhered to the bottom of the ship excluding oxygen from the steel.

Tidal estuaries have mudbanks which are exposed for long periods of time at low tide. These mudbanks are composed mainly of deposited clay, silt, sewage and oil and are frequently highly infected by bacteria. This mud provides ample nutriment for their metabolism. Among the bacteria which are known to exist in these muds are those which can bring about changes in sulphur compounds. The main types

are sulphate reducers which can reduce sulphates to sulphides, this process requiring hydrogen. There is a further group of bacteria which act upon sulphur containing organic matter and produce hydrogen sulphide gas.

We have ourselves investigated a case of severe marine corrosion in which a ship had been aground on a mudbank in a river in the East Indies. Severe corrosion had only occurred in the area that had been grounded and this area was still covered with a viscous, strong smelling, black mud at the drydocking in England despite the fact that it had occurred six months previously and the ship had travelled about eight thousand miles since grounding. The paint system had been severely abraded and the metal was heavily pitted. Ferrous sulphide was found in the mud. The remaining bottom plates showed only the normal red iron rust on damaged areas.

## MECHANISM OF ANAEROBIC BACTERIAL CORROSION

Where aerobic corrosion occurs, oxygen will depolarise the cell to allow the process to continue, whilst in neutral anaerobic conditions an alternative cathodic depolarising mechanism must be sought.

Van Wolzogen Kuhr and Van Der Vlugt<sup>2</sup> in Holland showed that an environment in which this type of corrosion

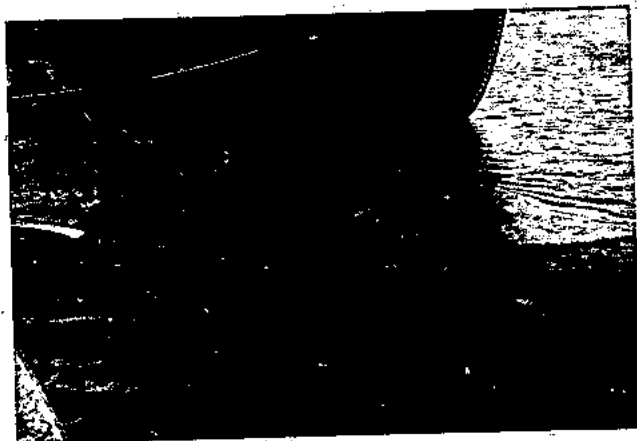


Fig. 1.



Fig. 2. Typical Mudbanks at low tide.



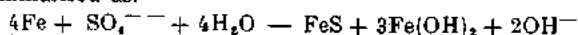
Fig. 3.

occurs, provides active conditions for the growth of sulphate reducing bacteria of the genus *DESULPHOVIBRIO DESULPHURICANS*. Moreover they stated that the bacteria were themselves able to enter into the corrosion process acting as cathodic depolarising agents and using the hydrogen to reduce sulphate to sulphide. This sulphide formed then reacted with metallic ions going into solution at the anodic areas giving a black deposit of ferrous sulphide. Table 1 shows the mechanism postulated by Kuhr and Vlucht.

TABLE 1

4Fe	4Fe <sup>++</sup> + 8e	Anodic reaction.
8H <sub>2</sub> O	8H <sup>+</sup> + 8OH <sup>-</sup>	Cathodic reaction.
8H <sup>+</sup> + 8e	8H	
SO <sub>4</sub> <sup>-</sup> + 8H	S <sup>-</sup> + 4H <sub>2</sub> O	Cathodic depolarisation by Bacteria.
Fe <sup>++</sup> + S <sup>-</sup>	FeS	Corrosion Product
3Fe <sup>++</sup> + 6OH <sup>-</sup>	3Fe(OH) <sub>2</sub>	Corrosion Product

Summarised as:



Recent work by Booth and Tiller<sup>8</sup> has confirmed this mechanism. Bunker<sup>4</sup>, showed that the sulphate reducers could be very active in areas of restricted oxygen supply, but that this could be in close proximity to an area of abundant oxygen supply. It can be seen that these conditions are fulfilled in the case of a ship's hull which is aerated by tidal river water, but which for long periods a low tide would be lying in mud. One characteristic of these muds additional to their bacterial content is the depletion of oxygen in them due to the action of organic matter. This anaerobic state is most pronounced in warm weather and affords the ideal conditions for the activity of the sulphate reducing bacteria. The activity of these bacteria allows the corrosion to continue, usually in a severe localised form producing a ferrous sulphide film on the metal surface. When this system is re-aerated it is possible that the ferrous sulphide is oxidised giving colloidal sulphur. This free sulphur can thus initiate a severe form of corrosion of iron and steel. It can thus be seen that the conditions to which steel may be exposed in tidal estuaries may be extremely corrosive. Patterson showed that the conditions could be simulated in the laboratory and suggested that one method of protection might be made by the incorporation of chemical inhibitors in paint films.

In this paper the work has been carried out in three stages:

1. The effect of bacterial action on paint films.
2. The effect of inhibitors on these paint films.
3. The protective effect of inhibitors when a bare metal area is deliberately left in the paint film.

#### EXPERIMENTAL

A simple method was devised to reproduce the conditions existing in the mudbanks. The mud samples were kept at 37°C in one litre screw capped glass Kilner jars to simulate conditions in summer when these muds are exposed for long periods, becoming heated, depleted of oxygen and corrosively aggressive. The panels used in all the experiments were very thin mild steel 10cm x 5cm (100 sq. cm in area), 0.25 mm thick. These panels were prepared by abrading both surfaces with grade 0, emery paper, thoroughly degreasing twice using A.R. xylene, dried between filter paper and weighed to the nearest milligram. Care was taken that the panel faces were not touched at any time during preparation. The panels which were painted were given one coat by brush at their normal spreading rate and single coats were used, to accelerate any attack as some of the multi-coat systems have a final thickness of .25-.375 mm. The painted panels were allowed to dry for 7 days at 21°C and 50% relative humidity before being reweighed. Panels were always prepared before mud samples were collected to ensure that the mud would be active. The mud was taken from a mudbank which is about three miles from the mouth of the River Wear, the river for the Port of Sunderland. This mudbank is exposed twice during a twenty four hour period and contains appreciable amounts of sewage, coal dust and large pieces of scrap steel. The latter is present, as the mudbank is in the vicinity of a ship fitting out berth. The samples were collected from a depth of two to three feet, taken to the laboratory and transferred to the glass jars as quickly as possible to prevent undue aeration. The jars were almost completely filled with mud, a small space being left to facilitate removal of the panels. The pre-weighed panels were pushed into the mud. When painted panels were used an unpainted control panel was always exposed in the same jar. The jars were tightly fastened placed in an oven at 37°C and left for a standard time of 50 days. At the end of this time the jars were taken out, cooled and the panels withdrawn. The corrosion products were carefully removed by scrubbing and washing in running water, the panels being finally washed in 20% (v/v) solution of hydrochloric acid inhibited with .2 cc. Quinoline per 100 cc. solution to remove any remaining corrosion products, dried and reweighed. The coated panels were cleaned photographed, the paint removed with a non-corrosive paint stripper, washed in A.R. xylene and finally reweighed.

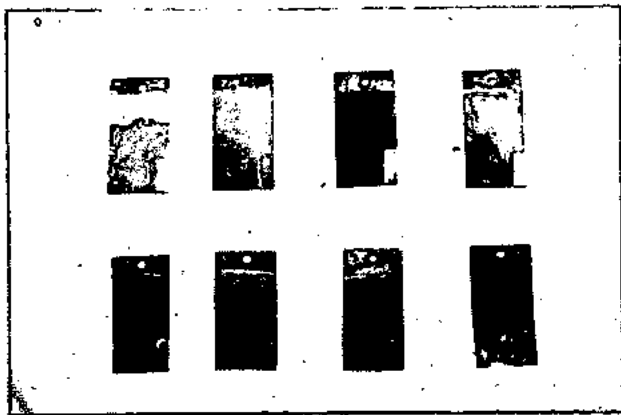


Fig. 4. First Series. Appearance of schemes after 50 days.

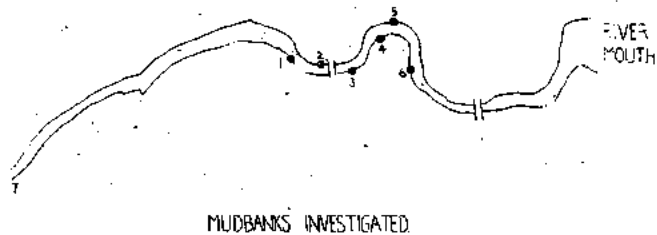


Fig. 5. Positions of various mudbanks investigated.

### FIRST STAGE TO DETERMINE THE EFFECT OF BACTERIAL ACTION ON PAINT FILMS

The initial investigation was to determine whether the mud would show bacterial activity and to observe the effect this attack had on several types of paint systems used as outer ships bottom protectives. Initially seven schemes were used.

- Scheme 1. Plasticised coal tar pitch, pigmented solely with aluminium powder at a dry film thickness of 0.04 mm.
- Scheme 2. Plasticised natural asphaltum, pigmented with aluminium powder and basic lead sulphate, at a dry film thickness of 0.05 mm.
- Scheme 3. Modified phenol formaldehyde, linseed, tung oil varnish pigmented with aluminium powder, iron oxide, basic lead sulphate and barytes at a dry film thickness of 0.10 mm.
- Scheme 4. Coal tar pitch/epoxy pigmented with iron oxide at a dry film thickness of 0.10 mm.
- Scheme 5. High Build Liquid pitch/epoxy pigmented with iron oxide at a dry film thickness of 0.15 mm.
- Scheme 6. High Build Epoxy coating pigmented with iron oxide and silica at a dry film thickness of 0.20 mm.
- Scheme 7. High Build Epoxy abrasion resistant coating pigmented with yellow oxide at a dry film thickness of 0.50 mm.

Schemes 1, 4, 5, 6 and 7 are proprietary materials, 7 specifically for use in condition of severe abrasion, whilst 2 and 3 are paints to Admiralty specifications and included as comparisons.

The standard procedure was carried out and Table 2 shows the results.

TABLE 2  
FIRST SERIES 50 DAYS

SCHEME	Weight Loss MGMS
Unpainted Control	3090
1	50
2	19
3	205
4	21
5	17
6	15
7	20

It can be seen that the unpainted control was severely attacked. The corrosion rate was approximately 62mgm/dm<sup>2</sup>/Day. Only scheme 3 showed any breakdown and this was in the form of severe blistering with pitting beneath the blisters. This breakdown was probably due to the medium, an oleo-resinous varnish, being less water resistant than other schemes. The aluminium pigment of schemes 1 and 2 was darkened but the schemes were otherwise good. The remaining schemes were unaffected.

It is apparent from the results, especially of the unpainted control, that the mud was very aggressive and that the procedure could be adopted to evaluate inhibitors.

Further mud samples from six other areas of the river were checked to establish if bacterial corrosion was general throughout the mudbanks of the river. All the areas were in the vicinity of sewage outlets and were sampled 20-25 yards downriver from these outlets. Four of the areas were heavy black viscous muds, one a yellow shingle and one sample was collected from an area well upstream where the river water is uncontaminated. This sample was brown and rather sandy. An analysis was carried out on the samples collected and the results are shown in Table 3.

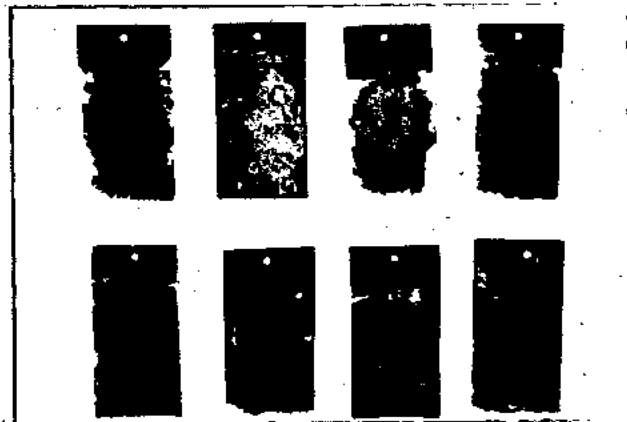


Fig. 6. Appearance of unpainted panels exposed to varying mud samples.

TABLE 3  
MUD ANALYSIS

Area	Appearance	Percent Moisture	pH of Aqueous Extract	Percent Loss on Ignition	Total Sulphur (as sulphide)	Weight Loss in MGMS
1a	Black Viscous	47	7.0	26	1.3	3090
1b	Black Viscous	47	7.0	22	1.04	2670
1c	Black Viscous	45	7.0	27	1.38	4600
2	Yellow Single	15	5.6	9	.40	2984
3	Black Viscous	30	7.0	4.7	.21	883
4	Black Viscous	37	7.0	7.7	.11	1298
5	Black Viscous	40	7.0	26	1.21	2584
6	Black Viscous	45	7.0	9	.94	1173
7	Brown Sandy	25	7.0	10	.07	401

The weight loss figures were determined on unpainted panels. Loss on ignition and sulphur determination were carried out after drying the muds for 30 mins. at 82°C. It can be seen that with the exception of two samples all were black viscous neutral muds. All were active, the most active giving the highest figures for loss on ignition and sulphur content. No colloidal sulphur was found in any of the samples. The high sulphur figures might be expected in muds supporting sulphate reducers and the high loss on ignition figures are probably due to organic matter, part of which could provide nutriment for the sulphate reducers. In the case of area 2, the yellow shingle, the high weight loss figure was found to be due to acid effluent from a nearby chemical works.

It might be expected that if the activity in these mud-banks was bacterial, lowering the temperature would in effect reduce the activity of the mud and would reduce the rate of corrosion. This was found to be true, since unpainted panels exposed in a mud sample from area 1a and placed in a refrigerator at 0°C gave a weight loss figure of 480 mgms against a weight loss figure of 3090 mgms for unpainted panels exposed in the same mud for the same period of time at 37°C. It can thus be seen that some of these muds if exposed for long periods of time during hot weather could become extremely aggressive.

#### SECOND STAGE

#### THE EFFECT OF INHIBITORS ON PAINT FILMS EXPOSED TO BACTERIAL ATTACK

It was important to know what effect the inhibitors might have as protection against bacterial attack and whether they would have any adverse effects on film properties or corrosion resistance of the schemes tested. Saleh<sup>5</sup>, carried out work on numerous additives that might have an effect on anaerobic bacteria. Tests were carried out on a total of twelve inhibitors. These are named in Table 4.

Six inhibitors B, C, D, F, G and M were found effective by Saleh and we included these in addition to A, E, H, J, K and L more recent compounds which we have evaluated as bacteriacides. The inhibitors were used at a concentration of

TABLE 4  
INHIBITORS SELECTED FOR EVALUATION

Inhibitor	Form
A Para Toluene Sulphonamide	Solid
B Cetyltrimethyl Ammonium Bromide	Solid
C Dichloro-dihydroxy Diphenylmethane	Solid
D Pentachlorophenol	Solid
E Potassium Tellurate	Solid
F Mixed mono and dialkyl Quaternary Ammonium Chloride	Liquid
G Dialkyl Quaternary Ammonium Chloride	Liquid
H Alkyl Quaternary Ammonium Chloride	Liquid
J Primary Amine of Dodecyl Fatty Acids	Liquid
K Aliphatic nitrogen inhibitor	Liquid
L Alkyl propylene diamine	Heavy Paste
M Tetra decyl pyridinium bromide	Solid

1% by weight of the dryfilm in schemes 1, 4, 5 and 6. Scheme 1 was included so that any inhibitor showing protective properties might become apparent in the thinner coating. The liquid inhibitors were added by simple stirring, the solids were ground into a small portion of the paint before being added to the bulk. The liquid inhibitors were incorporated in the activator of the two pack systems to prevent premature gelation due to the reaction of the amines with the epoxy resin. All the inhibitors used are available commercially. Panels were prepared as previously described and immersed in a fresh sample of mud taken from area 1 in July 1966. The results after 50 days are shown in Table 5.

TABLE 5  
SECOND SERIES 50 DAYS

Inhibitor	Weight Loss (Milligrammes)			
	Scheme 1.	Scheme 4.	Scheme 5.	Scheme 6.
Unpainted Control	Average Loss 2760 mgms.			
No Inhibitor	43	2	38	15
A	67	10	114	107
B	95	14	152	150
C	52	6	60	35
D	54	7	80	48
E	332	21	172	45
F	36	1	25	15
G	31	3	60	45
H	29	1	57	42
J	49	3	92	88
K	26	1	135	122
L	35	1	82	76
M	22	1	90	75

All the paints of scheme 1 showed the typical pitting attack due to bacterial corrosion. Three inhibitors A, B and E showed severe pitting and were worse than the uninhibited control paint, which showed only moderate pitting as did inhibitors C and D. Several paints containing inhibitors showed much better protection than the uninhibited control paint. These were inhibitors F, G, H, J, K, L and M, the panels only showing slight pitting. All the paints in scheme 1 showed darkening of the aluminium pigment.

All the inhibitors performed well in Scheme 4, with the exception of inhibitor E which showed blistering of the film and moderate pitting of the metal.

None of the paints of Scheme 5 showed any film defect but the metal substrate showed moderate pitting with in-

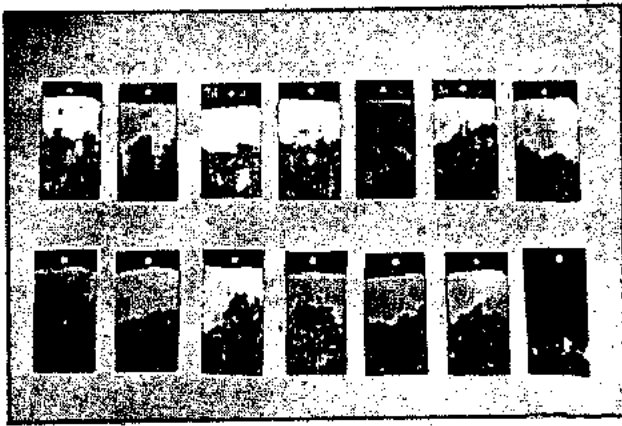


Fig. 7. Second Series. Typical attack on panels of Scheme 1.

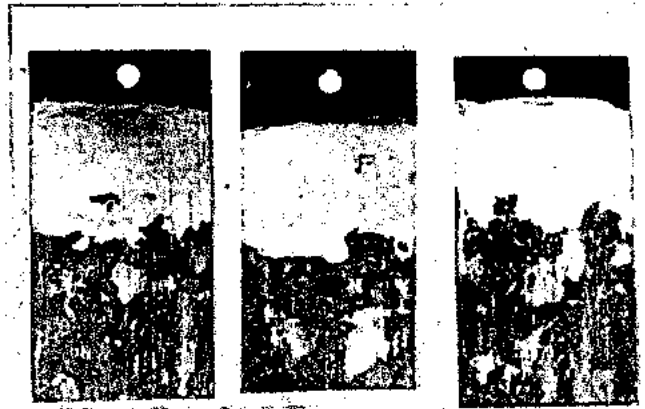


Fig. 8. Second Series. Panels of Scheme 1, showing varying degrees of pitting.

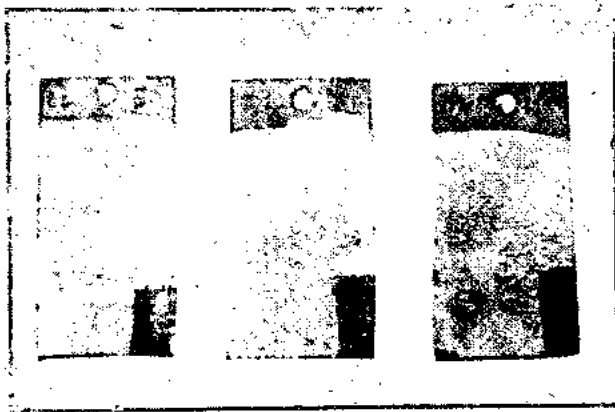


Fig. 9. Second Series. Panels of Scheme 6, showing varying degrees of blistering.



Fig. 10. Second Series. Panel of Scheme 1, showing pitting of Paint Film.

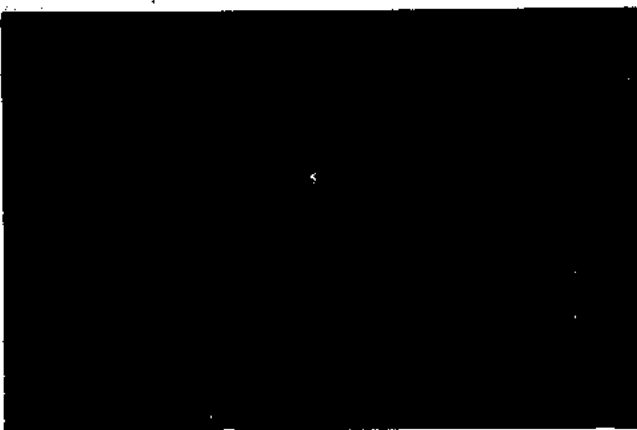


Fig. 11. Second Series. Panel of Scheme 1, showing pitting of metal substrate.

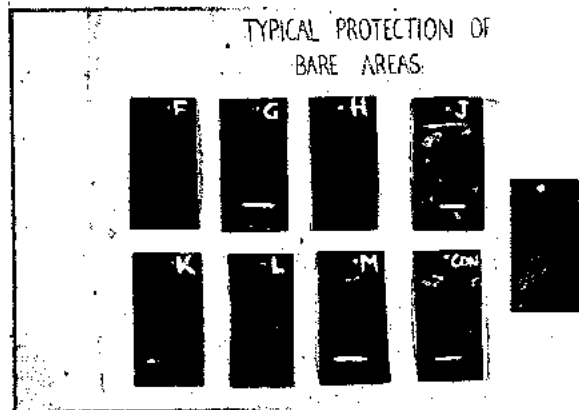


Fig. 12. Third Series. Showing typical protection of windows of panels of Scheme 1.

TABLE 6  
THIRD SERIES 40 DAYS

INHIBITOR	WEIGHT LOSS (MILLIGRAMMES)							
	Scheme 1	% Protect	Scheme 4	% Protect	Scheme 5	% Protect	Scheme 6	% Protect
Unpainted Control	Average Loss 4,600 mgms.							
Uninhibited Paint	332	—	223	—	388	—	120	—
A	—	—	235	—	—	—	—	—
B	—	—	174	22	—	—	—	—
C	—	—	350	—	—	—	—	—
D	—	—	134	40	—	—	550	—
E	—	—	226	—	—	—	—	—
F	61	82	36	84	366	6	185	—
G	479	—	315	—	215	44	—	—
H	160	52	172	23	185	52	—	—
J	218	34	74	67	237	49	—	—
K	284	14	55	75	212	45	—	—
L	147	56	76	68	181	53	—	—
M	276	17	91	59	286	26	—	—

hibitors A, B, E and K. The remaining inhibitors showed only slight pitting of the metal.

Scheme 6 was severely effected by the addition of inhibitors only inhibitors C and F and the uninhibited paint did not blister, whilst the remainder were heavily blistered and the metal showed severe pitting.

### THIRD STAGE

#### THE EFFECT OF INHIBITORS ON PROTECTION OF BARE AREAS OF METAL LEFT IN PAINT FILMS

It was found from the second stage of the work that some inhibitors performed well in certain schemes. The next step was to see if any of these inhibitors added to the paint would protect an area of exposed metal deliberately left in the paint film. The panels for this stage had a small window 25mm x 3 mm. in the film by masking with adhesive tape. Only the inhibitors showing promise from the second stage were used. A further fresh sample of mud was taken from area 1 in December 1966 for this stage. The results are given in Table 6.

The percentage protection figures were derived by subtracting the weight loss figures of the inhibited paint (where a protective effect was obvious) from that of the uninhibited paint of the same scheme then calculating this as a percentage.

Three inhibitors F, H, and L protected the «window» area and also prevented pitting of the painted area of scheme 1. The remaining inhibitors did not protect the «window» or prevent pitting of the paint film.

Only inhibitors A, C, E and G and the paint without inhibitor failed to protect the «window» area in scheme 4. Inhibitor E caused moderate blistering of the film.

The paint films of scheme 5 were unaffected but only inhibitors G, H, J and M protected the «window» area.

The paint films of scheme 6 showed slight blistering and only inhibitor F showed partial protection of the «window» area.

It is also important to know what effect the inhibitors might have on the corrosion resistance and film properties when schemes are immersed in sea water in the absence of mud.

Shotblasted 15 cm x 10 cm, 1.5 mm thick mild steel panels were prepared with the paints that had provided protection for the «window» areas of the painted panels in the

third stage of the work. The control paints without inhibitors were also applied. Single coats of the schemes were applied at their correct spreading rate and after drying for seven days were immersed in sea water. After eight months the paints of schemes 1, 4 and 5 showed no defects, but inhibitor F of scheme 6 showed slight blistering.

### CONCLUSIONS

The object of the work carried out was to provide a simple laboratory means of evaluating paint coatings to prevent the corrosion of steel by bacterial attack and to increase the anti-corrosive properties of these coatings by the addition of chemical inhibitors. The first problem was to establish that the corrosion was caused by bacteria. The mud samples used gave the typical pitting of mild steel associated with sulphate reducing bacteria and the neutrality, varying sulphur contents and the apparent inactivity of the samples at a low temperature are typical of muds containing sulphate reducers.

Any coatings that are to be used on metals exposed to active bacterial muds should preferably be thick, abrasion resistant and able to prevent the passage of water and hydrogen sulphide gas. It has been shown that whilst the particular control pitch/epoxy schemes without inhibitors were able to protect the metal when the films were continuous, corrosion resulted when the films were damaged.

The third stage of the work showed that several of the inhibitors could be added to schemes 1, 4 and 5, to give complete protection, even when the paint film was damaged. Not all inhibitors worked well in every scheme, but on the whole the liquid ones performed better than the solids. The best schemes were schemes 4 and 5 containing inhibitors G, H, J and M. Both are pitch/epoxy compositions, the better one being scheme 4 which dries, cures and would be abrasion resistant more quickly than the high build schemes. These two schemes would be preferred to the plasticised pitch, Scheme 1, which is less abrasion and water resistant than Scheme 4 and 5, although the addition of inhibitors F, H and L to this scheme would give complete protection. Scheme 2 has the same defects as scheme 1 and 3. The oleo-resinous varnish, is not to be recommended because of its rapid failure by blistering. The high build epoxy scheme 6 was not satisfactory even when inhibitors were added.

The work done in stage three needs much more investigation using other paint schemes and inhibitors and varying metal pre-treatments before any one paint scheme or inhibitor could be said to provide complete protection against bacterial corrosion, but it has been shown that suitable systems could be formulated to prevent severe attack at areas of paint film breakdown.

Further work is being carried out on abrasion resistant coatings and also on the various types of shop-primers used in the shipbuilding industry.

#### ACKNOWLEDGMENTS

We should like to thank Dr. W.S. Patterson for his interest and advice, and the Dredging Department of the River Wear Commissioners Sunderland for help in obtaining mud samples.

#### DISCUSSION

J. SPARROW (England): I would like to ask Mister Cameron if he has studied the effects of the anaerobic bacteria on antifouling paints in addition to his work on anticorrosives.

J. CAMERON: Yes we have done this and I remember that they are affected by sulfate reducing bacteria and darkening takes place especially in the case of antifouling paints which contain cuprous oxide and particularly those paints which are of the contact type, that is where nearly all the pigment is at the paint surface. Copper sulphide is formed and since this has very little antifouling activity, fouling can be expected subsequently. It would be advisable in such cases where constant immersion in these conditions may be expected, that some of the organic tin complex compounds should be used which are unaffected by this form of bacterial attack.

J. DEPIREUX (Belgium): I congratulate the authors for their very interesting work and I think that the influence on the microbiological corrosion is very important for the protection of hulls furthermore when they are found in the presence of copper based antifouling. I had the opportunity to verify some very important cases of hull's

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corrosion and the depolarisation effect of copper sulfide on the cathodic protection at a such degree that it was impossible to protect again the hull with the usual method and the normal power of the apparatus.

Please allow me to remember, on this subject, my paper delivered in the VIII<sup>e</sup> FATIPEC Congress, La Haye — Pays-Bas — 1966.

A. ROBINSON: As far as cathodic protection is concerned we have had some experience with impressed and fitted anodes and we find that where cathodic protection is able to protect the large damaged areas we feel that our inhibitor system would be able to protect damaged areas on vessels without either type of cathodic protection.

T. BIRKENHEAD (Great Britain): I would like to ask Mr. Cameron if he noticed any evidence of biological attack on the paint films.

J. CAMERON: In certain cases the films were affected, in the case of the aluminium paints the aluminium pigment was darkened in some places, also it may well be that in the case of the oleo resinous paint, that some bacterial degradation had taken place but we could not be sure about this.

# FOULING ORGANISMS IN THE NORTHERN ADRIATIC

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## SUMMARY

Investigations on the fouling of living organisms, sea vessels and other underwater objects were initiated with the aim to obtain an information on the qualitative characteristics of fouling communities in the Northern Adriatic. Observations were fulfilled on the hulls of wooden fisher boats, on neutral glass plates fixed on anchored rafts in the harbour of Rovinj, and on living specimens of shellfishes *Ostrea edulis*, *Mytilus galloprovincialis* and *Pinna nobilis*.

It is established that the most important foulers of the region are: molluscs *Ostrea edulis* and *Mytilus galloprovin-*

*cialis*, tubeworms *Pomatoceros triquetter* and *Filograninae* (*Salmacina* and *Filograna*), barnacles *Balanus amphitrite* and *B. eburneus*, polyzoans *Cryptosula pallasiana* and some species of the genus *Schizoporella*, and the polyzoan *Diplosoma listerianum*. The sea-weeds are not so common in a stable fouling communities, in spite of the fact that on the ship hulls *Enteromorpha* is one of the most common organisms.

The frequency values for fouling species are very different for various kinds of the substrate. Local differences were established even in fouling communities of living shellfish.

## INTRODUCTION

The quality and the intensity of fouling of vessels, sessile organisms and other underwater objects depend on numerous biotic and abiotic factors. The initial moment of the fouling is the time of settling of larvae of fouling organisms on the suitable substrate. This is considered to be the most important period in the fouling process. However, it depends on numerous factors, such as:

- 1) the reproductive period of fouling organisms,
- 2) the climate conditions of the environment,
- 3) the physical and the chemical properties of the surface available,
- 4) the time of exposure.

When the first foulers are settled, forthcoming development of the fouling community depends on the resistance of the settled organisms to the changes of environmental hydrographic conditions as well as on the interspecific relations of foulers. It is the fact that due to the biological exclusion (Harris 1946) many sessile species do not join in the fouling community when it is already established. Therefore it is of a greatest importance for future fouling studies to know in detail the sessile marine organisms which can take part in the fouling communities in various geographical regions.

It was our aim to list the most important fouling organisms of the Northern Adriatic. The complete insight into the quality of fouling communities was obtained by noting the species which have settled on ship hulls, on neutral experimental plates fastened on anchored rafts, and on living shellfish (oysters, mussels and *Pinna nobilis*).

Only wooden motor vessels were used in our studies, which were navigating in the North Adriatic region. Their speed does not exceed 10 Nm/hour and their draught was never greater than 3 m. The fouling of ship hulls was analysed when exposed in boat-sheds for cleaning.

The experimental plates of glass were used because of the neutral properties of the material. The plates were exposed on special rafts (Zavodnik & Igić 1968) which were anchored in the Bay Valdibora (Northern harbour of Rovinj) on the West coast of Istrian peninsula. These observations were initiated four years ago. Single plates were exposed from

one week to more than one year, and some of them were changed monthly. The fouling communities from the glass plates were analysed in the laboratory.

For comparison of the fouling of living benthic organisms, shellfishes *Ostrea edulis* L. (oyster), *Mytilus galloprovincialis* Lam. (mussel) and *Pinna nobilis* L. were chosen. While *Pinna* specimens were sampled only in the region of Rovinj, the oysters and the mussels derived from rearing places in Pomer, Valelonga, Limski kanal and Vabriga, which are situated on the western coast of Istria. The shellfish is usually reared on fixed parks, except in rearing place in Limski kanal, which is of a floating type (Nikolić & Stojnić 1962). The analyses of fouling of the shellfishes were fulfilled partly on field and in detail in a laboratory.

In total more than hundred fouling species, plant and animal, were identified. Unfortunately, some systematic groups are not studied in detail so far (Algae, Sponges, Hydroids). However, most of them are of minor interest for fouling studies, either due to their rareness or because of their small dimensions.

## SEA - WEEDS

In North Adriatic, the sea-weeds are not an important element in a stable fouling community. It is true that the first colonisers appearing in great quantities are bacteria and diatoms which were found on our experimental plates of glass already in the course of the first days of exposure. As well, the settling of spores of higher macro-algae occur at the early beginning of exposure. Before the fouling community consisting prevalently of animals is established, the sea-weeds can cover more than 80% of the surface of experimental plates, especially when immersed in small depths. The same is true for the hulls of wooden vessels but not for the fouling communities of living shellfish, where sea-weeds usually do not settle in great quantities. The species most frequently established in fouling communities are *Ulva lactuca*, *Enteromorpha* spp. (*E. intestinalis*, *E. prolifera*, *E. linza*, *E. clathrata* and others), and species of the genera *Ectocarpus* and *Melobesia*. It is interesting that *Ulva lactuca* settles more frequently on fixed experimental plates than on the hulls of travelling vessels, while on the shells of immotile



TABLE I

FREQUENCY DISTRIBUTION OF FOULING ORGANISMS ON VARIOUS SUBSTRATA (in %)

Substratum	Wooden vessels	Experimental plates	Living shellfish		
			Ostrea edulis	Mytilus galloprovincialis	Pinna nobilis
Number of observations	18	149	381	267	120
<i>Ulothrix implexa</i> Kütz.	—	0,7	—	—	—
<i>Ulva lactuca</i> L.	22,2	36,9	1,8	2,6	1,8
<i>Enteromorpha</i> spp.	94,4	28,2	—	—	—
<i>Cladophora</i> spp.	—	2,7	—	—	5,5
<i>Chaetomorpha aerea</i> (Dill.)	—	6,7	—	—	—
<i>Anadyomene stellata</i> (Wulf.)	—	2,0	—	—	1,8
<i>Pseudochlorodesmis furcellata</i> (Zgn.)	—	0,7	—	—	—
<i>Valonia utricularis</i> (Roth.)	—	—	10,0	—	31,4
<i>Acetabularia mediterranea</i> (Lm.)	—	—	+	—	18,5
<i>Halimeda tuna</i> (Ellis et Sol.)	—	0,7	—	—	3,7
<i>Ectocarpus</i> sp.	5,5	8,7	2,1	1,5	—
<i>Dictyota dichotoma</i> (Huds.)	—	1,3	0,3	—	1,8
<i>Padina pavonia</i> (L.)	—	—	—	—	7,4
<i>Cystoseira barbata</i> (Good. Wood.)	—	—	—	—	9,2
<i>Cystoseira adriatica</i> Sauv.	—	—	—	—	1,8
<i>Porphyra</i> sp.	—	0,7	—	—	—
<i>Peyssonnelia rubra</i> (Gr.)	—	0,7	—	—	—
<i>Lithothamnion</i> sp.	—	—	—	—	1,8
<i>Melobesia</i> sp.	22,2	61,1	7,3	32,9	25,9
<i>Ceramium</i> sp.	—	—	—	—	1,8
<i>Polysiphonia</i> sp.	—	—	3,9	—	—
<i>Laurencia obtusa</i> (Huds.)	—	—	—	—	55,2
<i>Laurencia paniculata</i> (J. Ag.)	—	—	—	—	16,5
<i>Laurencia</i> sp. - indet.	—	—	3,1	0,4	—
<i>Sycon raphanus</i> Schmidt	—	15,4	2,9	0,8	—
<i>Spongiaria</i> indet.	—	+	+	—	+
<i>Anemonia sulcata</i> Pennant	—	—	—	—	1,8
<i>Actionothoe clavata</i> Ilmoni	—	2,7	—	—	—
<i>Cladocora caespitosa</i> Milne-Edw.	—	—	—	—	1,8
<i>Balanophyllia verrucaria</i> Mich.	—	—	—	—	5,5
<i>Hydrozoa</i> spp.	16,6	61,8	4,2	—	—
<i>Vermetus triqueter</i> (Bivone)	22,2	—	0,8	1,9	—
<i>Vermetus glomeratus</i> Linne	—	—	—	—	3,7
<i>Vermetus arenarius</i> Linne	—	—	—	—	22,2
<i>Arca Noe</i> Linne	—	—	—	—	+
<i>Modiolus barbatus</i> (Linne)	—	0,7	4,7	—	—
<i>Musculus costulatus</i> (Risso)	—	4,7	2,3	0,4	3,7
<i>Mytilus galloprovincialis</i> Lam.	83,3	18,8	22,8	6,7	—
<i>Chlamys varius</i> (Line)	—	—	0,3	—	3,7
<i>Chlamys glabra</i> (Linne)	—	0,7	—	—	—
<i>Chlamys opercularis</i> (Linne)	—	0,7	0,3	—	—
<i>Spondylus guaderopus</i> Linne	—	—	—	—	1,8
<i>Anomia ephippium</i> Linne	—	19,5	2,1	9,7	18,5
<i>Ostrea edulis</i> Linne	50,0	19,5	0,8	16,8	42,0
<i>Chama gryphina</i> Lamarck	—	—	—	—	18,5
<i>Saxicava arctica</i> (Linne)	—	—	0,5	—	—
<i>Serpula vermicularis</i> Linne	22,2	26,8	6,8	3,7	+
<i>Pomatoceros triqueter</i> (Linne)	27,7	42,9	37,3	44,9	77,7
<i>Filigraninae</i> div. spp.	83,3	73,8	7,3	—	—
<i>Spirorbis</i> sp.	94,4	20,8	7,1	4,9	87,3
<i>Hydroides uncinnata</i> (Phil.)	—	1,3	—	—	—
<i>Hydroides norvegica</i> (Gunn.)	22,2	—	—	—	—
<i>Hydroides helmatius</i> (Iroso)	—	1,3	—	—	1,8
<i>Sabella pavonina</i> Savignyi	—	0,7	—	—	—
<i>Spirographis spallanzanii</i> (Viv.)	—	—	0,5	—	—

TABLE 1 (continued)

Substratum	Wooden vessels	Experimental plates	Living shellfish		
			Ostrea edulis	Mytilus galloprovincialis	Pinna nobilis
Number of observations	18	149	381	267	120
<i>Balanus amphitrite</i> (Darwin)	86,6	69,8	16,5	28,1	—
<i>Balanus eburneus</i> (Gould)	44,4	61,7	22,0	11,6	—
<i>Balanus perforatus</i> (Brug.)	—	—	4,5	14,6	—
<i>Balanus tintinnabulum</i> (Linne)	—	25,5	—	1,5	—
<i>Balanus</i> sp. - juv.	—	—	1,6	1,1	—
<i>Chthamalus stellatus</i> (Poli)	—	8,0	—	—	—
<i>Aetea truncata</i> (Landsbor.)	—	6,0	—	—	—
<i>Bugula neritina</i> Linne	11,1	12,1	—	—	—
<i>Bugula avicularia</i> Linne	—	0,7	—	—	—
<i>Bugula</i> sp.	5,5	—	3,9	—	—
<i>Scrupocellaria reptans</i> Linne	—	8,0	—	—	—
<i>Membranipora</i> sp.	—	—	—	—	58,0
<i>Schizoporella</i> div. spp.	16,6	71,8	44,1	32,9	62,0
<i>Cryptosula pallasiana</i> (Moll.)	68,6	—	21,5	—	—
<i>Lichenopora radiata</i> Audouin	—	—	—	—	5,5
<i>Didemnum fulgens</i> M. Edwards	—	—	—	—	5,5
<i>Diplosoma listerianum</i> (Edw.)	16,6	51,0	24,4	1,9	—
<i>Lissoclipum pseudoleptoclinum</i> Drasche	—	—	1,8	1,9	—
<i>Ascidella aspersa</i> (Müller)	—	0,7	0,8	0,8	—
<i>Phallusia mammillata</i> Cuvier	—	—	2,4	—	—
<i>Styela partita</i> (Stimpson)	16,6	—	2,1	1,9	—
<i>Polycarpa gracilis</i> Heller	—	0,7	—	—	—
<i>Polycarpa pomaria</i> (Savignyi)	—	0,7	—	—	—
<i>Botryllus schlosseri</i> (Pallas)	5,5	—	2,4	0,4	—
<i>Botrylloides leachi</i> (Savignyi)	—	—	6,8	1,9	—
<i>Halocynthia papillosa</i> Linne	—	—	—	—	1,8
<i>Microcosmus sulcatus</i> Coquebert	—	—	—	—	3,7

shellfishes it was found only extraordinarily. On the contrary, the *Enteromorpha* species were found in the water-line belt of nearly all wooden boats examined, but in much less frequency on experimental plates and not at all on the shellfish. Melobesias, which can cover great surfaces on the shellfish shells are like *Ulva* more frequently observed on experimental plates than on vessels, and significant frequential differences were found for mussels and oysters. The reason for this is not known. Other algal species are rarely found in fouling communities in Northern Adriatic; it is obvious that seaweeds prefer to settle on immovable objects such as experimental plates, shellfishes and other sessile animals. The permanent species of algal ship fouling seems to be only *Enteromorpha*.

#### SPONGES

Sponges were not observed on the hulls of examined wooden vessels. It is interesting that on glass plates the protuberated sponge *Sycon raphanus* was established in 15% of observations, while on shellfish it was found only rarely. Some other flat species were found on plates and shellfishes too (Zavodnik 1967, Zavodnik & Igic 1968) but the specimens sampled on oysters are unfortunately not identified till now.

#### HYDROIDS

Hydroids are rarely found on ship hulls and shellfish in North Adriatic but they were frequently observed on experimental plates. Consequently, the covering rates and the

biomass of these animals are insignificant in our region; in contrary to this, for example, in Baltic Sea hydroids can represent one of the most important animal groups in the fouling community (Arbuzova 1963). The following hydroid genusses were identified: *Eudendrium*, *Obelia*, *Laomedea*, *Gonothyrea*, *Kirchenpaueria*, *Ventromma* and *Plumularia*, of which *Plumularia* is most frequent.

It is worth to mention the fixation of the actinian *Actinothoe clavata* on some experimental plates of glass.

#### MOLLUSCS

Among molluscs, the most important fouling organisms are shellfishes, especially oysters, mussels and *Anomia ephippium*. This latest species was found frequently on experimental plates and in some cases on the shells of other shellfish studied, but it was never established on ship hulls. On the contrary, mussels and oysters settle most frequently on the hulls of wooden vessels and more rarely on glass plates. It is interesting that both species do not live frequently on the shells of other specimens of their own or other shellfish species, except of oyster, which was frequently found on *Pinna*. Occasionally also some other shellfish species were encountered in the fouling community of glass plates and sessile animals but never they were observed on ship hulls. Of the sessile gastropods, only *Vermetus triquetus* was found in approx. 1/5 of the vessels examined, but never on experimental plates and rarely it was observed on the shells of some shellfish.

## TUBEWORMS

Due to their frequency and to their covering rate, tube-worms are considered as one of the most important animal groups in fouling communities in the Northern Adriatic. On wooden ship hulls, most frequently was observed and in great quantities the small tubeworm *Spirorbis* sp., which was on the contrary less present on experimental plates and on living commercial shellfishes. *Filigraninae* (*Salmaeina* sp. and *Filigrana implexa*) were also rarely found on other sessile animals but their frequency and covering rate are very high for experimental plates and for ship hulls, where they were observed in more than 80% of the observations. The large species *Serpula vermicularis* was found in approx. 1/4 of the vessels and of the glass plates examined, while *Pomato-ceros triquetus* was more frequently observed on glass plates and on living shellfishes.

## BARNACLES

World wide, barnacles are supposed to be the most important animal group in the fouling communities. Our analyses show that on wooden vessels which navigated in the Northern Adriatic only *Balanus amphitrite* and *B. eburneus* were settled. Furthermore, the settling frequency of *B. amphitrite* is much greater on wooden vessels than it was found for *B. eburneus*. It is not the case for experimental plates of glass, where the frequency values are nearly the same for both species. On glass plates also *B. tintinnabulum* and *Chthamalus stellatus* were encountered while on ship hulls they were not present. It is interesting that barnacles usually settle more rarely on the shells of living mussels and oysters, while no one species could be identified in the fouling community of the shellfish *Pinna nobilis*, even in small depths.

## POLYZOANS

It is the fact that in fouling communities of the ship hulls prevalently flat formed colonies can be found in Northern Adriatic. Mostly it is the species *Cryptosula pallasiana* which was present on more than 65% of the vessels examined.

On the contrary, the species of the genus *Schizoporella* (*S. sanguinea*, *S. errata*) were found on ship hulls only in approx. 1/5 cases but they were much more frequently observed on the experimental plates or on the shells of living shellfish. Polyzoans with bush-formed colonies (*Bugula*, *Scrupocellaria*) were rarely or not at all registered on ship hulls. It is interesting that bush-formed Polyzoans very rarely settle on living shellfish in spite of the almost complete immovability of the hosts.

## ASCIDIANS

Generally, ascidians are not an important element in the fouling communities in the Northern Adriatic. Their frequency values are found to be less than 10% for living shellfish, except for the synascidian species *Diplosoma listerianum*. Its soft and semitransparent flat colonies were found on more than 50% of the glass plates examined, and they settle frequently on oysters too. The covering values of *Diplosoma* are remarkably great, such as 90% on glass plates and even 100% on oysters. It is believed that the mass mortality of oysters in some rearing places (Pomer near Pula) is caused in a great deal by this polyzoan species.

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## DISCUSSION

G. RELINI (Italy): I have to ask you some questions. At what depth the panel was exposed?

L. IGIĆ: The panels were exposed at the depth from ten to one hundred and fifty centimetres.

G. RELINI: Have you put your panels only in Rovinj Harbour or also in other Harbours of the Northern part of Adriatic?

L. IGIĆ: The experimental panels were immersed in Rovinj Harbour and in Pula Harbour — about twenty miles far from Rovinj.

G. RELINI: Have you found the absence of *Balanus trigonus*? this is very interesting because I have found it in Trieste Harbour.

L. IGIĆ: Although the investigations were carried on in different parts of Northern Adriatic, it is very interesting that never once and nowhere these species were found. I do not know what is the reason for this phenomenon, but I suppose that are local fluctuations, or perhaps unequal density of the populations of these species.

# TRIBUTYL TIN METHACRYLATE COPOLYMERS IN ANTIFOULING PAINTS

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## SUMMARY

Although organotin compounds are known to have great toxicity to many fouling organisms, it has proved difficult to make satisfactory antifouling paints by the addition of simple organotin compounds to paint media.

On the hypothesis that the short lives of such paints were due to a too rapid solution of the poison, experiments were done with polymers of tributyl tin methacrylate. It was found that by using co-monomers such as methyl methacrylate one could produce films of satisfactory strength, and flexibility could be imparted by adding plasticisers or using flexibilising co-monomers such as butyl acrylate. The polymers had little antifouling action as clear or lightly-pigmented

films, but when pigmented at high pigment volume concentration with cuprous oxide they gave paints of extraordinary effectiveness and length of life.

It was found possible to replace cuprous oxide wholly or partly by other sparingly soluble pigments, zinc oxide being particularly good. In all cases high pigment volume concentration was maintained. In order to maintain the effectiveness of paints with reduced copper content, or no copper at all, it was necessary to raise the concentration of combined organotin radical in the polymer.

The production of resins and paints on these lines has been carried out successfully on a commercial scale.

## INTRODUCTION

The effectiveness of organic compounds of tin as antifouling agents is now well known. A large volume of literature has been published on the subject, much of it emanating from the Miami Research & Test Station, Florida where M & T Chemicals Inc. have conducted an intensive programme of research<sup>1,2</sup>. These reports produce evidence that under the conditions obtaining at Florida organotin compounds, especially of the  $R_3SnX$  type, possess a high degree of antifouling activity against a wide range of organisms. Evidence that these findings applied to other parts of the world, including British waters, has been supplied by other workers<sup>3</sup> and unpublished work by the Authors' own Company.

The simplest way of using a poison such as tributyl tin oxide is to incorporate it in a paint by mixing or grinding, without chemical modification. Work on these lines has been published, and a useful summary is to be found in the paper of Bennett and Zedler<sup>4</sup>. Our own experience with such formulae has been rather discouraging. The best results have been obtained with vinyl/rosin and certain rosin-based media, but at best the life has been one six-month season at our testing site in Devon. Such a result has been uncommon; the majority of trials have been effective for three or four months only, and then have succumbed to weed fouling. The few paints which have lasted a season have contained between 5 and 10 per cent of tributyl tin oxide (by weight of the whole paint), and have been applied in two coats to give 20-36 gms. of poison per square metre: this represents a very uneconomical performance in comparison with cuprous oxide.

Another method of using the poison would be to add it to a conventional copper-bearing antifouling as a boosting poison; mercury salts are commonly used in this way. This method has been tested with several paints highly loaded with cuprous oxide, but the improvement in performance has been small, at best.

Other organo-tin compounds such as tributyl tin sulphide, fluoride, chloride and acetate, and triphenyl tin chloride, have been tested in similar ways, with no better results.

The reason for the failures cannot at this moment be definitely stated, according to our own knowledge. The pattern of failure suggests that it is due to a too rapid leaching of poison from the paint, and some preliminary analytical results support this hypothesis. The fact that tributyl tin oxide is incompatible with most paint media, and is readily exuded at the surface of a paint film, may have some responsibility for this.

This difficulty was encountered with vinyl, acrylic, alkyd, chlorinated rubber and ethylhydroxyethyl cellulose paints as well as with the more conventional rosin based materials. In many cases tributyl tin oxide visibly migrated to the surface of the dried paint to produce a tacky film. It is obviously difficult to control the leaching rate of the poison under these conditions.

A paper by Monterroso, Andrews and Marinelli<sup>5</sup>, which described polymers of tributyl tin acrylate esters, aroused our interest in that it provided a possible alternative to the simple addition of tributyl tin salts to conventional antifouling paint media. If the paint medium had the tributyl tin radical chemically bound to it the problem of incompatibility would not exist. In order that the poison should become available to the sea-water immediately adjacent to the film, the tributyl tin radical would have to dissolve in some form, and this might mean that it would have to be hydrolysed off the polymer backbone. Such a process might be slow, and might also be capable of control by varying the water-permeability of the paint.

When the first medium of this type had been made it was tested as an unpigmented film, also lightly pigmented with titanium dioxide, and heavily pigmented with cuprous oxide. The first two were failures, the third was remarkably successful. Subsequent experiments confirmed the fact that a high ratio of pigment to medium solids was necessary, and

furthermore that the pigment should be slightly soluble in sea-water: cuprous oxide and zinc oxide are outstanding examples of such pigments, and they also of course have their own toxic properties. The mechanism of poison release is imagined to be that the pigment slowly dissolves, leaving channels in the film, by means of which the sea-water can progressively get into contact with the paint medium and hydrolyse the tributyl tin radicals away from the polymers.

Since the investigation started patents have appeared describing the use of organo-tin polymers in antifouling paints<sup>8</sup>. They do not, however, explicitly or implicitly disclose the importance of this type of pigmentation.

#### THE PREPARATION AND TESTING OF A TBTM/MM COPOLYMER

We prepared tri-n-butyltin methacrylate by Montermoso's method<sup>4</sup>, and from this prepared a homopolymer, in a solution type polymerisation using benzoyl peroxide as initiator. A final viscosity of 0.5 poise/25°C was obtained at 40% solids in toluene. Clear films painted out from this solution remained soft. They showed rapid breakdown on sea-water immersion, with shrinkage, giving rise to a reticulated effect.

Attempts to toughen the film by blending the solution with xylol solutions of polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride/polyvinylidene chloride copolymer, chlorinated rubber or rosin were unsuccessful, due to incompatibility of the solutions. Cereclor 70, a chlorinated paraffin wax, could be mixed with the homopolymer solution but films painted out from the resulting solution dried with a milky appearance and remained very soft.

Tougher homopolymer films could no doubt be made by varying the reaction conditions to give a polymer having a higher molecular weight, but the poor film properties just described, together with Montermoso's description of his tri-n-butyltin methacrylate homopolymer as an elastomeric substance, led us to consider that copolymerisation would be more likely to give us the combination of film properties and organotin content which we required.

We considered that we would require a comonomer capable of adding to the hardness of the film, and methyl methacrylate seemed to be suitable for initial trials.

We attempted the copolymerisation of tri-n-butyltin methacrylate (TBTM)/methyl methacrylate (MM): 1/3.3, w/w (1/11.9, moles) at 100°C in toluene solution with benzoyl peroxide, 1% by weight of the monomer, as initiator. Details of this and other preparations are given in our Patent Application<sup>9</sup>. This preparation was not fully satisfactory in that some precipitated high molecular weight polymer had to be removed before clear films could be obtained from the remaining solution. The films thus obtained were extremely hard and brittle.

At this early stage it was considered essential to obtain, as quickly as possible, some indication of the practicability of using such a polymer as a toxic, film-forming antifouling medium. In order to do this we wished to take advantage of a full season's raft trials of paints based on such a medium, and this necessitated using the material immediately to hand. Fortunately it proved possible to plasticise our polymer with dibutyl phthalate, and with an addition of 25% by weight of the resin we obtained films that were both hard and tough.

Trials with this copolymer medium were first carried out on our rafts in the River Yealm during the 1962 fouling season. The unpigmented medium applied as a clear film at a rate of 120 gm./m<sup>2</sup> (equivalent to 7.1 gm./m<sup>2</sup> of TBT radical) had negligible antifouling properties, so that within a few weeks of immersion heavy fouling, both plant and animal, had accumulated. Laboratory tests using barnacle larvae tended to confirm this finding, since after shaking the finely-ground resin with sea-water for 24 hours the filtrate had no significant toxicity.

The same medium was pigmented with Anatase TiO<sub>2</sub> at 23% PVC and applied at a rate of 133 gm./m<sup>2</sup> (equivalent to 5.2 gm./m<sup>2</sup> of TBT radical). This paint was also a failure

with heavy settlements of both weed and animal fouling after only three or four months' immersion, but by comparison with the unpigmented copolymer medium the onset of fouling, particularly the weed, was much slower so that it took some two months longer to reach the same degree of intensity as recorded on the unpigmented composition, despite the fact that the amount of organotin applied per unit area was slightly less. This result suggested that incorporation of the TBT radical into the copolymer medium had not completely blocked the toxic effect and that given the right conditions it could, at least in some degree, be released to exert antifouling action.

The third paint of this series was pigmented with cuprous oxide at 48% PVC, and was immersed from our rafts in April 1962. Two patches of this paint (G. 519) were tested, one applied at a rate of 202 gm./m<sup>2</sup> (equivalent to 125 gm. Cu<sub>2</sub>O and 3.5 gm. TBT radical per m<sup>2</sup>) and another two-coat scheme at 377 gm./m<sup>2</sup> (to give 234 gm. Cu<sub>2</sub>O and 6.5 gm. TBT radical per m<sup>2</sup>). As a comparison, patches of two more conventional paints, on vinyl/rosin medium, were immersed at the same time; the first was a high copper content antifouling (G. 44) applied at 183 gm./m<sup>2</sup> (to give 102 gm./m<sup>2</sup> Cu<sub>2</sub>O) and the second was a similar composition but with the copper boosted by an organic mercurial poison (G. 195/2) applied at 362 gm./m<sup>2</sup> (to give 189 gm. Cu<sub>2</sub>O and 12.7 gm. organomercurial per m<sup>2</sup>). Both single and double coats of the copolymer antifouling were superior to either of the others. The first of the paints to show fouling was the unboosted, high-copper antifouling (G. 44), which after about six months started to pick up the settlements of stunted weed to which these paints are typically prone. By the end of the first season this type of fouling was heavy and it persisted thereafter with gradual increase for the remainder of the immersion period.

The boosted high copper antifouling (G. 195/2) resisted the stunted weed longer than the unboosted composition but by the end of the second season of immersion weed settlement was taking place and after this there was little to choose between the performances of the two paints.

The single coat of copolymer antifouling G. 519 was broadly speaking similar in performance to the double coat of the boosted high copper antifouling G. 195/2, on the whole being generally rated slightly superior throughout the four years' trial period. It should be mentioned at this stage that the film of the copolymer antifouling, both single and double coats, developed crazing after it had been immersed for some months and that a proportion of the fouling recorded was situated within the cracks rather than on the surface of the antifouling proper. The true antifouling performance of the composition was therefore probably somewhat better than the description given.

The double coat of G. 519 was quite outstanding in performance. At all stages of the four years' immersion this patch was the best and, during the final two years' immersion, continued to maintain a high degree of resistance when the other schemes had collected considerable settlements of weed and animal fouling. In the later stages some weed was recorded in the cracks but even at the final examination, after four years' immersion, weed settlement was not rated as more than slight. Fig. 1 illustrates the history.

In Table I, the fouling assessment numbers for the paints calculated at three-monthly intervals are shown. The number is calculated by rating the intensity of each type of fouling on a 0-8 scale, and multiplying this rating by a numerical factor which is greater the less resistant the type of fouling. Thus the larger the fouling assessment number the more severe the fouling, and when the number is rated continuously at 10-15 or more the paint is failing. On this basis the patch of G. 44 began to fail at the end of the first season of immersion, G. 195/2 towards the end of the second season, the single coat of G. 519 at the start of the third season while the double coat of G. 519 has still not failed by the end of the fourth season.

Scrapings from known areas of G. 519 were taken after

TABLE I  
FOULING ASSESSMENTS FOR A/F COMPOSITIONS  
G.44, G.195/2 AND COPOLYMER A/F G.519  
IMMERSION PERIOD FROM APRIL 1962 - APRIL 1966

A/F	Spreading Rate gm./m <sup>2</sup>	Months Immersion															
		3	6	9	12	15	18	21	24	27	30	33	36	39	42	45	48
G.44	183	2	9	20	26	13	16	17	17	18	32	25	26	28	/	/	44
G.195/2	362	0	0	5	22	8	9	13	17	20	21	16	23	36	/	/	48
G.519	202	0	0	10	22	6	9	10	15	12	15	23	19	29	24	38	54
G.519	377	0	0	0	22	0	0	0	0	9	11	9	11	6	5	9	9

TABLE II

	Immersion Period					
	0 days		1208 days		1585 days	
	Cu.	TBT	Cu.	TBT	Cu.	TBT
G.519. Single coat 202 gm./m <sup>2</sup>						
Poison: gm./m <sup>2</sup>	106.5	3.5	28.3	2.23	10.9	1.97
Poison: % leached	-	-	73	36	90	44
Average leaching rate, overall (micrograms/cm <sup>2</sup> /day)	-	-	6.5	0.10	6.0	0.09
G. 519. Double coat 377 gm./m <sup>2</sup>						
Poisons: gm./m <sup>2</sup>	200	6.57	108	5.47	73.6	4.9
Poison: % leached	-	-	46	17	63	25.5
Average leaching rate, overall (micrograms/cm <sup>2</sup> /day)	-	-	7.6	0.09	8.0	0.10

1208 and 1585 days' immersion and analysed for copper and tin. From these data calculations giving some idea of the rate of poison depletion and therefore the leaching rate can be made. The results of these calculations are given in Table II.

Too much should not be read into these analytical figures but they do suggest that considering the long period of immersion a satisfactory leaching rate of copper has been maintained, also that the tin leaches at an extremely low rate.

#### FURTHER DEVELOPMENT OF THE MEDIUM

The original paint, G. 519, was based on a TBTM/MM: 1/3.3, w/w copolymer of fairly low molecular weight, with a viscosity of 8 poises/25°C. at 38% solids in toluene. This resin, like TBTM/MM copolymers in general, was brittle unless it was plasticised. The first plasticiser we used was dibutyl phthalate (DBP) and the optimum amount was

determined by air drying and sea-water immersion of clear films. These tests showed that an addition of 25 parts DBP to 100 parts copolymer resin gave a tough film which did not embrittle after a month's immersion in sea-water. This plasticisation treatment was therefore used in G. 519. The cracking which occurred on immersion of this paint, however, pointed to the fact that this plasticiser was insufficiently permanent, and that the attainment of satisfactory mechanical properties in the paint would be a problem.

It is a general property of addition polymerisations that the average molecular weight can vary over a wide range, depending on the conditions rather than the extent of reaction. It was therefore necessary to decide what would be best in this respect, and to choose the reaction conditions accordingly. It was found, as might be expected, that higher molecular weights gave stronger films than did lower molecular weights, but on the other hand the latter gave better antifouling performance. It was essential to achieve an antifouling per-



(a) July, 1964 (28 months). A = G. 195/2 — Cu<sub>2</sub>O/Hg — 2 coats  
C = G. 519 — Cu<sub>2</sub>O/TBT copolymer — 2 coats.



(b) October, 1965 (43 months).  
Key to position: four patches A B C D.

Fig. 1. This shows the condition of the plate carrying the double coat of G. 519 after immersion for 28 and 43 months. The lighter square at the bottom of the patch is where paint had been scraped off for analysis of residual poison.

formance of comparable excellence to that of G. 519, so a low level of viscosity was chosen (ca. 3.5 poises/25°C/40% solids in xylol/Pentoxone: 4.5/1)<sup>10</sup>. Dioctyl phthalate (DOP) was chosen as plasticiser, being more permanent than DBP, and clear film tests were carried out to determine the optimum amount required for a TBTM/MM 1/3 copolymer. This turned out to be somewhat critical; ideally the film should be tack-free and tough at normal temperatures (20°C) without becoming brittle at sea-water temperatures (say 5°C) even after prolonged immersion. This was not fully achieved, but a reasonable compromise was made by using 50 parts DOP to 100 parts of copolymer resin solids. This gave a rather soft, slightly tacky film at 20°C, only slightly brittle at 4°C which retained its flexibility during 16 weeks' sea-water immersion. When suitably pigmented quite tough tack-free films were obtained.

At this point, the possibility of increasing the tin content was considered. This should give a more toxic medium, and the higher proportion of tributyltin methacrylate should help to plasticise the film, thus reducing the need for added plasticiser. An upper limit is set by the weakness and deterioration on immersion of the TBTM homopolymer itself. These ideas were largely borne out in practice, but unfortunately we encountered difficulties with regard to film strength at the low molecular weight which had been chosen for optimum antifouling properties. For example, a 1/1 w/w copolymer, plasticised with 20% DOP, gave a soft film which nevertheless embrittled on immersion. This type of result encouraged us to turn our attention to copolymers which would include an 'internal plasticiser', i.e. a flexibilising monomer copolymerised with the methyl and tributyltin

methacrylates. This was expected to give better mechanical properties and resistance to deterioration on immersion in water.

Among the methacrylates themselves some increase of flexibility can be obtained by incorporating some higher alkyl esters e.g. butyl methacrylate, but acrylates are much more effective since they are much softer than the corresponding methacrylates. Butyl acrylate (BA) was found to be a suitable plasticising monomer and a typical composition is TBTM/MM/BA: 5.0/3.5/1.5, w/w.

The manufacture of these copolymers on a large scale has proved fairly simple. Tributyltin methacrylate monomer is readily made in xylol solution at 50-85°C. from tributyltin oxide and methacrylic acid. The water of reaction is removed as it is formed by azeotropic distillation under reduced pressure. In the early work it appeared that some oxygenated solvent must be present to ensure good clarity but later results have shown that this is unnecessary providing the tributyltin oxide is of good quality. Since the final polymer is required in solution the polymerisation has been conducted in solution, using the solution of monomer prepared as above and adding co-monomers, catalysts and moderators as required. The main difficulty in practice has been that long times are often required in order to reach the desired viscosity, and this difficulty increases as the proportion of tributyltin methacrylate in the copolymer increases.

#### PIGMENTATION

The success of G. 519, based upon the copolymer medium heavily pigmented with sparingly soluble cuprous oxide,



(a) = «Waterline»



(b) = «Turn of Bilge»



(c) = «Flats» facet

Fig. 2. Panels exposed on Turtle at Newton Ferrers, photographed in October (27 weeks). Left-hand and middle panels, PhHgCl paints. Right-hand panel, ZnO/TBT copolymer paint (G. 511).



prompts speculation as to the relative proportions of the toxic action derived from the copper and the organotin respectively; in other words, whether the «opening up» of the copolymer medium by a comparatively inert pigment of low solubility might produce a composition which derived its toxic effectiveness from the tributyl tin radical alone.

Work on these lines is still in progress so that it is not possible to make any positive statements, but nevertheless sufficient information has been gained to point out the trends.

A preliminary series of trials in the TBTM/MM: 1/3 medium was carried out by reducing the cuprous oxide and replacing it with equivalent amounts of an inert but practically insoluble pigment, iron oxide. The results showed that even with the copper oxide as low as 18% w/w of the paint ( $\text{Cu}_2\text{O}$  PVC = 16%; total PVC = 54%) reasonable antifouling properties were retained. On the other hand the indications were that the additional «boost» which the organotin radical had conferred to G. 519 was in these cases lacking, and the antifouling properties were little if at all superior to what would be expected from the copper alone.

Later trials were carried out using more soluble inert pigments such as  $\text{BaCrO}_4$ ,  $\text{CaSO}_4$  and  $\text{As}_2\text{O}_3$ , in which one third by volume of the cuprous oxide content of copolymer antifouling was replaced by the pigment. Once again results were not conclusive, but the fact that the antifouling performances of these modified compositions were at least equal to that of the control copolymer antifouling, with full copper content, over an immersion period of six months, is consistent with the «opening up» hypothesis.

Theoretically it is very desirable to find out whether «opening up» the copolymer medium will enable it to function as an antifouling composition without the assistance of other toxins, but from the practical standpoint the most pressing reason for seeking a substitute for the copper-pigmented antifouling of the G. 519 type is the high price of copper. From the latter point of view the inertness or otherwise of the sparingly soluble «opening up» pigment is of far less importance than its price, but of course a toxic pigment which combined cheapness with the other desired properties would be preferred. Considerations of this kind gave rise to the idea that the compounds of zinc might bear investigation, since it is well known that zinc is toxic to many organisms. In the laboratory, solutions of zinc have a toxicity to barnacle (*Elminius*) larvae of only about one quarter and one twenty-fifth of solutions containing the same concentrations by weight of copper and mercury respectively. This is, however, based on a killing time of one hour, and it is easy to confuse slowness of action with low toxicity. For antifouling work a rapid toxic effect is not essential; copper is by far the most widely used antifouling poison, yet it is slow-acting and much less toxic than mercury calculated on a time-and-concentration basis.

For these reasons zinc compounds have always had potential interest as antifouling poisons, but the generally lower order of effectiveness as compared with copper has necessitated the use of large quantities of boosting poisons, which has tended to offset the price advantage. The copolymer medium, however, appeared to offer a possible route whereby the potential antifouling properties of both zinc and organic tin might be realised.

The first trials in this direction involved the substitution of part of the cuprous oxide by equivalent weights of zinc oxide, and a series of paints were tested with ratios of  $\text{Cu}_2\text{O}$  to  $\text{ZnO}$  of 60/0, 40/20, 20/40 and 10/50 by weight (total PVC 49%; TBT radical approx. 1.7% by weight of whole paint) in the TBTM/MM: 1/3 medium. The results from these trials were interesting since broadly speaking, the composition containing  $\text{Cu}_2\text{O}/\text{ZnO}$ : 40/20 was little, if at all, inferior to the control even after nearly two years' immersion, with both paints giving very good performances. The other two paints containing greater amounts of  $\text{ZnO}$  were not such good antifouling, but were still quite effective. On the whole, resistance to weed fouling appeared to deteriorate more rapidly with the reduction of the copper than resistance to barnacles and hydroids.

Having established that antifouling properties were retained even with severe reduction of the copper content, the next step was to eliminate the copper altogether and formulate a paint pigmented with zinc oxide only. In order to compensate for the absence of copper pigment the quantity of organotin was raised, by using a TBTM/MM: 1/1 medium.

Fig. 2 shows the three facets of a Turtle raft trial<sup>11</sup> of such a paint (G. 811), after immersion for 27 weeks at Newton Ferrers. This paint was applied on the right-hand panels at an average rate of 400 gm./m<sup>2</sup>. (210 gm. of  $\text{ZnO}$  and 12 gm. of TBT radical per m<sup>2</sup>). At this time there was only slime on the surface, nor had any other fouling been registered. For comparison, the other two panels of the three on each facet carried phenyl mercury chloride in different media, applied to give an average of 24 gm.  $\text{PhHgCl}$  per m<sup>2</sup>; both of these paints began to pick up hydroids after 21 weeks.

A large amount of work has been done in order to find the best levels of pigment, organotin radical and plasticiser, and it has been confirmed that a level of organotin similar to that in G. 811 is about the minimum if an effective paint is to be made. The goal of a really effective white antifouling has been attained in commercial practice by this means.

## CONCLUSIONS

The work described in this paper started as a pure speculation, prompted by the failure of conventional additions of organotin poisons to antifouling paint media to provide the length of life required. The hypothesis that such paints failed by too rapid an exhaustion of poison, and that the organotin copolymers succeeded by slowing down the release of poison, has received some support from other work (leaching-rates and residual analyses), but the success of the copolymer approach is not in itself a proof of the hypothesis. Its merit lies in the fact that it has produced commercially practical paints with great toxicity and long life.

This approach therefore has to a large extent realised the potential of organotin antifouling poisons, but the authors do not claim that it is the only way to do so. There are moreover certain disadvantages: the amount of organotin poison that can be incorporated in a paint by this means is limited, and there has been a great deal of difficulty in attaining satisfactory mechanical film properties. Other equally effective means may well be found, but this work has shown the concept of chemically combining the poison with the paint medium to be fruitful.

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## DISCUSSION

Dr. LITTAUER (U.S.A.): I would like to congratulate Mr. Sparrow and his group on the sophisticated coatings research which they have performed. I have three points to present.

1. Mr. Sparrow remarked that one of the main reasons for using TBTO as a toxin is the high price of copper, but actually a major use of TBTO containing paints is on aluminum pleasure boats where copper-based coatings can cause serious corrosion problems. TBTO paints can also be made in any color which is appealing to this market. Copper-based paints can, of course, be corrosion stimulators on steel hulls and when equivalent antifouling longevity is obtained, TBTO-based paints could be serious competition to copper-based paints.

2. The results obtained in the South of England of three or four seasons antifouling effectiveness are remarkable, but I wonder what the life will be under higher temperature conditions accompanied usually by more severe fouling and more rapid toxic leach rate.

I am also interested in your opinion concerning static versus dynamic testing of antifouling coatings. So many investigators rely on raft tests when repetitive dynamic-static testing gives a totally different picture concerning leach rate and coating life.

3. Finally, do you have any opinion concerning the toxic mechanism of TBTO? What I mean is, do you feel that the organometallic complex is toxic or could it be that tin itself is the toxic agent and the organic ligand is merely a convenient way to present the tin in a soluble and readily ingestible form? A similar question could also be posed concerning the organolead complexes which were described yesterday.

J. SPARROW: Thank you very much for your kind remarks at the beginning.

With regard to the first of your three points. I entirely agree with

you about the corrosion problem associated with the use of copper and this is a point which I should have mentioned.

The second point you raised concerned performance in tropical waters and under practical conditions. We have tested organotin copolymer antifoulings under both these conditions and although in the tropics the length of life has not been as great as described in this paper, they have nevertheless given performances comparable with the strongest antifoulings. As I have explained in the paper, we have also devoted a lot of time to improving the film strength of these antifoulings while at the same time maintaining their antifouling properties. Work on these lines is still in progress, but we already have evidence to show that paints of this kind will function satisfactorily under the conditions you mention.

Your third point was on the significance of the metal ion in the functioning of organometallic poisons. I regret to say that as I am a biologist, rather than a chemist or biochemist, I cannot really answer your question adequately but my feeling is that part of the explanation may lie in the penetration of the poison into the organism. It is certainly the case that those organometallic poisons which are very fat soluble tend to show enhanced toxicity coinciding with an increased rate of penetration of the poison into the organism.

I would rather leave it to a biochemist to say whether there is still a difference in toxicity once the compounds have entered the organism. Certainly inorganic compounds of tin are, in laboratory tests, much less toxic than their organic derivatives. According to our tests tributyltin oxide in the laboratory is about 7-9 times as toxic to barnacle larvae and about 14 times as toxic to *plumaria* sporelings as mercuric chloride, while mercury itself is very much more toxic than inorganic tin.

# PRELIMINARY NOTES OF THE MARINE FOULING AT THE PORT OF MAR DEL PLATA ARGENTINA

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## SUMMARY

Reference is made in this note to the qualitative and quantitative composition of the benthic communities of the Mar del Plata Harbour (Argentina). Researches on the fouling organisms were carried out based in our former studies of the area. This is the first time that fouling studies are being done in our country.

Studies in detail of the fouling organisms constitute the present stage of the investigations, and are made over an experimental raft.

As at the present time we have only reached up to the 6th month of observations we are given a preliminary idea of the fouling development.

We include the diagrams of the monthly main species frequency. Data of the accumulative panels are excluded.

Preliminary conclusions on monthly fouling obtained through half-year researchs are given below:

a) There are alternative periods of intense and weak fouling

attachment during summer and winter respectively.

b) The fouling organisms succession follows the same mechanism as in other latitudes. It starts with bacteria-diatoms-protozoa complex, finishing with higher organisms associations.

c) Many of the organisms show an accentuated growth and the vital cycle is completed in a short period of time. This involves a great possibility of substitution which is proved in practice since many organisms die before a month of attachment and are substituted by others.

d) The fact that it can be observed the attachment of organisms on the accumulative panels, not recorded on monthly panels, proves that certain species requires an established community to continue their development after the attachment.

These studies have relations with a research about properties of antifouling paints which is made simultaneously.

## INTRODUCTION

The studies on marine biology of this American South Atlantic area deal mainly with the taxonomic aspects, in spite that many plant and animal groups are practically unknown.

On the other hand it must be considered that benthic-ecological studies have going on for only a few years. Initially the investigations were carried out in the Patagonian coasts and lately in the Mar del Plata area.

This is the first time that fouling studies are being done in our country.

## LOCALITY

The Mar del Plata harbour is located at 38°08'17" S. and 57°31'18" W. For its construction and naval traffic it ranks as one of the most important ports of Argentina.

From the biological and hydrological points of view it has specific characteristics which differentiate it from the neighbour ports.

Some variations of the sea water of this area are noticeable throughout the year. During winter-months the Malvinas Current, which flows along this coastal region of the Buenos Aires province, brings cold waters very rich in nutrients. During summer-months this current sinks to deeper zones remaining at a certain distance from the coast and some branches of the northern warm-waters from the Brasil Cur-

rent affect the coastal area. The latter is not a pure mass of sea water as it is exposed to the influence of fresh water apports, to the differential heating produced by shallow depths and to the many other factors which have a great influence over the coastal regions. It modifies among other things salinity and temperature.

Even though the harbour area is affected by the dynamics surrounding waters it shows, because of its sheltered construction, special characteristics which make it different from the natural neighbour localities.

The surface water temperature suffers an annual variation of about 14°C (7-21°C). Temperatures tend to be higher in summer and lower in winter in 1 or 2°C than those of surface waters beyond the harbour entrance.

Salinity ranges from 32 to 34 ‰ and the pH is of about 7.7.

The pollution is appreciable because of the industrial discharged sewage and other apports of water which are common in ports. For its influence over the organisms it has to be always under control.

The surface water oxygen contents ranges among normal values decreasing somehow during those periods of maximum pollution intensity.

The vertical range of tide is of about 90 cm and practically there are not conspicuous currents.

Turbulence is minimum compared with the one of the outside harbour area, but is anyway more important than that of the Mediterranean.

TABLE I

RESULTS OF THE BENTHIC COMMUNITIES STUDIES AT THE PORT OF MAR DEL PLATA, ARGENTINA  
(February 1964)

Key: R Rare  
C Common  
VC Very common  
A Abundant

SAMPLES		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
ALGAE :	<i>Ulva lactuca</i>	C	VC	A	A	C	R	R	R	R	-	-	-
	<i>Enteromorpha</i> sp.	C	VC	VC	-	-	-	-	-	-	-	-	-
	<i>Bryopsis</i> sp.	-	-	-	-	C	C	C	VC	R	R	-	-
	<i>Ceramium</i> sp.	-	-	-	-	C	VC	VC	VC	-	R	-	-
COELENTERATA :	<i>Tubularia</i> sp.	-	-	-	10	-	-	-	-	-	-	-	-
BRYOZOA :	<i>Bugula</i> sp.	-	-	-	-	-	C	A	VC	VC	A	-	-
MOLUSCA :	<i>Pachysiphonaria lessona</i>	3	16	1	-	-	-	-	-	-	-	-	-
	<i>Mytilus platensis</i>	-	10	217	200	134	90	58	30	10	9	9	1
	<i>Brachyodontes rodriguezii</i>	-	-	-	54	71	42	18	8	3	2	2	-
ANNELIDA :	Polynoinae	-	-	-	-	2	9	15	11	7	6	4	2
	Serpulidae	-	-	-	-	3	27	27	10	10	2	6	1
	Spionidae	-	1	-	-	4	-	-	-	-	-	-	-
	Polychaeta errantia	-	-	-	-	-	40	40	74	74	27	32	15
PYCNOGONIDA :	<i>Anoplodactylus</i> sp.	-	-	-	-	1	15	23	8	2	-	5	2
CRUSTACEA :	<i>Balanus</i> spp.	470	590	500	450	285	370	421	280	150	193	29	140
	<i>Exosphaeroma calcarea</i>	-	393	390	477	5	5	2	-	-	-	-	-
	<i>Cyrtograpsus angulatus</i>	-	-	25	19	5	-	2	1	1	-	-	1
	<i>Halicarcinus planatus</i>	-	-	-	-	-	-	1	-	-	-	-	-
	<i>Cyrtograpsus altimanus</i>	-	-	3	27	9	9	16	10	5	13	7	8
	Amphipoda	-	-	-	-	15	56	75	50	24	34	6	10
	<i>Coenophthalmus tridentatus</i>	-	-	-	-	-	-	-	-	-	1	1	-
<i>Plathyxantus crenulatus</i>	-	-	-	-	1	-	-	-	-	-	-	1	
TUNICATA :	<i>Molgula robusta</i>	-	-	-	-	41	30	41	25	14	18	14	12
	<i>Ciona intestinalis</i>	-	-	-	-	-	280	420	330	125	358	317	152

## PRELIMINARY COMMUNITIES STUDIES

Earlier observations on harbour communities were carried out by the author in 1964. On that occasion quantitative and qualitative records on the organisms attached to the harbour breakwaters were made from the high tide line to 3.50 m depth, close to the bottom. For this purpose the aid of SCUBA equipment was necessary.

Samples were taken over a 25 × 25 cm square frame. Values thus obtained are reported in table I.

These data show the evidence of marked quantitative and qualitative differences with data of the outside harbour communities. These differences are due in part to the vertical condition of the substratum which limits the inter-tidal zone to the harbour environmental characteristics.

The Mytilidae communities: *Brachyodontes rodriguezii* and *Mytilus platensis* covers the rocks of the inter-tidal zone except inside the harbour where they have a less importance since they are not dominant species. By other way there is a conspicuous inversion in the vertical distribution of these two species, since in the harbour *Mytilus platensis* appears at higher levels than *Brachyodontes rodriguezii*, while on coastal shores *B. rodriguezii* is the one who covers the upper zones.

At a later date a buoyant substratum kept submerged

from October 1964 to October 1965 was used.

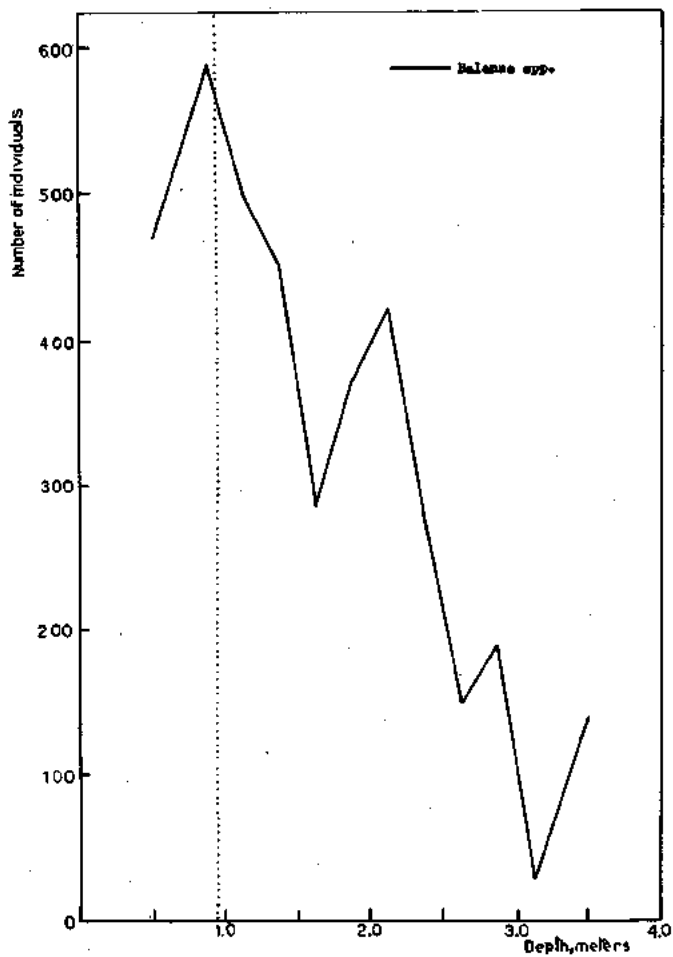
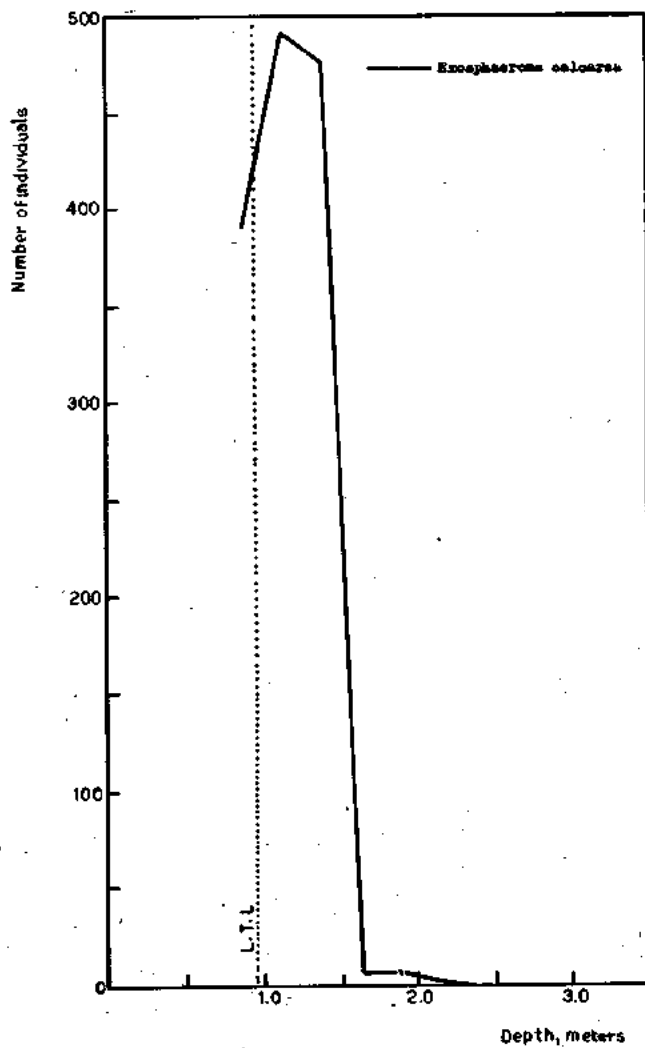
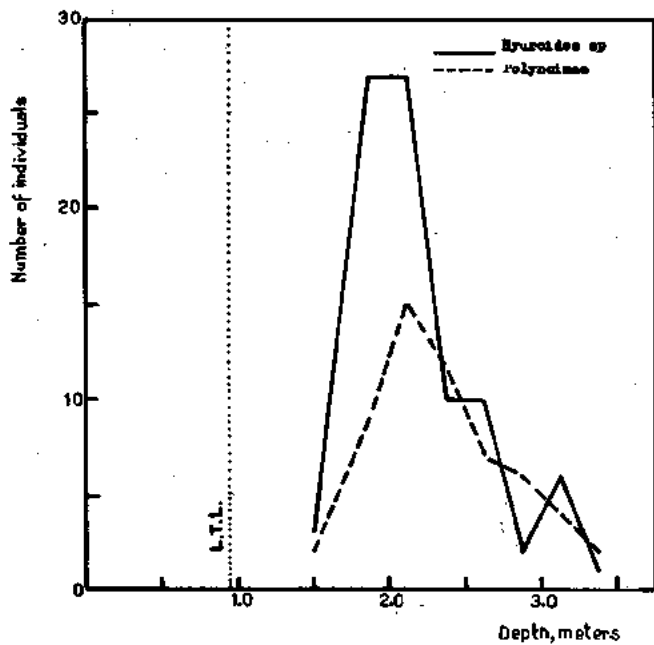
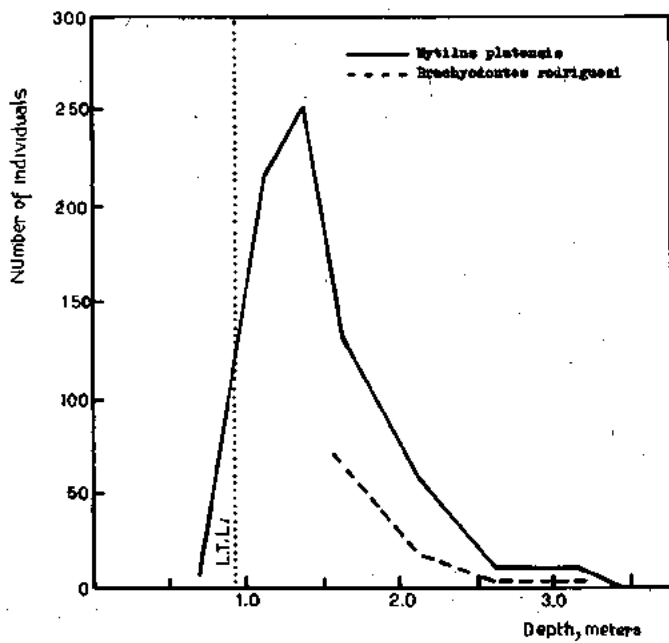
Fouling samples were taken over three 20 × 30 cm panels vertically placed from surface to 1.20 m depth. Data thus obtained are reported in table II. In table III are also included volume, ashes, dry and wet weight determinations data from the principal species.

The results obtained differs in some aspects from those of the former essay. This differences are due to the substratum buoyant condition, which eliminates the tide influence and to the fact that the attachment surface was isolated from the bottom.

## STUDIES ON EXPERIMENTAL RAFT

Studies on experimental raft constitute the present stage of our investigations based on a community biological view as seen through preliminary studies.

The following research plan of investigations has been carried out by members of two institutions, Laboratorio de Ensayo de Materiales e Investigaciones Tecnológicas (LEMIT) and the Instituto Interuniversitario de Biología Marina (IIBM), with the economic aid of the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).



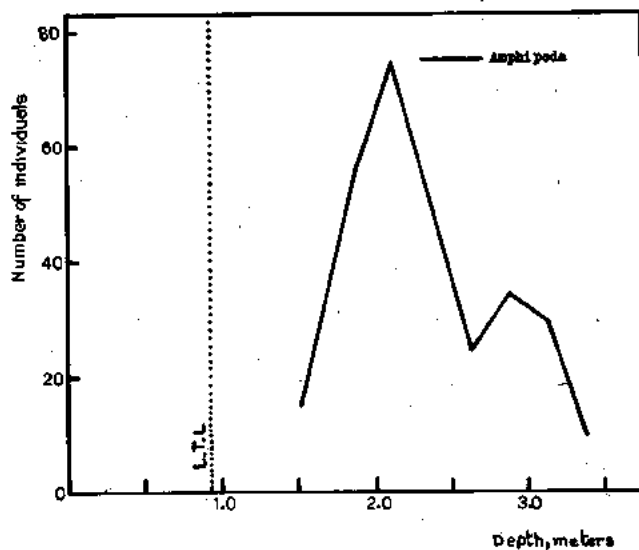
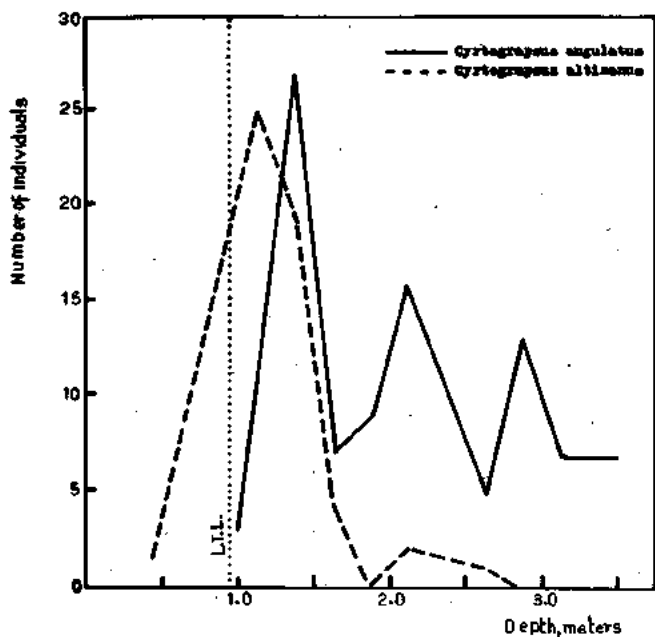
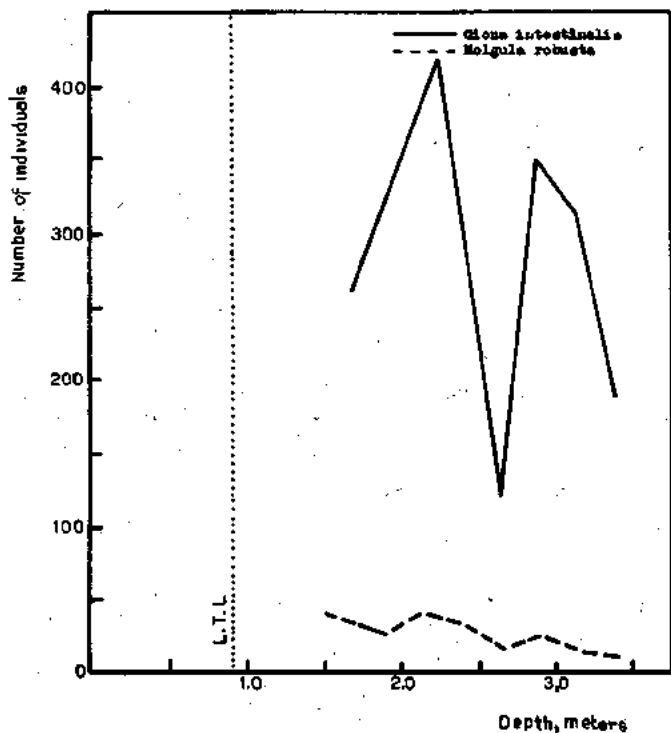


TABLE II

RESULTS OBTAINED ON THE ANNUAL FOULING (OCTOBER 1964/OCTOBER 1965) ATTACHED TO A BUOYANT SUBSTRATUM AT THE MAR DEL PLATA HARBOUR (ARGENTINA)

Key: the same of table I



Panel	A	B	C
<b>ALGAE :</b>			
Ulva lactuca	VC	—	—
Ceramium sp.	C	A	C
<b>COELENTERATA :</b>			
Tubularia sp.	5	—	—
<b>BRYOZOA :</b>			
Bugula sp.	VC	A	A
Membranipora sp.	VC	A	A
<b>MOLLUSCA :</b>			
Mytilus platensis	7	35	21
Brachyodontes rodriguezii	1	22	9
<b>ANNELIDA :</b>			
Polynoinae	6	12	6
Hydroides sp.	2	28	40
Polychaeta errantis	30	39	48
<b>PYCNOGONIDA :</b>			
Anoplódaetylus sp.	1	5	1
<b>CRUSTACEA :</b>			
Balanus spp.	30	49	99
Idothea sp.	5	1	1
Exosphaeroma calcarea	2	—	—
Pachycaeles halgae	1	—	—
Cyrtograpsus altimanus	—	5	9
Amphipoda	3000	5000	3000
<b>TUNICATA :</b>			
Molgula robusta	123	200	181
Ciona intestinalis	13	57	250

TABLE III  
WEIGHT AND VOLUME OF SOME OF THE SPECIES  
REPORTED IN TABLE II

	Wet weight g	Dry weight g	Ashes g	Volume ml
<i>Ulva lactuca</i>	4,130	0,680	0,120	4
<i>Bugula</i> sp.	7,010	0,780	0,490	3
<i>Membranipora</i> sp.	4,130	1,150	0,980	2
<i>Amphipoda</i> (for 500 individuals)	—	2,400	0,645	2
<i>Molgula robusta</i>	83,400	5,710	1,391	100
<i>Ciona intestinalis</i>	24,320	1,200	0,160	30

The first part of the plan consists in monthly investigations throughout a year (september 1966/september 1967) which will give an idea of the development of the fouling community from its initial attachment and also a monthly attachment information for each species.

At the same time periodical records of the medium abiotic conditions are being carried out.

#### METODOLOGY

Thirteen frame panels containers from the raft for biological studies were used. The rest of them were kept for paint tests.

Each frame holds four 30 × 40 cm sanded acrylic panels vertically placed from surface to 1.50 m depth. Twelve of the frames are used to record the annual accumulative fouling and the remaining one is used for monthly attachments. Before sampling each panel, photographs are taken to document the distribution of the principal species.

At present we have only reached up to the 6th month of attachment investigations (september/march). For this reason we are only giving a general scheme with diagrams showing the monthly attachment for the main species while the data on the community development obtained from the accumulative panels, which are still incomplete, are excluded.

A great number of the organisms recordered through these investigations are rather unknown in our country. The sistematic work presents some difficulties because of the lack of specialists in this subject. For this reason many of the organisms are included in the present paper as genus or in higher taxonomic categories. Their definitive taxonomic place will be determined at the end of the investigations.

#### CONCLUSIONS

Preliminary conclusions on monthly fouling obtained through half-year researchs are given below:

- There are alternative periods of intense and weak fouling attachments during summer and winter respectively.
- The fouling organisms succession follows the same mechanism as in other latitudes. It starts with bacteria-diatoms-protozoa complex, finishing with higher organisms associations.
- Many of the organisms shows an accentuated growth and the vital cycle is completed in a short period of time. This involves a great possibility of substitution which is proved in practice since many organisms die before a month of attachment and are substituted by others.

- The fact that it can be observed the attachment of organisms on the accumulative panels, not recorded on monthly panels, proves that certain species requires an established community to continue their development after the attachment.

#### APPENDIX

MONTHLY ATTACHMENT FREQUENCY OF MAIN ORGANISMS ALONG FOUR VERTICAL PANELS (ABCD), PLACED ON EXPERIMENTAL RAFT FROM SURFACE TO 1,50 m DEPTH (Mar del Plata, September 1966/September 1967).

- ALGAE: Bacillariophyta.
- ALGAE: Chlorophyta - *Enteromorpha intestinalis*
- ALGAE: Chlorophyta - *Ulva lactuca*.
- ALGAE: Chlorophyta - *Bryopsis plumosa*.
- ALGAE: Rhodophyta - *Polysiphonia* sp. + *Ceramium* sp.
- COELENTERATA - *Tubularia crocea*.
- COELENTERATA - *Gonothyrea inornata* + *Obelia angulosa*.
- NEMATODA.
- BRYOZOA - *Bugula* sp.
- BRYOZOA - *Bowerbankia gracilis*.
- MOLLUSCA - *Eubranchus* sp.
- ANNELIDA - *Eupomatus* sp. + *Hydroides norvegica* + *Mercierella enigmatica* + *Serpula vermicularis*.
- CRUSTACEA: Copepoda - *Tisbe furcata* + *Harpacticus* sp.
- CRUSTACEA: Amphipoda - *Corophium* sp.
- CRUSTACEA: Cirripedia - *Balanus trigonus* + *Balanus amphitrite*.
- CRUSTACEA: Decapoda - *Cyrtograpsus angulatus*.
- TUNICATA - *Ciona intestinalis*.
- TUNICATA - *Molgula robusta* + *Molgula manhattensis*.

LIST OF SPECIES SETTLED MONTHLY DURING SEPTEMBER 1966/SEPTEMBER 1967.

#### ALGAE

*Bacillariophyta*  
*Amphora* sp.  
*Cocconeis* sp.  
*Grammatophora* spp.

*Licmophora lyngbyei* fa. *elongata*  
*Licmophora lyngbyei* fa. *abbreviata*  
*Licmophora lyngbyei* fa. *minor*  
*Navicula* spp.  
*Nitzschia closterium*  
*Nitzschia longissima*

*Pinnularia* sp.  
*Plagiogramma* sp.  
*Thalassiothrix nitzschoides*  
*Pleurosigma* sp.  
*Synedra affinis*  
*Coccinodiscus* sp.  
*Melosira sulcata*

#### Cyanophyta

*Lyngbia lutea*  
*Microcoleus tenerrinus*  
*Phormidium corium*

#### Chlorophyta

*Cladophora* sp.  
*Enteromorpha intestinalis*  
*Ulva lactuca*  
*Bryopsis plumosa*

Rhodophyta

*Polysiphonia* sp.  
*Ceramium* sp.

PROTOZOA

*Peridinium* sp.  
*Amoeba* sp.  
*Zoothamnium* sp.  
*Vorticella* sp.  
*Euplotes* sp.  
*Frontonia* sp.  
*Trachelonema* sp.  
*Lacrymaria* sp.  
*Mesodinium* sp.

COELENTERATA

*Tubularia crocea*  
*Gonothyrea inornata*  
*Obelia angulosa*

NEMERTEA (in litt.)

ROTIFERA (in litt.)

NEMATODA (in litt.)

BRYOZOA

*Bugula* sp.  
*Bowerbankia gracilis*  
*Membranipora* sp.

MOLLUSCA

*Eubranchus* sp.

*Siphonaria lessoni*  
*Buccinanops* sp.  
*Saxicava solida*

ANNELIDA

*Eupomatus* sp.  
*Hydroides norvegica*  
*Mercierella enigmatica*  
*Serpula vermicularis*  
*Polydora ciliata*  
*Syllis robertianae*

CRUSTACEA

Copepoda  
*Tisbe furcata*  
*Harpacticus* sp.

Amphipoda  
*Corophium* sp.

Cirripedia

*Balanus amphitrite*  
*Balanus trigonus*

Decapoda

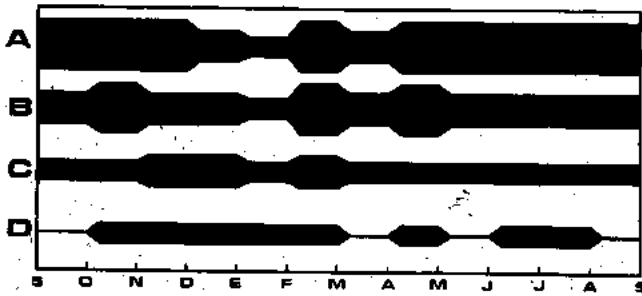
*Cyrtograpsus angulatus*  
*Cyrtograpsus altimanus*

TUNICATA

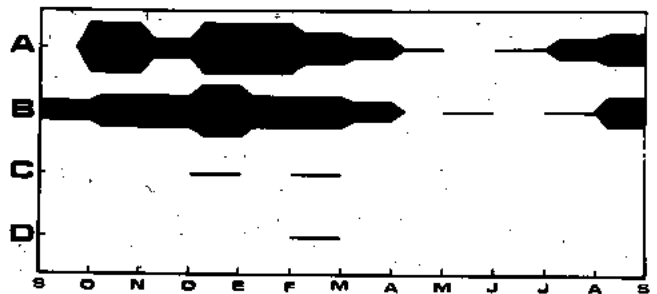
*Ciona intestinalis*  
*Molgula robusta*  
*Molgula manhattensis*  
*Molgula occidentalis* (?)

Note: The Graphs on pages 559 and 560 are referring to vertical distribution based on the results reported in Table 1.

GRAPHS OF MONTHLY ATTACHMENT FREQUENCY OF MAIN ORGANISMS (APPENDIX p. 561).

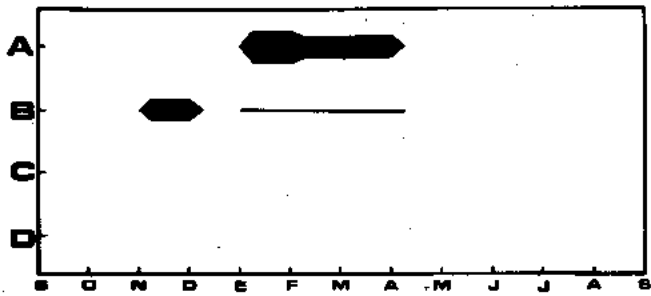


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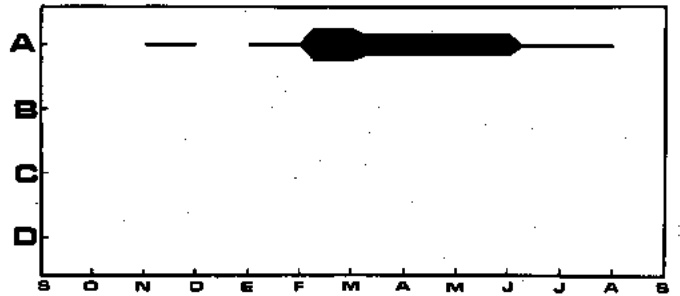


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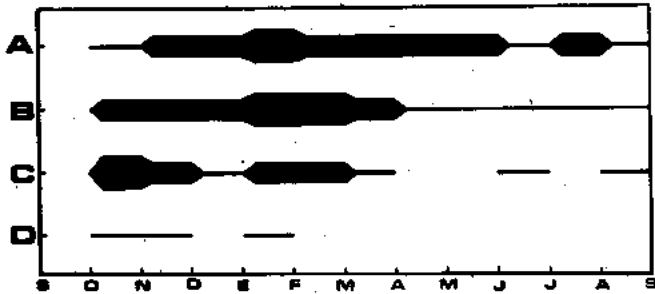




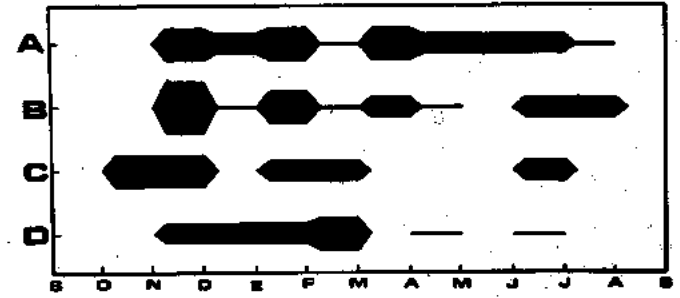
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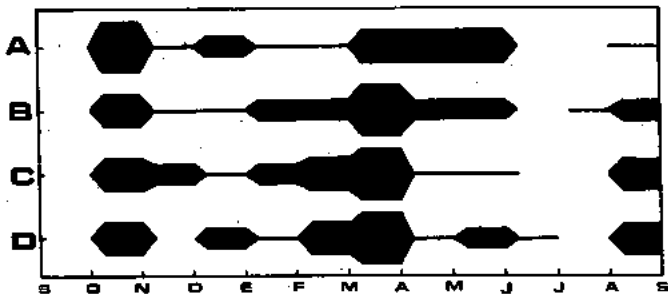
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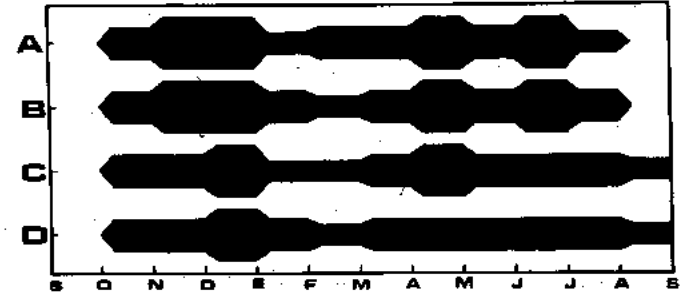
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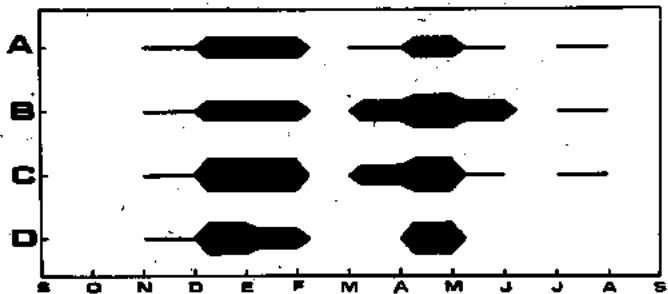
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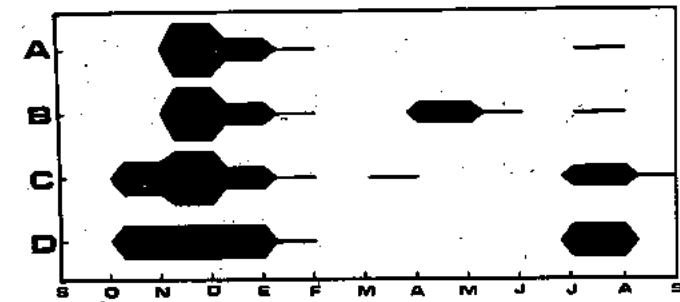
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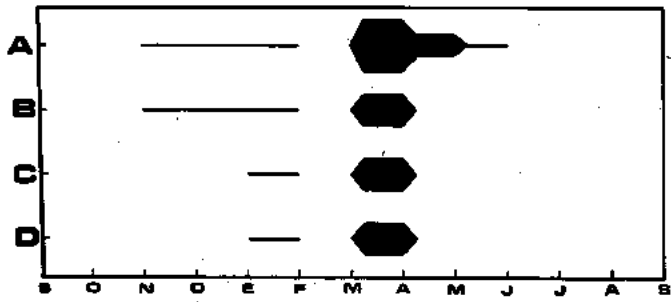
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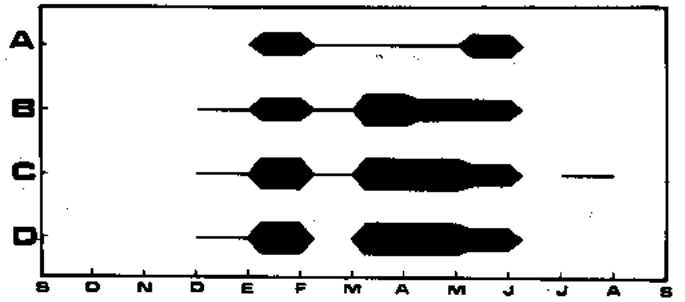
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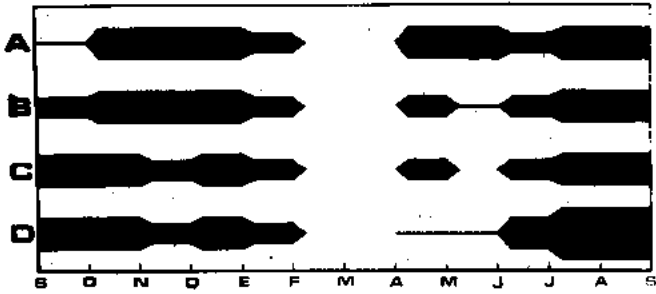
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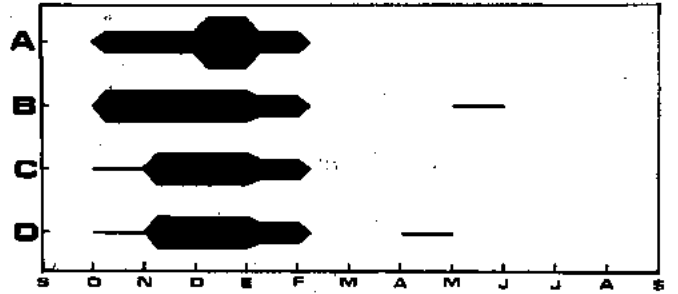
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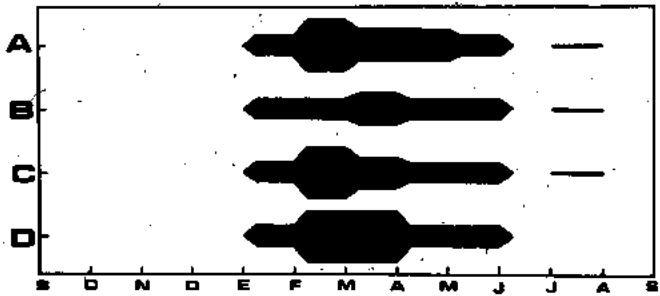
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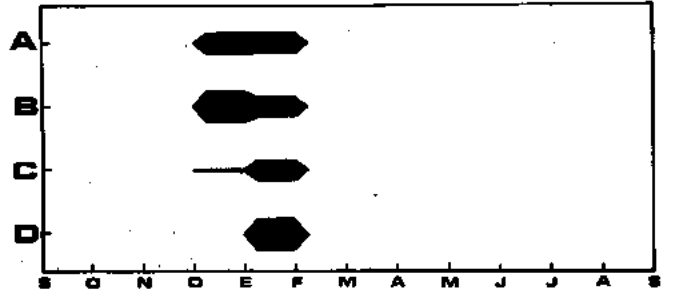
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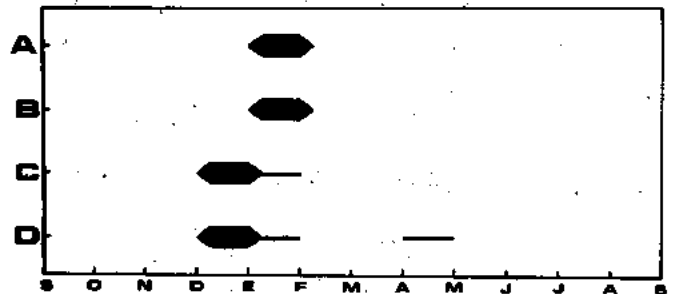
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18

# STUDIES ON MARINE FOULING AND BORING ORGANISMS IN BOMBAY HARBOUR

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## SUMMARY

The development and composition of the fouling on any submerged structure in the sea depends on the type of natural fauna or population locally present. It has been accepted that the underwater deterioration caused by the fouling organisms is far more severe in tropical waters than in temperate waters. The study under report has indicated that the major fouling species in Bombay harbour belong to class hydrozoa, cirripedia, polychaeta, bryozoa and tunicata.

It is observed that barnacles from Bombay chiefly comprise the Indo-Pacific forms with Malayan elements. Some of them are widely distributed and are reported from Malay Archipelago, Pacific Ocean, Mediterranean, Atlantic Ocean and Indian Ocean.

Year to year observations on incidence of fouling growth have shown that there is a good uniformity in the species involved and also in their abundance. The seasonal variations as a result of varying salinity and temperature have been,

however, observed.

In Bombay, fresh settlements of tunicates, hydrozoans and bryozoans may occur during the monsoon since these organisms can sustain low salinity conditions. It is observed that *Electra* spp. are the early settlers on the underwater structures protected with antifouling paints containing copper.

A preliminary study of micro-organisms has revealed the presence of 15 species of cellulolytic bacteria that bring about deterioration of cellulosic material. Fungal species associated with similar type of deterioration have also been identified. A composition of the primary film that induces marine fouling has been studied in detail.

*Teredo furcifera*, a common wood borer in Bombay waters, is found to be a fast growing species that attains maturity only after 20 days of growth. It liberates young-ones continuously and more than 7000 of them are liberated at a time.

## INTRODUCTION

The underwater deterioration caused by the marine organisms is far more severe in tropical than in temperate waters<sup>1</sup>. The tropical water is considered to be very productive and hence supports a rich and varied animal life. However, very little is known about these organisms and only a small number of them have been identified and described<sup>2-3</sup>. The taxonomic and life-history studies in respect of these organisms, particularly, are far from complete. Occurrence of some destructive fungi, crustacean borers and copper resistant bryozoans in Indian waters has added to the severity of the fouling and borer problem in this region. The object of this work was to identify major fouling and boring species incident in Bombay harbour and to collect information on their breeding and settlement characteristics.

## EXPERIMENTAL

For these observations, non-toxic panels were immersed at three different localities viz (a) experimental raft in the middle ground, (b) Burmah Shell Refinery jetty at Trombay, (c) breakwater area at Naval Dockyard. Test boards were examined at weekly intervals. For trapping the wood worms, timber panels of Himalayan fir (*Abies pindrow*) were used.

## RESULTS

List of marine fouling organisms encountered during the present study.

### 1) Primary film

#### a) Bacteria

*Achromobacter pestifer*

*A. superficialis*

*A. aquamarinus*

*A. guttatus*

*A. sp.*

*Bacillus coagulans*

*Cellulomonas acidula*

*C. galba*

*C. gelida*

*Flavobacterium peregrinum*

*F. okeanoites*

*Micrococcus luteus*

*Kurthia zophii*

### b) Diatoms

*Melosira* sp.

*Navicula* sp.

*Bacillaria* sp.

*Amphora* sp.

*Nitzschia* sp.

*Surirella* sp.

*Rhopalodia* sp.

*Mastogloia* sp.

### c) Fungi

*Plectomycetes* sp.

*Aspergillus* sp.

*Cladosporium* sp.

*Halosphaeria* sp.

### d) Protozoans

*Stylonychia* sp.

*Zoothamnium* sp.

*Euploes* sp.

*Epistylis* sp.

*Vorticella* sp.  
*Laxodes* sp.

2) *Coelenterata*

*Pennaria* sp.  
*Alcyonaria* sp.  
*Actinaria* sp.  
*Plumularia* sp.  
*Hydractinia* sp.  
*Sertularia* sp.  
*Telesio* sp.

3) *Polychaeta - Annelida*

*Nereis* sp.  
*Dasychone* sp.  
*Hydroides* sp.  
*Sabellid* sp.  
*Pomatoceros* sp.  
*Polynoe* sp.  
*Spirorbis* sp.

4) *Bryozoa*

*Amathia* sp.  
*Victorella* sp.  
*Zoobotryon* sp.  
*Nolella paupensis*  
*Nolella* sp.  
*Mammillopora* sp.  
*Membranipora savarti*  
*Scrupoecellaria scruposa*  
*Acanthodesia* sp.  
*Bugula neritina*  
*Electra* sp.  
*Caulibugula* sp.  
*Schizoporella* sp.  
*Conopeum* sp.  
*Bowerbankia* sp.  
*Alserina smithi*

5) *Cirripedia*

*Balanus tintinnabulum tintinnabulum*  
*B. tintinnabulum zebra*  
*B. amphitrite variegatus*  
*B. a. communis*  
*B. a. hawaiiensis*  
*B. a. cochinchensis*  
*B. a. denticulata*  
*B. a. insignis*  
*Balanus calidus*  
*B. amaryllus eumaryllis*  
*B. amaryllus nivea*  
*Chthamalus malayensis*  
*Ch. withersi*  
*Tetraclita purpurascens*

6) *Marine borers*

a) *Teredid worms*

*Teredo furcifera* M = (*T. parksi*)  
*Teredo* (*Kuphus*) *manni* Wright  
*Teredo elongata*  
*Lyrodus pedicellatus*  
*Bankia* (*Bankiella*) *consularis*  
*Bankia campanellata*

b) *Pholads*

*Martesia fragilliss*  
*Pholad* sp.

c) *Crustaceans*

*Limonoria indica*  
*Sphaeroma* sp.

*Details of fouling examination in Bombay harbour 1962-66.*

The test boards holding non-toxic experimental panels were periodically examined during the period 1962-1966. The following are the results of this examination.

Month	Observations
January	Heavy growth of hydroids, barnacles and amphipods. Settlement of encrusting bryozoa moderate. Other organisms noted are polychaete worms, gastropods, <i>Mytilus</i> and <i>Scapharca</i> .
February	Hydroids and barnacles dominate general fouling; amphipods observed. Sabellid worm, sea anemone and encrusting bryozoan attack moderate. Other organisms noted are Oysters, <i>Mytilus</i> , <i>Scapharca</i> and gastropods.
March	Heavy barnacle and hydroid growth noted; sabellid settlement moderate. Other organisms: sea anemone <i>Alcyonaria</i> and gastropods.
April	Heavy growth of hydroids; barnacle settlement moderate to heavy; moderate settlement of <i>Hydroides</i> sp., encrusting bryozoa and sea-anemone.
May	Heavy settlement of hydrozoans and amphipods; barnacle settlement moderate. Sea-anemone attack and bryozoan settlement moderate; ascidians noted.
June	Hydroid and barnacle settlement moderate; sea-anemone settlement poor; bryozoan settlement occurs; other organisms are ascidians, <i>Alcyonaria</i> , oysters and <i>Hydroides</i> sp.
July	Fresh hydrozoa and sea-anemone settlement occurs and survives monsoon. Encrusting bryozoa noted; other organisms are <i>Alcyonaria</i> etc.
August	Hydroid settlement heavy; a large number of encrusting bryozoa noted. Sea-anemone growth moderate. Barnacle settlement poor.
September	Hydrozoa and ascidian settlement heavy; fresh polyzoan settlement occurs; barnacle settlement moderate; Other organisms noted are <i>Hydroides</i> sp. and oysters.

Month	Observations
October	Very heavy growth of hydrozoa, barnacles and sea-anemones noted. Other organisms noted are sponges, ascidians and <i>Scapharca</i> .
November	Heavy hydrozoa and sea-anemone growth noted. Barnacle settlement moderate to heavy.
December	Hydrozoa growth exuberant; sea-anemone growth heavy; barnacle settlement moderate and bryozoan growth in patches. Other organisms noted are oysters, amphipods, sponges and ascidians.

The causes of annual variations in fouling are unknown<sup>4</sup>. In Bombay harbour, however, it is noted that the scarcity or poor occurrence of one species may increase the number of others. This is particularly true in respect of softer organisms such as bryozoans and tunicates. Besides this inter-relationship the varying salinity of the seawater also influences the quality and quantity of the fouling in Bombay harbour (Table 1). It influences particularly the breeding potential in certain sedentary forms<sup>4</sup>.

*General observations on settlement and growth.*

All the major fouling groups have been encountered in Bombay harbour. Amongst these, however, Hydroids, Poly-

TABLE 1

SHOWING MONTHWISE MEAN SEAWATER TEMPERATURE, MEAN ATMOSPHERIC TEMPERATURE AND TOTAL HOURS OF SUNSHINE IN BOMBAY HARBOUR DURING 1963-64

Sr. No.	Period	Mean seawater temperature	Mean atmospheric temperature	Range maximum temperature (°C)	Mean sunshine (hours)
1	March	27.0	30.7 <sup>+</sup>	27.6 - 35.0	9.3
2	April	31.4	32.1	29.6 - 35.4	10.1
3	May	33.0	33.4	32.6 - 34.1	10.4
4	June	30.6	32.0	27.7 - 35.0	5.75
5	July	29.0	30.0	26.7 - 31.7	3.0
6	August	26.9	29.0	26.4 - 31.3	2.0
7	September	28.1	30.5	26.5 - 32.8	5.4
8	October	29.1	32.1	29.6 - 34.7	8.4
9	November	28.0	32.9	27.2 - 35.5	7.9
10	December	26.4	28.5	27.4 - 35.6	7.4
11	January	24.4	27.7	23.8 - 34.6	9.0
12	February	24.4	28.5	25.3 - 34.2	9.3

chaeta, Hydrozoa, Cirripedia and to a certain extent, Mollusca are the important groups that cause severe fouling of the ships and water-front constructions (Fig. 1). A general account of each of these groups with respect to their biological activity is given below:

- (a) *Hydroids*. The hydroid fouling in Bombay harbour is both rich and varied. Dense growths of *Pennaria*, *Plumularia*, *Sertularia*, *Alcyonaria*, *Hydractinia* and *Actinaria* have been observed generally throughout the year. A very heavy growth of *Pennaria sp.* and *Sertularia sp.* is noted during January to May and again during October - November. A single colony may attain a size of 4" in length, only within four to five weeks. Hydroids together with barnacles and amphipods, therefore, can cause severe blockage of the conduits and filters. Hydroids are also the major ship fouling species in Bombay harbour and are responsible to a very great extent, for the damage of the protective coatings on the ships' hulls. It was noted that the settlement of *Actinaria sp.* invariably checked the settlement of other major fouling species. The fresh occurrence of hydrozoans in Bombay harbour even during heavy monsoon is of interest. Many of the species examined show preference for the edges of the test blocks and experimental panels.
- (b) *Polychaeta*. As many as seven different species are commonly noted in the Bombay harbour. Of these, however, *Hydroides sp.* and *Sabellid sp.* are the major fouling organisms. The attack of these polychaete worms is severe during the warmer months and although many of them survive the monsoon, a fresh settlement during this period is uncommon. Luxuriant growth of *Hydroides sp.* is noted in the wet-basin at the Naval Dockyard Bombay, where the water is comparatively stagnant. Barnard<sup>6</sup> has suggested that tubicolous worms normally grow abundantly in highly polluted waters. This has also been noted in Bombay. It has been observed with interest that calcareous tubeworms settle and grow in great abundance on the blades of the propellers of the I.N. Ships. Sabellid worms occur throughout the year and may attain a size of 5" in tube-length even during the monsoon months.
- (c) *Bryozoans*. Quite a large number of both erect and encrusting bryozoans are encountered in Bombay

harbour. Systematic study of this group has revealed the presence of nearly seventeen or more species. This is a major fouling group in Bombay water and fresh occurrence, particularly of the encrusting forms is noted throughout the year, even during the monsoon. A very heavy and crowded growth is, however, noted during the month of October. The growth of encrusting polyzoa is largely dependent on the occurrence of other fouling organisms, at least in respect of certain species. For example, during the monsoon when the settlement of barnacles, hydroids and other organisms is poor, the encrusting bryozoans, particularly *Electra spp.*, are amongst the first few early settlers on newly painted hulls of the ships in



Fig. 1. Marine fouling growth in Bombay harbour six week exposure.



Fig. 2. *Acanthodesia* sp., an encrusting-bryozoan grows six to seven inches in diameter in six weeks period.

Bombay harbour. In Australian waters also the occurrence of copper resistant species of bryozoa viz. *Watersipora cuculata* has been reported<sup>7</sup>. Of the 17 polyzoan species, *Bugula* sp., two *Electra* spp., *Membranipora* sp. and *Acanthodesia* sp. are common ship fouling forms in Bombay harbour. Erect species such as *Zoobotryon*, *Amathia*, *Bowerbankia*, *Bugula*, *Scrupocellaria* and *Caulibugula* are encountered, both in inshore waters and in the open sea. The first three forms are, however, more common in inshore region. *Acanthodesia* sp. may attain very big dimensions and is perhaps the biggest single encrusting colony noted in the Bombay harbour (Fig. 2). As mentioned earlier, the bryozoan settlement also occurs during monsoon and the forms encountered are *Acanthodesia* sp., *Electra* sp. and *Membranipora* sp. Amongst the erect forms *Caulibugula* sp. and *Nolella paupensis* may settle and grow during the monsoon.

(b) *Cirripedia*. Barnacles constitute a major group of fouling organisms in Bombay harbour. As many as 15 species of these shell-dwelling crustaceans have been reported from Bombay waters<sup>8,9</sup>. Species such as *Balanus amphitrite variegatus*, *B. a. communis*, *B. amaryllus euamaryllis* and *B. tintinnabulum tintinnabulum* largely contribute to the fouling community on ships' hulls (Fig. 3). *B. a. euamaryllis* and *B. t. tintinnabulum* besides being present on the ships' hulls are also found plentifully on surf-washed rocky shores at various localities around Bombay. Of these seven varieties of *Amphitrite* series, *Balanus amphitrite variegatus*, *B. a. insignis*, *B. a. venustus* and *B. a. denticulata* are essentially off-shore species. On the otherhand, *B. a. communis*, *B. a. hawaiiensis* and *B. a. cochinensis* are intertidal barnacles.

Inter-relationships in respect of eight varieties of *Amphitrite* series have been discussed in earlier papers<sup>8,10</sup>. A plate (Fig. 4) showing variations in opercular valves of eight varieties encountered at Bombay is given here. It is felt that illustrations such as this may help to identify these varieties and may throw some light on «*communis-denticulata-hawaiiensis*» problem confronting cirriped biologists. These three varieties can be separated from one another at Bombay. However, as suggested by Stubbings and others, a further study on this aspect of cirriped taxonomy is necessary.

From a general literature survey of the cirriped



Fig. 3. *Balanus amphitrite communis*, six weeks exposure. Life span of this species is more than two years. *B. tintinnabulum* (left), *B. a. euamaryllis* (right).

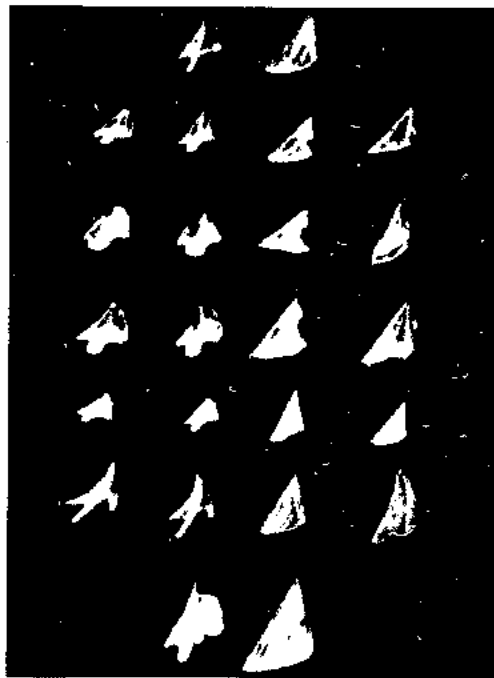


Fig. 4. Opercular valves of *Balanus amphitrite* varieties. From top to bottom row, *variegatus communis*, *hawaiiensis*, *cochinensis*, *denticulata*, *insignis* and *venustus*.

fauna, it is observed that the barnacles from Bombay chiefly comprise the Indo-Pacific forms with Malayan elements. Of the fifteen barnacles encountered at Bombay, two viz. *B. a. cochinensis* and *B. a. insignis*, both originally described by Nilsson-Cantell<sup>2</sup> exclusively belong to the Indian ocean. The former is recorded from Cochin and the latter from Sumatra. The *Chthamaliid* barnacles described here have been earlier reported from Malaya Archipelago, Formosa and Japan. Two *Chthamaliid* varieties viz. *Ch. moro* and *Ch. malayensis* have been found to be synony-

TABLE 2

SHOWING MEAN OVARY INDEX (GROWTH), MEAN MATURITY INDEX AND PERCENTAGE OF FERTILIZED INDIVIDUALS IN FOUR SPECIES OF BARNACLES

Period	B. a. communis			B. a. hawaiiensis			Ch. malayensis			Ch. withersi		
	Mean ovary growth index	Mean ovary maturity index	% fertilized	Mean ovary growth index	Mean ovary maturity index	% fertilized	Mean ovary growth index	Mean ovary maturity index	% fertilized	Mean ovary growth index	Mean ovary maturity index	% fertilized
1) March	3.3	2	66	3.0	2.24	63	3.16	2.0	56	1.25	1.89	38
2) April	3.0	2.1	64	3.3	2.08	68	3.0	2.4	40	1.4	0.84	3
3) May	2.88	1.1	13	1.0	0.96	6	2.7	3.0	64	2.22	1.02	8
4) June	2.1	1.86	44	3.0	2.22	66	2.05	2.5	60	1.16	0.85	0
1) July	2	1.3	20	2.0	1.24	18	0.74	0.65	2	0.46	0.69	11
2) August	2.8	1.0	13	1.6	1.12	30	0.81	0.60	0	0.72	0.54	1
3) September	1.8	1.65	30	1.8	1.1	3	2.02	1.28	10	1.15	1.35	21
4) October	3.0	2.22	64	3.0	2.65	70	2.21	1.26	38	2.32	1.08	16
1) November	1.22	0.98	16	2.2	1.28	25	0.78	0.56	5	0.98	1.04	6
2) December	1.73	0.94	19	—	—	—	0.79	0.80	6	0.92	0.92	0
3) January	2.41	1.48	32	—	—	—	0.73	0.64	0	1.07	0.96	1
4) February	2.44	1.2	23	—	—	—	2.46	1.2	13	1.07	1.1	18

mous<sup>8</sup>. Among others *B. a. hawaiiensis*, *B. a. variegatus*, *B. a. euamaryllis*, *B. a. nivea* and *Tetractita purpurascens* have been recorded from the Indian ocean. In view of the synonymy between *B. a. hawaiiensis* and *B. a. denticulata*, Utinomi<sup>11</sup> records a world wide distribution of the former species. Three other barnacles viz. *B. a. communis*, *B. a. venustus* and *B. t. tintinnabulum* are also widely distributed and have been reported from the Malaya Archipelago, Pacific Ocean, Mediterranean sea, Atlantic Ocean and Indian Ocean.

In Bombay harbour, the settlement of barnacles occurs throughout the year. However, during the monsoon, the barnacle fouling is considerably low. It is during February to June and October - November, the settlement activity is very intense. The poor settlement noted during the monsoon can easily be attributed to the low salinity. It is known that most of the organisms do not survive under low salinity conditions. Iyengar and others<sup>12</sup>, while reporting on fouling in Bombay harbour, noted stunted growth during period of low salinity. Under these severe conditions, cessation of gametogenesis and fertilisation leading to the failure of breeding activities can easily be understood. A detailed account of breeding in respect of four common barnacles has been published earlier<sup>5, 10</sup>. Table 2 gives a summary of the same.

e) *Mollusca*. Some of the important fouling molluscan species noted in Bombay harbour are Oysters, Mytilus and Scapharca. Of these three, first two are of fairly common occurrence although not a very serious pest. Oyster growth is generally heavy during the warmer months (February to June). No Oyster growth was recorded during the monsoon period. As mentioned earlier, Mytilus is not a serious pest but whenever they occur, particularly on ships hulls, they predominate over other fouling species. A very thick mat of Mytilus growth often completely covers the underwater surface of the ship, leaving no free space for the settlement of other organisms. This, however, has been noted on the hulls of small ships, particularly those plying in the coastal waters only.

f) *Ascidians*. Six different species of simple and Compound Ascidian foulers have been noted in Bombay harbour. Of these, three compound ascidians were encountered in the water-front constructions and these did not settle either on moving structures or on the experimental raft in the middle ground. Simple ascidian, *Ascidialla* sp. is very common form in the Bombay harbour. Ascidian growth is very intense during March to June and they survive early monsoon also. In July i.e. in the midst of monsoon, all six species may occur on one and the same exposure panel. Like encrusting bryozoans, it seems, the settlement and particularly the growth of the ascidians is influenced by the presence of other fouling groups. During the monsoon, compound-ascidians may settle and grow very fast.

g) *Primary film*. As a first step in understanding the role of micro-organisms, if any, in conditioning the timber for attack by marine foulers, the sequence of settlement of micro-organisms was also investigated at this Laboratory<sup>13</sup>. Examination of the glass panels after first 24 hours showed the presence of only a few species of bacteria and detritus. After 48 hours diatoms appeared gradually increasing in number with the period of exposure. The genera of the diatoms encountered on the glass panels in order of their abundance were *Melosira*, *Navicula*, *Achnanthes*, *Bacillaria*, *Amphora*, *Nitzschia*, *Surirella*, *Rhopalodia* and *Mastogloia*. Amongst protozoans encountered and identified *Epistylis* and *Verticella* sp. were dominant. The fungi isolated from wood submerged in the sea included species belonging to genera *Plectomycetes*, *Aspergillus*, *Cladosporium* and *Halosphaeria*. The soft, rot fungus *Halosphaeria quadriocornuta* has been reported earlier from Catamaran fishing boats in South India. In the present investigation also this fungus was observed only on wood immersed in surface waters. The fungi were present only on the superficial layers of the submerged wood.

The laboratory investigations were undertaken with a view to ascertaining the role of primary film in inducing settlement of marine fouling and boring organisms. It has been observed that larvae of *Teredo furcifera* do not show any particular

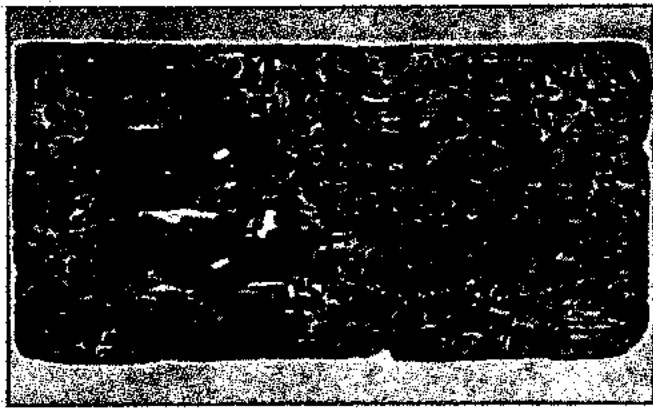


Fig. 5. *Teredid* attack in Bombay harbour, six to seven week exposure.

preference for «filmed» blocks over clean ones, the latter being sterilized at 15 lb/sq. in. for 20 minutes<sup>14</sup>. The settlement of fouling organisms such as *Hydroides* sp. *Spirorbis* sp., *Asciodiella* sp. and *Nolella* sp. has occurred readily on sterilised microscope slides under laboratory conditions.

h) *Wood borers*. The marine borer damage in Bombay harbour and adjoining areas is very severe (Fig. 5). *Bankia* sp. for example, burrows twelve inches long tunnels in barely six weeks period. Green-heart timber, which has a reputation of being *Teredo* resistant is also affected by borers in Bombay harbour (Fig. 6). Incidentally, an indigenous timber *Tetrameles nudiflora* has been found to be naturally resistant to *Teredid* attack<sup>15</sup>. Amongst molluscan borers, *T. furcifera* is widely distributed and is more destructive than other species encountered at Bombay.

Attack of *T. furcifera*, though with varying intensity, occurs all the year round in Bombay harbour. It is the seasonal change in gonadal activity rather than change in salinity or temperature that determines the intensity of borer attack. This is evident by the fact that in any month the

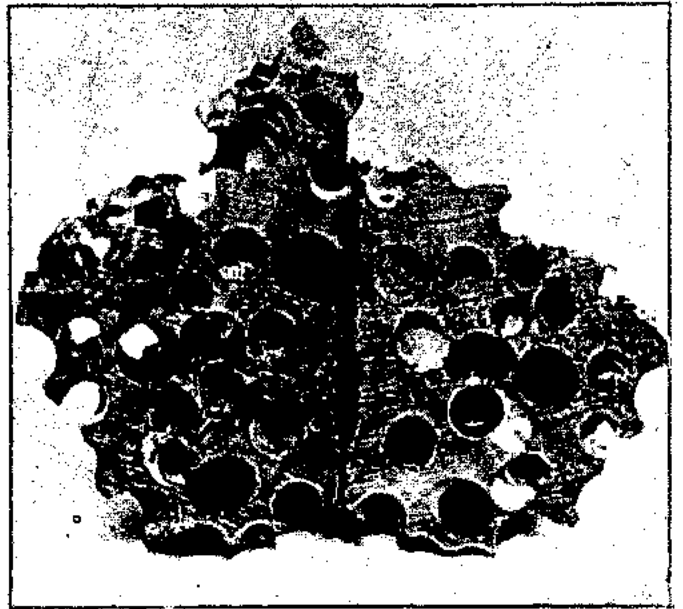
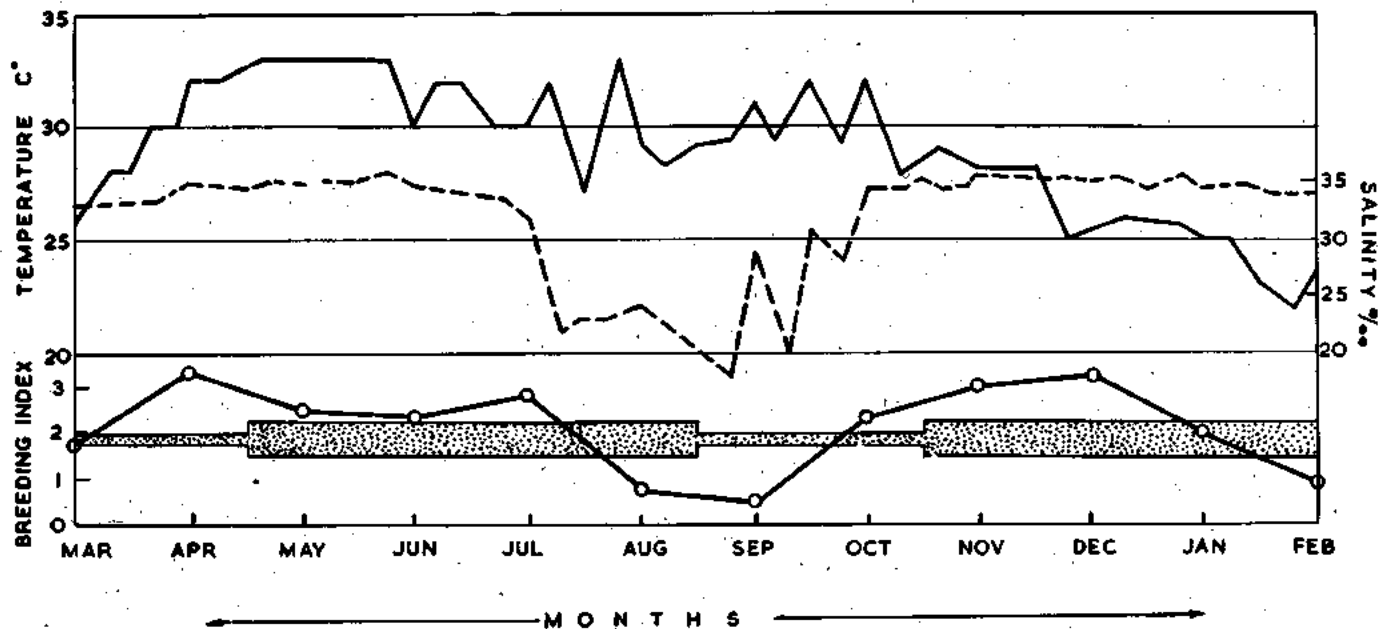


Fig. 6. Green heart timber, a reputed borer resistant species suffers damage in Bombay harbour.

borer damage, heavy or moderate, is determined by the figure of breeding index in the preceeding month (Fig. 7). The larvae may settle and metamorphose when the salinity of ambient water is as low as 10-15‰.

The development of gonads and the subsequent metamorphosis of larvae in the brood during the first fifty days of growth of this borer has been summarised in Table 3. It is evident that this species becomes sexually mature when it is barely twenty days old. This is of interest since the same species in Hawaiian waters, as reported earlier<sup>16</sup>, attains

#### TEREDO ATTACK IN BOMBAY HARBOUR



Broad and narrow dotted stripes denote heavy and moderate attack respectively; (----) Salinity, (—) temperature, (°—°) breeding index.

Fig. 7. *Teredo furcifera* attack in Bombay harbour.



TABLE 3

BREEDING INDEX IN *T. FURCIFERA* DURING THE FIRST 50 DAYS OF GROWTH

Exposure period (Days)	Average breeding index	Predominant stage
20	0.71	Developing ova.
30	1.08	Unfertilized eggs.
40	2.11	Early veliger
50 - 55	2.73	Veliger or Pedi-veliger

sexual maturity after sixty days. *T. furcifera* in Bombay waters liberates pediveligers 55 to 60 days after its settlement. The fastest growing *Teredo sp.*, however, appears to be a native of Pago Pago, American Samoa Island, where according to one report<sup>17</sup>, wood-worms liberate swimming larvae after twenty four days of growth.

The breeding potential of *T. furcifera* increases as the animal grows older and it is estimated that one single brood may hold at a time more than 30,000 pediveligers. The highest number of pediveliger larvae, individually counted from the first brood of fifty days old organism was found to be 7,000. During the development of the larvae, three distinguishing growth stages viz. early veliger, veliger and pediveliger, measuring  $73,221 \pm 0.02$  and  $285 \pm 0.03$ , respectively, can be identified. Pediveligers of *T. (Lyrodus) pedicellatus* measure  $175 \mu$ . This size difference being definite can be advantageously used in identification of *Teredo* larvae in drift at Bombay.

## CONCLUSIONS

The following are some of the observations of interest made during the course of this investigation on marine fouling organisms incident in Bombay harbour.

- i) The major fouling organisms incident in Bombay harbour belong to class hydrozoa, cirripedia, polychaeta, bryozoa and tunicata and prevail in that order of abundance. The heavy settlement of the fouling organisms occurs throughout the year. In monsoon, however, the settlement is moderate.
- ii) The fouling organisms settled well before the onset of monsoon may perish soon after the first few showers. However, the same species may settle and grow during the monsoon and continue to grow under varying salinity conditions.
- iii) A preliminary study of the «primary film» has revealed the presence of fifteen species of cellulolytic bacteria. Fungal species indulging in underwater deterioration of the timber are also identified. In Bombay waters primary film has very little or no significance in effecting the settlement of the fouling and boring organisms.
- iv) Amongst fifteen binnacle species encountered at Bombay *B. a. communis*, *B. a. variegatus*, *B. amaryllus euamaryllis* and *B. tintinnabulum tintinnabulum* are major ship fouling species. Taxonomic comments on inter-relationships of *Amphitrite* varieties have been made which may throw some light on «*communis denticulata hawaiiensis*» problem confronting cirriped taxonomists.
- v) At least two bryozoan species namely *Electra sp.* and *Membranipora sp.* have been found to be copper resistant forms.
- vi) Wood borer *Teredo furcifera* attacks, although with varying intensity, all the year round. It is a fast growing

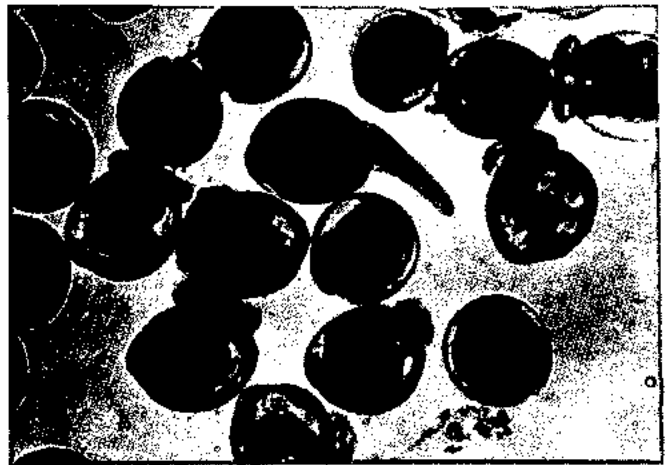


Fig. 8. The laboratory observations have shown that the settlement of *T. furcifera* larvae is independent of salinity values, temperature, light intensity, food and a primary film (actual size of larvae is  $285 \mu$ ).

borer which liberates about 7,000 young-ones, 50-55 days after its initial settlement. Breeding potential increases as the animal grows older.

- vii) Settlement of *Teredo* larvae is found to be independent of salinity and temperature variations of ambient waters in Bombay harbour.

## ACKNOWLEDGEMENTS

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# THE FOULING ON SHIPS AS THE CONSEQUENCE OF THEIR NAVIGATION IN THE ADRIATIC AND OTHER WORLD SEAS

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## SUMMARY

Observations were carried out on the fouling of vessels sailing in the Adriatic Sea in order to find out the quantitative and qualitative characteristics of this sea. The fouling of iron ships which had sailed the three oceans have been used as a means of comparison.

The typical fouling organisms are cosmopolitans, and according to their frequency and abundance the most important are: the sea-weed *Enteromorpha sp.*, the tubeworm *Hydroides norvegica*, the barnacles *Balanus amphitrite* and *Balanus eburneus*, the mussel *Mytilus galloprovincialis* and the polyzoan *Cryptosula pallasiana*. In the fouling of vessels sailing in the Adriatic the following species are the most characteristic *Filograna implexa*, *Ostrea edulis*, *Schizoporella sanguinea* and *Diplosoma listerianum*.

The total fouling of iron ships is greater and it is about 5-95%, while that of the wooden vessels is between 3% and 85%. On iron ships the stern, the stern post and the propulsive system were most fouled, while the bow and the rudder registered the lowest degree of fouling; on wooden ships the propulsive system and the iron rudder were most fouled, while on the bow and the wooden rudder the slightest fouling was observed.

Various organisms are characterized by the distribution between the hull and the propulsive system. The upper part

of the water line is colonized by the sea-weeds, while on the lower parts of the hull there settle mainly the other organisms. The tubeworms and the mussels are mostly concentrated on the keel of the ship. On almost the whole surface of the propeller wings there settle the sea-weeds, while the animals fasten on the proximal parts of the wings and on the shaft of the propeller; the mussel *Mytilus galloprovincialis* settles only on the shaft.

The highest degree of resistance to the copper of the anti-fouling paints has been observed in the following species: *Enteromorpha sp.*, *Hydroides norvegica*, *Balanus amphitrite* and *Cryptosula pallasiana*, while the inhibitory effect of the toxins is particularly characteristic at the ascidians and at *Ostrea edulis*. A less lethal effect of these poisons was noticed at some species of tubeworms and of flat polyzoans.

The most significant influence upon the decrease of the speed of ships among all the components of the fouling community, is represented by the tubeworms and the barnacles.

The quality and the quantity of the fouling community is not essentially influenced by the type of vessel or by the geographic zone of sailing; a long navigation and a longer period of anchorage in the mouths of rivers influence upon the mortality and the dropping off of various fouling species.

## INTRODUCTION

Although the problem of fouling has been investigated for a great deal, yet most of the contemporary researches concern the fouling studies on experimental plates resp. rafts, while a certain weaker attention is paid to the researches of fouling on ships and boats. The Adriatic Sea has been particularly neglected. So, only works by Nümann and Beth (1955) and Nikolić (1959) can be cited. In the course of the last three years researches on these problems have been started at the Institute for marine biology in Rovinj. The aim of these studies is to learn on the characteristics of ship fouling in the Adriatic. The quality, the dominance and the distribution of fouling organisms on the vessels are noted. Besides, these inquiries have the aim to acquaint with the organisms having the highest degree of resistance towards the toxic substances of anti-fouling varnishing as well as with those which are the most noxious, i.e. those mostly influencing upon the decrease of the speed of the ship or causing the penetration of the ship hull. As a means of comparison, the fouling of vessels which had sailed the three oceans (and mostly had crossed the Eastern Mediterranean) has been used.

## METHODS OF RESEARCHES

The fouling of the ships which had sailed outside the Adriatic Sea was analysed upon iron ships in dry docks immediately after the emptying, while the fouling of the Adriatic was registered upon wooden ships in boat-sheds. There were examined 18 ironships of three different types: 12 motor-cargo vessels, three traders and three passenger ships with full draught between 310 and 791 cm. There were examined also 18 wooden ships: 11 fishing, one cargo vessel while the remaining were tourist boats. The full draught of wooden vessels varied between 92 and 290 cm. On the occasion of the survey of each vessel, the fouling was registered qualitatively and the distribution of the species was noted; besides, the covering of the organisms has been expressed in percentages and in relation with the surface available the covering values of all parts of the ship were calculated.

## RESULTS

In the fouling of all the examined ships, certain organisms appeared very frequently and with high covering rate. Such species will be treated separately, considering their high

frequency and abundance. The organisms of primary importance are:

*Enteromorpha* sp. The frequency for both kinds of vessels was high-94.4%. *Enteromorpha* settles along the upper part of the water line determining a belt about 70-100 cm. wide on iron ships (fig. 1) whilst on wooden boats the wideness of the belt varied between 10 and 30 cm. (fig. 2). The fouling rate of the various parts of ships, particularly of wooden ones is rather unequal. It is characteristic for both kinds of ships that the *Enteromorpha* sp. fouls mostly the propeller, the rudder and the bow and very little the stern post, while the bottom is completely unfouled by it (table 1). It mostly settles over the propulsive system on the wings of the propeller, while the shaft is practically unfouled. The *Enteromorpha* colonizes the shaft only when there are no other organisms settled there. On iron and wooden vessels it fouls approximately 15% more the outer side of the wings of the propeller along almost the whole length of the wings, except those most distal parts which are most exposed to the dynamics of water masses. It is interesting that on the hulls of both kinds of vessels, the bow was heavier fouled than the middle of the hull; this fact does not coincide with observations of some other authors (Harris 1946, Zevina 1957, Nikolic 1959) according to which *Enteromorpha* settles mostly in the middle of the hull and less on the bow. This phenomenon

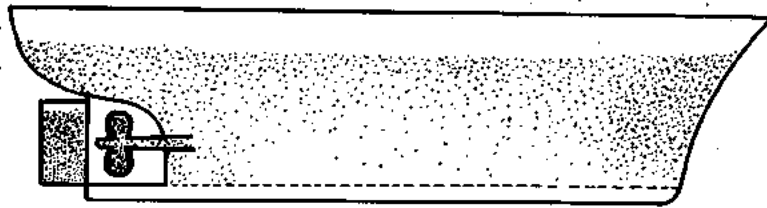
can not be interpreted with Zevina statement (1957) that the configuration of the vessel is the main factor influencing the fouling rate of *Enteromorpha*. It is the fact that at many studied by us, of almost the same configuration and the same sailing route during the same season had a quite different fouling was registered. In all probability the phenomenon of intraspecific relationships has to be taken into consideration. In fact it was noticed that the bow was completely covered by the *Enteromorpha* when the other organisms were absent.

*Hydroides norvegica* (Gunnerus): This tube-worm settles three times more frequently on iron vessels than on wooden ones. On both kinds of boat hulls, it mostly settles on the bottom without any significant difference between the kinds of ships, then on the stern and the middle of the hull, while all the other parts are very differently fouled. Consequently, all ships parts were more covered by specimens of this species on iron ships, except of the keel (table 1). On the propulsive system *Hydroides* colonized for 20% more on the shaft than on the wings of the propeller of iron ships, while there was no difference on wooden ships. In most cases it settles on the proximal parts of the wings; exceptionally it expands towards the middle part of the wings if it is not covered by sea weeds or when there exist a dense population of other organisms on the proximal parts or on the shaft.

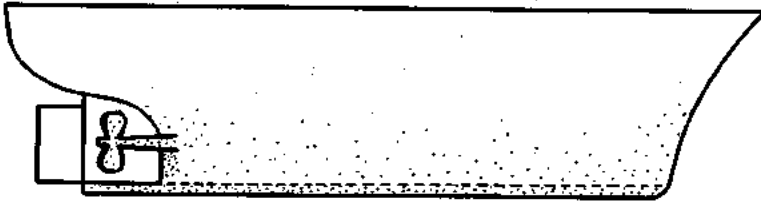
TABLE 1  
AVERAGE VALUES OF THE SURFACE OCCUPIED BY FOULING ORGANISMS  
(IN %)

FOULING ORGANISMS	IRON SHIPS							WOODEN SHIPS									
	FREQUENCY TOTAL	covering						FREQUENCY TOTAL	covering								
		RUDDER	PROPULSIVE SYSTEM	STERN POST	STERN	MIDDLE OF THE HULL	BOW		KEEL	IRON	WOODEN	PROPULSIVE SYSTEM	STERN POST	STERN	MIDDLE OF THE HULL	BOW	KEEL
<b>SEA WEEDS</b>																	
ENTEROMORPHA SP.	94,4	52,8	54,8	25,0	31,0	31,3	40,6	—	94,4	19,6	39,4	52,5	5,5	19,6	18,7	31,6	—
CHLOROCOCCUS SP.	5,5	—	68,0	—	—	—	—	—	—	—	—	—	—	—	—	—	—
ULVA LACTUCA (Linnaeus)	5,5	0,5	—	—	—	—	—	—	22,2	2,1	—	8,0	—	—	—	—	—
BRYOPSIS SP.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
ECTOCARPUS SP.	—	—	—	—	—	—	—	—	5,5	—	—	—	—	8,0	10,0	8,0	—
MELOBESIA SP.	5,5	—	2,0	—	—	—	—	—	22,2	—	—	5,2	—	—	—	—	—
<b>HYDROIDS</b>	11,1	—	2,0	1,0	—	—	—	—	16,6	—	—	+	+	—	+	—	5,0
<b>MOLUSCS</b>																	
MYTILUS GALLOPROVINCIALIS (Lamarck)	22,2	—	5,0	7,0	—	7,0	2,0	14,0	83,3	4,5	5,0	15,0	18,2	11,7	6,5	5,0	17,8
OSTREA EDULIS (Linnaeus)	5,5	—	—	—	—	—	—	1,0	50,0	15,7	—	10,2	7,5	—	—	—	—
VERMETUS TRIQUETER (Bivone)	—	—	—	—	—	—	—	—	22,2	6,7	—	6,1	—	—	—	—	—
<b>TUBEWORMS</b>																	
SPIROBIS SP.	22,2	2,0	1,5	2,5	2,0	8,7	—	3,0	94,4	12,2	4,5	9,7	12,0	4,6	3,2	4,9	6,4
HYDROIDES NORVEGICA (Gunnerus)	66,6	11,4	14,3	24,4	40,7	23,7	18,7	48,0	22,2	1,0	—	3,5	9,0	22,5	19,7	5,0	50,0
POMATOCEROS TRIQUETER (Linnaeus)	16,6	6,0	10,4	14,0	4,0	6,0	4,0	6,0	27,7	1,0	—	0,1	3,0	5,0	—	—	—
SERPULA VERMICULARIS (Linnaeus)	—	—	—	—	—	—	—	—	22,2	—	—	0,4	3,0	—	—	1,0	—
MERCIERELLA ENIGMATICA (Fauvel)	5,5	25,0	48,0	40,0	10,0	15,0	7,0	10,0	—	—	—	—	—	—	—	—	—
FILOGRANA IMPLEXA (Berkeley)	—	—	—	—	—	—	—	—	83,3	11,8	5,0	20,4	30,0	10,7	4,9	4,2	8,5
<b>BARNACLES</b>																	
BALANUS AMPHITRITE (Darwin)	100,0	3,7	16,6	19,8	19,9	7,7	10,2	7,5	86,6	10,8	6,2	15,0	9,7	10,6	8,1	4,7	4,5
BALANUS EBURNEUS (Gould)	27,7	3,0	4,8	8,5	2,0	3,7	3,0	9,5	44,4	4,2	5,5	15,1	10,2	3,7	4,4	2,3	5,4
TETRALITA SQUAMOSE (Pilsbry)	5,5	—	—	60,0	3,0	2,0	2,0	1,0	—	—	—	—	—	—	—	—	—
<b>POLYZOA</b>																	
CRIPOTOSULA PALLASIANA (Moll)	33,3	6,0	5,3	18,0	21,5	14,7	8,0	6,7	66,6	32,0	1,0	20,2	20,2	3,0	6,7	5,0	5,0
SCHIZOPORELLA ERRATA (Waters)	5,5	3,0	1,7	5,0	—	7,0	3,0	1,0	22,2	22,5	11,5	8,7	—	—	—	—	—
SCHIZOPORELLA SANGUINEA (Norman)	—	—	—	—	—	—	—	—	16,6	—	—	20,3	6,0	—	5,0	3,0	13,0
SCHIZOPORELLA UNICORNIS (Johnston)	5,5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
WATERSIPORA SUBVOIDEA (d'Orbigny)	5,5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
BUGULA NERITINA	5,5	—	—	15,0	5,0	15,0	7,0	15,0	11,1	—	—	1,0	—	—	—	+	—
BUGULA SP.	—	—	—	—	—	—	—	—	5,5	—	—	—	—	—	—	—	1,0
<b>ASCIDIANTS</b>																	
DIPLOSOMA LISTERIANUM (Milne-Edwards)	—	—	—	—	—	—	—	—	15,5	27,8	—	26,5	29,3	—	5,0	—	7,0
BOTRYLUS SCHLOSSERI (Pallas)	—	—	—	—	—	—	—	—	5,5	5,0	—	—	—	—	—	—	—
STYELA PARTITA (Simpson)	—	—	—	—	—	—	—	—	16,6	7,0	—	+	+	—	—	—	+

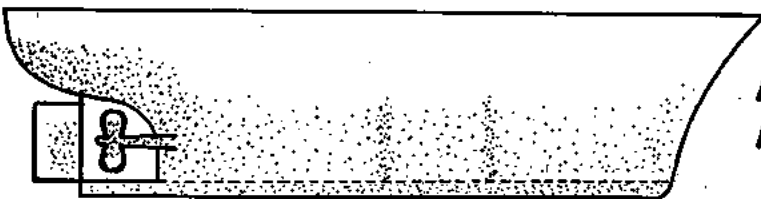
# IRON SHIPS



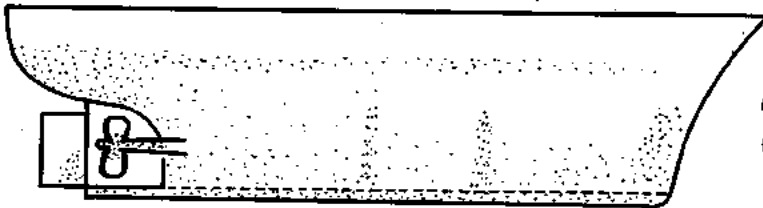
*Enteromorpha* sp.



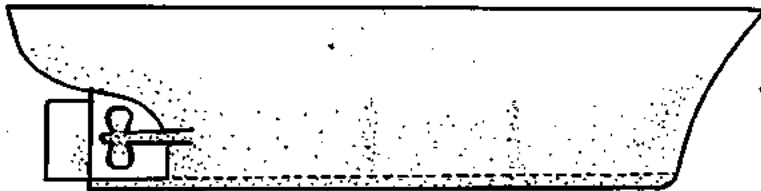
*Mytilus*  
*galloprovincialis*



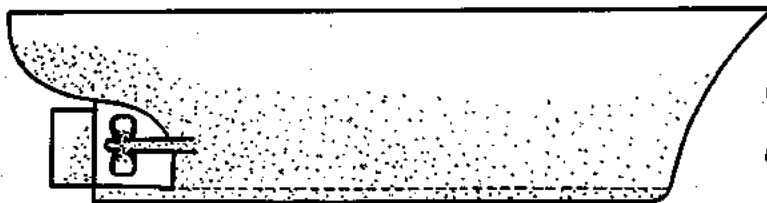
*Hydroides*  
*norvegica*



*Balanus*  
*amphitrite*



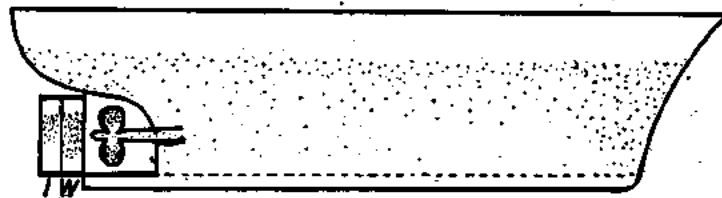
*Balanus*  
*eburneus*



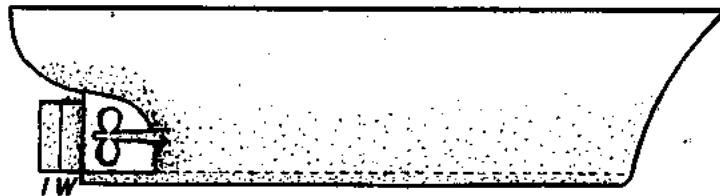
*Cryptosula*  
*pallasiana*

Fig. 1. Distribution of fouling organisms on the iron ships.

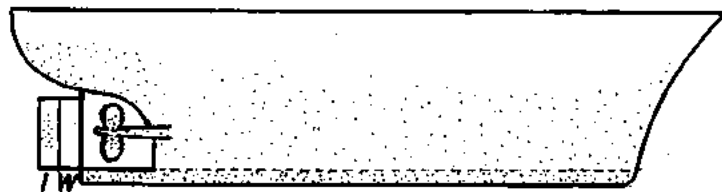
# WOODEN SHIPS



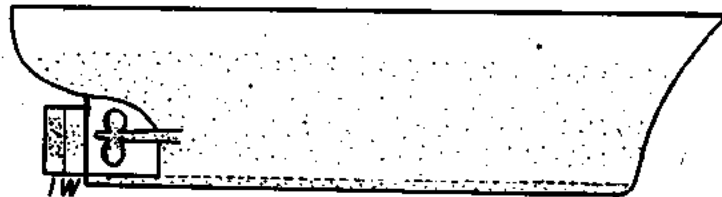
*Enteromorpha* sp.



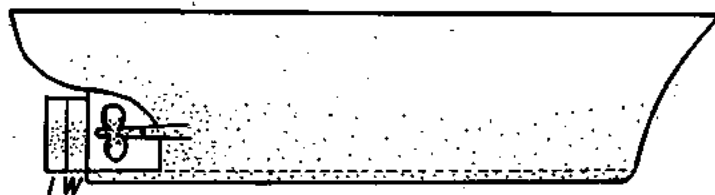
*Mytilus*  
*galloprovincialis*



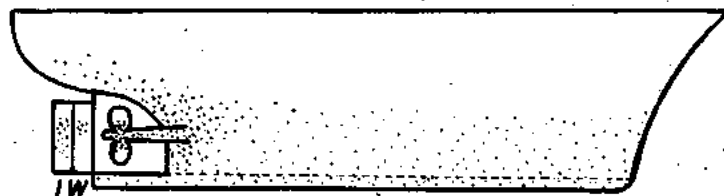
*Hydroides*  
*norvegica*



*Balanus*  
*amphitrite*



*Balanus*  
*eburneus*



*Cryptosula*  
*pallasiana*

I = IRON RUDDER

W = WOODEN RUDDER

Fig. 2. Distribution of fouling organisms on the wooden ships.

Otherwise, the *Hydroides* settles about 5% more on the inner part of the propeller than on the outer one. The zonal distribution on the hull starts under the water line about 70-100 cm. and further on it increases towards the bottom where the settlement is at its densest (fig. 1, 2). In the cases when the fouling complex is heterogeneous and dense, the settlement is very uneven, i.e. the specimens are concentrated on the lower parts of the stern, under the inlet valves, immediately above the bilge keel, and mostly on the keel.

*Balanus amphitrite* (Darwin). This species is characterised by the 100% frequency for the fouling on iron vessels, while on wooden ones it is for 12% smaller. The settling of specimens over the various parts of both kinds of vessels is very unequal: only in the middle of the hull they settle almost uniformly. Otherwise all the parts, except the rudder, are more fouled on iron ships where this barnacle mostly settles on the stern, stern post and on the propeller, and less on the keel and on the rudder. On wooden boats the *Balanus amphitrite* mostly settles on the propulsive system, the stern, iron rudder and stern post, while the sparsest settling has been noticed for the keel and the bow (table 1). In the middle of the hulls the distribution is very similar, to that of *Hydroides norvegica*. When the populations of seaweeds are rare *B. amphitrite* colonises also the upper part of the water line. In regard to the fouling of the propulsive system, the shaft of the propeller at iron and wooden vessels is more fouled than the wings (for 20% on iron and 13% on wooden ships). The specimens settle insignificantly more on the outer sides of the wings, concentrating on their proximal parts (fig. 1, 2).

*Cryptosula pallasiana* (Moll). Flat colonies of this species settle twice more on the wooden vessels than on the iron ones and that happens very unequally for both kinds of ships. For example, some parts (propulsive system, rudder) can be fouled even five times more on wooden ships, and the stern of iron vessels is over seven times more fouled by colonies of this species as it is the case for wooden boats (table 1). The vertical distribution of colonies on the hulls is very similar to that of the tubeworm *H. norvegica*. Settlements of *Cryptosula* begin at a distance of 100-130 cm. from the upper part of the water line at iron vessels, and at a distance of 50-70 cm. at the wooden vessels. On iron ships, the shaft outer and inner side of wings of the propeller are equally fouled; but the outer side of the wings of wooden boats is for 3% more fouled than the inner one there is also characteristic the concentration of colonies on the proximal parts of the wings (fig. 1, 2).

*Balanus eburneus* (Gould). As a component of the fouling community of vessels this barnacle is met rarely in compare to the above cited species. On iron ships the highest covering is found on the bottom and on the stern post, while at wooden ships it is the case for the propulsive system and the stern post. All other parts of both kinds of vessels are less colonised and without any significant difference (table 1). On the hulls, specimens predominantly concentrate towards their lower parts and similar to the species *H. norvegica* and *B. amphitrite*, can settle more density under the inlet valves and above the bilge keel. As it happened with other mentioned species, it settles on the proximal parts of the wings and over the shaft of the propeller twice more than over its wings (fig. 1, 2).

*Mytilus galloprovincialis* (Lam.). This species is primarily significant for wooden vessels because of its frequency, abundance and settling on all parts of the ship. This shellfish settles less on the iron vessels; the specimens were not found at all on the rudder and on the stern. Mussels mostly settle on the keel on both kinds of ships. Besides, a larger number of specimens is registered on the stern post and the propeller shaft of wooden ships (table 1). On all the vessels the same distribution of specimens has been noticed

and this did not occur in one of other species. The mussels settle always in shadier and darker places, while on the propulsive system it fouls only the shaft (90% of cases on the lower part (fig. 1, 2).

*Other organisms*: Some more species were registered in the fouling community, whether common to both kinds of vessels or to one of them only. Some of these fouling species have only a qualitative significance because of their low frequency and insignificant covering values, or because they settle only on some parts of the ships. For example, some tubeworms are important only from the qualitative point of view (*Spiroris* sp. for iron ships, *Pomatoceros triquetus* and *Serpula vermicularis* for wooden vessels). The tubeworm *Mercierella enigmatica* is distinguished in the quantitative point of view for iron ships (table 1) while the *Filograna implexa* is characteristic for the wooden vessels. These species are very important in the fouling of the Adriatic Sea, since it very often appears as the predominant organism in the fouling different substrata and on some organisms (table 1).

Among the molluscs besides, the mussel *Mytilus galloprovincialis*, the Oyster (*Ostrea edulis*) has been found on both kinds of ships, while the snail — *Vermetus triquetus* was observed on wooden vessels only. *Ostrea edulis* is completely insignificant for the iron vessels because of the very rare settling rate and the slightest surface covering, but it settles in a greater degree on some parts of wooden boats (table 1). It is interesting that *Vermetus triquetus* settles only on some distinct parts of the boat, such as rudder and propeller shaft.

On one of the iron vessels which had sailed across the Red Sea there were found some specimens of the barnacle *Tetraclita squamosa*. It is characterized by the large dimensions of the basis of the shells (up to 3 cm. in diameter (and cover therefore some parts of the ship up to 60% when the population is dense (table 1). Further more, the height of the shells of *Tetraclita* (up to 10 cm.), exerts a significant increase in the friction and due to it, the speed of the vessel can be considerably reduced.

In the ship fouling the polyzoans are represented prevalently by some flat species. Amongst the bushy species only the *Bugula* was registered with a very low frequency values. Among the flat colonial forms, the following species were observed: *Schizoporella unicornis*, *Watersipora subovoidea* (on iron ships only, very rare and with an insignificant covering) and the *Schizoporella errata* which is a common element in the fouling of both kinds of vessels, although its frequency is 4 times higher on wooden vessels (table 1). As well, the species *Schizoporella sanguinea* is very important in the fouling of wooden boats, especially on some parts of the vessels (table 1). This species is also an almost regular member of the fouling community on nearly all underwater objects and on numerous unmovable organisms in the Northern Adriatic.

The Ascidians, have been found exclusively on wooden boats: According to the degree of surface covering and the frequency the Synascidian *Diplosoma listerianum* is marked. The species *Botryllus schlosseri* and *Styela partita* are important from the qualitative point of view.

*General characteristics of the fouling*: The total fouling of the whole vessels as well as that of the various parts of iron and of wooden ships is different. The entire covering of the iron ships is higher and it is around 5-95%; between 5% and 10% in 3 ships, between 10% and 30% in 8 ships and between 60% and 95% in 7 ships. The total covering of wooden boats is around 3-85%; between 3% and 12% in 5 boats, between 20%-35% in 7 ships, between 40% and 45% in 4 ships and between 80% and 85% in 2 ships. On iron ships the covering values of the various parts grouped as follows: the stern, the stern post and the propulsive system are equally fouled, the middle of the hull and the keel have no significant difference, while the slightest fouling is found on the rudder and the bow, with insignificant differences, too. On wooden ships the propulsive system is most covered (about twice more than on iron ships) then the rudder (about 1.5 times more

than on iron ships), the stern post and the keel (it has on average the same value as on iron ships), the stern (it is about 1/3 less fouled than on iron ships). The middle of the hull and the bow wooden vessels are somehow less fouled, while the slightest settlement is characteristic for the wooden rudder. The reciprocal relation among the covering of all parts of iron ships is more uniform.

When the geographic zone of sailing is considered as a supposition of a possible influence on the quality and abundance of the fouling species, frequently it was possible to notice that different geographical zones exert the same influence on the quality of the fouling at iron vessels (for example —the route to the Guinean Gulf and Aden or to Scotland and the Black Sea). On the contrary it was noticed that the composition of the fouling can be completely different for the vessels which have sailed inside the same zone, e.g. to the Black Sea or to Eastern Mediterranean. The most convincing indicator of this fact are the wooden vessels which have sailed inside a limited zone (the surrounding of Rovinj) and yet their fouling communities were completely different. Although it is considered that the number of the species in a fouling community depends upon the higher temperature and the higher salinity (O.E.C.D., 1966), our results do not confirm this. So, for instance a ship which had sailed from Venice to Tripoli was covered by two species only, while the fouling of the ships which had sailed to the Northern Europe was much more various. Considering the influence of the length of sailing on the qualitative-quantitative composition of the fouling community, we can agree with some authors (Harris 1946, Bishop et al. 1949) that a long sailing influences the removal of the settlement. On the vessels which had been cruising for a longer period, a mortality rate of 100% and traces of drop-off organisms were noticed. In our opinion a long sailing is not of principal importance; more essential are the environments through which the ship had sailed, that is the heterogeneity and the fluctuations of hydrographic factors of the environment. Since we have not at our disposal the dates concerning the quality of ports in relation to the salinity or the water pollution we cannot establish with certainty the positive effect of water pollution to the fouling and or what is the negative influence of the brackish waters. Consequently, it is known to us that on the hull of the vessel which had been anchored in the mouths of the Dnjester for more than a month, only traces of earlier settled organisms were found.

When analysing the fouling of some types of vessels, no significant qualitative and quantitative differences in the distribution of organisms were noticed. Only passenger ships revealed an insignificantly slighter settlement in the middle of the hull, and the reason for this can be searched in the higher speed of those ships.

The resistance of the fouling organisms was determined on the basis of their settling on coloured surfaces. Wooden ships have been smeared all over with anti-fouling varnishing «copperpaint», containing copper, while the iron ships were smeared all over with the anti-fouling paint «supertropical» (with copper, too) in 85% of the cases we have analysed. The highest degree of resistance among all the species of organisms for both kinds of ships has been noticed for the *Enteromorpha* sp. and the *Hydroides norvegica*. As far as iron vessels are concerned, less resistant are *Cryptosula pallasiana* and *Balanus amphitrite*, while the slightest resistance appeared to be for *Mytilus galloprovincialis* and *Balanus eburneus*. On wooden ships the following resistance scale was established: *Mytilus galloprovincialis*, *Balanus amphitrite* and *Balanus eburneus*, while *Cryptosula pallasiana* is least resistant to toxic surfaces. A high degree of resistance is characteristic for the tubeworms *Filograna implexa* and *Mercierella enigmatica*. *Pomatoceros triquetter* has shown the weakest degree of resistance to toxic substances (particularly on wooden ships) while the *Spirorbis* sp. is characteristic for its smallest tolerance to toxine on both kinds of ships. The barnacle *Tetractita squamosa* is resistant as much as *B. amphitrite*. Among all the species of polyzoa only *Schizoporella sanguinea*

reacts similarly towards toxine as *Cryptosula pallasiana* does, while all other species are almost completely unresisting. The toxine has a totally lethal effect for the following species: *Vermetus triquetter*, *Styela partita* and *Botryllus schlosseri*. If we compare the settlement of the *Diplosoma listerianum* on painted (7%) and unpainted (30%) surfaces, or the settlement of the *Ostrea edulis* where the settlement ratio between painted and unpainted surfaces is 1:20, we can conclude that the copper of the anti-fouling paints has an inhibitory effect on these species. It is obvious that the same organisms behave differently toward the same kind of toxine. As well, lesser resistance was observed at some animal groups which were believed till now as the most resistant animals, i.e., barnacles (Harris 1946, Komarovskij 1957) and even Cypris-larvae (*Dolgopoljskaja* 1959). An opposing phenomenon has been noticed at the tubeworm *Pomatoceros triquetter* and the *M. galloprovincialis* which were up to now regarded as almost completely unresistant to poisons (Harris 1946). Since we are not informed on the quality of the painting system and neither we know the quantity of toxins that the paint contains, we may only suppose that the value of the «Leaching rate» of the anti-fouling paints for iron ships grew weaker when exposed to the action of various hydrographic factors and their variations. This argument the qualitative enfeeblement of the painting system could be considered as the only possible cause of the increased covering of iron ships. But, if on the basis of this assumption we keep that the painting system of wooden ships is better preserved, that is not enough to explain why the tubeworms have settled more than the barnacles. Very probably the intraspecific relationships have exerted their influence on the smaller quantity or on the predominance of single species in the fouling of wooden ships. According to Harris (1946) and Bishop et al. (1949), the settling of the first colonizers is very important. For example, after a strong settling of tubeworms an unequal surface is not suited for the settling of barnacles. As well factor reproduction period is a very important. All the analyzed ships started their journey at the end of winter or at the beginning of spring, and we can suppose that this factor is one of the causes of the predominance of *Enteromorpha* sp. and *Hydroides norvegica*, since their reproduction period falls exactly in that time, while for the barnacles this period begins a bit later. The cause for a more frequent settlement on wooden ships for the mussels *Mytilus galloprovincialis* is probably caused by the denser populations in the Adriatic. The presence of the ascidians on wooden ships may be probably explained by its weak vital and adaptive capabilities.

The way and the speed of growth, the manner of fastening on the surface and the resistance of the various organisms indicate which organisms are to be considered most noxious for the speed of ships. The barnacles and the tubeworms are important. The barnacles fasted by a wide basis on the surface of the hull and their shells are turned outwards; furthermore, their settlements in a form of epibioses of first, second and even third degree give rise to a significant friction to ships. It is worth to mention that the paint under the basis of barnacle shells had been absorbed and somewhere even damages to the ship surface were noticed. The tubeworms can also cause a more considerable friction when their population are very dense and when as a result of the epibiosis—they grow vertically outwards. It is believed that the worms represent the most serious fouling component on the propulsive system. Since their settling with a relatively long basis enables them to hold during the rotation, it causes a decrease of the propulsive force of the system itself. As well because of the shapes of their bodies, their consistence and the possible appearance of the epibioses, shellfish could probably exert a negative influence on the speed of ships. No epibiosis phenomenon in the ship fouling community was noticed for the oyster *Ostrea edulis*, while it was very frequently observed at the mussel *Mytilus galloprovincialis*. This species prefers shadow places and avoids the fast water currents (Zevina 1957); it mostly settles on the bottom of the vessel and that can not increase considerably the friction. Seaweeds have

secondary significance in regard to resistance, frequency and broadness of the covering zone, because their soft thaluses are pressed on the hull surface in the course of sailing and therefore do not influence the rise of resistance value; only exceptionally the population is so dense that thick layers of several centimeters are formed. Flat polyzoa are of no importance for the ship's friction, as their colonies are very flat, but they can damage the film of the paint when their colonies drop off.

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#### DISCUSSION

Prof. KONOFAGOS (Greece): I think that all that you have said are extremely interesting. I am a metallurgist and consequently that what I have understood, are two things. First there is an enormous difference, sometimes, in the way, on which the organisms are fixed on the iron ships and on the wooden ships, and second there is an enormous difference relative to the keel. A first question is this: for what reason a given organism at first is fixed differently on the ships made of wood, and the ones made of iron, secondly for what reason is fixed differently at different points of the wood of the ship and a third question will be this: Have you found a difference between the way with which the organisms are fixed on the propellers of the wooden ships and of the iron ones?

L. IGIC: The manner of the fixation of a particular sessile organism is specifically characteristic regardless the kind of the substrate. However, considerable differences in qualitative and quantitative composition of fouling communities are established for wooden and iron boats. These differences are probably caused by various distincts of navigation, length of the routes, various anchoring-places etc. The fouling of the wooden fishing boats is more heterogeneous and not so uniformly distributed as it is on the iron boats, probably due to the presence of metal parts (rudder, stern post, propeller) which are not protected by anti-

fouling paints. Therefore these metal parts of wooden boats are regularly more fouled than the wooden hull. Moreover on unprotected surfaces other organisms frequently settle, which are not resistant to toxins of antifouling paints. Consequently, the relative uniformity of fouling communities of iron boats can be also a result of considerable mortality and falling off of settled organisms at the time of long navigation.

G. RELINI (Italy): Don't you think that any difference may be due also to different paints?

L. IGIC: The quantitative differences in fouling of the keels of iron and wooden boats, as well as in fouling of the keel and other parts of the same ship are insignificant. On the contrary, considerable differences in qualitative composition of fouling communities on the keels are observed.

G. RELINI (Italy): Yes but all ships were treated with different kind of paints.

L. IGIC: The individuals of the particular fouling species settle on the propeller of wooden and iron boats on the same manner. However, the distribution of these species on the propellers, as well as the qualitative and quantitative composition of fouling communities on the propellers of wooden and iron boats are not identical.



**Séance - Meeting - Sitzung - Συνεδρίασις**  
**24.9.1968**

**Présidence - Presidency**  
**Präsidium - Προεδρείον**

**Prof. BALAKRISHNAN NAIR (India)**  
**Prof. E. VOYATZAKIS (Greece).**  
**Dr. E. LITTAUER (U.S.A.).**

# FOULING ORGANISMS IN THE HARBOR AT MONTEREY, CALIFORNIA

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## SUMMARY

1. A series of 162 plywood and asbestos board panels were exposed in the water under Monterey Municipal Wharf No. 2 at various positions and water depth from October 1, 1966 to October 1, 1967.

2. Short term panels (exposed for one month) made it possible to determine season of setting of fouling and boring organisms, while long term panels (exposed for from 3 to 12 months) made it possible to measure rate of growth and determine the dominant foulers.

3. On the short term panels, a total of 70 species of animals and plants settled on the surface, while on the long term panels 81 species were recorded.

4. With few exceptions on both the short term and long term panels, encrusting and erect bryozoans were the dominant fouling organisms. These included *Hippothoa hyalina*,

*Lyrula hippocrepis*, and *Crisulipora occidentalis*.

5. *Balanus crenatus* was the dominant barnacle, and was found on panels at all positions throughout the year.

6. Calcareous serpulid worms, *Spirorbis spirillum* and *Serpula* sp., were the most common annelids found.

7. Water temperature and salinity records were kept throughout the year but no clear correlation between these physical factors and the rate of fouling was noted with the possible exception of the influence of a generally higher temperature in late June and early July, 1967, on the settling of *Balanus crenatus*.

8. Plywood and asbestos board, when exposed at 14 feet depth, collect essentially the same organisms and at the same rate.

## INTRODUCTION

The presence of fouling organisms in a harbor is not only of interest to the marine biologist but is of considerable economic importance to harbor engineers and maintenance personnel and to boat owners. On the Pacific Coast of North America relatively few published studies on fouling organisms have been made. These include investigations in Washington at Admiralty Inlet (de Palma, 1966) and Friday Harbor (Johnson and Miller, 1935) and in California at Oakland (Graham and Gay, 1945), Port Hueneme (Drisko, 1964), Newport Harbor (Scheer, 1945) and several studies in the La Jolla-San Diego area (Coe, 1932; Coe and Allen, 1937; Whedon, 1937, 1943; Aleem, 1957).

Until recently no systematic investigation of marine fouling had been made in Monterey Bay, California. —Mommson (1966) and Miller (1966) carried out two short term studies in Monterey Harbor, and the present paper presents the results of a full year's observations in the same area. The object of the study was to obtain information concerning the kinds of organisms that settle on test panels exposed in the water at various depths, to learn something of the season of attachment or settling, to note any correlation between settling of organisms and the temperature and/or salinity of the water, to determine choice of substrate for individual organisms, to measure the rate of growth of dominant forms and to study seasonal progression over the year. Other workers have found great variability from year to year in the results obtained from such studies, and the present investigation is planned to continue for several years. This contribution is therefore to be viewed as an interim report on the first year study. Additional systematic observations are being made at various places in open water in Monterey Bay down to depths of 100 feet and will be reported on in due time.

The author wishes to acknowledge the following colleagues for help in the identification of various fouling organisms:

Dr. E.N. Kozloff (Suctorians), Dr. Z.M. Arnold and Mr. Jack Gougé (Foraminiferans), Mr. G.F. Kelso (juvenile barnacles), Dr. I.A. Abbott (Algae) and Dr. D.P. Abbott (Ascidians). Mr. J.R. Lance assisted in resolving nomenclature problems with opisthobranchs. Acknowledgement is also due my wife, Mrs. A.E. Haderlie, for assistance in the laboratory work, and to the Office of Naval Research for financial support.

### Area of Study

The site chosen for this study was near the outer end of Monterey Municipal Wharf No. 2, about 1000 meters from the shore (Figure 1). This wharf was constructed in 1926 and is supported by concrete piles about 8 to 10 feet apart and has rows of creosoted wooden fender piles along each side. All of the piles are covered with a luxuriant growth of attached organisms dominated by acorn barnacles (*Balanus nubilus*, *B. glandula*, *B. crenatus* and *B. tintinnabulum*), anemones (*Metridium senile*, *Anthopleura xanthogrammica*, *Corynactis californica*) bay mussels (*Mytilus edulis*) and numerous hydroids, bryozoans, polychaetes and tunicates. The depth of the water at the test site is about 21 feet at mean low tide. The maximum tidal fluctuation is 8 feet. The test site is at the outer edge of the harbor and pollution is not excessive; the water is often so clear that the sandy bottom can be seen easily. Throughout the period of study surface water temperature was recorded and salinity determinations were made every two weeks (Figure 2). Most of the test panels were exposed under the eastern edge of the wharf. The water in this area receives very little direct sunlight and then only in the morning. One group of panels, to test for the effect of more light, was placed on the western edge of the wharf where the water receives direct sunlight for several hours in the afternoon.

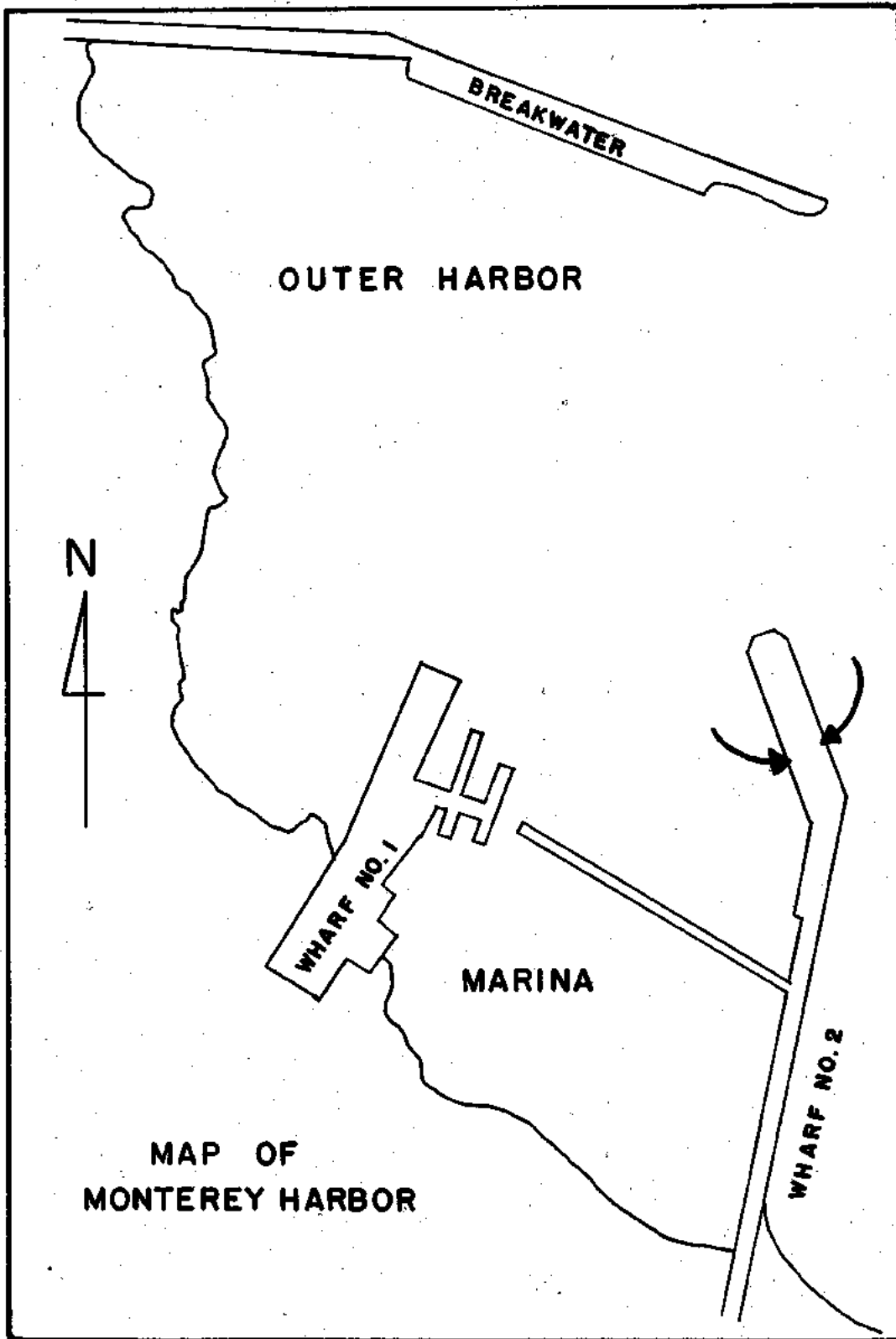


Figure 1  
Test sites under Municipal Wharf No. 2 indicated by arrows.

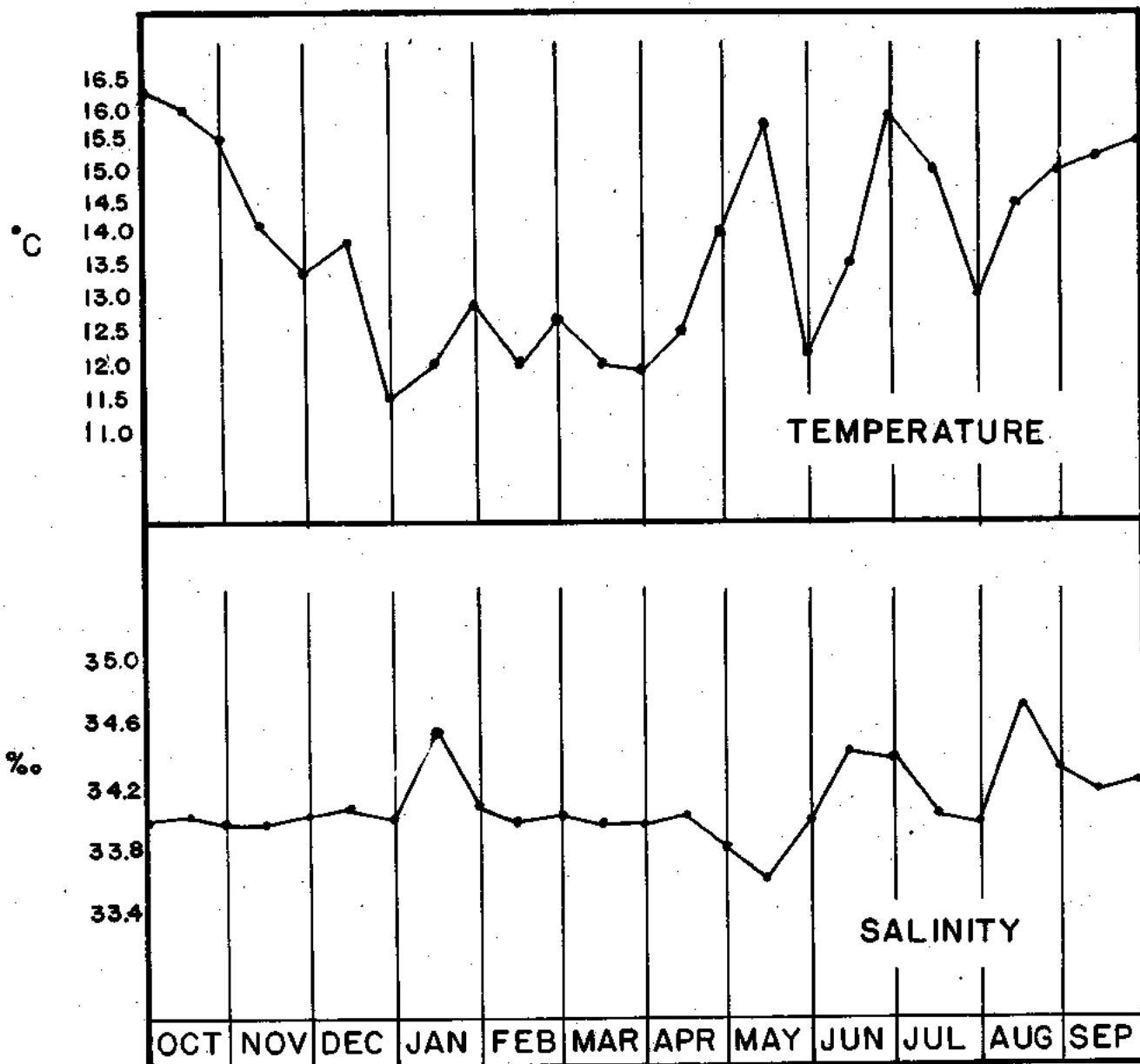


Figure 2  
 Biweekly morning temperatures and salinities at test site  
 for the year October 1, 1966 - October 1, 1967

In their short term studies of fouling organisms in Monterey Harbor, both Mommson (1966) and Miller (1966) tried a variety of test panels such as glass, plywood, stainless steel, masonite, fiberglass, and aluminum coated with Teflon. They both found that 1/4 inch douglas fir plywood was the best all-round collector, and this material had the added advantage of collecting wood-boring organisms. In the present study standardized 8 inch by 10 inch panels of 1/4 inch marine grade douglas fir plywood were used as the primary collecting surfaces. Some workers have reported that asbestos board was the most promising material for maximum attachment of foulers. To test and compare asbestos board with wood in Monterey Harbor one set of collecting panels consisted of asbestos board of the same size as the plywood panels with one smooth and one roughened side (Johns-Manville Colorlith).

The collecting panels were supported vertically in racks similar to those employed by Coe and Allen (1937) for the last 3 years of their study. All of the submerged racks were constructed of stainless steel (see Figure 3) and each held six 8 inch by 10 inch panels spaced at 3 inch intervals. One rack designed to float on the surface regardless of tidal level was made of 3/4 inch redwood slats. All racks were supported by a bridle and were held in position by 3/32 inch stainless steel bathythermograph wire. The racks were free to swing and rotate in the slight tidal currents found at the site.

A total of six racks were employed in this study. Five of the racks contained plywood panels, one contained asbestos board, and they were positioned as follows:

- I. Floating Rack. Constructed of wood and tethered with counterweights so that it floated with the top edge of the plywood collecting panels at the water's surface.
- II. Intertidal Rack. Positioned about 4 feet above the lowest low tide level. The plywood panels in this rack were submerged approximately one half the time and exposed to air the other half.
- III. Shallow Rack. Located 1 foot below lowest tide level; plywood panels always submerged.
- IV. Deep Rack. Positioned 14 feet below lowest tide level and about 7 feet off the bottom. Plywood panels.
- V. Deep Asbestos Rack. This rack contained the asbestos board panels and was positioned at the same depth and close to the Deep Rack containing plywood panels.
- VI. Lighted Rack. This rack of plywood panels was positioned 1 foot below lowest tide level on the western side of the wharf where the panels were exposed to afternoon sunlight.

The period covered by this study was from October 1, 1966 to October 1, 1967. Of the six panels in each of the racks, there were four that were left in place for 3 months (Panel 3P), 6 months (Panel 6P), 9 months (Panel 9P) and 12 months (Panel 12P) respectively. These were designated as Long Term panels. The remaining two panels in each rack were designated Short Term panels (T panels): one was put in on the first of each month and retrieved for study on the first of the next month, the second was put in on the fifteenth of each month and retrieved a month later. These short term panels therefore overlapped one another and made possible more exact determination of settling time. A total of 162 panels were exposed and examined during the year. Two of the panels from the 3 month series were lost. The length of exposure of the various panels in each rack is shown diagrammatically in Figure 4.

In many of the previous studies on fouling organisms on this coast, investigators have found it expedient to scrape the fouling organisms off the panels and preserve the entire lot in formalin or alcohol for later sorting and identification. In a preliminary pilot study carried out two years ago in Monterey Harbor this technique proved to make identifica-

tion very difficult and often impossible, especially for small, delicate, recently-settled forms. Throughout this study, therefore, the retrieved panels were placed in tubs of sea water or in aquaria with running sea water immediately after removal from the racks and were examined as soon as possible, usually within 3 hours of being removed from the sea. For examination each panel was placed in a pan of sea water and the entire surface surveyed with a binocular stereoscopic microscope (7x to 30x magnification). This made it possible to see and record very small living organisms such as some of the protozoans and newly settled stages of bryozoans and barnacles. This technique not only made identification easier but made it possible to observe the behaviour of the organisms, determine where on the panel they tended to settle, their size, relative abundance, what their associates were, etc. Proper identification of the fouling organisms, especially the very young stages, was constantly a problem, but with experience and the help of specialists it became easier. In some cases panels with juvenile organisms of questionable identity were kept in aquaria or were returned to the original racks for additional periods during which time the organisms in question matured enough to make identification possible. Representative organisms were then removed from the panel and preserved for later study and reference. The entire wooden panel of the short term series was air dried and retained for reference. In the case of the panels in the long term series that had been in the water from three months up to a full year, a careful study was made to determine which organisms were dominant, their size and shape and the percentage of the surface each species covered. After examination, one of the flat surfaces of each of these panels was scraped clean of attached organisms and the scrapings were oven dried at 100° C until the weight was constant. The results are expressed as grams of dry weight tissue per panel side (80 square inches or 512.75 square centimeters). This provides a rough statistical measure of concentration and an index to productivity of the environment for the specific time period of exposure (see bottom line Table 3). In many cases, however, the older panels had obviously suffered loss of part of the fouling growth due to periodic buffeting of the racks against piles when wave action was severe. The panel with the remaining organisms intact on one side was air dried and saved for reference.

## THE FOULING COMMUNITY

### I. Discussion of Organisms settling on Short Term Panels

During the year of observation a total of 70 different kinds of organisms, identified at least to genus, were found on the short term panels. Some organisms were found to have settled during every month of the year, indicating either a continuous breeding cycle or larval forms that can live free for some time before settling. Others settled only seasonally. The truly sessile organisms (primary foulers) received the most attention and a serious attempt was made to identify to species all such forms, but many of the more easily identified motile organisms (secondary foulers) that were found on the panels were also recorded. Numbers of diatoms, tiny flatworms, nematodes, small errant polychaetes, minute snails, mites, free-swimming copepods and crustacean larval forms were often observed but few of these were identified.

Table 1 is an example of how the data were collected and recorded for one common fouling organism, *Balanus crenatus* Bruguière, 1789. Similar tables were prepared for each of the 70 organisms. For bryozoans, hydroids, etc. numbers of discrete colonies were counted rather than individuals.

The data from the entire observation period are summarized in Table 2. This table lists the identified organisms, the numbers of individual test panels where the organisms settled, and the period of the year when the organisms occupied the panels. Also indicated are those panels that carried the greatest number of individuals or colonies of organisms, and at the bottom of the table the number of

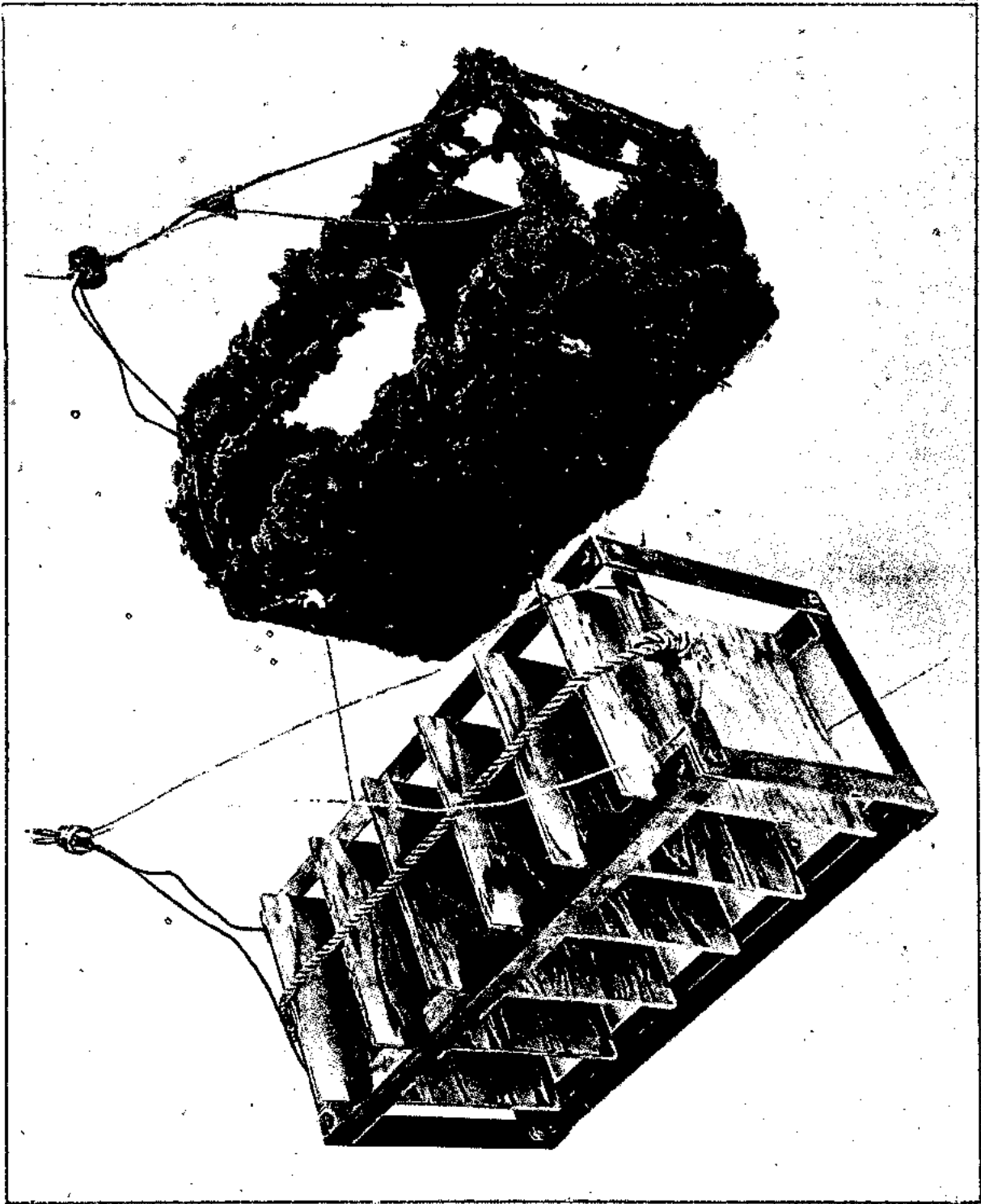


Fig. 3 Photograph of test racks and panels. Left, rack and 6 panels in place ready for exposure. Right, deep rack following removal from water after 12 months exposure. The 12 months panel and the last temporary panel (23-T) still in place. Fouling growth primarily *Cristatipora occidentalis*

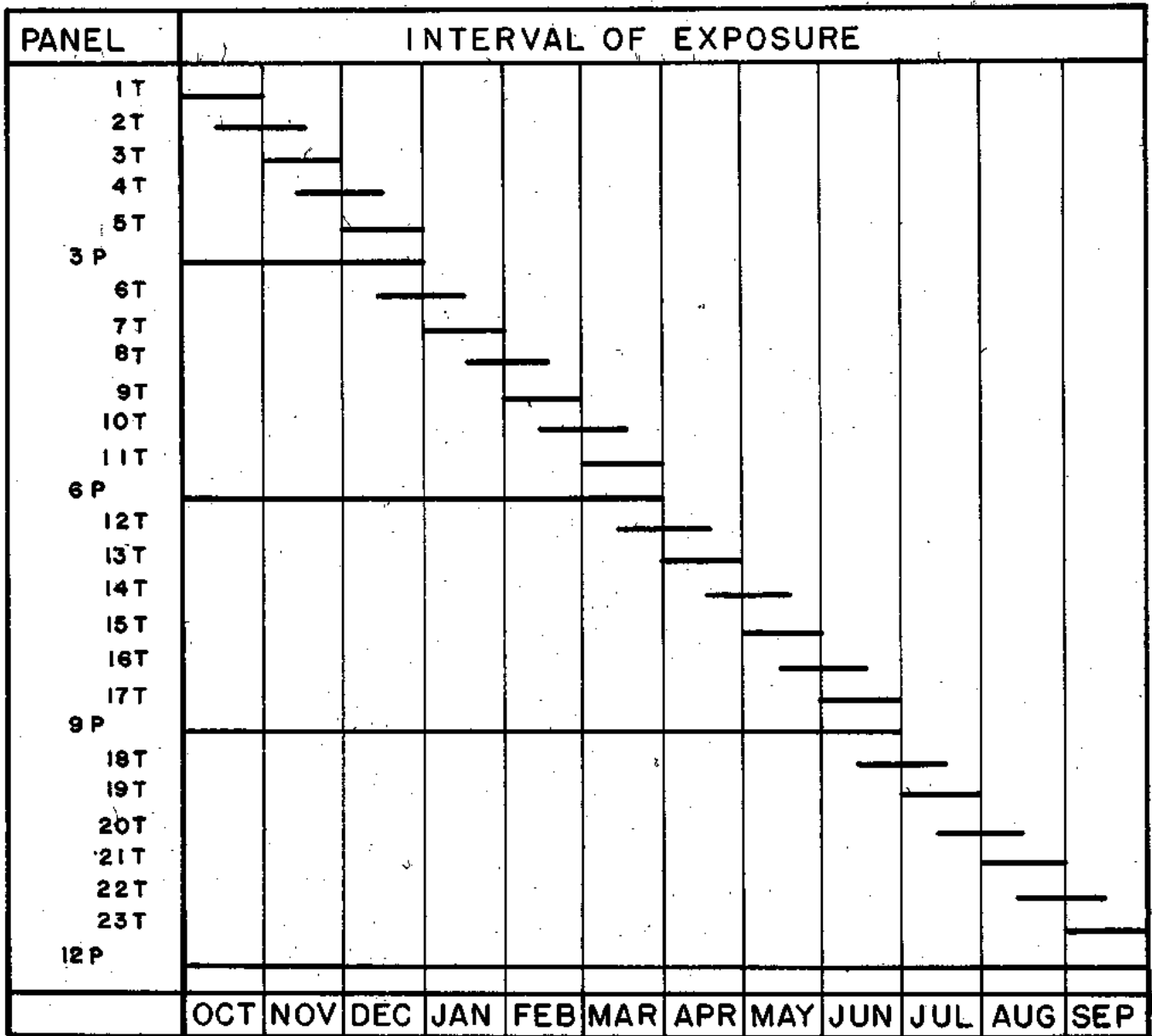


Figure 4

Diagram illustrating period of exposure for test panels from  
October 1, 1966 to October 1, 1967

T = short term panels

P = long term panels

TABLE 1

THE NUMBER OF BARNACLES (*BALANUS CRENATUS*) THAT SETTLED ON VARIOUS PANELS THROUGHOUT THE YEAR. A TABLE SIMILAR TO THIS WAS PREPARED FOR EACH OF THE 70 ORGANISMS ENCOUNTERED.

Panel Number	Lighted Panel	Intertidal Panel	Floating Panel	Shallow Panel	Deep Panel	Asbestos Panel
T - 1		20				
T - 2		1	1			1
T - 3				1		2
T - 4				1	1	3
T - 5			1			
T - 6		1	1	2		
T - 7	1	3	1			4
T - 8	1	2		1		4
T - 9		4				6
T - 10		30	150	100	160	
T - 11	1	25	20	8	10	5
T - 12	2	100	10	5	5	
T - 13		3	50		2	
T - 14		4	12	10	2	
T - 15	1	20	40	3	1	1
T - 16		10	100	1	1	
T - 17	1	25	25		2	
T - 18		20	10			
T - 19		5	10			
T - 20	3	20	25	50	5	20
T - 21	2	20	20	100	4	1
T - 22	1	2	10	10		10
T - 23		6	15	10		
Total panels fouled	9	20	18	14	11	11

species collected by each type of panel.

As can be seen from an examination of Table 2, the most common fouling organisms encountered on the short term panels were encrusting cheilostomate and cyclostomate bryozoans, calcareous serpulid worms, the acorn barnacle *Balanus crenatus*, foraminiferans, ciliates, the nestling clam *Hiatella arctica* and the opisthobranch *Hermisenda crassicornis*. The following discussion will briefly review the most common organisms of each of the major groups listed in Table 2.

#### Algae

None of the short term panels ever had an extensive growth of algae. After one month in the water all panels usually had a slippery surface film that probably consisted of microorganisms too small to be seen, and on many of the panels in racks near the surface, chains of colonial diatoms were observed but not identified. On the rack suspended just below low tide level on the western side of the wharf (the lighted rack) where afternoon light was greatest, it was expected that the panels would collect algae and during the summer months small sprigs of green and red algae were often found. *Ulva* sp., *Polysiphonia pacifica* and *Herposiphonia parva* were the only plants identified. In all cases the growth was very sparse. On one panel, numerous fans of the colonial diatom *Licmophora* sp. were observed.

#### Protozoa

Three species of foraminiferans were observed on various panels. The most common by far was *Cornuspira tajollensis*. This foram was found throughout the year on panels at all depths and positions, but was especially abundant on the intertidal and floating panels. The next most abundant protozoan was the large pink or reddish ciliate *Folliculina* sp. which again was found throughout the year and often in such numbers as to make the panel look dark to the naked eye. The suctorian *Ephelota gemmipara* was sometimes seen as a small forest on the surface of the panels and especially as a fuzzy growth on the clam *Hiatella arctica* and on hydroids. Ciliated swimmers were seen leaving *Ephelota* during February. The stalked colonial ciliate *Zoothamnium* sp. was fairly common and was most clearly seen on the roughened edge of the panels.

#### Porifera

The only sponge that was common on the short term panels was *Leucoselenia eleanor*. In the time available this sponge never was able to form dense masses of anastomosing tubes, but consisted of a few short tubes tightly pressed on the panel surface. A few small specimens of *Leuconia heathi* were occasionally observed, especially on the deep panels.



TABLE 2

## LIST OF ORGANISMS AND PANELS IN SHORT TERM SERIES WHERE ORGANISMS SETTLED

Organisms	Number of test panels on which organism settled 1						Total panels occupied	Interval test panels were occupied (Oct. 1, 1966—Oct. 1, 1967)
	L	I	F	S	D	A		
<b>ALGAE</b>								
<i>Licmophora</i> sp.	1 <sup>2</sup>	0	0	0	0	0	1	September
<i>Uloa</i> sp.	8	0	0	0	0	0	8	January-October
<i>Polysiphonia pacifica</i> Hollenberg, 1942	4	0	0	0	0	0	4	July-September
<i>Herposiphonia parva</i> Hollenberg, 1943	4	0	0	0	0	0	4	July-September
<b>PROTOZOA</b>								
<i>Cornuspira lajollaensis</i> Uchio, 1960	11	18	11	14	14	13	81	October-October
<i>Rosalina columbiensis</i> (Cushman, 1925)	2	2	1	5	3	1	14	June-October
<i>Spirillina revertens</i> Rumbler, 1906	2	0	2	0	1	0	5	July-September
<i>Zoothamnium</i> sp.	7	4	1	8	4	3	27	October-October
<i>Folliculina</i> sp.	15	4	3	16	21	9	68	October-October
<i>Vorticella</i> sp.	0	0	0	0	1	0	1	September
<i>Ephelota gemmipara</i> (Hartwig, 1876)	1	5	5	5	3	2	21	October-October
<b>PORIFERA</b>								
<i>Leuconia heathi</i> (Urban, 1905)	0	1	0	2	2	1	6	January-July
<i>Leucosolenia eleanor</i> Urban, 1905	5	7	8	7	8	6	41	February-October
<b>COELENTERATA</b>								
<i>Obelia</i> sp.	9	15	9	0	1	1	35	October-October
<i>Hydractinia</i> sp.	0	1	1	0	0	0	2	May
<i>Syncoryne mirabilis</i> (Agassiz, 1862)	5	7	8	3	0	1	24	November-October
<i>Companularia</i> sp.	1	0	0	0	0	0	1	July
<i>Anthopleura</i> sp.	0	0	0	1	1	0	2	November-December
<b>PLATYHELMINTHES</b>								
<i>Stylochoplana gracilis</i> Heath & McGregor, 1912	7	7	4	5	9	12	44	October-October
<i>Notoplana acticola</i> (Boone, 1929)	0	2	1	0	1	6	10	February-October
<i>Thysanozoon californicum</i> Hyman, 1953	1	0	1	1	1	0	4	March; May-June; Sept.
<i>Stylochus tripartitus</i> Hyman, 1953	0	0	2	0	0	0	2	June
<i>Stylochus</i> sp.	1	0	1	0	0	0	2	March; July
<b>NEMERTEA</b>								
<i>Emplectonema gracile</i> (Johnston, 1837)	0	0	2	0	0	0	3	March-May
<b>ECTOPROCTA (Bryozoa)</b>								
<i>Bowerbankia gracilis</i> O'Donoghue, 1926	6	16	12	7	6	9	56	January-October
<i>Filicrisia franciscana</i> (Robertson, 1910)	4	1	1	4	1	4	15	May-October
<i>Crisia</i> sp.	1	0	0	0	0	1	2	June-August
<i>Crisulipora occidentalis</i> Robertson, 1910	1	1	1	10	7	2	22	November-October
<i>Tubulipora pacifica</i> Robertson, 1910	17	2	2	22	20	20	83	October-October
<i>Bugula neritina</i> (Linnaeus, 1758)	8	4	1	16	11	9	49	January-October
<i>Bugula californica</i> Robertson, 1905	4	0	0	3	4	6	17	Nov.-Jan.; May-Oct.
<i>Hippothoa hyalina</i> (Linnaeus, 1767)	21	10	10	21	22	22	106	October-October
<i>Lyrula hippocrepis</i> (Hincks, 1882)	13	8	8	12	5	19	65	November-October
<i>Scrupocellaria californica</i> Trask, 1857	0	0	0	0	0	2	2	May
<i>Scruparia ambigua</i> (d'Orbigny, 1841)	17	2	1	11	11	12	54	October-October
<i>Holoporella brunnea</i> (Hincks, 1884)	13	7	4	19	14	19	76	November-October
<b>ENTOPROCTA</b>								
<i>Barentsia gracilis</i> (Lomax, 1886)	0	0	0	0	0	1	1	January

TABLE 2 (cont.)

Organisms	Number of test panels on which organism settled 1						Total panels occupied	Interval test panels were occupied (Oct. 1, 1966—Oct. 1, 1967)
	L	I	F	S	D	A		
<b>ANNELIDA</b>								
<i>Nereis</i> sp.	0	1	0	0	0	0	1	August
<i>Platynereis agassizi</i> (Ehlers, 1868)	0	0	0	1	0	4	5	April-July
<i>Pectinaria californiensis</i> Hartman, 1941	1	0	0	0	0	0	1	August
<i>Halosydna brevisetosa</i> Kinberg, 1855	0	1	1	0	2	1	5	March; August-October
<i>Sabellaria cementarium</i> Moore, 1906	0	0	0	0	1	0	1	March
<i>Spirorbis spirillum</i> (Linnaeus, 1758)	21	8	9	22	23	22	105	October-October
<i>Serpula</i> sp.	7	7	3	13	13	16	59	October-October
<i>Polydora brachycephala</i> Hartman, 1936	3	1	1	0	1	5	11	February-August
<i>Thelepus</i> sp.	0	0	0	0	0	1	1	August
<b>ARTHROPODA</b>								
<i>Balanus crenatus</i> Bruguière, 1789	9	20	18	14	11	11	83	October-October
<i>Balanus glandula</i> Darwin, 1854	0	1	1	0	0	0	2	June; August
<i>Chthamalus</i> sp.	1	1	1	1	0	0	4	July-September
<i>Idothea</i> sp.	0	1	0	0	1	0	2	February; May
<i>Limnoria quadripunctata</i> Holthuis, 1949	8	13	10	19	10	0	60	October-October
<i>Caprella</i> sp.	5	5	2	6	3	5	26	Nov.; Feb.; May-Oct.
<i>Corophium insidiosum</i> Crawford, 1937	0	0	5	0	0	1	6	March-July; August
<b>MOLLUSCA</b>								
<i>Pododesmus cepio</i> (Gray, 1850)	2	1	0	5	3	1	12	October; July-Sept.
<i>Mytilus edulis</i> Linnaeus, 1758	2	5	9	1	2	0	19	Oct.; Jan.; July-Sept.
<i>Pecten</i> sp.	1	0	0	0	0	2	3	July-September
<i>Hiatella arctica</i> (Linnaeus, 1771)	6	12	12	11	13	9	63	October-October
<i>Bankia setacea</i> (Tryon, 1863)	0	0	0	2	0	0	2	February-April
<i>Hermisenda crassicornis</i> (Eschscholtz, 1831)	10	12	11	13	10	12	68	October-October
<i>Doto kya</i> Marcus, 1961	0	0	1	0	0	0	1	May
<i>Dendronotus frondosus</i> (Ascanius, 1774)	0	3	3	1	0	1	8	January-July
<i>Acanthodoris brunnea</i> MacFarland, 1905	0	0	1	0	0	0	1	June
<i>Triopha grandis</i> MacFarland, 1905	2	0	0	2	0	0	4	December; Feb.; April
<i>Cratena albocrusta</i> MacFarland, 1966	2	1	0	0	3	0	6	January; May; August
<i>Polycera atra</i> Mac Farland, 1905	1	1	1	2	1	0	6	February-August
<i>Acmaea</i> sp.	0	3	1	1	0	0	4	March-July
<i>Mopalia</i> sp.	0	0	0	1	0	0	1	May
<b>ECHINODERMATA</b>								
<i>Strongylocentrotus</i> sp.	9	8	9	7	8	8	49	January-October
<i>Eupentacta quinquesemita</i> (Selenka, 1867)	0	0	0	0	0	1	1	June
<i>Pisaster</i> sp.	1	0	0	1	2	2	6	June-September
Total species collected by each type panel	46	41	44	39	41	41		

- (1) Panel designations are as follows: L = Lighted Panels  
 I = Intertidal Panels  
 F = Floating Panels  
 S = Shallow Panels  
 D = Deep Panels  
 A = Asbestos Board Panels

- (2) An underline indicates the group of panels with the greatest numbers of individuals or colonies.

#### Coelenterata

In most fouling studies, investigators have reported hydroids as among the most common organisms. This was not found to be true under the Monterey wharf. *Obelia* sp. was found throughout the year, but was usually a very sparse

growth except for a few of the intertidal panels where it formed a flourishing colony with stalks 2 cm high. Maximum growth was in May, and medusae were released at that time. The only other hydroid found in any significant numbers was

*Syncoryne mirabilis* and it was found as a very sparse growth except on a few floating panels in June. Small anemones (*Anthopleura* sp.) were found on only two occasions on the short term panels. It is surprising that more anemones did not settle on the panels, for several species are found growing in great numbers on nearby piles.

#### Platyhelminthes

Flatworms were common secondary foulers on many of the panels, but some of the worms were so minute as to make identification impossible. The most consistent and conspicuous form was the small cuneate *Stylochoplana gracilis* which was present all year. It was abundant on the deep panels, especially those of asbestos board, and was always seen gliding in and among the bryozoans and barnacles. An interesting flatworm encountered only rarely was *Thysanozoon californicum*. This small worm has a papillated dorsal surface and its color and texture often closely matched the bryozoan colonies (*Holoporella brunnea*) it lived among.

#### Nemertea

Small specimens of *Emplectonema gracile* were found on two panels in the floating rack in March and April. This was the only nemertean found on the short term panels.

#### Ectoprocta (Bryozoa)

During the period of this study, bryozoans clearly constituted the dominant fouling organisms on the short term panels in terms of numbers of species involved, number of panels fouled and numbers of individual colonies. The single species that was dominant on all the submerged panels throughout the year was *Hippothoa hyalina*. This organism forms a circular colony that is hyaline and appears as delicate silvery patches on test surfaces. On many of the shallow and deep panels there were hundreds of colonies up to 5.0 mm in diameter on each side of the panel. Next in importance was *Tubulipora pacifica*. This cyclostomate bryozoan forms a colony that when small is a fan-shaped mat of calcareous tubes with the open ends pointing upward. On the short term panels these colonies never were more than 1-2 mm in diameter, but on deep wooden and asbestos panels in June there were hundreds of colonies which made the test surface feel rough like sandpaper. *Tubulipora* was found on the floating and intertidal panels only in August and September, but on others it was found throughout the year. Two other encrusting bryozoans that were a conspicuous part of the fouling community throughout most of the year were *Lyrula hippocrepis* and *Holoporella brunnea*. These colonies were often colored yellow or orange and after being on the panel one month or less were up to 4 or 5 mm across. One large *Lyrula* colony, however, reached a diameter of 10 mm in a month or less.

Erect bryozoans were less common on the short term panels than the encrusting forms, yet many of these had formed small colonies. *Scruparia ambigua* was never abundant on any one panel, but it was found throughout the year on all submerged panels. The site of growth of *Scruparia* was most often on the roughened edge of the panel and it was never more than a few millimeters high. *Bowerbankia gracilis* was found from January through September and was represented on panels at all depths. The creeping stolons of *Bowerbankia* often gave rise to only a few zoecia, but in some cases on intertidal panels in February and again from May to July a thick furry coating was found. *Bugula neritina* is easily recognized by its purplish color, and was found as small sprigs from January to October. *Crisulipora occidentalis* was the only other bryozoan that occurred with any regularity. It was found throughout most of the year on many of the submerged panels, but was most common on the shallow ones.

#### Entoprocta

The only entoproct observed during the year of study was *Barentsia gracilis*, and it was seen as a small colony only once on an asbestos panel in February.

#### Annelida

*Spirorbis spirillum* was second only to the bryozoan *Hippothoa hyalina* in number of panels fouled and it settled on the surfaces throughout the year. It was least common on the floating and intertidal panels, but was abundant on all of the submerged ones, both wood and asbestos. On some panels, over 50 tubes per side was not uncommon. Most of the tubes were tightly spiraled and averaged 0.5 mm in diameter but some were up to 1.0 mm. Both sinistral and dextral tubes in about equal numbers were represented. The twisted but not coiled tubes of another serpulid (*Serpula* sp.) were also found throughout the year, but these were less abundant than *Spirorbis* both as individuals and in terms of number of panels settled on. The maximum growth of *Serpula* sp. in one month was up to 6 mm in tube length. The only other annelid that occurred regularly was the tube-building *Polydora brachycephala*. The tubes built of silt and debris were fairly common, especially on the asbestos panels. Many tiny errant polychaetes were observed on nearly every test surface, but none of these were identified.

#### Arthropoda

As was to be expected, the dominant arthropod foulers were acorn barnacles. On the piles of the wharf *Balanus glandula*, *B. crenatus*, *B. tintinnabulum* and *B. nubilis* are common, yet, except for a few specimens of *B. glandula* and *Chthamalus* sp., *Balanus crenatus* was the only barnacle that was found as a significant fouler on the test surfaces. Throughout the entire year and on panels at all depths, small specimens of *B. crenatus* could be found. Many were recently settled forms 0.1 mm across, but others were up to 2.5 mm after being on the panel one month or less. As a rule any one panel had only a few barnacles, but enough to show that *B. crenatus* settles throughout the year (see Table 1). The period of maximum settling was from mid-February through March. This was also found to be the period of maximum settling of *B. crenatus* by Mommmsen (1966). It is interesting to note that during late February and early March the maximum settling of up to 25 barnacles per square inch was on the floating, shallow and deep wooden panels, but in late March the maximum settling was on the intertidal panels. In late May and early June another period of intense settling of *B. crenatus* occurred on the floating panels and in late July and August a heavy settling on the shallow panels.

In a survey in the same area during the previous summer, Miller (1966) found massive settling (up to 50/square inch) of *B. crenatus* in late June and early July, and the deep panels were most heavily fouled. In contrast to this, the present study found practically no barnacles settling on the deep panels during late June and July, and only a few on the intertidal and floating panels. The explanation of this might be found in differences in water temperature. In Miller's study the temperature fluctuated between 12.5° and 14.0°C during this period, whereas in 1967 the temperature varied between 13.5° and 15.3°C (Figure 2).

In terms of choice of color of substrate, no significant differences were found in the rate or season of settling of *B. crenatus* on the dark asbestos panels and the lighter wooden panels at 14 feet depth. On the upper panels subject to more light, however, it was found that the larvae tended to settle most abundantly on darker parts of the wood and on dark ink lines drawn on the wood.

As will be noted later, *Balanus tintinnabulum* settled on the long term panels and on the stainless steel racks, but this barnacle was never seen on the short term panels. Perhaps this barnacle, like some other fouling organisms, requires the presence of living organisms on a surface before it will settle.

Other arthropods recorded on the short term panels were secondary foulers. Various copepods were found on practically every test surface, but none were identified. The skeleton shrimp *Caprella* sp. and the tube-building amphipod *Corophium insidiosum* were occasionally present as was the isopod *Idothea* sp. Mites and crustacean larvae were common and abundant and the wood boring gribble *Limnoria quadripun-*

*ctata* was often seen crawling over the surface or in shallow burrows in the wood.

#### Mollusca

The attached mollusc most often encountered on the short term panels was the nestling clam *Hiatella arctica*. This white, rectangular clam was found throughout the year on panels at all depths, but the greatest number of individuals was on the floating panels. Most of the animals were very small (2 mm and less) and were usually seen creeping over the test surface, but larger clams (10 mm and more) were often attached by bisal threads. The clams were most common in depressions in the wood surfaces.

Small numbers of the bay mussel *Mytilus edulis* were also found on wooden panels at all depths throughout most of the year. Most of these were small and mobile, but others were up to 10 mm long and attached. Never were there more than four or five animals on a panel. *Pododesmus cepio* was also found attached to or moving over the panels. These were invariably very small.

Opisthobranchs were encountered on the test surfaces throughout the year. By far the most common and abundant species was *Hermisenda crassicornis*. Each panel occupied normally carried from one to five animals, and egg masses of *Hermisenda* were found during every month of the year. *Dendronotus frondosus* was seen on only a few panels, but when seen it was very abundant. *Cratena albocrusta* and *Polycera atra*, although not seen often, were abundant on certain panels. Other opisthobranchs listed in Table 2 were found only rarely. Except for *Hermisenda crassicornis*, which appeared on panels regardless of what other organisms were present, most of the nudibranchs found were on panels which supported colonies of *Obelia* or other hydroids.

Other molluscs encountered on the temporary panels were gastropod snails of a variety of forms but invariably small and none were identified. Also found one or more times were tiny limpets (*Acmaea* sp.) and very small chitons (*Mopalia* sp.).

#### Echinodermata

From January through September, small sea urchins (*Strongylocentrotus* sp.) averaging 0.5 mm in diameter were frequently encountered in small numbers on panels at all depths. Tiny asteroids (*Pisaster* sp.) appeared on a few panels from June to September and a single specimen of the sea cucumber *Eupeniacta quinquesemita* was seen in June.

#### Chordata (Tunicata)

As will be seen later, three species of tunicates settled on the long term panels and on the stainless steel and wooden racks. Yet, no tunicates were ever observed on the short term panels. It is possible that these animals are not pioneers in the fouling community, but settle only after the surface has been «prepared» by other organisms.

### II. Depth and Surface Preference

At the bottom of Table 2 is a summation of the total number of species of fouling and boring organisms collected by each category of test panel. There are only slight differences in the total number of species each collected. As has been pointed out in the above discussion of the organisms that settled on the short term panels, some definitely preferred one depth to another, but the preference varied from species to species. One of the purposes of this study was to determine the type of surface that would collect the maximum number of fouling organisms, and to get data relative to this problem, panels of two different materials (plywood and asbestos board) were submerged to identical depths in the same area to test their relative effectiveness as collectors. As can be seen from Table 2, there was no difference in the number of species of organisms collected by these different materials, and in settling most foulers did not seem to distinguish between the two. Some organisms, however, (e.g.

*Folliculina* sp.) seemed to prefer plywood to asbestos board, whereas the reverse was true for others (e.g. *Lyrula hippocrepis*). The asbestos board had one smooth and one rough surface but these difference had no effect on rate of settling or foulers except there was a tendency for more barnacles (*Balanus crenatus*) to settle on the rough surface than the smooth, and encrusting bryozoa seemed to prefer the smooth surface. These differences, however, were only slight.

### III. Discussion of Organisms Settling on Long Term Panels.

Table 3 lists the fouling and boring organisms observed on the long term panels. As can be seen, the list is similar to that of the organisms on the short term panels (Table 2). It is a longer list, however, containing 81 organisms identified at least to genus, and several organisms were found in fair numbers on the long term panels that were never encountered on panels in the water for only one month. As Sheer (1945) and others have pointed out, this is to be expected, for many organisms settle on surfaces only when these surfaces have been colonized by pioneering foulers.

The long term panels presented many difficulties in analysis. Very often one or two species of bryozoans, for example, were the dominant organisms at the time the panels were removed for study, and these had overgrown and completely smothered earlier populations of barnacles and serpulid worms. In the case of panels practically covered with a foliaceous growth of erect bryozoans, it was impossible to locate all the organisms living in and around the bryozoans. It was obvious that very often the growth of organisms had become so heavy on a panel that large slabs of fouling growth had broken off and the area was being recolonized by other forms. This explains why the weight of the fouling mass on a 9 month panel might be less than on one of 6 months (see Table 3, bottom). As before, each of the major groups and dominant organisms will be discussed briefly.

#### Algae

Five species of green and red algae were found on the long term panels in the lighted rack. Even after 12 months, the growth of algae was very sparse and did not constitute a dominant part of the fouling mass. Diatoms were observed attached to bryozoans and other fouling animals but none of these were identified.

#### Protozoa

It was very difficult to detect protozoans in the mass of multicellular foulers, yet essentially the same forms were found as on the short term series. *Cornuspira lajollaensis* was the dominant foraminiferan, and on the 12 month floating panel was found in thousands. *Folliculina* sp. was the most commonly encountered ciliate.

#### Porifera

On the long term panels *Leucoselenia eleanor* appeared as large masses of anastomosing tubes, and was often covered with silt and debris. At one time or another it was found on panels at all depths and was also abundant on the floating and intertidal racks. *Leuconia heathi* was a common sponge on the submerged panels and racks but was not found on those in the intertidal or the floating series. On some of the 12 month panels single specimens of this sponge were often up to 8 cm long, but most were globular and about 3 cm in diameter. *Rhabdodermella nuttingi* was found only on 9 month and 12 month test surfaces. It was never abundant, and was found in small clumps, the individuals reaching a maximum length of 5 cm.

#### Coelenterata

The only consistent hydroid fouler on the long term

TABLE 3  
LIST OF ORGANISMS AND PANELS SETTLED ON IN LONG TERM SERIES  
OCTOBER 1, 1966 - OCTOBER 1, 1967

Fouling and boring organisms	3-months						6 months						9 months						12 months																	
	L	I	F	S	D	A	L	I	F	S	D	A	L	I	F	S	D	A	L	I	F	S	D	A												
<b>ALGAE</b> <i>Ulva</i> sp. <i>Giffordia sandriana</i> (Zanardini) Hamel, 1939 <i>Polysiphonia pacifica</i> Hollenberg, 1942 <i>Pterosiphonia dendroidea</i> (Montagne) Falkenberg, 1901 <i>Brachioglossum woodii</i> (Agardh) Kylin, 1924	No data		No data									+						+							x <sup>4</sup>											
<b>PROTOZOA</b> <i>Cornuspira bajollaensis</i> Uchio, 1960 <i>Rosalina columbiensis</i> (Gushman, 1925) <i>Zoothamnium</i> sp. <i>Folliculina</i> sp. <i>Ephelota gummipara</i> (Hartwig, 1876)	No data		No data			x	x			x		x			x	x									x	x	x	x			x	x	x	x		x
<b>PORIFERA</b> <i>Leuconia deatzi</i> (Urban, 1905) <i>Leucosolenia eleanor</i> Urban 1905 <i>Rhabdoderma nuttingi</i> Urban, 1902	No data		No data	++	+	+	+		x	x	+	+	+	+	x	+	x	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	x
<b>COELENTERATA</b> <i>Obelia</i> spp. <i>Syncoryne mirabilis</i> (Agassiz, 1862) <i>Hydractinia</i> sp. <i>Corynactis californica</i> Carlgren, 1936	No data	x	No data						x				x	x	x										x	x								+		+
<b>PLATYHELMINTHES</b> <i>Stylochopiana gracilis</i> Heath & McGregor, 1912 <i>Notoplana acticola</i> (Boone, 1929) <i>Thysanoxon californicum</i> Hyman, 1953 <i>Stylochus tripartitus</i> Hyman, 1953	No		No			+		+			+							+																		+
<b>NEMERTEA</b> <i>Micrura verilli</i> Coe, 1901 <i>Euplecionema gracile</i> (Johaston, 1837) <i>Tetrastemma nigrifrons</i> Coe, 1904	data		data																																+	+
<b>ECTOPROCTA (BRYOZOA)</b> <i>Bowerbankia gracilis</i> O'Donoghue, 1926 <i>Filicerisia franciscana</i> [Robertson, 1910] <i>Crisia</i> sp. <i>Criuslipora occidentalis</i> Robertson, 1910 <i>Tubulipora pacifica</i> Robertson, 1910 <i>Bugula neritina</i> (Linnaeus, 1758) <i>Bugula californica</i> Robertson, 1905 <i>Hippothoa hyalina</i> (Linnaeus, 1767) <i>Lyruria hippocrepis</i> (Hincks, 1882) <i>Serupocellaria californica</i> Trask, 1857 <i>Seruparia ambigua</i> (d'Orbigny, 1841) <i>Haloporella brunnea</i> (Hincks, 1884)	No		No																																	
<b>ANNELIDA</b> <i>Nereis vesillosa</i> Grube, 1854 <i>Nereis</i> sp. <i>Platynereis agassizi</i> (Ehlers, 1868) <i>Halosydna brevisetosa</i> Kinberg, 1855 <i>Pseudognamptilla ocellata</i> Moore, 1905 <i>Sabella</i> sp. <i>Spirobia spirillum</i> (Linnaeus, 1758) <i>Serpula</i> sp. <i>Polydora brachycephala</i> Hartman, 1936	data		data																																	
<b>ARTHROPODA</b> <i>Balanus crenatus</i> Brugiere, 1789 <i>Balanus glandula</i> Darwin, 1854 <i>Balanus tintinnabulum</i> (Linnaeus, 1758) <i>Chthamalus</i> sp. <i>Limnoria quadripunctata</i> Holthuis, 1949 <i>Corophium insidiosum</i> Crawford, 1927 <i>Capsella</i> sp. <i>Cancer antennarius</i> Stimpson, 1856 <i>Pachygrapsus crastipes</i> Randall, 1839 <i>Pugettia producta</i> (Randall, 1839) <i>Loxorhynchus crispatus</i> Stimpson, 1875	No data	x	No data			+	x	x	x	x	x	+			x	x	x														+	+	+	+	+	+

TABLE 3 (cont.)

Fouling and boring organisms	3 months						6 months						9 months						12 months																		
	L <sup>1</sup>	I	F	S	D	A	L	I	F	S	D	A	L	I	F	S	D	A	L	I	F	S	D	A													
<b>MOLLUSCA</b>																																					
<i>Pododesmus cepio</i> (Gray, 1850)																																					
<i>Mytilus edulis</i> Linnaeus, 1758						+																															
<i>Pecten</i> sp.																																					
<i>Hiatella arctica</i> (Linnaeus, 1771)						+																															
<i>Benkia setacea</i> (Tryon, 1863)						+																															
<i>Hemissenda crassicornis</i> (Eschscholtz, 1831)						+																															
<i>Doto kya</i> Marcus, 1961																																					
<i>Dendronotus frondosus</i> (Ascanius, 1774)																																					
<i>Acanthodoris brunnea</i> MacFarland, 1905																																					
<i>Triopha grandis</i> MacFarland, 1905																																					
<i>Cratens alborusta</i> MacFarland, 1906																																					
<i>Polycera atra</i> MacFarland, 1905																																					
<i>Aegires albopunctatus</i> MacFarland, 1905																																					
<i>Dirona picta</i> MacFarland, 1905																																					
<i>Acmaea</i> sp.																																					
<i>Ischnochiton</i> sp.																																					
<b>ECHINODERMATA</b>																																					
<i>Strongylocentrotus purpuratus</i> (Stimpson)																																					
<i>Strongylocentrotus</i> sp.																																					
<i>Ophiotrix spiculata</i> LeConte, 1851																																					
<i>Pycnopodia helianthoides</i> (Brandt, 1835)																																					
<i>Pisaster</i> sp.																																					
<i>Eupentactia quinquearmata</i> (Selenka, 1867)																																					
<b>CHORDATA (TUNICATA)</b>																																					
<i>Aplidium solidum</i> (Rittler & Forsyth, 1917)																																					
<i>Ascidia ceratodes</i> (Hunziman, 1912)																																					
<i>Styela montereyensis</i> (Dall, 1872)																																					
<i>Styela truncata</i> Rittler, 1901																																					
Weight of dried organisms scraped from one side of 8 inch by 10 inch panel																																					

(1) Symbols used at head of columns mean: L = Lighted panels; I = Intertidal panels; F = floating panels; S = Shallow panels; D = Deep wooden panels; A = Asbestos board panels.

(2) Symbols in columns mean: + = organism present in numbers of from 1 to 10 individuals or colonies. \*  
 x = organism present in numbers of from 10 to 20 individuals or colonies.  
 xx = organism present in numbers of from 20 upward (individuals or colonies).

panels was *Obelia* sp. It was most abundant on the intertidal panels, and on the deep asbestos panels. The anemone *Corynactis californica* was found in small numbers on one asbestos panel at 9 months and on one deep wood panel at 12 months and was found attached to the wood bottom plates of the intertidal, shallow and deep racks. This anemone is common on the wharf pilings, but was never encountered except in these few instances sited.

#### Platyhelminthes

Essentially the same group of flatworms inhabited the long term and short term panels. Much larger worms, however, especially *Stylochus tripartitis*, were found on the long term surfaces, and in all cases the flatworms were more abundant on the older, more heavily fouled surfaces.

#### Nemertea

The three species of nemerteans found on the long term series were few in number but large in size. One *Emplectonema gracile* reached a length of over 30 cm. These worms often occupied open burrows that had been excavated by *Limnoria* or the dead shells of barnacles.

#### Ectoprocta (Bryozoa)

The bryozoans again were the dominant organisms on all of the long term panels and on most of the racks. On the submerged panels and racks *Crisulipora occidentalis* was

often so dominant as to make the surface appear to be covered with nothing else (see Figure 4). The thickness of the *Crisulipora* growth often exceeded 5 cm, and on the deep panels this growth made up more than three fourths the weight of the entire fouling community. *Crisia* sp., *Filicrisia franciscana* and *Bugula neritina* often grew abundantly with *Crisulipora*, but never were any of these dominant. Under the *Crisulipora* growth, and encrusting the surface of all submerged panels of 6 months age and older and all racks was *Lyrula hippocrepis*. *Holoporella brunnea* and massive fans of *Tubulipora pacifica* were also found in abundance. *Lyrula* was in all cases, however, the dominant encrusting bryozoan.

On the floating panels and those in the intertidal position, *Crisulipora* was usually completely replaced by *Bowerbankia gracilis* as the dominant erect bryozoan, and many panels and the racks in these positions had a thick furry growth of *Bowerbankia*. Under this blanket, however, was the ubiquitous *Lyrula hippocrepis* and, except on the intertidal and floating panels, *Holoporella brunnea*. The encrusting bryozoan *Hippothoa hyalina*, the most conspicuous organism on practically all of the short term panels, was found on a few panels of the 3 month and 6 month series, but after this was not seen on the panels as a living organism. The dead remains of *Hippothoa* were often seen on 9 and 12 month panels under a smothering encrustation of *Lyrula hippocrepis*.

#### Annelida

The dominant annelids were again, as before, the serpulid

worms *Spirorbis spirillum* and *Serpula* sp. They were found on all panels except those in the intertidal series, but on the older panels were often smothered by *Lyrula* growth. On some of the 12 month panels, *Serpula* sp. reached a length of 8 cm and up to 0.5 cm in diameter.

#### Arthropoda

*Balanus crenatus* was fairly common on only the intertidal panels at 3 months, but at 6 months this barnacle was very abundant on all except the deep wooden and asbestos panels. From then on, as the bryozoan growth increased, the barnacles declined. Under the layer of *Lyrula hippocrepis* could be seen the dead shells of many *Balanus crenatus*. *Balanus tintinnabulum* was never abundant, but on many of the panels except the deep ones from one to five large *B. tintinnabulum* could be found. The largest of these from the 12 month panels were 3 cm in diameter. A small number of *Balanus glandula* was found on the 12 month panels of the intertidal series, and a few were also observed on the stainless steel rack of the intertidal series and the wooden floating rack.

#### Mollusca

The dominant mollusk on the long term panels was, as on the short term ones, the nudibranch *Hermisenda crassicornis*. The dominant attached mollusk was *Hiatella arctica*. This nestling clam was found embedded in the fouling growth of panels at all depths, but was most abundant and reached the largest size on the floating panels. On some of these, and in crevices in the floating rack, after 12 months this mollusk reached a length of 3 cm and had siphons up to 5 cm long.

*Mytilus edulis* is a common wharf piling dweller, yet it was found only in small numbers on the test panels and racks during this study. Never were more than five mussels found on any one panel, but they were sometimes of large size. Several mussels attached to the floating rack were 5 cm long when the rack was removed after 12 months.

In addition to *Hermisenda crassicornis*, many species of nudibranchs were observed on the long term panels, but always in small numbers.

#### Echinodermata

The only echinoderms to appear regularly on the test surfaces were small green sea urchins. In the older panels these became purple and could be identified as *Strongylocentrotus purpuratus*. They were especially abundant on the floating rack and panels.

#### Chordata (Tunicata)

No tunicates were observed on any of the short term panels nor on those in the water for 3 months. On older panels, however, four species of tunicates were encountered. *Ascidia ceretodes* was on many of the panels of 6 months age and older and at one time or another was found on panels

at all depths. It was never a dominant organism, and reached a maximum size at 12 months of about 3 cm across.

*Aplidium* (formerly *Amaroucium*) *solidum* made an inconspicuous first appearance on a deep asbestos panel at 9 months. At 12 months this tunicate was found in large numbers attached to all the racks and to panels in the intertidal, floating and shallow positions. On the intertidal rack and the 12 month intertidal panel, *Aplidium solidum* was clearly the dominant organism, forming large massive slabs up to 10 cm across.

*Styela truncata* and *Styela montereyensis* were found in small numbers on several of the 12 month panels and rack. On the floating panel and rack *S. montereyensis* reached a maximum length of 8 cm.

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# A STUDY OF DEEP - OCEAN FOULING

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## SUMMARY

A deep water sampling program was conducted in the Straits of Florida and in the Tongue of the Ocean during 1961-1968 to determine distribution patterns of offshore fouling communities. Test panels and other substrates were exposed at various depths to 1,737 meters and distances to

five miles from shore. The rate of fouling diminished toward the bottom and in a seaward direction. No fouling occurred below the mixed layer, except for trace amounts very close to the bottom.

## INTRODUCTION

The luxuriant growth of marine biological fouling in near-shore waters is well known and poses a major problem for marine engineers. Biofouling at offshore locations is generally thought to be very much reduced, by nearshore standards, but this belief has rarely been quantitatively confirmed by long term investigations.

In 1961 the U.S. Naval Oceanographic Office undertook a

sampling program in the Straits of Florida and in the Tongue of the Ocean (TOTO), Bahama Islands (Fig. 1) to determine the distribution pattern of offshore biofouling communities. Previous investigations of biofouling communities in the South Florida/Bahamas region have been carried out only at shallow water sites in Biscayne Bay (Weiss 1948, Smith and others 1950) and at Daytona Beach, Florida (Richards and Clapp 1944).

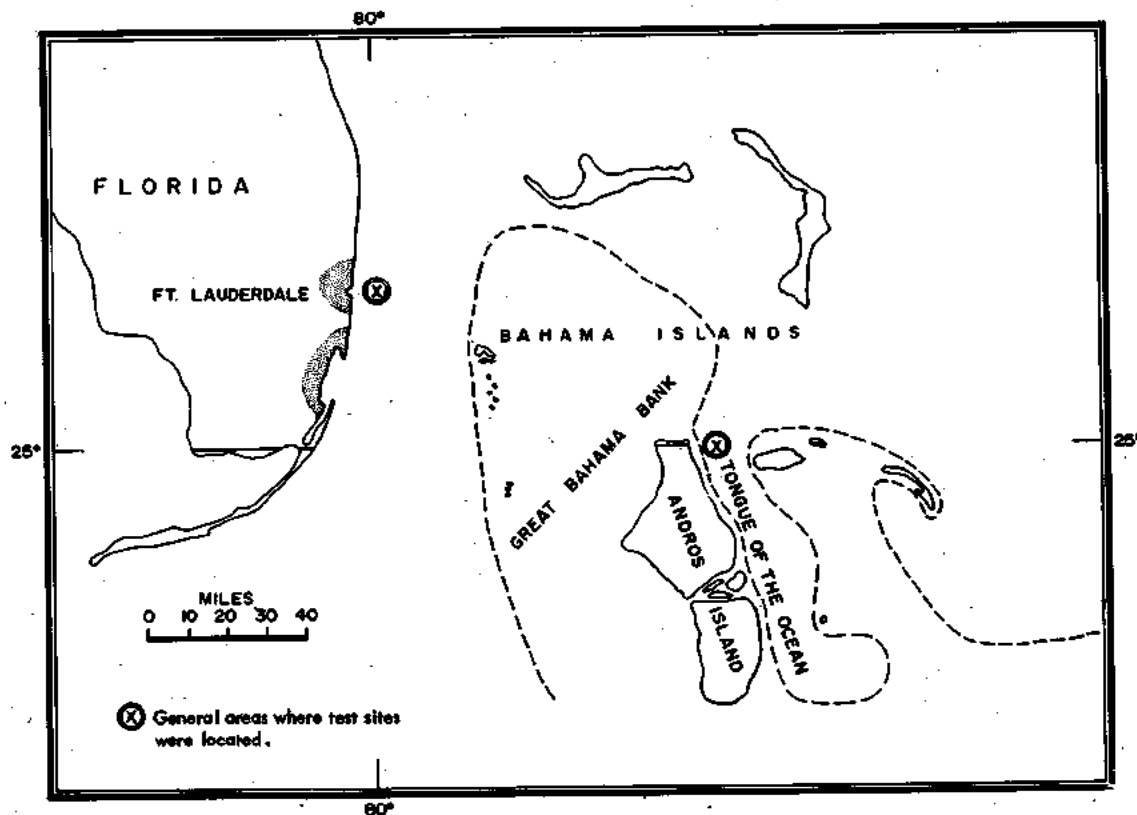


Figure 1. Map of Study Area Showing Approximate Location of Test Sites



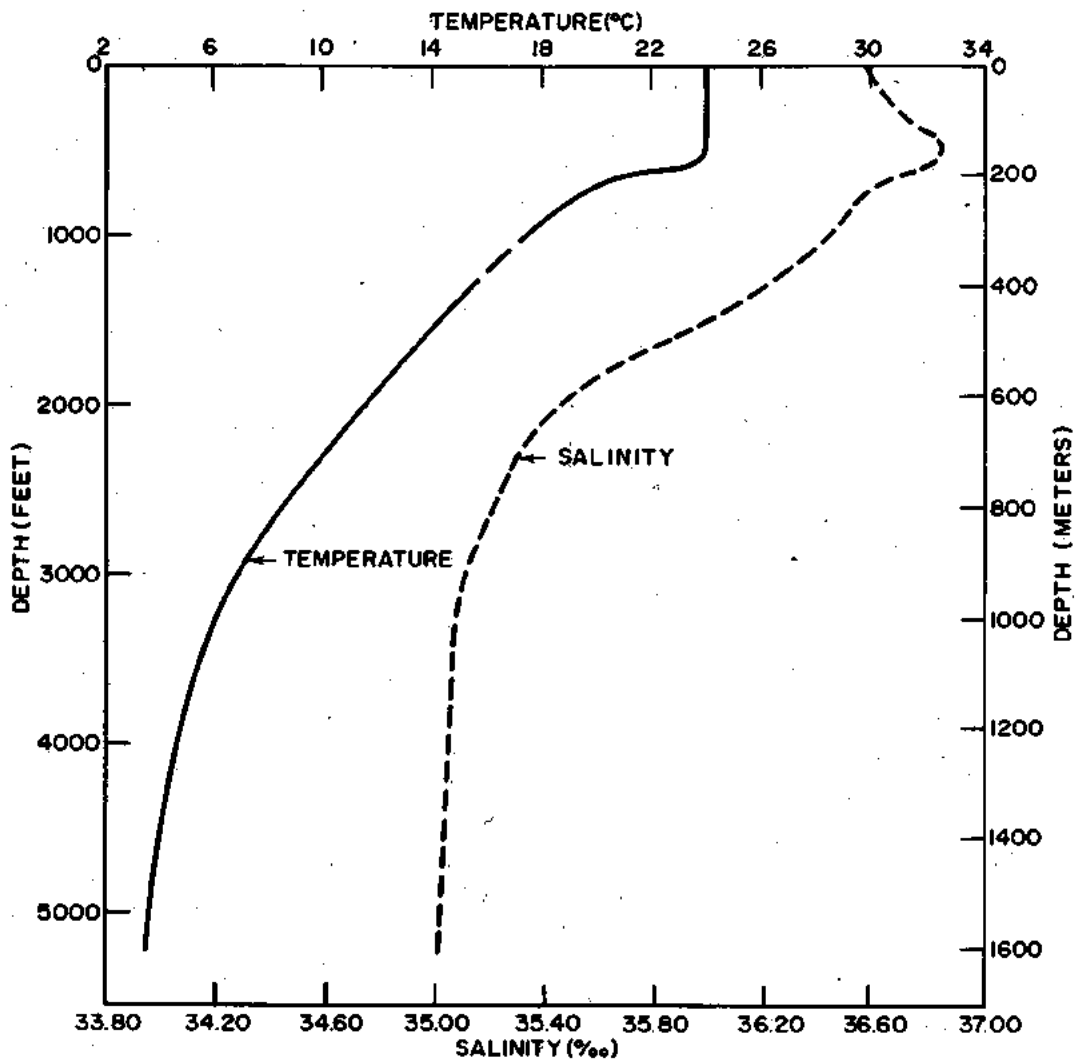


Figure 2. Typical Temperature and Salinity Profiles, Upper TOTO

This is a report of the fouling investigations carried out off Fort Lauderdale, Florida and off Andros Island, Bahamas between June 1961 and January 1968. Interim reports are available which discuss early aspects of these programs (DePalma 1962, DePalma 1963a).

I am indebted to Dr. Ruth D. Turner of the Harvard Museum of Comparative Zoology, Dr. Victor Zullo of the Woods Hole Marine Biological Laboratory, Dr. Arnold Ross of the American Museum of Natural History, and Dr. James B. Rucker and Mr. Edward R. Long of the Naval Oceanographic Office, for assisting in the identification of various organisms.

#### EXPOSURE SITES

South Florida and the Bahama Islands together make up the northern edge of the broad, tropical, Caribbean biological province which extends from Florida to Brazil and from Central America to the Windward Islands.

The marine environment in the Florida Straits is open sea in character with a normal salinity of 35.5 to 36.5 parts per thousand. The outstanding feature of this environment is the northflowing Florida Current, whose speeds vary greatly but average 1.5 knots at the test panel exposure sites. Tem-

peratures range annually from 24°C. to 30°C. at the surface and from 20°C. to 25°C. near the bottom. The bottom slopes gently to the eastward and is composed of a fine grained calcareous sand.

The Tongue of the Ocean is a long, narrow, deep trench lying roughly north and south, with the northern end open to the deep sea. It is bordered on the south and east by the shallow Great Bahama Bank and on the west by Andros Island (Fig. 1).

In the upper layers, the warm saline waters of the TOTO (Fig. 2) are very much similar to those of the Straits of Florida. The currents are generally weak and variable and the bottom consists of a dominantly silt size calcareous ooze.

#### METHODS

Six inch by twelve inch wood-asbestos test panels were used as collecting surfaces. These were exposed vertically from moored arrays or horizontally on the bottom, for one month or cumulatively longer periods up to 31 months. Fouling organisms were also collected from other substrates (oceanographic sensors and hardware) exposed in the study areas for various periods of time. Test panel arrays were moored at four sites off Fort Lauderdale, Florida and two

TABLE I  
LIST OF SPECIES AND SITES AND DEPTHS WHERE COLLECTED

Species	Site and Depth (see Fig. 3)	Species	Site and Depth (see Fig. 3)
<b>Algae:</b>		<i>Balanus venustus niveus</i>	A1, B3, C4
<i>Dilophus ahernans</i>	B2, C2, E2, E3	<i>Balanus</i> sp.	E3, E4, E5, F2
<i>Heterosiphonia</i> sp.	C2, D2, E2, F2, F3, G2, G3	<i>Heteralepas cornuta</i>	C4, D4, D5
<i>Spyridia</i> sp.	C2, D2, E2, E3	<i>Conchoderma virgatum</i>	D2, F2, F3, F4, G2, G3, G4
<i>Sargassum filipendula</i>	B2, D2, E2, G2	<i>Scalpellum portoricanum</i>	E7
<i>Cladophora</i> sp.	B2, C2, D2, E2, E3, F2, F3, G2	<i>Poecilasma inaequilaterale</i>	E7
<i>Zonaria variegata</i>	C2, D2, E2	<i>Lepas anatifera</i>	D2, E2, F2, F3, F4, F5, F6, F7, G2, G3, G4, G5, G6, G7
<i>Jania</i> sp.	B2, D2, E2		
<i>Gracilaria</i> sp.	B2, C2, D2, E2	<b>Mollusca:</b>	
<i>Padina vickersiae</i>	B2, C2, C3, D2, D3, G2, G3	<i>Ostrea frons*</i>	B2, B3, C2, C3, C4, D2, D3, E2, E3, F2, F3, F4, F5, G2, G3, G4, G5
<i>Ulva</i> sp.	B2, C2, C3, D2, D3, E2, E3	<i>Ostrea equestris*</i>	B2, B3, C2, C3, C4, D2, D3, D4, E2, E3, F2, F3, F4, G2, G3, G4
<i>Chrysonohos lewisii</i>	B2, B3, C2, D2, E2, F2, F3, G3	<i>Pinctada radiata*</i>	A1, B2, B3, C2, C3, C4, D2, E2, F2, F3, F4, G2, G3, G4
<b>Protozoa:</b>		<i>Pycnodonta thomasi*</i>	B2, B3, C2, C3, C4, D2, D4, D5, E3, E4, E5, F3, F4, F5, G4, G5
<i>Trochammina compacta</i>	F14, G14, G15	<i>Pteria colymbus</i>	B2, C3, C4, D3, D4, D5, E2, E3, E4, E5, F2, G2, G4
<i>Homotrema rubrum</i>	G5	<i>Anomia simplex*</i>	A1, B2, B3, D2, E2, E3, F2, F3, F4, F5, G2, G3, G4, G5
<b>Porifera:</b>		<i>Pinna carnea</i>	B2, B3, C2, D2, F2, F3, F4, G3, G4
<i>Spongia officinalis</i>	B2, B3, C2, D2	<i>Crassostrea rhizophorae*</i>	A1
<i>Grantia</i> sp.	B2, B3, C2, C3, D2, D3, D4, E2	<i>Chama macrophylla*</i>	B2, B3, C2, C3, D2, E2, F2, F3, F4, G2, G3, G4, G5
<b>Coelenterata:</b>		<i>Arca zebra</i>	B2, D2, E2, F3, G2, G3
<b>Campanulariidae*</b>	A1, B2, B3, C2, C3, C4, D2, D3, D4, D5, E2, E3, E4, E5, F2, F3, F4, F5, F6, F7, G2, G3, G4, G5, G6, G7	<i>Musculus lateralis</i>	B2, C2, C3, C4, D2, E2, E3
<b>Tubulariidae</b>	D5, E4, E5, E6, E7, F11, G14, G15	<i>Spondylus americanus*</i>	B2, B3, D5, F2, F3, F4, F5, G2, G3, G4
<b>Sertulariidae</b>	D5, F2, F3, F4, F5, F6, F7, G2, G3, G4, G5, G6, G7	<i>Aequipecten muscosus</i>	B2, B3, C2, C3, C4, F2, F3, F4, G3, G4
<i>Oculina diffusa</i>	C3, F3, F5, G3, G4, G5	<i>Brevimalleus candeanus</i>	B2
<i>Acropora</i> sp.	C3, F3, F4, G3, G4	<i>Hiatella arctica</i>	E2
<i>Porites</i> sp.	D3, F3, F4, F5, G3, G4, G5		
<b>Gorgoniidae</b>	B2, C2, D2, D3, F2, G2	<b>Molluscan borers:</b>	
<b>Bryozoa:</b>		<i>Lyrodus pedicellatus</i>	B2, B3, C2, C3, D2, D3
<i>Microporella trispinosa</i>	B3	<i>Teredo bartschi</i>	B2, B3, C2, C3
<i>Harmerella dichotoma</i>	B3	<i>Teredo clappi</i>	B3
<i>Schizoporella unicornis</i>	A1, D4, D5	<i>Teredo fulcifera</i>	E2, E3, E4
<i>Parellisina latirostris</i>	D5	<i>Teredo fulleri</i>	E4
<i>Celleporella vagans</i>	D5	<i>Teredo navalis</i>	E3
<i>Parasmittina spatularia</i>	D5	<i>Teredo</i> sp.	F2
<i>Biflustra tenuis</i>	E2	<i>Teredothyra matocotana</i>	B2, B3, C2, C3, C4, D2, D3, D4
<i>Bugula</i> sp.	B3	<i>Teredora malleolus</i>	D2, D3, D4, E2, E3, E4
<b>Annelida:</b>		<i>Notoreredo knoxi</i>	D3
<i>Hydroides parous</i>	A1, B2, B3, C2, C3, C4, D2, D4, D5, E3, E4, E5	<i>Bankia gouldi</i>	B2, D2
<i>Hydroides norvegica</i>	B3, C4, F2, F3, F4, F5, G2, G3, G4, G5	<i>Bankia fosteri</i>	C2, C4, D2, D4, E2, E4
<i>Pomatoceros</i> sp.	B3, C4, D4, D5, E4, F2, G2, G4	<i>Bankia carinata</i>	B2, B3, C2, C3, C4, D2, D3, D4, D5, E2, E3, E4, E5, E6, E7
<i>Vermiliopsis infundibulum</i>	A1, F3, G3		
<i>Pomatostegus latiscapus</i>	B3, E7, F3, F5, G3, G5	<i>Xylophaga a</i>	C3, C4, D3, D4, D5
<i>Serpula vermicularis</i>	C2	<i>Xylophaga b</i>	E6, E7
<i>Salmacina incrustans</i>	A1, B2, B3, C4, D5, F4, G4	<i>Xylophaga c</i>	E7
<i>Serpulid</i> s	G14, G15	<i>Xylorredo noti</i> , Turner	G15
<b>Sabellidae</b>	G14, G15		
<b>Arthropoda:</b>		<b>Chordata (Tunicata):</b>	
<i>Balanus improvisus*</i>	A1, B2, B3, C3, D3, D4	<i>Botryllus</i> sp.	B2, B3, C2, C3, D2, D3, D4
<i>Balanus trigonus*</i>	A1, B2, B3, C2, C3, C4, D2, D3, D4, D5	<i>Styela</i> sp.	A1, B2, B3, C2, C3, D2, D3, E3, F2, F4, G2, G3
<i>Balanus tintinnabulum</i>	B2, B3, C2, C3, C4, D3		
<i>Balanus eburneus*</i>	A1, B3, D2, D3	<i>Ciona intestinalis</i>	A1, B2
<i>Balanus calidus</i>	B3, C4, D3, D4	<i>Ascidia nigra</i>	B2
		<i>Asciidiidae</i>	C2

\* Dominant species; i.e. occupied greater than 50% of surface on one or more test panels.

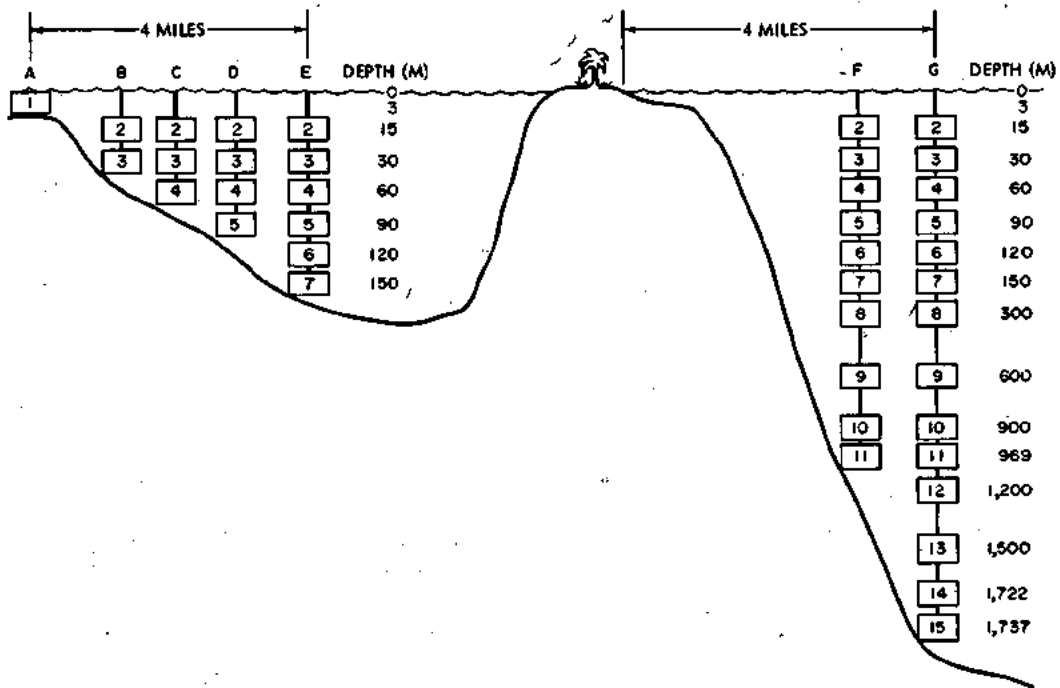


Figure 3. Map of Study Area in Cross Section Showing Simplified Bottom Profile and the Sites and Depths of Panel Exposure

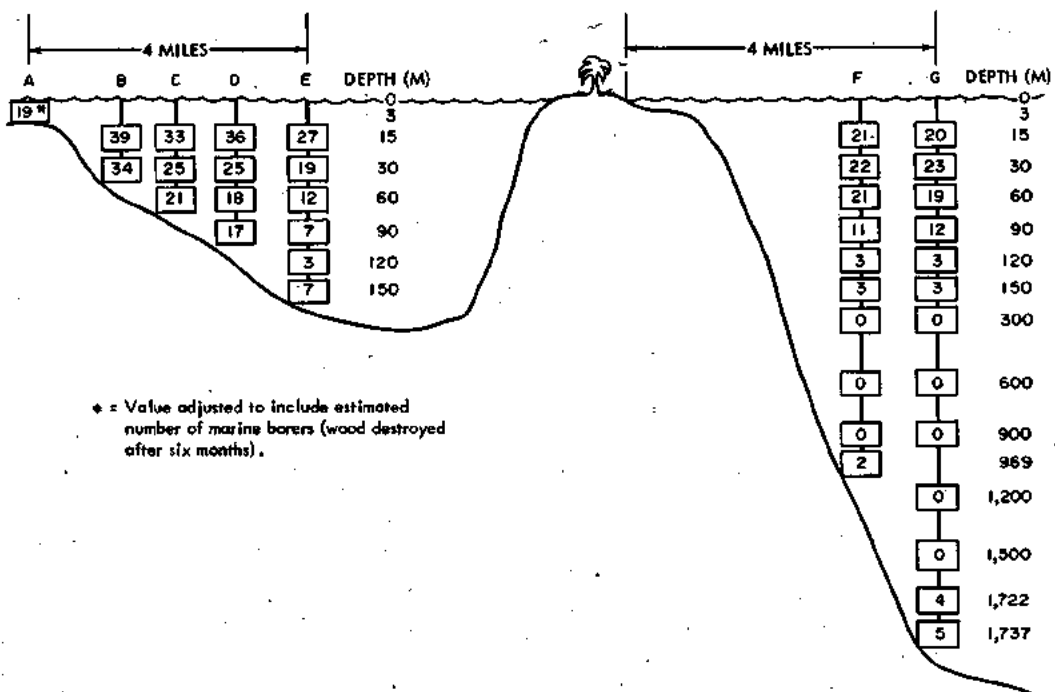


Figure 4. Distribution of Taxa on Test Panels Exposed in the Study Area.

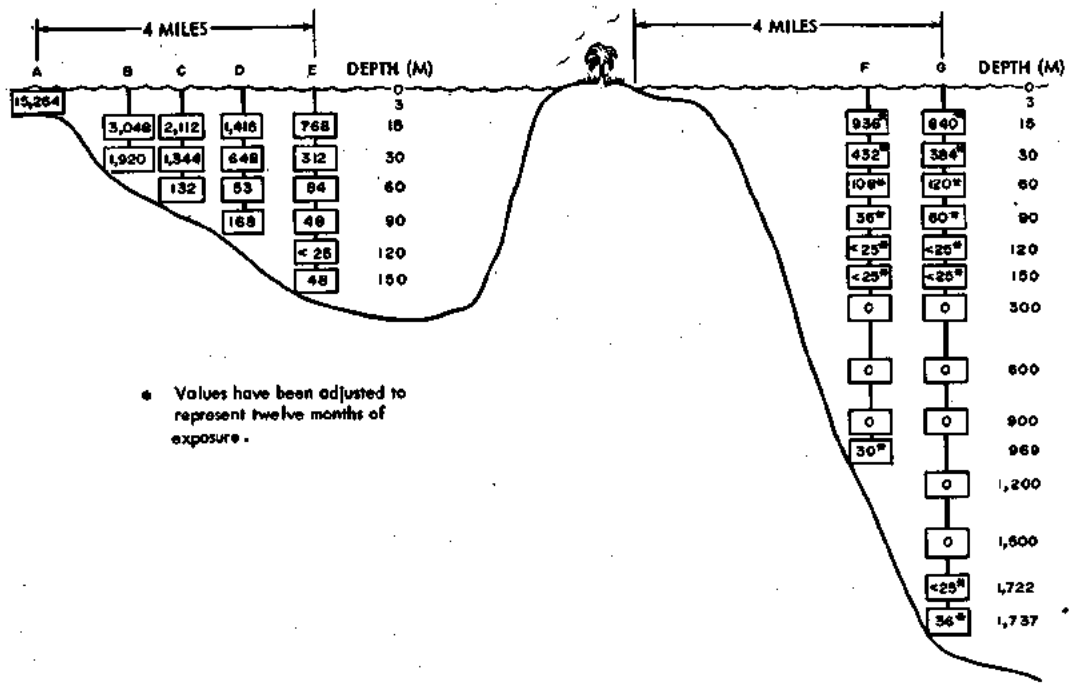


Figure 5. Dry Weight of Biofouling (gms/m<sup>2</sup>) on Test Panels Exposed in the Study Area

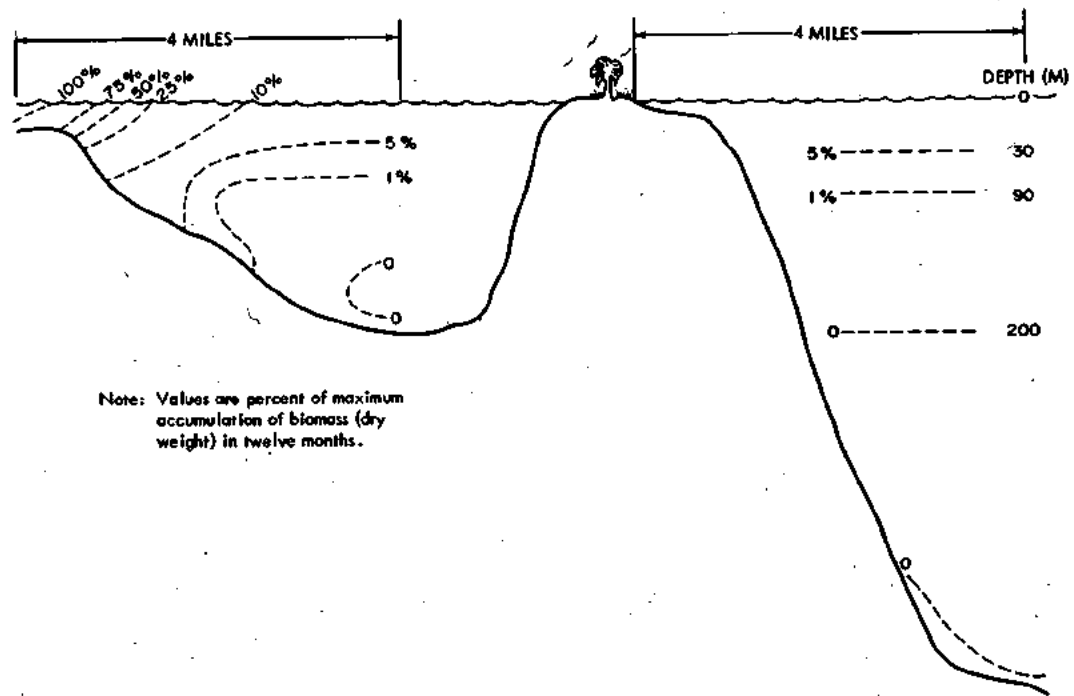


Figure 6. Biofouling Distribution Patterns in the Straits of Florida and in the Tongue Of The Ocean

sites off Andros Island. Panels were hung at 15, 30, and 150 meter intervals along the mooring line, from near the surface to the bottom. Panels were also exposed nearshore in three meters of water to obtain a standard measurement for offshore comparisons. Temperature, salinity, and current data were also collected at the test sites.

After recovery, the test panels were photographed and preserved in ethyl alcohol. The fouling organisms were then identified, measured, counted, dried, and weighed.

## RESULTS AND DISCUSSION

A total of eighty-eight species of fouling organisms were collected at the test sites. A list of these organisms and their local distribution are given in Table 1. The seaward deployment of the sites and the depths where the test panels were exposed are shown in Figure 3.

There is a general decline in the species diversity toward the bottom and in a seaward direction. This trend is shown in Figure 4. The exception to this occurred on panels exposed close to shore, where great numbers of available larvae plus interspecific competition for available space tend to limit the number of species which are able to attach. The total annual biomass (dry weight in  $g/m^2$ ) at each test site is indicated in Figure 5, and in general the total biomass accumulation is proportional to the species diversity shown in Figure 4. A representative pattern of biofouling distribution for this region may be developed by contouring the dry weight values in Figure 5 and expressing them as percent of maximum accumulation for a twelve month period (fouling rate) as in Figure 6.

The maximum accumulation of fouling occurred in the shallow waters of the Florida coast. The rate of fouling diminished toward the bottom and in a seaward direction to a point about four miles offshore, where the biomass values leveled off at about 10% of the maximum. Frequency of attachment to the test surfaces decreased in proportion to the distance the larvae had to travel to find suitable substrates. After attachment these organisms were able to complete life processes equally well at all sites, based on growth rate measurements, indicating that the rate of fouling offshore is limited by the number of available larvae rather than any deficiency in the environment.

In the TOTO the rate of fouling diminished rather uniformly from values of less than 10% of maximum at the surface to virtual extinction at about 200 meters. Two hundred meters is also the average depth of the mixed layer for this region, based on temperature-salinity profiles (Fig. 2). On test surfaces exposed within a few feet of the bottom, however, a measurable quantity of fouling persisted even into the deepest parts of the TOTO. This near-bottom fouling community consisted principally of tubeworms and hydroids and its persistent occurrence appears related to the proximity of an impoverished broodground.

From the limited information available, it appears that the pattern of offshore biofouling in the South Florida/

Bahamas region is typical of many other offshore areas. Turner (1963), for instance, reported a zone of no-fouling in deep water off Bermuda. Muraoka (1966) reported very light fouling on objects exposed near the bottom in deep areas of the Pacific Ocean. The diminution of fouling away from shore and shoal areas has also been reported by Ayers (1951) and the Woods Hole Oceanographic Institution (1952). Dolgopolskaya (1959) reported that in the Black Sea, biofouling intensity similarly decreased from the surface toward the bottom.

It is interesting to note, however, that local conditions can sometimes produce strikingly different results. Off the south coast of Sardinia, for instance, biofouling has been found to be five times more abundant near the bottom than near the surface, for reasons not readily apparent (DePalma 1963b).

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## DISCUSSION

Dr. HOUGHTON (England): You said in comparing the fouling mass from jetties and your deep water site that you only got about one per cent settlement near the bottom in deep water, is this correct?

J. DePALMA: Yes, one percent or less.

Dr. HOUGHTON (England): That was on the surface of the panel?

J. DePALMA: Right. This included the tubeworms and hydroids which were attached to the surface of the asbestos panel; not the marine borers in the wooden panels.

Dr. HOUGHTON (England): Can I then ask you if you have any information on what relative proportion of borers were there, is it similar?

J. DePALMA: I haven't shown this but I do have a very complete series on marine borers provided by Ruth Turner which I will be happy to provide you with.

G. RELINI (Italy): I wish to ask Mr. DePalma some details in determination of Bahamas he used the dry weight or not?

J. DePALMA: Yes I used the dry weight.

G. RELINI: Have you used the dry weight of all organisms? Have you taken it from the panels?

DePALMA: That is correct; these measurements do not include the weight of the panels.

G. JONES (England): Do you have any information on the pre-

sence of bacteria or fungi on these panels?

J. DePALMA: Jan Kohlmeier in North Carolina has examined some of these panels and found bacterial degradation. I can't remember now what species were involved.

E. LINDNER (U.S.A.): What was the deepest ocean water where you collected barnacles, or, rather, did you find any depth limit for the acorn barnacle?

J. DePALMA: If I remember correctly we found *Balanus trigonus* to a depth of about 100 meters. You may also be interested to know that I collected only one small *Balanus* barnacle on all of the panels exposed in the Bahamas area. I also found no mention of *Balanus* in any of the literature on the Tongue-of-the-Ocean area.

Dr. ROMANOVSKY (France): I would like to ask two questions. First, at what distance from the bottom were the deepest panels placed? Second, if the panels were in the Gulf Stream or closer to shore?

J. DePALMA: In the Florida Straits area, the jetty panels were close to shore at the entrance to Port Everglades. The first set of offshore panels were generally influenced by a southflowing countercurrent, and the rest of the panels were well into the Florida Current, which becomes the Gulf Stream farther north. The deepest panels were right on the bottom; in contact with the bottom.

# PROTECTION AGAINST BORERS, FOULERS AND CORROSION THROUGH THE USE OF ALUMINIUM ALLOY SHEATHING IN A MARINE ENVIRONMENT

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## SUMMARY

Timber and other metallic structures in a marine environment are liable for rapid deterioration due to the ravages of marine borers, marine foulers and marine corrosion. The problem of their proper protection is so severe, concerning all the maritime nations of the World, that millions and millions of rupees are being spent annually, for repairs, renewals, maintenance and preventive research. This phenomena of deterioration of materials in sea-water is known for ages and attempts to minimise and prevent the catastrophe is still going on in the countless laboratories of the World with some success.

In India, the coastal waters are severely infested with a number of destructive marine organisms whose pattern of living has been well adjusted to the prevailing hydrographical conditions. The quality and quantity of the marine borers and foulers in Indian waters are very much varying with time and space that all timber structures including wooden hulls of fishing boats are seriously affected resulting in a big economic loss.

The fishing fleet of India comprising of wooden boats of various sizes and shapes represent the largest single collective investment in to-day's fishing industry and upon their efficient service depends the economy of millions of people and lives of number of fishermen. Wood still continues to be one of the most widely used building materials for boats in India. For obtaining long and trouble free service from wooden fishing boats, adequate care has to be taken in the proper protection of the hulls against the damages caused by the marine organisms.

Experiences have shown the long lasting protective value of a metallic sheathing on the wooden hull below water line and copper plates in particular have been very much relied

upon as the material against marine borers and foulers. Also they are very slow in their wear in sea-water under normal conditions.

Of late there is a world-wide scarcity for all non-ferrous metals, copper, in particular. India has to import copper from outside at a very high cost and their restricted supply and nonavailability have very much retarded the expansion of the fishing fleet. A substitute for copper was carefully looked into.

The Central Institute of Fisheries Technology, at Cochin a Government of India research organisation, as a result of intensive studies and investigations has now recommended the use of aluminium-magnesium alloy as a sheathing material in a marine environment. Laboratory investigations, field studies and service trials were conducted following standard procedures based on which two prototype boats have been sheathed with Indian made aluminium-magnesium alloy. Though the versatility of this marine alloy is well known by now, certain practical difficulties were encountered during their use as a sheathing material on the wooden hulls of motorized boats necessitating a delicate handling of this material in the tropical waters of India in particular.

Choice of compatible fastenings, avoidance of bi-metallic contacts in sea-water and the proper painting schedule on the sheathing were standardised. The use of aluminium-alloy in lieu of the imported copper with specific advantages has been demonstrated to an acceptable level. This import substitution is likely to relieve the strain on Indian finance to the tune of rupees 6,00,00,000 and lot of precious copper is spared for a better use. The Indian fishing fleet can now expand with assured supply of indigenous building materials at all times.

## INTRODUCTION

The Indian sub-continent has a vast coastline of 5689 km. bordering her eight maritime states. Nearly 1.33 million tons (1965) of fisheries wealth are being exploited annually from her abundant aquatic resources. There are innumerable types of wooden fishing crafts, both indigenous and modern, engaged in the fishing operations. With plenty of timber resources in India, wood will continue to be on great demand for boat-building purposes for many years to come. But the tropical seas around India are so very heavily infested with marine wood borers and foulers that even timbers having high natural resistance do not last longer under prolonged immersion in any marine environment. As such all wooden fishing crafts in India have to be protected carefully against these ravages till such time when, entirely new and better construction materials come into use.

The repeated introduction and use of metallic sheathing, culminating in the use of copper plates as an effective protection against both marine borers and fouling organisms on wooden hulls is an event of historical importance dating back to 18th century. Advantages on the use of copper and its alloys for marine purposes were thought of in greater details in the subsequent years that copper plates and nails were extensively used in wooden boat construction thereafter. Of the many known methods of protection, sheathing the wooden hull with copper plates has been the most preferred one by the Indian shipwrights for ages past.

In India, the indigenous resources for copper being very much limited most of our demands are met from the imported stock. Of the Rs. 30 crores worth of non-ferrous metals imported into India, copper alone has been valued at Rs. 20 crores. Due to the increase in use of copper in the various other essential industries, its present limited supply and

import restrictions, the price of copper sheets suitable for sheathing of fishing boats has shot up from Rs. 6/- to Rs. 18/- per kg. within a period of 8 to 10 years. The boat building industry finds it very difficult and expensive to use copper materials as a result of which the overall cost of fishing boats is rapidly increasing and the expansion of the fishing fleet is, thereby, retarding. This crisis has necessitated a search for an easily available, cheap and effective substitute for copper.

Since 1960, detailed investigations and experiments were carried out both under laboratory and field conditions at the Central Institute of Fisheries Technology, Cochin, a research organisation under Government of India. The project ended with a finding that indigenous aluminium alloyed with magnesium and rolled in the form of sheets can be used in a marine environment as an effective substitute to the imported copper sheets for the protection of the wooden hulls of fishing boats only at one fifth the price of copper. The growing demand for a metallic hull sheathing material that will stand continuous sea-water immersion has now been met with by the introduction of the special aluminium-magnesium alloy. Also during the Third F.A.O. Technical Meeting on Fishing Boats held in Gothenberg, Sweden, late in 1965 opinions were unanimous with the experts as to the versatility and free use of aluminium alloys in fishing boat construction without any reserve.

In the following pages of this paper, a general account on the reaction of aluminium magnesium alloy to marine borers, foulers and corrosive conditions and problems encountered during the hull sheathing work in a prototype fishing boat with this new material are presented. The authors are very much thankful to Dr. A.N. Bose, Director, Central Institute of Fisheries Technology, for his useful suggestions and helpful criticism during the course of this project study.

### MARINE WOOD BORERS

In the tropical warm coastal waters around India, the damages caused by the marine borers and the marine fouling organisms to the unprotected wooden hulls of fishing boats are comparatively very high. Almost all the wooden structures under immersion in sea water are attacked by these pests constantly and as a result of annual maintenance, repairs and renewals millions of rupees are being spent by various agencies.

The problem of protecting boat building timbers from their biological deterioration was taken up for detailed investigations at the Central Institute of Fisheries Technology. Selected varieties of home grown timbers constantly in demand by the boat building industry were assessed for their natural resistance against the attack of the destructive marine organisms. Prolonged immersion tests were carried out at various locations employing different wooden test blocks of standard sizes (Figure 1). Both qualitative and quantitative studies were made on the settling organisms besides the collection of their vital biological details and hydrographical features of their living environment.

Timber destruction is caused by two groups of marine organisms, the molluscs and the crustaceans. The molluscs, represented by the well known ship-worms are of the genera *Teredo*, *Nausitora*, *Bankia*, *Uperous* and *Lyrodus*. The Pholadid molluscan form is represented by *Martesia*. Of the crustaceans, the most important genera, *Limnoria* and *Sphaeroma* are the Isopods. Of these, *Shipworms* and *Martesia* have been found to inflict the maximum amount of damage to wooden hulls of fishing boats even though the other forms are also met with. The very conducive living media with abundant feeding material available throughout the year keeps up the population of these marine pests beyond depletion. The endemic stock has become so well adapted through years of acclimatization and physiological adjustments that they have been able to tolerate wide fluctuations in water salinity and temperature. A good number of them have established well in estuarine waters and a few have at-

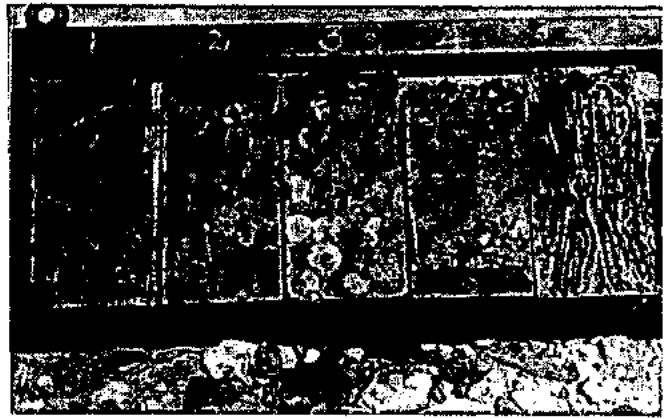


Fig. 1. Untreated wooden test blocks damaged by marine borers in less than 8 months.

tempted ingress into fresh-water river mouths. 28 species of ship-worms, 2 species of *Martesia*, 3 species of *Sphaeroma* and 9 species of *Limnoria* are known to be active in the Indian waters.

Investigations so far conducted have only revealed that none of the approved boat building timbers can withstand continuous sea-water immersion for more than 6 to 7 months without undergoing 50% deterioration on them. The most common timbers that are now in use in the construction of modern mechanised fishing boats are «Teak» (*Tectona grandis*); «Aini» (*Artocarpus hirsuta*) and «Venteak» (*Lagerstroemia lanceolata*) though other cheap and lighter woods are also in use for catamarans and other indigenous fishing crafts. Successful wood protection in sea-water is, therefore, of very great economic importance and the problem very much concerns all wooden boat owners.

Most of the unprotected wooden hulls of fishing boats are severely infected by marine wood borers in varying degrees within a period of one year. Such crafts have to be hauled ashore for repairs or for replacing the affected structures. On the wooden hull, the stem, keel, stern areas, rudder and bottom hull planks are the worst affected parts. Since the damages are mostly internal the extent of timber destruction as is seen from outside does not provide a true guidance for an accurate evaluation of the total deterioration.

It is the common practice of the coastal fishermen of India to apply various indigenous preparations as surface coatings on their wooden fishing crafts. These preparations, on careful test, have been found lacking in their protective efficacy against marine borers and as such cannot reliably protect the mechanised modern vessels. However, a few of the selected toxic chemical wood preservatives (Heavy creosote oil and copper-arsenic-chrome compound) when fixed into timber structures in adequate quantities, have been found to enhance the natural durability of the treated timber and resist the borers successfully. The best treating technique and an efficient toxic preservative against all the forms of marine borers have still to be worked out on account of certain practical limitations in their use in sea-water. Wooden hulls sheathed with copper plates have been free from the settlement of marine organisms.

### MARINE FOULING

Marine fouling results from the growth of certain sessile and sedentary animals and plants on all types of submerged surfaces in a marine environment. This large assemblage include microscopic forms such as bacteria, fungi, diatoms, protozoans, rotifers as well as macroscopic forms like sponges, coelenterates, flatworms, bryozoans, tube-worms, amphipods,

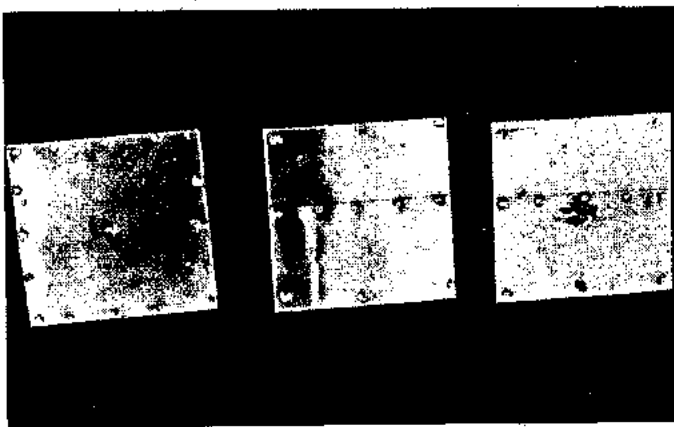


Fig. 2. Pattern of sheathing wooden test blocks with aluminium alloy for borner protection



Fig. 3 Immersion rack and test panels for assessing the quality and quantity of marine fouling.

barnacles, molluscs etc. Animals that foul are principally the attached forms occurring in the shallow coastal waters and estuaries. Of these fouling organisms barnacles, mussels, oysters, tubeworms, hydroids and sea-weeds are the most important forms from the point of surface coverage, volume and weight.

Any non-toxic newly exposed surface, may be of wood, metal, mineral or synthetic material, under immersion gets rapidly coated with a slimy primary film composed of bacteria, diatoms, algal spores mixed with organic and inorganic detritus, mud, sand and other particulate materials suspended in sea-water. This primary film in due course is followed by waves of other fouling forms. There is also a biological sequence and succession involved in the settlement of these organisms in space and time which is often influenced by the environmental conditions, hydrographical features etc. Finally there is the establishment of a climax community comprising of forms which are slow growing and probably long living. Marine fouling organisms settle on submerged surfaces during their early larval period and their settlement can be prevented only during this stage in their life cycle by providing toxic surfaces.

The problem of marine fouling is more severe in Indian harbours than it is in temperate waters (Figures 2, 3, and 4). Unprotected wooden hulls form an ideal substratum for the fouling organisms. Copper sheathed wooden vessels are free from fouling because of the toxic nature of the surface that is in contact with sea-water, or else fouling can be prevented by the use of special type of paints containing certain inorganic and organic chemicals which provide toxic material near the surface, lethal to the larval growth of the marine fouling organisms. Antifouling paints suitable for temperate waters show poor performance under Indian tropical conditions and as such copper sheathing the wooden hull has been in vogue for a long time and both marine borers and foulers have been kept away simultaneously from the wooden hull.

In the accompanying tabular statement (Table No. 1) details are furnished as regards the degree of natural resistance of the most important boat-building timbers against marine borers and foulers at a test site.

#### ALUMINIUM FOR MARINE USE

Aluminium is widely used in many fields due to its lightness and high strength-to-weight ratio, its resistance to corrosion and for the ease with which it can be fabricated. Aluminium is being manufactured in India with indigenous resources and the industry is showing great signs of progress and has all plans to face the present copper crisis. Sea-water is a highly corrosive medium, the corrosion behaviour of which is greatly influenced by salinity, pH, dissolved oxygen,

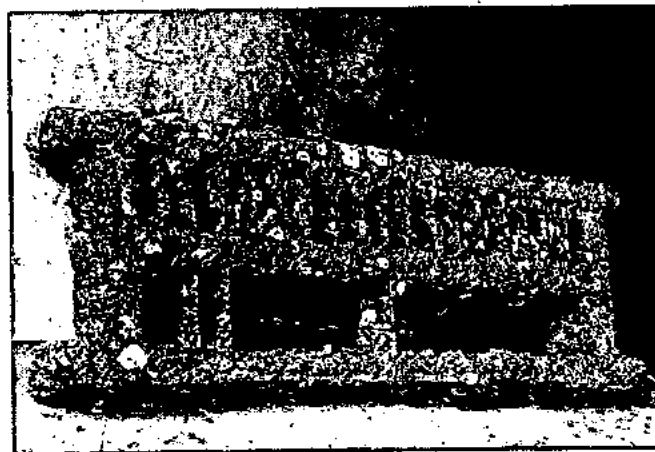


Fig. 4. The amount of fouling gathered in less than one year in a tropical test site (C.I.F.T. Cochin-India)

carbon dioxide etc. Metals and alloys to be used in such a destructive environment requires, a careful selection, proper protection and service maintenance.

Unalloyed aluminium is soft and ductile for working with low strength. By the addition of copper, magnesium, manganese, silicon, nickel and chromium to aluminium a wide range of alloys can be produced to meet the varying requirements of strength, ductility, corrosion resistance and weldability. High strength aluminium-magnesium-manganese marine alloys provide adequate strength and offer greater protection against seawater corrosion.

A number of all aluminium fishing boats and other commercial crafts have been built in recent years. Aluminium-magnesium alloys conforming to approved ship-building standards as the American 5083, 5086 alloy and the British MG5-MG5S alloy are being used for hull construction elsewhere. In India such alloys with 3.5 to 5% magnesium are also manufactured for shipbuilding purposes as Indal 54S and A56S.

For initial tests in the laboratory, in the field, for the subsequent trials under service conditions and for the prototype work, Indian aluminium-magnesium alloy M57S of the following specifications was selected and used.



T A B L E No. I

STATEMENT SHOWING THE DEGREE OF NATURAL RESISTANCE OFFERED BY THE COMMON BOAT-BUILDING TIMBERS AGAINST MARINE BORERS AND FOULERS UNDER CONTINUOUS IMMERSION AT A TEST SITE

Sl. No.	Botanical Name	Family	Indian trade name	Condition of test block	Specific weight at 12% moisture	Total area 2000 sq. cm. Time taken for 50% borer destruction	Main borers responsible	General fouling	Hydrographical details at the test site Oct.-May
1	<i>Tectona grandis</i>	Verbenaceae	Teak	Seasoned heartwood	42 Lb/c.ft	7 months	Shipworms / Martesia	Heavy	Salinity: 16‰ to 35‰ pH: 7.5 to 7.8 Water temperature: 28°C Dissolved oxygen: 3.6 ml/L to 6.5 ml/L
2	<i>Artocarpus hirsuta</i>	Moraceae	Aini	"	37 "	5 "	Martesia / shipworms	Heavy	
3	<i>Lagerstroemia lanceolata</i>	Lythraceae	Venteak	"	42 "	6 "	"	Heavy	
4	<i>Pterocarpus dalbergioides</i>	Leguminaceae	Andaman Padauk	"	45 "	6 "	Martesia	Heavy	
5	<i>Pterocarpus marsupium</i>	"	Bijasal	"	50 "	5 "	"	Heavy	
6	<i>Dalbergia sissoo</i>	"	Sissoo	"	49 "	"	"	Heavy	
7	<i>Dipterocarpus sp.</i>	Dipterocarpaceae	Gurjan	"	47 "	6 "	Martesia / shipworms	Heavy	
8	<i>Shorea robusta</i>	"	Sal	"	55 "	5 "	Martesia	Heavy	
9	<i>Hopea parviflora</i>	"	Hopea	"	59 "	6 "	Shipworms / Martesia	Heavy	
10	<i>Terminalia paniculata</i>	Combretaceae	Kindal	"	49 "	5 "	Martesia	Heavy	
11	<i>Terminalia tomentosa</i>	"	Laurel	"	54 "	6 "	"	Heavy	
12	<i>Terminalia dialata</i>	"	White chuglam	"	44 "	7 "	Martesia / shipworms	Light	
13	<i>Dysoxylum malabaricum</i>	Meliaceae	White cedar	"	45 "	5 "	Martesia	Heavy	
14	<i>Cedrus deodara</i>	Coniferae	Deodar	"	34 "	6 "	"	Moderate	
15	<i>Artocarpus chaplasha</i>	Moraceae	Chaplash	"	32 "	4 "	Shipworms / Martesia	Heavy	
16	<i>Mangifera indica</i>	Anacardiaceae	Mango	"	43 "	3 "	"	Light	
17	<i>Albizia lebbek</i>	Leguminaceae	Kokko	"	40 "	6 "	Martesia	Heavy	
18	<i>Adina cordifolia</i>	Rubiaceae	Haldu	"	43 "	5 "	Martesia / shipworms	Heavy	
19	<i>Grewia tilaefolia</i>	Tiliaceae	Dhaman	"	49 "	4 "	"	Light	

Aluminium	—	97.0%
Magnesium	—	2.0%
Copper	—	0.2%
Iron	—	0.2%
Silicon	—	0.2%
Chromium	—	0.2%
Manganese	—	0.1%
Zinc	—	0.1%

decreases and practically stops due to the formation of the protective corrosion products around each pit.

2. *Galvanic corrosion*: Aluminium and its alloys are anodic to most structural metals and alloys. Especially in a highly conducting sea-water medium aluminium and its alloys will suffer galvanic corrosion when in contact with nobler metals like copper, bronze or brass or even steel. Generally bi-metallic couples are undesirable. At the stern quarter of a motorised boat, where dissimilar metals such as aluminium on the hull, bronze propeller and its shaft and other mild-steel or cast iron rudder fittings, are in close proximity, galvanic corrosion will result (Figure 6). Aluminium sheathing has to be protected by installing sacrificial zinc anodes. So also all fastenings used on aluminium should be made compatible. Aluminium (tacks or screws) or stainless-steel fastenings would do well under these circumstances. The conventional boat fastenings made of copper, brass or mild steel should never be used in conjunction with aluminium sheathing. Even woods treated with preservatives containing copper or mercury compounds should not be in contact with aluminium.

3. *Crevice corrosion*: Aluminium sheathing when in direct contact with wet wood will suffer from corrosion in the form of pits. Certain extractives of wood are injurious to aluminium and as such contact between wood and the metallic sheathing has to be suitably prevented. Any bitumastic coating or tough insulating paint composition, and Kraft tar paper or tar coated hebbian may be interposed between the wooden hull and the sheathing. The inside face of the aluminium sheathing can be painted with zinc chromate primer which goes well with aluminium under all circumstances.

4. *Deposition attack*: Pitting on aluminium surfaces will be caused by the deposit of heavy metals like copper or mercury when paints containing such toxic compounds are applied directly over the metal. Since all commercial antifouling paints are likely to contain any one of these salts along

### SPECIAL PROBLEMS WITH ALUMINIUM ALLOY

1. *Pitting corrosion*: Bare unprotected aluminium alloy has a low rate of pitting corrosion in sea-water. The amount of pitting and the retention of mechanical properties indicates an extremely high resistance to sea-water corrosion. The average depth of a pit is about 2 to 3 mils in a period of about two years. Most of the pitting occurs in the first two to three years of service and later the rate of attack

or in combination, the base metal has to be properly primed and insulated. Hence particular attention should be paid in the selection and application of metal primers.

Depending on the severity of the working conditions any one or a combination of the following methods of care may be adopted to minimize the bimetallic corrosion in sea-going vessels.

- (a) Coat the aluminium surface facing the joint with 2-coats of zinc chromate primer,
- (b) apply zinc chromate primer in all crevices,
- (c) prevent metal to metal contact (dissimilar) by proper non-conducting insulants like bitumen treated or zinc chromate treated non-metallic washers or felts,
- (d) and finally paint the completed joints with adequate coats of zinc chromate paint.

It is thus possible to maintain aluminium-magnesium alloy in a marine environment particularly in a fishing boat when used for sheathing the wooden hull, by carefully avoiding all bimetallic contacts and by following the specially recommended painting schedule.

### PAINTING OF ALUMINIUM SURFACES

One of the main practical difficulties in painting non-ferrous metals like Aluminium is to obtain a good adhesion of the priming paints to the very smooth and shining surface of the rolled sheets. Surface sandering cannot be done to perfection. Recent experiments have revealed that some form of uniform metal etching treatment enhances the adhesive properties of paints coated on aluminium surfaces.

Such a *Metal Wash Primers* is a development of the well known phosphoric acid wash incorporated with special synthetic resins and rust inhibiting pigments. They are commercially available in two pack system — the acid part and the pigmented resin solution which have only to be mixed when required. (*Always manufacturer's directions for use have to be followed*).

When the *wash primer* is applied to well cleaned aluminium surfaces, the chromate in presence of phosphoric acid forms a chromate sealed phosphate film on the metal surface. A complex compound is also formed by the interaction of the resin and chromium phosphate. The thin film so produced is firmly bonded to the metal surface which holds on tenaciously the subsequent paint coats. Wash primer dries very quickly in about 15 minutes in open air. Even though this wash primer is applied as a very thin coat, it is important that no place on the hull sheathing is missed. The wash primer coat must be followed with 2 coats of zinc chromate primer. Now the base metal is adequately protected against its coming in direct contact with the copper or mercury containing anti-fouling paint coatings which when applied at the end before launching will protect the hull against the settlement of the fouling organisms during service.

The best commercial antifouling paint used during the present investigation gave a fouling free life of 7 to 8 months over the well primed aluminium sheathing. The boat with aluminium sheathing has to be hauled ashore once a year for the renewal of bottom paints (Figures 7, 8), till such time more efficient and long lasting under water paints are put in the Indian market.

Paints containing lead, copper, mercury or graphite should not come in direct contact with aluminium as either of these is liable to set up galvanic attack on aluminium resulting in the formation of corrosion pits. Zinc chromate pigmented paints are the best as they supply the required chromate ions for passivation which prevents the corrosion of the metal. Whenever zinc anodes are employed for cathodic protection only high purity zinc with an iron content less than 15 ppm has to be installed. Aluminium, no matter how successful as a light and cheap substitute, does require a careful handling to get the best results.

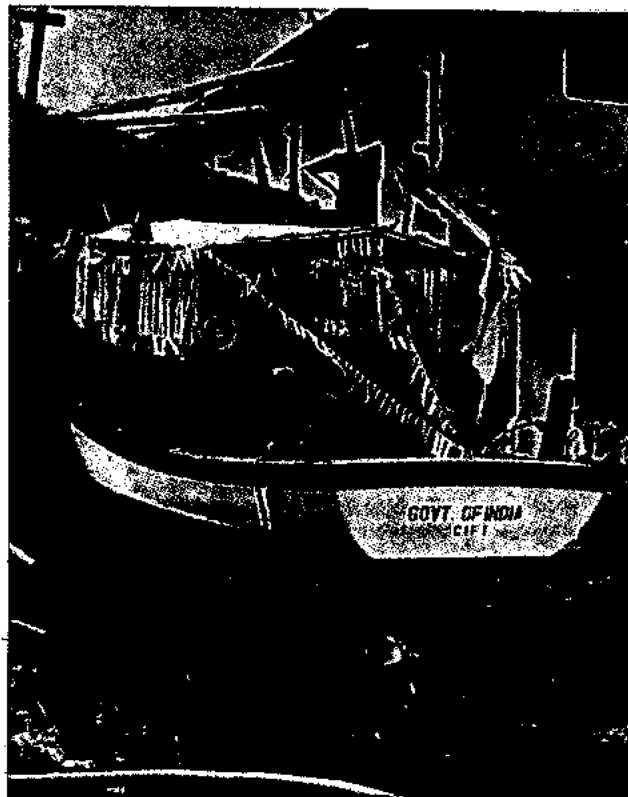


Fig. 5. A 30' prototype coastal fishing boat with aluminium alloy hull sheathing ready for launching (1963)



Fig. 6. The stern quarter of the prototype with the aluminium alloy sheathing after one year of service (before renewing the painting 1964).

## PROTOTYPE STUDIES

During the year 1963, a prototype mechanised wooden fishing boat of 30' overall length (Figure 5) was commissioned and its hull below waterline was fully sheathed with aluminium-magnesium alloy containing 2% Mg and of 22SWG thickness. Taking all precautions in the selection of proper aluminium fastenings, in the avoidance of bi-metallic contact—particularly at the stern area and by following the recommended schedule of protective painting, the successful protection of wooden hulls with aluminium sheathing in lieu of the conventional copper material was demonstrated. During the past four years' of service life, the hull was inspected annually at the end of every fishing season and no major break down has been noticed and the wooden hull is completely free from borer attack. A second boat of 50' length has also been launched during early 1967.

It is now believed that aluminium as a sheathing material like copper, will last better than any other metallic substitutes. (The normal life of copper sheets in fishing boats is known to be between 6 to 8 years). In case of renewal of affected aluminium plates in between its normal service life the expenditure is negligible. If few basic principles in handling aluminium as a material in boat construction are carefully followed the best life out of aluminium is always assured at a comparatively low cost. Adequate inspections during the different stages of boat construction at the yards and thereafter during service life are always necessary and useful. The technical know-how as regards to the right handling of aluminium in a marine environment was clearly demonstrated in a recent seminar attended by many prospective users of this new material.

### ECONOMICS

The following is the comparative cost of expenditure involved in protecting an area of one square foot of the wooden hull in a fishing boat for different materials used (as per 1966 price pattern).

Material	Cost per sq. foot
Copper sheet 24 SWG	Rs. 14.00 (Imported)
Aluminium-magnesium alloy 22 SWG	Rs. 3.50 (Indigenous)
F.R.P. Fibreglass chopped strand mat and polyester resin	Rs. 7.25 (Indigenous)
Nylon/Epoxy resin covering	Rs. 15.00 (Imported)
Heavy cresote oil at 20 Lb/cu. foot loading: (studies incomplete) (Indigenous).	

### CONCLUSION

During the five years between 1966-1971, 8000 wooden fishing boats, based on modern designs, ranging in size from 30' to 50' will be added on to the existing fishing fleets in India. About 60,00,000 square feet area of exposed wood has to be protected against the ravages of marine borers and foulers. The entire requirement of copper for the sheathing if required, has to be imported into India at a very exorbitant price. By substituting copper by the indigenous aluminium as detailed out in the present communication, a total saving of nearly Rs. 6,00,00,000 can be realised and a good amount of copper is spared for better use in the other vital industries.

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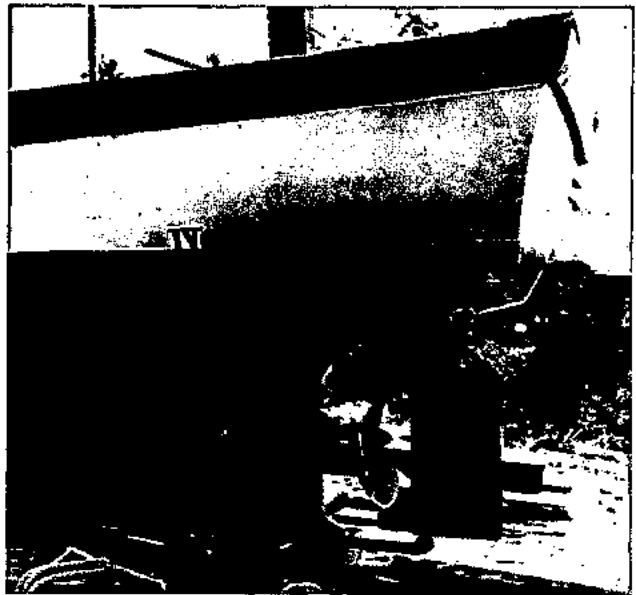


Fig. 7. The stern of the prototype after two years of service (paint renewed 1965)



Fig. 8. The prototype boat with the hull sheathing repainted - after three years of service - 1966.

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# A FUNDAMENTAL APPROACH TO MARINE FOULING STUDIES USING LABORATORY-REARED ORGANISMS

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## SUMMARY

Fouling accumulations on shipbottoms, a problem since ancient times, can result in increased fuel consumption and hull corrosion, and in other losses in time, money, and reduced efficiency in the operation of a vessel. In the past, the development and study of antifouling materials and devices has been mainly empirical. The objective of the work described herein is to develop new methods and materials for greater fouling control, using techniques which permit observation of the fouling organisms and the evaluation of antifouling materials in the laboratory. The mass-rearing of barnacles in the laboratory is shown in a 12-minute long motion picture film, and some of the work which is being done with these laboratory-reared barnacles is described in

this paper. A bioassay technique using second stage barnacle nauplii to evaluate the relative biological activity of potential antifouling toxicants is described. The results of 23 such bioassays is presented. The techniques for a bioassay evaluation of antifouling coating formulations are set forth. Here, newly attached and metamorphosed juvenile barnacles are used to provide information on the effectiveness and life expectancy of antifouling coatings. A ten-point index of barnacle response to poisoning is described. Preliminary test results of several coatings indicate that a good correlation between the new laboratory bioassay and the old inspection evaluation of a raft trial is being achieved.

Fouling results from the growth of animals and plants on the surfaces of submerged objects. On shipbottoms, such an accumulation can result in increased fuel consumption due to additional resistance to the movement of the hull through the water, losses in time and money for hull scraping and the application of remedial measures, reduction in the efficiency of various underwater sensing devices, and an increase

in hull corrosion. The increase in shaft horsepower needed to maintain speed of a U.S. Naval vessel is shown in the graph of Figure 1, and loss of speed of another Naval vessel as fouling accumulated is shown in Figure 2. The development of antifouling materials has been going on since ancient times, and in the past twenty-five hundred years we have progressed at a slow pace from the use of oils and tars, through

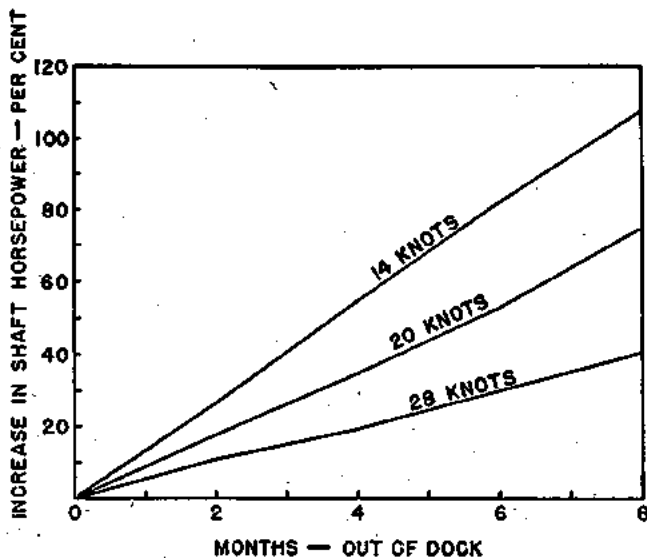


Fig. 1

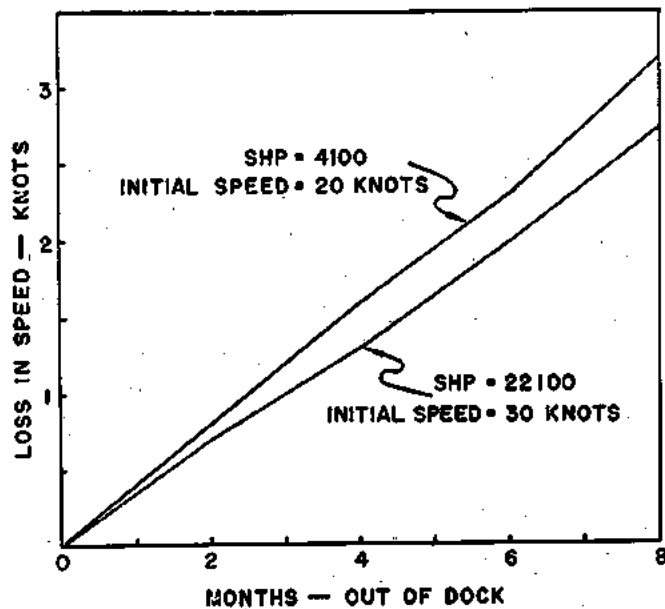


Fig. 2

the application of copper sheathing, to the development of paints containing copper and other compounds which are toxic to marine life.

The study of antifouling coatings has been mainly empirical. Toxic chemicals are incorporated into formulations whose ultimate usefulness is determined by the rate at which the toxic chemical leaches out into the surrounding environment. The leaching rate should be high enough to poison the fouling community and low enough to provide a desirable service life. As a rule, the effectiveness of antifouling formulations is expressed in terms of how long they may be expected to work. This is generally determined by exposure of such formulations to a natural marine environment for periods of up to several years.

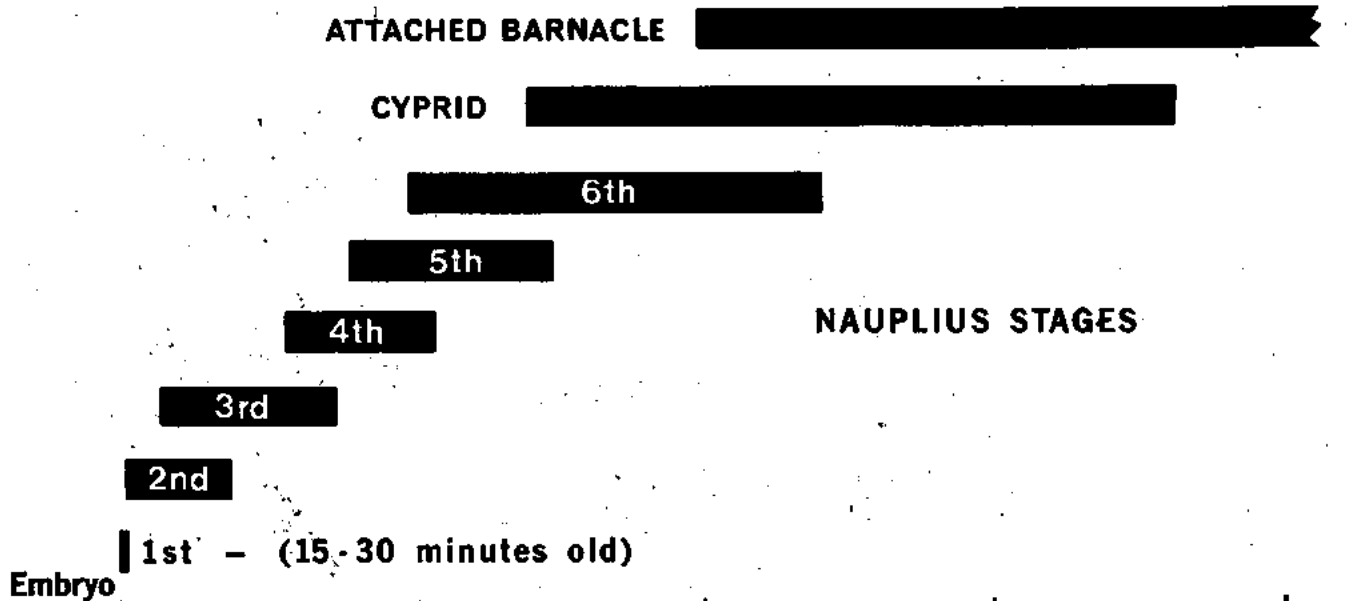
In recent years attempts have been made to reduce the evaluation time and increase the precision of antifouling materials studies. Investigations by de Wolfe<sup>1</sup> on the accelerated aging of coatings, and Miller<sup>2</sup> on the use of impregnated porous carbon to evaluate toxicants, and by others, indicate that there is a recognized need to replace, or at least supplement, harbor-test-rack studies with standardized, repeatable laboratory methods.

Laboratory studies of fouling, such as close observation of the setting and attachment of the organisms, and the development of laboratory methods to evaluate antifouling materials have, until recently, been retarded by the difficulties involved in rearing and maintaining the necessary marine organisms. Attempts at mass rearing the larval stages of barnacles were generally unsuccessful<sup>3,4,5</sup> until the procedures of Freiberger and Cologer<sup>6</sup> were developed. A brief description of the rearing techniques used, and first photomicrographs of the embryonic and larval stages of *Balanus eburneus* are shown in a 12-minute long motion picture film which is presented as part of this paper. This development of the barnacle larvae from embryo to attached young adult is also shown by means of a bar-graph in Figure 3.

Now with large quantities of barnacle larvae available, a wide variety of studies relating to fouling and antifouling are possible. In this paper we describe some of the work currently underway at the U.S. Naval Applied Science Laboratory on the development of a new bioassay approach for evaluating antifouling coatings, and present a discussion of studies which may lead to better materials and methods for fouling prevention.

# BARNACLE DEVELOPMENT

## BALANUS EBURNEUS, B. IMPROVISUS, B. AMPHITRITE



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Fig. 3

Other work, previously described by the authors, but not covered in detail in this paper, includes an investigation of the effect of light on barnacle attachment, Figure 4, and the results of experiments on the growth rate of newly settled young barnacles before and after exposure to cuprous oxide, Figure 5 and 6, respectively.

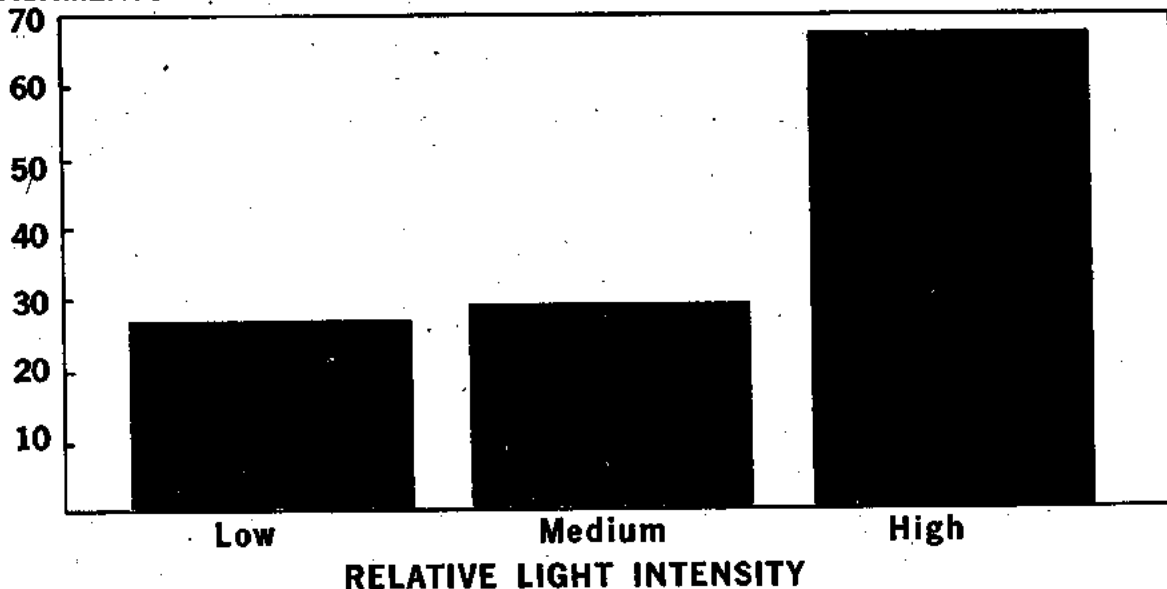
STUDIES OF TOXICANTS FOR ANTIFOULING COATING FORMULATION

One of the uses for laboratory-reared barnacle larvae is to determine quickly the relative biological activity of toxic compounds employing a bioassay technique. For this purpose, second stage nauplii are used to test the toxicity of a 3% of-saturation solution of the candidate toxicants. A controlled laboratory procedure has been developed which results in determination of the time it takes to kill one-half of a population of 26 nauplii. The results of a series of such bioassays of 23 toxicants is shown in Figure 7. It should be noted that the amount of toxicant available in this test is dependent upon the solubility; a condition which allows the absolute concentration to vary from sample to sample, but which follows closely the true toxic-release situation which occurs in the field.

Our primary objective, however, is the use of laboratory reared barnacles for determining the effectiveness of anti-fouling coatings and methods. A study of this kind, outlined by Cologer and Freiberg, is currently underway and is discussed in this paper. This is a new and fundamental approach to the problem of marine fouling made possible not only because of the Laboratory's development of barnacle-rearing techniques, but also because of the ensuing increased knowledge on the biological behavior of these animals. Live, adult barnacles are collected on panels in Biscayne Bay, Florida, and are shipped by air freight to our marine biology facility which is located at the New York Aquarium. The compacted masses of embryos, when present, are removed from the barnacle's mantle cavity and placed into a beaker of seawater where they continue to develop and hatch into naupliar larvae. The larvae are cultured as described in reference 6 and progress through the six naupliar stages, the cyprid stage, and then settle and metamorphose to become attached barnacles. These newly attached barnacles have been selected as the organisms for bioassay because they are sessile and easy to observe, feed voraciously and thus inject toxins present in the environment, grow at a measurable

**ATTACHMENT RESPONSE OF BARNACLES TO LIGHT  
BALANUS EBERNEUS - TWENTY DAYS AFTER HATCHING**

AVERAGE NUMBER OF ATTACHMENTS



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Fig. 4

# ATTACHMENT & GROWTH OF BALANUS EBURNEUS

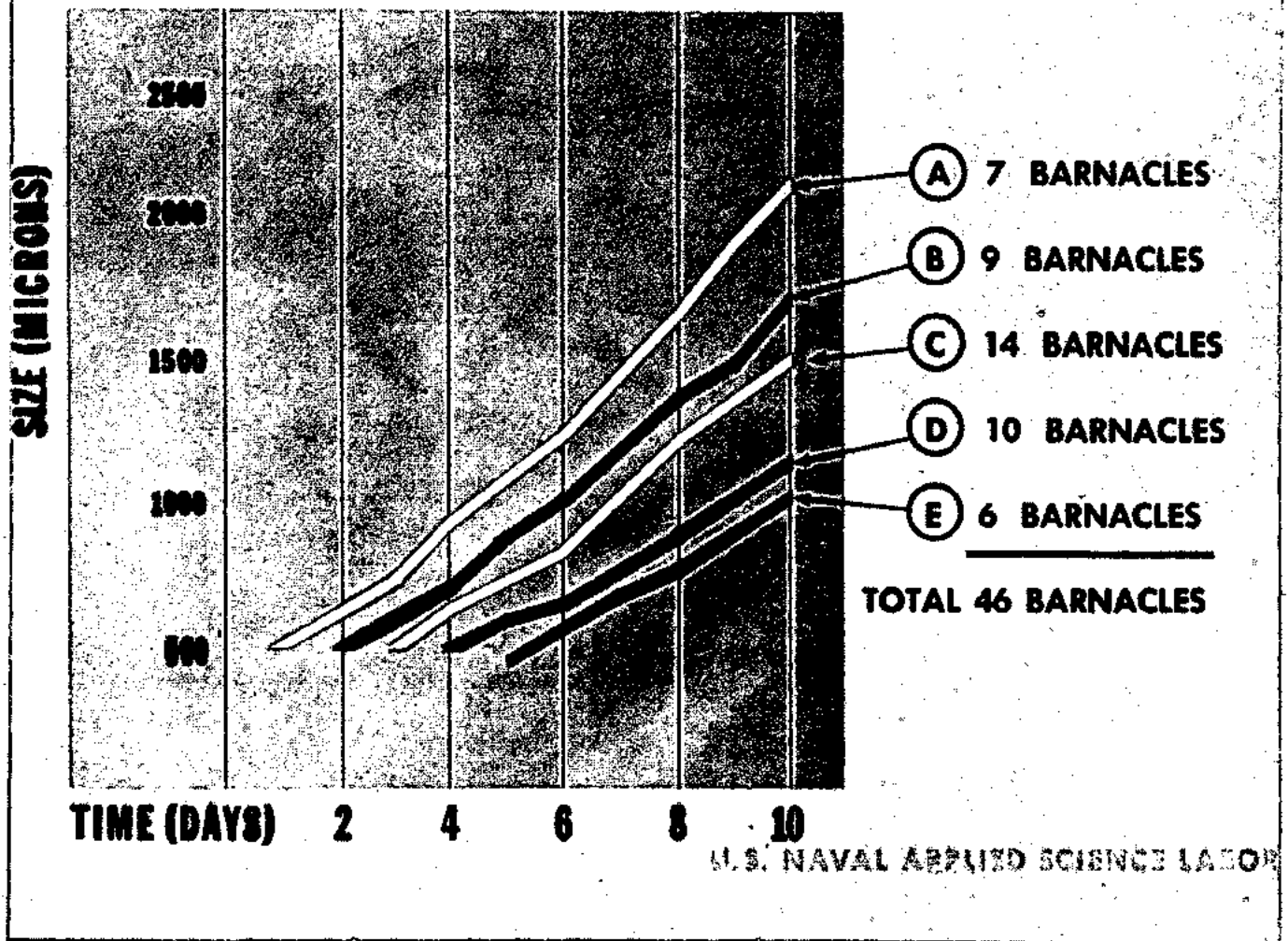


Fig. 5

rate, and respond to poisoning in accordance with a recognizable pattern. In practice, the bioassay of a given antifouling paint involves several populations of laboratory reared young barnacles whose growth rate and behavior in the absence of toxins can be predicted, and whose individual members display recognized patterns of activity. However, it should be noted that exposure of such populations to a freshly and newly applied toxic coating may quickly result in high mortality rates even through the coating may have a short service life which would preclude its consideration for antifouling use. It is therefore recognized that evaluations of toxic coatings must be made with samples which have been treated in some manner to simulate long-term marine exposure. The response of laboratory reared barnacles to these treated coatings could then be compared with the known responses of barnacles to coatings of known age and effectiveness. Since a coating will approach borderline effectiveness during the end of its service life, a precise and sensitive method is required to mark the end of the paint's usefulness. Such a test of the effectiveness of aged antifouling coating samples will be correlated with the results of similar tests of coatings of known service life. Interpretation of these data will provide

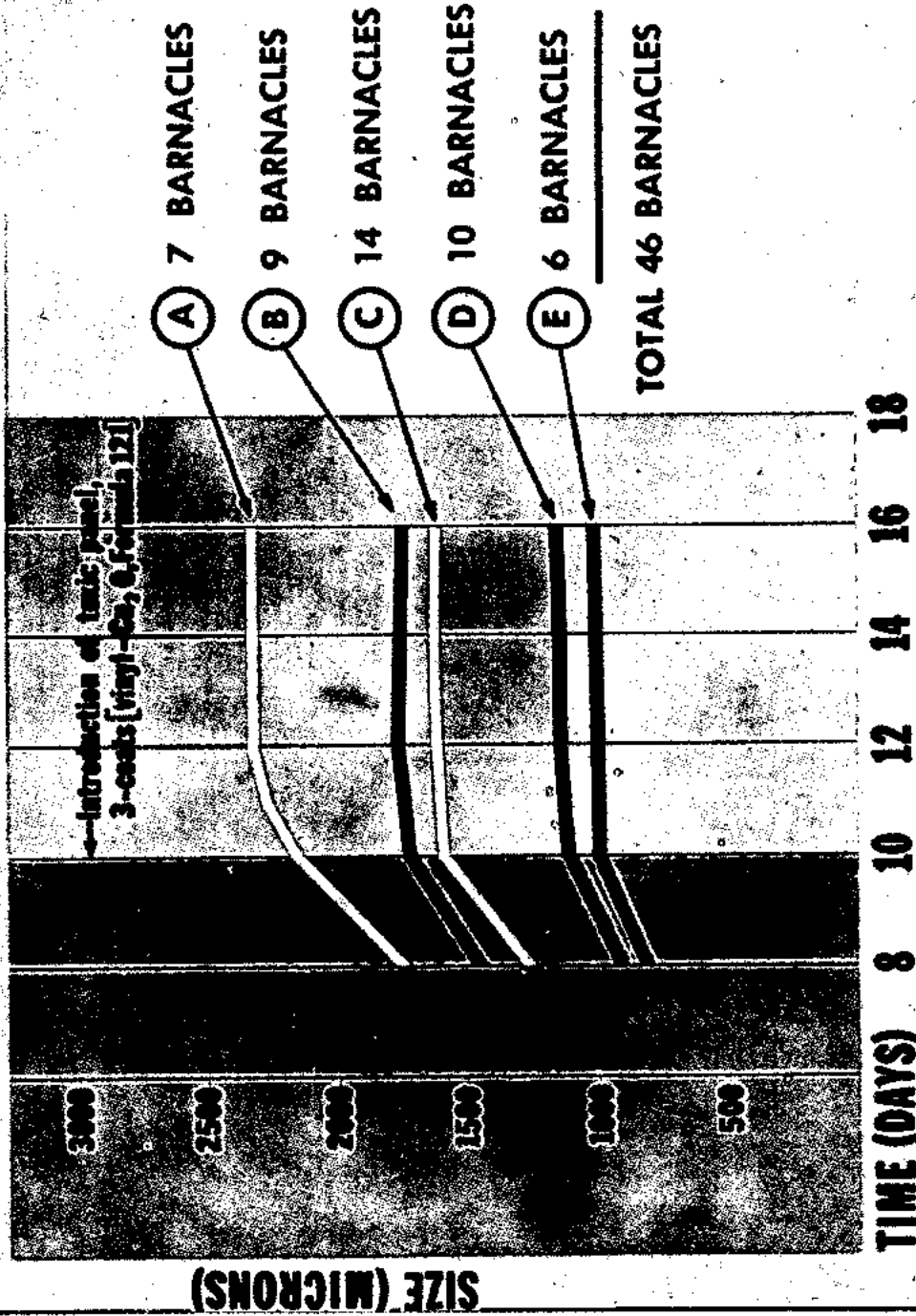
an indication of the service life of the coating sample under test.

## BARNACLE BEHAVIOR AS A MEASURE OF ANTI-FOULING EFFECTIVENESS

Antifouling coating test samples are evaluated by exposing them to a laboratory-reared population of newly attached young barnacles. The test coatings are applied to one-inch-square glass panels (microscope slide cover glasses) and then exposed to the desired amount of natural or laboratory aging. The aged coating samples are then introduced into a petri dish containing a population of young barnacles in a natural sea-water environment. The barnacles are observed regularly once each 24 hours in order to determine their response to the presence of the test coating. These observations involve, mainly, those parts of the anatomy, indicated in Figure 8, which are grossly affected by the presence of toxicant in the environment. A ten-point scale evaluating barnacle response to toxicants has been devised to provide a basis for a sensitive, repeatable bioassay test. This scale is shown in Figure 9.



# RESPONSE OF BALANUS EBURNEUS TO TOXIC



U.S. NAVAL APPLIED SCIENCE LABORATORY

Fig. 6

# RESPONSE OF BARNACLE LARVAE TO TOXICS

TIME REQUIRED TO KILL ONE HALF THE POPULATION

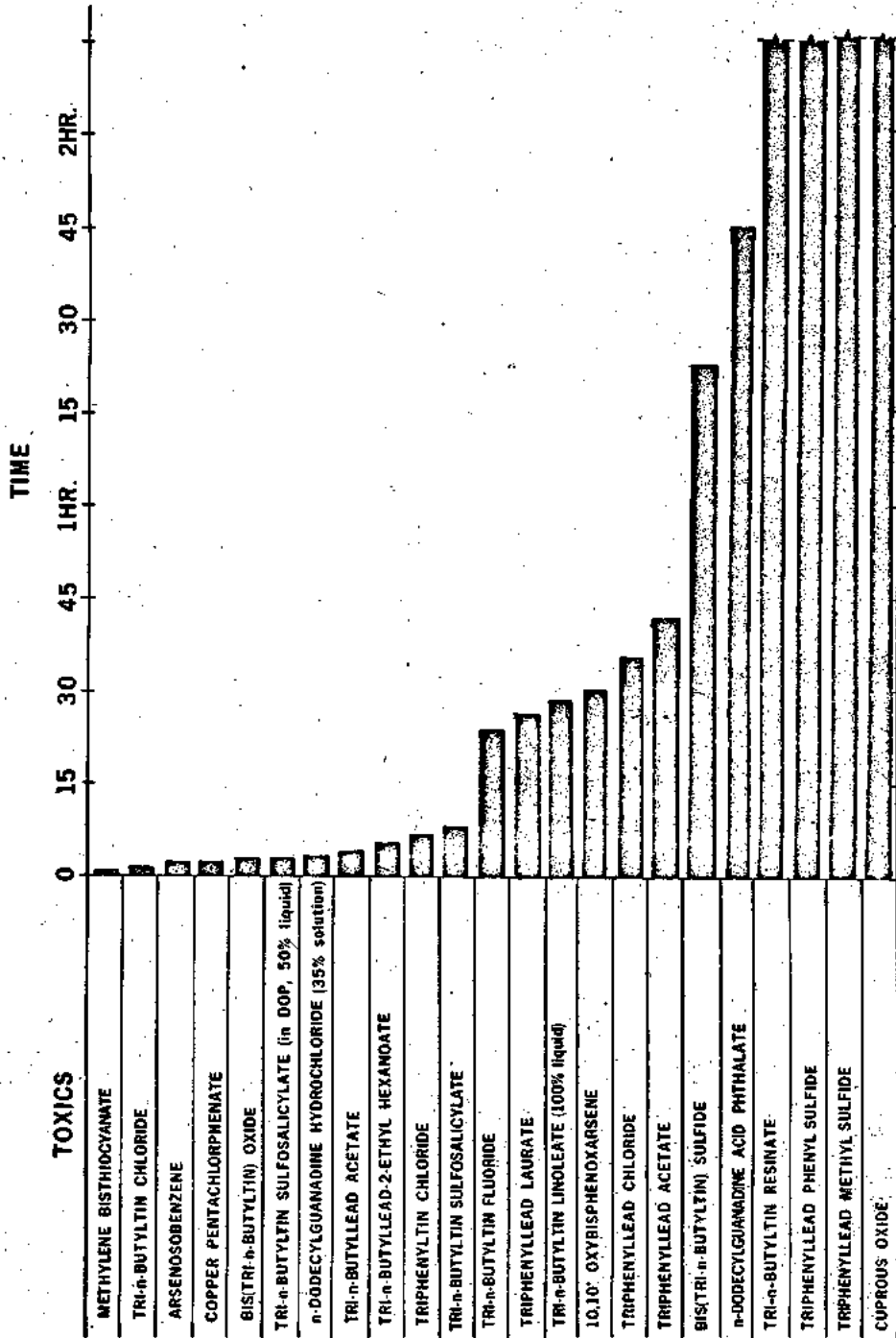


FIG. 7

## PRELIMINARY TEST RESULTS

Using the bioassay technique and the response scale described in the previous paragraphs, two coatings were evaluated. Test panels coated with two antifouling formulations and a non-toxic control coating were exposed in the sea at Miami Beach, Florida for periods of up to 6 months. The preparation details and dimensions of the test panels are shown in Figure 10. The coatings were applied to 1 inch square glass panels which were affixed to 8 by 10 inch aluminium panels in the manner shown. The resultant fouling growth after one month is shown in Figure 11. A close-up view of the coated glass panels is shown in Figure 12. The glass panels were then placed in petri dishes together with laboratory populations of newly attached young barnacles and Barnacle Response Numbers were determined by inspection. These numbers, as well as data similarly obtained for two to six month material exposures are shown in Figure 13.

The response, over a four day period, of the barnacles to the nontoxic control, demonstrates that average response numbers of 3.0 or below may be interpreted as an indication of normal barnacle behavior in a laboratory environment. For the antifouling coatings this response number was exceeded by the first day for all of the samples tested. It is interesting to note that with the cuprous oxide coating, the antifouling effectiveness actually increased during the six month exposure period. Visual examination of the antifouling test samples showed that all were effective against the attachment of fouling for the full exposure periods. Ad-

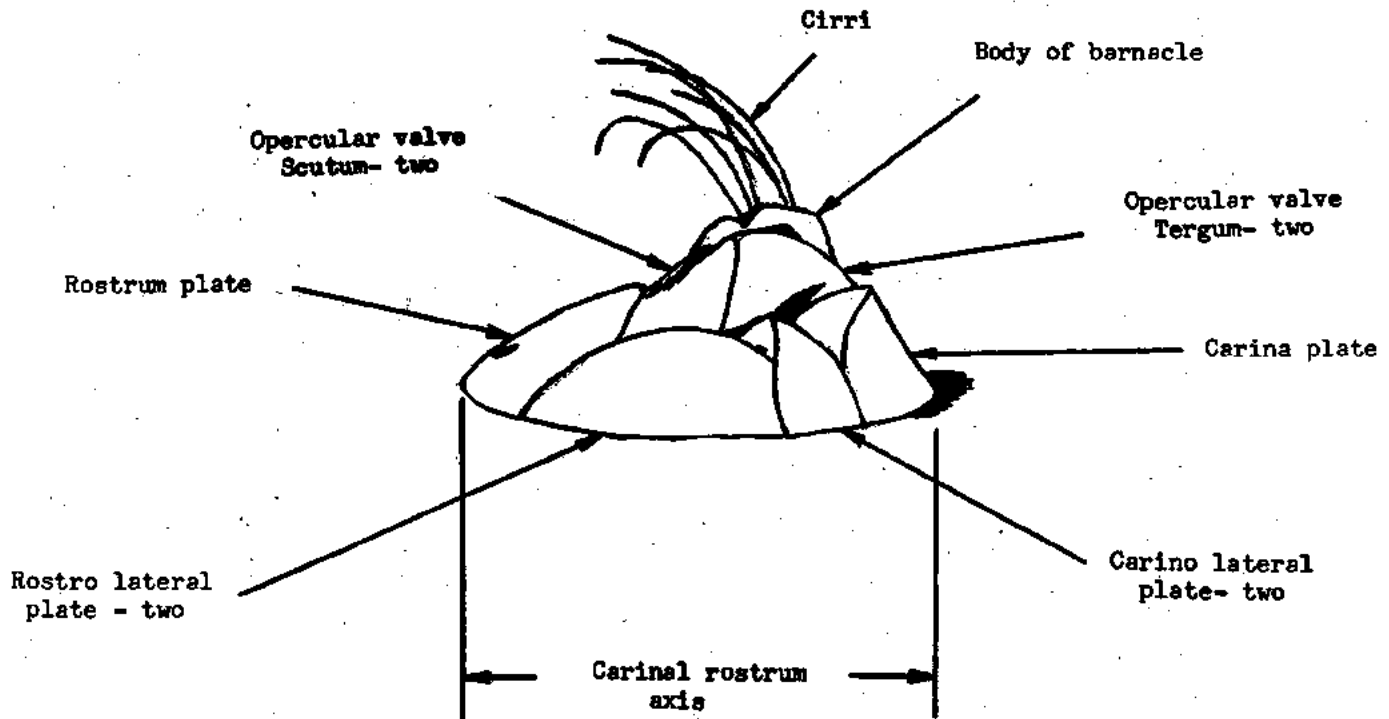


Fig. 8

## SCALE OF BARNACLE RESPONSE TO TOXICS

RESPONSE NO. / NAME	DESCRIPTION
1. NORMAL	NORMAL, COORDINATED, FULL-SWEEP CIRRAL ACTIVITY.
2. PUMPING	RHYTHMIC MOVEMENT OF ANIMAL. OPERCULAR VALVES SLIGHTLY OPEN.
3. CIRRI SLUGGISH	CIRRI COILED OR UNCOORDINATED OR SLUGGISH. CIRRI ENCLOSED IN SHELL WHEN CONTRACTED.
4. VALVES CLOSED— CIRRI IN	OPERCULAR VALVES CLOSED. CIRRI ENCLOSED WITHIN SHELL. ANIMAL SENSITIVE TO VIBRATION, LIGHT, AND GENTLE PRODDING.
5. VALVES CLOSED— CIRRI OUT	OPERCULAR VALVES CLOSED. CIRRI PROTRUDING. VALVES RESPOND TO PRODDING.
6. VALVES OPEN— CIRRI IN	OPERCULAR VALVES OPEN. CIRRI COILED WITHIN SHELL. VALVES DO NOT RESPOND TO PRODDING.
7. VALVES OPEN— CIRRI OUT	OPERCULAR VALVES OPEN. CIRRI PROTRUDING OUT OF SHELL.
8. BODY PROTRUDING	BODY AND CIRRI PROTRUDING OUT OF SHELL
9. MANTLE PROTRUDING	MANTLE, BODY AND CIRRI PROTRUDING.
10. DEAD	DEAD ANIMAL. OR— 24 HOURS AFTER NO. 9.

FIG. 9

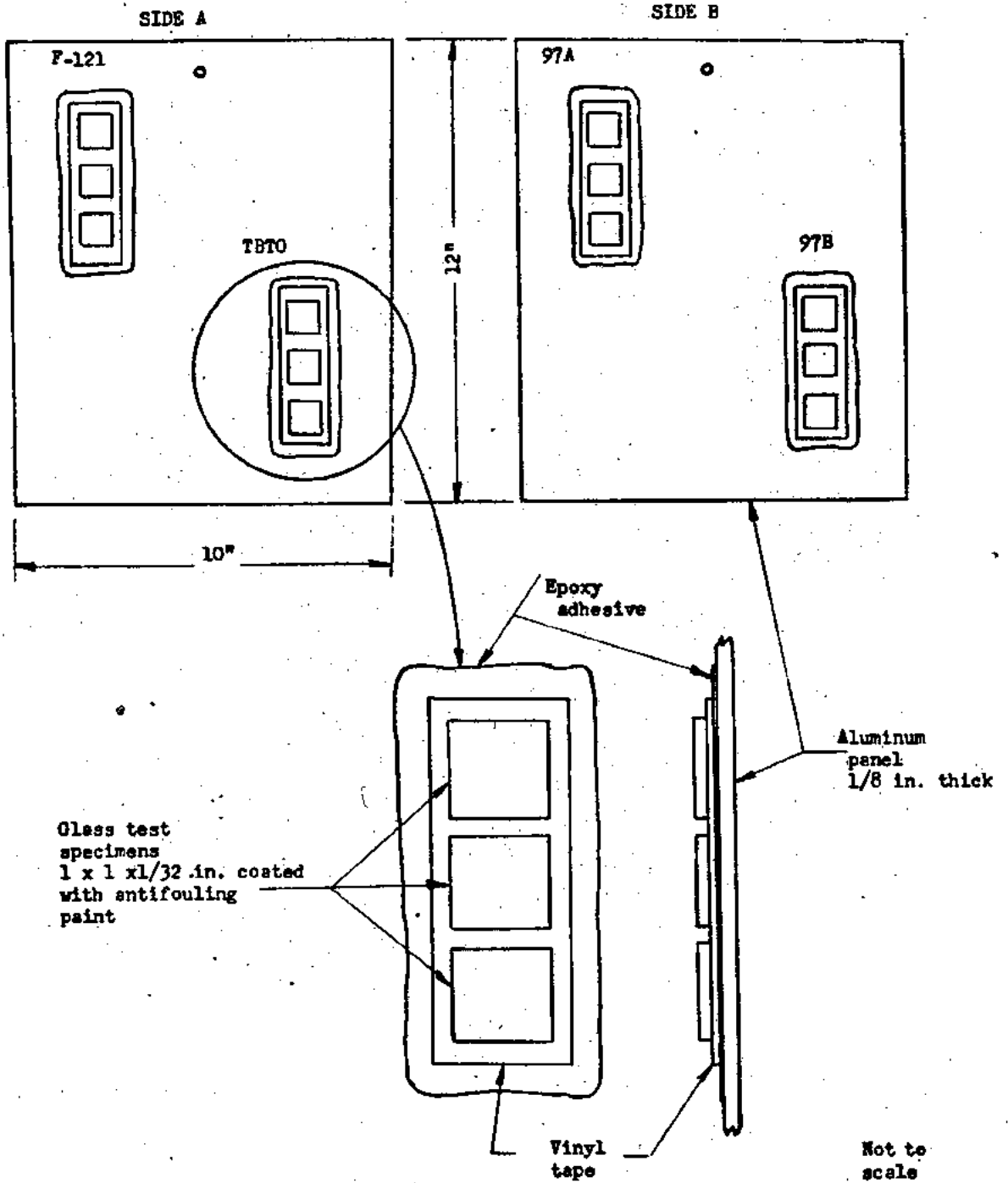
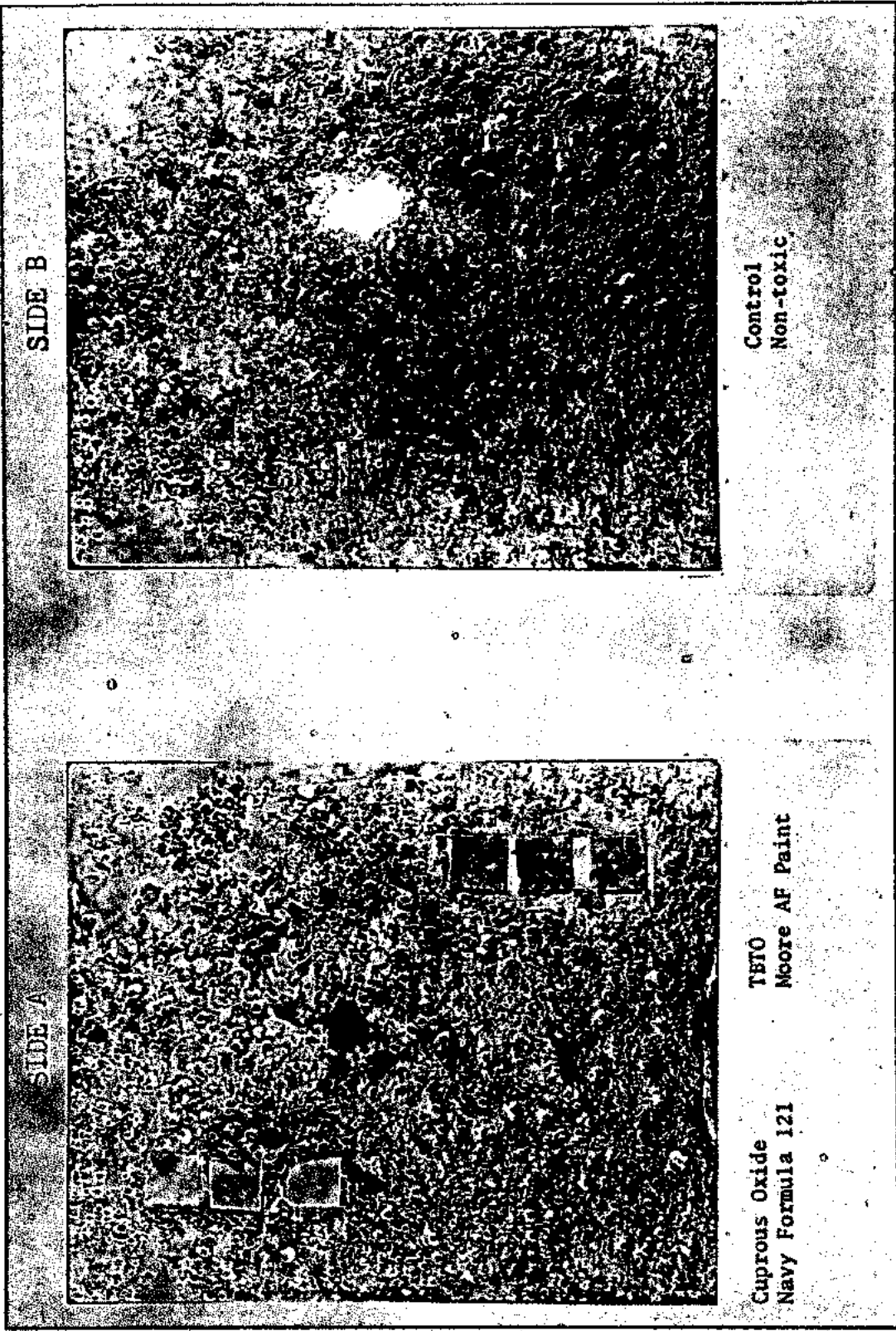


Fig. 10



SIDE B

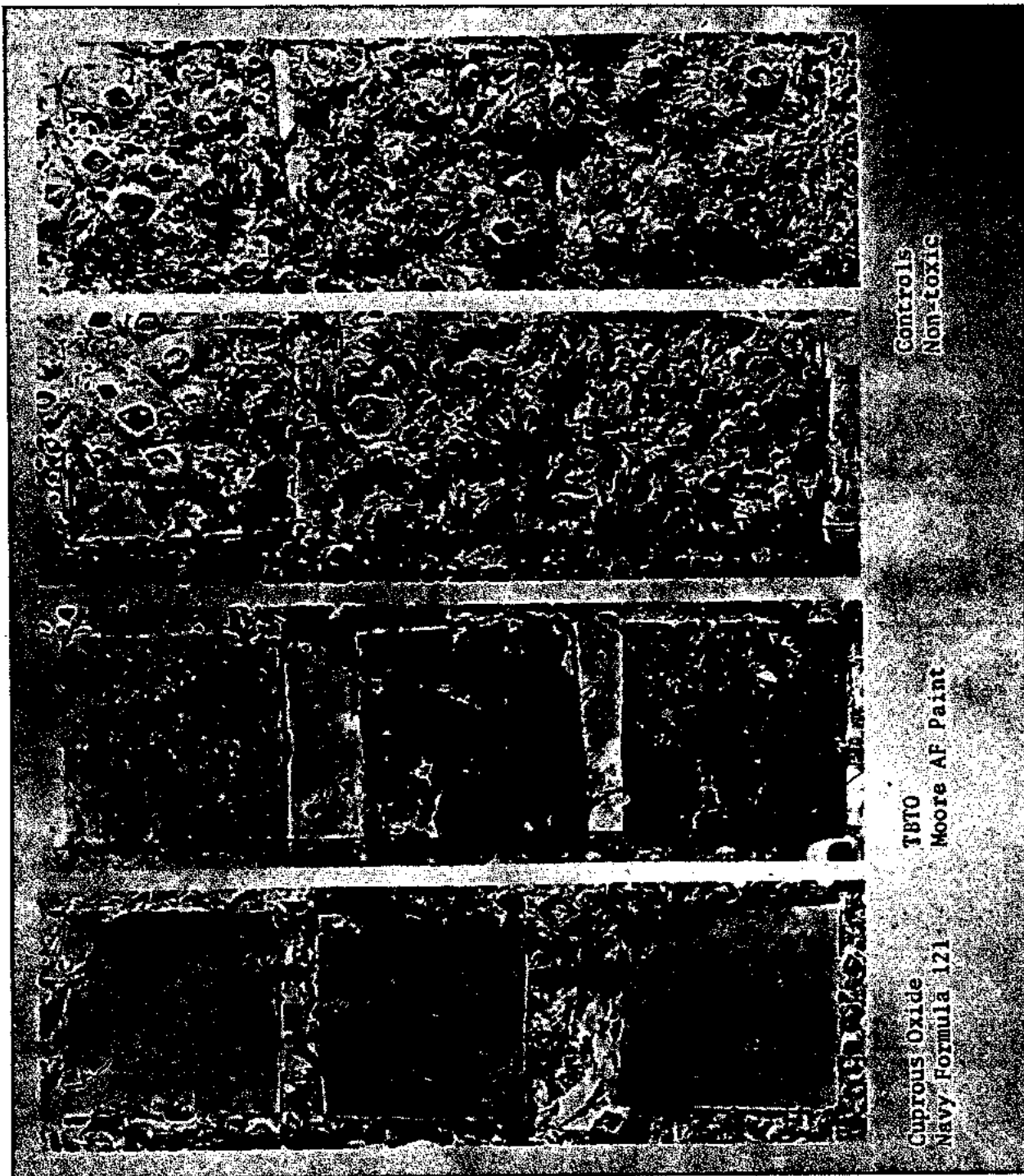
Control  
Non-toxic

SIDE A

TBTO  
Moore AF Paint

Cuprous Oxide  
Navy Formula 121

Fig. 11



Controls  
Non-toxic

TBTO  
Moore AF Paint

Cuprous Oxide  
Navy Formula 121

Fig. 12

## BIOASSAY OF TWO COATINGS

COATING	NATURAL EXPOSURE TIME MONTHS	NUMBER OF BARNACLES	AVERAGE RESPONSE NUMBER				
			INITIAL	1 DAY	2 DAYS	3 DAYS	4 DAYS
CUPROUS OXIDE FORMULA 121	0	59	1.1	3.8	4.7	5.7	6.8
	1	60	1.2	4.7	6.2	7.8	8.4
	2	78	1.1	5.0	6.4	8.1	8.6
	3	64	1.3	3.8	5.1	6.0	7.3
	4	60	1.1	4.9	7.1	8.6	9.4
	5	64	1.0	4.7	6.5	8.8	9.6
	6	65	1.0	4.4	6.5	8.7	9.4
TBTO BENJAMIN MOORE ANTIFOULING PAINT	0	10	1.0	4.0	5.1	8.6	9.8
	1	10	1.0	3.7	4.1	5.8	8.7
	2	10	1.1	3.6	4.6	7.2	8.3
	4	10	1.0	3.8	5.6	6.4	8.8
CONTROL NO TOXIC		50	1.0	3.0	3.0	2.8	2.9

Fig. 13

ditional studies, some of which are currently underway on a variety of antifouling toxicants indicated in Figure 14, and with exposure periods long enough to produce failure of the coating's antifouling effectiveness, will ultimately yield data in the initial range necessary to the development of a correlation between service life and laboratory response number.

### ACCELERATED AGING

In order to fulfill the goals set forth for the development of a methodology for evaluating marine antifoulants, a technique for the accelerated aging of antifouling coatings will also have to be devised. It is desired that such a labor-

atory process should accelerate the aging of antifouling coatings by a factor of at least 100 so that an equivalent of 3 years of natural exposure could be produced in less than 2 weeks. In addition, such a process should reproduce the natural aging characteristics of the coating. Some of the laboratory operations to provide accelerated aging of coatings which are to be studied, singly and in combination, include: increase in temperature of the seawater surrounding the test panels, changes in the pH of the seawater, high velocity movement of seawater across the test surface, agitation of the coatings at high frequency using ultrasonics, exposure of test coatings to intensive ultraviolet radiation, the use of surfactants and solvents, and techniques for extraction and absorption. These factors are outlined in Figure 15.



## ANTIFOULING COATINGS CURRENTLY UNDER INVESTIGATION

<u>COATING DESIGNATION</u>	<u>MANUFACTURER OR SUPPLIER</u>	<u>RESIN TYPE</u>	<u>TOXIC</u>
NAVY FORMULATION F121		VINYL	CUPROUS OXIDE
NAVY FORMULATION F134		POLYISOBUTYLENE	CUPROUS OXIDE
NO FOUL	B.F. GOODRICH CO.	NEOPRENE	NOT SPECIFIED
EXPERIMENTAL COATING	M&T CHEMICALS INC.	POLYURETHANE	TRIBUTYL TIN SULFIDE
EXPERIMENTAL COATING	M&T CHEMICALS INC.	HYPALON	TRIBUTYL TIN SULFIDE
EXPERIMENTAL COATING	M&T CHEMICALS INC.	MODIFIED NEOPRENE	TRIPHENYL TIN CHLORIDE
EXPERIMENTAL COATING	M&T CHEMICALS INC.	MODIFIED NEOPRENE	TRIBUTYL TIN SULFIDE
FORMULA DIS66F494	GOODYEAR TIRE AND RUBBER CO.	NEOPRENE	TRIBUTYL TIN OXIDE
EXPERIMENTAL COATING	M&T CHEMICALS INC.	MODIFIED NEOPRENE	TRIBUTYL TIN OXIDE
EXPERIMENTAL COATING	M&T CHEMICALS INC.	MODIFIED NEOPRENE	TRIPHENYL TIN CHLORIDE

Fig. 14

# DEVELOPMENT OF TECHNIQUES FOR ACCELERATED AGING OF ANTIFOULING PAINTS

## REQUIREMENTS

1. DUPLICATE THOSE AGING CHARACTERISTICS WHICH RELATE TO ANTIFOULING ACTIVITY
2. ACCELERATE AGING BY A FACTOR OF AT LEAST 100 EQUIVALENT TO 2 YEARS NATURAL AGING IN ABOUT ONE WEEK
3. BE APPLICABLE TO A WIDE VARIETY OF ANTIFOULING PAINTS

## POSSIBLE APPROACHES

1. INCREASE IN TEMPERATURE
2. CHANGES IN pH
3. WATER VELOCITY
4. ULTRASONICS
5. RADIATION
6. SURFACTANTS AND SOLVENTS
7. EXTRACTION AND ABSORPTION

## CALIBRATION

1. LAB DATA
2. RAFT TRIALS
3. SHIP SERVICE TRIALS

Fig. 15

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## DISCUSSION

Dr. LITTAUER, President (U.S.A.): If I may take the liberty, I would like to submit the first question. How representative is the barnacle in an overall assessment of antifouling characteristics?

D. KALLAS: It isn't necessary representative. We have found that in fouling we had algae, molluscs, tubeworms and barnacles, but we had to start somewhere and we started with the barnacle and the balanus berius. We were wondering if we used the right species, but I think with the methodology which we developed, we can move to the other forms of animal life.

E. LINDNER (U.S.A.): Mr. Kallas, you demonstrated here how you use the second stage nauplius and metamorphosed adult barnacle as an indicator for the toxic materials. I would like to ask three questions: First, if you have any experience in this line with the cyprid stage of the barnacle, since this is the attaching form;

Second, if you have any knowledge about whether or not the cyprid consumes any food. The literature has some contradictions about this question and most investigators agree that the cyprid does not feed;

Third, in the event that you have experience with the cyprid and also agree that the cyprid does not feed, therefore it does not ingest the toxics, are the toxics still effective by acting, for example, through the respiratory system or any other way?

D. KALLAS: The first question was about studying the cyprid stage. I was fascinated with Dr. Kühl's paper about the cyprid stage. According to my mind this stage should be studied because it is the point at which the barnacle attaches. When it is a swimming nucleus it does not bother us until it attaches after his metamorphosis. It is the right thing to get it at the cyprid stage and this is where I think that our efforts should be concentrated. Now your second question is does the cyprid feed? Colozier tells that it does not feed, because he has observed it carefully and after a certain period if he doesn't attach, it dies. Also he has not seen it to grow. So we don't think it feeds. Dr. Kühl's work seems to suggest that in the cyprid stage the poison was absorbed by some sort of osmosis.

We do not have any further experience with cyprid and I believe that is a gap, and one of the things I have gained of this meeting is to go back and ask, our people to spend some more time on the cyprid, just before and after metamorphoses. As I said before I was fascinated with what Dr. Kühl has spoken about and I wish if he were here, if he would possibly say something about how the cyprid is doing the metamorphosis.

Dr. KÜHL (Germany): I saw many thousands of cyprids with my own eyes never could I observe any uptake of food but nevertheless the cyprids metamorphosed very well. During a long time I had them in glass dishes with clear water without any food and the metamorphosis could be stated in each case. I think this fact is very clear.

Prof. EVANS (Canada): Mr. Kallas, you were suggesting that when barnacles settle they are oriented for life. I may be wrong, but in my observations I have noted that the barnacles which settle on rocky shores are oriented so that they face the flow of water as it recedes. Do you know anything about larval orientation at the time of settling?

D. KALLAS: I don't know, I am certain that they are other reasons why the barnacle settles and arranges itself in a certain way. You must remember that the barnacle attaches when it is a separate, and when it attaches and orients itself, it then metamorphoses but it orients itself with its eyes towards the light and its eyes are where the carina plate is in the acorn barnacles. We have also observed that the more light we have the more barnacles we will get.

Dr. HOUGHTON (England): There are several comments and a question I would like to make. I agree with Dr. Kühl that cyprids do not feed, and I think support for this view will be re-evaluated in a

paper by Walley which will be published shortly. As to the question of light, work carried out by Dr. Stubbings and myself suggested that in *Elminius modestus* there is an optimum light intensity for settlement. If however you look at conduits, you find that there is tremendous settlement of *E. modestus* in the absence of light, I think this question of the effect of light is very complicated. We need to know a lot more about it. The question I would like to ask you is, that we have been devotely successful with rearing *E. modestus*, but have had a lot of trouble with *Balanus balanoides* particularly with regard to temperature. Have you had any experience which could help us in this field.

D. KALLAS: In regard to the question of light, I agree with you hardly. Apparently the barnacle is interested in other things besides lights, you know food and sex and all other things that barnacles are interested in. May be in that pipe is something more attractive than light.

QUESTION unregistered.

Dr. LITTAUER (U.S.A.): Can you answer that perhaps Dr. Kühl. Dr. KÜHL (Germany): This is possible. In the cyprids we find yellow concretions— under normal microscopic lighting they seem black — in the anterior and posterior ends of the larval body. These spots are the calcareous reserve for the primary calcification of the plates and are distributed a short time before or whilst the metamorphosis. They are formed in the first metanauplius stage. Also the oily globules in the cyprids are stocked by the nauplius. These fat-reserves enable the cyprids to search for a suitable settling place by swimming and crawling for a period up to 3-4 weeks. By my own experiments in glass dishes the decrease of the oil reserves could be stated. In this way the duration of the planktonic life of the cyprids can be estimated by the quantity of the oil globules.

Concerning the first question I believe that the poisoning of the cyprids is effected by osmosis mainly at the attaching point or at the basis of the metamorphose young barnacle.

Dr. BALAKRISHNAN NAIR N. (India): Mr. Kallas have you any data on the slime film and the settlement of barnacles?

D. KALLAS: No, except we found that as we grow barnacles that the way to do it is to have a slime film, because they will settle on the slime film rather than settle on just playing.

Dr. BALAKRISHNAN: And would you kindly tell us something about the effect of colours of this substratum.

D. KALLAS: Yes, we have done some experiments on colours and I don't think we have found any dramatic differences, we have also done some experiments on sound, the imposition of ultrasonic and sonic influences. I think that all of this has to be looked better.

B. CALLAME (France): To answer the question of Dr. Balakrishnan on the subject of colours, I can say that I have done experiments on this question by myself and I get results which were not very clear. The light colours seems to be the less attractive. During night all colours are black and the fixation takes place for more than fifty per cent.

By this occasion I would like to ask this question: On what way do the Larvae and Balanac grow up from the point of view of their nourishment.

D. KALLAS: I would like to say that the next film will answer many of your questions, although it is a review of the film you have seen but it does have more definite information on the feeding of the over and the nauplius stages.

Prof. EVANS (Canada): Have you ever tested to see if they would settle on teflon?

D. KALLAS: We have had very limited experiments with teflon and we found no major differences.

**SÉANCE DE CLOTURE  
CLOSING SESSION  
SCHLUSSSITZUNG  
ΣΥΝΕΔΡΙΑΣΙΣ ΛΗΞΕΩΣ**

**24 Septembre 1968**

SEANCE DE CLOTURE  
CLOSING SESSION  
SCHLUSSSITZUNG  
ΣΥΝΕΔΡΙΑΣΙΣ ΑΘΗΝΩΝ

*Prof. Dr. Skoulikidis:* Chers Congressistes c'était pour moi un grand honneur et un grand plaisir, d'être pendant tout ce temps en contact avec les congressistes éminents du 2<sup>e</sup> Congrès International de la Corrosion Marine et des Salissures.

Je crois que ces mêmes sentiments ont régné aussi pendant le contact que vous avez eu entre vous.

De tous parts l'on me dit que le congrès est réussi tant du point de vue scientifique, que de celui de l'organisation.

Ce qui m'a aussi convaincu. Ce résultat n'est pas dû seulement aux efforts de tous ceux qui ont contribué à la réalisation du Congrès mais aussi, à votre présence. Car le Congrès, c'est vous, chers Congressistes.

C'est pourquoi je renouvelle mes remerciements à vous tous d'être venus à Athènes. Mes remerciements s'adressent aussi aux nombreux congressistes Hellènes.

Je crois, que grâce aux communications très intéressantes présentées tout le long du Congrès, il a été prouvé ce que j'ai dit à mon allocution, il y a quatre jours que le progrès dans la recherche sur la Corrosion et les Salissures, effectué depuis le premier Congrès est très important.

Monsieur Romanovsky, Président du Comité Permanent International pour la Recherche sur la Préservation des Matériaux en Milieu Marin, va maintenant, nous donner un rapport sur les communications présentées pendant le Congrès.

Ce rapport a été fait par Monsieur le Docteur Romanovsky en collaboration avec Monsieur le Docteur Déchaux, Petrocokinos et Monsieur le Docteur Callame.

Je souhaite un bon séjour à ceux qui resteront pour quelques jours encore à Athènes et un bon voyage à ceux qui partiront.

Chers Congressistes Au-Revoir jusqu'au Troisième Congrès dont nous fixerons le lieu ayant déjà deux Candidatures.

*Prof. Dr. Skoulikidis:* Je prie le Dr. Romanovsky de prendre la parole.

*Dr. Romanovsky:*

Monsieur le Président, Mesdames, Mesdemoiselles, Messieurs.

Vous me voyez arriver ici avec un papier, ce qui n'est pas mon habitude et je vous prie de m'en excuser; mais le rapport que je vais vous lire a été fait par mes éminents Collègues, Messieurs Déchaux, Petrocokino et Callame et je ne voudrais déformer ni leur pensée ni leur écrit.

C'est un grand honneur pour moi de vous présenter ce rapport, mais c'est une tâche également très périlleuse car on m'a demandé de faire une sorte de résumé, bref et rapide, étant donné que vous devez vous rendre encore à vos hôtels avant d'aller à la réception de ce soir; je vais essayer de m'en acquitter au mieux.

Je voudrais d'abord, avant de commencer à lire l'exposé des rapporteurs, les remercier très sincèrement pour cette tâche qu'ils avaient à accomplir, en restant continuellement dans les salles de travail et en prenant des notes, et c'est le résultat de ces notes que je vais vous lire maintenant.

*Section I.* — dont les rapporteurs étaient Messieurs Déchaux et Petrocokino.

Après une introduction magistrale de Monsieur le Prof. Chaudron, des Conférenciers successifs nous ont donné les résultats de leurs essais sous différents climats, dans les latitudes allant de 36 Sud à 60 Nord.

Ces essais portaient sur les métaux, alliages ou assemblages des métaux les plus divers, soit nus, soit recouverts de peintures, en contact avec l'eau de mer, naturelle ou artificielle.

Ces essais étaient effectués aussi bien au Laboratoire, sur radeaux que sur des câbles immergés, des navires, des docks flottants ou des bouées.

Nous avons pu constater avec satisfaction que le nombre d'essais en eau de mer naturelle allait en croissant, comme nous le connaissons tous et en particulier le Professeur Chaudron.

La lutte contre la corrosion a été examinée de différents points de vue: passivation, inhibition, protection cathodique, revêtement seul ou sous protection cathodique.

Dans ce dernier domaine, les Conférenciers ont comparé les métaux sacrificiels, donné des exemples de protection et codification et étudié la remise en peinture après action de la protection cathodique.

Les communications ne se sont pas bornées au cas de l'eau de mer, mais ont fourni des renseignements précieux sur la corrosion dans l'eau saumâtre chaude et dans les installations de dessalement de l'eau de mer.

Des idées nouvelles ont été émises au sujet de l'influence des dépôts paraffinés que laisse le pétrole brut sur les piqûres des citernes des pétroliers.

Ces idées s'appuyaient sur des expériences directes, ce qui permet d'éclaircir certaines observations restées inexplicables.

L'érosion due à la cavitation a été étudiée en détail par deux méthodes de laboratoire; les résultats ont été comparés entre eux et avec la pratique.

En matière de constructions navales et des réparations, les études ont porté sur la préparation des tôles neuves ou anciennes. Trois communications ont été consacrées à ce sujet.

On y a de nouveau attiré l'attention sur la difficulté de mise à nu adéquate des surfaces corrodées par leur séjour antérieur dans l'eau de mer.

Je crois que les dernières communications nous ont montré l'importance de l'agressivité de l'eau de mer sur un matériau moderne qui est le béton.

L'intérêt de ces communications a été tel que, le plus souvent, le Président était obligé de limiter le nombre des interventions pour ne pas prolonger outre mesure les séances de travail.

Dans le cadre de la *Section II* consacrée aux salissures, le rapport a été établi par Monsieur Callame.

L'ensemble des idées générales qui découlent de l'audition des diverses communications, peut se résumer en sept points:  
1<sup>o</sup> — De nombreuses informations sur la répartition géographique des salissures, ont été apportées, notamment sur les côtes de l'Adriatique, de la Baltique, de l'Inde, de l'Europe du Sud et de la Californie à Monterey.

2° — En ce qui concerne la biologie des salissures, des données très importantes ont été apportées sur le mécanisme de fixation des balanes et sur l'influence des toxiques dans la métamorphose des cypris en balanes.

Les travaux ont été effectués sur les larves obtenues au laboratoire et enfin sur la concentration de substance radioactive par certains organismes salissants.

3° — Le rôle des bactéries, vis-à-vis de la corrosion, et du conditionnement du milieu a été également abordé au cours de trois communications.

4° — L'intérêt porté en technologie des peintures anti-fouling, sur les composés organo-métalliques d'étain et de plomb, a été particulièrement développé.

Une étude intéressante semble démontrer que la protection cathodique n'a pas d'effet sensible sur les performances des peintures antisalissures; c'est ce que nous avons tous pensé antérieurement.

5° — Parmi les procédés de protection, autres que les peintures antisalissures, on remarque le développement des recherches, notamment par utilisation des dispositifs susceptibles de modifier localement le pH du milieu. On a cité également l'emploi d'alliages de cuivre, du courant électrique et enfin du recouvrement par des feuilles d'aluminium pour la protection du bois.

L'action du Chlore pour la destruction du *Mytilus edulis* a également été évoquée.

6° — D'importantes informations ont été apportées sur le perforant marin, non seulement en ce qui concerne le bois, notamment aux Indes et en France, mais aussi à propos de la pierre, aux Indes et au Canada.

7° — Un travail très important nous a été présenté cet après-midi sur l'influence de la profondeur, en ce qui concerne le développement des salissures, ce qui attire particulièrement l'attention sur ce travail, car nous avons relativement peu d'informations jusqu'ici sur l'influence des grandes profondeurs.

Au total, une trentaine de communications ont montré la diversité des problèmes posés par la lutte contre les salissures et leur actualité est due à la très grande importance économique que peut avoir la résolution de nombreux problèmes soulevés par cette question.

Bien des mers du Globe sont encore inexplorées en ce qui concerne les salissures.

Bien des améliorations et bien des procédés nouveaux de protection sont encore à apporter.

Ce sera la tâche des prochaines années et, nous l'espérons, la matière du prochain Congrès.

Ainsi donc soixante-trois communications, provenant de dix-neuf Nations ont été présentées.

On m'a demandé ce matin, (il s'agissait d'un représentant de la Presse), quelles étaient les solutions définitives et pratiques que nous avons apporté au cours des travaux de ce Congrès pour résoudre les problèmes de la corrosion?

Car ces gens là s'imaginent toujours qu'une fois qu'il y a un certain nombre de scientifiques et de techniciens réunis ensemble, ils vont immédiatement leur apporter sur un plateau d'argent la solution idéale qui supprime la corrosion et tous ses problèmes.

Or évidemment, vous le savez, beaucoup mieux que moi, ce sont des choses impossibles.

Et je lui ai répondu simplement ceci: «Lorsque les savants ont commencé à étudier le courant électrique, d'abord sous

sa forme statique, est-ce qu'en ce moment-là ils pouvaient prévoir que ce courant électrique leur fournirait de la glace pour rafraîchir leurs boissons?»

C'est pour bien leur faire comprendre que ce que nous faisons ici nous permet de faire avancer la science, qui à son tour fait avancer la technique et celle-ci, à son tour, apporte des solutions économiques de plus en plus précises et de plus en plus fructueuses.

Donc ce Congrès a été un pas de plus vers des solutions pratiques.

Avant de terminer mon exposé, que j'aurai voulu encore plus court, je tiens, au nom de tous les Congressistes ici présents, à exprimer mes remerciements, tout d'abord à Monsieur Skoulikidis qui, depuis des mois se consacre à la tâche de ce Congrès, qui a maigri de je ne sais combien de kilos, qui n'a pas pris de vacances, qui a abandonné sa femme (c'est une façon de parler) et qui s'est donné corps et âme à ce Congrès. Pendant ce Congrès il a été vraiment, comme il le disait lui-même, le Magicien. Chaque fois qu'on lui demandait quelque chose celle-ci se réalisait.

Ce Congrès a été vraiment extrêmement sympathique, contrairement à certains grands congrès où vous avez deux mille ou trois mille personnes, qui sont des machines où on ne sait pas trouver le responsable. Ces grands congrès n'ont plus ce contact humain comme nos congrès, qui sont beaucoup plus petits.

Au cours de notre Congrès les participants se sont fait des amis.

Je tiens également à remercier le Président et les Membres des Comités et plus particulièrement Monsieur le Président Koronaïos qui préside la Chambre Technique de Grèce, pour toute l'aide qu'il a apportée à Monsieur Skoulikidis. Je crois qu'à un certain moment Monsieur Skoulikidis était dans une situation très difficile, désespérée peut-être, et Monsieur Koronaïos s'est trouvé là pour faire le miracle, il a été aussi un peu le magicien.

J'aurais voulu remercier tout le monde, mais j'ai peur d'en oublier. Néanmoins je voudrais remercier la Commission de l'Énergie Atomique qui a aidé Monsieur Skoulikidis et qui continue à collaborer avec lui. Je l'ai d'ailleurs déjà remerciée au cours du dîner à l'Hôtel Hilton. Je voudrais remercier également tout le personnel du laboratoire de Monsieur Skoulikidis qui a apporté une aide unique, sans laquelle il n'aurait jamais pu faire ce qu'il a fait. Je voudrais remercier aussi les interprètes qui ont travaillé quelque fois dans des conditions très difficiles. Ils n'étaient pas assez nombreux pour assurer la traduction en quatre langues. Si nous avions respecté les conventions internationales, nous serions arrivés à un chiffre astronomique d'interprètes que nous ne pouvions pas avoir ici. Aussi, je tiens tout particulièrement à les remercier ici. Je voudrais aussi remercier le personnel de l'Agence Valcania qui vous a permis de faire des excursions qui ont favorisé votre séjour ici.

Je suis navré si j'ai oublié quelqu'un dans mes remerciements mais je crois avoir fait un petit peu le tour d'horizon.

Je renouvelle moi, à titre personnel, tous mes remerciements à Monsieur Skoulikidis et à Monsieur Koronaïos et je suis très heureux d'avoir pu parler devant vous en dernier.

Je vous donne rendez-vous au prochain Congrès qui aura lieu probablement dans quatre ans.

Je vous remercie.

