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Torres A. Lewis

TUESDAY 27TH JULY 2004

PLENARY PRESENTATION

MOLECULAR CROSS-TALK BETWEEN SPECIES IN THE FORMATION OF MARINE FOULING COMMUNITIES

J A Callow, School of Biosciences, University of Birmingham, UK
A S Clare, School of Marine Science & Coastal Management, University of Newcastle, UK

Settlement of the dispersal stages of marine organisms typically involves exploration and sensing of a surface, followed by temporary and permanent phases of adhesion. Spores of algae and larvae of invertebrates respond to cues presented by a surface, e.g., wettability, roughness, surface chemistry, diffusible molecules. In the natural environment, this range of cues may be presented by other organisms that have already colonised a surface and evidence from several research groups is now accumulating to show that this level of communication occurs between widely different phylogenetic groups. This has profound implications for our understanding of how marine fouling communities develop and these insights may suggest novel methods of control. In this presentation we explore the scope of this type of communication by reference to interactions between spores of green algae, barnacle cypris larvae and biofilms formed from specific strains of marine bacteria.

In the case of zoospores of the green alga, Ulva, we have shown that biofilms of specific bacterial strains stimulate spore settlement and that spores preferentially attach to bacteria; biofilms of other strains inhibit settlement. One mechanism behind the settlement-promoting effect is the detection, by spores, of acylated homoserine lactones (AHLs); a class of diffusible signals used by bacteria during quorum-sensing. This is the first demonstration that eukaryotes can recognise this class of prokaryote signals.

In the case of the barnacle, Balanus amphitrite, biofilms of bacterial strains that promote settlement of Ulva, generally inhibit settlement of the cypris larvae. Although the mechanism(s) of action is unclear, it is not unreasonable, based on prior work, to postulate a chemical modulation of settlement. For one selected strain, Vibrio anguillarum, AHLs have been implicated in the inhibition of settlement.

This ability to 'listen in' on bacterial communication is unlikely to be confined to Ulva and B. amphitrite. Can the response of fouling organisms to AHL or other signalling systems, therefore, be exploited to provide a non-toxic solution to control fouling? On the one hand, the disparity in response between Ulva and B. amphitrite is not promising. On the other hand, lessons learned from research on the halogenated furanones - molecules that interfere with AHL signalling and possess broad-spectrum antifouling activity - should encourage this line of enquiry.

STREAM 1 – SESSION: FOULING CONTROL ON SHIPS SESSION CHAIR: COLIN ANDERSON

OVERVIEW OF THE U.S. OFFICE OF NAVAL RESEARCH PROGRAM ON MARINE BIOFOULING CONTROL

S McElvany, L Chrisey and P Armistead, Office of Naval Research, USA

The US Navy's Office of Naval Research is supporting the research and development of environmentally friendly marine hull coatings. The Navy is seeking new ship coatings capable of meeting current and anticipated performance specifications (e.g., 12-year repainting cycle, compatibility with existing spray systems) and global regulatory standards, which will enable the Navy to train and operate worldwide, in an unrestricted fashion.

Specific objectives of the ONR program will be described; the program invests in both basic and applied research on the development of novel foul-release and foul-resistant coatings (elastomers, nanostructured coatings, polymers with patterned surface chemistries, fluoropolymers, coatings with tethered biocides). Supporting research activities to the development of coatings include: surface characterization; fracture mechanics/tribological studies of organism adhesion and debonding processes; and interactions of biofouling organisms with surfaces and with each other. A variety of laboratory and field exposure-based tests are used to characterize the performance of these coatings, and will be described in the presentation. The ONR program is unique in that it tightly couples the study of biofouling biology/ecology with the development and characterization of novel surfaces, in an iterative fashion, to maximize the potential for developing a non-toxic coating that exhibits desired fouling-control and durability qualities. The ONR coatings program is addressing the Navy's intermediate through long-term coating needs for environmentally benign yet operationally acceptable marine hull coatings.

PERFORMANCE OF BIOCIDE-FREE ANTIFOULING PAINTS – TRIALS ON DEEP-SEA GOING VESSELS

B Daehne, B Watermann and M Wiegemann, LimnoMar, Germany S Sievers and R Dannenberg, Umweltbehörde Hamburg, Germany H Michaelis, NLÖ – Forschungsstelle Küste, Germany

From 1998 to 2003 a total of 117 test patches were tested on 20 ships. 45 inspections took place in this period (DAEHNE et al. 2000, 2002, WATERMANN et al. 1999, 2001, 2003). The <u>ship types</u> included: container ships, tanker, bulk carrier, cruiser, ferries, research vessels, patrol- and fishing boats. The ships were painted with test patches or fullcoated. The <u>types of test paints</u> can be summarised as: 16 non-stick coatings (silicones, semisilicones and teflon coatings), 16 erodable/self-polishing paints, 2 fibre coatings, 7 anticorrosive paints (epoxies, rubber-like PU coatings). The performance was tested according to type of paint and ship after 4 - 60 months. The <u>evaluation criteria</u> for the surveys of test coatings were: Fouling degree/coverage by visual estimation according to STG 2111, dry weight of fouling/m², measurement of the adhesion force of barnacles according to ASTM method D 5618-94. In addition the condition of the paint was recorded and samples of fouling organisms were sampled for taxonomic determination

Results of different biocide-free coatings

Silicone coatings

The application was performed in routine dock-practice but required specific protection measurements to prevent overspray in addition to a limited range of humidity and temperature. The airless spray application of transparent silicones finishes required far more surveillance to avoid holidays than pigmented finishes. Removal of silicones was successfully tested without succeeding problems at recoated areas. It is highly recommended to remove silicone coatings by high water pressure (1200 - 2000 bar) instead of grit/sand blasting, thus creating a higher effort in time and money than for erodable paints. The performance of silicones was positively correlated with the condition of paint. Undamaged test patches performed well up to 60 months. The antifouling performance of unfilled silicones was superior to filled and pigmented products. When exposed to mechanical impact like abrasion, scratching or pressure, filled and pigmented silicones endured these impacts far better than unfilled products.

Silicone-free non-stick coatings

For these coatings basing on semisilicones or teflon a low efficacy was recorded. Only one coating displayed a reduced adhesion force of barnacles.

Erodable coatings

This type of coatings created no problem and no additional protective measurements in application, removal and overpainting. As the mode of action of this paint is directly related to the erosion rate a calculation of minimal dry-film thickness and the survey of applied dry-film thickness is strongly recommended. Out of 16 erodable paints, 8 displayed a good performance on coastal operating vessels

Fibre coatings

Fibre coatings based on an epoxy glue and fibres in different lengths had to applied with special devices and specially trained applicators. From the beginning of the project to the last application the quality of this type of coating could be improved. A critical density and their homogenous distribution of fibres is crucial for the performance. Removal of fibre-coatings can be effected by hydro- or sand-blasting following normal dock practice.

Test patches with short fibre length (1.1 mm) and high density of fibres performed effectively to prevent fouling by barnacles, but not by algae.

Anticorrosive paints

All anticorrosive paints tested in this project displayed no inherent antifouling properties. They can be used without an additional antifouling paint on top, exclusively on ships with suitable operational profile. Or they can be used in combination with ICCP systems which probably have a fouling reducing side effect. Both solutions are in practice.

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THE ROLE OF UNDERWATER CLEANING IN CONTROLLING MARINE FOULING

S Moore and J Jackson, UMC International Plc, UK

Marine fouling has long been a problem for mobile and static marine structures, and a lot of research, development, and money have been expended to combat its effects, generally by utilising antifouling products. Now that the environmental lobby has become so powerful due the consciousness of public opinion, the use of biocides whose sole aim is killing living organisms has been brought into question. For many years underwater cleaning has been used purely as an expedient for shipowners, to be used when the life of their antifouling coating has been spent. Likewise, the thought of cleaning the underwater parts of static structures has only been considered when crucial inspections or maintenance are required.

Underwater cleaning techniques are now highly developed and fouling can be removed without damage to the underlying substrate, including the cleaning, where necessary, of low surface energy silicon paints. Consequently the use of toxic antifouling paints that are damaging to the environment should be a thing of the past, and there are considerable dividends available to those who embrace underwater cleaning as a method of controlling marine fouling.

Cleaning underwater should be carried out early and often when the marine fouling is in its early stages of growth, thus mitigating against most of the problems associated with the migration of species. To be able to abolish all biocide based antifouling paints and still control marine fouling should be the aim of the industry over the next 10 years!

This paper will put forward the technologies, the experience of over 30 years in the industry, and the financial case for looking seriously at this most attractive option to conventional thinking.

PERSPECTIVES IN TECHNOLOGY, MANAGEMENT AND ECONOMICS OF TBT FREE ANTIFOULING FOR COMMERCIAL SHIPS

A Touzot, Center for Corrosion and Biofouling Control/Florida Institute of Technology, USA:

One of the challenges of operating ships is how to efficiently protect these valuable assets from fouling organisms and to control the associated cost. This paper examines the methods and technology used for achieving optimum antifouling selection for commercial ships. This was achieved by matching the basic requirements from different types of ship operations (Tanker and Containership) with available antifouling technologies (CDP, SPC and Silicone base); understanding the structure and interaction between stakeholders of the antifouling market (Ship Owners, Paint companies, and Research); and creating managerial and economic models for decision-making (technology matrix and Net Present Value).

WORLDWIDE PERFORMANCE PROJECT FOR TBT-FREE ANTI FOULING SYSTEMS.

L Kolle, the Norwegian Marine Technology Research Institute (MARINTEK), Norway H Vold, Det Norske Veritas (DNV), Norway.

Many ship owners have for several years tested tin-free Anti Fouling paint systems, both in form of test areas and for full hull bottoms, with varying success. Some ships have experienced severe fouling and speed loss. Hence, many ship owners ask for thorough documentation regarding the performance of the new Anti Fouling systems.

The test programme is part of a research project called "Green Efforts for Existing Ships", operated and managed by the Norwegian Marine Technology Research Institute, MARINTEK. The project is funded by the Research Council of Norway and the Norwegian Shipowners' Association in addition to support from all participating partners. Det Norske Veritas (DNV) participates as specialist in Coating and Material Protection. They are prime responsible for all laboratory activities and in addition for all final dry-dock inspections and evaluation of obtained results.

The overall objective of this TBT-free Anti Fouling paint test programme is to perform testing and establish documentation on performance of last generation tin-free Anti Fouling paint systems, based on application of test patches on ships in normal operation. Ship owners participate by offering test ships and arrange for test areas. The composition of test ships should be sufficiently broad to reflect operational conditions for the world fleet both regarding trades, trading waters, speed, activity levels, docking intervals etc, and also most demanding operational conditions for Anti Fouling systems to be covered. All major suppliers of Anti Fouling paint systems participate with their last generation products, designed for the actual ship and trade.

Test patches have been applied on a total of sixteen test ships. Of these, fourteen ships have patches of last generation self-polishing (SP) Anti Fouling systems and the last two have patches with biocide-free paint systems. Six paint suppliers are participating with their products in the project. The SP products all utilize copper-oxide as biocide, but in other respects the composition and properties between them are quite different compared to the existing TBT based technologies, which are fairly common in formulation. The biocide-free products are all based on silicone technology.

By November 2003 the programme has been running for in excess of three years, and during the last 18 months there are performed intermediate sub-sea inspections of five test ships, and eight test ships with the shortest docking intervals, up to 30 months, have passed final dry-dock inspection.

MECHANICAL CLEANING OF PLEASURE BOATS: A VIABLE ALTERNATIVE TO BIOCIDAL ANTIFOULINGS?

J C Overbeke, G M Ferrari and P R Willemsen, TNO Industrial Technology, Antifouling and Corrosion, The Netherlands

There is increasing legislative pressure in The Netherlands on the use of copper and other biocide containing antifoulings on pleasure boats. One of the alternatives considered by authorities, boat owners and researchers is mechanical hull cleaning through brushing. Three demonstration projects were conducted by TNO between 1998 and 2003 to assess the feasibility of this approach.

The conventional antifouling system present on the hulls was removed from a total number of 120 pleasure crafts. The boats were re-coated with either a biocide-free hard topcoat (epoxy and 1-component) or a silicone based fouling-release coating. Fouling rate and composition on these non-toxic coatings was monitored during the project. The boats were periodically cleaned throughout the project and the following cleaning methods were compared: manual cleaning, high-pressure water jetting and automatic brushing using two different boat washers.

The tested boat washers were able to clean pleasure boats, but the efficacy was limited. A cleaning frequency of once a month in marine environments is necessary during the fouling season. In fresh water environments, were the fouling pressure is limited, mechanical cleaning is a suitable alternative to antifoulings. The silicone coatings did not fully withstand the abrasion forces resulting from the automatic boat washers. Discharge of removed biomass and organic sludge at cleaning sites was assessed and found to be a minor problem.

The overall conclusion is that mechanical hull cleaning potentially is a viable option for pleasure boats, but that there are still a number of technical limitations to be overcome. Logistics of boat washing in marinas is of critical importance to the public acceptance of boat cleaning.

THE ANTIFOULING PERFORMANCE OF BIOCIDE FREE SILICONE FOULING RELEASE COATINGS APPLIED TO A 6.4 METER POWER BOAT

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C Darkangelo-Wood, Judith Stein and Kathryn Truby, GE Corporate Research and Development, USA

This paper discusses the performance of a 6.4 meter power boat that was coated with the General Electric RTV11 + 10% DMSC15 oil Duplex fouling release coating in June of 1998. The boat has been monitored for biofouling, barnacle adhesion strength, hydrodynamic self cleaning and powering efficiency. It was found that during periods of low usage, the hull became fouled by both hard and soft organisms. The initial power trials demonstrated that a high percentage of the fouling fell away at high speed (24 knots) and that drag penalties were small. Barnacle adhesion strength measurements showed that there was a decrease in the fouling release properties with time and this was reflected by a reduction in performance as measured by subsequent power trials. The reduction in fouling release performance led to recoating the boat with a different formulation (RTV11 + 10% SF1147 fluid) in August 2001. This system has continued to perform well and the physical condition of the coating has remained good with no blistering, delamination or peeling.

STREAM 1 – SESSION: ALIENS AND INTRODUCTIONS SESSION CHAIR: BOB FLETCHER

CHARACTERISATION AND MANAGEMENT OF BIOFOULING IN SHIPS OF THE ROYAL AUSTRALIAN NAVY

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J A Lewis and L Montelli, Defence Science and Technology Organisation, Australia

B Wykes, Defence Corporate Services and Infrastructure Group, Australia

The Royal Australian Navy (RAN) has initiated a suite of pro-active measures to identify and evaluate operational and marine species invasion risks via the biofouling vector and to develop a set of risk reduction and response measures aimed at combating marine biofouling.

The RAN has a fleet of over 50 ships and submarines operating predominantly around Australia, the South-West Pacific, South and East Asia, and in the Gulf. Underwater hull surfaces are protected by new technology anti-fouling coatings, but biofouling continues to occur within internal seawater systems and in unpainted or poorly anti-fouled niches on the external hull. Fouling induced interference with operational capabilities is not uncommon, and can occasion significant degradation of cooling, propulsion, combat and fire fighting systems. Biofouling also poses the risk of transferring potentially harmful and unwanted non-native species among Australian and overseas ports visited by RAN vessels.

This paper outlines the particular fouling characteristics of naval vessels and presents results from recent baseline hull fouling surveys of around 25 RAN ships and submarines. The results have allowed specific vulnerabilities in ship design, construction and maintenance to be identified, as well as relationships between hull fouling assemblage characteristics and vessel operating profiles. Response measures undertaken by the RAN for two frigates returning to Australia from the Middle East with suspected pest mussel fouling are also described.

STREAM 2 – SESSION: MICROFOULING SESSION CHAIR: PETER STEINBERG

BIOFILM DISPERSAL DURING BACTERIAL COMPETITION

L Yan, A Wobker and J Grant Burgess, Heriot-Watt University, UK

The development of microbial biofilms is an important step in corrosion and fouling of marine structures. Much attention has been directed towards the inhibition of biofilms and we are also developing strategies to prevent biofilm growth and encourage biofilm dispersal. We have studied the ability of bacteria to disrupt biofilms produced by other species. To do this, biofilms of *Bacillus licheniformis* were grown in an Air-Membrane Surface (AMS) bioreactor (1); and a *Microccocus sp.* biofilm was grown in a roller slide bioreactor (RSB) (2). Chemicals released by the *B. licheniformis* biofilm led to the complete dispersal of the established *Micrococcus* biofilm, and this was not due to antimicrobial compounds or surfactants to which the micrococci are susceptible. Preliminary studies showed that this dispersal only occurred when the *Micrococcus* cells were viable, suggesting an active, inducible and physiologically mediated process. This is the first report of bacterial compounds that can elicit the active dispersal of biofilms established by other species of bacteria. Thus aquatic bacteria appear to have evolved mechanisms to disperse biofilms of other competing bacteria. These biofilm dispersing compounds are being chemically characterised.

STREAM 2 – SESSION: MICROFOULING & PROKARAYOTE-EUKARYOTE

SIGNALLING

SESSION CHAIR: MAUREEN CALLOW

HOST PLANT VS. BIOFILM DERIVED SETTLEMENT CUES; A TALE OF TWO URCHINS.

P Steinberg, R Swanson, M Watson and N Kumar University of New South Wales, Australia R de Nys, James Cook University, Australia J Williamson, Macquarie University, Australia

Cues for selective settlement are critical for understanding colonisation of surfaces by marine invertebrate larvae, in the context of both applied systems and the dynamics of natural ecosystems. Two important sources of cues in natural systems are marine eukaryotes and the ubiquitous bacterial biofilms which coat most surfaces in the sea. Here we compare the response of larvae from two sea urchins (echinoids) to algal and biofilm derived cues. Larvae of the specialised urchin *Holopneustes pupurascens* exhibit strong settlement preferences among different potential host algae, and metamorphose rapidly in response to histamine, which is present in high quantities in *Delisea pulchra*, the main juvenile host plant for this species. In contrast, larvae of the generalist urchin *Heliocidaris erythrogramma* show much less preference for individual host species, but require a biofilm for normal rates of metamorphosis. When isolated and cultured as laboratory biofilms, a wide range of bacterial strains induce high rates of metamorphosis in this species, suggesting that this urchin responds generally to biofilms in the environment rather than to a few, specific strains of bacteria. This difference in the response of habitat specialists vs. generalists to host plant vs. biofilm derived cues is consistent with the model proposed by Steinberg et al. (2001), and has implications for our view of the mostly generalist biofouling fauna and flora which colonise artificial surfaces worldwide.

CULTURABLE MARINE BACTERIA CONCERNED IN BIOFILM FORMATION

K K Kwon, Y K Lee, K H Cho, S J Lee and H K Lee, Marine Microbial Diversity Lab., Korea Ocean Research & Development Institute, Korea

The formation of biofilm in marine environments is starting point of biofouling and/or biocorrosion. However there was not enough information about the bacteria concerned in early phase of biofilm formation and its control in marine environments. To procure standard bacterial strains for biofilm studies, we isolated bacteria from early phase of biofilm and characterized their properties related with biofilm formation. Acrylic surfaces were emerged for 3 days in near shore seawater at five areas of Korean Peninsula. Bacterial isolates were obtained using ZoBell 2216e agar medium. Based on morphological characteristics, 76 strains were selected and partial sequences of 16S rDNA (300 to 500 bps) were analyzed. Attachment properties on polystyrene surface according to Loo et al. (2002) and cell surface hydrophobicity by BATH method were analyzed. The isolates could be assigned to 26 known genera which have been reported as widespread in marine environment. Approximately 35% of the isolates had been reported previously as uncultured or unidentified in GenBank database. Properties related to biofilm formation of each strain will be described.

STREAM 2 – SESSION: NATURAL PRODUCTS SESSION CHAIR: PETER STEINBERG

SCREENING FOR MARINE NATURAL PRODUCTS AS ANTIFOULANTS IN BRAZILIAN MARINE ORGANISMS

R C Pereira, B A P da Gama, V L Teixeira and B G Fleury, Universidade Federal Fluminense, Brazil R Coutinho, Instituto de Estudos do Mar Almirante Paulo Moreira, Brazil

The worldwide ban of organotin-containing paints is now prompting the quest for safe and effective alternatives. New tin-free paints are arising, combining the known effects of copper with other biocides of unknown toxicity and environmental effects. However, there is serious concern over the effect of heavy metal compounds on the marine environment and less toxic substances than these organometallic chemicals are urgently required. One promising alternative is the development of antifouling coatings whose active components are naturally occurring compounds from marine organisms. As part of a research aimed at the discovery of new metabolites active as antifouling agents from organisms of the Brazilian littoral, natural concentrations of extracts of several species of seaweeds and marine invertebrates are being tested in the laboratory through the "mussel test" and in the field through the "phytagel method". More than 50 extracts, fractions and/or pure compounds from seaweeds and 20 from marine invertebrates have been tested to date. In general, our findings suggest that effective antifouling chemical defenses are not as widely spread as previously thought. The 'mussel test' used in the laboratory seems to be a reliable time and cost-saving screening method for antifouling substances, but field assays comprise a more sensitive method to detect broad spectrum activity. To date, we found that some seaweeds produce secondary metabolites with a broad spectrum antifouling activity, i.e., compounds which are effective against the settlement of many fouling species. On the other hand, invertebrates seem to produce narrow spectrum antifoulants, effective only against a specific organism. Probably the use of synthetic analogues of marine natural products will be the alternative to obtain new safe and effective antifoulants. In other words, the determination of natural chemical antifouling mechanisms and substances will constitute a basis to apply marine natural products or derived chemicals into antifouling paints, with possibly less or no negative effects on the marine environment.

SEASONAL VARIATION IN ANTIFOULING ACTIVITY OF CRUDE EXTRACTS OF THE BROWN ALGA, *BIFURCARIA BIFURCARTA* (CYSTOSEIRACEAE), AGAINST BARNACLE (*BALANUS AMPHITRITE*) CYPRIDS AND MARINE BACTERIA (*HALOMONAS MARINA* AND *PSEUDOALTEROMONAS HALOPLANKTIS*).

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A Ortalo-Magne

In previous studies, it was demonstrated that macroalgae from Brittany contain products with antifouling activity against marine bacteria, fungi, diatoms, seaweeds and mussels. Little is known regarding the ecological function of these compounds and insufficient attention has been paid to evaluating the possible temporal variation in antifouling activity. Studies of chemical defences in terrestrial and marine organisms suggest that organisms vary widely in the production of chemical defences associated with physical (temperature, light) and biological (e.g. grazing pressure) factors, season and geographical location. The present study aimed to investigate the antifouling activity of crude extracts of the brown alga, *Bifurcaria bifurcata*, collected monthly, against 2 marine bacteria, *Halomonas marina* and *Pseudoalteromonas haloplanktis*, and the the barnacle, *Balanus amphitrite*. The toxicity of extracts was determined with a *B. amphitrite* nauplius assay.

The antimicrobial activity of the extracts were found to be subject to seasonal variation, with the highest level of antifouling activity recorded from samples collected between April and September. No activity against H. marina was observed in samples collected between October and January. Intermediate levels of inhibition (minimum effective concentration [MEC] >50 μ g/ml) were recorded for samples collected in February, March and September. High level of toxicity were noted (MEC <50 μ g/ml) for samples harvested from to August with the lowest MEC (12.2 μ g/ml) recorded for the June sample. All samples tested on P. haloplanktis were inhibitory with MECs <100 μ g/ml. Medium values (MEC >50 μ g/ml) were recorded for samples collected from October to February. High activity (MEC <50 μ g/ml) was recorded for samples harvested between March and September. Samples collected from May, to July showed particularly high MECs (<10 μ g/ml).

Results of the anti-settlement experiments showed that the extracts (when tested from 0 to $100 \,\mu\text{g/ml}$) could be divided into three groups on the basis of their MECs: (1) Extracts collected from September to March reduced settlement at non-toxic concentrations (50 to $100 \,\mu\text{g/ml}$); (2) extracts collected from April to July (which were the most active extracts) reduced settlement significantly when tested at >5 $\,\mu\text{g/ml}$ but were toxic at $100 \,\mu\text{g/ml}$; and (3) the extract prepared in August was inhibitory at >25 $\,\mu\text{g/ml}$, but was toxic at $100 \,\mu\text{g/ml}$.

Toxicity tests showed that for samples collected from September to March LC₅₀s were >100 μ g/ml, demonstrating that they were non-toxic to nauplii. In contrast, samples collected from April to August were toxic to nauplii; the more toxic samples being collected in May (LC₅₀ = 55.6 μ g/ml) and in June (LC₅₀ = 38.3 μ g/ml).

These experiments showed that the antifouling activity of extracts reached a peak in summer corresponding to maximal values for water temperature, light intensity and fouling pressure. It remains to be investigated whether this activity has an ecological role in the alga.

STRUCTURE-ACTIVITY RELATIONSHIP STUDIES TOWARD ANTI-BARNACLE ACTIVITY AND BIOORGANIC STUDIES FOR THE ELUCIDATION OF ANTI-FOULING MECHANISM WITH ISOCYANO COMPOUNDS

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Y Nogata and I Sakaguchi, Abiko Research Laboratory, Central Research Institute of Electric Power Industry, Japan E Yoshimura, SERES Inc., Japan

We disclose structure-activity relationship studies toward anti-barnacle activity with various isocyano compounds and bioorganic studies for elucidation of fouling mechanism with fluorescence-labeled isocyano compounds.

In order to apply to a creation of an efficient antifoulant, we have studied on the structure-activity relationships based on antifouling active natural compounds and synthesized compounds in terms of anti-barnacle activity. Various types of isocyao compounds were synthesized and evaluated for their antifouling activity against the larvae of the barnacle Balanus amphirite. The anti-barnacle effect of the synthesized compounds was in the EC_{50} range about $0.01-20\mu gml^{-1}$. And, almost of the compounds showed no significant toxicity in high concentration. Our structure-activity relationships studies suggested that isocyano function would be important for potent anti-barnacle activity.

As a further investigation, the elucidation of the antifouling mechanism was envisaged. We tried to synthesize fluorescence-labeled isocyano compounds which would be able to visualize the working point of antifouling active isocyanides. Several fluorescence-labeled compounds were synthesized and evaluated for their antifouling activity. The bioassay with bioactive fluorescence compounds was observed under fluorescence microscope.

STREAM 2 – SESSION: BIOMETRICS AND SETTLEMENT CUES SESSION CHAIR: TONY CLARE

THE EFFECTS OF TEXTURE AND PHEROMONES ON EXPLORATION AND SETTLEMENT OF CYPRIDS.

G Prendergast, L Hannsen, R Head, V Bers, C Zurn and J Thomason, University of Newcastle, UK

Larvae of fouling species utilise a range of physical and chemical cues to determine where to settle. These experiments aimed to examine the effects of two important cues to barnacle settlement: texture and conspecific pheromones. Two complementary experiments were carried out in the Clyde Sea, West coast of Scotland, during the April settlement season of Semibalanus balanoides. Textured surfaces (smooth to coarse) were treated with conspecific adult or cyprid settlement factor, Chthalamus montaguii settlement factor, or left untreated, in a split plot design. Cyprid settlement was assessed after one tidal immersion; this was repeated three times. In total we analysed the settlement of over 20,000 larvae. Similarly treated tiles were immersed and filmed using a remotely controlled underwater video camera and the number of explorers and their behaviour were quantified. The settlement results were interpreted in the context of the analysis of the exploratory behaviour.

INTERSPECIFIC DIFFERENCES IN THE ANTIFOULING PERFORMANCE OF MYTILID MICROTOPOGRAPHIES

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L Hansson, Danish Institute for Fisheries Research, Denmark

R M Head, Materials Technology Division, TNO Industry, The Netherlands

G S Prendergast, J C Thomason and C Zürn, University of Newcastle upon Tyne, UK

Previous studies have shown that the surface microtopographies of Mytilus edulis and M. galloprovincialis reduce fouling of Balanus improvisus and B. amphitrite (Bers & Wahl in press, Scardino et al. 2003).

The aim of this study was to investigate whether the microtopographies of mytilid species from different regions differ in their repellency when exposed to identical fouling pressure by barnacle cyprids. To distinguish microtopography effects from other potential antifouling properties of the shell, replicas of individual valves of mytilids from the UK, Germany, Brazil and Russia were made using high resolution epoxy resin. Positive controls were roughened using sandpaper, and negative controls were smoothed by an additional layer of resin. Resin replicas and controls were exposed in situ at Millport, Isle of Cumbrae, Scotland, in April 2003. Settlement of the acorn barnacle Semibalanus balanoides on the resin casts was recorded. The results illustrate how different microtopographies perform differently with regard to fouling by S. balanoides.

Bers AV & Wahl M (2003) The influence of natural surface microtopographies on fouling. Biofouling in press

Scardino A, de Nys R, Ison O, O'Connor W, Steinberg PD (2003) Microtopography and antifouling properties of shell surface of the bivalve molluscs Mytilus galloprovinvialis and Pinctata imbricata. Biofouling 19 (Supplement): 221-230.

MOLECULAR CHARACTERIZATION OF THE SETTLEMENT INDUCING PROTEIN COMPLEX (SIPC) IN BALANUS AMPHITRITE

C Dreanno, and A S Clare, School of Marine Science and Technology, University of Newcastle, UK R R Kirby and S Hawkins, Marine Biological Association of the United Kingdom, UK K Matsumura, Himeji Kisho Co Ltd, Japan

Understanding the chemical basis of barnacle gregariousness has been a focus of ecological research over the last 50 years. We have previously identified a glycoprotein termed Settlement Inducing Protein Complex (SIPC), which is involved in the conspecific settlement in *Balanus amphitrite*. In the present study, we describe the molecular structure of SIPC and the isolation of a cDNA clone that contains the entire coding region. The quaternary structure of the SIPC was examined by native and SDS/Page electrophoresis using various conditions of reduction. The SIPC disulfide bridge pattern was proposed by comparison of specific conserved cysteine residues between SIPC and the alpha 2 macroglobulin (A2M) to predict the SIPC molecular arrangement. Enzymatic deglycosylation by N-glycosidase F and H demonstrated that SIPC is a glycoprotein. The SIPC sequence was determined by cloning and sequencing of overlapping polymerase chain reaction (PCR) and rapid amplification of cDNA ends PCR products. The cDNA sequence is 4,693 bp long and contains one open reading frame coding for a protein precursor composed of 1,548 amino-acid residues, including a 17-residue signal sequence. The phylogeny analysis revealed that SIPC is closely related to the thiol-ester protein family and shares the highest homology with the tick A2M (31%) and the horseshoe crab A2M (29%). The northern hybridization with an homologue cDNA probe detected a single 5.2 kb polyadenylated sense RNA.

EPITAONDIOL, A NEW ATTACHMENT INDUCER FROM THE BROWN ALGA STYPOPODIUM ZONALE (DICTYOTACEAE)

A R Soares, A P da Cunha, V L Teixeira, R C Pereira and B A P da Gama, Universidade Federal Fluminense, Brazil

Most marine invertebrates undergo planktonic larval stages prior to settlement and metamorphosis into adult forms. Both larval settlement and metamorphosis are often induced by exogenous species-specific chemical and physical cues, which are believed to originate from a variety of sources, including algae, conspecifics, microbial films or even a suitable food source. In response to the aquaculture challenge of producing constant numbers of juveniles of cultured species, natural inducers have been screened in the laboratory for their ability to induce larval settlement and metamorphosis. Stypopodium zonale (Lamouroux) Papenfuss is a brown alga abundantly found along the Brazilian coast, and is chemically characterized by the production of diterpenes of mixed biosynthesis (meroditerpenes). The thalli of this seaweed are frequently found covered by fouling organisms, and preliminary assays using the crude extract of S. zonale showed significantly stimulated settlement. The goal of this work was to isolate the secondary metabolites responsible for this activity. S. zonale was collected at Praia Rasa, Armação de Búzios, Rio de Janeiro State. The specimens were air dried at room temperature and submitted to exhaustive extraction in dichloromethane. The bioassay-guided fractionation of the organic extract was performed using the attachment of juveniles of a common fouling mussel, Perna perna, as a model. The extract was chromatographed over silica gel with a gradient from nhexane to EtOAc. The active fractions were rechromatographed to yield an active compound that was purified by crystallization. The active metabolite was identified as the meroditerpenoid epitaondiol (1) by comparison of IR, UV, NMR and mass spectral data with previously reported data. Very few chemical inducers of settlement and methamorphosis of marine invertebrates have been identified, and even less of these were secondary metabolites.

IN VITRO EVIDENCE FOR THE INFLUENCE OF EXUDATES FROM MACROORGANISMS ON RECRUITMENT DYNAMICS IN WESTERN BALTIC BENTHIC ASSEMBLAGES

M Lenz, M Heede and M Wahl, Institute of Marine Research, University of Kiel, Germany

The observation that the composition of benthic assemblages on similar substrates seem to differ among microhabitats, e.g. blue mussel beds or eelgrass communities, suggested that recruitment dynamics are influenced by secondary metabolites, that are exudated by these macroorganisms. To test this assumption, water samples from 5 different but adjacent microhabitats were sterile filtered (0.8 µm) and incubated with natural plankton communities for 72 hours. Settlement rates of three predominant larvae species, the barnacle *Balanus improvisus*, the periwinkle *Littorina littorea* and the blue mussel *Mytilus edulis*, were recorded and compared to settlement rates in control assays, that contained filtered seawater from the water column above a sandy patch within the same location. Water samples were tested biweekly from April to September 2002.

At least at 6 of the 8 sampling dates, settlement densities of all larvae species were lower in microhabitat water samples than in the control assays. Settlement of barnacle larvae was significantly reduced at one or more sampling dates by exudates from the red alga Ceramium strictum, the green alga Enteromorpha sp., the brown alga Fucus vesiculosus and the eelgrass Zostera marina. Settlement oft M. edulis post-larvae and of larvae of L. littorina were significantly reduced at two or more sampling dates by exudates from Enteromorpha sp., F. vesiculosus, Z. marina and M. edulis. These results support the assumption, that as yet unidentified secondary metabolites derived from dominant macroorganisms are substantially contributing to the generation of small-scale recruitment patterns in Western Baltic benthic communities.

WEDNESDAY 28TH JULY 2004

PLENARY PRESENTATION

BIOFOULING, ANTIFOULING, AND THE ENVIRONMENT: WHERE BIOLOGY AND CHEMISTRY COLLIDE.

J A. Lewis, Maritime Platforms Division, Defence Science and Technology Organisation, Australia

The degradation of ship performance by marine biofouling has motivated seafarers across the centuries to seek antifouling solutions to try and keep their vessel hulls fouling free. Biocidal antifouling coatings have proven to be the most effective means of biofouling control, and coatings such as the organotin self-polishing copolymers could provide effective antifouling protection for 5 or more years. However, antifouling effectiveness has generally equated with biological toxicity, and one of the challenges to the antifouling technologist has been to find biocides that are toxic at the paint surface, but benign once in the water column. Environmental concerns have led to many effective antifoulants being deemed unacceptable, the most recent and well known the IMO action to globally ban organotin antifouling biocides under the International Convention on the Control of Harmful Anti-Fouling Systems on Ships, 2001. Alternative antifouling biocides continue to be under close scrutiny, and there is a strong push towards non-toxic solutions.

However, ship performance and maintenance is not the only impact of biofouling, and ships are now recognised to have facilitated the spread of many marine species around the globe, some with serious economic and ecological consequences. Regulation of one vector, ships' ballast water, is planned under a new IMO convention drafted for consideration in 2004, but fouling is considered to be as important a vector for species translocations. Consideration is therefore needed of both chemical and biological impacts of changing antifouling technologies, be they antifouling coatings, pipework treatment systems, or hull husbandry practices.

STREAM 1 – SESSION: ENVIRONMENTAL AND LEGAL REQUIREMENTS SESSION CHAIR: JULIAN HUNTER

ENVIRONMENTAL RISK ASSESSMENT – AN ESSENTIAL PART OF REGULATORY DECISION MAKING

J Chadwick, Health and Safety Executive (HSE), UK.

Not all chemicals are designed to be toxic to living organisms. There are probably in excess of 100,000 general chemicals on the market worldwide, and the Chemicals White Paper has identified 30,000 that are in need of testing for their hazard and risks to people and the environment. The indicative List of existing non-agricultural pesticide actives stands at a mere 2000 only about half of which have received ultimate support for Annex 1 authorisation and notified to the authorities. However, these actives are specifically designed to be toxic to natural organisms in some 23 product types. It is likely that a significant element in the decline of biodiversity and the loss of individual species is due to the introduction of these chemicals into the environment. Antifouling products represent a specific group (Product type 21 under the Biocides Products Directive (BPD) which have their own associated environmental problems. Also In the past a chemical used in antifouling products have caused massive population declines in predatory molluscs and disastrous declines in commercial fisheries until legislation came into force. The chemical Tri butyl Tin, which is now being, phased out internationally has caused molluscs to permanently change sex and had a catastrophic effects on oyster fisheries in the 1970s. Without international legislation and more importantly the power to enforce it, the unchecked release of chemical Biocides into the environment can have serious environmental consequences. The UK. Has recognised this and since the late 1980's has embarked on a major national review programme for all antifouling products registered in the UK. We started with the reviews of TBTO and Copper, which have now been almost brought, up to date with the reviews of all remaining booster biocides. An update on the progress of this and details of our revised risk assessment strategy is given in a second presentation.

The UK risk assessment strategy developed for the booster biocides review used both measured and predicted environmental concentration (MEC and PEC) alongside predicted no effect data (PNEC) and applied the standard risk quotient approach (MEC:PNEC and/or PEC:PNEC). The successful development and validation of the Regulatory Environmental Modelling of Antifoulants (REMA) was an example of what can be achieved by collaboration between government departments. The UK regulatory authority is also very grateful for the technical input freely given by the industry on the REMA project. The risk assessment strategy developed by the UK concentrated on the impact from leisure crafts used in and around coastal estuaries. The main areas for concern were identified as coastal estuaries, and where boats were pontooned within an estuary. It was agreed, that enclosed or locked marinas (which are often manmade) were not a cause for concern provided the immediate estuary surrounding such sites did not suffer harm from the release of the elevated levels of biocides as a consequence of flushing. Elevated levels of biocides in enclosed freshwater sites would be a cause for concern. However, at the initial review in 2000 information to address this environment was not available but usage data for enclosed freshwater systems has since been considered by the UK and proposals for monitoring this environment are presently being considered by the relevant authority. Unfortunately to date no resolution has been obtained on this work and earlier initiatives for HSE to develop a risk model for aquaculture is very unlikely to be completed by HSE.

The UK reviews were carried out under our national regulations covered by the Food and Environmental Protection Act 1985 and enshrined under the enabling parliamentary Statutory Instrument 'The Control of Pesticides Regulations 1986 'These regulations are now being superseded by the BPD. However, as we have seen from our review programme very toxic chemicals can be used without serious risk to the environment. Hazardous chemicals if used under restricted conditions can bring about very real financial and environmental benefits. Regulatory environmental risk assessment employs a balanced view looking at the hazards of chemicals in the light of possible exposure routes while also considering the costs and benefits of their use. This paper describes the multi-disciplinarian tiered approach to hazard and risk assessment under the UK national regulatory scheme and how this compares to the approach adopted by the EU for Biocide products. Antifouling products Europe has developed technical guidance to estimate environmental exposure from the use of Biocides and this paper compares how we have done things at a national level and how we see things changing under BPD.

The OECD with Haskoning has recently been developing an OECD emission scenario document for antifouling products (due for completion by July 2004) The strict interpretation of this will have far reaching ramifications and strict interpretation of BPD data requirements and technical guidance may effect the authorisation of antifouling products at a national and international and may effect the future of antifouling products in a world market.

ENVIRONMENTAL EMISSION SCENARIOS FOR ANTIFOULING PAINTS – AN OECD PROJECT WITH RAMIFICATIONS FOR COUNTRIES REGULATING ANTIFOULING PRODUCTS

E van der Aa, Royal Haskoning, The Netherlands

The OECD has recently published the first Environmental Emission Scenario Document (ESD) on wood preservatives under its biocides programme. The Biocide Steering Group chose antifouling products as the second biocidal product type for which an ESD is to be produced. The aim of the project is to produce an ESD for active ingredients used in antifouling products that is harmonised and applicable in all EU Member States and non-EU OECD Member countries. Production of the ESD will result from adaptation and harmonisation of existing scenarios or models or, if necessary, development of new ones. This work is done in close co-operation with similar work being done in the European Union to develop ESDs for use under the regulatory scheme of the Biocidal Products Directive (EC/98/8). The actual work of producing the ESD is done by a consortium of two consultants: Royal Haskoning and the Institute of Public Health and the Environment (RIVM), both from the Netherlands. Their work is overseen by a Steering Group composed of regulators from Australia, Canada, Finland, France, Germany, the Netherlands, Switzerland, the UK, the USA, and the European Commission together with industry representatives (CEPE and ACC). The work is financed by the European Commission. The ESD is planned to be discussed and agreed with the appropriate bodies in the OECD and approved by the European Commission. The Steering Group has it's last meeting in Ispra in February 2004.

The content of the ESD produced will be presented. Elements of this presentation are: purpose of an ESD (realistic worst-case approach), scope of the ESD for antifouling products (application, use phase and removal), scenario development: where is scenario development considered necessary and where were scenarios developed, presentation of scenarios developed within the project, testing of scenarios. Use of these scenarios - especially within the EU relating to the BPD - will be discussed.

MEASURING BIOCIDE RELEASE RATES FROM ANTIFOULING COATINGS – WORK OF THE ISO/ASTM COMMITTEES

A Finnie, Chairman ISO Working Group on Biocide Release Rates from anti-fouling coatings

Biocide release rate data is increasingly used by regulatory authorities in environmental risk assessments as part of the antifouling product registration process. In response to this, internationally recognised standard methods for quantifying biocide release rates from antifouling coatings are being developed by ISO and ASTM in order to meet the needs of the coatings industry.

Methods have previously been published for copper and organotin, and the relevant ISO and ASTM committees are currently working together to develop methods for a number of organic booster biocides. Specifically, these are dichlofluanid, tolylfluanid, zineb, and pyridine triphenylborane (ISO), and dichloro-octylisothiazolone, zinc pyridinethione, copper pyridinethione and cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine (ASTM). To-date, all of these procedures are based on the standard "rotating cylinder method". This method was originally developed as a cost-effective and practical means of characterising biocide release rates in the laboratory, rather than providing reliable estimates of environmental inputs. Several investigations have since highlighted some important limitations of this method – in particular that the reproducibility of the method is relatively poor, and that results are generally significantly higher than direct measurements of true environmental inputs from the same coating. Future method development should therefore be directed towards improved alternative methods which are better able to provide reliable estimates of true environmental inputs, but which are also practical and cost-effective.

CHOOSING ANTIFOULINGS FOR MINIMAL ENVIRONMENTAL IMPACT – A SHIP OWNERS PERSPECTIVE

C Nygren, Wallenius Lines, Sweden

Due to the strict environmental policy within Wallenius Lines and Wallenius Marine, only tin free antifoulings have been applied since 1997. The experiences accumulated on choosing and applying different types of tin-free and biocide-free antifouling will be presented. When choosing an antifouling system the environmental impact needs to be taken into consideration as well as the technical performance. The latest internal antifouling policy will be presented as well as its background.

DEVELOPING GLOBALLY COMPLIANT ANTIFOULINGS

J Hunter, International Coatings Ltd, Akzo Nobel, UK

At present (2004), antifouling paints are regulated under national laws as biocidal products and require registration before sale in USA, Canada, Hong Kong, New Zealand, UK, Sweden, Finland, Malta, Eire, the Netherlands, and Belgium. Although bureaucracy associated with assembly and presentation of application dossiers is different in each case, the principles adopted in evaluation of antifouling products prior to registration follow common aims and themes. The overriding common aim is to ensure products on the market can be applied safely and used with minimum impact on the environment. Risk assessment is the tool by which risk to humans and environment is evaluated, and as methods are evolving a degree of harmonisation of approach is evolving. The OECD Environmental Scenario Document (ESD) will increase the degree of harmonisation in approach. The paper will review evolution in regulation of antifouling paints with reference to provision of compliant and effective products for the future.

RIP TBT – IS COPPER NEXT?

C Mackie, CSI Europe, Copper in anti-foulings Task Force Co-ordinator

The title of this talk may encapsulate the thoughts of some regulators as TBT products are phased out and other active substances come into under the spotlight. However, unlike some other biocides, copper has not just entered the antifouling paint market, it has been used successfully for 100 years as a biocide in antifouling paints. During this time, no adverse environmental effects have ever been proven against copper in the marine environment. This in itself should be a good indication that copper is an excellent antifouling biocide, however, there is a perception that copper can cause harm due to its classification as a "heavy metal" and in addition, to low ecotoxicity values observed by many workers in laboratory ecotoxicity studies using soluble copper salts and clean laboratory waters.

An extensive copper risk assessment programme being conducted in Europe and the US in both fresh and marine waters should hopefully dispel this perception. This presentation will describe some aspects of the risk assessment programme and present an appropriate methodology for evaluating copper in the environment.

COPPER IN THE ENVIRONMENT – A BIOAVAILABILITY/ECOTOXICITY STUDY.

B Jones, Centre for Environment, Fisheries and Aquaculture Science (CEFAS), UK

This study evaluates the possible input of copper from antifouling paints into UK Harbours and Marinas. Copper is a ubiquitous element present in all marine waters, sediment and marine life. Copper occurs in marine waters in many different chemical species including free copper ions, inorganic salts and complexes and organically-bound forms, Free copper + and copper++ ions are the most toxic forms and the toxicity decreases in the order: copper ions Cu+ and Cu++> inorganic copper> organic copper. The approach taken within this study has been to measure the concentrations of Total Dissolved Copper and the Electrochemical Labile Copper (inorganic fraction) with the concentrations of relatively non-toxic Organic Copper derived by subtraction. Three types of boat usage were considered: - Estuarine Harbours, Commercial Harbours and Marinas. At each sampling location three stations were sampled so as to provide a putative concentration gradient away from the likely source of copper. E.g. for a harbour, one sampling station would be in the inner harbour, one in middle of the harbour and one located outside the harbour mouth. Sampling took place in all the four seasons of the year.

The results indicate that, at the sampling times chosen, concentrations of total dissolved copper are generally below the UK environmental quality standard of 5 ug/l at the sites tested. Only one value exceeded this, inside one marina in the autumn 6.68 ug/l. The highest concentrations found were, in general, in marinas with one high concentration found in a commercial harbour. The mean range for total dissolved copper in commercial harbours was 1.0-2.75 ug/l, in estuaries 0.7-1.80 ug/l and marinas 0.98-2.39 ug/l. The mean range for labile copper in commercial harbours was 0.24-0.84, in estuaries 0.12-0.43 ug/l and marinas 0.17-0.65 ug/l. The maximum concentration of labile copper was 2.69 ug/l.

PHOTODEGRADATION OF ZINC AND COPPER PYRITHIONES IN AQUEOUS ENVIRONMENTS

Y Yamaguchi, A Kumakura, M Isshigami, Y Yamada, H Shibata and T Sunda, Marine Pollution Prevention Group, Environment and Energy Department, National Maritime Research Institute, Japan

Zn and Cu Pyrithiones (ZnPT and CuPT) are widely used antifouling booster biocides in TBT-free paints. Photodegradation behaviour of ZnPT or CuPT in the aquatic environment was investigated by ultraviolet-visible spectroscopy. The half lives of them were estimated as 32.3 min. and 59.6 min., respectively, for the natural sunlight during August at 35°40'55" north latitude. The major degradation product was identified as pyridine-2-sulfonic acid based on the spectrum. The decomposition rate constants were determined as a function of intensity of light and temperature, assuming the first order kinetics, based on change in the intensity of spectrum.

COMPUTER MODELLING FOR ENVIRONMENTAL EXPOSURE ASSESSMENT OF ANTIFOULING BIOCIDES

R J Fenn and G Polson, Arch Treatment Products, USA

In order to estimate the impact of exposure to antifouling biocides on non-target organisms in the aqueous environment, a risk assessment is required. In this process the predicted environmental concentration (PEC) of the biocide is compared with its predicted no-effect concentration (PNEC). PEC is most often estimated using environmental exposure modelling software, and PNEC is derived from ecotoxicology studies. The resulting ratio of PEC / PNEC is called the Risk Quotient (RQ)0000000, and in a scenario in which the RQ>1 the biocide is considered to pose a risk.

Of the software available in recent years for estimating PEC for antifoulants, "MAM-PEC", "REMA", "Luttik-Johnson" and "EXAMS" are prominent examples. They differ in their ease of use, in their flexibility, their ability to handle input data, and in the scope of their output data. At the present time, none of these programs fulfils all the requirements for a comprehensive treatment of the variables for the calculation of a realistic PEC for pyrithione biocides. We would like to discuss the major programs available today, focusing on their strengths and weaknesses, and relating our experience on how to utilize the best features of each for modelling of pyrithione antifoulants.

Of equal importance to risk assessment as the use of appropriate computer models, is the use of accurate data. Since the results cannot be any more accurate than the input parameters, nor more valid than the correct application of the output data, we will briefly discuss the importance of some of the key variables involved in antifoulant modelling, and demonstrate the effect of the use of inaccurate and misapplied data on the risk quotient.

THE ENVIRONMENTAL FATE AND EFFECTS OF SELECTED ANTIFOULING PAINT BOOSTER BIOCIDES

K Thomas, Centre for Environment, Fisheries and Aquaculture Science (CEFAS) UK

The International Maritime Organisation (IMO) ban on tributyltin (TBT) as an antifouling paint biocide has raised the profile of the environmental acceptability of alternative organic booster biocides. In this paper we consider work conducted by CEFAS in the UK to establish the occurrence, fate and effects of selected antifouling paint booster biocides in docks, harbours and marinas. Of the eight booster biocides that have been commonly used in the UK, Irgarol 1051 and diuron have been regularly detected in coastal surface water and sediment samples. None of the other biocides targeted have been detected. Laboratory degradation studies showed that Irgarol 1051 and diuron are very stable, whilst other biocides, such as Sea-Nine 211, zinc pyrithione and dichlofluanid rapidly degrade under both aerobic and anaerobic conditions. The persistence of Irgarol 1051 and diuron led to restrictions in their use in antifouling paints being imposed. The affinity of biocides to partition between water and sediment was shown to be an important factor when considering the fate of biocides associated with dredged material. Sea-Nine 211 has the greatest affinity for sediments, but rapidly degrades. Irgarol 1051 has a lower sediment specific equilibrium sorption constant (K_d) and a higher persistence resulting in potentially higher sediment concentrations. Contamination of sediments with antifouling biocides incorporated within paint particles significantly increases their persistence of biocides no matter what their K_d value is. The toxicity of biocides to primary producers is such that low ng l^{-1} concentrations of some biocides can pose a risk to certain micro- and macroalgae species that are important primary producers. Irgarol 1051 was also shown to bioaccumulate in higher marine plants and algae, although Irgarol 1051 exposed to plants in the form of paint particles was not as bioavailable as free dissolved Irgarol 1051. Modelling the input of diuron and Irgarol 1051 following the disposal of dredged material showed that very little diuron enters the sea via this pathway because of its low K_d. Due to Irgarol 1051's higher K_d and anaerobic persistence, the disposal of dredged material can potentially contribute up to 50% of the Irgarol 1051 that enters the sea. The data reported within this paper will be used to assess the overall impact of antifouling paint booster biocides in dredged material.

DETERMINATION OF RESIDUES OF THE BOOSTER BIOCIDE DICHLOFLUANID IN WATER AND MARINE SEDIMENT OF GREEK MARINAS

C Hamwijk, TNO Chemistry Physiological Sciences Department, Zeist, The Netherlands

re in the right.

Dichlofluanid is used as booster biocide in antifouling paints. The presence of dichlofluanid and its metabolite DMSA was monitored in seawater and marine sediment from three Greek marinas, in accordance with the OECD Principles of Good Laboratory Practice. Seawater and sediment samples were collected at three representative positions and one suspected hotspot in each marina and shipped to the laboratory for chemical analysis. As part of the project, an analytical method had been developed and validated. Furthermore, some additional experiments were carried out to investigate the potential influence of possible paint particle bound dichlofluanid.

BIOTESTS AND SELECTED CHEMICAL ANALYSIS OF BIOCIDE FREE ANTIFOULING COATINGS REGARDING TOXIC COMPOUNDS

B Waterman, LimnoMar, Germany

S Sievers and R Dannenburg, Hamburg Department of Environment and Health - Environmental Analysis, Germany

J Overbeke and J Klinstra, TNO Industrial Technology, The Netherlands

O Heemken, GALAB, Geesthacht, Germany

Several types of biocide-free antifouling paints were subjected to bioassays and selected chemical analysis of incorporated and leaching substances. Non-erodable coatings (silicones, fibre coats, epoxies, polyurethane, polyvinyl) and erodable coatings (SPCs, ablative) were tested to exclude the presence of active biocides and dangerous compounds. The paints were subjected to the luminescent bacteria test and the cypris larvae settlement assay, the latter delivering information on toxicity as well as on efficacy.

Chemical analyses of selected compounds of dry-film were performed:

- Leaching-rate of organotin compounds from silicones
- Leaching-rate of nonylphenol and Bisphenol A from epoxy and vinyl based coatings
- Concentration and leaching rate of selected organic compounds in polyurethane
- Concentration of heavy metals erodable coatings

The determination of leaching-rates was performed using glass microslides covered by the paint system. Additionally, microslides covered by TBT-SPCs/sealer/tie coat/ biocide-free top coat were subjected to the measurements of leaching rates of organotin.

The results of the bioassays indicated that none of the submitted paints contained leachable biocides. Nevertheless, some products contained or leached dangerous compounds. The analyses revealed leaching of nonylphenol (up to 74.7 $\text{ng/cm}^2/\text{d}$ after 48 hrs) and Bisphenol A (up to 2.77 $\text{ng/cm}^2/\text{d}$ after 48hrs) from epoxy resins used as substitutes for antifouling paints. The heavy metal zinc was analysed in the dry paint film up to 576,000 ppm in erodible coatings not incorporated as a biocide but to control the erosion rate. Values for TBT in silicone elutriates were mostly below the detection limit of 0.005 mg/kg. Values for DBT ranged from <0.005 – 6.28 mg/kg deriving from catalysts used as curing agents.

Implications to environmental requirements and legislation are discussed

KEY ISSUES IN AUTHORISATION OF ANTIFOULANTS UNDER EU LAWS: THE OUTCOME OF THE REVIEW OF BOOSTER BIOCIDES IN THE UK

J Chadwick, Health and Safety Executive (HSE), UK.

In 2000, the Health and Safety Executive (HSE) finalised a UK review of the Booster Biocide active substances approved for use in antifouling paint products. Previously, HSE has undertaken reviews of products containing TBT and copper, which have been considered by the Advisory Committee on Pesticides in the 1990s. In 1992 the ACP considered that from the data available there did not appear to be a significant concern regarding the impact of copper based paints on the aquatic environment (although there remain some significant areas of uncertainty such as bioavailability), but requested that an assessment of the booster biocides be undertaken as the revocation of TBT on vessels < 25 m could result in an increased use of products containing the active ingredients.

The review initially included 12 booster biocides, which by the time of the environmental review was completed had decreased to only 8 active ingredients; Irgarol 1051, Diuron, TCMTB, Chlorothalonil, Dichlofluanid, Zinc pyrithione, RH-287 and Zineb. The main outcomes of the review were that two boosters were revoked with data requirements being set for the remaining 6. However, manufacturers have only supported 4 booster biocides leaving: Dichlofluanid, RH-287, Zinc pyrithione and Zineb. In addition, there were some outstanding/unresolved issues regarding the use of booster biocide products in enclosed freshwater environments and the additional risks posed by the identified metabolite(s).

The revocations of Irgarol 1051 and diuron were as a result of a fairly comprehensive package of Government sponsored monitoring in UK waters at the time of the review. Usage data gathered as part of a UK Environment Agency (EA) survey informed us that diuron and Irgarol 1051 were the main market leaders at the time (1998/9) with approximately 52 and 32 % of vessels being treated with paints containing these boosters respectively. The risk assessment approach considered the individual monitoring data points (MECs – measured environmental concentrations) against the defined predicted no effect concentrations and used the % of MEC:PNEC values > 1. The decision to revoke these boosters was based on the exceedence of acceptable risk in the estuary and open marina scenarios. This decision was not taken lightly, however faced with the measured values, which were resulting from the current use levels and the fact that post-approval control on usage was not practicable, revocation on environmental grounds was accepted by the Ministerial committee (ACP).

The UK has defined its risk assessments around the booster biocide review, which initially went to the UK advisory committee on pesticides in 2000. The UK specific scenario is centred very much around the leisure craft market, which has the potential to impact on the coastal and inland water bodies due to the sheer number of vessels, which are present in UK waters. Unfortunately our knowledge of shipping is much reduced by comparison, in addition to which the restriction of use in the UK on ships would not prevent incoming ships with the restricted product being applied outside the UK (thereby disadvantaging UK ship yards). However, restriction to use on ships in the UK will occur where worker safety issues cannot be resolved.

The protection goals in the UK are largely dictated by the environmental protection bodies (EA, English Nature, Countryside council for Wales, Scottish Environment Agency and Scottish Natural Heritage) who have advised the HSE on which areas are of concern within the UK, in order to meet requirements set out by conservation legislation the UK is signed up to. These include:

- 1. Freshwater enclosed water bodies such as the lakes where there is significant use by antifouled vessels
- 2. Estuarine including marinas and harbours, which can be closed, open/pontooned or inlet. The main protection goal for the UK is the open/pontooned moorings within UK estuaries, which can serve as refuge for developing fish and invertebrates.
- 3. Marine Coastal (shallow shelf-line)
 - Open sea (difficult)

It has been assumed that the estuarine situation is worst-case and provided the risk assessment is acceptable it is likely that in other areas where the density of vessels becomes reduced, will have greater dilution and be less of a concern. However, monitoring in areas where usage levels are high remains desirable for confirmation of this assumption particularly with persistent or metal compounds due to the potential accumulation from estuarine inputs.

For the booster biocides there were no monitoring data were available, predicted environmental concentrations (PECs) were required. These were calculated using the REMA model (Regulatory Environmental Modelling of Antifoulants),

which requires inputs of basic chemical properties, usage data and leaching rate inputs for the individual antifouling products. The leaching rate has been shown to be a key parameter for the calculation of environmental concentrations during the validation of REMA. In particular the use of the ASTM/ISO study endpoints caused REMA to significantly over-predict the environmental concentrations of Irgarol 1051 and diuron. The reasons for this over-prediction was largely due to the REMA model being a steady-state system (taking no account of potential reductions over time) and the available laboratory method being more indicative of the leaching rate from a freshly painted surface. Therefore, the validation was repeated using a simple calculation assuming that all the active substance was lossed from the surface within the in-service lifetime. In addition, a similar exercise was undertaken using a long-term leaching rate endpoint (90 days) gathered for Irgarol 1051 and a standard leaching rate for diuron (30 days), both obtained using a modified method devised as part of a HSE funded research program (flume method). Both these approaches gave excellent validation reducing the predicted concentrations to within a factor of 1.5 – 7 of the measured data.

As a result of the experience gained from the validation exercise and the lack of progression of standard leaching rate methodology that HSE has considered the use of the calculation approach, devised by the EU paint manufacturers group CEPE. The CEPE model is frequently used by manufacturers in support of their products, but to date HSE has not received any validation of the underlying assumptions and until these are proven with supporting data – this approach will continue to be treated with caution.

In 2004, the ACP has considered the data submitted to support the post-review data requirements for booster biocides and agreed that no further regulatory action should taken under national regulations. However, the ACP has supported the request for further data requirements to be submitted with the product review and/or reregistration under the Biocidal Products Regulations. This approach allows manufacturers time and flexibility to address the remaining issues, but that without this information products simply would not be reregistered in the UK.

STREAM 2– SESSION: FLOW EFFECTS AND SURFACE INTERACTIONS SESSION CHAIR: ROBERT WOOD

THE EFFECT OF BIOFOULING ON FRICTIONAL DRAG AND TURBULENT BOUNDARY LAYER STRUCTURE

M P. Schultz, United States Naval Academy, Naval Architecture & Ocean Engineering Department, USA

The increase in frictional resistance that results from ship hull fouling is well established. However, few data are available to compare the hydrodynamic performance of modern antifouling coating systems. Results of an experimental towing tank study measuring the frictional resistance of both biocide-based and fouling-release coatings are discussed. The results show little difference in frictional resistance among the coating types in the unfouled condition, ignificant differences are observed among the coatings in the fouled condition, with the fouling-release surfaces showing the largest increase in frictional resistance. Subsequent cleaning returns the resistance of most of the coatings to near their unfouled level. Characterization of coating roughness is then discussed and used to relate these laboratory results to performance penalties of the coatings at ship-scale. Finally, results of detailed velocity measurements in turbulent boundary layers developing over fouling using laser Doppler velocimetry are presented and the ensuing changes in the boundary layer structure discussed.

FLOW, DEPTH AND FOULING: THE EFFECTS OF LOCAL HYDRODYNAMICS ON SETTLEMENT OF MARINE ORGANISMS

T M Sin and S LM Teo, National University of Singapore, Singapore D Rittschof, Duke University Marine Laboratory, USA

Variation in larval settlement and recruitment has longer-term implications for the structure of developing epifaunal assemblages. While the influence of hydrodynamics on settlement and recruitment has been extensively examined at larger spatial scales, very little information exists on the effects of small-scale hydrodynamics operating the scale of centimetres. While physicochemical features control the deposition of passive particles, cyprids have well-documented behavioural responses to shear forces. We utilised cylinders of varying sizes (0.8 cm, 1 cm, 5 cm, 10 cm and 30 cm) to examine the effects of complex natural flows on the capture of passive particles and settlement of barnacle cyprids at Beaufort, North Carolina and Singapore. Specifically, we examined the variation in fouling of surfaces by particulates and barnacles with respect to depth in different current flows, turbulence and wave action generated shear forces. Although the results differed at the sites, some generalities emerged. Patterns of barnacle settlement around cylinders were consistently different from that of particulate fouling. Cylinder size had significant, but complex effects on the patterns of barnacle settlement along the surface of the cylinders at any depth. The data suggest that each size of cylinder in flow set up specific small-scale hydrodynamic features that cyprids responded to. The two-way interaction between depth and facing was also found to have significant effects on barnacle settlement. Patterns of settlement around the surface of cylinders varied with depth, and these appeared to be independent of cylinder size.

The results demonstrate that barnacle cyprids responded to small-scale hydrodynamic features at low Reynolds numbers below the theoretical minimum for separation. This study has provided evidence for the importance of small-scale flow (cms) on the settlement responses of active larvae, and has implications for models of settlement of active larvae in 3-dimensional flow

FLOW EFFECTS ON CORROSION OF STAINLESS STEELS

A Neville and X Hu, University of Leeds, UK

The corrosion behaviour of stainless steels in marine environments is dependent on the passive film remaining intact and offering resistance to charge transfer. The nature of the passive film is known to depend on the alloying additions, in particular Cr, Mo and N.

The disruption of the passive film due to the effects of a flowing liquid, free from or containing solids, can cause accentuation of corrosion. The ability of the stainless steel to then perform depends on a number of factors such as the rate of depassivation, the charge transfer during depassivation and the rate of repassivation.

In this paper results from a study covering aspects of flow-induced corrosion and erosion-corrosion of high alloy (UNS S32654, UNS S31254 and UNS S32750) and standard grade stainless steels (UNS S31603) will be reported. The paper will demonstrate that alloying additions, specifically intended for enhancing localised corrosion resistance, will offer benefits in terms of corrosion resistance under flow-induced and erosion-corrosion conditions.

The APPLICATION OF ROTATING CYLINDER ELECTRODES TO MARINE CORROSION MONITORING

F Walsh and G Kear, University of Southampton, UK K Stokes, DSTL Porton Down, UK.

D Barker, University of Portsmouth, UK

A number of electrode geometries have been widely used to simulate electrochemical corrosion of marine alloys under well defined flow conditions. The most popular of these 'hydrodynamic electrodes' are channel flow electrodes, pipe flow electrodes, rotating disc electrodes (RDEs) and rotating cylinder electrodes (RCEs).

The RCE has progressively developed since quantitative measurements of mass transport to smooth electrodes in turbulent flow were made in the early 1950s. The inner RCE in a concentric flow field has a number of key characteristics: (a) it normally experiences turbulent flow, (b) mass transport can be directly related to peripheral velocity by empirical (dimensionless group) correlations, (c) current density and electrode potential are uniform over the electrode surface and (d) it has a relatively large electrode surface (in comparison to the RDE). The applications of a single, smooth, macro electrode RCE can be considerably extended by using roughened surfaces, bimetallic RCEs (BRCEs) and micro/macro RCEs. These features make the RCE a key choice for laboratory studies on flow corrosion.

This paper illustrates the application of simple and modified RCEs to marine corrosion via studies on the dissolution of cupro-nickel alloys in synthetic and real seawater. Both oxygen reduction and cupro-nickel dissolution are considered together with the effects of (i) RCE velocity, (ii) film formation and (iii) bimetallic coupling. This paper highlights the advantages of a potential step, hydrodynamic step, current transient approach, which is capable of producing fast, accurate and reproducible data on mass transport controlled corrosion rates.

MODELLING EROSION-CORROSION OF PURE METALS IN AQUEOUS SLURRIES

B.D. Jana and M.M. Stack, University of Strathclyde, UK

There has been much interest in recent years in mapping tribo-corrosion mechanisms, where the wear process involves sliding wear, micro-abrasion or solid particle erosion. In particular, there is now a methodology for mapping slurry erosion-corrosion phenomena based on mathematical models in the literature for particulate erosion and for aqueous corrosion. However, the important effect of material composition on the boundaries of such maps has not been investigated to date.

In this work, predictive models were used to predict the erosion-corrosion performance of a range of e metals i.e. Cu, Al and Ni at various pH and potential values. The results were compared to those of a reference material, Fe. Erosion-corrosion mechanism maps were constructed based on the results

The maps generated demonstrated differences in erosion-corrosion mechanisms for the various pure metals. Changes in electrochemical variables had a significant effect on the transitions between the individual erosion-corrosion regimes for the pure metals. The implications of such results for erosion-corrosion issues involving metallic materials are addressed in this paper.

EROSION AND EROSION-CORROSION PERFORMANCE OF CAST AND THERMALLY SPRAYED NICKEL-ALUMINIUM BRONZE

R C Barik, J A Wharton and R J K Wood, University of Southampton, UK K R Stokes, DSTL Porton Down, UK

Nickel-Aluminium Bronze (NAB) is widely used for propulsion and seawater handling systems in naval platforms. It is selected because of its attractive combination of toughness and shock resistance but it has inherent susceptibility to selective phase corrosion and erosion-corrosion. In order to extend the life of NAB components, modern coating techniques are being considered to confer wear and corrosion resistance and also cost effective refurbishment. This paper presents research into erosion and erosion-corrosion of both "as cast" and thermally sprayed NAB. The synergistic effects based on mass loss and electrochemical measurements obtained from pure erosion (E), flow corrosion (C) and erosion-corrosion (T) experiments are presented under a range of energies that relate to maritime operating conditions. Novel analysis of electrochemical measurements based on the ratio of the standard deviation of current noise under flow to that under erosion-corrosion is used to define limiting conditions. The influence of synergy was found to be dependent on flow energy and could be either beneficial or detrimental. The results of this work assist with material selection for controlled or reduced material loss in marine vessels.

STREAM 2- SESSION: FOULING CONTROL USING SURFACE EFFECTS SESSION CHAIR: STEVEN MCELVANY

NANOPOROUS THIN FILMS FOR NON-TOXIC ANTI-FOULING SURFACES WITH LOCALIZED PULSED ELECTRIC FIELD CAPABILITY

M A Anderson, University of Wisconsin, USA

Biofilm formation on ships in the marine environment has promoted extensive research in this area to find out viable option to prevent/slough off biofilm from such water bodies. The current research is one of the research efforts to investigate the effect of pulse electric field on biofilm prevention/sloughing. The present research explores the possibility of using inter digital electrodes to generate the pulse electric field, which makes it a unique attempt in its approach. The electrode system used in this study consists of 8 µm, 25 µm and 300 µm spacing electrodes. The main electrode material employed is gold on an inert support media, which is glass in this case. For better adhesion of gold over glass substrate, Chromium is used in between the glass and the Gold. The required electric field under varying conditions is produced by a pulse electric generator, regulated by a user friendly interface. Pseudomonas aeruginosa is used as a model organism in this study. Baclight method, which takes advantage of two fluorescent dyes, is used to test the baterial viability. Preliminary results showed that the present system is capable of killing P. aeruginosa at applied field strengths ranging from 0.45 V/µm to 1.42 V/µm. Operational difficulties like dissolution and sloughing of electrode material and poor adhesion of Gold over glass were encountered during these experiments. Hence, the modification of electrode system and a better design of electric circuit to measure other parameters like changes in electric current pattern, waveform and circuit voltage are needed. On going research focuses on better design of the electrode system, biofilm experiments to achieve biofilm prevention/sloughing at low voltages instead of killing the microorganism and an improved electric circuit to monitor other parameters required to efficiently define the mechanism behind the biofilm experiments. The current research also focuses on the application of the approach in real world, where the sole objective is to develop a spray paint, which will contain the micro spheres to act as micro electrodes. The results of the on going research will be presented in the upcoming conference session.

ENGINEERING SURFACE TOPOGRAPHIES TO CONTROL MARINE FOULING

A Brennan, T Estes and L Hoipkemeier-Wilson, University of Florida, USA

M Carman, A Feinberg and J Schumacher, Department of Biomedical Engineering, University of Florida, USA

In recent decades, there has been considerable research into cellular responses to topographical cues on both nanometer and micrometer scales. This concept is now being employed to develop engineered surface topographies that reduce marine fouling by optimizing mechanical and energetic effects. It has long been known that surface roughness affects wettability. Wenzel first proposed an equation for this relationship in 1936, which was later modified by Cassie in the 1940s. Wenzel's equation applies when a liquid is able to follow the contours of the topography. Cassie's equations fit when either the liquid cannot follow the contours and instead rests upon a composite surface of solid and air or when the liquid is wicked into the recesses of the topography ahead of the drop. The combined model takes into account both the roughness ratio and the solid surface fraction and predicts that roughness tends to push surfaces to the extremes of wettability. The accuracy of the model was tested against previously engineered silicone topographies including pillars, ridges, channels and ribs. The contact angles of five liquids were measured on each surface. A high level of correlation (coefficient of determination of 0.89) with the model was found. In order to maximize the effect of topography on wetting, a large roughness ratio and small solid fraction is needed. Minimizing the wettability of a substrate would limit the ability of marine organisms to contact and adhere to the surface, but mechanical contributions must also be considered. For very fine features, it is conceivable that fouling organisms could exert enough force as they settle to alter the topography to something more amenable. The forces needed to shift the tops of 4 micron high features by 1 micron were calculated for 2 µm diameter pillars as well as 2x4, 2x8, 2x12, and 2x16 µm ribs. The necessary force to shift the pillar was at least an order of magnitude smaller than any of the ribs. This led to the development of a biomimetic surface topography which is based on the scales of fast moving sharks. It is composed of diamond packed $2.5 \ \mu m$ wide ribs spaced $1.5 \ \mu m$ apart. The dimensions of the topography were altered in order to maximize changes in wettability as well as remain sensitive to fouling organisms. This topography has a high roughness factor (5.0) and moderate solid fraction (0.47). The biomimetic topography has yielded promising bioassay results, leading to ~85% reduction in *Ulva* settlement compared to smooth silicone.

CONTROL OF ULVA ZOOSPORE SETTLEMENT VIA MICROTOPOGRAPHIC CUES

A Brennan, T Estes and L Hoipkemeier-Wilson, Department of Materials Science and Engineering, University of Florida, USA

J Callow and M Callow, School of Biosciences, The University of Birmingham, UK

M Carman, A Feinberg and J Schumacher, Department of Biomedical Engineering, University of Florida, USA

Micropatterned silicone elastomers were characterized and evaluated for control of biological settlement and adhesion with respect to zoospores of the macrofouling alga, Ulva. Dow Corning's Silastic T2 was chosen as the base substrate and both bulk and surface properties have been examined. The bulk elastic modulus was found using tensile testing to be ~1.5 MPa, while the surface modulus was measured using atomic force microscopy to be roughly 1-2 orders of magnitude smaller than the bulk elastic modulus. The low modulus accounts for the enhanced foul release properties of silicone compared to more rigid substrates such as glass. The topographical features studied included 5 μm wide ridges, 5 µm diameter pillars, and a biomimetic engineered surface topography. For 5 µm tall and 5 µm spaced features, settlement increased relative to an unpatterned silicone control by 150% for ridges and 80% for pillars. The spores tended to settle within the valleys and against the walls created by the topographical features. Most spores were able to squeeze in between features and against two side walls. Additionally, spores packed closely into the valleys thereby minimizing their exposed surface area to achieve an energetically favorable situation Increasing feature spacing, resulted in decreased settlement that approached that of smooth silicone. Spores still tended to settle against feature walls, but each spore could only press against one wall. These results led to the next generation of topographies which intended to probe feature spaces smaller than the spore body. These topographies would require the spores to bridge features, an energetically and mechanically unfavorable situation. The first of these topographies tested was the biomimetic engineered surface topography, also known as the sharklet. It is based on the scales of fast moving sharks and is composed of diamond packed 2.5 µm wide ribs spaced 1.5 µm apart. This topography yielded a ~85% reduction in spore settlement compared to the control. This is the first definitive example that minimally fouling substrates can be produced via microtopographies. The majority of spores that settled on this pattern rested in the ~3 µm spaces between each diamond. Future studies will eliminate these areas and evaluate if the spacing of the biomimetic pattern is the critical factor.

FOULING RELEASE COATINGS OF CONTROLLED SURFACE ENERGY BASED ON THERMOPLASTIC ELASTOMERS

C K. Ober and S Krishnan, Department of Materials Science and Engineering, Cornell University, USA A Hexemer and E J. Kramer, Department of Materials, University of California, USA J A. Finlay, J A. Callow and M E. Callow, School of Biosciences, the University of Birmingham, UK

Recent results of fouling release behaviour will be described for a series of coatings obtained from surface engineering block copolymers. Surfaces based on poly(ethylene glycol) (PEG) and short perfluorocarbon segments are compared when attached to the same elastomeric underlayer. Evaluation of these materials includes both physical (AFM, contact angle, NEXAFS) and biological characterization. It was observed that settlement of Ulva zoospores (an indicator of biofouling tendencies) was higher on the PEG surface compared to the fluorinated surface. The residual biomass after the spores were cultured for 10 days was correspondingly higher. AFM studies have shown a correlation with the uniformity of the surface with fouling release. These and other aspects of the surface behaviour of these materials will be discussed.

NOVEL ANTIFOULING SURFACES MODELED FROM NATURE

A Scardino and R De Nys, School of Marine Biology & Aquaculture, James Cook University, Australia J Lewis, Maritime Platforms Division, Defence Science Technology Organisation, Australia; E Harvey, MINIFAB, Australia

The antifouling properties of marine bivalves and gastropods of the Great Barrier Reef (GBR) were investigated. Field collections of bivalves and gastropod species that are naturally clean *in-situ* were undertaken on selected reefs of the GBR. The surfaces of all collected species were characterized using light microscopy, scanning electron microscopy and laser scanning confocal microscopy. A range of micro (<100µm) and macro (100µm-1mm) textures and shapes were discovered. The surfaces of selected species were modeled using high-resolution resin casting and laser ablation of polymers. Models, which are accurate to within 1µm, were tested. The modeled surfaces were exposed to high fouling pressure in laboratory assays and in the field. Surfaces modeled from natural microtextured surfaces were significantly less fouled than smooth controls over time. The relationship between the shell surface microtexture and the intensity of fouling is discussed.

SURFACE PROPERTIES OF MARINE ORGANISM ADHESIVES AND THEIR POSSIBLE ROLES IN ORGANISM RELEASE FROM ANTIFOULING COATINGS

G C Walker, University of Pittsburgh, USA

The modulus of coatings influences the release properties of those materials. Lower modulus coating materials are expected to release barnacles more easily than high modulus coatings. Predictions along these lines have been made by a number of previous researchers, using the Kendall equation. One assumption in the most general application of the Kendal equation to the release of barnacles is that the barnacle substrates are much harder than the coatings. We present results that illustrate that barnacle bases exhibit base-plates with heterogeneous modulus, and we explore the hypothesis that the modulus of the outermost skin of the baseplate, which can be soft, correlates with the adhesion strength of barnacles to easy-release coating substrates. This would imply the need for alternative model for hard fouling release. We also discuss the modulus properties from traditional soft foulers, such as *Ulva sp.*, and discuss possible mechanisms for their release from marine coatings.

KINETICALLY-TRAPPED SEGREGATING MIXTURES OF FLUOROPOLYMERS AND LINEAR POLY(ETHYLENE GLYCOLS): NANOSCOPICALLY-RESOLVED AMPHIPHILIC SURFACES: THAT PRESENT TREACHEROUS TERRAIN TO INHIBIT BIOFOULING.

K L. Wooley, C S. Gudipati, J A. Johnson, K T. Powell and G O. Brown, Washington University, USA

This presentation will describe the preparation and study of marine antifouling coatings, comprised of nanoscopically-resolved morphological and topographical surface domains, capable of inhibiting protein adsorption to limit adhesion of marine organisms. In order to generate complex nanoscale surface features across films of sufficient mechanical integrity, composite crosslinked networks are prepared from combinations of polymers having different molecular architectures, physical properties and chemical compositions. In particular, hyperbranched fluoropolymers (HBFP) and linear poly(ethylene glycol) (PEG) are used as hydrophobic and hydrophilic components, respectively, to generate an amphiphilic surface profile. The combination of these two materials to generate complex nanometer-scale surface topographies and morphologies is an entirely new concept in the development of non-biofouling coatings materials.

The preparation of complex nanostructured materials is being advanced rapidly with the development of a methodology that relies upon two fundamental techniques in polymer chemistry: (1) the phase segregation of incompatible block copolymers or polymer mixtures to produce well defined nanoscopic domains over long ranges; and (2) crosslinking within selective regions of those phase segregated assemblies to provide robust materials comprised of regions that exhibit contrasting chemical, physical and mechanical properties. Although the phase segregation of incompatible polymers is not a new phenomenon, the regionselective crosslinking of the segregated assemblies is only recently being realized as a versatile methodology by which to tune the size, shape and behaviour of materials. In this presentation will be described the formation of surfaces patterned with nanoscopic arrays of topographic and morphologic complexity. The preparation of non-fouling and foul-releasing surfaces is accomplished by the bulk-state phase segregation and covalent crosslinking of hyperbranched fluoropolymer and linear poly(ethylene glycol) mixtures. The nanostructured surface features in this case are dictated mainly by the stoichiometries of two components and the coating thickness, which is driven by compositional and topological differences. Detailed characterization of these surfaces, including interesting surface reorganization events for these materials, will be discussed. Furthermore, data collected from experiments that extend this methodology to other compositions, including those that incorporate linear fluoropolymers will be presented.

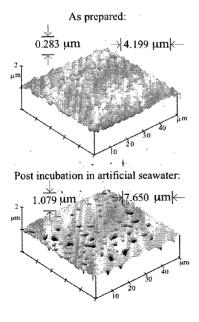


Figure 1. Atomic force microscopy images of the surface characteristics of the amphiphilic crosslinked network materials upon preparation and after incubation under artificial seawater (upper and lower panels, respectively). Inversion of the surface occurs due to conformational reorganization, which occurs upon swelling of the poly(ethylene glycol) rich domains. Each of these images illustrates the amphiphilic surface features, and serves as a measure of the nature of the phase segregated domains.

THURSDAY 29TH JULY 2004

PLENARY PRESENTATION

RECENT DEVELOPMENTS IN MICROBIOLOGICALLY INFLUENCED CORROSION: A SERIES OF PARADOXES

B Little, Naval Research Laboratory, USA

Since 1934 it has been recognized that microorganisms could produce corrosive metabolites, e.g., acids, bases and sulfides, influencing corrosion of some alloys. Recent developments in microbiology, surface chemistry, microscopy and electrochemistry have contributed to our understanding of microbiologically influenced corrosion (MIC) but have also produced a series of paradoxes. For many years the major emphasis in MIC studies has been development of synthetic media for detection and enumeration of specific types of bacteria associated with corrosion products. Using genetic techniques, researchers determined that is possible to culture only about 1% of the organisms from a natural population. Use of microelectrodes to measure biofilm/metal interfacial dissolved oxygen and pH established that biofilms create environments that cannot be predicted from parameters measured in the bulk medium. Environmental electron microscopy enabled one to image bacteria in hydrated corrosion products. With this improved technology came the realization that in many circumstances, bacteria are attracted to corrosion products. Investigators using electrochemical techniques have recently established that the same organisms and mechanisms that cause MIC can also inhibit corrosion. Furthermore the composition of the synthetic medium may be more important to electrochemical measurements than the presence or activities of the microorganisms. For many alloys, oxyanions, e.g., sulfate, phosphate and nitrate are corrosion inhibitors. When the Cl⁻¹ to oxyanion ratio is low, pits and crevices will not propagate. As microorganisms consume or reduce oxyanions, the corrosivity of the medium may increase. Researchers found that chloride must be present in a concentration at least comparable to that of all other anions combined; otherwise corrosion was inhibited even at hydrogen sulfide levels up to 500 ppm. MIC researchers are left with the following paradoxes: many naturally occurring organisms cannot be cultured, interfacial chemistry cannot be predicted, corrosion products influence the distribution of bacteria, bacteria can inhibit corrosion and electrolyte composition may be more important to localized corrosion than metabolites.

STREAM 1– SESSION: FOULING CONTROL USING CHEMICALS SESSION CHAIR: DAVID ARNOLD

ANTI-MICROFOULING ACTIVITY OF THREE EXTRACTS OF MARINE ALGAE FROM BRITTANY, FRANCE.

A Bazes, M Lartigue, E Quéméner, J-P Braud and N Bourgougnon, Université de Bretagne Sud, France

The inhibitory effects of ethanolic and dichloromethane fractions from Sargassum muticum and Polysiphonia lanosa from the Atlantic shores of South Brittany, have been investigated against representative species of the major groups of fouling organisms, viz. bacteria, diatoms, and spores and zygotes of macroalgae. A third algae has also been used. Ceramium botryocarpum which appeared in 2001 in culture pools used by Innovalg for algae production, seems to inhibit the settlement of green algae and barnacles. The annual variation of in vitro activity of these extracts has been also investigated. All extracts showed good levels of inhibitory activity and no toxicity against Vero cells, which may suggest a potential for active ingredients in antifouling paints. Further work is now needed to identify the compounds causing the activity, to evaluate specific antimicrobial activity against marine bacteria specially implicated in biofilms and to examine the precise role of such activity in nature.

ANTIFOULING ACTIVITY OF NEW THIENOPYRIDINE DERIVATIVES

B A P da Gama, L C S Pinheiro, A R Azevedo, A M R Bernardino and R C Pereira, Universidade Federal Fluminense, Brazil

The search for effective, environmentally safe antifoulants has been prompted by the proposed ban of organotin-based antifouling paints, on the basis of their high toxicity to non-target marine organisms. Many research fronts have been initiated so far, and one of the most promising in the short term seems to be the use of new synthetic, metal-free organic products as antifoulants. Synthetic substances have an obvious advantage over natural products, since they can be quickly obtained in relatively large amounts at a low cost. This is the main reason why many research institutes worldwide are now focusing on synthetic substances as medicines. When a new substance is tested against some pathogenic agent, and the results are negative, it is generally put aside. The aim of this study is to test new organic substances, originally designed to work as medicines, as antifouling agents. Five new thienopyridine derivatives and four pyrazolopyridines were tested against the common fouling mussel, Perna perna, in laboratory experiments. Waterproof filterpaper circles were embedded in each substance (1 mg.disk-1), cut in a chessboard pattern, and then offered to detached juvenile mussels in Petri dishes previously covered by an entire circle of clean filterpaper, so that each mussel could choose to attach to the same area of treated and untreated surfaces (N = 10 replicates treatment⁻¹). A control experiment without substances was performed for comparison. The total number of byssal threads attached to each substrate was counted after 12 h. This assay has been demonstrated to be an effective screening method for antifouling substances. Interestingly, only the 5-cyano-4-chlorothieno[2,3-b]pyridine, the key intermediate for the synthesis of the new 4-(phenylamino)thieno[2,3-b]pyridines, and the 4-(phenylamino)thieno[2,3-b]pyridine with chlorine in a meta position showed significant activity against fouling (p < 0.01, ANOVA followed by Tukey test). A single change in chlorine position to para led to the opposite activity, significantly stimulating mussel attachment (p < 0.001). The carboxylic acid derivatives of these substances and all the pyrazolopyridines had no significant influence on mussel attachment (p > 0.05). Both active substances presented low toxicity to mussels after a period of 24 h from exposition. The present results may lead to new antifoulants with low toxicity and good antifouling performance in the near future, and can contribute to a better understanding of structure-activity relationships.

EXTENDED ANTIFOULING COATING PERFORMANCE THROUGH MICROENCAPSULATION

E Haslbeck, Naval Surface Warfare Center Carderock Division, USA

In anticipation of even tighter environmental actions being taken at the international level, reducing or eliminating the use of heavy metals as biocides in antifouling (AF) hull coatings is being considered. In many cases, this is being done by incorporation of rapidly biodegradable organic pesticides. At the same time, the US Navy is extending the drydocking interval for the majority of its fleet, and, as a result, is pushing for extended AF coating system performance life. Microencapsulation of biocides offers the potential for greater formulation versatility and improved, environmentally friendly, and extended performance of AF coating systems.

Microencapsulation of biocides offers several advantages. First, encapsulation controls the rate of biocide release, resulting in highly predictable, steady state release rates. Second, encapsulation ensures more biocide remains in the coating over longer periods of time, which results in extended effective performance. Thus, AF coatings incorporating microencapsulated biocides can realize an environmental benefit over today's copper ablative and self-polishing systems.

Our focus has been on encapsulation of products related to Sea-Nine 211TM (Rohm and Haas). These microcapsules have been formulated into three commercial binder/resin systems as a booster biocide to the cuprous oxide. The binder/resin systems included one "ablative" technology, one "tin-free self-polishing" technology, and one "hybrid" of the two technologies. Compatibility studies demonstrated the capsules and binder/resin systems co-mixed without degrading liquid or applied coating properties including storage stability, polishing rate, and cracking tendency.

Test panels were prepared for field evaluation of antifouling performance in accordance with established ASTM methods. In addition, biocide release rate (both the copper and organic biocide) were measured in accordance with established and draft ASTM methods respectively. Comparisons of field performance, release rate, and dry film physical properties were made between unencapsulated and encapsulated booster biocides in all three coating binder/resin systems. To date, after more than 24 months of field exposure, two of the three coating systems containing encapsulated organic biocides remain free of significant hard fouling. Also, the release rate data show that microencapsulation results in highly controlled and significantly lower release of biocide from the coating system when compared to unencapsulated biocide in the same binder/resin system.

ESTIMATION OF ANTIFOULING PAINT ACTIVITY BY MEANS OF MATHEMATICAL MODELLING AND SELECTED ROTARY EXPERIMENTS: FROM TIN-BASED TO TIN-FREE SYSTEMS

D M Yebra, S Kiil and **K Dam-Johansen**, Department of Chemical Engineering, Technical University of Denmark, Denmark

C Weinell, Hempel's Marine Paints A/S, Denmark

As a result of the imminent worldwide ban on the very efficient but environmentally harmful tributyltin self-polishing copolymer (TBT-SPC) antifouling (A/F) systems, the marine paint companies have been forced to renew their efforts in the development of more benign alternatives. In contrast to the time-consuming empirical tests used by the paint industry, mathematical models of A/F coatings have been demonstrated to constitute a promising tool for accelerated product testing at different operational conditions and screening of new ideas for potential product optimisation.

The adaptation of the previously developed TBT-SPC model (Kiil et al. 2001) to tin-free products with binders based on mechanisms similar to those of the TBT-based A/F paints (Cu-, Zn- or Si-acrylates), should not entail significantly different modelling concepts. On the other hand, the description of tin-free rosin-based self-polishing (TF-RSP) systems is somewhat more troublesome. Because rosin-based compounds are often used in both technologies (as either co-binders or as main active binder component), the attainment of a reliable mathematical model for the activity of TF-RSP coatings would provide useful information for both SP product families.

In the present study, the first efforts made to characterise the working mechanisms of model paints based on a synthetic derivative of rosin (Zn-carboxylate) are presented. This information is needed to model the paint behaviour. First, the

polishing mechanisms of their binder system is studied by means of SEM-EDX studies of paints exposed to rotary experiments in artificial seawater under controlled conditions. The degree of depletion of the Zn-containing molecules in the leached layer is used to investigate the polishing pattern of the coating. A study of the role of insoluble pigment particles and retardants on the polishing behaviour is also provided. Finally, a mention is made to the studies performed on the reactivity and mechanisms (i.e. reaction products) of the binders of interest and published elsewhere.

Kiil, S., Weinell, C.E., Pedersen, M.S., Dam-Johansen, K. Analysis of Self-Polishing Antifouling Paints Using Rotary Experiments and Mathematical Modeling. Ind. Eng. Chem. Res. 40(2001), pp. 3906-3920.

SYNTHESIS AND EVALUATION OF ISOCYANOBENZEN DERIVATIVES FOR ANTIFOULING ACTIVITY AGAINST THE BARNACLE BALANUS AMPHITRITE

Y Nogata and I Sakaguchi, Abiko Research Laboratory, Central Research Institute of Electric Power Industry, Japan Y Kitano, T Suzuki and R Kobayashi, Laboratory of Bio-organic Chemistry, Tokyo University of Agriculture and Technology, Japan

E Yoshimura, SERES Inc., JAPAN

We have studied on the structure-activity relationships based on antifouling active natural compounds and synthesized compounds in terms of anti-barnacle activity. Recently, we have reported the synthesis of isocyano compounds, such as 3-isocyanotheonellin, its analogues, and simple liner isocyanides, which showed potent antifouling activity against barnacle larvae without significant toxicity. These results suggest that the isocyano group is important for non-toxic antifouling activity.

In continuation of our research to create new potent anti-barnacle activity compounds, we tried to synthesize various types benzene compounds, which consisted mainly of isocyanobenzene derivatives. Several benzene compounds, containing isocyano function or acetamide function, showed potent anti-barnacle activity, while their toxicity to larvae were much less than that of CuSO₄. Especially, 4-[(E,E)-1,5-dimethl-hexa-1,3-dienyl]isocyano benzene was more active than CuSO₄ with EC₅₀ values 0.0078 μ g ml⁻¹, but they were not lethal to cypris at high concentrations. On the other hand, benzene compounds, of which isocyano group was converted to other function groups, were moderately active or showed high toxicity as same as CuSO₄. Present structure-activity relationships studies provided further evidence of strongly relation between isocyano function and potent anti-barnacle activity with low toxicity.

THE POTENTIAL USE OF PROTEOLYTIC ENZYMES TO CONTROL FOULING BY THE GREEN ALGA, ULVA SP., AND THE BARNACLE, BALANUS AMPHITRITE.

M E Pettitt, J A Callow and M E Callow, School of Biosciences, University of Birmingham, UK S L Henry and A S Clare, School of Marine Science and Technology, University of Newcastle upon Tyne, UK I Schneider and K Allerman, BioLocus ApS, Denmark

Effective antifouling measures are estimated to save the EU shipping industry £1billion annually in reduced operating costs. Environmental and health and safety concerns surrounding current tin- and copper-based biocides are mounting, however, fuelling the legislative process (EU biocides directive No98/8/EC) and the search for effective, 'green', nontoxic alternatives.

Marine macrofouling organisms frequently colonise surfaces by temporary, and if the surface is suitable, permanent attachment of the spore or larva. This critical phase of the life cycle may thus involve one of more adhesives, which are often proteinaceous in character. It is logical, therefore, to explore technologies that offer the potential to interfere with this adhesive stage, by either blocking the binding of the adhesive or by degrading it. Biolocus has patented the concept of employing enzymes in antifouling coatings (PCT/DK01/00202) and promising preliminary data resulted in EU support for a 2-year CRAFT project with a key objective to investigate how enzymes might interfere with adhesive functions of fouling organisms. In this presentation we communicate findings from a range of experiments which suggest that the commercial protease Alcalase has a significant effect on the adhesion of zoospores from a major macrofouling green alga, *Ulva* (syn. *Enteromorpha*) and, through its action on at least one adhesive, settlement of the cypris larva of the major fouling barnacle, *Balanus amphitrite*.

ENVIRONMENTALLY FRIENDLY ABLATIVE FOULING DETERRENT COATING

G Seabrook and E Soeterik, Magellan Companies Inc., USA

Abstract: An environmentally friendly ablative fouling deterrent coating has been developed and tested, which controls hard and soft fouling. Developmental patented technology using ecologically safe phytochemicals (plant extracts) has been successfully formulated into marine underwater hull ablative coatings. A series of tests have been conducted in two global marine test laboratory locations. In each test trail and in each test location the results show consistent fouling deterrent capabilities.

ANTIFOULING EFFICACY OF ORGANIC COATINGS: NEW AF COATING FORMULATIONS AND THEIR PERFORMANCES AT AYAJIN HARBOR, EAST COAST OF SOUTH KOREA

M Sidharthan, H D Bhattarai and H W Shin, Soonchunhyang University, South Korea

In Korean peninsula increasing maritime activities proportionately increase the AF coating usage and its production to solve the vessel hull fouling problems. Toxic booster biocides are indiscriminately used in many of the AF coatings but their fate in seawater is not clearly known. These toxic chemicals environmentally persistent in seawater for long time and their increasing load into the marine environment become great concern in the recent years. In order to phase out such toxic AF coatings, 94 new organic AF candidates and their combinations were tested in this static panel investigation. AF test candidates include different groups of organic chemicals; terrestrial plants and soil extracts. Each AF candidate (three concentrations) was incorporated in a conventional matrix type of coating base paint. Toxicity and nontoxic AF (repelling) activity of new AF candidates and their combinations were compared with some commercial AF coatings. Significant differences in AF efficacy were observed on panels coated with AF candidates such as *Euonymus* sp extract, two aliphatic acids and its derivatives, an aromatic dicarboxylic acid ester and three commercial test formulations. The environmental variables of the Ayajin harbor (static panel immersion site) greatly influenced the fouling rate. Results obtained were discussed through experimentation under laboratory and field conditions.

HIGH THROUGHPUT METHODS IN THE DEVELOPMENT OF NOVEL MARINE COATINGS

D C Webster, P S Majumdar, A Ekin, J A Bahr and **D A Christianson,** Department of Polymers and Coatings, Center for Nanoscale Science and Engineering, North Dakota State University, USA

Coatings are complex materials comprised of numerous polymers, crosslinkers, catalysts, additives, and pigments and fillers. Development of a coating often involves a tedious cycle of formulation, preparation, application and testing of formulations one at a time. Time and material constraints often limit the number of materials that can be prepared and tested. The development cycle can be significantly accelerated using automated methods for most of the key steps needed in developing a coating.

A complete workflow for the development of novel marine coating compositions has been developed. Polymer synthesis is carried out in parallel using an automated batch reactor system. The preparation of coating formulations is also carried out using an automated system that dispenses and mixes formulation ingredients. Viscosity of each formulation is measured and can be adjusted as well. The formulations are then applied in array format to either standard coating test panels or microtiter plates using an automated application system.

Key coating properties are then measured using automated systems. Surface energy of coatings is measured by determining the contact angle of liquid droplets on the coating surface. Pseudo-barnacle adhesion is measured on the coating array using a novel automated pull-off adhesion testing system. Viscoelastic properties of the coatings are measured using a parallel DMTA system. All of these systems are connected through a common database in order that all information about a material is saved and retrievable. Software for experimental design, experiment execution, and database searching is an integral part of the overall system.

For the development of novel silicone fouling release coatings, key parameters involving the molecular weight of the silicone, crosslinkers, solvents, catalysts, etc., are evaluated in experiments consisting of 24 coatings. Key compositions are identified and further refinements are made in subsequent experiments. Screening of properties using laboratory methods results in the identification of robust coating candidates for testing with marine organisms.

THE TRANSITION TO TIN-FREE COATINGS AND FUTURE DIRECTIONS FOR BIOFOULING CONTROL

J A Lewis, Maritime Platforms Division, Defence Science and Technology Organisation, Australia

In anticipation of entry-into-force of the International Convention on the Control of Harmful Anti-Fouling Systems on Ships, 2001, the Royal Australia Navy (RAN) implemented a program in 2002 to replace antifouling coatings containing tributyltin with tin-free products throughout the fleet. Self-polishing copolymer coatings with copper as the primary biocide have been adopted on the basis of comprehensive panel, patch and hull trials undertaken by DSTO with support from the RAN. A patch trial project on Australian commercial ships has also been undertaken to verify the efficacy of tin-free products in the Australian environment. However, with all biocidal antifouling coatings under scrutiny for their possible environmental impact, research is continuing into the performance of biocide-free coatings and novel methods of biofouling control. Trials of silicone-based foul release coatings have been underway for more than 10 years but, so far, these are seen as practical only for vessels with particular operational profiles. Further developments in methods of biofouling control are therefore warranted and are being pursued.

STREAM 1– SESSION: DECAY OF WOOD IN THE MARINE ENVIRONMENT SESSION CHAIR: ANDY PITMAN

A LABORATORY BIOASSAY FOR ASSESSING THE RESISTANCE OF TROPICAL HARDWOODS TO THE WOOD-BORING CRUSTACEAN *LIMNORIA*

S M Cragg and L M S Borges, University of Portsmouth, UK J R Williams, TRADA Technology, UK G S Sawyer, Buckinghamshire Chilterns University College, UK

Feeding by the marine wood borer Limnoria quadripunctata can be measured by measuring the rate of production of faecal pellets, which are roughly cylindrical and of a predictable size. Limnoria ingests the wood in which it burrows and is thus subjected to any bioactive compounds contained within the wood. The resistance of certain timbers to this borer is probably due to such compounds. A short-term bioassay has been developed which can be used to predict the resistance of timbers to Limnoria, by comparing faecal pellet production rate and mortality in contact with those timbers with that on non-resistant Scots pine sapwood. This screening test permits the evaluation and comparison of large numbers of timbers much more rapidly than is possible with traditional marine trials. The experimental approach reveals the optimum temperature for feeding in L. quadripunctata to be between 18 and 22°C. The experimental approach permits the distinguishing of the effects of water-soluble and ingested compounds. The results from these tests suggest that certain lesser known timber species promise as good or better performance than species widely used as durable timbers for marine construction.

WOOD BORING ACTIVITY ON TROPICAL COAST OF RIO DE JANEIRO, BRAZIL.

L F Skinner, Universidade do Estado do Rio de Janeiro, Brazil S H G Silva, and H P Lavrado, UFRJ, Departamento de Biologia Marinha, Brazil

Rio de Janeiro coast has three large bays: Sepetiba, Ilha Grande and Guanabara Bay and all of that have many areas of mangrove forest with wood supply, besides the use of wood artifacts in many activities. Among these, Guanabara Bay is poorly affected by wood boring due to pollution and fouling communities. Conversely, wood boring activity on Sepetiba and Ilha Grande Bay is high, mainly by Teredinidae mollusks. In this work we evaluate the specific composition related to saline gradient and the potential for wood destruction at Sepetiba and Ilha Grande Bay. Panels of *Pinus* (80cm³) were used to collect wood boring organisms. Nine species of bivalve mollusks from Teredinidae family were found: *Teredo furcifera, T.bartschi, Bankia fimbriatulla, B.gouldi, B.carinata, B.destructa, Lyrodus floridanus, L.massa* and one unidentified *Nototeredo spp.* It was found also *Martesia striata* bivalve and *Limnoria tripunctata* crustacean. Density and specific composition was strongly related to salinity, with low density of wood borers and low wood destruction rates at low salinity places. Opposite was observed were salinity is higher than 25 PSU. Wood boring activity was lower on spring-summer (rainy season) than on autumn-winter (dry season) and there is no difference on potential of wood destruction between Sepetiba and Ilha Grande Bay.

STREAM 2– SESSION: BIOCORROSION SESSION CHAIR: SHEELAGH CAMPBELL AND IWONA BEECH

ANAEROBIC IRON CORROSION BY NOVEL MICROORGANISMS -A NOVEL MECHANISM AND STRATEGIES FOR THEIR DETECTION

J Kuever, Department of Microbiology, Institute for Material Testing Foundation Institute for Materials Science, Germany

Sulphate-reducing bacteria (SRB) are well known for causing microbial corrosion. Beside the production of hydrogen sulphide as corrosive agent they effectively consume hydrogen produced by cathodic depolarisation. Previous studies focussed on *Desulfovibrio* spp. as most efficient hydrogen scavenging SRB. A newly isolated SRB belonging to a different family showed that there are other SRB which are more corrosive than all known *Desulfovibrio* spp. Growth of this strain on iron was much faster than with molecular hydrogen suggesting a direct utilisation of electrons from metallic iron. In addition, a newly isolated *Methanobacterium*-like archaeon showed a similar behaviour.

Because of their ecological relevance and their economic impact a set-up of modern molecular tools was developed for a successful and rapid detection.

LONG- TERM EXPOSURE TRIALS EVALUATING THE BIOFOULING AND CORROSION RESISTANCE OF COPPER NICKEL ALLOY SHEATHING MATERIALS.

S Campbell, Portsmouth University, UK C Powell, Consultant Metallurgist to the Nickel Development Institute, UK

The modern equivalent of copper sheathing, so successful on Nelson's ships, is the use of a 90-10 copper nickel alloy applied as an adhesive backed foil to ships and as granules embedded in polychloroprene rubber used on legs and risers of offshore structures. The 10% nickel alloy is reported to have better corrosion resistance than copper whilst maintaining similar biofouling resistance. While independent long term evaluation studies for copper nickel itself are widely available, little data exists for these types of composite products.

A 7 and 8 year raft exposure trial study in Langstone Harbour, UK, evaluating the corrosion and biofouling behaviour of the foil and granule composite products respectively has now been completed. Removals of panels for destructive assessment after 1, 4/5 and 7/8 years were made. In addition, a third product under development at the start of the study, involving expanded mesh with a neoprene backing, and a single sample of hot rolled plate were included. The adhesion of the foil product was measured by peel resistance tests on 3 occasions over the exposure time.

This paper will detail the results of the study. These will essentially show that all products showed restricted colonization of fouling species and remained largely free of macrofouling. Where present it could be wiped away fairly readily. The foil product had thinned $5.5 \mu m$ per annum when averaged over a 7 year period. Some reduction in bond strength was observed for the foil, being less pronounced on steel than GRP.

STREAM 2- SESSION: MODERN TECHNIQUES IN BIOFOULING SESSION CHAIR: SHEELAGH CAMPBELL AND IWONA BEECH

COMBINATORIAL HIGH-THROUGHPUT BACTERIAL BIOFILM SCREEN FOR ASSESSMENT OF ANTIFOULING AND FOUL-RELEASE PERFORMANCE OF MARINE COATINGS

S J. Stafslien, T Ready, J A. Bahr, D A. Christianson and P Boudjouk, Center for Nanoscale Science and Engineering, North Dakota State University, USA

Fouling inhibits the performance and increases the expense of all maritime operations. It also forms a conduit for the introduction of invasive nuisance species to non-indigenous waters. New coatings are needed to combat the fouling phenomena, especially in light of the recent ban on tributyl-tin containing paints. Combinatorial high-throughput materials synthesis and analysis capabilities for the discovery of novel marine coatings has recently been established within the Center for Nanoscale Science and Engineering at North Dakota State University. To identify superior foul-resistant candidates from substantial numbers of new coatings, a novel biological laboratory assay is currently being developed as a screening protocol. Modified 24-well polystyrene plates are robotically deposited with resin and challenged with marine bacterial biofilms. Biofilm growth is obtained on the coating surface only by adapting a novel growth template to the polystyrene plates. The initial amount of biofilm obtained on each resin material (antifouling performance) is determined by first staining each well with a UV/Visible absorbent or fluorescent dye followed by analysis utilizing a BIO-TEK Synergy HT microplate reader. Foul-release performance of each resin material is assessed by quantitating the amount of biofilm remaining after water jet treatment of the initial biofilm growth obtained. Results and current status on method development and implementation of the biological assay will be discussed as well as attempts to correlate the laboratory assay data to coating physical properties and ocean immersion testing data.

APPLICATION OF AFM TO STUDYING ADHESION, DETERIORATION AND MICROELASTIC PROPERTIES OF FOULING-RELEASE SURFACES IN SIMULATED MARINE ENVIRONMENT.

F T Arce, R Avci, K Cooksey and B Cooksey, Montana State University, USA I Beech, University of Portsmouth, UK

Atomic force microscopy (AFM) has been applied to the study of a number of issues concerning adhesion properties of commonly used antifouling surfaces. Macroscopic studies on fouling-release surfaces indicate that the macroelastic properties of such surfaces relate to the fouling-release properties of the surfaces through Kendal's model. However, to the best of our knowledge no study exists that addresses whether there is any relation between the microelastic properties of a surface and its micro adhesion properties. Here we study these issues by taking advantage of liquid AFM and other analytical techniques to address the microelastic, microadhesion and microdeterioration properties of Intersleek TM and RTV11TM surfaces exposed to artificial seawater. An atomically flat mica surface was used as the control surface because its physicochemical, morphological and microelastic properties are the complete opposite of those of the fouling-release surfaces. The patchy distribution of microelastic regions on fouling-release surfaces was correlated with the locations of subsurface filler particles in the coatings. While the properties of Intersleek remain largely unchanged, significant degradation in the form of morphological changes, embrittlement and stiffening is observed in RTV11 surfaces depending on their preparation. It is now well established that in marine environments, interactions between extracellular polymeric substances (EPS) secreted by microorganisms and inanimate surfaces are critical to the initial biofouling events at microscopic scale. We probed adhesion events between a live diatom (Navicula genus) and IntersleekTM (highly hydrophobic) surfaces and compared these results with similar studies conducted on mica (highly hydrophilic) surfaces. Viable diatoms were immobilized onto tipless AFM cantilevers and adhesion force measurements were taken in artificial seawater into which both Intersleek and mica surfaces were immersed, simultaneously. It was observed that, on either surface, EPS polymers associated with the diatom were able to stretch up to several microns. The strength of adhesion (unbinding) forces varied from ~ 100 pN to 50 nN, for both surfaces. These surfaces were found to be indistinguishable in terms of measured adhesion forces and average work of adhesion, despite the significant differences in the physicochemical, mechanical and morphogical properties of the two surfaces. Adhesion at the microscopic scale appears to be dominated by the conditioning of these surfaces, and no relation could be found between the microelastic properties of the surface and the adhesion events associated with the

STREAM 2– SESSION: MARINE CONSERVATION

SESSION CHAIR: FRANK WALSH

RNLI PERSPECTIVE ON BUILDING RESTORATION: ANCIENT AND MODERN.

H Richings, RNLI, UK

This presentation will review the RNLI's current programme of maintenance, modernisation and rebuilding of lifeboat stations with specific reference to uses to which old lifeboat houses are put. The RNLI has 231 operational lifeboat stations around the coastline of the UK and the Republic of Ireland. The number and location of lifeboat houses has varied throughout the RNLI's 180-year history. Many were constructed in the mid to late 1800s, some from that period are still in use, others have passed into other uses, and some have returned to lifeboat use and been restored for use by modern lifeboats.

The RNLI continues to build new buildings to a high standard using both traditional building design and more contemporary methods. The presentation will aim to show how making best use of existing buildings through modernisation and restoration is combined with building new to ensure that, where practical, buildings of historical value are given a new lease of life and new buildings are created that will justify heritage status in the future.

MARINE CONSERVATION USING MODERN METHODS & MATERIALS

L Townsend, Coating Consultants Ltd., UK

The lecture will cover the author's early experience with HOLLAND 1, followed by work on HMS CAROLINE (WW1 Cruiser). Then it will cover HMS BELFAST camouflage and later docking. It will then discuss the forthcoming docking of HMS WARRIOR; and the proposed preservation of a WW1 aircraft lighter (from which the first wheeled take off at sea was made). Mention will be made of possible pitfalls in materials used, and of past dialogues with historians wishing to employ "traditional" methods and materials.

FRIDAY 30TH JULY 2004

PLENARY PRESENTATION

IN SEARCH OF THE PERFECT SHIP HULL COATING

G Swain, Florida Institute of Technology, USA

The perfect ship hull coatings would be non-fouling, provide corrosion control and be hydrodynamically smooth for the lifetime of the vessel; it should be compatible with the materials and methods of construction, be easy to apply, be cost effective and have no adverse environmental impacts. In spite of the efforts and creativity of scientists, engineers and laymen it appears that we are still a long way from a coating that meets these criteria. The self polishing copolymer tributyltin paints came close, and for many years have provided excellent service, however, they failed to pass the environmental requirements and now must be considered unacceptable as an antifouling coating. This leaves navies, ship owners and operators once more looking for a universal solution. This paper will explore the technologies that are presently being used and those that have been attempted or are under development. They include the biocide based systems, the non-stick and fouling release coatings, systems based on natural antifouling mechanisms, and alternative technologies that include the use of electricity, radiation, thermal activity and surface composition and texture. It will discuss the potential and limitations of these technologies and attempt to identify future solutions.

STREAM 1– SESSION: FOULING CONTROL USING SILICONES SESSION CHAIR: JOHN LEWIS

IN SITU RELEASE BEHAVIOUR OF BARNACLES FROM SILICONE COATINGS.

I L Singer, Naval Research Lab, USA G Kowalke and D Wendt, Cal Poly State University, USA J Kim, Lehigh University, Bethlehem PA

The growth and development of barnacles (B. amphitrite) settled on transparent silicone coatings was monitored in the laboratory from larval metamorphosis to maturity, at which point barnacles were removed. The coatings, Sylgard 184 (Dow Coring), and a "pure" PDMS (Gelest), were deposited on microscope glass slides, and then allowed to soak in filtered seawater for 6 days before being exposed to the larval culture. Time-lapse video recordings of the barnacle baseplates were made during growth. Removal of adult barnacles was performed in, situ (in vivo) using a digital force gauge mounted on a motorized stand. Barnacles were removed by applying a shear force to the baseplate. Two video cameras were used during the shear test: one to record the barnacle/coating interface and the other to record the digital force output. The two video signals were mixed in real-time and sent to a video recorder for playback analysis. Barnacle baseplates attached to the Gelest PDMS coating sheared cleanly, by interfacial peeling. On Sylgard 184, by contrast, baseplates adhered strongly and barnacle shells were crushed, similar to earlier field-study findings of barnacles (B. improvisus) on Sylgard 184. Tests are now underway with three thicknesses of Gelest PDMS coatings, 0.1, 0.5 and 2 mm, to investigate the effect of coating thickness on the growth, baseplate development and removal of barnacles. The results will be discussed in terms of the compliance of the coating/barnacle joint and fracture mechanics models of release.

ADHESION OF SOFT FOULERS TO SILICONE COATINGS.

M E Callow, JA Finlay and JA Callow, School of Biosciences, University of Birmingham, UK. M Chaudhury, Department of Chemical Engineering, Lehigh University, USA.

The green alga *Ulva* (Enteromorpha before recent taxonomic revisions) colonises new surfaces by producing microscopic, motile (5 µm diam.) spores, which release an adhesive glycoprotein on settlement. This adhesive is a space-filling, hydrophilic material, which undergoes cross-linking (curing) processes within minutes of release from the spore. The tenacity of spore adhesion on a range of different surfaces, including foul-release materials, has been assessed by hydrodynamic methods. Adhesion strength is strongly influenced by the time the cells are in contact with the surface, surface energy and whether or not the spores settle in groups. There appears to relatively little influence of coating modulus and thickness on the release of *Ulva* spores although these parameters do influence the release of sporelings (young plants). The relevance of the Kendall's model for microscopic, compliant 'soft-fouling' organisms will be discussed.

ORGANICALLY MODIFIED SILICONE POLYMERS FOR ANTIFOULING / FOULING RELEASE COATINGS.

J Thomas, S-B Choi and P Boudjouk, Center for Nanoscale Science and Engineering, North Dakota State University, USA

Modification of silicone polymers by covalently attaching organic biocides is being carried out to simultaneously incorporate antifouling/fouling release properties to silicone based marine coatings. Synthetic control over the incorporation of hydrophilic/hydrophobic moieties, crosslink type and crosslink density with in the polymer resins allows tuning of the resulting coating's surface and mechanical properties. Initial tests of these coatings included static contact angle measurements, dynamic mechanical thermal analysis and leaching studies on biocide. Tests against marine fouling organisms were performed using settlement and adhesion bioassays using Zoospores of the green alga *Enteromorpha* at the School of Biosciences, The University of Birmingham, UK and tubeworm attachment strengths at the University of Hawaii, Honolulu, USA. Field immersion tests carried out at Florida Institute of Technology, Melbourne, Florida, USA, ascertained the antifouling/fouling release properties of the coatings to barnacles. Results will be discussed in terms of biocide content and surface properties.

This research is sponsored by the Department of the Navy, Office of Naval Research, Grant N00014-02-1-0702.

PEEL RELEASE STUDIES OF DOPED SILICONE COATINGS AGAINST EPOXY (PSEUDOBARNACLES).

J Kim and M K. Chaudhury, Lehigh University, USA I L. Singer, Naval Research Lab, USA

Peel tests of silicone from epoxy were performed to better understand the kinetics of release of barnacles from silicone coatings. Silicone strips of a commercial silicone, Dow Corning Sylgard 184, and a "pure" PDMS (Gelest) were modified by adding non-reactive oils or silica filler. The strips were cured, attached to epoxy, then peeled at a fixed angle (30 degrees) and at loads from 0.1 to 5N (10g - 500g) force. Some strips were also exposed to Bovine Serum Albumin (BSA) in water before attaching to epoxy. Peel speed vs. load data were obtained by analyzing videos taken during peeling. The strain energy release rate (fracture energy) was computed as a function of load and geometry. Fracture energies of Sylgard 184 were reduced by adding oils to the network, but increased by solvent extraction; solvent-extracted Sylgard 184 exposed to BSA had a much higher fracture energy than BSA-exposed Sylgard 184 with and without dopant oil. Fracture energies of the "pure" PDMS were much lower than that of the Sylgard 184, and also less affected by extraction or by dopant oils. Fracture energies of both silicones were not affected by silica filler loaded up to 4 parts per hundred (by weight). Optical microscopy and XPS suggest that oil segregation to the surface might be responsible for reducing the fracture energy of oil-doped and BSA-exposed silicones.

PROPELLER FOULING CONTROL USING FOUL RELEASE COATINGS

R Mutton and M Atlar, University of Newcastle upon Tyne, UK C D Anderson, International Paint Ltd., UK

The ban on TBT antifouling coatings on ships, introduced by the IMO, has led to the development of a number of new antifouling systems. Prominent among these are the Foul Release systems, which now have a proven track record in preventing the fouling on certain types of ships hulls. Previous work has shown that in addition to proven antifouling abilities these ultra-smooth coatings have a lower drag than other antifouling coatings. This research has led to their trial on marine propellers where high water velocities around the blades allow low-drag, fouling-free coatings to have a significant effect on the propeller efficiency leading to economic advantages.

Investigations with a number of full-size ships that have had their propellers coated with Foul Release systems showed that advantages could be obtained. In order to quantify these advantages, sea trials have been conducted over a measured mile, using Newcastle University's dedicated research vessel 'Bernicia', both before and after the propeller was coated with a Foul Release system. This paper describes the conduction of these trials, using an automated data collection system to record the propeller torque, power and rpm of the propeller shaft, and the ships onboard computers to record position, vessel speed and heading, wind speed and direction and depth of water. The results of these trials will be presented along with discussion of the continued monitoring of the full-size vessels.

RELEASE BEHAVIOUR OF EPOXIED PSEUDOBARNACLES FROM SILICONE COATINGS IN HIGH SPEED BOAT TESTS.

R Quinn and G Swain, Florida Institute of Technology, USA I L Singer, Naval Research Lab, USA

Pseudobarnacles (cylinders of various diameter and length) were epoxied to transparent silicone (Dow Corning 3140 RTV) coatings (0.1 to 2 mm thick) on glass. The glass panels were attached to a thick plexiglass plate, and the plate was secured to the hull of a power boat. Video cameras at low (30 fps) or high (500 - 1000 fps) frame-rates recorded the epoxy/silicone interface as the boat speed increased from 1 to about 40 knots, as measured by a GPS receiver. Release occurred in less that 1/30 second. High frame-rate videos indicated three stages of release: 1) crack initiation at the epoxy/silicone interface; 2) crack propagation; and 3) lift off of the cylinder shortly before the crack propagated across the interface. Videos of the GPS speed were mixed in real-time with videos of the interface. Release ranking vs. speed data were obtained from the synchronized videos. Cylinders of a given length and diameter released sooner on thicker coatings than on thinner coatings, consistent with behavior seen in much lower speed (20 - 200 microns/s) shear and pull tests. At a fixed coating thickness and a fixed cylinder diameter, longer cylinders released sooner than shorter cylinders. These results will be discuss in terms of the fracture mechanics expected of a glued joint subjected to the shear and lift forces of water flowing past a boat hull.

STREAM 2– SESSION: CORROSION CONTROL TECHNIQUES AND MATERIALS SESSION CHAIR: KEITH STOKES

IMPRESSED CURRENT CATHODIC PROTECTION EQUIPMENT

B Torrance, Low Signature Cathodic Protection, Aish Technologies, UK

ICCP systems have been around for a long time, and are available in many forms, from the very simple to the highly sophisticated. This presentation will outline the principles of ICCP and look in detail at the system components (control systems and 'rectifiers', anodes, reference electrodes, shaft and rudder grounding). The relative merits of various types of each will be compared. The importance of system layout will be emphasised, and methods available for achieving good layout discussed. Some ideas for future applications will be tabled. The presentation will provide guidelines for those concerned with the prevention of marine corrosion on how to specify ICCP systems (and importantly how not to over- or under-specify them), and highlight some pitfalls to be avoided.

COMPUTER SIMULATION OF RESITOR CONTROLLED CATHODIC PROTECTION OF STEEL IN SEA WATER

S Paul. and P K Mitra, Jadavpur University, India

Carbon steel and various alloys steel are very much prone to different forms of corrosion in marine environment. Localized corrosion of stainless steel in the form of crevice and pitting corrosion is a major problem of it in seawater and hence cathodic protection, using Zn or Al sacrificial anode is conventionally adopted to restrict the perforation stainless steel structure. It is observed from the cathodic polarization curve of this steel in seawater that higher the polarization more is the current density and grater will be anode consumption. Both Zn and Al cause the steel to polarize too much negative potential, giving rise to higher consumption of them. Moreover at higher negative potential the cathodic reaction shifts from usual

$$2H_2O + 2[O] + 4e \rightarrow 4OH$$
 to $2H_2O + 2e \rightarrow H_2 + 2OH$

Causing hydrogen embrittlement of steel. Thus it is necessary to control the polarization of steel, using sacrificial anode so that the current sent by the anode is just sufficient to prevent the localized corrosion of the steel and with no over polarization. A suitable resistor can be put between the anode and steel to control the current. But depending on chemistry, speed of fluid movement and presence of microorganisms in the seawater, corrosion rates will vary and resistance of the resistor.

In the present investigation, attempts are being made to develop a model, using numerical and computational methods to obtain values of sacrificial anode size and resistance, given fluid properties and structure dimension.

TESTING METHODOLOGIES, ACCEPTANCE CRITERIA AND A CRITICAL EVALUATION OF HYDROCHLORIC AND PHOSPHORIC ACID BASED CHEMICALS FOR DESCALING OF SEAWATER PIPING MATERIALS.

E J Lemieux and K E Lucas, Naval Research Laboratory, USA T Wolejsza, Geo-Centers, Inc., USA

Use of copper-nickels alloys in seawater-cooled heat exchangers is common due to the inherent properties of these alloys, namely, a relatively low corrosion rate, anti-fouling properties and erosion corrosion resistance relative to other alloys. The corrosion behavior of these alloys is strongly dependant on the formation of a "protective film" on the underlying metal. In addition, alloying of copper with nickel increases these alloys tendencies towards passivity as compared to pure copper and has beneficial effects on their erosion-corrosion resistance. Erosion-corrosion is also improved by addition of iron and manganese. The ability to form a protective film in seawater is influenced by various parameters which include:

- Alloy-related properties (microstructure, chemical composition)
- Seawater properties (oxygen and contaminant content)
- Physical conditions (design, temperature, flow velocity)

The main causes of failure of cupro-nickel alloy components in seawater are usually attributed to either erosion-corrosion at extreme velocities or pitting phenomena. It is well established that these failures are generally due to detrimental seawater conditions, such as the presence of sulphides, or poor designs resulting in flow velocities too high and highly turbulent conditions. Periodic cleanings are necessary on seawater cooling systems, due to the gradual formation of scaling and macro-fouling during operation. Several chemicals and procedures can be used to remove these deposits and growths, the most common products being hydrochloric, citric or sulfamic acids. Hydro-lancing and mechanical cleaning are currently in use but have major drawbacks in costs and labor hours. In addition, most of these methods raise some safety and environmental issues.

Currently, two commercial water scale solvents have been identified that claim to be safe, environmentally friendly, inexpensive and exhibit no detrimental effects on the materials. However, demonstrations have noted an appreciable metal loss during cleanings. As a result of these demonstrations, the Naval Research Laboratory in Key West, FL (NRLKW) has conducted research to determine the characteristics of both hydrochloric acid and phosphoric acid based cleaning compounds which are commercially available. The objectives of this work reported in the current document were to identify the effect of cleanings on the corrosion behavior of 70/30 Cu/Ni, on the existing protective oxide film and evaluate the subsequent reformation of 70/30 Cu/Ni in seawater after cleaning with descalant. A compilation of these results is given in the current document. Additionally, the methods for evaluation of descaling chemicals and the acceptance criteria are presented.

UNDERSTANDING CORROSION ISSUES IN ALUMINIUM CAR FERRIES: CORROSION PREVENTION AND CONTROL TECHNIQUES

A Duran, Pechiney Marine, France C Henon, I Ronga, Pechiney CRV, France C Waddington, Hart, Fenton & Co. Ltd., UK

Properly designed and maintained, aluminium vessels require much less upkeep for corrosion matters when compared to steel ships, though they are not impervious to degradation from corrosion. It is important to identify how, when and where corrosion affects aluminium marine structures so that the excellent corrosion resistance of the material can be fully exploited.

This paper will firstly recall the main corrosion modes with respect to aluminium alloys used for marine applications: galvanic, aesthetic, crevice, pitting, intergranular, exfoliation and stress corrosion. Typical corrosion examples, as they've occurred in normal service conditions on existing aluminium car ferries, are then presented. Some corrosion cases found in these craft are investigated and the phenomena behind these corrosion issues are explained. The diagnosed corrosion problems are treated from a preventive maintenance approach and long-term solutions are applied.

As a naval architectural and marine engineering consultancy, Hart, Fenton's extensive experience in the inspection and refit supervision of aluminium car ferries has provided the basis the investigations presented. From this and in contrast to existing standard laboratory tests for aluminium corrosion, ongoing corrosion testing at Pechiney's Research Centre attempts to imitate actual conditions encountered in service to better estimate the long-term service performance of marine grade aluminium alloys. This partnership has resulted in the following presentation that will attempt to promote aluminium usage in marine applications through observation and a better understanding of the corrosion phenomena. The authors present solutions to these issues so that corrosion need not be considered an affliction in aluminium car ferries.

MITIGATION OF HYDROGEN EMBRITTLEMENT BY POTENTIAL CONTROL OF SACRIFICIAL ANODE CATHODIC PROTECTION

W R Jacob, The Corrosion Consultancy Limited, UK

Conventionally designed sacrificial anode systems produce potentials more negative than those strictly necessary to protect steels from seawater corrosion. In general, potentials will be in the range -950 to -1100 mV dependent on anode type and the presence and integrity of coatings. Such negative potentials can have a number of undesirable effects, including hydrogen embrittlement of some engineering materials [e.g. high strength steels] and premature deterioration of coatings. The presentation will describe a method of controlling the potentials produced by sacrificial anodes to values closer to those strictly required for protection. By the use of Schottky barrier rectifiers [SBR] in conjunction with the anodes, together with careful design, potentials in the range -775 to -825 mV can be ensured. At these potentials, the risk of embrittlement is much reduced. In order to establish a design methodology for such limited potential systems, experiments have been carried out using different types of SBR in a number of configurations. Details of the trial, and the results obtained, will be discussed. Sufficient information is now available to allow the design of limited potential cathodic protection systems operating within a closely controlled potential range.

STREAM 2– SESSION: MACROFOULING SESSION CHAIR: CLAIRE HELLIO

THE INFLUENCE OF EPIBIOSIS ON SUSCEPTIBILITY TO HERBIVORY AND FOULING OF THE RED SEAWEED CRYPTONEMIA SEMINERVIS

B A P da Gama, R P de A Santos, N G Silveira, J H S Miyamoto, M A O Lacerda, L Avellar and R C Pereira, Universidade Federal Fluminense, Brazil

Benthic marine macroalgae are particularly susceptible to biofouling (epibiosis) because they are sessile and are restricted to the photic zone, where conditions for the growth of fouling organisms are optimal. Epibiosis may provide a "protective coating" to the basibiont alga, but generally seems to be detrimental: the negative effects of fouling on host plants have been extensively documented in marine systems, and include a decrease of light and nutrient availability, a loss of flexibility resulting in increased brittleness, mechanical damage of host surfaces, changes of surface pH, and changes in drag which can cause breakage during storms. Host plants can also be fouled by higher preference epibionts, thus suffering not only the direct negative effects of being fouled, but also experiencing increased rates of grazing. The seaweed Cryptonemia seminervis (Rhodophyta, Halymeniaceae) is usually collected with a high percent cover of epibionts (> 50%), namely bryozoans and sponges. In order to assess the effect of epibiont cover on the susceptibility to herbivory and fouling of this seaweed, we compared herbivore consumption (amphipods and seaurchins) of fouled and non-fouled live specimens and extract-containing pellets of C. seminervis, as well as tested the influence of extracts on attachment of the fouling mussel Perna perna. The consumption of specimens fouled by the bryozoan Membranipora sp. (the more abundant epibiont on C. seminervis) was significantly higher than the consumption of surface-free ones, either by the amphipod community dominated by Elasmopus sp or by the sea-urchin Lytechinus variegatus (p < 0.05). Epibiosis by unidentified sponges also increased consumption of C. seminervis (p < 0.05). 0.05), suggesting that the common epibiont cover of this seaweed may really act as a lure to herbivores, i.e., epibionts may attract consumers that otherwise would not feed significantly on the host plant. This effect was also observed with the extracts of fouled and non-fouled specimens, i.e., extracts from fouled seaweeds were more prone to be consumed by herbivores (p < 0.05). On the other hand, fouled specimens were more chemically defended against fouling, since the mussel P. perna attached significantly more to surfaces coated with the extract of non-fouled Cryptonemia (p < 0.05). The results suggest that epibiosis is indeed onerous to this alga, and may somehow trigger the production of chemical defences against fouling organisms.

LINKING BARNACLE LARVAL AVAILABILITY TO SETTLEMENT ON ROCKY SHORES OF TROPICAL AND UPWELLING SHORES OF BRAZIL.

L F Skinner, Universidade do Estado do Rio de Janeiro, Brazil R Coutinho, IEAPM, Brazil

Barnacles are the most important species of fouling communities and its control on man-made structures spends large amounts of money every year. Usually, they reproduce on substrata and after development of egg to a nauplius stage, they are released to water column where they feed on phytoplankton to develop to a cyprid settling stage. In this work we relate the barnacle larval availability (nauplius and cyprids) to settlement season and to oceanographic characteristics of Cabo Frio region on Brazil. This region shows a contrasting between tropical and upwelled waters, mainly on spring-summer and development or transport of larvae are different. In this experiment, barnacle colonization on rocky shore was observed and also larval availability on plankton. Two species of barnacles were chosen: *Tetraclita stalactifera* and *Chthamalus bisinuatus*. Besides these two species do not occur on fouling communities of immersed structures, on rocky shores they are easily found and no other barnacle species colonize substrata on the same place. The results show differences on larval availability (nauplius or cyprid) due to the season of the year and to upwelling effect, with an influence on settlement. Also, different colonization strategies for *T. stalactifera* and *C. bisinuats* were observed.

SPATIAL PATTERNS IN TROPICAL FOULING ASSEMBLAGES ON NAVIGATIONAL BUOYS WITHIN THE COASTAL WATERS OF SINGAPORE

T M Sin, and S L M Teo, National University of Singapore, Singapore

This study examined spatial patterns in the fouling assemblages on navigational buoys in four geographic sectors in the coastal waters of Singapore. These buoys differed in physical characteristics, timing and length of deployment, all of which are expected to influence the structure of subtidal epibenthic communities. However, analysis of the assemblages using higher taxonomic resolution yielded clear spatial patterns. There were distinct differences in the structure of offshore and nearshore assemblages. Nearshore assemblages were dominated by the green mussel, Perna viridis and relatively high abundances (>20%) of Balanus reticulatus, while offshore assemblages were characterised by calcareous algae and ostreid molluscs. Among-sector differences were also observed, although there was greater overlap in assemblages on buoys in the two offshore sectors. In general, assemblages on buoys within a sector were more similar than were buoys among sectors. These differences were due in part to the composition of the assemblages, but were also distinguishable on the basis of relative percent cover of taxa such as P. viridis. Correspondingly, the largest spatial scale (kms) accounted for most of the variation in percentage cover of most taxa. The intermediate scale only accounted for the greatest amount of variation in cover of bryozoans and ascidians. The results of this study provide evidence that spatial differences in late-stage epibenthic assemblages may override initial differences due to the physical characteristics of the settlement substrata, as well as differences in timing and length of deployment. The mechanisms for this are still unclear, but differences in environmental conditions and larval availability are possible causes. The data presented here provides valuable information for subsequent studies on patterns of variation in the structure of epibenthic assemblages. . . .

RECRUITMENT AND SUCCESSION OF A FOULING COMMUNITY IN A STRESSING ENVIRONMENT IN THE NORTH COAST OF RIO DE JANEIRO STATE. BRAZIL

I Rosental Zalmon and W Krohling, Universidade Estadual do Norte Fluminense, Brazil

Sedimentation and turbidity can interfere negatively in the recruitment and succession of epibenthic species by closing and clogging the responsible structures for feeding and breathing. In the north of Rio de Janeiro State, Paraíba do Sul river increases the sedimentation and the turbidity of the coastal region mainly in summer months when the river discharge increases due to the rainy season. The environmental parameters salinity, pH, dissolved oxygen, nutrients and chlorophyll a present very reduced temporal fluctuations in the region. The hypotheses to be tested are: i) the seasonality in the recruitment of the fouling species occurs due to the temporal variation of rainfall and Paraiba do Sul river discharge; ii) changes in the succession process occur due to the submersion time and the colonization history of the organisms. A total of 36 reefballs, 100 meters apart from each other, were immersed 9 meters deep, 3 miles away from the coast in the north shore of Rio de Janeiro State (21°29 S', 41°00 W'), with concrete plates fixed in the external surface of each structure. Monthly, from January 2002 to February 2003, four recruitment plates and four succession plates were withdrawn from distinct modules. To preserve the sampling temporal independence, the plates were analyzed by destructive method through the point-intersection technique to obtain the cover percentage of the fouling organisms. The community structure descriptors were richness and Brillouin diversity. The influence of the environmental parameters in the recruitment and the relationship of the recruits versus residents were analysed through Pearson's correlation coefficient. The structural changes of the community were investigated by the turnover and the degree of structural difference index. Rainfall and Paraiba do Sul river discharge values reflected the two seasons that characterize the region: a period of severe and prolonged rain, mainly during the summer and a dryer one on the remaining months. The most abundant recruiter groups were Hydrozoa (7 taxa) and Cirripedia (5 taxa), while on the succession plates Hydrozoa (10 taxa) and Ectoprocta (6 taxa) were the dominant. The empty space did not present itself as a limiting factor for the recruitment of species with a cover percentage higher than 40%, while on the succession plates revealed a decreasing tendency, with less than 10% from the sixth month. The taxa Balanus spp, Clytia spp, Obelia spp, Bougainvillia sp and Ostrea sp alternated themselves in dominance, following irregular patterns and showed no definite period of recruitment. Although a significant correlation of the environmental parameters was not found with the abundance of the most representative taxa, it was observed higher levels of rainfall related to cover percentage of empty space. Other factors, besides sedimentation and turbidity, contribute in a negative way to the recruitment and development of the local fouling community: (1) the artificial reef is located in an area subjected to a high abrasion; (2) the local presents a low primary productivity (chlorophyll a) and (3) the region presents a lack of natural consolidate substrate. Such factors resulted in low abundance (maximum cover percentage lower than 40% on the recruitment plates), richness values (average number on the recruitment plates = 5 and on the cumulative plates = 10) and species diversity (average H on the recruitment plates = 1.3 and on the cumulative plates = 1.8), in comparison to the other fouling communities of Rio de Janeiro State. Concerning the interactions between recruits and residents it was observed mainly the facilitation mechanism between organisms of the same taxonomic category. Among the residents, the inhibition mechanism occurred more frequently between Balanus and Bougainvillia, Balanus and Ostrea, Bougainvillia and Obelia and Ostrea and Obelia. The facilitation and/or tolerance mechanisms were identified particularly between Balanus and Obelia and between Bougainvillia and Ostrea, respectively. The increasing tendency of richness values on cumulative plates (average number = 4 in the first month and 16 in the twelfth month), the significant alterations in the abundance of the main taxa Balanus, Bougainvillia, Obelia and Ostrea, the increase in the turnover rate and in the degree of structural difference index specially in the later stages (9 to 12 months) suggest that the community did not achieve a climax or a final stability. Paraiba do Sul river showed a negative influence in the recruitment of the local fouling species. In that local a simultaneous action of physical and biological factors occurs (sedimentation, turbidity, lack of natural consolidate substrate and low primary production) that overlap the temporal recruitment patterns of the epibenthic species. The monthly plates reflected the available larvae in the plankton in the different months of the year capable of overcoming the stressing factors. On the cumulative plates, the changes in the community structure and on turnover rate were constant through all the study. reflecting the substrate colonization history and the predominant species interactions.

Studies on the introduced kelp *Undaria pinnatifida* (Harvey) Suringar. The effect of reduced salinity on sporophtye production.

Fletcher, R L, Farrell, P and V. M. Capel Institute of Marine Sciences University of Portsmouth Ferry Road, Portsmouth, PO4 9LY UK

Abstract

The large, adventive, fouling kelp <u>Undaria pinnatifida</u>, (Harvey) Suringar was first reported for the British Isles in June 1994, growing on the sides of floating pontoons of a marina in the Hamble Estuary, on the south coast of England. As a result of a monitoring programme, it is now known to have spread to eleven other south coast marina sites, from Torquay in the west to Ramsgate in the east. In addition, <u>Undaria</u> has been found in the Channel Islands, growing at two marina sites in the Port of St Helier, Jersey. Despite its abundance at many of these marinas, <u>Undaria</u> has been very slow to colonise adjacent shores, and populations have only just been established to date in the benthos at the entrance to the Hamble Estuary and just outside Torquay Marina.

It is probable that small boats were responsible for the original introduction of Undaria from Brittany, and for the subsequent spread of the plants along the south coast. With very little competition from the native kelp species, the Undaria plants have flourished at the marina sites, especially in sheltered areas in the reduced salinity environments. The Undaria plants occur in quite high biomass levels, and have a wide seasonal distribution and phenology, with reproductive spore production extending well into the winter months. Plants show a marked preference for attachment to the introduced sea-squirt Styela Clava and may be responsible for the loss of the latter from marina sites in the Hamble. The distribution of Undaria in the Hamble has been borne out by laboratory culture studies which confirm Undaria to be more euryhaline than native kelp species, notably Saccorhiza polyschides.

Hull Fouling and Biological Invasions

Stephan Gollasch GoConsult Bahrenfelder Str. 73a 22765 Hamburg Germany

12th International Congress on Marine Corrosion and Fouling, University of Sc

Content

- · Biological Invasions Dimension of the Problem
- Invasion Vectors
- Relative Importance of Hull Fouling as Invasion Vector in Europe
- Case Study Hemigrapsus penicillatus
- Outlook
- Summary

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Biological Invasions -Dimension of the Problem

- Biological invasions are considered as one of the top four anthropogenic threats of the world's oceans
- World-wide a new aquatic invader is recorded in average every 9 weeks
- Approx. 100 introduced aquatic species are known from northern Europe (coastal waters)
- Costs to manage and eradicate unwanted introduced species (incl. terresrtrial habitats) world-wide are estimated as more than one billion Euro (!) annually

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Invasion Vectors

- · Key invasion vectors are shipping (ballast water and hull fouling) and intentional species introductions for e.g. aquaculture and research purposes
- · The world's merchant fleet consists of more than 40,000 vessels

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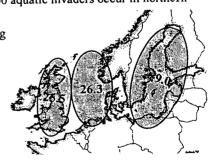
Importance of Hull Fouling as **Invasion Vector in Europe**

- · Ballast water is into focus today as the IMO Ballast Water Management Convention was signed in February 2004
- · However, many severely impacting invaders arrive in the hull fouling of ships (e.g. the Zebra Mussel Dreissena polymorpha, the barnacle Balanus improvisus and the hydroid Cordylophora caspia)

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Aquatic Invaders in Europe

- Approx. 100 aquatic invaders occur in northern Europe
- Hull fouling invaders in % of all invaders
- Mean = 20.3 %



Relative Importance

- Hull fouling is the most important invasion vector (approx. 20 %)
- However, this number may be an underestimate as invasion vectors for some species are not clear
- Just one example: Mussels may be introduced as larvae in ballast water or as adult specimens dropping of a ship hull
- Species with unclear invasion vectors are excluded from the number given above!

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Hull fouling on "cleaned" ships

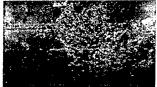
- Even on cleaned and antifouling painted ships hull fouling occurs at docking support strips
- No access during cleaning and painting in dock
- Up to 40 strips are in use
- Each strip measures up tp 40 x 150 cm
- 40 strips cover 240 m²

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Hull fouling at Support Strips

- This underwater image shows dense fouling (almost 100 % coverage) at docking support strip
- Up to 23 species were found during a German hull fouling study on a single ship

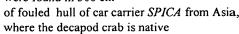


 Approx. 20 % of the hull fouling species are mobile, i.e. not attached to the hull

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Hemigrapsus penicillatus

- One of the most recent invaders in Europe
- First recorded in French waters in 1994
- During a German shipping study 6 crabs were found in 300 cm² of fouled hull of car ca



· This vessel likely introduced the crab to Europe

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Hemigrapsus penicillatus con't

- · Crabs were found in empty barnacle shells
- The crab is still spreading in Europe and reached the Dutch coasts in 2001. It is expected to arrive in Germany very soon
- Up to 20 indivduals are found per m² in France impacting upon native species by predation
- Concerns are expressed, especially for mussel culture sites

Please feel free to download the full report at www.gollaschconsulting.de

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Antifouling Paints

- According to an IMO Convention TBTpaints cannot be used anylonger
- Today, alternative paints are not as effective as TBT-based paints, especially in terms of the interdocking interval until paints need to be renewed
- As a consequence: Is there a higher invasion risk with TBT-free paints towards the end of the usual interdocking interval?

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Outlook

- Historically, the invasion rate increased towards the end of the 20th Century
- Future ship design improvements may result in an increased invasion rate
 - faster ships result in more frequent ship visits
 - larger ships increase the invasion probability (larger hull surface, higher ballast water capacity)
- Impact of TBT-free antifouling paints
- As result aquatic invasions are expected to continue

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Summary

- Most aquatic invaders in Europe are introduced by ships
- Within shipping, hull fouling is the dominating vector
- Solving the ballast water problem will not solve the problem of biological invasions
- Even cleaned ships show hull fouling at parts covered by docking support strips

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...my apologise for not being able to join the conference...

Thank you very much for your attention!

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		Stream i	The stand of the standard stan	· · · · · · · · · · · · · · · · · · ·		
0830-0930		Registra	ition & Coffee	The second secon		
0930-0940	Opening Address by Trevor Blakeley					
0940-1000	The Changing Face of Marine Corrosion and Biofouling: 50 Years of the COIPM (Gareth Jones & Bob Fletcher)					
1000-1045	PLENARY PRESENTATION - Molecular Cross-Talk between Species in the Formation of Marine Fouling Communities (James Callow Tony Clare)					
1100-1120	Fouling Control On Ships (Colin Anderson)	Keynote: Overview of the U.S. Office of Naval Research Program on Marine Biofouling Control (Stephen McElvany, Linda Chrisey and Paul Armistead, ONR)	Microfouling (Peter Steinberg)	Keynote Speaker: Biofilm dispersal during bacterial competition (<i>Liming Yan, Anja Wobker and J. Grant Burg</i> ess)		
1120-1140		Performance of biocide-free antifouling paints – Trials on deep- sea going vessels (B. Daehne, B. Watermann, M. Wiegemann, S. Sievers, R. Dannenberg & H. Michaelis)				
1140-1210		CALL THE STATE OF	offee			
1210-1230		Meeting the Fouling & Corrosion Needs of the US Navy (Ingle)		Host plant vs. biofilm derived settlement cues; a tale of two urchins (Peter Steinberg, Rebecca Swanson, Megan Watson, Rocky de Nys, Jane Williamson, and Naresh		
1230-1250	Fouling Control On Ships (Colin Anderson)	The role of underwater cleaning in controlling marine fouling (S. Moore & J. Jackson)	Microfouling & Prokarayote- Eukaryote Signalling Maureen Callow)	Kumar)		
1250-1310		Perspectives In Technology, Management and Economics and of TBT Free Antifouling for Commercial Ships (A. Touzot)		Culturable marine bacteria concerned in biofilm formation (Kae Kyoung Kwon, Yoo Kyung Lee, Kyeung Hee Cho, Soon Jae Lee and Hong Kum Lee)		
1310-1410			unch			
1410-1430	george and a second of the sec	Worldwide Performance Project for TBT-free Anti Fouling Systems (L. Kolie & H. Vold)		Screening for Marine Natural Products as Antifoulants In Brazilian Marine Organisms (Pereira, R.C, da Gama, B.A.P, Teixeira, V.L, Fleury, B.G & Coutinho, R)		
1430-1450		Mechanical cleaning of pleasure boats: a viable alternative to biocidal antifoulings? (P. Willemsen)	Natural Products (Peter Steinberg)	Seasonal variation in antifouling activity of crude extracts of the brown alga, Bifurcaria bifurcarta (Cystoseiraceae), against barnacle (Balanus amphitrite) cyprids and marine bacteria (Halomonas marina and Pseudoalteromonas haloplanktis). C Hellio, G Culioli, J-P Marechal, S Henry, H Thomas-Guyon, A S Clare and A Ortalo-Magne)		
1450-1510		The Antifouling Performance of Blocide Free Silicone Fouling Release Coatings Applied to a 6.4 Meter Power Boat (Geoffrey W Swain, Chris J Kavanagh, Brett S Kovach, Christina Darkangelo-Wood, Judith Stein, Kathryn Truby)		Structure-activity Relationship Studies toward Anti- barnacle Activity and Bloorganic Studies for the Elucidation of Anti-fouling Mechanism with Isocyano Compounds (Yoshikazu Kitano, Yasuyuki Nogata, Erina Yoshimura, Kazuhiro Chiba, Masahiro Tada, and Isamu Sakaguchi)		
1510-1540			Coffee			
1540-1600		Title TBA (Stephan Gollasch)		The effects of texture and pheromones on exploration and settlement of cyprids. (Gabrielle Prendergast, Lars Hannsen, Ritchie Head, Valeria Bers, Constanze Zurn, Jeremy Thomason)		
1600-1620		Environmental assessment and prediction of fate of ballast water in Europe (S Leweyr S Belson, F Fernandez Estarlich, P Wybrow, Z Sabeur T Laiz Alonso, A Morall)	Helder Undane.	Interspecific differences in the antifouling performance of mytilid microtopographies (A. V. Bers, L. Hansson, R. M. Head, G. S. Prendergast, J. C. Thomason, M. Wahl, C. Zürn)		
1620-1640	Aliens & Introductions (Bob Fletcher)	Characterisation and Management of Biofouling in Ships of the Royal Australian Navy (J F Polglaze, P R Smith, R H Hilliard, J A Lewis, L Montelli & B Wykes)	Biomimetics & Setttlement Cues (Tony Clare)	Molecular Characterization of the Settlement Inducing Protein Complex (SIPC) in Balanus Amphitrite (B. Dreanno, R.R. Kirby, K. Matsumura, S. Hawkins And A.S. Clare)		
1640-1700				Epitaondiol, a new Attachment Inducer from the brown alga Stypopodium Zonale (Dictyotaceae) (Angélica R. Soares, Andrea P. da Cunha, Valéria L. Talxeira, Renato C. Pereira & Bernardo A. P. da Gama)		
1700-1720				In vitro evidence for the influence of exudates from macroorganisms on recruitment dynamics in Western Baltic benthic assemblages (Mark Lenz, Monja Heede & Martin Wahl)		
1930-		Confer	ence Dinner			

1730 Louno Mar neely

0900-0945		PLENARY PRESENTATION - Biofouling, Antifouling and the	Environment: Where Biology and Chem	Tracking at the Nation of the Control of the Contro
1000-1040	Environmental & Legal Requirements (Julian Hunter)	Keynote Speaker: Global regulation of antifoulings – the IMO Antifouling Systems Convention (Heinz-Jochen Poremski)	Flow Effects & Surface Interactions (Robert Wood)	KEYNOTE: The Effect of Biofouling on Frictional Drag and Turbulent Boundary Layer Structure (Michael P. Schultz)
1040-1100		Environmental Risk Assessment – an essential part of regulatory decision-making (John Chadwick)		Flow, Depth and Fouling: The effects of local hydrodynamics on settlement of marine organisms (T. M. Sin, D. Rittschof and S.L.M Teo)
1100-1130			offee	
1130-1150	*	Environmental Emission Scenarios for antifouling paints – an OECD project with ramifications for countries regulating antifouling products (Eefje van der Aa)		Flow Effects on Corrosion of Stainless Steels (A Neville and X Hu)
1150-1210	Environmental & Legal - Requirements (Julian Hunter)	Measuring blocide release rates from antifouling coatings – work of the ISO / ASTM committees (Alistair Finnle)	Flow Effects & Surface Interactions (Robert Wood)	The Application of Rotating Cylinder Electrodes to Marine Corrosion Monitoring (Frank Walsh and Gareth Kear)
1210-1230		Choosing antifoulings for minimal environmental impact – a ship owners perspective (Christer Nygren)		Modelling erosion-corrosion of pure metals in aqueous slurries (B.D. Jana and M.M. Stack)
1230-1250		Developing globally compliant antifoulings – a coatings supplier perspective (Julian E Hunter)		Erosion and Erosion-Corrosion Performance of Cast and Thermally Sprayed nicket-aluminium bronze (R.C. Barik, J.A. Wharton, R.J.K. Wood and K.R. Stokes)
1250-1350			unch	
1350-1410		RIP TBT - is copper next? (Carol Mackle)		Nanoporous Thin Films for Non-Toxic Anti-Fouling Surfaces with Localized Pulsed Electric Field Capability (M. Anderson)
1410-1430		Copper in the Environment – a bloavailability/ecotoxicity study (Bryn Jones)	Fouling Control Using Surface Effects (Steven McElvany)	Engineering surface topographies to control marine fouling (Anthony Brennan, Michelle Carman, Thomas Estes, Adam Feinberg, James Schumacher, Leslie Holpkemeier-Wilson)
1430-1450		Photodegradation of Zinc and Copper Pyrithiones in Aqueous Environments (Yoshiłaka Yamaguchi, Akira Kumakura, Maki Isshigami, Yasuhiro Yamada, Kiyoshi Shibata, Tetsuya Sunda)		Control of ulva zoospore settlement via microtopographic cues (Anthony Brennan, James Callow, Maureen Callow, Michelle Carman, Thomas Estes, Adam Feinberg, James Schumacher, Leslie Hoipkemeier-Wilson)
1450-1520			offee	
1520-1540		Computer Modelling for Environmental Exposure Assessment of Antifouling Blocides (Robert J Fenn, George Polson)		Fouling Release Coatings Of Controlled Surface Energy Based On Thermoplastic Elastomers (Christopher Ober, Sitaraman Krishnan, Alexander Hexemer, Edward Kramer, John Finlay, James Callow, Maureen Callow)
1540-1600	٠	The environmental fate and effects of selected antifouling paint booster blocides (Kevin Thomas)		Novel antifouling surfaces modeled from nature (Andrew Scardino, John Lewis, Erol Harvey & Rocky De Nys)
1600-1620	Requirements (Julian	Determination of residues of the booster biocide dichlofluanid in water and marine sediment of Greek marinas (Casper Hamwijk)	Fouling Control Using Surface Effects (Steven McElvany)	Surface Properties of Marine Organism Adhesives and Their Possible Roles in Organism Release from Antifouling Coatings (G. Walker)
1620-1640		Biotests and Selected Chemical Analysis of Biocide-Free Antifouling Coatings Regarding Toxic Compounds (B T Waterman, S Sievers, R Dannenburg, J C Overbeke, J W Klinstra, O Heemken)		Kinetically-Trapped Segregating Mixtures Of Fluoropolymers And Linear Poly(Ethylene Glycols): Nanoscopically-Resolved Amphiphilic Surfaces: That Present Treacherous Terrain To Inhibit Blofouling (Karen L. Wooley, Chakravarthy S. Gudipati, Jeremiah A. Johnson, Kenya T. Powell, Gerald O. Brown)
1640-1700		Key Issues in Authorisation of Antifoulants under EU Laws:The outcome of the review of booster biocides in the UK (John Chadwick)		
1700-1830		· ·	r Session	

Thursday 29th July Stream 2 Stream 1 PLENARY PRESENTATION - Recent Developments in Microbiologically Influenced Corrosion: A Series of Paradoxes (Brenda Little) 0900-0945 Anaerobic fron Corrosion by Novel Microorganisms: Anti-microfouling activity of three extracts of marine algae from 1000-1030 Brittany, France (Alexandra Bazes, Magali Lartigue, Eric Mechanisms and Strategies for their Detection (J. Quémèner, Jean-Paul Braud, Nathalie Bourgougnon) Kuever) **Fouling Control Using** Biocorrosion (Sheelagh Chemicals (David Campbell & Iwona Beech) Arnold) Antifouling Activity Of New Thienopyridine Derivatives Accelerated Low Water Corrosion: Causes and Concerns (Bernardo A.P. da Gama, Luiz C.S. Pinheiro, Alexandre R. 1030-1100 (I.B.Beech, S.Gillard and S.A.Campbell) Azevedo, Alice M.R. Bernardino & Renato C. Perelra) Coffee 明和新疆 1100-1130 Fundamental Research at CORRODYS, the Centre for Marine and Biological Corrosion of Cherbourg (Jacques Extended Antifouling Coating Performance Through Daret, Delphine Bermond-Tilly, Emilie Dajoux, Isabelle Dupont, Christelle Ott, Samuel Pineau) 1130-1150 Microencapsulation (E. Haslbeck) Estimation of Antifouling Paint Activity by Means of Long-term Exposure Trials Evaluating the Biofouling and Corrosion Resistance of Copper Nickel Alloy Sheathing Mathematical Modelling and Selected Rotary Experiments: 1150-1210 from Tin-Based to Tin-Free Systems (Diego Meseguer Yebra, Materials. (S.A.Campbell and C.A.Powell) Søren Kill, Kim Dam-Johansen, Claus Weinell) **Fouling Control Using** Biocorrosion (Sheelagh Chemicals (David Campbell & Iwona Beech) Arnold) Synthesis and Evaluation of isocyanobenzen derivatives for Close-up of condenser biofouling and corrosion - old and antifouling activity against the barnacle Balanus amphitrite 1210-1230 (Yasuyuki Nogata, Yoshikazu Kitano, Erina Yoshimura, (P. Christiani) Takehiro Suzuki, Rie Kobayashi, and Isamu Sakaguchi) Testing Methodologies, Acceptance Criteria and a Critical Evaluation of Hydrochlone and Phosphoric Acid Based The potential use of proteolytic enzymes to control fouling by the green alga, Ulva sp., and the barnacle, Balanus amphitrite (ME Pettitt, SL Henry, JA Callow, ME Callow, AS Clare, I Schneider and K Allerman) 1230-1250 Chemicals for Descaling of Seawater Piping Materials (E. J. Lemieux K.E.Lucas, T.Wolejsza) - 45. Lunch 1250-1350 Saving sv Cutty Sark: Electrochemistry in Action (P Environmentally Friendly Ablative Fouling Deterrent Coating 1350-1410 Lawton, S A Campbell, I B Beech, S Gillard) (Guy Seabrook & Ernie Soeterik) Combinatorial High-Throughput Bacterial Biofilm Screen Antifouling Efficacy of Organic Coatings: New AF Coating for Assessment of Antifouling and Foul-Release Formulations and their Performances at Ayajin Harbor, East Performance of Marine Coatings (Shane Stafslein, 1410-1430 Coast of South Korea (M. Sidharthan, H. D. Bhattarai and Thomas Ready, James Bahr, David Christianson, Philip H.W. Shin) Modern Techniques in Biofouling Boudjouk) **Fouling Control Using** (Sheelagh Campbell & Iwona Chemicals (David Beech) Arnold) High Throughput Methods in the Development of Novel Marin Modern Surface Techniques in Biofouling (Recep Avcl) 1430-1450 Coatings (Dean C. Webster, Partha S. Majumdar, Abdullah Ekin, James A. Bahr, David A. Christianson) Application of AFM to Studying Adhesion, Deterioration and Microelastic Properties of Fouling-Release Surfaces The Transition to Tin-Free Coatings and Future Directions for in Simulted Marine Environment (Fernando Teran Arce. 1450-1520 Biofauling Control (John A. Lewis) Recep Avci, Iwona Beech, Keith Cooksey, Barbara Coffee 1520-1550 A Laboratory Bioassay for Assessing the Resistance of RNLI perspective on building restoration: ancient and Tropical Hardwoods to the Wood-Boring Crustacean Limnoria 1550-1610 modern (Howard Richings) (Simon Cragg, L Borges, J Williams, G Sawyer) Decay of Wood in the Conservation of Ships in the Solent: Electrochemical and Marine Conservation (Frank

Phsical Studies (F C Walsh, K Patterson)

Walsh)

Evening Reception at SOC

Donner

(L Skinner, S Silva, H Lavrado)

1610-1630

1630-1650

1800-2000

Marine Environment

(Andy Pitman)

Wood boring activity on tropical coast of Rio de Janeiro, Brazil

Stream 2

		Stream 1		
0900-0945	Called Services of the Services	PLENARY PRESENTATION - In Search	of the Perfect Ship Hull Coating (Geoff	Swaln)
1000-1030	Der.	In situ Release Behavior of Barnacles from Silicone Coatings (I. Singer, Greg Kowalke, Dean Wendt and Jongsoo Kim)		Impressed Current Cathodic Protection Equipment (Barry Torrance)
1030-1050		Adhesion of soft foulers to silicone coatings (Maureen E Callow, JA Finlay, M Chaudhury, JA Callow) Mauree -		Computer Simulation of Resistor Controlled CP of Steel in Seawater (S Paul, P Mitra)
1050-1110	Fouling Control Using Silicones (John Lewis)	Organically Modified Silicone Polymers for Antifouling/Fouling Release Coatings (Johnson Thomas, Saok-Bong Choi and Philip Boudjouk)	Corrosion Control Techniques and Materials (Keith Stokes)	Understanding Corrosion Issues in Aluminium Car Ferries: Corrosion Prevention and Control Techhniques (A Duran)
1110-1130				Mitigation of Hydrogen Embrittlement by Potential Control of Sacrificial Anode Cathodic Protection (W Jacob)
1130-1150		light B	uffet Lunch	
1235-1255	,	Peel release studies of doped silicone coatings against epoxy (pseudobarnacles) (I. Singer, Jongsoo Kim and Manoj K. Chaudhury)		The Influence of Epiblosis on Susceptibility to Herbivory and Fouling of the red seaweed Cryptonemia seminervis B A.P. da Gama, R P. de A. Santos, N G. Silveira, J H.S. Miyamoto, M A.O. Lacerda, L Avellar & R C. Pereira)
1255-1315	Fouling Control Using	Propeller Fouling Control Using Foul Release Coatings (R. Mutton, M. Allar, C.D. Anderson) Lobert Muffor	Macrofouling (Claire Hellio)	Linking Barnacle Larval Availability to Settlement on Rocky Shores of Tropical and Upwelling Shores Of Brazil (L. F. Skinner & R. Coutinho)
1315-1335	Silicones (John Lewis)	Release Behavior of Epoxied Pseudobarnacles from Silicone Coatings in High Speed Boat Tests (R. Quinn, Geoffrey Swain & I. Singer)	<u>.</u>	Spatial patterns in tropical fouling assemblages on navigational buoys within the coastal waters of Singapore (Sin, T.M. and S.L.M. Teo)
1335-1355				Recruitment And Succession Of A Fouling Community in a Stressing Environment in the North Coast of Rio De Janeiro State, Brazil (Ilana Rosental Zalmon& Werther Krohling)

1430 UMC-

The Royal Institution of Naval Architects

The 12th Congress on Marine Corrosion & Fouling, 27 - 30 July 2004

DELEGATE LIST

Delegates	Organisation	Country
		UNITED KINGDOM
ALDRED, Mr Nicholas	University of Newcastle upon Tyne	DENMARK
ALLERMANN, Mr Knud	Biolocus AS	U.S.A.
AMEY, Dr Ronald	Invista Inc	U.S.A.
AMOS, Mr Stuart	HRP Technology Inc	UNITED KINGDOM
ANDERSON, Mr Colin	International Coatings Ltd	NORWAY
ANDREASSEN, Mr Petter	Jotun A/S	UNITED KINGDOM
ARMITAGE, Miss Sophie	The Royal Institution of Naval Architects	UNITED KINGDOM
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BEACHAM, Ms Rachel	North Atlantic Fisheries College	UNITED KINGDOM
BEHRENDS, Dr Brigitte	University of Newcastle upon Tyne	GERMANY
BERS, Ms Anna	IFM - Geomar University of Newcastle upon Tyne	UNITED KINGDOM
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BOWMER, Dr Tim	TNO Chemistry	U.S.A.
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BROOKS, Dr Steve		U.S.A.
BROWN, Mr Richard	University of Rhode Island University of Strathclyde	UNITED KINGDOM
BUDDHADEV, Mr Jana	Heriot-Watt University	UNITED KINGDOM
BURGESS, Dr Grant	Naval Undersea Warfare Centre	U.S.A.
BURGESS, Dr Michelle	University of Birmingham	UNITED KINGDOM
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CHAPMAN, Mr John	Turkish Navy	TURKEY
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DUPLESSIS, Mr Hugo	Independent Surveyor	UNITED KINGDOM
ELBOURNE, Mr Peter David	University of Newcastle upon Tyne	UNITED KINGDOM
FARRELL, Mr Peter	Leigh Paints	UNITED KINGDOM
FENN, Dr Robert	Arch Chemicals Inc	UNITED KINGDOM
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ZURN, Miss Constanze

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Lewis, John

From:

Sophie Armitage [sarmitage@rina.org.uk]

Sent:

Saturday, 3 July 2004 2:04 AM

To:

'iohn.lewis@dsto.defence.gov.au'

Subject: The 12th International Congress on Marine Corrosion and Fouling

Dear Mr Lewis

Thank you I have received your registration form and I can confirm that your place has been booked for The 12th International Congress on Marine Corrosion and Fouling conference, 27th - 30th July 2004, Southampton University.

The conference is being held in the Physics Building (No 46). Registration, refreshments and lunch will all be held in the Staff Social Centre. Map 1 shows Highfield Campus and denotes the Physics Building (no 46) and the Staff Social Centre.

Please register at the Garden Court Restaurant in the Staff Social Centre to pick up your delegate pack before attending the conference. Registration is from 15:30 to 18:30 on Monday 26th July and from 08:30 - 09:40 on Tuesday 27th July 2004.

If you have requested accommodation, four nights (26th to 29th July) will be reserved for you at the Glen Eyre Complex (see enclosed map). If you are staying in en-suite accommodation you will be staying in South Hill Halls A, B or C (you will be advised of your exact location when you collect your room key). If you have reserved standard accommodation you will be staying in either Chamberlain Halls or J block behind the Central Reception (again you will be advised when you arrive to pick up your key).

Please note that you have to pick up your key for your accommodation <u>AFTER</u> 12 noon on the 26th July, if you will be arriving earlier please let the conference dept know so we can arrange individual room registration for you. When you arrive you will need to go to the *Central Reception & Key Collect Point* - denoted by a key on Map 2. They will then let you know which halls you are staying in. Breakfast and dinner will be served in the Chambers Restaurant which is located in Chamberlain Hall next to South Hill Halls. Breakfast will be served from 07:30 - 08:30 Tuesday morning to Friday morning. Dinner will be served on Monday 26th and Wednesday 28th at 19:30 and Thursday 29th at 20:30. The conference dinner will be held on Tuesday eve at 17:00 at the Garden Court Restaurant at in the Staff Social Centre.

I have also enclosed a dietary requirement form; if you have any special requirements please let me know as soon as possible.

If you have any further queries please do not hesitate to contact me on +44 (0)20 7201 2401 or visit www.soton.ac.uk/~marine04

Kind Regards

Sophie Armitage

Conference Organiser
The Royal Institution of Naval Architects
10 Upper Belgrave Street
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