

15th International Congress on Marine Corrosion and Fouling

organised by Newcastle University on behalf of

Comité International Permanent pour la Recherche sur la Préservation des Matériaux en Milieu Marin (COIPM)

PROGRAMME and ABSTRACTS

The Sage Gateshead 25-29th July 2010

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Programme

	SUNDAY	, 25 th JULY			
16.00-19.00	Registration (Concourse, Th		ad)		
		, 26 th JULY	•		
08.00-08.45	Registration (Concourse, Th		ad)		
08.45-09.00	Welcome				
09.00-09.40	26-H2-P:Plenary session (Ha	ll Two) - Schultz	:: Economic impact of		
	biofouling on a naval ship	.,	p		
09.40-10.00	Refreshment break				
	Session 1 (Hall Two)		Session 2 (Barbour)		
	Hydrodynamics & ship		Biofouling in industrial		
	efficiency (Swain)		cooling water systems (Bruijs)		
10.00-10.15	26-H2-1-1:Haslbeck: US Navy evaluation of a fouling release coating: biofouling control, physical performance, and impact on fuel economy	10.00-10.30	26-B-1-1: Rajagopal (keynote): Biofouling and its control in industrial cooling water systems: an overview of the present and a peek into the future		
10.15-10.30	26-H2-1-2:Hasselaar: Investigation into the development of an advanced ship performance monitoring and analysis system				
10.30-10.45	26-H2-1-3:Yebra: Fouling control products: value proposition and associated atmospheric pollution profile	10.30-10.45	26-B-1-2: Wither: Industrial cooling water systems: discharge controls in the European Union		
10.45-11.00	26-H2-1-4:Klijnstra : Rapid screening of friction drag properties	10.45-11.00	26-B-1-3: Venhius : Root-cause analyses of corrosion in heat-exchangers: a case study		
11.00-11.15	26-H2-1-5: Kanar: Innovative hydrodynamic approaches for drag properties evaluation of advanced antifouling coatings elaborated in nanotechnology fields, on basis of AMBIO project results	11.00-11.15	26-B-1-4: Christiani: Monitoring by an electrochemical integrated system of corrosion and antifouling treatments on aluminum brass condenser tubes		
11.15-11.30	26-H2-1-6: Atlar: Boundary layer drag and surface roughness characteristics of nanostructured coatings	11.15-11.30	26-B-1-5: Lamb : Electrolytic anti-fouling systems for pumped water intakes in the oil + gas industry		

	on an axysymmetrical slender body tested in a		
11.30-11.45	cavitation tunnel 26-H2-1-7: Gysel: The environmental benefits of surface treated coatings (STCs)	11.30-11.45	26-B-1-6: Glazer: Characterization of the marine organisms on artificial substrates in a power plant in the southeastern Mediterranean
11.45-12.00	26-H2-1-8: Senda: Drag reduction for ships due to polymer release from painted surface by Toms effect	11.45-12.00	26-B-1-7: Venugopalan: Biofouling in Indian nuclear power plants – an overview of problems encountered and lessons learned
12.00-12.15	26-H2-1-9: Sampson: Cavitation and open water performance analysis of two types of antifouling propeller coatings	12.00-12.15	26-B-1-8: Macdonald: Industrial Cooling Seawater in the Middle East - a case study of operation optimisation and reduced environmental impact
12.15-12.30	26-H2-1-10: Swain: The mechanics and hydrodynamics of fouling release coatings	12.15-12.30	General discussion
12.30-14.00	Lunch	I	6 1 4/5 1
	Session 3 (Hall Two) Regulatory and		Session 4 (Barbour) Marine bioadhesion
	environmental (Hunter)		(Wilker)
14.00-14.30	26-H2-2-1: Hunter (keynote): Antifouling regulations – regulatory approach to minimise their impact on the environment – how far have we come	14.00-14.20	26-B-2-1: Wahl : Interfacial spectroscopy: in situ approaches to understand sticky contacts
	since TBT?		
14.30-14.50	since TBT? 26-H2-2-2: Low: Current regulatory issues for antifouling products under the EU Biocidal Products Directive	14.20-14.40	26-B-2-2: Aldred: Imaging temporary adhesion and surface exploration by barnacle cyprids
14.30-14.50	26-H2-2-2: Low: Current regulatory issues for antifouling products under the EU Biocidal Products	14.20-14.40	temporary adhesion and surface exploration by

	antifordings in Californian		the corpulid <i>Undraides</i>
	antifoulings in Californian marinas		the serpulid <i>Hydroides</i> dianthus
15.30-16.00	Refreshment break	I	
16.00-16.20	26-H2-2-5: Blanck: A	16.00-16.20	26-B-2-5: Stewart : The
	proposed strategy for risk		Sandcastle glue of
	assessment of antifouling		Phragmatopoma californica
	combinations in paint		
	products		
16.20-16.40	26-H2-2-6: Shibata:	16.20-16.40	26-B-2-6: Flammang : The
	Prediction of		cement of sabellariid tube-
	environmental		dwelling polychaetes: A
	concentration for a photo-		complex composite adhesive material
	degradable anti-fouling		adnesive material
16.40-17.00	agents 26-H2-2-7: Long: Advances	16.40-17.00	26-B-2-7: Elwing:
10.40-17.00	in understanding of copper	10.40-17.00	Adsorption and cross-
	in the environment and the		linking of marine
	impact on its regulation		bioadhesives
17.00-17.20	26-H2-2-8: Lindblad:	17.00-17.20	26-B-2-8: Cha : Mussel
	Environmental risk		bioadhesion: Study using
	assessment of		recombinant mussel
	Metatomodine – an		adhesive proteins and their
	effective metal-free		coacervated forms
	antifouling biocide		
17.20-17.40	26-H2-2-9: Taylor : Release	17.20-17.40	26-B-2-9: Wilker: Chemical
	rate of copper pyrithione		insights on how marine
	from coated fish nets –		biological materials stick
	comparison of results from		
	a modified test procedure modelled after ASTM		
	D6903		
18.00-20.00	Welcome reception – Discov	v erv Museum (si	ponsored by International
	Paint Ltd.)	(-)	,
	Buses leave The Sage at 17.4	5-18.00	
	TUESDAY	, 27 th JULY	
09.00-09.40	27-H2-P: Plenary session (Ha	all Two) – Willia	ms : Fouling Control
	Technology: Changes throug	h Tyne	
09.40-10.00	Refreshment break	I	
	Session 5 (Hall Two)		Session 6 (Barbour)
	A) Industry perspective		Lab/field assessments of
	(Pereira)		antifouling coating
10.00-10.15	B) Aquaculture (Dürr) 27-H2-1-1: Tomasgaard:	10.00-10.30	technologies (Stafslien) 27-B-1-1: Rittschof
10.00-10.13	New generation of copper	10.00-10.50	(keynote): A perspective
	(I) oxide for antifouling		from 2 decades of academic
	paints		lab and field-testing of
10.15-10.30	27-H2-1-2: Lindblad:	1	experimental and
	Medetomidine – from lab		commercial coatings
	bench research towards		
	market introduction		
10.30-10.45	27-H2-1-3: Yebra : The	10.30-10.45	27-B-1-2: Callow:

	winding road to commercial products - Hempel's experience		Integration of laboratory and field testing within the AMBIO project
10.45-11.00	27-H2-1-4: Risberg: Water uptake of commercial antifouling coatings with binders based on trialkylsilyl acrylates or metal acrylates/carboxylates	10.45-11.00	27-B-1-3: Coutinho : Testing an analogue of antifouling from a marine sponge
11.00-11.15	27-H2-1-5: Touzot : A point at the operation for containership	11.00-11.15	27-B-1-4: Anton: ECOPAINT PACA Project: Antifouling activity of biocidal compounds through bioassays and field immersion test
11.15-11.30	27-H2-2-1: Dürr : Biofouling pressure at European aquaculture facilities over a 2-year period	11.15-11.30	27-B-1-5: Webster: Correlation between lab assays and field testing results for siloxane- polyurethane fouling- release coatings
11.30-11.45	27-H2-2-2: Guenther: The development of biofouling on commercial salmon cage nets in Mid-Norway	11.30-11.45	27-B-1-6: Teo : Rapid field testing of foul-release coatings using a novel waterjet testing apparatus
11.45-12.00	27-H2-2-3: Powell: Innovation in aquaculture cages using copper based alloys	11.45-12.00	27-B-1-7: Stafslien: Rapid biological laboratory assessments of antifouling marine coating performance: their utility and relationship to static ocean immersion testing
12.00-12.15	27-H2-2-4: Woods: Biofouling on Greenshell™ mussel (Perna canaliculus) farms: a preliminary assessment and potential implications for sustainable aquaculture practices	12.00-12.15	27-B-1-8: Salta: Bioassay screening and imaging for antifouling performance of novel natural products
12.15-12.30	27-H2-2-5: Filtridge: Foul play or facilitation? The impact of hydroid biofouling on mussel aquaculture in Port Phillip Bay, Australia	12.15-12.30	27-B-1-9: Camps : A reliable marine antifouling bioassay based on in vitro adhesion: comparison of the response of five pioneer bacteria
12.30-14.00	Lunch		
	Session 7 (Hall Two)		Session 8 (Barbour)
	New technologies to		General aspects of fouling I

	control fouling (Callow)		(tbc)
14.00-14.30	27-H2-3-1: Brennan	14.00-14.20	27-B-2-1: Zargiel: Variation
	(keynote): Biomimetic		in diatom community
	microtopographies – A		structure on antifouling and
	green, antifouling		fouling release coatings
	technology		from three static immersion
			test sites in Florida
14.30-14.45	27-H2-3-2: Walker : Waterstable diblock polystyreneblock-poly(2-vinyl pyridine) and diblock polystyrene-	14.20-14.40	27-B-2-2: Briand: What is the influence of the nature of submerged artificial surfaces on the structure of
	block-poly(methyl methacrylate) cylindrical patterned surfaces inhibit		microbial biofilm communities?
	settlement of zoospores of		
	the green alga <i>Ulva</i>		
14.45-15.00	27-H2-3-3: Galli: Macromolecular engineering of nanostructured-surface films with amphiphilic copolymers for application in marine biofouling release coatings	14.40-15.00	27-B-2-3: Satheesh: Extracellular polymeric substance synthesis by bacteria during adhesion on surfaces: Influence of substratum variability and environmental factors
15.00-15.15	27-H2-3-4: Ober: Ambiguous, amphiphilic surfaces for fouling resistant coatings	15.00-15.20	27-B-2-4: Dreanno : A new marine biofilm forming model: <i>Pseudoalteromonas haerens</i>
15.15-15.30	27-H2-3-5: Wooley: Nanoscopically-complex, amphiphilic, non-toxic antifouling marine coatings: From hyperbranched fluoropolymer- poly(ethylene glycol)- derived networks to new generation materials		
15.30-16.00	Refreshment break		
16.00-16.15	27-H2-3-6: Majumdar: Polysiloxanes with tethered quaternary ammonium salts as novel antifouling/fouling-release coatings	16.00-16.20	27-B-2-5: Goodes: Determination of distribution of paint additives and assessment of their leaching rates using Laser Scanning Confocal Microscopy
16.15-16.30	27-H2-3-7: Jiang: Development of environmentally benign, durable and effective ultra low fouling marine coatings	16.20-16.40	27-B-2-6: Dobretsov: Inhibition of biofouling by quorum sensing inhibitors

16.30-16.45	27-H2-3-8: Scardino: Novel technologies to reduce biofouling on vessels when in port	16.40-17.00	27-B-2-7: Palanisamy: A comparative study on the antifouling activity of Indian and Caribbean Sea grasses extracts	
16.45-17.00	27-H2-3-9: Wang: Preparation and topography observation of faveolate microstructure surface antifouling material	17.00-17.20	27-B-2-8: da Gama: Antifouling activity in Sargassum vulgare: within- thallus variation and polyphenolic content	
17.00-17.15	27-H2-3-10: Jonsson: A new antifouling technology based on oxygen depleted surfaces	17.20-17.40	27-B-2-9: Thabord: Sargassum polyceratium chemical and physical impact on major coral reef invertebrate recruitment in Martinique (FWI)	
17.15-17.30	27-H2-3-11: Dahlström: Anti-barnacle effect of medetomidine in soft and hard coatings			
18.30-10.00	Poster session (Northern Ro	ck Foundation H	all)	
	P1: CUMBOR ET AL.: EVALUATION OF HEAVY METAL AND TBT CONTAMINATION ASSOCIATED WITH SHIPPING IN MUSSELS AND SEDIMENT ALONG THE WEST COAST OF THE UK			
	P2: ZHANG XIAODAN: AN ANTIFOULING-PAINTS PROJECT IN CHINA AND CHINA GREEN LABELING STANDARD FOR ANTIFOULING PAINTS			
	P3: SUGDEN ET AL.: COMPLEX INTERACTIONS BETWEEN ABIOTIC DISTURBANCE AND SURFACE REFUGE AND SHAPE DETERMINE THE			
SETTLEMENT OF MARINE PROPAGULES P4: VON WALDEGGE: VARIABILITY AND SUCCESSION OF FO CORROSION ON COATINGS AND ADHESIVES AT DIFFERENT THE GERMAN NORTH SEA				
	P5: SOLOMON: FOULING CONTROL: MAKING THE ECO-EFFICIENT CHOICE P6: PENG ET AL.: EFFECT OF INHIBITING WASHES ON COATING			
	P7: BIN ET AL.: STUDY ON THE ANTI-CORROSION PERFORMANCE OF			
	ORGANIC COATINGS UNDER SIMULATED DEEP SEA ENVIRONMENT			
	P8: MESSANO ET AL.: THE INFLUENCE OF MARINE MICROFOULING			
	COMMUNITY ON THE OPEN CIRCUIT POTENTIAL BEHAVIOR OF A DUPLEX			
	STAINLESS STEEL UNDER FIELD AND LABORATORY CONDITIONS P9: MCBETH ET AL.: IRON-OXIDIZING ZETAPROTEOBACTERIA ASSOCIATED			
	WITH STEEL CORROSION IN NEARSHORE MARINE ENVIRONMENTS			
	P10: CHAW ET AL.: FEASIBILITY STUDY OF AN AUTOMATED ONLINE			
	CLEANING SYSTEM FOR SEAWATER HEAT EXCHANGERS			
	P11: DÜRR ET AL.: SILICONE COATINGS AND CLEANING - ANTIFOULING STRATEGY FOR FISH NETS AND OYSTER TRAYS			
	P12: MARTIN: ANTIFOULING			
	P13: MARIMUTHU ET AL.: EF		, ,	
	AGAINST THE FOULER – AN A			
	P14: MARANDA ET AL.: EFFIC	CACY OF AN ISOT	HIAZOLIN COMPOUND AS A	

FOULING DETERRENT: RESPONSE OF A PENNATE DIATOM

P15: YANG ET AL.: LARVAL METAMORPHOSIS OF THE MUSSEL *MYTILUS GALLOPROVINCIALIS* LAMARCK, 1819 IN RESPONSE TO

NEUROTRANSMITTER BLOCKERS AND TETRAETHYLAMMONIUM

P16: THOMÉ ET AL.: CHEMISTRY-DEPENDENT SURFACE CONDITIONING AND ITS IMPLICATION FOR SETTLEMENT OF SPORES OF THE GREEN ALGA *ULVA*

P17: PETRONE ET AL.: IN SITU ATR-IR SPECTROSCOPIC AND ELECTRON MICROSCOPIC ANALYSES OF *UNDARIA PINNATIFIDA* SPORE SETTLEMENT

P18: MCMONAGLE: OUTER SHIP HULL CHARACTERIZATION USING PHOTOMETRIC ANALYSIS

P19: COOGAN & SWAIN: MACROFOULING COMMUNITIES ON FOULING RELEASE COATINGS FROM THREE STATIC IMMERSION TEST SITES IN FLORIDA

P20: RAHMAN ET AL.: WATERBORNE POLYSILOXANE-URETHANE-UREA FOR POTENTIAL MARINE COATINGS

P21: ALDRED ET AL.: EFFECTS OF SURFACE TEXTURE ON THE ATTACHMENT STRENGTH OF BARNACLES AND THEIR LARVAE

P22: FINLAY ET AL.: THE MAPPING OF ALGAL ATTACHMENT SITES ON MICRO-PATTERNED SURFACES

P23: COOPER ET AL.: KINETIC ATTACHMENT OF *ULVA* ZOOSPORES TO TOPOGRAPHICALLY MODIFIED SURFACES

P24: RAMASUBBURAYAN ET AL.: EVIDENCE FOR THE ANTIFOULING ACTIVITY OF SELECTED MANGROVES

P25: HAYES ET AL.: POTENTIAL OF MICROALGAE EXTRACTS FOR ANTIFOULING APPLICATION: PRELIMINARY RESULTS

P26: VANCE & THOMASON: AN ENVIRONMENTALLY BENIGN METHOD FOR PREVENTING FOULING

P27: XUE & JIANG: ZWITTERIONIC-BASED MATERIALS AS ENVIRONMENTALLY BENIGN, DURABLE AND EFFECTIVE ULTRA LOW FOULING MARINE COATINGS

P28: COLAK & TEW: NOVEL DUALLY FUNCTIONAL ZWITTERIONIC POLYMERS AND THEIR ANTI-BIOFOULING PROPERTIES

P29: BRYANT ET AL.: SURFACE CHARACTERISTICS OF MULTI-COMPONENT XEROGELS WITH AND WITHOUT SEQUESTERED SELENOXIDE CATALYST AND THEIR EFFECTS ON BIOFOULING

P30: SOKOLOVA ET AL.: ALKYL CHAIN LENGTHS AND RATIOS: FACTORS IN CREATING A XEROGEL WITH SURFACE CHARACTERISTICS SUITABLE FOR BARNACLE REMOVAL

P31: GARCIA ET AL.: INHIBITION OF BYSSAL THREAD FORMATION OF LIMNOPERNA FORTUNEI BY NATURAL PRODUCTS ISOLATED FROM THE BROWN ALGA *DICTYOTA DICHOTOMA*

P32: PÉREZ ET AL.: APPROACHES TO MARINE BIOFOULING CONTROL BY THYMOL BASED PAINTS

P33: STUPAK ET AL.: EFFECT OF THYMOL ON INVASIVE GOLDEN MUSSEL *LIMNOPERNA FORTUNEI*

P34: YUNLU ET AL.: NOVEL BORON CONTAINING ANTIFOULING PAINTS **P35: BLIHOGUE & ILAN:** ANTI-MICROFOULING ACTIVITY FROM MARINE SPONGE-ASSOCIATED BACTERIA

P36: BLIHOGUE ET AL.: ANTIFOULING ACTIVITY OF TERPENES ISOLATED FROM MARINE INVERTEBRATES

	P37: ZHENG JIYONG ET AL: AI			
	COATINGS CONTAINING CRU	DE EXTRACT OF (GREEN ALGAL <i>ULVA PERTUSA</i>	
	P38: BLIHOGUE ET AL.: ARE A	ALKYLPYRIDINE-B	ASED COMPOUNDS SUITABLE	
	BIOCIDES FOR ANTIFOULING	PAINTS?		
	P39: ANTON ET AL.: ECOPAINT PACA PROJECT: NEW TECHNOLOGIES OF			
	NON-TOXIC ANTIFOULING PAINTS			
	P40: ARRHENIUS: COMBINED EFFECTS OF ANTIFOULANTS – SYNERGISTIC,			
	ADDITIVE OR ANTAGONISTIC EFFECTS?			
	P41: WENDT ET AL.: THE EFFICACY OF ANTIFOULING BIOCIDES: A			
	SYSTEMATIC APPROACH			
	P42: KANIA & KANAR: MEASUREMENTS OF ROUGHNESS OF NEW			
	ANTIFOULING COATINGS FOR		NDUSTRY ELABORATED	
	WITHIN THE AMBIO PROJECT			
	P43: BENDAOUD ET AL.: PHC			
	CHARACTERISATION AND IMI			
	P44: MARIMUTHU: BIOFOUL			
	GRANDE ISLAND OF GOA, WE			
	P45: GOHAD ET AL.: VISUALIZ			
	SENSORY ORGANS OF OYSTEI	R AND BARNACLI	SETTLEMENT STAGE	
	LARVAE		DECEDED IN THE CARRIE OF	
	P46: GALLUS ET AL.: PRESENCE BALANUS AMPHITRITE (=AMI			
	CIRRIPEDIA)	PHIDALANUS AIVI	PHITKITE) (CROSTACEA,	
		STICKING! NITRI	OVIDE REDUCES THE	
	P47: THOMPSON ET AL.: NO STICKING! NITRIC OXIDE REDUCES THE ADHESION OF FOULING ALGAE			
	P48: HOLM & HASLBECK: EFFECT OF REPEATED CLEANINGS USING			
	MULTIPLE TOOLS ON CONDITION OF A FOULING-RELEASE COATING			
	P49: QUINIOU ET AL.: TESTIN	IG METHODS TO	ASSESS BOTH THE EFFICACY	
	AND ECOTOXICITY OF ANTIFO	DULING COATING	iS	
	P50: SHANKAR & PUNITHA: ANTIFOULING ACTIVITY OF THREE BACTERIAL			
	STRAINS ASSOCIATED WITH MARINE SPONGE			
	P51: STAPATHY ET AL.: BIOF			
	WATER SYSTEM OF PROTOTY		R REACTOR - A TROPICAL	
	MARINE ENVIRONMENT CASI			
		POSTERS IN WE	LCOME PACK	
	WEDNESDA	•		
09.00-09.40		=	The Study of Microbiologically	
	Influenced Corrosion in Marin	ne Environments	– A Sea Change	
09.40-10.00	Refreshment break			
	Session 9 (Hall Two)		Session 10 (Barbour)	
	New developments in		Marine corrosion -	
	fouling-release technology		materials (Little)	
	(Webster)			
10.00-10.30	28-H2-1-1: Anderson	10.00-10.15	28-B-1-1: Francis : The	
	(keynote): Innovation in		performance of	
	foul release: more about		superduplex stainless steel	
	doing, less about dreaming		in different types of	
		10.15.10.20	seawater	
		10.15-10.30	28-B-1-2: Powell: Long term	
			studies of the performance	

10.30-10.45	28-H2-1-2: Lin: Study on the antifouling ability	10.30-10.45	of copper-nickel alloy sheathing for the splash zone corrosion protection of offshore structures 28-B-1-3: Xiaoyan: Material database on corrosion
	improvement of silicone- based coating with poly (acrylamide-silicone)		control technology and protection of ocean engineering structures
10.45-11.00	28-H2-1-3: Baum: Foul release performance of flow point defined physical gels prepared from poly(dimethylsiloxane)	10.45-11.00	28-B-1-4: Kanematsu: Biofouling of chromium and nickel based materials in marine environment
11.00-11.15	28-H2-1-4: Chisholm: Novel, amphiphilic polysiloxane fouling- release coatings	11.00-11.15	28-B-1-5: Kawakami : Bacterial adhesion to copper alloyed antibacterial stainless steel surfaces
11.15-11.30	28-H2-1-5: Tribou: Investigation of grooming tools for ship hull coating maintenance	11.15-11.30	28-B-1-6: Kanematsu : Biofouling on EAF stainless steel oxidizing slag in marine environment
11.30-11.45	28-H2-1-6: Murosaki: Observation of barnacle settlement and growth process on soft and wet hydrogels	11.30-11.45	28-B-1-7: Makama: Cathodic delamination of cable connector assemblies: mechanisms, materials and testing protocols
11.45-12.00	28-H2-1-7: Majumdar: Novel antimicrobial, antifouling/fouling-release coatings containing quat- functional POSS compounds	11.45-12.00	28-B-1-8: Bruin: Using electrochemical impedance spectroscopy and microscopy for evaluation of ballast tank coating degradation by microorganisms
12.00-12.15	28-H2-1-8: Webster : Tough fouling-release coatings based on self-stratification	12.00-12.30	Q&A
12.15-12.30	28-H2-1-9:Conlan: The effect of modulus and thickness of polydimethylsiloxane coatings on the settlement and adhesion of <i>B. amphitrite</i>		
12.30-14.00	Lunch	I	
	Session 11 (Hall Two)		Session 12 (Barbour)
	Biocidal antifouling technology (Finnie)		Microbiologically - influenced corrosion (Little)
14.00-14.30	28-H2-2-1: Ashmore : Sea-Nine(TM) CR: a new, microencapsulated marine	14.00-14.30	28-B-2-1: Johnston : Biodeterioration of the RMS Titanic, microbiological

	antifouling product		assessment, 1996 to 2010
14.30-14.45	28-H2-2-2: Nydén (on	14.30-14.45	28-B-2-2: Rao: Microbially
	behalf of Nordstierna):		induced localized corrosion
	New approach to		of type 316L stainless steel
	microcapsule synthesis –		in a recirculating seawater
	replacement of a		system
	hazardous chemical		3,000
14.45-15.00	28-H2-2-3: Nydén: Release	14.45-15.00	28-B-2-3: Campbell:
	from painted surfaces: Free		Electrochemical and
	and encapsulated biocides		microbiological
	·		contributions to the
			corrosion of 70/30 CuNi
			Alloys in seawater
15.00-15.15	28-H2-2-4: Backhaus:	15.00-15.15	28-B-2-4: Jeffrey: The effect
	Employing classical mixture		of sterilisation on the
	toxicity concepts for the		corroding of mild steel in
	optimization of biocide		coastal seawater
	combinations for		
	antifouling paints		
15.15-15.30	Q&A	15.15-15.30	Q&A
15.30-16.00	Refreshment break		
16.00-16.15	28-H2-2-5: Jackson:	16.00-16.15	28-B-2-5: Duan: Corrosion
	Development of antifouling		mechanism driven by
	paints for newbuildings -		marine electro-active
	more than just good		biofilm
15 15 15 20	antifouling performance	46454630	20 0 0 0 0 0 0
16.15-16.30	28-H2-2-6: Bressy:	16.15-16.30	28-B-2-6: Miyano: The
	Aqueous-based acrylic		study of biofilm formation and the electrochemical
	miniemulsions: a family of seawater erodible		behavior of some metals in
			natural marine water
	polymers with tunable mechanical and erosion		natural marine water
	properties		
16.30-16.45	28-H2-2-7: Hellio: New	16.30-16.45	28-B-2-7: Kumar: Etching
10.30-10.43	functionalized	10.50-10.45	initiated corrosion of
	oligoisoprenes based		stainless steel 316L by the
	flexible antifouling coatings		cement of the barnacle,
	with antimicrobial		Amphibalanus reticulatus
	properties		Ampinibalanas reticulatas
16.45-17.00	28-H2-2-8: Pinori : Post	16.45-17.00	28-B-2-8: Lee: Novel MIC
	Settlement Inhibition (PSI)	10.15 17.00	mechanisms associated
	of barnacle growth,		with storage of alternative
	Balanus improvisus. A		fuels in marine
	novel approach in marine		environments
	anti-fouling control		
17.00-17.15	28-H2-2-9: Ramotowski:	17.00-17.15	28-B-2-9: Duan: Application
_	New, biofouling-resistant		of atomic force microscopy
	elastomers for acoustic		in the study of sulfate-
	applications		reducing bacteria biofilm
17.15-17.30		17 15 17 20	-
17.13 17.30	Q&A	17.15-17.30	Q&A

	Buses leave The Sage at 18.3		
	THURSDAY	•	
09.00-09.40	29-H2-P: Plenary session (Havector of invasions: risky beh	=	_
09.40-10.00	Refreshment break		
	Session 13 (Hall Two)		Session 14 (Barbour)
	Fouling as a vector for invasive species (Ruiz)		General aspects of fouling II (Swain)
10.00-10.20	29-H2-1-1: Teo: Survey of sessile marine fouling organisms found on navigational buoys in Singapore's coastal waters	10.00-10.20	29-B-1-1: Vance : The effect of ocean acidification upon macrofouling in a temperate marina
10.20-10.40	29-H2-1-2: Wendt: Invasive bryozoans transported via hull fouling initiated a phase shift in a small California (USA) estuary	10.20-10.40	29-B-1-2: Greco: How do crabs keep their eyes clean? The synergistic antifouling approach of Carcinus maenas
10.40-11.00	29-H2-1-3: Davidson: Commercial ship biofouling as a transfer mechanism for species inoculations of the US Pacific Coast	10.40-11.00	29-B-1-3: Pagett: Understanding the settlement of <i>Balanus</i> amphitrite though the characterisation of glycans involved in gregariousness
11.00-11.20	29-H2-1-4: Johnson: Integrating antifouling strategies to minimize transport of marine invasive species by recreational boats	11.00-11.20	29-B-1-4: Rosenhahn: Influence of physicochemical surface properties on the settlement of spores of the green alga <i>Ulva</i> studied by three dimensional holographic tracking
11.20-11.40	29-H2-1-5: Ralston: The ghost of fouling communities past: evidence for carry-on effects on transplanted panels	11.20-11.40	29-B-1-5: Birch : Exploratory response of <i>A. amphitrite</i> cyprids on micro pillars
11.40-12.00	29-H2-1-6: Thomason: The relative risk of antifouling technologies for the transport of invasive species	11.40-12.00	29-B-1-6: Magin: A predictive model for the attachment of marine organisms to microtopographies
12.00-12.20	29-H2-1-7: Campbell: Slow moving barges: a risk assessment across domestic Australian borders	12.00-12.20	29-B-1-7: Barlow : Functional amyloid in the adhesive of the barnacle <i>Balanus amphitrite</i>
	END OF CONGRESS (S	_	
	See web site for po	_	-

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26-H2-P: Plenary

ECONOMIC IMPACT OF BIOFOULING ON A NAVAL SHIP

Michael P Schultz, John A Bendick, Eric R Holm, and William M Hertel

United States Naval Academy and Naval Surface Warfare Center - Carderock Division mschultz@usna.edu

Various approaches can be used to mitigate underwater hull fouling. Minimizing fouling reduces ship operating costs by decreasing power demand. Common mitigation approaches include antifouling coatings, fouling-release coatings, in-water hull cleaning and dry-dock maintenance. Each approach has associated capital, operational, and maintenance costs. The United States Navy continually investigates emerging underwater hull coating and maintenance technologies for cost savings and mission benefits. In this paper, a cost-benefit analysis (CBA) for underwater hull coatings and maintenance is presented. The CBA evaluates potential benefits to rationally guide research investments. Its inputs include data on ship performance (e.g. powering, operational tempo, coating life), in-water maintenance (e.g. frequency, type), and dry-dock maintenance (e.g. frequency, coating removal, coating application). The present analysis focuses on the Arleigh Burke class destroyer (DDG-51), a mid-sized surface combatant, which is the largest class of conventionally-powered ships in the U.S. Naval fleet. Predictions of ship resistance and powering penalties as a result of fouling are made based on laboratory-scale drag measurements and a similarity-law scaling analysis. The procedure, which was reported on previously in Schultz (2007) Biofouling 23: 331-341, is linked with the Navy's fouling rating system. The powering penalty prediction is used along with the specific fuel consumption data, fuel costs, operational and cleaning data to assess the overall economic impact of the hull fouling. The analysis of several hull conditions will be presented in this work, including a hull coated with an ablative copper antifouling having typical fouling levels.

US NAVY EVALUATION OF A FOULING RELEASE COATING: BIOFOULING CONTROL, PHYSICAL PERFORMANCE, AND IMPACT ON FUEL ECONOMY

*Elizabeth Haslbeck, Douglas Griggs, Jennifer Gardner, Eric Holm, David Stamper, Dana Lynn, Crystal Peyton, Joseph Curran, Jacob Vestal, and **Steven Lawrence

*Naval Surface Warfare Center, Carderock Division (NSWCCD), **Naval Research Laboratory elizabeth.haslbeck@navy.mil

Accumulation of fouling on ship hulls and propellers increases roughness resulting in increased fuel use and decreased speed and range. Currently the US Navy uses biocide-based antifouling coatings to control fouling on hulls, while propellers are left uncoated but are cleaned regularly. Non-toxic, fouling release (FR) coatings are smoother than current antifouling coatings and slough accumulated biofouling. Utilization of these coatings may reduce the frequency with which US Navy vessels operate with rough hulls and propellers, resulting in decreased fuel costs. Although commercial fleets report fuel savings when employing these coatings, the operational profiles of Navy vessels present risks that will require new approaches to hull and propeller maintenance. We are investigating the performance of fouling release coatings to determine if they can be utilized as effective hull or propeller coatings throughout the US Navy fleet. A test FR coating system has been applied to the hulls of an Arleigh Burke Class Destroyer (DDG), a Ticonderoga Class AEGIS Cruiser (CG), and to the propellers of a Whidbey Island Class Landing Ship Dock (LSD) vessel. These ships and a control ship from each class have also been equipped with the Ship Propulsion Condition Monitor (SPCM), to track changes in efficiency of vessel operation and thus fuel usage over time. Results from FR coated ships are compared to those for paired control ships utilizing current-generation paints, and for the LSD class vessel with uncoated propellers. The underwater hulls and propellers of test and control ships are inspected regularly so that ship performance data can be related to extent of fouling. Preliminary results confirm that biofouling accumulates on FR coatings at widely variable rates depending on harbor. In addition, effective biofouling release is dependent on biofouling type, age, and density as well as ship operational tempo. We will present the latest results of the project, and discuss development of condition-based maintenance approaches and maintenance technologies that will facilitate more widespread use of these materials. This work is funded by the Fleet Readiness Research and Development Program out of the Naval Sea Systems Command (NAVSEA) and by the Biofouling Program out of the Office of Naval Research.

26-H2-1-2

INVESTIGATION INTO THE DEVELOPMENT OF AN ADVANCED SHIP PERFORMANCE MONITORING AND ANALYSIS SYSTEM

T.W.F. Hasselaar, M. Atlar, E. Mesbahi

Newcastle University, School of Marine Science and Technology twfhasselaar@planet.nl

The complete ban on TBT in marine antifouling coatings in 2008, souring fuel prices over the past six years and upcoming energy efficiency indices for ships have resulted in a strong interest of the shipping industry to monitor, evaluate and optimise ship performance. Existing systems to monitor and analyse ship performance often act as a black box, showing little insight in data analysis and paying insufficient attention to data quality. The reliability of performance indicators (PIs) is therefore often poor, making the evaluation of anti-fouling coatings difficult. As response, Newcastle University, in collaboration with International Paint and OSG Ship Management, has started a 4-year research project in 2005 to investigate the development of a reliable, realtime and transparent ship performance monitoring and analysis (PM&A) system. A novel onboard and realtime PM&A system has been designed, implemented and evaluated on a 16m research vessel and 300.000dwt VLCC. Most attention was focussed on improving data quality; the identification of transient conditions (acceleration, deceleration, course deviation) where performance changes must be filtered out, and the reliability of power and speed readings should be evaluated. Speed logs, the most important sensors for performance analysis, are affected by many environmental conditions and are often unreliable. Other ways to determine speed through water, e.g. using the propeller inflow speed, heavily rely on an accurate definition of the wake fraction. Prediction of the wake to account for hull fouling based on statistics can result in large errors in PI's. A method is therefore described to utilise the speed log in periods where it can be considered most reliable. Performance data is corrected to standard conditions (no wind and waves, in deep water and at design draft) using propeller operating characteristics. Corrections are proposed to account for propeller fouling when periodical diver inspections are performed. Evaluation of the PM&A system on the research vessel and VLCC show that using a dedicated automatic data acquisitioning system, rational data conditioning, automatic performance analysis, reliable performance indicators can be obtained. Yet, deviations in performance up to ±15% cannot be avoided due to measurement errors from speed logs and environment.

FOULING CONTROL PRODUCTS: VALUE PROPOSITION AND ASSOCIATED ATMOSPHERIC POLLUTION PROFILE

Diego Yebra

Hempel A/S, Denmark dmy@hempel.com

No assessment of the environmental profile of novel "greener" products will be complete without knowledge of the impact that a potential loss of performance will have on increased emissions of Green House Gases. Similarly, the chances of commercial success for such greener technologies depend greatly on the industry's ability to demonstrate that their use will not involve higher fuel bills for ship owners/managers. Using Fouling Release coatings as an example, the challenge today is about demonstrating the sustained fuel saving benefits of this technology, which key for its progressive conquer of the biocidal market. In this presentation, we will use equivalent sand roughness figures as presented by Schultz (2007) to estimate the role of fouling on a range of trading vessels (ITTC extrapolation standards by FORCE technology). Initial differences in skin friction coefficient between conventional copper-based AFs and fouling release technologies from towing tank tests will also be taken into consideration. Different fouling scenarios will be simulated and its impact on the fuel consumption discussed.

26-H2-1-4

RAPID SCREENINGOF FRICTION DRAG PROPERTIES

Job W. Klijnstra¹, Mark Bakker¹, Anouk Bruin¹, Klaas Kooiker² & Pierre Emmanuel Guillerm³

¹TNO Science & Industry, Den Helder,The Netherlands; ² Marin, Wageningen,The Netherlands; ³Bassin d'essais des Carenes, Val de Reuil, France

job.klijnstra@tno.nl

Friction drag increase by macro roughness and macro fouling like algae and barnacles on ships hull is known for a long time and has been detailed extensively in literature. Far less is known on friction drag increase due to "micro roughness" in the form of slime biofilms. Previous publications have shown that slime fouling may give added drag effects between 9 and 29 % (Holm et al., 2004) and 11 – 21 % increase in shaft power (Schultz, 2007). But the relationship between slime fouling and coating properties such as roughness and surface energy and the consequences for friction drag increase is still poorly understood. A rotational disk set up is used to get more insight into this relationship. Differential measurements can be made to establish drag differences between disks with various roughness profiles, different types of coatings and various degrees of slime fouling. Drag data from disk tests can be translated, using similarity law assumptions as developed by Granville (1987), to more universal boundary layer shifts that are applicable under different hydrodynamic flow regimes. Increasing sand roughness of disks gives higher drag values corresponding to friction lines as determined for flat plates in towing tank tests. Coated disks with different roughness patterns are investigated on drag properties prior to and after certain degrees of slime fouling. Similarly, the system can be used for screening different surface types and coating formulations on drag (reduction) properties. This way the rotational disk set up has clear value in down selection of relevant flat plate test conditions and as a screening tool in coating development.

INNOVATIVE HYDRODYNAMIC APPROACHES FOR DRAG PROPERTIES EVALUATION OF ADVANCED ANTIFOULING COATINGS ELABORATED IN THE FIELD OF NANOTECHNOLOGY: RESULTS FROM THE AMBIO PROJECT

Jan Kanar

CTO S.A., Gdansk, Poland jan.kanar@cto.qda.pl

The paper intends to present the scope of hydrodynamic tests in the assessment of anti-fouling coatings, based on advanced nanostructured materials, created by molecular surface engineering, elaborated within the EU sponsored AMBIO Project. The subject coatings are addressed to the maritime sector which puts very high requirements in scope of coating prop-erties and ship hull drag reduction, seen from the point of view of costly fuels savings. Widely understood hydrodynamic investigations are a group of the complex field testing which aims to quantify a relationship between widely understood surface roughness and hy-drodynamic performances so as to determine the branch usefulness of new products. In detail, they have been performed to establish main surface characteristics of selected coated surfaces and understand how these characteristics interact with fundamental properties of these surfaces. Since, the hydrodynamic tests have been conducted in different sizes, testing facilities like the big towing tank and cavitation tunnel, a series of samples including: flat plates, axisymmetric bodies and hydrofoils models had been selected for these investigations - each sample demands different quantities of antifouling materials. Apart from newly elaborated coatings, a group of reference commercial ones has been applied so as to compare results with existing data bases. The received results are to make recommendation for their full scale applications and further improvement for their surface characterisation and hydrodynamic testing methods.

26-H2-1-6

BOUNDARY LAYER, DRAG AND SURFACE ROUGHNESS CHARACTERISTICS OF NANOSTRUCTURED COATINGS ON AN AXY-SYMMETRICAL SLENDER BODY TESTED IN A CAVITATION TUNNEL

Uğur Oral Ünal¹, Burcu Ünal², George Politis³, Mehmet Atlar³

¹Istanbul Technical University, ²Istanbul Technical University and ³Newcastle University mehmet.atlar@ncl.ac.uk

AMBIO is an integrated R&D project funded by European Commission's Framework Programme 6 during 2006-2010. The project aimed to develop new types of surface coating to prevent the growth of biofouling on the surfaces such as ship hulls in the marine environment. Whilst the majority of anti-fouling coatings sold today are based on toxic anti-fouling paints, a further distinguishing feature of the AMBIO project was the development of non-toxic anti-fouling paints with taking full advantage of nanotechnology. Accordingly, several new nanostructured paints were developed and the best performers were further investigated for their hydrodynamic characteristics. Since the frictional component of water resistance makes the most important contribution to the total drag of marine vessels, the effect of the coating on the boundary layer flow of the vessel and hence the frictional drag of the hull is also directly related with the required energy for the propulsion. This study covers an experimental research conducted at Emerson Cavitation Tunnel (ECT) of Newcastle University to investigate the boundary layer, drag and surface roughness characteristics of three newly developed nanostructured anti-fouling coatings along with some key reference coatings to be able to provide useful and reliable data with comparisons. The study, in fact, follows a similar experimental research with the same new coatings which were hydrodynamically tested at the ECT by the authors, with flat plate boundary layer measurements. Hence, as a further support to the previous findings this 2nd group of tests was conducted in the ECT using an axy-symmetrical testing body which also included a load cell facility to measure the frictional drag simultaneously while measuring the boundary layer. A specifically designed axy-symmetrical slender body of 175 mm in diameter and of 2708 mm in length with an interchangeable floating circular cylindrical sleeve was used as the testing body in the experiments. Boundary layer data was collected with a DANTEC 2D LDV (Laser Doppler Anemometry) system at 4 different flow velocities for each experimental case. These measurements did not only provide to capture several boundary layer characteristics of the different coatings such as boundary layer, momentum, displacement thicknesses, but also very critical quantities such as roughness functions and local skin friction coefficients. To provide further understanding of the effect of different coatings to the boundary layer flow of the slender body, two-way ANOVA analysis was also carried out with multiple pairwise comparisons for the key boundary layer parameters as well as the roughness functions. Careful and systematic skin friction drag measurements were also conducted at 5 different flow velocities for each coating by using a high-quality HBM load-cell mounted in the nose of the slender body. These tests provided further support to the boundary layer measurements. The surface roughness and texture characteristics of the tested coatings were also analysed using the contact and non-contact measurement devices to support the experimental analysis and discussion of the results. The tests and subsequent analysis revealed some critical conclusions about the hydrodynamic performances of the new anti-fouling coatings.

THE ENVIRONMENTAL BENEFITS OF SURFACE TREATED COATINGS (STCS)

Maxim Candries

Hydrex nv / Subsea Industries nv, Belgium mcandries@hydrex.be

Surface treated coatings (STCs) are formulated to protect ship hulls and other submerged surfaces against fouling and corrosion for prolonged periods. Antifouling efficiency is maintained by regular in-water treatment which consists of a cleaning aspect that removes fouling and a conditioning aspect that involves special maintenance tools to improve the surface characteristics. STCs offer several environmental benefits which are discussed here. A first environmental benefit is that STCs last significantly longer than other coatings and are expected to match the lifetime of the vessel on which they are applied. The paint application process can therefore be limited to a single event at newbuilding stage. Full repainting in drydock is no longer required, which reduces the emissions of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs). A second benefit is that STCs are entirely free of biocides. Experiments were carried out in collaboration with the Dutch Ministry of Transport, Public Works and Water Management to analyze the effluents released during the underwater treatment of STCs. The experiments demonstrated that STCs are totally free of biocides and that the underwater treatment of STCs will not affect the local water quality. The underwater treatment in itself offers a third significant advantage. Special maintenance tools have been developed so that the coating can simultaneously be cleaned and conditioned, which changes the roughness characteristics. The effects of conditioning on the drag characteristics of STCs have been studied by means of large-scale towing tank experiments using a 6.3m long friction plane. Between Reynolds numbers of 2.9 • 10^7 and 5.1 • 10^7, the frictional resistance of a conditioned STC was on average 5.3% lower compared to a newly applied and unconditioned STC. As a consequence, regular underwater cleaning and conditioning of STCs will lower the fuel consumption and reduce the carbon footprint of a vessel.

26-H2-1-8

DRAG REDUCTION FOR SHIPS DUE TO POLYMER RELEASE FROM PAINTED SURFACE BY TOMS EFFECT

Tetsuya Senda*, Hirotomo Ando*, Chiori Takahashi*, Hideki Kawashima*, Eiichi Yoshikawa**, Toshihiko Ashida**, Yasuo Kawaguchi***, Masaaki Motozawa*** and Kaoru Iwamoto****

*National Maritime Research Institute, **Chugoku Marine Paints, ***Tokyo University of Science and ****Tokyo University of Agriculture and Technology

senda@nmri.go.jp

Toms effect is known as a drag reduction mechanism obtained by adding a small amount of appropriate polymer, even as small as less than 1 ppm, to turbulent flow. Applications of this effect to ships would result in a significant reduction of fuel consumption and have been attempted by injecting polymer solution along the hull surface from the bow of the vessel. However, in those studies, no successful technologies have been proposed for commercial ships probably because such polymer solution rapidly diffuses away from the hull surface. This study explores advanced paints leaching out such polymers gradually with a similar behavior to the release of biocidal chemicals from anti-fouling coatings. Experiments, as well as corresponding numerical simulation, have revealed that supplying the polymers from coating surface to the near-the-surface region (buffer region) of the turbulent flow could effectively reduce the friction resistance. Analysis of polymer solution by GPC-MALS (Gel Permeation Chromatography Multi-Angle Light Scattering Method) has shown that polyethylene-oxide (PEO) is the most promising for drag reduction and the drag reducing rate is highly dependent on molecular weight. Mechanical or chemical degradation of polymers often observed during the experiments have been found related to the decrease in molecular weight. At least one million g/mol would be necessary for drag reduction, suggesting that high molecular weight would be needed for formation of a network-like structure to interact with the flow resulting in suppression of the turbulence and a low frictional resistance. Based on these findings, several paints containing PEO have been prepared and tested in a towing tank using plate-type models. Finally, prototype paints have been obtained exhibiting a significant drag reduction (>10%) in comparison with a conventional self-polishing type anti-fouling paint.

CAVITATION AND OPEN WATER PERFORMANCE ANALYSIS OF TWO TYPES OF ANTIFOULING PROPELLER COATINGS

R. Sampson, M. Atlar

Science & Tech Corp. & University of Newcastle rsampson@stcnet.com

A series of open water propeller tests were conducted in the Emerson Cavitation Tunnel at the School of Marine Science and Technology, University of Newcastle as part of the AMBIO project. The tests were designed to assess the influence of different types of state-of-the-art antifouling propeller coatings on the open water performance and observed cavitation patterns of a typical merchant ship propeller. The model propeller selected for the experiment is currently fitted to a 95,000 dwt tanker vessel "Guardian" which has been successfully coated with silicone based antifouling paint for approximately 5 years. The operation and performance of this propeller has been the subject of several international research projects including AMBIO, which involve the antifouling expertise of the Emerson Cavitation Tunnel. Two propellers were manufactured and tested for the project in an uncoated and coated condition using two very different types of antifouling technology, based on Nano-surface technology and silicone paint technology respectively. This presentation reports on the findings from this state-of-the-art study, which includes both an analysis of the open water propeller performance changes due to the different coatings on the thrust and torque of the propeller and the effect of the coatings on the cavitation inception and level of the cavitation developed by the propeller during representative conditions.

26-H2-1-10

THE MECHANICS AND HYDRODYNAMICS OF FOULING RELEASE COATINGS

Geoffrey Swain

Florida Institute of Technology swain@fit.edu

Silicone fouling release coatings are now offered by all the major coatings companies and there is interest in understanding the speed at which the vessel must travel to remove fouling. We have been measuring the fouling release properties of this family of coatings for twenty years and we have collected a large amount of data both relating to biofouling adhesion and to the hydrodynamics of removal. This paper will combine the data to produce simple models that will help in the understanding of ship velocities required for fouling release.

26-H2-2-1: Keynote

ANTIFOULING REGULATIONS – REGULATORY APPROACH TO MINIMISE THEIR IMPACT ON THE ENVIRONMENT – HOW FAR HAVE WE COME SINCE TBT?

Julian Hunter

Akzo Nobel, International Paint julian.hunter@akzonobel.com

Since the TBT ban antifouling paints have become the focus of significant attention from regulators and environmentalists and are now probably the most scrutinised group of coatings in the world. Antifouling paints are now regulated globally (through IMO), regionally (federal US law and EU regulation), nationally and locally (eg Californian state law) which presents a scientific and bureaucratic challenge for the coatings industry and for researchers alike. In this presentation an overview of key developments in regulations and regulatory approach to antifoulings will be discussed in the context of overall benefit to human and environmental safety.

26-H2-2-2

CURRENT REGULATORY ISSUES FOR ANTIFOULING PRODUCTS UNDER THE BIOCIDAL PRODUCTS DIRECTIVE

Andrew Low

Health and Safety Executive andrew.low@hse.gsi.gov.uk

The aims of the Biocidal Products Directive (98/8/EC) are to harmonise the EU market for biocidal products (including antifouling products) and their active substances, whilst providing a high level of protection for man, animals and the environment, and ensuring that products are sufficiently effective. There are ongoing efforts to reach agreement on the details of how assessments (such as risk assessments, for example) will be carried out. Given that the Directive covers 23 Product Types and that there are 27 Member States to gain agreement between, this is a major undertaking. This presentation will highlight a number of the current issues relating to the areas of environmental assessment, efficacy and operator exposure as they relate to antifouling products and their active substances.

MAMPEC: A GENERIC MODEL FOR ENVIRONMENTAL EXPOSURE MODELLING OF ANTIFOULING BIOCIDES. INTRODUCTION TO VERSION 3

Bert van Hattum, Arthur Baart*, Jos van Gils*

Institute for Environmental Studies, Vrije Universiteit, Amsterdam, The Netherlands; * Deltares, Delft, The Netherlands bert.van.hattum@ivm.vu.nl

Against the background of the requirements of the EU Biocidal Products Directive (BPD) and the IMO International Maritime Organisation (IMO) Antifouling Convention of 2001 there is a need for reliable modelling tools for the prediction of exposure and risks of new antifoulants in the marine environment. In 1999 the first version of MAMPEC was released. The study was sponsored by the Antifouling Working Group of the European Paint Makers Association (CEPE / CEFIC) with a contribution from the European Commission (DG XI). The model has since been improved with regular updates of the model. The latest release of MAMPEC version 3.0 is compatible with Windows Vista/ 7 and includes some important new features. The model predicts concentrations of antifoulants in generalised 'typical' marine environments (open sea, shipping lane, estuary, commercial harbour, yachting marina, open harbour). The user can specify: emission factors (e.g., leaching rates, shipping intensities, residence times, ship hull underwater surface areas), compound-related properties and processes (e.g., Kd, Kow, Koc, volatilisation, speciation, hydrolysis, photolysis, biodegradation), and properties and hydrodynamics related to the specific environment (e.g. currents, tides, salinity, DOC, suspended matter load, port dimensions). MAMPEC includes options for advanced photolysis modelling, and incorporation of wind-driven hydrodynamic exchange and other non-tidal exchange processes important for areas without tidal action, or inland freshwater environments. Included are also the service-life emmission scenarios developed by OECD and adopted by EU as the standard environmental emission scenarios, to be used for evaluation of the biocides under the Biocidal Products Directive. The model has been validated for a number of compounds and is today recognized by regulatory authorities in EU, USA and other OECD countries. MAMPEC is currently also used in authorisations by GESAMP and IMO for the assessment of active ingredients in ballast water. In version 3.0 the .net framework is implemented to improve compatibility with current IT developments. Additional languages can be chosen (Japanese, Chinese). New functionalities are: the OECD-EU standard emission scenarios for application and removal of paint during docking operations, an improved speciation scheme for Copper, analysis of fluxes and final fate of model compounds, options to run multiple combinations model settings useful for sensitivity analysis. The model is freely available from the software support site $\underline{\text{http://delftsoftware.wldelft.nl.}}$

26-H2-2-4

REMEDIATION OF COPPER IMPAIRED MARINAS: PREDICTING ENVIRONMENTAL LOADING USING SCENARIO MODELLING.

Gareth Prowse, Emma Grange

International Paint Ltd Gareth.prowse@akzonobel.com

In enclosed marinas with high vessel occupancy and limited water exchange, concentrations of copper can exceed national water quality standard limits. This situation can be exacerbated by localised inputs of copper from diffuse sources (such as municipal waste water) and cultural practices for maintaining vessels such as hull scrubbing. In such circumstances action (remediation) may be required to reduce the level of copper in that environment. Given that antifouling products typically contain a copper based biocide, restriction of the use of copper based paints has been identified as a key factor in the reduction of copper levels in the environment. This paper presents a case study for such a situation, where an action plan for reducing copper levels in the environment has been defined by a regulatory authority. By using environmental modelling with the Marine Antifoulant Model to Predict Environmental Concentrations (MAMPEC), copper concentrations were predicted in a typical marina under different product-type scenarios and compared with the action plan targets. From this study it was concluded that the promotion and adoption of emerging controlled-release technologies could be a viable regulatory approach to reducing copper loading in affected marinas.

A PROPOSED STRATEGY FOR RISK ASSESSMENT OF ANTIFOULING COMBINATIONS IN PAINT PRODUCTS

Hans Blanck, Thomas Backhaus, Lars Förlin, Magnus Nydén, Björn Dahlbäck

University of Gothenburg and Chalmers University of Technology hans.blanck@dpes.qu.se

With complex antifouling combinations on the market there is a need to assess the potential environmental risk of paint products. An evaluation of leachates from painted surfaces account for mixture toxicity but is likely to ignore fate processes. Testing of aged leachates will account for the influences of degradation only if aging occurs under environmentally realistic conditions. We suggest a strategy involving (1) estimate of leakage rates for all antifoulants, (2) MAMPEC-model-based predictions of environmental mixture composition (3) mixture toxicity predictions for selected non-target organisms or communities, and/or (4) direct testing of predicted environmental mixtures. The suggested approach will improve the realism of the environmental assessment and account for the so-called cocktail effect of chemicals that are co-emitted from antifouling paints. When predictions are experimentally validated, any synergism or antagonism will be detected as mispredictions.

26-H2-2-6

PREDICTION OF ENVIRONMENTAL CONCENTRATION FOR A PHOTO-DEGRADABLE ANTI-FOULING AGENTS

Kiyoshi Shibata, Tetsuya Senda, Yoshitaka Yamaguchi, Ryuji Kojima, Shinobu Sugasawa, Osamu Miyata, Toshiaki Shibata

Chiba Institute of Technology and National Maritime Research Institute kyshibt@sky.it-chiba.ac.jp

Since the ban of organic tin compounds as an antifouling agent in ship hull paints, various new antifouling paints have been developed to substitute them. Some of them are containing photo-degradable anti-fouling agents, which are easily decomposes to less toxic substances in the environment. In fact, they have seldom been detected in the environment. But, the photo-degradation is not favorable in deep water or at night, and it may lead steep temporal and spatial concentration change. Thus, in this work, a numerical unsteady state model has been developed to predict the environmental concentration, focusing on the photodegradation rate. The model includes the following fate processes of the antifouling agent; release from ship hull paint, advection, diffusion caused by concentration gradient, photolytic, hydrolytic degradation. The rate of photo-degradation was expressed as quasi-first order kinetics and its rate constant was proportional to the light irradiation intensity, which is a function of depth and transparency of water, as well as time, date and geographical location. Temporal and spatial concentration distribution change of the anti-fouling agent around a large vessel mooring at a pier was calculated, changing the leaching rate, diffusion coefficients, decomposition rate, sunlight intensity, and water transparency. The highest concentration was observed at near the bottom of vessel and its value was influenced by mainly the diffusion coefficients, leaching rate and water flow rate. The decomposition rate only affects in the shallow water. However, it is almost impossible to evaluate absolute concentration and compare with environmental monitoring data, because some of the parameter's values are still not well known and they are changing with time and location. Therefore, it will be inevitable to apply the worst case scenario to predict the environmental concentration. In this presentation, the effects and significance of the parameters in this model are examined, and future task in the environmental fate study of antifouling agents to avoid the worst case scenario will be discussed.

ADVANCES IN UNDERSTANDING OF COPPER IN THE ENVIRONMENT AND THE IMPACT ON ITS REGULATION

Kevin Long

Regulatory Compliance Limited on behalf of the EU Antifouling Copper Task Force klong@regcs.co.uk

The regulatory status of copper has historically been the source of much debate, with much attention being focused on the perceived risk from the use of copper based products for a variety of biocidal functions, in particular in the field of antifouling. This focus has been centred upon derived threshold levels of effect from a variety of sources which indicated the use of copper may lead to detrimental effects on aquatic organisms during normal use. Within the last decade there has been a paradigm shift in the understanding of metal chemistry, driven by an improved understanding of the bioavailability of metals and our ability to model this in the receiving environment. This has lead to significant changes in the way regulatory systems are now addressing the issue of metals in the environment, allowing a more scientific approach to the regulation of metals in general, and copper in particular. A summary of the new concepts will be presented, with an emphasis on how various regulatory regimes around the world are incorporating this new knowledge into the assessment of copper as an active substance in antifouling paints.

26-H2-2-8

ENVIRONMENTAL RISK ASSESSMENT OF METATOMODINE – A METAL-FREE ANTIFOULING BIOCIDE

Cecilia Ohlauson, Dan Isaksson, Lena GE Mårtensson Lindblad

I-Tech AB Lena.Lindblad@i-tech.se

Environmental risk assessment is a key factor in developing new marine biocides. Regarding new biocides, it is also possible to be proactive. This can be done by continuously using risk assessment when evaluating overall decisions for further developments and investments. For new marine biocides, there is a long wish list to be granted. For example, broad efficacy, ready biodegradable, low water solubility, low cost, increased docking intervals, and human safety. It is impossible to fulfil all demands with one single molecule, but it is possible to make priorities and optimise between the different parameters. There are two main aspects regarding medetomidine and its risk assessment. First of all, it is extremely effective in prohibiting barnacle larvae from attaching to a marine surface. By being so effective, it is possible to dramatically reduce the amount of biocide used in the marine environment. Only 0.1% w/w is needed in a paint matrix compared to, for example, cuprous oxide, which needs hundredfold more to obtain the same result. Using such a small amounts of medetomidine calls for a very low leakage rate, which is favourable in a risk assessment. Secondly, when reducing the amount of cuprous oxide, new technological opportunities will be possible to explore. Much of the paint properties are restricted to the fact that it contains at least 30% of cuprous oxide. The replacement of cuprous oxide with very small amount of medetomidine needs further development in formulation technologies, but it may also open up possibilities to reduce the VOC content in paints and consequently, increase the dry weight. This new technological window allows for polymer development and control release systems which is independent on cuprous oxide and may create technical and market advantages, perhaps more flexible dry docking schedules. In the long run, this is probably more important for the environment than specific values within an environmental risk assessment.

RELEASE RATE OF COPPER PYRITHIONE FROM COATED FISH NETS – COMPARISON OF RESULTS FROM A MODIFIED TEST PROCEDURE MODELED AFTER ASTM D6903

Denise B. Taylor, Paul Kappock, Christopher Bannon, Vidya Sane, Richard Brien

Arch Chemicals, Inc., USA dbtaylor@archchemicals.com

The release rate of a biocidal active such as copper pyrithione from an antifouling coating is important in assessment of the potential environmental impact of that active. Laboratory methods are employed to determine release rates under controlled conditions. The results of these studies are then used in various models as part of the risk assessment. One generally accepted method for determining release rates in a laboratory is the rotating cylinder method, designed to model a treated ship's hull and its at-dock and at-sea behavior. In this test, painted cylinders are maintained in seawater at a controlled temperature, pH and salinity and tested at regular intervals by spinning them in fresh seawater which is then analyzed for the active ingredient. Evaluation of coatings designed for fish nets used in aquaculture has also been done using this method, but it is unclear if the painted cylinder represents leaching from a coating on a fish net. A modified testing device, modeled after the rotating cylinder described in ASTM D6903, was fabricated and used to test a commercial net coating containing copper pyrithione under controlled conditions. The results were compared to those obtained on the same type of coating using the traditional painted cylinder method. Results will be presented and discussed.

26-B-1-1: Keynote

BIOFOULING AND ITS CONTROL IN INDUSTRIAL COOLING WATER SYSTEMS: AN OVERVIEW OF THE PRESENT AND A PEEK INTO THE FUTURE

Sanjeevi Rajagopal

Department of Animal Ecology and Ecophysiology, Institute for Wetland and Water Research, Radboud University Nijmegen S.Rajagopal@science.ru.nl

In power plants using natural aquatic systems as heat sink, biofouling inside cooling system components is a major problem to be reckoned with. Irrespective of the type of the cooling water - fresh or saline - biofouling in the form of condenser slime and macrofouling presents formidable operational problems that need to be addressed in an environmentally sustainable manner. Use of injectable biocides has been an established method to control biofouling. However, better understanding and awareness of the environmental effects of chemical biocides have caused strict stipulations being placed with respect to the discharge limits. Consequently, industry is on the continuous lookout for ingenious methods to control biofouling and related problems. Continued R & D on the biology of major fouling organisms such as mussels using Mosselmonitor® has helped us understand the mechanism of the effect of chlorine. As a result, it has been possible to devise methods to enhance the efficacy of chlorine, even while reducing the total chlorine inventory used for biofouling control. Techniques such as Pulse-Chlorination® have gained industry acceptance in many European and Asian countries mainly due to improved biofouling control and reduced environmental discharge. Apart from traditionally used methods such as chlorination and heat treatment, use of advanced treatment chemicals (e.g. BioBulletsTM) and formulations is gaining currency. There are also well-established methods for automated mechanical cleaning, which supplement chemical dosing. Emphasis is also being placed on passive systems such as design improvements that entail minimal fouling development in CW systems. Advances in related areas such as coatings and paints are also expected to find applications in power plant environments, albeit in a limited manner. In future, cooling water systems would increasingly use non toxic coatings (foul-release coatings), physical techniques (e.g. nano-coated surfaces) or behavioural methods (e.g. pheromonal chemicals). The paper gives an overview of power plant biofouling and its control in European countries, emphasizing the recent advances with respect to operational control and environmental compliance. It also gives a glimpse into the future of antifouling technology with respect to cooling water systems.

26-B-1-2

INDUSTRIAL COOLING WATER SYSTEMS: DISCHARGE CONTROLS IN THE EUROPEAN UNION

Andrew Wither

Environment Agency, UK
andrew.wither@environment-agency.gov.uk

The discharge of effluent to surface waters is increasingly subject to international controls, primarily from the European Union but also other international bodies such as the OSPAR Commission. Despite European Union legislation driving environmental legislation the principal of subsidiarity means there can be significant differences in the application of European Directives between different member states. Specific environmental issues related to cooling water discharges are temperature and chemicals used for corrosion and fouling control. Under European legislation several common metals are identified as 'priority hazardous substances' with the object of phasing out discharges containing these elements and their compounds, whilst the remainder are 'priority substances' with an obligation to progressively reduce emissions to achieve 'good chemical status' in all water bodies. Chlorine and other antifouling chemicals are also subject to international legislation with tighter limits for chlorine and its derivatives being discussed. This presentation will review the primary legislation that impacts discharges from cooling water systems e.g. the Habitats and Water Framework Directives, the Integrated Pollution Prevention and Control Guideline as well as recent subsidiary legislation such as the Environmental Standards Directive. The importance of discharge regimes and mixing zones within the receiving water will be reviewed. Examples will be given of practice within the United Kingdom, and differences in approach from elsewhere within the European Union highlighted. Finally suggestions will be given of the key questions that should be considered by anyone proposing a new cooling water discharge.

26-B-1-3

ROOT-CAUSE ANALYSES OF CORROSION IN HEAT-EXCHANGERS: A CASE STUDY

Lars P. Venhuis, Isabelle Van der Maren

KEMA Nederland BV; Oman LNG LLC lars.venhuis@kema.com

A Liquid Natural Gas (LNG) production plant using once-through seawater fed cooling system showed scale formation and internal pitting in its Cupro Nickel heat exchanger tubes. KEMA was requested to investigate the cause and mechanism thereof. For the investigation KEMA performed microbial sampling and analyses during plant shutdown. During identification of the presence of microbial scale, boroscopic inspection was performed to select the tubes for pulling for further metallurgic investigation. Microbial activity and microbes associated with Microbial Influenced Corrosion (MIC) were identified by means of Adenosine-5'-trifosfate (ATP), MIC-kit and Polymerase Chain Reaction (PCR) techniques. For understanding the composition of the scale and its origin, KEMA performed light microscopic analysis and a technology called "KemPhase-analysis". From the investigation it was concluded that the scale and pitting was caused by manganese oxide (MnO₂) scale originating from biological oxidation by aerobic Manganese-oxidizing Bacteria (MOB) which accumulated the manganese from the seawater. This formed a galvanic coupling.

26-B-1-4

MONITORING BY AN ELECTROCHEMICAL INTEGRATED SYSTEM OF CORROSION AND ANTIFOULING TREATMENTS ON ALUMINUM BRASS CONDENSER TUBES

Pierangela Cristiani¹, Giorgio Perboni²

ENEA-Ricerca sul Sistema Elettrico SpA¹, CESI SpA² pierangela.cristiani@erse-web.it.

Condenser performance and reliability have a significant impact on the electric generation of a power plant in view of the present energy market. In recent years, the detection of many failure events in condensers drove the achievement of experimental monitoring setup regarding these phenomena. About the formation of protective oxide layers growing on Cu based alloys as Aluminum brass, commonly employed in seawater, the positive role of chlorination treatments and the addition of ferrous ions was addressed. For this purpose measurements were carried out in on-plant circuits, with different characterized environments. Our results confirm that chlorination treatments, continuously or discontinuously imposed depending on material and aqueous environment, promoted the formation of a protective layer on Cu based alloys. This layer, reinforced with the treatment of ferrous ions, was able to avoid the onset of localized corrosion phenomena even when seawater becomes of particular aggressiveness, as it happens in presence of or high flow of water with Al Brass. In the present paper, an innovative integrated equipment with wireless sensors specifically set for industrial application and suitable to monitor the corrosion (by Linear Polarization Resistance technique), the biofilm growth (by the BIOX electrochemical probe), the chlorination treatment and other physical-chemical parameters of the water is described in detail and commented.

26-B-1-5

ELECTROLYTIC ANTI-FOULING SYSTEMS FOR PUMPED WATER INTAKES IN THE OIL + GAS INDUSTRY

Matthew Lamb and Ross Fielding

Cathodic Protection Co. Limited, UK matthew.lamb@cathodic.co.uk

The use of copper to prevent hard fouling dates back many years, when copper clad wooden ships were used in the English Navy. Electrolytic marine anti-fouling systems have been utilised on intake pumping equipment since the early 1970's (Forties Platforms). By applying a small DC current to the copper anode, ions are released into the water in controlled amounts to prevent larvae settling on pump intakes and associated pipe work, keeping them clear from growth. Combining Copper with Aluminium anodes holds the copper ions in solution longer allowing greater flow around the pump intake equipment. Initial designs for Cu/Al electrode systems included installing an electrode unit to the pump intake. Further details provided on a brief case study. The requirement to use an alternative method of introducing the anti-fouling solution, lead to the use of a deck mounted tank pumping dosed liquid to the intake via small bore pipe work. Further details provided on a brief case study. The next development stage is to combine copper anodes with mixed metal oxide (MMO) anodes to produce copper-chlorine systems, which work in much the same way, but to greater affect. Rates of both Copper and Chlorine dissolution can be greatly reduced to suit higher flow rates. The reduction of the rate of dissolution protects non-metallic component parts from early replacement. Since inception Cu/Al systems have been competing with chemical dosing systems for both offshore and onshore applications. Onshore applications include cooling water intakes for power plants. Marine Applications are utilised in sea chests at vessel intake areas.

26-B-1-6

CHARACTERIZATION OF THE MARINE ORGANISMS ON ARTIFICIAL SUBSTRATES IN A POWER PLANT IN THE SOUTHEASTERN MEDITERRANEAN

Dr Anat Glazer

Marine Laborator, Israel Electric Corporations Ltd. glazer@iec.co.il

Marine and aquatic habitats include a large variety of natural and artificial substrates. These comprise piers, underwater pipes, artificial reefs and cooling water systems. The accumulation of biofouling depending on local conditions may reach heights of 10-100 cm above the substrate and decreases the efficiency of power plants. Since the development of biofouling has positive effects on other types of artificial structures, a comparison of biofouling development on a variety of man-made substrates may be useful for the optimal design of structures for specific purposes. The main goal of the present study was to examine the development of biofouling on different types of artificial substrates. Several substrate properties such as texture, adhesiveness, and heavy metals content were examined to evaluate their role in the species appearance, settlement rate, duration of the fouling community and toxicity (heavy metals accumulation) in soft tissues of biofouling organisms. The intention was on one hand to determine the optimal substrate on which fouling development is minimal - to be used in cooling water systems, while on the other hand to determine the maximal fouling biomass, for purposes such as artificial reefs. The study was performed at the "Orot Rabin" Power Station, near Hadera, Israel, the southeastern Mediterranean. The settlement of fouling organisms was examined on the following types of substrates, represented as plates: smooth concrete, rough concrete, smooth concrete mixed with coal fly ash and concrete coated with the foul-release silicone based - "Bioclean" (Chugoko). During the 18-months of research 79 sessile invertebrates and algae settled on the sampling plates. They appeared in four types of morphological categories (algae, solitary organisms, encrusting colonial organisms and bushy colonial organisms), represented by 8 major taxonomic groups (algae, sponges, hydroids, bryozoans, barnacles, mollusks, serpulids worms and ascidians). The build up of a fouling community from its pioneer stage up to the collapse stage lasted 7 months. The effect of the substrate was expressed differently in various developmental stages of the biofouling. In all stages, the coated plate was distinct from all the concrete plates. The environmental factors interacting with physical properties of the substratum can determine the community structure. Recognizing the fouling communities and its species composition regarding artificial substrates is important for designing specific underwater structures suitable to their designated purposes.

26-B-1-7

BIOFOULING IN INDIAN NUCLEAR POWER PLANTS – AN OVERVIEW OF PROBLEMS ENCOUNTERED AND LESSONS LEARNED

V. P. Venugopalan, P. Sriyutha Murthy, K. S. Krishna Rao and S.V. Narasimhan

Water and Steam Chemistry Division, BARC Facilities, Kalpakkam, India and Madras Atomic Power Station, Nuclear Power Corporation India Ltd., Kalpakkam, India

vpv@igcar.gov.in

India currently operates three (coastal nuclear power plants and will be soon commissioning the fourth one. The fifth one is being constructed and is expected to be completed by 2012. These plants are located on the east and west coasts of peninsular India. Seawater is used as the tertiary coolant in all these reactors by employing intake systems that vary from open channel and breakwater dyke to deep sub-seabed tunnel. Over the years, it has been the experience of the plant operators that biofouling has the potential to jeopardize the economic operation of the plants. The currently operated plants have been experiencing biofouling problems in the condenser cooling circuits, with the intensity of fouling varying with location. We have been monitoring the fouling scenario in some of these power plants for over two decades by way of regular filed sampling during normal operation as well as during shutdown periods. In addition, data have been generated on the anticipated fouling scenario in the upcoming plants. The plants employ biocide regimes depending on the severity of fouling encountered. Data have been generated on the response of the major fouling organisms to chlorine, which is used as the major biocide at all the stations. The power plants have fine-tuned appropriate chlorination regimes based on the biocide demand of the water and type and extent of biofouling involved. For example, continuous low dose chlorination is being employed at MAPS, Kalpakkam, where mussels are dominant. TAPS, Tarapore, on the other hand, encounters far less fouling problem and has been employing intermittent chlorination. Careful analysis of problems and judicious application of control strategies have ensured smooth operation of the plants over the years. The paper gives details of the fouling scenario at various stations and the chlorination regimes employed, along with data on the relative efficacy of the control programme ascertained by in-plant sampling during maintenance shutdowns. In addition, there is an ongoing programme on the environmental effects of biocidal residues and chlorination byproducts in the outgoing water. The paper gives an overview of the overall strategy employed in the management of the biofouling problem in cooling water circuits of Indian nuclear power plants.

26-B-1-8

INDUSTRIAL COOLING SEAWATER IN THE MIDDLE EAST - A CASE STUDY OF OPERATION OPTIMISATION AND REDUCED ENVIRONMENTAL IMPACT

Iain A Macdonald

Imperial College, London i.macdonald@imperial.ac.uk

The Middle East is dependant on the marine environment for providing mediums for transportation, fisheries and mariculture, drinking water, industrial and power plant cooling requirements and more recently tourism. This case study reviews these potentially conflicting resource users and the steps taken by an industrial facility in the north of Qatar to address both internal operational issues and regional concerns regarding cooling seawater discharges and particularly residual oxidants (chlorine). This facility reduced the quantity of sodium hypochlorite being used to inhibit biological fouling and the residual oxidant levels in cooling seawater returned to sea by > 50% through the adoption of a technique termed "Pulse-Chlorination". The issues management process both internal (Operations, Maintenance and Environmental Departments) and external stakeholders (e.g., local environmental regulator, other facilities following different strategies and researchers) will be described and lessons learnt highlighted. Further action plans were created and are being implemented to continually improve on the current status in terms of cooling seawater biofouling prevention strategy performance monitoring, biofilm monitoring, and impact of the cooling seawater discharge upon local marine resources. These are believed to be unique in the region and are routed in providing a local scientific basis for determining discharge limits rather than adopting sources available for guidance in the literature the currently non-targeted, unfeasible (in certain situations) and disparate environments suggested requirements. Jellyfish and algae tide blooms are another area of concern that have the potential impact on the marine environment and its derived services of significant economic value to resources users in this area.lt will be necessary of the countries surrounding the Gulf to acknowledge that the marine environment has a threshold for discharged loads of chemicals and heat, although the levels at which these become critical for marine biodiversity conservation are poorly understood and require significant multidisciplinary study and regional collaboration.

26-B-2-1

INTERFACIAL SPECTROSCOPY: IN SITU APPROACHES TO UNDERSTAND STICKY CONTACTS

Kathryn J Wahl, Daniel E Barlow, Richard K Everett, Christopher M Spillmann, Gary H Dickinson, Beatriz Orihuela, and Dan Rittschof

US Naval Research Laboratory, Washington DC USA; Duke University Marine Lab, Beaufort NC USA kathryn.wahl@nrl.navy.mil

Proteinaceous secretions are widely recognized to be significant contributors to marine biofouling. The resulting interfacial films can be physisorbed or chemisorbed, and have varying degrees of permanency – they may be highly polymerized and cross-linked, or simply sticky enough to allow surface exploration. Conventional approaches to examine interfacial films derived from bioadhesive junctions are forensic in nature – foulant removal (separating the surfaces) followed by ex situ examination of the adhesive composition and surface morphology. While "what" the adhesive is may be gleaned from ex situ approaches, "how" the adhesive is applied and cures cannot. These time dependent changes can't be examined "after the fact" and instead require real-time measures of interfacial interactions. At NRL, we have made significant progress in developing in situ methods to demonstrate the chemical, mechanical and rheological processes in interfaces. We are now applying and extending these approaches to examine underwater adhesion in marine organisms, specifically the little striped barnacle, Balanus amphitrite. We are developing in situ and in vivo spectroscopic approaches to determine how protein structure and chemistry influence marine foulant adhesion. We are particularly interested in determining the structure and chemistry of the cement, the biochemical processes influencing polymerization, cross-linking, and water displacement, as well as the physiochemical nature of the adhesion. Our in situ approaches include performing temporally- and spatially-resolved microscopy and spectroscopy through adhesive interfaces transparent at UV, visible, IR, and x-ray wavelengths. I will describe how we have used these tools to develop new understanding of the properties and development of the adhesive interface of barnacles.

26-B-2-2

IMAGING TEMPORARY ADHESION AND SURFACE EXPLORATION BY BARNACLE CYPRIDS

Nick Aldred¹, Tobias Ekblad², Olof Andersson², Bo Liedberg², Anthony S. Clare¹

¹Newcastle University, UK ²Linkopings University, Sweden nicholas.aldred@ncl.ac.uk

Barnacle cypris larvae explore immersed surfaces prior to permanent attachment and metamorphosis into a juvenile barnacle. Although their mechanism of temporary adhesion is poorly understood, it is a pivotal stage in surface colonisation by barnacles since, without temporary attachment, permanent attachment and growth to adulthood would be impossible. Direct observation of this phenomenon has previously been difficult due to the small size of the attachment organs and the transparent nature of the cyprid cuticle, as well as the adhesive itself, although progress has been made recently using modern surface sensing techniques. Atomic force microscopy (AFM) has allowed high-resolution imaging of adhesive 'footprints' deposited on surfaces and mechanical analysis of the constituent proteins however, in terms of antifouling coatings development, this technique has significant limitations. In order to observe adhesive deposition in real time, imaging surface plasmon resonance (iSPR) has recently been employed, allowing direct observation of surface exploration and adhesive deposition by cyprids. iSPR has the potential for use as a rapid-screening assay for candidate antifouling chemistries, allowing quantitative analysis of exploration and adhesive deposition by cyprids. Examples will be presented demonstrating the differences in attachment success between cyprids exploring on a number of different test surfaces, including self-assembled monolayers with methyl-, carboxyl-, amine- and poly(ethylene glycol) terminations.

26-B-2-3

BARNACLE GLUE CURING AND ORGANIZATION OF MARINE COMMUNITIES

Dan Rittschof, Gary Dickinson, Kathryn Wahl, Irving Vega, Richard Everett and Beatriz Orihuela

Duke University (DR, BO), Tropical Marine Science Institute, Singapore (GD) Naval Research Laboratory (KW,RE) Department of Biology, University of Puerto Rico (IV)

ritt@duke.edu

Our present model of barnacle glue curing has components that are similar to blood clotting. In the model, structural proteins and enzymes are activated from storage forms. Once activated, structural proteins can rearrange and present motifs to surfaces. At least one class of enzymes (Trypsin-like serine proteases) activates structural proteins and at least one other class of enzymes (Transglutaminases) cross links structural proteins and are a curing agent. Due to the pioneering work of Kamino and colleagues and others on the components of barnacle glue and other complex macropolymers, we know that barnacle glue and the curing process are more complex than our simplistic model. However, the model provides paths for research, an evolutionary context and mechanism for glue curing. Moreover, the model enables prediction that there are other glues that cure by a similar mechanism. A consequence is the predictable release of peptide hydrolysis products generated during the activation of structural proteins and enzymes and eventual degradation of glues. For barnacle glue, the peptide hydrolysis products function as pheromones, kairomones and other classes of signal molecules. Thus, in a broad sense, the processing, curing and breakdown of a variety of evolutionarily related macropolymers can function to literally and figuratively cement and organize marine communities.

26-B-2-4

INSIGHTS INTO THE COMPOSITION, MORPHOLOGY, AND FORMATION OF THE CALCAREOUS SHELL OF THE SERPULID *HYDROIDES DIANTHUS*

Adrienne E. Tanur, Nikhil Gunari, Ruby May A. Sullan, Christopher J. Kavanagh, Gilbert C. Walker

University of Toronto ailbert.walker@utoronto.ca

To date, the calcareous tubes of serpulid marine worms have not been studied extensively in a biomineralization context. The structure and composition of the tube shell and adhesive cement of the marine tubeworm Hydroides dianthus were studied using a variety of characterization techniques, including powder XRD, FTIR, SEM, EDX, and AFM. The tube and cement were determined to be inorganic—organic composite materials, consisting of inorganic aragonite and Mg-calcite crystals, and both soluble and insoluble organic matrices (SOM and IOM). SEM imaging revealed a variety of crystal morphologies. AFM nanoindentation of the inorganic components yielded Young's moduli of 20 GPa in the wet state, and 50 GPa in the dry state. Amino acid analysis of the SOM indicated substantial amounts of acidic and non-polar neutral amino acids. Part of the insoluble organic tube lining was identified as being composed of collagen-containing fibres aligned in a criss-crossed structure. The SOM and organic tube lining were found to contain carboxylated and sulphated polysaccharides. In an artificial seawater solution, the SOM and the organic tube lining mediated CaCO₃ mineralization in vitro. The relationship between these results, marine biofouling and antifouling strategies will be discussed.

THE SANDCASTLE GLUE OF PHRAGMATOPOMA CALIFORNICA

Russell J. Stewart, Kelli K. Svendsen, Ching Wang

University of Utah, Salt Lake City, UT, USA rstewart@eng.utah.edu

The marine Sandcastle worm (P. californica) and related species live in composite mineralized tubes for shelter. The mineral phase is gathered for free from the environment as sand grains and seashell bits by a crown of ciliated tentacles and passed to a pincershaped pair of dexterous palps called the building organ. Dabs (~100 pL) of adhesive are applied onto suitable particles before they are pressed onto the end of the tube with the building organ. The adhesive components are produced in clustered glandular tissue situated around the coelomic cavity of the first three parathoracic segments. The glands contain at least two major secretory cell types distinguished by their densely packed secretory granules: heterogeneous granules contain dense inclusions, homogeneous granules have a uniform appearance. The granules exit from their respective secretory cells through narrow cellular extensions that form bundled channels leading to the building organ. The two granule types travel intact and unmixed in single file columns through separate channels to the building organ. They appear to park, still intact, a few microns from the surface of the building organ until secretion is triggered. Other secretory cells in the vicinity of the building organ, distinguished by the size and staining of their secretory granules, may supply additional adhesive components. The granule types appear to mix like a multi-part adhesive during or shortly after secretion from the building organ. The secreted glue is initially fluid as evident from the contact angles on glass beads and sets into a force-bearing solid foam within 30 seconds—underwater. The glue is comprised of a set of oppositely charged proteins. The major protein component is a polyphosphoric acid containing serial runs of 10-14 serines of which more than 90% are phosphorylated. The polyacidic protein is stored, along with Mg²⁺, in the dense heterogeneous granule inclusions. Other pote ntial protein components identified biochemically and by sequencing random cDNAs from an adhesive gland library are generally polybasic. As part of our larger effort to create synthetic analogs of the natural sandcastle adhesive, our goal is to understand the events occurring in the first few seconds after secretion when a fluid adhesive forms and then turns into a solid foam.

26-B-2-6

THE CEMENT OF SABELLARIID TUBE-DWELLING POLYCHAETES: A COMPLEX COMPOSITE ADHESIVE MATERIAL

Patrick Flammang, Pierre Becker, Aurélie Lambert & Elise Hennebert

Université de Mons, Laboratoire de Biologie marine, Mons, Belgium Patrick.Flammang@umons.ac.be

Sabellariids are tube-dwelling marine polychaetes which live in the intertidal zone. They are commonly called honeycomb worms or sandcastle worms because they are gregarious and the tubes of all individuals are closely imbricated to form large reef-like mounds. To build their tube, they collect sand grains or mollusk shell fragments in their surroundings, dab them with spots of cement, and assemble them into a rigid composite tube. In Sabellaria alveolata, a common species along European coasts, the cement presents a porous aspect when fractured. SEM observations showed that it is in fact made up of hollow spheroids up to 3 μm in diameter embedded in a matrix. This particular ultrastructure was confirmed in TEM, the spheroid cortex consisting of an electron-dense fibrillar material disposed in concentric layers. In addition to the spheroids, the matrix also encloses small electron-dense granules and lacunae. The cement is produced by large unicellular glands housed in the anterior part of the animal and which open at the level of a specialized building organ made up of two lobes located near the mouth. These cement glands are of two types: those containing homogeneous granules and those containing heterogeneous granules. Both types of granules range from 2.5 to 4 µm in diameter and enclose a moderately electron-dense material but, in heterogeneous granules, very electron-dense fibrillar inclusions are embedded in this material. Comparison between the ultrastructure of the granules and that of the cement clearly indicates that the moderately electron-dense material from both types of granules forms the cement matrix while the hollow spheroids derive directly from the inclusions of the heterogeneous granules, which inflate through a still unexplained process. In the California sandcastle worm Phragmatopoma californica, the cement is comprised of three protein families, GY-rich, H-repeat and SY-rich proteins [Endrizzi & Stewart, J. Adhesion, 85:546-559, 2009]. The latter are unusually hyperphosphorylated, up to 90% of their serine residues being phosphorylated. By RT-PCR and cloning, we have identified homologous proteins in the cement of S. alveolata. Immuno-enzymatic and immuno-gold labelling of both cement and glands with anti-phosphoserine antibodies indicated that, in S. alveolata, SY-rich proteins are present in the moderately electron-dense material of both type of secretory granules, as well as in the cement matrix. This confirms the mode of formation of this complex composite cement.

ADSORPTION AND CROSS-LINKING OF MARINE BIOADHESIVES

Hans Elwing

Dept of Cell and Mol Biol/Interface Biophysics, University of Gothenberg, Sweden <u>hans.elwing@cmb.qu.se</u>

The establishment of the bond of sessile marine organisms such as barnacles, mussels, and algae in the marine environment starts with the secretion and the adsorption of the adhesive biopolymers to the substrate. Subsequently, this is followed by the formation of cohesive interactions with the next layer of adhesive biopolymers that are deposited adsorbed on top of the first layer. These two fundamental processes for the adhesive plaque buildup have been subjected to several investigations in recent years using model molecules, especially Mytilus edulis foot protein 1 (Mefp-1) from the blue mussel. With the introduction of optical surface-sensitive methods such as ellipsometry and surface plasmon resonance (SPR), it has been possible to elucidate both the kinetics of adsorption and structure of the Mefp-1 film. In contrast to adsorption, the cohesive interactions or the cross-linking are not easily followed with these optical methods and new approaches and techniques are required. One such technique that has been useful is the quartz-crystal microbalance with dissipation monitoring (QCM-D), which has been used for cross-linking studies of a variety of biopolymers including bioadhesives from mussel [1-2]and algae[3]. We re also developed new surface modifications method to learn more about the details the influence of surface chemistry and topography in the adhesion and cross-linking process of marine adhesives (4).

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26-B-2-8

MUSSEL BIOADHESION: STUDY USING RECOMBINANT MUSSEL ADHESIVE PROTEINS AND THEIR COACERVATED FORMS

Hyung Joon Cha, Seonghye Lim, and Yoo Seong Choi

Department of Chemical Engineering, Pohang University of Science and Technology hjcha@postech.ac.kr

Marine mussels attach to substrates using adhesive proteins. Mussel adhesive proteins (MAPs) have received increased attention as potential biomedical and environmentally friendly adhesives. However, practical applications of MAPs have been severely limited by uneconomical extraction and unsuccessful genetic production. Developing new adhesives requires access to large quantities of material and demonstrations of bulk mechanical properties. Previously, we designed fp-151, a fusion protein comprised of six MAP type 1 (fp-1) decapeptide repeats at each MAP type 5 (fp-5) terminus and successfully expressed it in Escherichia coli. This recombinant hybrid protein exhibited high level expression, a simple purification, and high biocompatibility as well as strong adhesive ability on a micro scale. In the present work, we performed investigations on the bulk adhesive properties of purified fusion fp-151 in air. The unmodified recombinant fp-151, as expressed, contains tyrosine residues and showed significant shear-adhesive forces. Adhesion strength was increased after enzymatic oxidation of tyrosine residues to L-3,4-dihydroxyphenylalanine (DOPA) groups. Addition of cross-linkers generally enhanced adhesion, although too much addition decreased adhesion. Taken together, we present the first bulk-scale adhesive force measurements for an expressed recombinant hybrid mussel adhesive protein. It has also been suggested that complex coacervation (liquid-liquid phase separation via concentration) might be involved in the highly condensed and non-water dispersed adhesion process of MAPs. However, as purified natural MAPs are difficult to obtain, it has not been possible to experimentally validate the coacervation model. In the present work, we demonstrate complex coacervation in a system including recombinant MAPs and hyaluronic acid (HA). We observed successful complex coacervation using cationic MAPs and an anionic HA partner. Importantly, we found that highly condensed complex coacervates significantly increased the bulk adhesive strength of MAPs in both dry and wet environments. Collectively, our results indicate that a complex coacervation system based on MAPs shows superior adhesive properties, combined with additional valuable features including liquid/liquid phase separation and appropriate viscoelasticity.

26-B-2-9

CHEMICAL INSIGHTS ON HOW MARINE BIOLOGICAL MATERIALS STICK

Jeremy R. Burkett, Allison O. Mattes, Cristina Matos-Pérez, James D. White, and Jonathan J. Wilker

Purdue University wilker@purdue.edu

Mussels, barnacles, Ulva, sea stars, tube worms, oysters, and kelp are examples of the many marine creatures producing adhesives and cements. Each organism can attach itself to surfaces with impressive tenacity. From an applications standpoint we would like to prevent this adhesion in order to develop antifouling surfaces for ship hulls. Conversely we would also like to mimic the properties of marine bioadhesives to generate new materials with wet bonding abilities such as those needed for surgical glues. Both preventing and mimicking bioadhesion requires fundamental understanding of the chemistry involved. Our laboratory is working to characterize marine bioadhesives from multiple organisms. Studies begin with the readily accessible adhesive of mussels and progress to other animals. Chemical insights on bioadhesion are sought from experiments with live animals, extracted proteins, peptide models, and synthetic polymers. Here we will combine data from these various studies to arrive at proposed mechanisms of adhesion. Both cohesive and adhesive interactions need to be considered. In the case of each bonding mode more than one type of chemistry may well be at play, especially when looking for themes between the adhesives of different organisms.

27-H2-P: Plenary

FOULING CONTROL TECHNOLOGY: CHANGES THROUGH TYNE

David N. Williams

International Paint Ltd.

David.williams@akzonobel.com

Paint making on the Tyne dates back 1881 when the Holzapfel brothers began to make their way in the world of marine paint. The marine coating brand they launched – International – is still going strong nearly 130 years later and the global organisation that developed from it has become known worldwide for innovative products, high-tech quality and on-the spot service wherever ships ply their trade. This presentation looks back at the history of antifouling paint making on the Felling-on-Tyne from the introduction of the first Self-Polishing Copolymer (SPC) antifouling in 1974 through to the launch of the innovative Intersleek 900 fouling release technology in 2007. The challenges associated with developing new antifouling coating technologies from registration, formulation and testing will be described. The current and future opportunities facing the antifouling market will be reviewed from a coatings industry perspective.

NEW GENERATION OF COPPER(I)OXIDE FOR ANTIFOULING PAINTS

Lars Tomasgaard

Nordox AS, Oslo lars.tomasqaard@nordox.no

A new generation of copper(I) oxide for antifouling paint will be presented. The patented production method involves granulation of copper oxide with a solvent resistant binder. The technology allows the addition of a number of compounds to the mixture. Granulation of a mixture of copper(I)oxide with copper OMADINE® causes an encapsulation of the active ingredients and a favorable classification allowing the use of this product in pleasure craft antifouling. The products are characterized by a low tinting strength allowing the use in yacht antifouling paints. Another characteristic is low specific gravity in the paint and high efficacy allowing the use of significantly lower w/w copper concentrations in the paint without sacrificing performance. The proprietary granulation method also results in the products having controlled release properties with stable and low leaching rates without the initial surge after immersion. This leads to a more favorable risk assessment and regulatory benefits should comparative assessment become a part of the future regulatory regime. Future work will involve further exploring the addition of other metal compounds such as zinc oxide and other inert fillers, as well as the addition of other biocides to take advantage of the control release properties.

27-H2-1-2

MEDETOMIDINE – FROM LAB BENCH RESEARCH TOWARDS MARKET INTRODUCTION

Lena Lindblad

I-Tech AB, Sweden Lena.Lindblad@i-tech.se

Medetomidine was discovered ten years ago to be a substance that in very low concentrations, selectively inhibit barnacle settlement without harming the organism. The reasoning behind the discovery was to use receptor selectivity. Receptor selectivity has been a successful concept within the pharmaceutical industry; effective with limited side effects. However, the pharmaceutical concept relies on in-depth knowledge of human and animal physiology. The overall knowledge about barnacles is less extensive if compared to man, rat or other mammals or invertebrates such as the fruit fly. Our scientific approach was to find a specific and selective compound that regulated a key physiological output that could be manipulated and consequently, in low concentration inhibit barnacle settlement. Medetomidine proved to be such a substance. Besides its biological activity, physical and chemical properties suitable for incorporation in a paint During the past ten years working with Medetomidine, in my opinion it can be concluded that there are some key issues regarding development of new antifouling substances. (a) Effective not only in lab but in also in paint formulation (b) Mode of action as an important factor for toxicological assessments (c)Large scale synthesis (tons). The most difficult issues have not been correlated so much to science, but rather market related concerns. The available resources for developing new antifouling substances and products are less compared to other biotechnology sector. This is becoming even more accentuated due to new regulatory demands that have increased the costs dramatically and therefore, hampered innovations. To overcome these difficulties, I believe that fewer regulatory demands are not to wish for. Instead, rather explore the possibilities to develop the marine antifouling industry towards the biotechnology sector where industry, regulatory authorities and academia interact in taking steps forward towards future product developments. That responsibility must be shared by many and not by industry alone.

THE WINDING ROAD TO COMMERCIAL PRODUCTS- HEMPEL'S EXPERIENCE

Diego Meseguer Yebra, Pere Catala, Santiago Arias

Hempel A/S dmy@hempel.com

Over the course of the last decades, Hempel has had an active role in the research and development of novel Fouling Control products. The first part of this presentation will go through 40 years of intense research covering Krøyer's 1970 patent on the use of PDMS as alternative to biocidal coatings, research on the biology of fouling and on the screening of natural AF active compounds, development of novel self-polishing binder systems and model-based accelerated design processes, design and construction of novel lab-scale ageing setups, drag studies on both biocide-based and fouling release coatings, the use of enzymes as environmentally-friendly ingredients, unique tie-coats for silicones, etc. The presentation will end up presenting our expanding biocide-free assortment and the promising features of our hydrogel-based fouling release top-coats. Along the presentation, we will highlight key lessons learnt, often painfully, in the process of developing better and environmentally friendlier coatings with prospects of commercial success. We hope to provide the audience a better understanding of our industry's business models as a starting point for shaping a better future.

27-H2-1-4

WATER UPTAKE OF COMMERCIAL ANTIFOULING COATINGS WITH BINDERS BASED ON TRIALKYLSILYL ACRYLATES OR METAL ACRYLATES/ CARBOXYLATES

Erik Risberg, Anita Koop, Kari Dahl and Roar Hem

Jotun, Norway erik.risberg@jotun.no

Hydrolyzing or self polishing copolymer (SPC) coatings are a frequently used group of antifouling coatings provided by all major paint suppliers. This technology is based on the reaction of the antifouling coating with seawater, which converts the polymer from an insoluble matrix to a slightly soluble one. A suitable and well defined polishing rate leads to a controlled release of the biocides present in the coating. Three countries, China, South Korea and Japan represent 91% of the new building market based on dead weight tonnage (dwt). In China, with a market share of 36 %, 268 shipyards out of 343 are located along freshwater rivers. During the outfitting period these vessels are exposed to freshwater for extended periods. Within the segment of hydrolyzing antifouling coatings there are two main polymer technologies on the market today. These are based on trialkylsilyl acrylates and metal acrylates/ carboxylates (Fig. 1). In the present work the water uptake of commercial antifouling coatings, based on these two technologies, has been investigated. One interesting aspect is how the outfitting period in freshwater will affect the performance of a coating after launch.

Figure 1. The reaction between seawater and silyl acrylates (a) and metal acrylates (b).

A POINT AT THE OPERATION FOR CONTAINERSHIP

Arthur Touzot

CMA CGM, France ho.atouzot@cma-cgm.com

2009 has been a challenging year for the containership industry. The first 20 companies aggregated loss up to 12 billion dollars. This made each and every carriers change their way of operating vessels commercially and technically. This presentation gives a general overview on containership commercial organization/operation from an insider, its latest evolution and the impact on the present antifouling solution and marketing. This is a short abstract however some critical elements will be in the presentation as i am working in a specific position in operation at CMA CGM. The aim is for me to give a follow up to the speech i gave in southampton but with 3 years of experience with CMA.

27-H2-2-1

BIOFOULING PRESSURE AT EUROPEAN AQUACULTURE FACILITIES OVER A 2-YEAR PERIOD

S Dürr^{1,3}, D I Watson², E Bergtun², C Blair², J Cebriá², J Davenport², J Icely³, J Maguire³, A Manjua, M Marhuenda³, H Mortensen³, J Murphy³, J Newman³, A Pereira³, J Power³, S Prieto³, J Watters³ & J C Thomason³

¹School of Natural Sciences and Psychology, ²Liverpool John Moores University, UK; Department of Zoology, Ecology and Plant Science, University College Cork, Ireland; ³School of Biology, Newcastle University, UK s.t.durr@ljmu.ac.uk

In aquaculture high costs are caused by fouled equipment and infrastructure but also by the product itself being fouled. Aquaculture is part of the food industry and any antifouling strategy used is under regulation by the law. The aim of this study was to determine differences and similarities in spatfalls, problematic fouling species and fouling community development on a pan-European scale in order to define a baseline that establishes the biofouling pressure in the region but can be applied in non-toxic antifouling strategy testing. This was part of the CRAB (Collective Research on Aquaculture Biofouling) European biofouling baseline study. Recruitment and development of biofouling at 11 aquaculture sites across Europe was surveyed for 26 months from February 2005 to March 2007. The sites were Val Akva AS (Mid-Norway), Bømlo Skjell AS (S-Norway), Lakeland Marine Farms Ltd (W-Scotland), Curryglass Enterprises Ltd (SW-Ireland), Fastnet Mussels Ltd (SW-Ireland), James Newman (SW-Ireland), Cudomar S.L (E-Spain), Promociones Marsan S.L (E-Spain), Viveiros Ana Manjua Unipessoal Lda (S-Portugal), Sagremarisco-Viveiros de Marisco Lda (S-Portugal), Alevines Y Doradas SA (Canary Islands). As the field component was to be undertaken by aquaculture workers, standardisation of the survey was achieved through central coordination of the survey design, equipment used and analytical procedures undertaken. Monthly recruitment was measured on ten 20x20 cm² PVC panels at each site. These were exchanged for new panels after each assessment. Development of biofouling was measured on 50 identical panels at each site. Ten were permanently removed every 6 months. Recruitment of fouling species and development of the biofouling community was assessed on the panels using carefully standardised digital photography plus measurement of wet weight. Digital images were analysed using semi-automated image analysis with a stereological approach. Data have been analysed using multidimensional community analysis, and identification of the patterns and processes of fouling with a pan-European perspective will be presented.

THE DEVELOPMENT OF BIOFOULING ON COMMERCIAL SALMON CAGE NETS IN MID-NORWAY

Jana Guenther, Ekrem Misimi, Leif Magne Sunde

SINTEF Fisheries and Aquaculture, Trondheim, Norway jana.quenther@sintef.no

The Norwegian fish farming industry mainly uses copper-based coatings on nets combined with washing to reduce the amount of biofouling. This study quantified the net aperture occlusion at 1, 5, 10 and 15 m depth of two cages, which were irregularly washed in situ, at a commercial salmon farm in Mid-Norway over 5 months. The net aperture occlusion varied significantly with time for both cages, and also with depth for one cage, which had significantly higher net aperture occlusions at lower depths. Laboratory experiments quantified the regrowth of the dominant fouling organism, the hydroid Ectopleura larynx, because some damaged hydroids may remain on the nets after in situ washing and then regrow. Two experiments, determining the effects of different numbers of polyps cut off (all, half and none of the polyps cut off) and different time intervals between cuttings (all polyps cut off on days 0, 2, 4 and 6, on days 0 and 6, and not at all) on the regrowth of E. larynx, were conducted. Both experiments demonstrated that E. larynx can regrow its polyps. Five days after cutting, the hydroids with all of their polyps cut off (99 \pm 10 polyps) and the control hydroids (88 \pm 8 polyps). Similarly, six days after the final cutting, the hydroids repeatedly cut had more than twice the amount of polyps (90 \pm 8 polyps for the hydroids cut on days 0, 2, 4 and 6; and 101 \pm 6 polyps for the hydroids cut on days 0 and 6) than the control hydroids (41 \pm 3 polyps). The results of these experiments suggest that in situ washing of nets is only a temporary measure to control biofouling as E. larynx regrows and occludes the net apertures rapidly.

27-H2-2-3

INNOVATION IN AQUACULTURE CAGES USING COPPER BASED ALLOYS

¹Carol Powell and ²Hal Stillman

¹CDA, UK; ²ICA, USA <u>carol.powell@btinternet.com</u>

Copper alloys used in sea water service have low general corrosion rates but also a high resistance to many localised forms of corrosion which can lead to rapid failure. These properties, together with an inherent high resistance to macrofouling, have led to an interest in their application for Aquaculture cages for many years. However, in more recent times, a co-ordinated effort has been made by the copper industry, producers and end users to further develop designs and sound engineering practices for both surface and submersible enclosures to enable such innovation to become a commercial reality. Three alloys are currently of particular interest: (a) UR 30*, a 64% Copper-Zinc brass alloy with 0.6% tin, 0.3 % nickel and effective microelements; a proprietary trademarked product from Mitsubishi-Shindoh. (b) 90-10 Copper-Nickel, CA 70600. This alloy contains 10% nickel and small amounts of iron and manganese which are important in providing high corrosion resistance. (c)Seawire*, a Copper-3% Silicon alloy containing manganese and micro-alloying elements; a proprietary trademarked product from Luvata. The coppernickel is in the form of an expanded mesh, Seawire* is a welded wire mesh, and the UR 30* is a chain link mesh. UR 30* is already well established and there are around 300 cages installed today. The mechanical, corrosion and biofouling properties of these alloys will be described as well as types of cage design. Several international exposure trials are underway and available results will be discussed. These will include: (1) An aquaculture cage constructed with UR30* brass netting which was deployed in the Gulf of Maine and stocked with cod in June 2009. (2) Development activities in China occurring in the Copper Sea project under the leadership of the East China Sea Fisheries Research Institute and the International Copper Association. Three different types of antifouling copper alloy cages for different sea conditions and fish species are being developed. (3) The results of trials using copper alloy mesh attached to submerged geodesic spherical enclosures provided by Ocean Farm Technologies and deployed at an offshore fish farm in Panama. (4) The antifouling and environmental performance of large scale installations in Chile using UR30* brass netting.

* Trade mark

BIOFOULING ON GREENSHELL™ MUSSEL (PERNA CANALICULUS) FARMS: A PRELIMINARY ASSESSMENT AND POTENTIAL IMPLICATIONS FOR SUSTAINABLE AQUACULTURE PRACTICES

C. Woods, B. Hayden and O. Floerl

National Institute of Water & Atmospheric Research Ltd c.woods@niwa.co.nz

To date, our knowledge of the biofouling associated with Greenshell™ (Perna canaliculus) mussel longline farms, and the contribution of biofouling to the wider ecotrophic effects of mussel farms, is depauperate. This preliminary study examined the development of biofouling over a single crop cycle at two sites in Pelorus Sound, the main growing area for P. canaliculus in New Zealand. This crop cycle covered a 6-month initial seed period and a 6-month final seed period following reseeding of mussels onto new culture ropes. A diverse range of biofouling organisms (69 distinct taxa) were encountered on the mussel ropes, including sessile taxa (algae, sponges, hydroids, anemones, bivalves, bryozoans and ascidians) and mobile taxa (flatworms, polychaete worms, amphipods, isopods, crabs, shrimps, starfish, brittle stars and fish). Biofouling biomass was dominated by suspension-feeding organisms (~88%) such as bivalves, ascidians and, to a lesser degree, bryozoans. Biofouling biomass and taxon richness increased with culture time, although the practice of reseeding dramatically reduced the overall relative and total contribution to mussel line biomass from biofoulers. Averaged relative dry weight contribution of biofoulers to total mussel rope biomass at the beginning and end of both the initial and final seed crop periods was 92.9, 53.4, 8.6, and 11.2%, respectively. Biomass and proportional representation of biofouling and the abundance of major biofouling groups generally varied between the two sites, crop periods, time, and/or the sample depths. Based on biofouling biomass data obtained, we provide an example of calculated suspension-feeding effects of Greenshell™ mussel longlines based on the target crop of P. canaliculus alone, and with two other dominant biofoulers (the blue mussel Mytilus galloprovincialis and the solitary ascidian Ciona intestinalis) factored-in as an example of the possible wider ecotrophic effects of Greenshell ™ mussel farms when biofouling is considered for carrying capacity models. Our study provides preliminary data on the extent of biofouling associated with Greenshell™ mussel farms and the results suggest that biofouling assemblages could affect the ecotrophic effects of mussel farms have. This should be further examined to ensure sustainable aquaculture practices.

27-H2-2-5

FOUL PLAY OR FACILITATION? THE IMPACT OF HYDROID BIOFOULING ON MUSSEL AQUACULTURE IN PORT PHILLIP BAY, AUSTRALIA

Isla Fitridge & Michael Keough

Department of Zoology, University of Melbourne i.fitridge@pgrad.unimelb.edu.au

Marine biofouling - the development of sessile species assemblages on submerged surfaces over time - is a challenge to marine aquaculture operations around the world. Biofouling can severely affect the economics of aquaculture operations through lost stock, extra maintenance costs and compromised health of the species being cultivated. Many biofouling species are non-native and have been introduced from other parts of the world. Preventing and/or managing the impacts of biofouling organisms on farmed species requires an understanding of the ecology and dynamics of biofouling assemblages, and how the composition of these assemblages may evolve in the future as a result of events such as climate change. Hydroids (Cnidaria: Hydrozoa) are a frequently abundant component of marine sessile communities associated with natural and artificial habitats. Many hydroids have the potential for economic impacts through extensive fouling of piles, pontoons, aquaculture facilities and vessel hulls. In Port Phillip Bay, Australia, hydroids are commonly found associated with the culture of blue mussels (Mytilus sp.) The presence of a non-indigenous filamentous hydroid (Obelia dichotoma) on mussel ropes in the bay has historically been noted to substantially increase mussel spat yields, providing an attractive settlement surface for juvenile mussels. However, this species is now being replaced by a stolonal non-indigenous species (Ectopleura crocea). The presence of E. crocea has coincided with a sharp decline in mussel production, related to consecutive years of poor mussel larvae recruitment. E. crocea also heavily fouls mussel ropes and the shells of adult mussel stock. The economic losses for farmers in the bay could be substantial in terms of lost stock, increased operating costs and the inability to catch adequate spat. Detrimental effects of hydroid biofouling on mussel aquaculture have been documented overseas, yet little is understood about the relationship between hydroids and juvenile/adult mussels, or of the role of hydroids in biofouling assemblages. We here present preliminary data on the recruitment of hydroids and mussels in Port Phillip Bay aquaculture facilities and on the impacts of E. crocea on mussel larvae and adults. We also discuss the potential implications of biofouling on the sustainable future of mussel farms and other aquaculture operations in Port Phillip Bay.

27-H2-3-1: Keynote

BIOMIMETIC MICROTOPOGRAPHIES - A GREEN, ANTIFOULING TECHNOLOGY

Anthony Brennan

University of Florida, Gainesville, FL, USA abrennan@mse.ufl.edu

The complexity of the biofouling community challenges our technical solutions for an effective antifouling strategy. At the same time, mother nature provides numerous examples of highly efficient antifouling surfaces. The shark is one natural surface that we have studied and integrated into micro-topographical patterns. The patterns of the shark placoids have been attributed to a combination of antifouling mechanism, but more importantly highly efficient hydrodynamic surfaces that enable the fast moving animals their evolutionary persistence. In this plenary lecture, I will outline our approach to the use of the principles in our designed Sharklet surfaces that exhibit interesting and highly effective antifouling performance for a number of organisms. I will also describe other natural surfaces as well as the potential for application of these surfaces in the marine environment.

27-H2-3-2

WATER-STABLE DIBLOCK POLYSTYRENE-BLOCK-POLY(2-VINYL PYRIDINE) AND DIBLOCK POLYSTYRENE-BLOCK-POLY(METHYL METHACRYLATE) CYLINDRICAL PATTERNED SURFACES INHIBIT SETTLEMENT OF ZOOSPORES OF THE GREEN ALGA *ULVA*

Claudia M. Grozea, Nikhil Gunari, John A. Finlay, Daniel Grozea, Maureen E. Callow, James A. Callow, Zheng-Hong Lu, and Gilbert C. Walker

University of Toronto and University of Birmingham gilbert.walker@utoronto.ca

Nanopatterned surfaces with hydrophobic and hydrophilic domains were produced using the diblock copolymer polystyrene-block-poly(2-vinyl pyridine) (PS-b-P2VP) and polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA). The PS-b-P2VP diblock copolymer, mixed with the cross-linker benzophenone and spin-coated onto silicon wafers, showed self-assembled cylindrical structures, which were retained after UV treatment for crosslinking. The thin films displayed cylindrical domains after immersion in water. This study shows that pattern retention in water is possible for a long period of time, at least for two weeks in pure water and three weeks in artificial seawater. The PS-b-PMMA diblock showed self-assembled cylindrical structures. PS-b-P2VP and PSb-PMMA cylindrical patterned surfaces showed reduced settlement of zoospores of the green alga UIVa compared to unpatterned surfaces. The copolymers were investigated using atomic force microscopy and X-ray photoelectron spectroscopy.

MACROMOLECULAR ENGINEERING OF NANOSTRUCTURED-SURFACE FILMS WITH AMPHIPHILIC COPOLYMERS FOR APPLICATION IN MARINE BIOFOULING RELEASE COATINGS

Giancarlo Galli, Mahesh S. Kumar, Elisa Martinelli, Emo Chiellini

Università di Pisa, 56126 Pisa, Italy gallig@dcci.unipi.it

With an increasing drive towards environmentally benign, non-toxic marine coatings, we are interested in developing novel coatings in which a nanostructured surface can result in improved resistance to and release of marine biofoulig organisms. Most recent and innovative advances include use of hybrid polymer nanocomposites, biomimetic polymer-analogue platforms, lithographically patterned monolayers and plasma assisted chemical vapor deposition on metal surfaces. Although highly diversified in their individual architecture and function, all such technologies share the underpinning concept to exploit the interactions intervening between the fouling organisms and the specific surface features at the nanoscale. Surface segregation of low surface tension polymers may be an additional powerful tool to nanostructure a coating in such a way to comply with the nanosized cues of the foulants, thereby affecting antifouling activity or favouring removal of those foulants that do adhere. In keeping with this last rationale, we devised new low elastic modulus and low surface energy coatings by the homogeneous dispersion of a fluorinated amphiphilic polymer additive in an elastomeric commercially available polymer matrix. We show how the surface morphological, topological and compositional nanoscale complexities add to enhance release of marine micro- and macro-organisms in laboratory bioassays. The 'ambiguous' character of the coating surfaces, due to the simultaneous presence of hydrophibic and hydrophobic domains, resulted in distinct biological performances against organisms with contrasting tendencies to interact with the substratum. The amphiphilic polymers can be formulated in fouling release coatings for application in the marine environment with a proven potential in field trials, namely for shipping.

Acknowledgments. The work was funded by the EC Framework 6 Integrated Project 'AMBIO' (Advanced Nanostructured Surfaces for the Control of Biofouling). The results presented stem from collaboration with the partner groups at the Universities of Birmingham and Newcastle (UK), the Nancy Université-CNRS, BASF, International Paint and Argus Chemicals.

27-H2-3-4

AMBIGUOUS, AMPHIPHILIC SURFACES FOR FOULING RESISTANT COATINGS

Christopher K. Ober¹, Hari Sundaram¹, Youngjin Cho¹, Marvin Paik¹, Edward J. Kramer², Mike Dimitriou², Maureen Callow³, James Callow³ and John Finlay³

¹Cornell University, ²University of California at Santa Barbara, ³University of Birmingham <u>cko3@cornell.edu</u>

Amphiphilic surfaces that present both polar and non-polar components have shown superior fouling resistance as test coatings. One way to achieve such coatings is to make use of block copolymers with a surface active component that contains both polar and non-polar units. Such an amphiphilic coating surface can be easily coated using the self-assembling character of the block copolymer. Amphiphilic triblock surface active block copolymers (SABCs) were prepared through chemical modification of polystyrene-block-poly(ethylene-ran-butylene)-block-polyisoprene ABC triblock copolymer precursors. In one series, the methyl ether of poly(ethylene glycol) [Mr≈ 550 g/mol (PEG550)] and a semifluorinated alcohol (CF3(CF2)9(CH2)100H) [F10H10] were attached at different molar ratios to impart both hydrophobic and hydrophilic groups to the modified isoprene segment. A second series of amphiphilic materials was prepared by attachment of non-ionic surfactants consisting of PEG with one of a fluorinated, silicone or hydrocarbon segments. Coatings on glass slides consisting of a thin layer of the amphiphilic SABC deposited on a thicker layer of an ABA polystyrene-block-poly(ethylene-ran-butylene)-block-poly(styrene) thermoplastic elastomer were prepared for biofouling assays with algae. Dynamic water contact angle analysis, X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) measurements were utilized to characterize the surfaces. Clear differences in surface structure were realized as the composition of attached side chains was varied. In biofouling assays, the settlement (attachment) of zoospores of the green alga Ulva was higher for surfaces incorporating a large proportion of the hydrophobic side chains, while surfaces with a large proportion of the PEG side chains inhibited settlement. The trend in attachment strength of sporelings (young plants) of Ulva did not show such an obvious pattern. However, amphiphilic SABCs incorporating a mixture of PEG550 and non-polar side chains performed the best. The number of cells of the diatom Navicula attached after exposure to flow decreased as the content of PEG550 to non-polar side chains increased.

NANOSCOPICALLY-COMPLEX, AMPHIPHILIC, NON-TOXIC ANTIFOULING MARINE COATINGS: FROM HYPERBRANCHED FLUOROPOLYMER-POLY(ETHYLENE GLYCOL)-DERIVED NETWORKS TO NEW GENERATION MATERIALS

Jeremy W. Bartels, Christopher Fidge, Phillip M. Imbesi, Jun Ma, Karen L. Wooley

Texas A&M University wooley@chem.tamu.edu

This presentation will detail amphiphilic nanostructured material systems, constructed from a general methodology that involves the kinetic, in situ crosslinking of thermodynamically-driven phase segregated states of polymer assemblies. Macroscopic crosslinked networks composed of amphiphilic nanodomains presented on the surface and dispersed throughout the material are obtained by crosslinking of the assemblies in bulk samples. Of particular interest for these materials are the complex surface topographies and morphologies that allow for the materials to exhibit antifouling characteristics. The crosslinked macroscopic networks have been focused upon compositions that include hyperbranched fluoropolymers and linear poly(ethylene glycol)s, although the compositional profiles are being expanded. Unique anti-fouling performances and mechanical properties have been observed, and these data will be presented for a series of the original and new generation materials.

27-H2-3-6

POLYSILOXANES WITH TETHERED QUATERNARY AMMONIUM SALTS AS NOVEL ANTIFOULING/FOULING-RELEASE COATINGS

Partha Majumdar, Elizabeth Crowley, Shane J. Stafslien, Justin Daniels and Bret J. Chisholm

North Dakota State University, USA <u>Partha.Majumdar@ndsu.edu</u>

Polysiloxane coatings with tethered quaternary ammonium salt (QAS) moieties were investigated for potential application as environmentally-friendly, antifouling/fouling-release coatings to combat marine biofouling. Tethering of QAS moieties was achieved by mixing trialkoxysilane-functional QASs into a solution blend of silanol-terminated polydimethylsiloxane, methylacetoxysilane, and a catalyst. A combinatorial/high-throughput approach was applied to the investigation to enable multiple variables to be probed simultaneously and efficiently. The variables investigated were molecular weight of the silanolterminated polydimethylsiloxane, length of the N-substituted alkyl chain of the QAS, counter-ion of the QAS, alkyl chain length between the nitrogen atom and trialkoxysilane group of the QAS, alkoxysilane group of the QAS, and concentration of the QAS in the coating. Antifouling and fouling-release properties of the coatings were determined using a suite of organisms which included the marine bacteria, Cellulophaga lytica and Halomonas pacifica, the diatom, Navicula incerta, and the macrofouling alga, Ulva. So far, over 150 unique compositions were investigated. The results of the investigation enabled the identification of the primary compositional variables that affect activity toward marine microorganisms as well as the production of optimized coating compositions with broad-spectrum activity. Surface morphology of the coatings played an important role in antifouling/foulingrelease performance. Overall, the coatings with heterogeneous surface morphologies were found to be more active as compared to coatings with homogeneous surface morphologies. Incorporation of fumed silica into these QAS-modified, moisture-cured polysiloxanes provided a major enhancement in both tensile modulus and toughness. This allowed the design of oil-modified, silica-filled PDMS-QAScoatings with improved mechanical and fouling-release properties as co mpare to standard silicone coatings.

DEVELOPMENT OF ENVIRONMENTALLY BENIGN, DURABLE AND EFFECTIVE ULTRA LOW FOULING MARINE COATINGS

Shaoyi Jiang

University of Washington, Seattle, USA sjiang@u.washington.edu

Biofouling on ship hulls and other marine surfaces has become a global environmental and economic issue. We have been developing a new type of ultra low fouling marine coatings, to which marine microorganisms can not attach. These nonfouling coatings are as effective as anti-fouling coatings, but do not contain or leach any biocides while they are much more effectively in both performance and cost than environmentally benign fouling-release coatings, particularly for low ship moving speeds. In this talk, I will update our recent R&D progress in two areas - (a) design of ultra low fouling materials to resist nonspecific protein adsorption, bacterial adhesion/biofilm formation, and marine microorganism attachment, and (b) development of non-toxic, durable, effective, and low-cost ultra low fouling coatings with excellent mechanical strengths for marine applications. Under support from the Office of Naval Research (ONR), we have demonstrated that several zwitterionic-based materials are ultra low fouling and have developed several nontoxic and stable ultra low fouling coatings based on these zwitterionic materials. Marine laboratory tests have confirmed the outstanding performance of our coatings against a variety of marine microorganisms. We have developed paints and spray-coated them onto surfaces covered with an epoxy primer. Field tests of these panels clearly demonstrated that our coatings are very effective to defer the settlement of biofoulants. Our current focus is on the development of long-lasting coatings that are capable of effectively deferring biofouling under static conditions over a long period of time.

27-H2-3-8

NOVEL TECHNOLOGIES TO REDUCE BIOFOULING ON VESSELS WHEN IN PORT

Andrew Scardino

Defence Science Technology Organisation Australia andrew.scard<u>ino@dsto.defence.gov.au</u>

Biofouling is of particular concern for military vessels as they have very different operational tempos than commercial ships. The Royal Australian Navy (RAN) faces severe biofouling pressures, particularly when vessels are stationary for extended periods. The RAN operates in varying geographical localities, often in tropical waters were biofouling can be extreme. Some common problems have occurred with fouling-release coatings in that not all organisms are released at operating speeds. Issues with traditional antifouling coatings include copper tolerant species, poor application and unscheduled dry dockings. DSTO has developed novel technology to reduce biofouling on vessel hulls when in port. The use of a fine stream of air bubbles, released from spargers positioned underneath the hull has been trialled over several fouling seasons. The air bubbles scour the surface of the hull and also act as a barrier to most organisms settling on the hull. The air bubbles are most effective when used in combination with a fouling-release coating. A substantial reduction in species diversity and thickness is reported with a notable absence of calcareous fouling species. The air bubble treatment reduces the roughness of the hull as only a thin layer of slime and hydroids develop. The reduction in hull roughness is anticipated to translate into significant fuel savings, increase top speed and range as well as reduce maintenance costs. Other novel technology discussed in this paper includes the use of low frequency vibration to control fouling and bio-inspired surface modifications for fouling resistance.

PREPARATION AND TOPOGRAPHY OBSERVATION OF FAVEOLATE MICROSTRUCTURE SURFACE ANTIFOULING MATERIAL

Wang Li, Lin Cunguo, Duan Dongxia, Zheng Jiyong

State Key Laboratory for Marine Corrosion and Protection, Luoyang Ship Material Research Institute (LSMRI), Qingdao 266071, China wanql@sunrui.net

The settlement of microorganisms on artificial surfaces immersed in sea water, usually termed as marine biofouling, has enormous harm upon ships and other sea facilities. Usually, the marine biofouling can be reduced markedly or resisted by the use of the antifouling coatings. Along with the ban of traditional antifouling coatings containing organotin compounds, Current antifouling strategies are focused on the development of environmentally friendly coatings that protect submerged surfaces from the accumulation of colonizing organisms (i.e., biofouling). Bioadhesion and surface wettability are influenced by microscale topography. One ecofriendly approach is the manipulation of the surface topography on nontoxic materials to deter settlement of the dispersal stages of fouling organisms. The fabrication method of microstructure material mostly depend on the etching, microcontact printing, replica molding etc. These methods are applicable for the theories research, but make against mass production and application. Molecular self-assembly offers unique directions for the fabrication of novel supramolecular structures and advanced materials. In this paper, several kinds of acrylic resin and silicone were successfully synthesized. The faveolate microstructure surface was prepared by blending the acrylic resin and silicone without containing any toxic biocide, then the mechanism of this faveolate microstructure coming into being was analyzed.

27-H2-3-10

A NEW ANTIFOULING TECHNOLOGY BASED ON OXYGEN DEPLETED SURFACES

 $^{1}\text{Lindgren JF, }^{2}\text{Haeffner M, }^{2}\text{Ericsson CT, }^{1}\text{Jonsson PR and }^{3}\text{Elwing H}$

¹Univ Gothenburg, Dept Marine Ecol Tjarno, SE-45296 Stromstad, Sweden, ²R&D Ekomarine AB, SE-13102 Nacka, Sweden ³Univ Gothenburg, Dept CMB SE-40530 Gothenburg, Sweden <u>per.jonsson@marecol.qu.se</u>

A novel, non-toxic strategy to combat marine biofouling is presented. The technology is a paint with additions of up to 43% of industrial protein. Through microbial degradation of the protein component, an oxygen-depleted layer rapidly forms in a 0.2 mm layer close to the paint surface. With the present paint formulations, a stable, O_2 -depleted layer can persist for 16 weeks. Barnacle larvae (cyprids) did not settle on panels where oxygen saturation was 20%, and cyprids were killed when exposed to O_2 -free water for more than 1h. It is also shown that the O_2 -depleted layer will rapidly reform (within 15min) after exposure to turbulent flow. Field exposure of panels for 16 weeks showed that paint with protein reduced fouling by barnacles and bryozoans by 80% and close to 100%, respectively. The results suggest that this novel technology may be developed into a non-toxic alternative to copper-based antifouling paints, especially for pleasure boats in sensitive environments. There is clearly potential for further development of the paint formulation, and a full-scale test on a boat-hull suggested that service-life under realistic operations needs to be improved.

Lindgren, JF; Haeffner, M; Ericsson, CT, et al. "Oxygen-depleted surfaces: a new antifouling technology" BIOFOULING (2009) 25, 455-461

ANTI-BARNACLE EFFECT OF MEDETOMIDINE IN SOFT AND HARD COATINGS

Mia Dahlström, Martin Sjogren, Per R Jonsson, Mattias Berglin and Hans Elwing

Department of Cell and Molecular Biology, University of Gothenburg, Sweden mia.dhalstrom@fiskeriverket.se

The acorn barnacle remains to be a serious fouling organism in the marine environment. Previous research at our lab has lead to the discovery of a pharmacologic substance, Medetomidine, (4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole) which is very effective in repelling barnacle larvae in antifouling paint formulations. In this investigation we studied the release of medetomidine from two different coatings, one "soft" rosin-containing formulation and one "hard" Teflon-based matrix ("VC 17 without copper") formulation. The formulations were painted at solid surfaces yielding a concentration of about 17 ug medetomidine/cm² at the experimental surfaces. High performance liquid chromatography (HPLC) was used for the quantification of the release rate of medetomidine under standardized condition at 1, 2, 4, 8, 16 and 32 days. We found that the release rate of medetomidine from the hard surface was fast from day 1 to day 16 and peaked at about 300 ng/cm²/day at day 1. At day 32 the release rate was about 10 ng medetomidine/cm². Corresponding data on the soft surfaces indicated that the release rate of medetomidine was slow and about 10 times lower from day 1 to 16. At day 32 the release rate was about 5 ng/cm²/day. The same coatings were also checked for the colonization of the barnacle Balanus improvisus during field condition. Adult barnacles appeared at the coated surfaces day 16 and 32. It was obvious that medetomidine had a significant anti-barnacle effect when present in the rosin-based coating since the control surfaces (soft surfaces without medetomidine) was densly colonized with barnacles. The number of attached barnacles at the hard control surfaces was similar to the soft surfaces. In contrast to the soft coatings the presence of medetomidine in the hard surfaces had no apparent anti-barnacle effect. We concluded that the release of "free" medetomidine from the coating was not related to the anti-barnacle effect of the coatings. Instead it seems that the anti-barnacle effect of the medetomidine is related to the aviability of the medetomidine within the coating layer.

Dahlström M, Mårtensson LGE, Jonsson PR, Arnebrant T and Elwing, H., (2000) Biofouling 16, 191-203

27-B-1-1: Keynote

A PERSPECTIVE FROM 2 DECADES OF ACADEMIC LAB AND FIELD-TESTING OF EXPERIMENTAL AND COMMERCIAL COATINGS

Dan Rittschof

Duke University ritt@duke.edu

My research in the process and management of biofouling and corrosion spans over 25 years with over 25 years of continuous use of fouling testing in the laboratory and field and over two decades of testing of foul release surfaces. This talk will provide data that highlight two main points: 1. Laboratory study can inform theory and technology development. 2. Field studies are necessary to confirm laboratory results and are essential to the demonstration of efficacy. Additional studies are necessary to determine the impact of management approaches with respect to existing business models and to understand environmental impacts if the technology gains market share.

27-B-1-2

INTEGRATION OF LABORATORY AND FIELD TESTING WITHIN THE AMBIO PROJECT

J A Callow

University of Birmingham <u>i.a.callow@bham.ac.uk</u>

In the EC-funded Integrated Project 'AMBIO', approximately 500 coatings intended for a number of end-uses, including ship hulls, boats, fish nets, power inlets, optical windows, heat exchangers and membranes, were evaluated in laboratory assays for resistance to settlement/adhesion of fouling organisms. Assays employed a freshwater bacterium, two marine bacteria, the green alga Ulva and *Balanus amphitrite*. The biological evaluations were selected so that promising coatings for various end-uses could be identified. In addition, the surface properties of the majority of the coatings were determined. A number of specific examples of coatings that proceeded through laboratory evaluations to field trials will be given.

TESTING AN ANALOGUE OF ANTIFOULING FROM A MARINE SPONGE

¹Ricardo Coutinho, ²Cláudio Cerqueira Lopes, ²Rosangela Sabattini Capella Lopes, ¹Willian Romão, ¹José Eduardo Arruda Gonçalves, ³Renato Crespo Pereira

¹Division of Biofouling,Instituto de Estudos do Mar Almirante Paulo Moreira, Brazil, ²Laboratory of Analytical Chemistry, Federal University of Rio de Janeiro, Brazil, ³Federal University of Fluninense, Rio de Janeiro, Brazil rcouitnhosa@yahoo.com

The use of natural products as antifoulants has been an active research area for the last 30 years. However, little advances has been achieve in order to produce an antifouling paint with a natural substance in their matrix. Research in natural products in Brazil started in 1995 in the Brazilian Navy and Federal University Fluminense with emphasis in the field and laboratory test of antifouling (AF) activity extracted. More recently we synthesized a Glycerophospholipids with a chemistry structure analogue that produce by a marine sponge genera Crella, incorporated it in a paint matrix and tested in the field during one year. The results showed a significant reduction in the fouling growth with compared with a painel control without antifoulouling paint but, the performed was lower that obtained by a commercial paint control. Nevertheless, the results are promising and may contribute in finding of environmentally friendly marine coatings.

27-B-1-4

ECOPAINT PACA PROJECT: ANTIFOULING ACTIVITY OF BIOCIDAL COMPOUNDS THROUGH BIOASSAYS AND FIELD IMMERSION TEST

¹Charlène Anton, ¹Mercedes Camps, ²Romain Davy, ¹Sandra Lafond, ¹Brigitte Tanguy, ¹Lydia Horatius, ³Régis Delesmont, ¹Jean-François Briand, ²Françoise Quiniou, ¹Christine Bressy, ¹Yves Blache

¹Laboratoire Matériaux Polymères Interfaces Environnement Marin, Université du Sud Toulon-Var, France; ²IFREMER Centre de Brest, France, ³Institut Pasteur de Lille, Laboratoire Littoral, France charlene.anton@univ-tln.fr

In the past decade, the antifouling paint industry has been totally disrupted with the ban of tributyltin oxide by the International Maritime Organisation (IMO). To be effective in an environmentally friendly manner, the tin-free systems have to replace the harmful TBTO biocide by new biological active compounds which are under the European Biocidal Products Directive (BPD). In accordance with this new regulation, the substances have to show an inhibition effect of the settlement of target species on immersed structures without having toxicity and negative consequences on non-target marine organisms. The approval for a marketing authorisation will be given only to the products which have proved their activity and their lack of toxicity. Knowing that the impact of a substance on the environment depends on different parameters (concentration, solubility, accumulation, diffusion, etc), tests have to be realised on the active substance, on the coating containing the active substance and on the released substances. The Ecopaint PACA project aims at developing innovative paint technologies with long-time efficiency and limiting toxic products. One part of the project is focused on the activity of the biocide and its impact on the antifouling performance of the coating. The activity and the toxicity of biocidal compounds registered under the BPD and molecules coming from synthetic pathways or available on the market are assessed through in vitro adhesion and ecotoxicity tests. The inhibition of the adhesion of pioneer bacteria was performed using a multi-well plate method. Ecotoxicity was evaluated against several non-target species representing five trophic levels. In addition, the macrofouling on coatings containing the active molecules was assessed through raft immersion test. Finally, a parallel was drawn between the results obtained through bioassays and through field immersion test concerning the activity of the biocides.

CORRELATION BETWEEN LAB ASSAYS AND FIELD TESTING RESULTS FOR SILOXANE-POLYURETHANE FOULING-RELEASE COATINGS

Dean C. Webster, Abdullah Ekin, Rajan Bodkhe, Stacy Sommer, Shane Stafslien, Justin Daniels, Maureen Callow, James Callow, Franck Casse, Stephanie Thompson, Emily Ralston, Geoffrey Swain, Brian Nedved, Michael Hadfield, Lenora Brewer, Dean Wendt

North Dakota State University, University of Birmingham, Florida Institute of Technology, University of Hawaii, California Polytechnic State University

dean.webster@ndsu.edu

Siloxane-polyurethane coatings were screened using laboratory assays and selected coatings were also subjected to field testing to determine the viability of laboratory screening to identify coatings having good performance properties. While field immersion testing of new marine coatings compositions is the only reliable testing method available to date, laboratory assays are of critical importance in identifying those compositions suitable for field testing. This is especially true when carrying out high throughput synthesis of hundreds of coatings compositions in the laboratory. A large number of siloxane-polyurethane coating compositions were prepared and subjected to screening using surface energy analysis and pseudobarnacle adhesion. A subset of coatings was subjected to testing using marine organisms in the laboratory. These included algae, bacteria, and barnacles. Set of coatings having a range of performance in laboratory assays were tested using field immersion testing at three different test sites for up to 24 months. It was observed that coatings which performed poorly in laboratory assays also had poor performance in field testing. Thus, the laboratory assays are able to clearly eliminate poor performing coatings. Within the good performing coatings, the barnacle readhesion assay was the best in being able to predict the variations observed in organism adhesion over long-term field testing.

27-B-1-6

RAPID FIELD TESTING OF FOUL-RELEASE COATINGS USING A NOVEL WATERJET TESTING APPARATUS

¹Chin Sing Lim, ¹Gary H. Dickinson, ¹Serena Teo, ²Stacy A. Sommer, ²Dean C. Webster

¹Tropical Marine Science Institute, National University of Singapore, ¹Center for Nanoscale Science and Engineering, North Dakota State University

tmsteolm@nus.edu.sg

Foul-release technology is a promising alternative to broad-spectrum biocides for the control of marine fouling. Foul-release coatings, which are typically composed of low surface energy silicone or polyfluoro polymers, impede secure attachment of marine organisms. Fouling organisms can be cleaned easily from effective foul-release polymers, often for extended periods of time. Assessment of foul-release formulations typically proceeds through a series of laboratory assays, followed by marine static immersion testing of the most promising coatings. This process, however, can be expensive and time consuming, particularly during the static immersion phase; static immersion testing takes months to years to complete and requires a large amount of polymer (i.e. enough to coat replicate full size panels). To address these issues, we have developed a rapid field testing procedure, which incorporates a novel waterjet testing apparatus. Polymer formulations are coated onto 1 x 3 in. coupons (the size of a microscope slide), loaded into a slide box, and immersed at our static immersion test site in Singapore. After 3-4 weeks in Singapore waters, slides are typically fouled with various juvenile invertebrates and a thick layer of slime. Following immersion, slides are subjected to waterjet testing using an integrated waterjet screening system, designed in collaboration with Aromatrix Consulting Engineers Pte. Ltd. The waterjet system directs a steady stream of water from a multi-stage pump onto coated slides, which are mounted on an automated speed-controlled moving rack. Pressure of the waterjet can be precisely controlled. Removal of biofouling can than be quantitatively scored and compared among coating formulations. The major advantages of this procedure are that it is quick (generally completed in 3-4 weeks), only requires a small amount of polymer, and it consumes negligible space at static immersion test sites. In collaboration with NDSU, we are currently assessing how results of rapid tests correlate to those of long-term static immersion by testing the same set of siloxane-polyurethane coatings using both methods. We predict that pre-screening of foulrelease formulations prior to full scale static immersion testing will be a valuable tool for the prediction of coating success.

RAPID BIOLOGICAL LABORATORY ASSESSMENTS OF ANTIFOULING MARINE COATING PERFORMANCE: THEIR UTILITY AND RELATIONSHIP TO STATIC OCEAN IMMERSION TESTING

Shane J Stafslien

Center for Nanoscale Science and Engineering, North Dakota State University, USA Shane.Stafslien@ndsu.edu

The development of new and effective antifouling marine coatings requires a considerable amount of time, effort and resources to successfully transition a technological concept to the hull of a sea going vessel. In most instances, the end product available for distribution to the consumer has been carefully developed through several iterations of performance evaluations and subsequent coating reformulations. Although the application and long-term exposure on a vessel hull is the most effective way to evaluate broad-spectrum antifouling performance, this is only employed for the most mature coating technologies. More often, coatings that are in the earlier stages of development are assessed with a combination of laboratory assays and static ocean immersion testing to gauge their antifouling potential. A suite of rapid biological laboratory assays have been developed at NDSU to accommodate the performance evaluation of large numbers of antifouling marine coatings generated with a combinatorial approach. These rapid screening assays employ the use of automated tools to quickly assess the antifouling performance of coating arrays with marine bacteria, microalgae and barnacles. The goal of these rapid laboratory screening assays is not to necessarily identify the most promising coating candidates, but more realistically, to "weed out" or eliminate subpar coating compositions to obtain more manageable numbers for advanced performance assessments. Coatings that show promise in the laboratory are scaled up, applied to large raft panels and sent out to field testing sites for static ocean immersion evaluations to facilitate the identification of lead candidates that may warrant consideration for further development. Several classes of experimental antifouling coating compositions have been evaluated with both the rapid biological laboratory assays at NDSU and static ocean immersion testing at Office of Naval Research funded field testing sites. In general terms, good agreement in antifouling performance between the laboratory and the field have been observed. Several critical factors, such as immersion time, coating preconditioning, coating durability and seasonality, can confound these comparisons and make absolute correlations difficult to establish. However, when partnered together, laboratory and field assessments are extremely effective tools that can be used to aid in the development of new antifouling coating technologies.

27-B-1-8

BIOASSAY SCREENING AND IMAGING FOR ANTIFOULING PERFORMANCE OF NOVEL NATURAL PRODUCTS

¹Salta M., ¹Wharton J.A., ¹Stoodley P., ¹ Dennington S., ² Iglesias-Rodriguez D., ¹Wood R.J.K., ^{1,3}Stokes K.R.

¹National Centre for Advanced Tribology, University of Southampton, UK; ²National Oceanography Centre, University of Southampton, UK; ³Physical Sciences Department (Dstl), Dstl Porton Down, UK ms2104@soton.ac.uk

The underwater hull of a ship is exposed not only to the corrosive seawater environment, but also to the constant accumulation of biofouling. Biofouling, or marine growth, includes any attaching organisms such as bacteria, diatoms, tubeworms, mussels, barnacles and algae. Marine growth is a major problem continually encountered when dealing with the underwater hull and platforms, which can affect a vessel's performance including: speed, hydrodynamic efficiency, fuel consumption and weight. The use of tributyltin (TBT), in coatings was widely used for its antifouling capacity. However, in September 2008 it was prohibited due to its toxic affects in the wider marine environment, requiring that structures must have all the coating removed or overlay a protective barrier to prevent the leakage of the TBT. Therefore, the need for new, effective and environmentally friendly coatings has been the focus and challenge for the scientific community. The ideal antifouling coating would prevent marine growth as well as maintain a long performance life, while keeping within increasingly strict environmental regulations. This study has assessed the antifouling performance of natural products (NP), both crude extracts and isolated compounds, from marine sources (i.e. the red seaweed Chondrus crispus) and a purified furan derivative (PFD) from a terrestrial source, against biofouling organisms which included marine bacteria (Cobetia marina ATCC 25374, Marinobacter hydrocarbonoclasticus ATCC 49840 and Pseudoalteromonas sp NCIMB 2021) and diatoms (Cylindrotheca closterium and Amphora coffeaeformis), as well as cyprids (Balanus amphitrite). The biofilm growth and adhesion kinetics were quantified using a multidetection microplate reader utilising nucleic acid based viability staining and natural bioluminescence. These bioassays were corroborated using a novel application of the imaging capability of the microplate reader, to quantify biofouling in real time over a 48h period. Laser scanning confocal microscopy was used to compare biofilm structures for the different microorganisms in the presence and absence of the NPs. It was found that the PFD inhibited biofilm attachment and growth for the selected bacterial and cyprid assays in a dose dependant manner, down to a concentration of 1 ppm. The crude C. crispus extract showed inhibitory effects on biofouling in some bacterial assays.

A RELIABLE MARINE ANTIFOULING BIOASSAY BASED ON IN VITRO ADHESION: COMPARISON OF THE RESPONSE OF FIVE PIONEER BACTERIA

¹Mercedes Camps, ¹Jean-François Briand, ¹Linda Dombrowsky, ¹Gerald Culioli, ²Alexis Bazire & ¹Yves Blache

¹ Université du Sud Toulon-Var, France; ²LBCM, Université de Bretagne Sud, Lorient, France <u>camps@univ-tln.fr</u>

Marine biofouling occurred naturally as a colonization process of immersed substrata, leading to major economic and ecological consequences. Identifying new antifouling biocides are necessary, in particular because of the recent banning of traditional biocides. Reliable laboratory tools are thus required, the direct assessment of coatings in situ being expensive and time consuming. Biofilm formation, which starts with the recruitment of pioneer bacteria, is a key step during the biofouling process. In this study, pioneer bacteria from marine biofilms have been used and their adhesion was monitored using a fluorescence-based assay. Five strains isolated from various artificial substrata and from three different French locations are subjected to this monospecific assays. Nine biocides including commercial, natural and natural-derived products were tested as antifoulant. Based on the utilisation of these strains and molecules, the reliability of the assay was evaluated. This study suggests that strains could be classified depending on their sensitivity to the biomolecules used. Considering the nine molecules, the most sensitive strains were a *Paracoccus sp.* strain isolated in Brittany and a *Polaribacter sp.* strain from the Toulon bay. However, strain sensitivity also depended on the molecules tested. Among the commercial antifoulants, TBTO and Sea Nine® showed a low EC50 (< 20μ M) for most of the strains, in contrast with others like Preventol®, which showed a very high EC50, overall except for one strain. The non commercial products showed significant activities, in particular TFA Z, which EC50 ranged between 63 and 130 μ M depending on the strains. In conclusion, this study shows that this assay is a reliable antifouling assay to test in vitro bacterial adhesion. Our results strengthen the need to perform antifouling bioassays with a panel of strains with complementary profiles of activity (ie adhesion).

VARIATION IN DIATOM COMMUNITY STRUCTURE ON ANTIFOULING AND FOULING RELEASE COATINGS FROM THREE STATIC IMMERSION TEST SITES IN FLORIDA

Kelli A. Zargiel and Geoff W. Swain

Department of Marine and Environmental Systems, Florida Institute of Technology <u>kzargiel@my.fit.edu</u>

Diatoms are primary colonizers of antifouling and fouling release ship hull coatings and cause increases in drag, fuel consumption, and exhaust gas emissions. There are few studies which report on diatom community development on modern ship hull coatings. This study looked at diatom communities on eight commercial ship hull coatings: three ablative copper surfaces, two copper free biocidal systems, three fouling release coatings, and one polyvinylchloride control surface. Coatings were exposed at 0.5 meter depth at three static immersion test facilities along the east coast of Florida (Daytona, Sebastian, and Miami) over a period of four months. The data were analyzed to address the following three objectives: to compare differences in diatom communities among the coatings, among the sites, and at different exposure times. Over twenty five genera of diatoms have been identified, including some of the more commonly known foulers: Achnanthes, Amphora, Cocconeis, Entomoneis, Licmophora, Melosira, Navicula, Nitzschia, Synedra, and Toxarium. The eight commercially available coatings tested in this study showed significant differences in diatom fouling after 60 and 120 days of exposure. Differences were seen in community structure with diversity changing among test sites and coating types, and between exposure periods. These results demonstrate difference in antifouling and fouling release performance and highlight the need to test coatings at geographically different static immersion test sites.

27-B-2-2

WHAT IS THE INFLUENCE OF THE NATURE OF SUBMERGED ARTIFICIAL SURFACES ON THE STRUCTURE OF MICROBIAL BIOFILMS COMMUNITIES?

¹Jean-François Briand, ^{1, 2}Ikram Djeridi, ³Dominique Jamet, ⁴Stéphane Coupé, ¹Christine Bressy, ⁵Brigitte Le Berre, ⁵Frédéric Rimet, ⁵Agnès Bouchez & ¹Yves Blache

¹Univ. Sud Toulon-Var, France; ²UMR CNRS 6117, LMGEM, Marseille, Fr; ³PROTEE-EA 3819-EBMA, USTV, La Garde, Fr; ⁴PROTEE-EA 3819-EB2M, USTV, La Garde, Fr; ⁵INRA-UMR CARRTEL-RITOXE, Thonon, Fr briand@univ-tln.fr

Biofouling is a natural process of colonization of submerged surfaces, involving a wide range of organisms, from bacteria to invertebrates. The biofilm formation starts with the recruitment of pioneer bacteria and rapidly evolves to a more complex structure, involving other microorganisms, including microalgae. The aim of this study was to assess the influence of the nature of six artificial substrata with different surface energies, including antifouling paints on the biofilm microbial communities of the biofilms. Six substrata (polystyrene, Teflon®, two commercial antifouling paints and two paints produced in our laboratory) were submerged in triplicate, in May 2009, during two weeks, at two localities near Toulon on the French Mediterranean coast. At those localities, water qualities were dissimilar as one was in the Toulon military harbor while the other was on the south coast of Porquerolles Island, which is a natural protected area. The bacterial and microalgal diversities were investigated by PCR-DGGE and microscopic identifications respectively. In addition, the relative abundance of microalgae was studied for a period of 45 days. . We showed lower fouling density at Porquerolles compared to Toulon harbor. The bacterial community shows similar trends. It appears to be structured both by the sites and by the type of substrata. Pioneer microalgal communities were dominated at the two sites, and whatever the surfaces involved, by the same two diatom species, Licmophora gracilis and Cylindrotheca closterium. Nevertheless, the fouling density showed the same tendency for the two sites with a significant antifouling effect of all the antifouling coatings compared to Teflon and even more to polystyrene. After the pioneer stage, both the efficacies (densities) and the dominance of the diatom community varied from a paint to another but always implicating other species than the pioneer ones (Nitzschia spp., Navicula spp.).

EXTRACELLULAR POLYMERIC SUBSTANCE SYNTHESIS BY BACTERIA DURING ADHESION ON SURFACES: INFLUENCE OF SUBSTRATUM VARIABILITY AND ENVIRONMENTAL FACTORS

S. Satheesh

Centre for Marine Science and Technology, Manonmaniam Sundaranar University, India satheesh s2005@yahoo.co.in

The adhesion of microbes on hard surfaces and the formation of biofilms are associated with the synthesis of extracellular polymeric substances (EPS). EPS are known to play a key role in the adhesion of microbes and also form a significant part in the biofilm matrix. The role of substratum variability and environmental factors on EPS production by marine bacteria during biofilm formation was studied under laboratory conditions. Glass, stainless steel, plastic, and smooth and rough polythene sheets were used as substratum for biofilm formation. EPS production was also assessed in different salinity, pH, and calcium and magnesium concentration of the aquatic medium. EPS was isolated from the biofilm formed on different surfaces and also under different environmental conditions. The total carbohydrate and protein content was estimated. The EPS sample was also subjected to thinlayer chromatographic (TLC) analysis and SDS-PAGE for qualitative study. Results showed considerable variation in the amount of EPS produced by the bacteria that adhered on different surfaces. The carbohydrate and protein content was high on the EPS isolated from the bacteria that settled on stainless steel and low in the biofilm developed on glass. The EPS isolated from the bacteria that adhered on rough surfaces showed a maximum of four distinct spots in TLC. SDS-PAGE also showed variations in the composition of proteins of the EPS synthesized by the bacteria isolated from different surfaces and also from the coupons submerged under various environmental conditions. In general, the present study indicates that substratum variability and environmental factors strongly influence the composition of EPS synthesized by the bacteria. Although characterization of EPS produced by bacteria is not novel, a comparative study of the bacteria isolated from different surfaces may improve our understanding of the mechanism of bacterial adhesion.

27-B-2-4

NEW MARINE BIOFILM FORMING MODEL: PSEUDOALTEROMONAS HAERENS

Dreanno C, Leroy C, Rubio C, Mazeas F, Compère C.

Service Interfaces et Capteurs, IFREMER catherine.dreanno@ifremer.fr

The surface colonisation by microorganisms is described as one of the first steps in marine fouling formation. At the beginning of adhesion, bacteria colonize the surface and then build up a biofilm. The formation of these biofilms is a complex phenomenon involving the environment, the bacteria, and the colonized surfaces. These marine biofilms influence the settlement of a variety of invertebrate larvae and macroalgal spores In order to develop new antifouling strategies, it is crucial to identify and understand the adhesion mechanisms, the biofilm dynamic and chemical signals released by pioneer bacteria. In the frame of a long term study of biofilm formation in marine environment few species were isolated from stainless, steel, glass coupons immersed in natural seawater in the bay of Brest (France). A novel pioneer marine species, previously named D41, was selected for its high adhesion capacity on any types of material and its ability to produce extracellular polymeric substances (EPS). Based on cultures conditions, phenotype characteristics, and phylogenetic analysis of 16s rRNA, DNA G+C content and DNA-DNA hybridization, a new name was proposed for this strain: Pseudoalteromonas haerens. The surface chemical composition was investigated and showed evidence of proteins on membrane, explaining its high ability of adhesion. The composition of the EPS was studied and show high level of proteins and glycoproteins in contrast to other biofilm forming model. Moreover, the adhesion of P. haerens is inhibited by subtilisin, a protease with a broad substrate spectrum and active in seawater conditions, demonstrating a major role of proteins of EPS in the bacterial adhesion. In order to get a better understanding of adhesion mechanisms and biofilm regulation and competition, the "surfaceome" and secretome are currently investigated by a genomic and proteomic approach. The genome of P. haerens has just been sequenced de novo by pyrosequencing. Recent progress in genome sequence analysis and comparison will be presented and discussed.

DETERMINATION OF DISTRIBUTION OF PAINT ADDITIVES AND ASSESSMENT OF THEIR LEACHING RATES USING LASER SCANNING CONFOCAL MICROSCOPY

¹Liam Goodes, ¹Simon Dennington, ¹Julian Wharton, ¹Robert Wood, ²Keith Stokes

¹University of Southampton; ²Defence Science and Technology Laboratory lrq104@soton.ac.uk

The recent tributyltin ban, coupled with increasing concerns on copper oxide and booster biocide persistence and toxicity, has been a driver for the development of new and effective biocides to meet ever more stringent legislation. Natural products (NP), derived from marine organisms with their own chemical anti-fouling defences, have been identified as active anti-foulants. However, the integration of these compounds is hindered by their large size, complex chemistry and poor compatibility with the traditional polymeric binders that are used to deliver biocides. Short life-time in exposure trials is therefore symptomatic of most NP-based coatings, which often persist for 2 months at best. NP leaching mechanisms and binder distribution are poorly understood; even when binder depletion is controlled by use of self-polishing copolymers, depletion of NP additives during immersion may be nonsynchronous. This work provides greater insight on NP behaviour and integration in polymeric binder systems, and on leaching mechanisms of these novel biocidal compounds. Laser Scanning Confocal Microscopy has been used as a novel method to determine NP distribution within paint film binders. This technique allows the visualisation of paint film structure to a depth of around 100 µm, and permits the resolution of NP crystals in the binder. Furthermore, many NPs contain aromatic structures which demonstrate autofluorescence. Certain natural compounds are therefore discernable from the binder when an excitation is applied, after absorption/emission spectra are determined for NP additives in the paint film. The method is applied to anti-fouling paint samples of different binder types ranging from insoluble to self-polishing, which are incrementally exposed to dynamic accelerated erosion methods. These are examined to resolve leach fronts of binder and biocide separately. Copper oxide-based analogues are evaluated with Scanning Electron Microscopy/Energy Dispersive X-ray spectroscopy for comparison of leaching rate with NP-based formulations (Fy et al., 2005). In time, this methodology could be extended to analysis of more traditional biocidal additives as well.

FÄY, F., LINOSSIER, L., LANGLOIS, L., HARAS, D. & VALLÉE-RÉHEL, K. (2005) SEM and EDX analysis: two powerful tools for the study of antifouling paints. Progress in Organic Coatings, 54, 216-223.

27-B-2-6

INHIBITION OF BIOFOULING BY QUORUM SENSING INHIBITORS

¹Sergey Dobretsov, ²Max Teplitski, ³Valerie J. Paul, ⁴Peter Proksch

¹Sultan Qaboos University, Oman; ²University of Florida, USA; ³Smithsonian Marine Station, USA; ⁴Institut für Pharmazeutische Biologie und Biotechnologie, Germany sergey_dobretsov@yahoo.com

Quorum sensing (QS) is a phenomenon that involves production and release of low molecular weight bacterial signal molecules. QS is very important for regulation of bacterial adhesion, growth and biofilm formation. It has been shown that QS is a common phenomenon in marine biofilms and can play an important role in interactions between bacteria and higher organisms. Marine organisms have evolved effective mechanisms to regulate epibiosis by interference with bacterial QS signals. In our study we have been looking for QS inhibitors from marine organisms. Two approaches have been used: 1) we have been isolating and identifying QS inhibitors from cyanobacteria, seaweeds and sponges; 2) we have been screening marine natural products libraries. We found several compounds that inhibit QS at uM and nM level. Laboratory and field experiments demonstrated that QS inhibitors are not only controlling formation and composition of microbial biofilms but also preventing settlement of invertebrate larvae. In conclusion, QS inhibitors might be a good alternative to traditional antifouling compounds.

A COMPARATIVE STUDY ON THE ANTIFOULING ACTIVITY OF INDIAN AND CARIBBEAN SEA GRASSES EXTRACTS

¹P. lyapparaj, ¹A. Palavesam, ¹G. Immanuel, ¹R. Ramasubburayan and ²C. Hellio

¹Manonmaniam Sundaranar University, India and ²University of Portsmouth, United Kingdom bioiypps@yahoo.co.in

All marine infrastructures, installations and shipping industries are faced with the deleterious problems of biofouling and related high economical losses on removal and maintenance of this. The TBT antifouling paints have been banned due its non targeted toxicity threat to many marine organisms. Hence it is an imperative need to look for an eco-friendly antifouling compounds from bioresources to develop new paint formulations. Many of the marine organisms can resist the assault of biofouling by releasing antifouling compounds to its surrounding water and remains foul free. The associated microflora of those organisms also plays a vital role in repelling biofouling. Sea grasses, gorgonians, holothurians etc. are included amongst the foul free communities but this is an area which has been under researched. Bearing the above in mind, present investigation is progressing with the aim to find out a non toxic, novel antifouling compound from the sea grasses and its epiphytic bacteria and also to compare the antifouling efficacy of extracts of Indian, Caribbean sea grasses and its epiphytic bacteria. For this study, Indian sea grasses such as Syringodium sp, Cymodocea sp and Caribbean sea grasses of Syringodium sp and Thalassia sp were selected and extracted with solvents of increasing polarity like hexane, dichloroethane, acetone and methanol. Similarly for extraction, the epiphytic bacteria will be mass cultured. Then the culture supernatant will be extracted with Ethyl alcohol and the bacterial pellet will be extracted with Dichloroethane. Crude extracts with different concentrations (0.01, 0.1, 1.0, 10, 25, 50 and 100 μg/ml) are tested for antimicrofouling activity against the marine and coastal bacteria like Roseobacter litoralis, Vibrio estuarians, Shewanella putrefaciens, Pseudomonas fluorescens, Pseudoalteromonas elyakovii, Halomonas aquamarina, Escherichia coli, Salmonella typhimurium, Staphylococcus aureus, Alcaligenes faecalis and Acinetobacter baumanii and also the antimicro-algal assay is being performed over Cylindrotheca cloisterium, Exanthemachrysis gayraliae, Chlorarachnion globosum and Thalassiosira pseudonana. The antimacrofouling activity of extracts will also be screened against mussel. Results will be presented during the conference.

27-B-2-8

ANTIFOULING ACTIVITY IN SARGASSUM VULGARE: WITHIN-THALLUS VARIATION AND POLYPHENOLIC CONTENT

Erwan Plouguerné, Bernardo A.P. da Gama, Criscia Cesconetto, Renato C. Pereira

Departamento de Biologia Marinha, Universidade Federal Fluminense, Brazil bapqama@pq.cnpq.br

Phlorotannins are compounds found exclusively in brown algae (Phaeophyceae) that have been shown to deter herbivores or protect algae against UV radiation, but little is about their involvement in defence against fouling. In this study, we evaluated the antifouling activity of phlorotannin extracts from different parts of the thallus of the brown seaweed Sargassum vulgare from the coast of Rio de Janeiro (Brazil). Two collections were realized at the site Ilha de Itacuruçá (baia de Sepetiba), the first in May 2009 (E1) and the second in October 2009 (E2). The plants were separated in four parts according to tissue specialization: air-bladder, receptacles, leaflets, and axes. Extraction of the total phenolic compounds was performed using acetone/H₂O (7/3) as a solvent. Total phenolic contents (TPC) were quantified, and antifouling activity of each extract was evaluated against the common fouling mussel, Perna perna. The results showed that the polyphenol extracts from the air bladder and leaves strongly inhibited the fixation of byssus for both seasons studied. These structures are very important to the survival of S. vulgare. Air bladders guarantee the buoyancy of the algae and keep it upright in the water column, while leaflets are essential for photosynthesis. Specific defenses may have been developed or allocated by S. vulgare in order to protect these essential parts from the adhesion of macrofoulers. The antifouling activity of the phenolic extract from the receptacles rises from 27 to 80% between the two collections, indicating strong seasonal variation. For both seasons, TPC was higher in receptacles and axes than in air bladders and leaflets. Therefore, no positive correlation between concentration of phlorotannins and antifouling activity was observed. The differences observed in terms of antifouling activity between different parts of Sargassum thalli may be linked to a qualitative variation of the pool of phenolic compounds pre sent in each extract, or even to the presence of compounds other than phlorotannins. A chemical work regarding the isolation and identification of the antifouling compounds present in the acetone/H₂O extract from S. vulgare is under way.

SARGASSUM POLYCERATIUM CHEMICAL AND PHYSICAL IMPACT ON MAJOR CORAL REEF INVERTEBRATE RECRUITMENT IN MARTINIQUE (FWI).

M. Thabard, C. Hellio, O Gros, A.H. Engelen, M. Schaefer, JP Marechal.

School of Biological Sciences, University of Portsmouth, UK. and Observatoire du Milieu Marin Martiniquais, Martinique.

marie.thabard@port.ac.uk

Marine invertebrate colonisation on reefs is complex and relies on larval production, migration and settlement processes. Competition for space is crucial in ecosystems harbouring a high biodiversity. Both mechanical and chemical defence mechanisms are employed to outcompete other reef organisms. Over the past decades increased anthropogenic activities along with major natural disturbances have degraded reefs in which macroalgae have replaced coral reef-builders. In the Caribbean, the brown macroalgae Sargassum spp. are one of the most important seaweeds on degraded reefs in term of biomasses and percentage cover. The present work combined laboratory and field experiments to decipher effects of Sargassum polyceratium (one of the most conspicuous seaweed on Martinique reefs) on keystone coral reef invertebrates by investigating: 1) the effect on settlement and recruitment of invertebrates in the field; 2) the effect of surface molecules and waterborne cues on the larval development of marine tropical invertebrates. ERDAS and Image J software were used to determine the percentage covers of the different organisms. Colonization of artificial substrates was lowest at S. polyceratium covered plots (6.11%± 5.33), intermediate at plots cleared of S. polyceratium (12.00%± 7) and highest at healthy reef plots without S. polyceratium (19.11%± 8,9). S. polyceratium hexane extracts were demonstrated to contain bioactive surface compounds with anti-bacterial activity against all bacteria strains tested when used at concentration of 150 and 300 µg.ml⁻¹ as well as activity against early developmental stages of Codakia orbicularis (Bivalvia) and Diadema antillarum (Echinoderm) (MIC=5 μg.ml⁻¹ - Minimum Inhibitory Concentration) and Pseudonereis sp. (Annelida) (MIC=100 μg.ml⁻¹) larvae. In conclusion, these preliminary results suggest the use of chemical defenses by S. polyceratium against substrate competitors. More tests are currently conducted to test the effects of conditioned water on invertebrates' development and recruitment as well as the mechanical effects the algal canopy.

28-H2-P: Plenary

THE STUDY OF MICROBIOLOGICALLY INFLUENCED CORROSION IN MARINE ENVIRONMENTS – A SEA CHANGE

Brenda J. Little, Jason Lee and Richard Ray

Naval Research Laboratory, Stennis Space Center blittle@nrlssc.navy.mil

Recent developments in the study of microbiologically influenced corrosion (MIC) in marine environments have demonstrated the need to shift the focus from the identity of individual microorganisms to the chemistries produced by microbial consortia under specific conditions. The availability of molecular techniques has made it possible, and almost routine, to identify both bacteria and archaea associated with corrosion to the taxonomic level of genus. The list of microorganisms influencing corrosion is constantly expanding with this information. Despite the advances in microbial identification techniques it is still difficult to predict the susceptibility of specific alloys to MIC in marine environments. Two microbiologically mediated processes dominate the literature on microbiologically MIC in natural marine environments - ennoblement and sulfate reduction. At temperatures below 60°C, resistance to crevice corrosion is the limiting factor for selecting alloys for seawater service and crevice corrosion is the most critical issue affecting the performance of stainless steels in seawater. Marine biofilms cause a noble shift, or ennoblement, in open circuit potential (Ecorr) for most passive alloys. Theoretically, Ecorr ennoblement should increase the probability for pitting and crevice corrosion initiation and propagation of some passive alloys. Numerous researchers have shown that increased cathodic reduction rates accompany ennoblement of Ecorr. However, attempts to relate ennoblement to increased localized corrosion have been inconsistent. Extent of ennoblement of Ecorr varies among locations and the extent of ennoblement for a particular material cannot be used to predict an increased likelihood of localized corrosion. There may be multiple site-specific mechanisms for ennoblement of Ecorr in coastal seawaters. Thermodynamic models cannot predict the susceptibility of low alloy and medium grade stainless steels exposed in marine environments to corrosion induced by sulfate reducing bacteria. Laboratory experiments designed to provide data on susceptibility have produced conflicting results because of the following varying chemical conditions maintained during the experiments: 1) laboratory media can contain anions that inhibit localized corrosion, 2) laboratory media can contain yeast extract that interferes with electrochemical measurements, and 3) deaeration procedures can produce environments that are not conducive for the growth on sulfate reducing bacteria.

28-H2-1-1 (Keynote)

INNOVATION IN FOUL RELEASE: MORE ABOUT DOING, LESS ABOUT DREAMING

Colin D. Anderson

International Paint colin.anderson@akzonobel.com

The history of Foul Release technology is reviewed, from its ingenious discovery in the 1970's by a Newcastle paint chemist to its present prominent position helping meet the economic and environmental aspirations of ship operators and owners globally. The technical and commercial barriers to the successful introduction of the technology are outlined, highlighting some of the successes and failures that took place along the way. This illustrates how innovation in the marine sector takes place and provides some useful insights into how future innovation might occur.

28-H2-1-2

STUDY ON THE ANTIFOULING ABILITY IMPROVEMENT OF SILICONE-BASED COATING WITH POLY (ACRYLAMIDE-SILICONE)

Cunguo Lin, Jinwei Zhang, Li Wang, Yanlei Peng, Jiyong Zheng, Dongxia Duan, Juan Zhou

State Key Laboratory for Marine Corrosion and Protection, Luoyang Ship Material Research Institute, China lincq@sunrui.net

Biological fouling can bring about some unwanted and detrimental consequences to marine ship. Usually, the ship hull will be painted an antifouling coating to prevent biological fouling. The best performing coatings are those containing metal based compounds like copper or tributyltin, however which can lead to serious irreversible adverse influence to marine ecological environment, so it is necessary to develop new eco-friendly antifouling alternatives to protect marine ecological environment. It is well known that silicone-based coatings act essentially by means of a barrier layer with a combination of properties including ultrasmooth surface, low surface energy and low elastic modulus, which can minimize chemical and mechanical locking of fouling species, and this makes silicone become a very attractive candidate in developing new eco-friendly antifouling materials. However, it is also a matter of fact that some marine organisms still can adhere onto the silicone surface, especially diatoms, which can develop slime films and do not release from vessels operating at high speeds over 30 knots. Since silicone-based materials is promising in developing new eco-friendly antifouling materials, it is very significant and necessary to take some ways to further improve its antifouling ability. In this paper, the antifouling ability of silicone-based coating was improved with an additive of poly (acrylamide-silicone) (PAS). The preparation of the additive and the coating was introduced and characterized. Test results showed that, in comparison with control silicone coating, this coating could improve its antifouling ability against diatoms by 59%, and also had a very good inhibition efficiency for mussels settlement. The results also verified that the polyacrylamide segment of PAS formed microhydrogels on the silicone surface after which was immersed into seawater. Not only the microhydrophilic environment the microhydrogels bring about is helpful to improve the coatings antifouling ability against diatoms, but also the dissolvement of microhydrogels can make the coating surface a dynamic state, and this can effectively lower the bonding force between foulers and coating surface, thus further improving the antifouling ability of silicone-based coating.

FOUL RELEASE PERFORMANCE OF FLOW POINT DEFINED PHYSICAL GELS PREPARED FROM POLY(DIMETHYLSILOXANE)

Christof Baum*, Tim Heusinger von Waldegge*, Herbert Barthel#, Torsten Gottschalk-Gaudig#, Erwin-Peter Mayer#

*IMARE GmbH (Institute for marine resources), #Wacker Chemie AG Christof.Baum@imare.de

The effect of flow point on the release of macrofouling organisms was investigated. Physical gels were prepared by blending linear poly(dimethylsiloxane) with fumed silica. The mechanical profile of the gels was measured employing stress-controlled rheometry and gels with a flow point between 400 – 600 Pa were used for field tests. In addition, the gels exhibited a 'Payne-Effect' of strain hardening between 800 and 1200 Pa. Coated panels and uncoated PVC controls were deployed in a tidal free stream current of 0.1 to 1.1 m/s at Wilhelmshaven, Germany, over a period of six month. The samples were monthly inspected and photographed in combination with weight measurements. During the time of deployment the weight of the control and coated panels increased to 800% and 20%, respectively. In the early months barnacles and hydroida dominated the fouling community forming a bottom layer for mussels, ascidia and associated fauna in the late summer. Every month all partly cleaned control areas were occupied by a new dense layer of barnacles, whereas many roundish craters and gliding marks in the size of 0.1 to 1 mm defined the surface of coated panels. Abundances of barnacles 1-6 mm in diameter were steady (approx. 120 per square meter). The majority of them had colonized the gels in the first month of deployment. Image analysis showed that the patchy release of leptomedusa and anthomedusa left free space which was re-occupied by the colony with the smaller stalks. The result obtained show that the flow point is a key parameter in the design of physical release gels. Being completely vanished by the rheological properties of strain hardening it is evident that the working principle of the release is coupled to the size of the organisms and the amount of drag and lift the organisms transmit from the water flow to the gel.

28-H2-1-4

NOVEL, AMPHIPHILIC POLYSILOXANE FOULING-RELEASE COATINGS

David Christianson, Christy Gallagher-Lein, Shane J. Stafslien, Justin Daniels, and Bret J. Chisholm

North Dakota State University, Center for Nanoscale Science and Engineering Bret.Chisholm@ndsu.edu

Novel amphiphilic polysiloxane coatings were investigated using a combinatorial/high-throughput approach. The coatings were derived from solutions blends of a silanol-terminated polydimethylsiloxane, a silanol-terminated polytrifluoropropylmethylsiloxane, a trimethoxysilane-functional poly(ethyleneglycol), and methyltriacetoxysilane. For these coatings, crosslinking occurred through a moisture-cure mechanism and both the very hydrophobic perfluorinated polysiloxane segments and the very hydrophilic poly(ethyleneglycol) segments were incorporated into the coating matrix through hydrolysis and condensation reactions involving silanol and methoxysilane functional groups. An array of 24 unique coatings were produced that possessed systematic variations in composition. Fouling-release was characterized using a suite of high-throughput measurements based on various marine organisms including the marine bacteria, *Halomonas pacifica* and *Cellulophaga lytica*, the diatom, *Navicula incerta*, and the barnacle, *Amphibalanus amphitrite*. Overall, the results of the study showed a synergistic relationship between the incorporation of the hydrophobic perfluorinated polysiloxane segments and the hydrophilic poly(ethyleneglycol) segments on fouling-release properties. In addition to fouling-release, the morphology of the coatings was characterized.

INVESTIGATION OF GROOMING TOOLS FOR SHIP HULL COATING MAINTENANCE

Melissa Tribou

Florida Institute of Technology <u>mtribou@fit.edu</u>

Ship hull grooming has been proposed as a proactive, in-water, mechanical method to maintain biocide-free marine coatings in a 'fouling-free' condition. Grooming may be defined as the gentle cleaning of an immersed surface at a frequency sufficient to prevent the permanent attachment and growth of fouling. For this reason grooming tools need to be developed that are less aggressive than the traditional ship hull cleaning brushes. A fiberglass raceway tank (8x1x1 meters) has been designed and constructed to accommodate four 60x100 cm test panels per side for the testing of grooming tools. The grooming tool is mounted to an instrumented carriage that runs the length of the raceway and controls the forces and speed at which grooming is performed. The test panels are coated and then subjected to fouling prior to testing. The fouling is characterized prior to each grooming test by visual assessment, biofilm adhesion and thickness measurements. Grooming tool performance is determined in terms of the fouling and physical condition to both the test surface and grooming tool after one grooming event. The results from five grooming tools on three biocide-free marine coating surfaces will be presented.

28-H2-1-6

OBSERVATION OF BARNACLE SETTLEMENT AND GROWTH PROCESS ON SOFT AND WET HYDROGELS

¹Takayuki Murosaki, ¹Nafees Ahmed, ¹Tomoya Ogawa, ¹Akira Kakugo, ^{1, 2}Takayuki Kurokawa, ¹Jian Ping Gong, ³Yasuyuki Nogata

¹Graduate School of Sciences, Hokkaido University, Japan; ²Creative Research Institution Sosei, Hokkaido University, Japan; ¹Central Research Institute of Electric Power Industry, Japan

murosaki@sci.hokudai.ac.jp

The fouling by marine sessile organisms causes serious economic problem. Many researchers try to find alternative green antifouling materials instead of Tributyltin (TBT). Most of existing antifouling technologies target application on solid surface. Recently, studies of antifouling using hydrogels have been reported. Some hydrogels inhibited the settlement of barnacle's cyprid larvae (i.e. settlement stage larvae) [1]. Recently, we reported that many synthetic polymer gels with various kinds of chemical structures have antifouling activities against barnacle cyprid larvae in vitro [2], and the long time antifouling properties of mechanically tough hydrogels against marine sessile organisms were tested in marine environment. The results show hydrogels exhibited antifouling activity against barnacles in marine environment [3]. These settlement tests had been evaluating antifouling properties by the number of settlement on substrates. However, there is few reports about the relationship between the antifouling property of substrates and barnacle settlement and growth process. In this study, we investigate cyprid exploring behavior and barnacle growing process on hydrogels. The cyprid exploring behavior on substrates was investigated by video tracking system under the microscopy. The number of exploring event and the exploring time were investigated. After cyprid settlement, barnacle growing process on substrates were observed. It was observed that the morphology of barnacle depends on the elasticity of substrates. On solid and rigid PS surface, the morphology of barnacle bottom plate is flat, and its shell wall has a smaller angle to the substrate. However, on silicone rubber and gel surface, the bottom plate is concave and the shell wall has a large angle to the substrate. When a barnacle secretes new cement onto the surface, the muscles contract, so the base is subjected to a pull-up force and the shell wall exerts a compressive stress on the substratum. PS surface may not be bended because of its high elasticity. Thus, barnacle grow parallel to the PS surface. However, the elasticity of silicone rubber and hydrogels is lower than PS surface, so these substrates may be bended. Thus, the shell wall has a large angle to the substrate because barnacle may be able to grow also vertically. Furthermore, on a hydrogel surface, barnacle embed in the gel due to the soft and weak mechanical nature of this gel. In this case, the embed shell wall might result in mechanical locking in the gel, and it leads to less detachment of barnacles.

- [1] K. Rasmussen, et. al., Biofouling, 18, 177 (2002).
- [2] T. Murosaki, et. al., Biofouling, 25, 313 (2009).
- [3] T. Murosaki, et. al., Biofouling, 25, 657 (2009).

NOVEL ANTIMICROBIAL, ANTIFOULING/FOULING-RELEASE COATINGS CONTAINING QUAT-FUNCTIONAL POSS COMPOUNDS

¹Partha Majumdar, ¹Elizabeth Crowley, ¹Shane J. Stafslien, ¹Justin Daniels, ²Maureen E. Callow and ¹Bret J. Chisholm

¹North Dakota State University, USA; ²The University of Birmingham, UK. <u>Partha.Majumdar@ndsu.edu</u>

Polysiloxane coatings containing quaternary ammonium salt (QAS)-functionalized polyhedral oligomeric silsesquioxanes (Q-POSS) as an additive were investigated for potential application as antimicrobial, antifouling/fouling release coatings. An array of Q-POSSs possessing systematic variations in chemical composition (alkyl chain length, counter ion, and extent of quaternization) was synthesized using a two-step process. First, octasilane POSS was functionalized with dimethylamino groups by hydrosilylation with allyldimethylamine. Next, quaternization of the tertiaryamino-functional POSS was achieved using an alkyl halide to produce the Q-POSS. Moisture-cured polysiloxane coatings were prepared by dispersing Q-POSS molecules into a solution blend of a silanol-terminated polydimethylsiloxane, methylacetoxysilane, and a catalyst. In order to evaluate the utility of the Q-POSS molecules as a broad spectrum antimicrobial additive, the antimicrobial activity of the coatings toward E. coli, S. aureus, and C. albicans was determined using the agar diffusion method. The results obtained showed that both the composition of the Q-POSS and the composition of the polysiloxane matrix affected antimicrobial properties. Compositions were identified that inhibited the growth of all three microorganisms on the coating surface. Selected Q-POSS containing coatings were also evaluated toward Ulva spores for potential application as antifouling/fouling-release coatings. The Q-POSS containing coatings had a lower biomass (Ulva) than the Q-POSS-free controls thereby indicating a significant antifouling effect. Fouling-release performance of these coatings was evaluated by measuring percentage biomass (Ulva) removal after spin-jet washing at three impact pressures of 18, 67 and 111 kPa. Two out of six Q-POSS-containing coatings showed better removal properties than Intersleek 700 and 900.

28-H2-1-8

TOUGH FOULING-RELEASE COATINGS BASED ON SELF-STRATIFICATION

Dean C. Webster, Abdullah Ekin, Stacy Sommer, Robert Pieper, Rajan Bodkhe, Shane Stafslien, Justin Daniels

North Dakota State University dean.webster@ndsu.edu

Low surface energy tough fouling-release coatings are able to be realized using the concept of self-stratification. Current fouling-release coatings technology relies on low surface energy elastomers with the leading technology being silicone elastomers. While these coatings generally perform well with regards to fouling-release properties, they are mechanically weak, have poor adhesion to common substrates and primers, and are easily damaged. Tough coatings having low surface energy can be prepared by incorporating a low surface energy reactive polymer into a tough coating system such as a two-component polyurethane. During coating curing and film formation, the low surface energy component tends to predominate on the surface in order to minimize overall surface energy. The reactive functional groups ensure that the low surface energy polymer is covalently bound to the network. Using this approach, reactive polydimethylsiloxane (PDMS) has been incorporated into a polyurethane system. The PDMS has functional groups reactive with the isocyanate groups of the crosslinker at either one end of the PDMS chain or at both ends. High throughput screening has been used to explore the effects of PDMS molecular weight, PDMS functional groups, PDMS level, polyol composition, and crosslinker on the properties of the resulting coating. Laboratory assays have been used to identify coatings suitable for field immersion testing. The coatings are tough and have good adhesion to marine corrosion primers, eliminating the need for a tie-coat. Field testing has shown that some compositions have performance similar to that of silicone fouling-release coatings and are easily cleaned without damage.

THE EFFECT OF MODULUS AND THICKNESS OF POLYDIMETHYLSILOXANE COATINGS ON THE SETTLEMENT AND ADHESION OF *B. AMPHITRITE*

SL Conlan, RC Herdman, E Evariste and AS Clare

Newcastle University s.l.conlan@ncl.ac.uk

Silicone polymers and fluoropolymers are currently the most effective fouling-release coatings available. The development of these coatings will benefit from improved understanding of the mechanisms that underpin their performance. This study altered the modulus of PDMS (Rhodosil 48v) by using different chain lengths of silicone and substituting 50% of the cross linker (tetraethoxysilane) with a part inactive linker (trimethoxymethylsilane). This resulted in one quarter fewer crosslinks formed during curing. These two methods resulted in six different moduli (0.06 to 0.38MPa) as determined by DMA. The coatings were applied at three different thicknesses: thin (30 μ m), medium (58 μ m) and thick (130 μ m). The adhesion strength of pseudobarnacles, attached to the surface using epoxy, reduced as the modulus increased to around 0.3 MPa but then increased at 0.38 MPa. This trend is the reverse of that found by Kim et al. (2007; 2008) though the moduli tested here were at the lower end of those tested by Kim et al (0.08 to 1.3 MPa). Coating thickness only affected adhesion strength at the lowest modulus tested, in line with the results of Kim et al. (2007), though the thicknesses tested were all considerably lower (30 to 130 μ m compared with 160 to 740 μ m respectively). Adult barnacles removed from coatings of different modulus showed a very similar trend to that seen with pseudobarnacles, except that thickness did not affect adhesion strength at any modulus tested. Finally, cyprids were allowed to permanently attach to each surface and ease of removal was compared using a water jet. Neither settlement nor removal of cyprids was affected significantly by modulus or thickness, except at the lowest modulus tested where the two thinner coatings had a lower percentage removal than the thickest coating.

Kim et al. (2007) Biofouling 23(2): 113-120 Kim et al. (2008) Biofouling 24(4): 313-319

SEA-NINETM CR: A NEW, MICROENCAPSULATED MARINE ANTIFOULING PRODUCT

John Ashmore

The Dow Chemical Company jashmore@dow.com

Sea-Nine TM 211N is an effective marine antifoulant but its potential has been limited due to film quality issues. Microencapsulation of DCOIT, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, has been found to be both effective in producing high quality films and also in extending the service life of films containing the microencapsulated form of DCOIT, Sea-Nine CR Marine Antifouling Agent. The difficult journey to develop a microcapsule that provides acceptable in-can stability in a solvent-based paint yet, when exposed to seawater, can release the active ingredient at a sufficient rate to provide good antifouling performance, will be presented. Use of microencapsulated actives offer additional benefits to marine paint developers. In the past, the film matrix had to control the release of the actives at a rate sufficient to provide biological performance yet not release the active so fast that the film becomes depleted in the active. Optimizing film performance has been a trade-off between active release rate and other film performance characteristics. Use of a microencapsulated active to control the active's release rate removes a key design constraint allowing the developer to focus on improving film performance and producing higher performing marine paints.

28-H2-2-2

NEW APPROACH TO MICROCAPSULE SYNTHESIS – REPLACEMENT OF A HAZARDOUS CHEMICAL

Lars Nordstierna, Alireza Movahedi, Magnus Nydén

Department of Chemical and Biological Engineering, Chalmers University of Technology lars.nordstierna@chalmers.se

Current protective coating applications using biocides lose the protection quite rapidly as small molecular size renders a fast diffusional biocide leakage. A promising improvement of anti-growth protection can be achieved by the use of encapsulated biocides in the paint. The candidate method to produce microcapsules has dichloromethane as a key constituent in the synthesis step (Loxley and Vincent (1998) J Colloid Interface Sci., 208:49-62). Dichloromethane is hazardous and thereby often not allowed to be used at industrial scale. Here we show that ethyl acetate has equivalent physiochemical properties as dichloromethane in the production of microcapsules and thus can be used in order to fulfill legislative criteria. This opens up for a microencapsulation approach towards the long-term use of biocides and the presentation summarizes our recent lab-scale results on microencapsulation of several antifouling substances as well as large-scale production results.

RELEASE FROM PAINTED SURFACES: FREE AND ENCAPSULATED BIOCIDES

Magnus Nydén, Alberta Mok, Lars Nordstierna

Department of Chemical and Biological Engineering, Chalmers University of Technology mnyden@chalmers.se

Here we investigate a method for prolongation of the coating protection by slowing down the release rate of biocides in a controlled way. The biocide is placed into microspheres, from where it is slowly distributed into the coating. By different microscopic techniques the microspheres were found to be compatible (i.e. no phase separation was observed) both with the coating material and the paint. Biocide release from the coating is recorded by various analytical techniques and it is shown that the release is considerably slower from coatings with microspheres compared to an ordinary formulation with freely dispersed biocides. We suggest that microspheres are very efficient for controlling biocide release from protective coatings since they allow for optimization of biocide concentrations. They also increase the lifetime of the protective coating independent on the type of paint system used.

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EMPLOYING CLASSICAL MIXTURE TOXICITY CONCEPTS FOR THE OPTIMIZATION OF BIOCIDE COMBINATIONS FOR ANTIFOULING PAINTS

Thomas Backhaus, Åsa Arrhenius, Annelie Hilvarsson, Kristina Holm, Ida Wendt and Hans Blanck

University of Gothenburg, Sweden thomas.backhaus@dpes.qu.se

The classical mixture toxicity concepts of Concentration Addition (CA) and Independent Action (IA) have been successfully used in the past for modeling the joint action of pesticides, pharmaceuticals and other biologically active compounds. Here we report on their application for the environmental optimization of biocide combinations for antifouling purposes. Both concepts make use of efficacy data of individual compounds and allow the prediction of the total efficacy of all possible mixtures that can be composed from a given set of compounds. This enables a systematic and unbiased in silico exploration of the complete space of possible combinations. By applying a risk weighting function that accounts for the environmental risks of each individual compound in each mixture it is then possible to rank the mixtures according to their predicted total environmental risk. This provides a detailed map for selecting the most promising combinations for further studies, e.g. for field tests. The developed algorithms were applied to a set of 7 common and novel antifouling biocides. We experimentally recorded their individual toxicity and efficacy for representatives of the most common fouling organisms (Barnacles, Mussels, Sea Squirt, Bryozoans, Sea Lettuce and Biofilms (slime)) and then modeled the joint efficacy of all possible combinations of the 7 biocides. All combinations with a sufficient efficacy (at least 99% effect on the settling of each test organism) were then ranked according to their modeled environmental risk. We will present the results of this optimization procedure and will relate the efficacy of the modeled mixtures to their environmental risks. In particular we will highlight whether and to what extent combination products can be expected to have lower environmental impacts than products with only one or a limited number of active ingredients, while still providing the same efficacy. The study is part of the Swedish Marine Paint program which is sponsored by Mistra, the Foundation for Strategic Environmental Research.

DEVELOPMENT OF ANTIFOULING PAINTS FOR NEWBUILDINGS - MORE THAN JUST GOOD ANTIFOULING PERFORMANCE

Seamus Michael Jackson

Jotun seamus.jackson@jotun.no

In the development of antifouling paints the main factor that many consider is that of fouling control. However, there are many other properties that have to be considered when developing a coating. This is especially true when it comes to the paints developed for newly constructed ships. Today most of the newbuilding industry is concentrated in Korea, China and Japan. Commercial available antifouling paints were collected in Korea and tested in a series of tests to ascertain their mechanical properties. These tests included hardness measurements and block testing at different temperatures. A further property that was evaluated was colour stability after application. These results demonstrated that colour retention was very poor in many of these coatings. A development program was established to improve the colour stability of an antifouling paint while retaining the required fouling performance. Colour stability was evaluated by outdoor exposure and in accelerated testing in the laboratory. It was found that colour stability was dramatically improved by adjusting several parameters in a paint formulation. The antifouling performance of modern antifouling paints is obtained through a balance between the polishing rate and release rate of the biocides from the paint matrix. To establish this polishing rate testing and raft exposure trials are required. Polishing rate testing was carried out under controlled laboratory conditions and at different water velocities. The results from a range of formulations are presented. Factors that have a major impact on the polishing rate are also shown. Antifouling performance trials were carried out under static conditions. Several different biocide combinations were tested and the results from these are reported. As many newbuilding yards in China are in rivers the newly painted ships are often exposed in these for protracted periods. The most promising coatings were also tested under the se conditions. The final stage of the development program was in-service trials on a limited number of vessels and finally full scale application of the best formulation.

28-H2-2-6

AQUEOUS-BASED ACRYLIC MINIEMULSIONS: A FAMILY OF SEAWATER ERODIBLE POLYMERS WITH TUNABLE MECHANICAL AND EROSION PROPERTIES

C. Bressy; G. Kermabon-Avon; B. Tanguy; A. Margaillan

Université du Sud Toulon-Var, France christine.bressy@univ-tln.fr

A growing concern for environmental issues is observed in the development of marine paints and coatings. Biodegradable polymers are watched with interest as self-polishing binders for chemically-active paints. In addition, the use of water in the continuous phase of paints is a way to improve the safety in application, limiting the emission of volatile organic compounds and irreversible health effects. Water-based antifouling paints have been scarcely investigated. Two major drawbacks are reported (i) as polymer particles in aqueous solution need to be stabilized using surfactants, the resulting coatings tend to be seawater sensitive and the water absorption could increase upon immersion. (ii) slow drying and formation of weafilms in humid conditions are highlight ed compared to solvent-based paints leading to poor mechanical properties of the resultant coating in long-term service. In this paper, an innovative strategy was used to develop aqueous-based antifouling paints. Core-shell polymer nanoparticles were synthesized through the miniemulsion polymerization technique to get nanoparticles and to limit the use of surfactants in comparison with the emulsion process. Core-shell morphology was selected for the latex particles to form nanostructured films with suitable mechanical properties and erosion properties. The core is mainly composed of hydrophobic methacrylic monomer units whereas the polymer backbone of the shell bears carboxylic acid pendant groups. The methacrylic acid (MAA) monomer unit was chosen for its hydrophilic character and enables the formation of the well-known carboxylate sodium salt moieties, which contribute to the erosion mechanism. The interest of these novel binders is shown through water uptake measurements and erosion tests under dynamic conditions. The effect of parameters including the hydrophobic/hydrophilic character of the polymer nanoparticles, its molecular weight, and its core-shell morphology is discussed. Field tests on raft are performed to assess the antifouling performance of the resulting aqueous-based coatings.

NEW FUNCTIONALIZED OLIGOISOPRENES BASED FLEXIBLE ANTIFOULING COATINGS WITH **ANTIMICROBIAL PROPERTIES**

¹Claire Hellio, ²Rachid Jellali, ²Faten Sadaka, ²Irene Campistron, ¹Marie Thabard, ¹Rizlene Id Daoud, ²Frederic Gohier, ³Jean-Luc Mouget, ²Jean-Francois Pilard

> ¹School of Biological Sciences, Portsmouth University, UK; ²Université du Maine, France. claire.hellio@port.ac.uk

The accumulation of microorganisms, algae and invertebrates on immersed man-made surfaces leads to many economical and environmental problems, especially for the maritime industry. The total ban of tributyltin based paints from 2008 has oriented the research toward the development of new environmentally friendly solutions. One of the most attractive alternatives consists of attaching the active functions on the polymer chains by covalent bonds to avoid releasing of biocidal products, and to keep continuous activity. With this aim, the films studied in this work were synthesized from photocrosslinkable oligoisoprenes bearing quaternary ammonium groups. Firstly, a controlled degradation of a high molecular weight polyisoprene led to carbonyltelechelic oligoisoprenes with well defined molecular weight and functionality. Photocrosslinkable functions (acrylates and/or epoxides), and biocidal functions (quaternary ammoniums) were then introduced at the chain-ends and/or along the chain by chemical modification. Photocrosslinking under UV irradiation led to flexible films. The biological activities of these films were evaluated both in the laboratory (against marine bacteria, microalgae, fungi & macroalgae) and in the field. Results will be discussed regarding the variation of bioactivity in relation to the different composition of the films. Promising antifouling activities were recorded towards the growth bacteria, the adhesion of microalgae and the germination of macroalgae.

28-H2-2-8

POST SETTLEMENT INHIBITION (PSI) OF BARNACLE GROWTH, BALANUS IMPROVISUS. A NOVEL APPROACH IN MARINE ANTI-FOULING CONTROL

^{1, 2}Emiliano Pinori; ¹Mattias Berglin; ²Peter Sjövall; ¹Mia Dahlström; ¹Hans Elwing

¹University of Gothenburg; ²SP - Technical Research Institute of Sweden emiliano.pinori@cmb.qu.se

In the search for new antifouling technologies we have been inspired by the brown alga "Fucus evanescens" which in contrary to

many other sea organism, allows barnacles "Balanus improvisus" to colonize on its leaves, but prevent them to grow to adult animals. This phenomenon is called Post Settlement Mortality (1). Inspired by (1) we tested the anti-barnacle effect of avermectins, a group of biocides produced by a bacteria called "Streptomyces avermitilis". The acute toxicity level (LD50) of avermectins against "Artemia Salina", and "Balanus improvisus", are in the same range as Zn- or Cu-Pyrithione (2). The Avermectins have low water solubility and a very high molecular weight and it was therefore supposed that the emission levels from avermectin-containing paints should be low. The avermectin preparations were tested in rosin-based paint-formulations at different concentrations (0,1% and 0,01% w/v). The avermectin was added dissolved in xylene or dissolved in a co-solvent commonly used for avermectin preparations in veterinary medicine. A static panel antifouling study was carried out in the Swedish costal water, under a period of three summer months. After 5 weeks of immersion, the number of juvenile barnacles/surface area was approximately similar on the Avermectin-containing paint surface as compared to the control paint surface. After 10 weeks, was noted that cyprids attached to the avermectin-containing surfaces did not continue to grow, while those attached to control surfaces grew into Newly Metamorphosed and Juvenile stage (NM=0.2-5mm2; J=5-20mm2). Our results indicate a mechanism of action of avermectins entailing that of barnacle's growth inhibition rather than larval settlement inhibition. Thus, the mechanism of action of avermectins as revealed in our studies, closely resembles that of (1), i.e., Post Settlement Inhibition (PSI). Work is now in progress to determine the emission-level of the avermectins and their possible risk regarding non-target sedentary organisms.

^{1.} Wikstrom SA and Pavia, H (2004) "Chemical settlement inhibition versus post-settlement mortality as an explanation for differential fouling of two congeneric seaweeds" Oecologia 138, 2, 223-230

^{2.} Koutsaftis, A; Aoyama, I (2007) "Toxicity of four antifouling biocides and their mixtures on the brine shrimp Artemia salina" Sci Total environ. 387, 166-174

NEW, BIOFOULING-RESISTANT ELASTOMERS FOR ACOUSTIC APPLICATIONS

¹Thomas Ramotowski, ¹Wayne Tucker, ¹Matthew Rice, ²Elizabeth Haslbeck and ³Lucie Maranda

¹NUWC, Division Newport; ²NSWC Division Carderock; ³GSO University of Rhode Island thomas.ramotowski@navy.mil

The U.S. Navy has long used biocide-impregnated elastomers for a number of specialty applications including surface ship SONAR domes and small acoustic windows/domes. In most cases, conventional antifouling paints and coatings do not work well in these applications due to the extensive flexing of the rubbery substrates and the need for smooth water-elastomer boundaries for good acoustics. Cavitation induced by the underlying acoustic source, or high speed maneuvers can also damage/dislodge externallyapplied paints and coatings. Traditionally, these applications were met with rubbers containing tributyltin oxide (TBTO) an effective, but toxic and environmentally unfriendly biocide. International agreements banning the sale and use of TBTO have forced the U.S. Navy to eliminate the use of TBTO-containing elastomers in its fleet with the exception of bow SONAR domes for certain destroyers and frigates. We have been working on a more environmentally friendly alternative for the TBTO-containing rubber. A greener biocide for marine applications, DCOIT, (4,5-dichloro-2-n-octyl-4-isothiazolin-3-one; Dow Chemical Company) has been successfully incorporated into EPDM, neoprene, and polyurethane elastomers. DCOIT breaks down very quickly in sea water and sediments, exhibits essentially no bioaccumulation factor, and has a maximum allowable environmental concentration about 300 times greater than TBTO. Test panels containing between 3% - 6% by weight of DCOIT in EPDM rubber have been deployed for 3 years in temperate waters (Narragansett Bay, RI) and over one year in semi-tropical waters (Melbourne, FL) without developing any significant biofouling. Testing is underway at these and other locations for DCOIT/neoprene and DCOIT/polyurethane panels. The relatively low effective concentration of DCOIT within these elastomers allows them to remain free of unwanted, deleterious marine growth while at the same time, retaining their desirable physical and ac oustical properties.

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THE PERFORMANCE OF SUPERDUPLEX STAINLESS STEEL IN DIFFERENT TYPES OF SEAWATER

Roger Francis Glenn Byrne

RA Materials, UK rfrancis@rolledalloys.com

The superduplex stainless steels offer the combination of high strength, ready availability in a wide range of product forms and excellent corrosion resistance in a wide range of environments. The present paper shows that the open circuit potential depends on the redox potential and in seawater this can result in a wide range of potentials. The conditions that produce these potentials are discussed and the typical corrosion resistance under these conditions is presented. They cover the range from stagnant deaerated conditions where microbial activity is high, to chlorinated flowing seawater, where the risk of crevice corrosion is high. Finally, some service experiences are presented showing the high resistance of superduplex stainless steel to all of these conditions.

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LONG TERM STUDIES OF THE PERFORMANCE OF COPPER-NICKEL ALLOY SHEATHING FOR THE SPLASH ZONE CORROSION PROTECTION OF OFFSHORE STRUCTURES

Carol Powell

Copper Development Association

In recent times, there has been renewed interest in copper-nickel sheathing for protection of splash zone areas on offshore wind turbine towers. This has led to the review of existing trials and service performance over the last 25 years in similar applications. In 1984, 90-10 Cu-Ni (C70600) was installed for splash zone protection on the legs of Stage 1 of the Morecambe Gas Field platforms in the Irish Sea and is still in service today. At the start of this project and to examine the performance of Cu-Ni in close detail, a comprehensive study was initiated by the LaQue Center for Corrosion Technology in North Carolina, USA. The LaQue trials commenced in November 1983 with a series of 26 test pilings exposed to Banks Channel at Wrightsville Beach. Ten had Cu-Ni welded directly to steel, seven had the sheathing insulated from the steel with concrete and seven were bare steel. Some possessed cathodic protection and others did not. Two pilings were clad with 65%Ni-Cu alloy 400(N04400) and cathodically protected. Shortly afterwards, the programme was extended to include 14 pilings with a layer of butyl rubber acting as insulator between the steel and Cu-Ni sheathing. The pilings were systematically removed and examined over the next ten years leaving four for even longer term exposure. The piles were sectioned transversely to determine corrosion loss around the circumference and also as a function of elevation. In addition, anode consumption rates and biofouling levels were calculated. The site suffered the ravages of extreme weather including hurricanes to which the area is prone, but the piles survived. After 20 years exposure, the test site was abandoned and final long-term investigations were carried out. This paper reviews the results of this long term exposure work, compares it to the in-service performance experienced in the Morecambe Field and examines the case for the use of copper alloy sheathing in the Renewable Energy industry sector.

MATERIAL DATABASE ON CORROSION CONTROL TECHNOLOGY AND PROTECTION OF OCEAN ENGINEERING STRUCTURES

Tong Xiaoyan, Lv Shengli, Yao Leijiang, Li Zheng, Gao Xiang

Northwestern Polytechnical University, Xi'an 710072, P.R.China tonqxy@nwpu.edu.cn

In this paper, the material database on corrosion control technology of ocean engineering structures is developed according to related national standard and criterion on software development. Consider the corrosion influence degree on ocean engineering structures, which the situation of corrosion damage and graphic information in its splashed zone are investigated and collected, will be mainly focused in this aimed database. According to the specification on corrosion damage of ocean engineering structures and servicing objectives as well as its user's groups, the data flow is analyzed and data structure is designed based on definition of data code, design of data model, planning data criterion and standard, policy of data integrity and consistency, criterion of data cleaning and collection and inspection. In accordance with various application objectives, the different visiting control's criterion are established in order to run it efficiently and safety. In order to opening the database and sharing data resources, the www site is applied and home page oriented user is designed, the client can browse it through the www site www.dematers.com and more than 40,000 items on corrosion properties, corrosion environments and corrosion evolution models are collected in it. The date environment data recorded in Tsingdao, Xiamen, Zhoushan and Yulin ocean environment observation station are collected more than 20,000 items.

28-B-1-4

BIOFOULING OF CHROMIUM AND NICKEL BASED MATERIALS IN MARINE ENVIRONMENT

Hideyuki Kanematsu, Hajime Ikigai, Daisuke Kuroda, Akiko Ogawa

Suzuka National College of Technology kanemats@mse.suzuka-ct.ac.jp

Due to the accelerated movement for environmental protection energy problems, marine structures e.g those for off shore wind power or atomic generation, as well as conventional ones such as ships, bridges, oil tanks will be much more important in the near future. From the viewpoint, effective countermeasures for marine corrosion are urgently required, since they will lead to great economic effects. The difficulty of analyses for marine corrosion can be attributed to the complicated factors involved in the process. The investigation should be carefully divided into several steps and fixed which step one would deal with. In this experiment, we prepared three categorized experimental assay systems. The immersion experiment in a pure culture system where only single variety of bacteria, Pseudomonas aeruginosa, was active (Type 1). Marine immersion where metallic materials were immersed in shallow water along a Japanese coast in a certain time (Type 2). And the immersion tests in a simulated laboratory solution (Type 3). We focused on chromium and nickel based metallic materials for the series of experiments, since our pilot study in the past showed a significant advantage of those metallic materials in the first assay system and the third. As specimen, plain carbon steel (JIS SS400, control), chromium plated steel(the substrate: JIS SS400), nickel plated steel(the substrate: JIS 33400), stainless steels (JIS SUS304) were used. Those were immersed in pure culture of P. aeruginosa, simulated static artificial sea water with condensed marine bacteria and shallow water of Ise Bay in Japan (Pacific Ocean). In all assay systems, the plain carbon steel showed significant corrosion products composed of brown iron oxides generally. On the other hand, nickel and chromium plated steels showed the dominated biofilm formation and the extents of corrosion product formation were not so significant, compared to the results for plain carbon. Stainless steels showed the highest anti-corrosion properties. The analysis by a confocal laser scanning microscopy in Type 1 assay system showed that pitting corrosion occurred dominantly for carbon steels and also that a tiny hunch deriving from organism appeared on the surfaces of chromium and nickel based materials. The mechanism and the anti-bacterial properties were discussed from the viewpoint of materials.

BACTERIAL ADHESION TO COPPER ALLOYED ANTIBACTERIAL STAINLESS STEEL SURFACES

Hiroshi Kawakami, Kenji Kittaka, Yoshihiro Sato, Yasushi Kikuchi

Osaka City University, Japan hkawakam@mech.eng.osaka-cu.ac.jp

Type 304 stainless steel, copper alloyed stainless steel, and oxygen free copper were subjected to antibacterial tests and short term exposure experiments in a laboratory. The model bacteria used were Pseudomonas sp., that were isolated from residual water in a water system where microbially influenced corrosion (MIC) was suspected and were used in previous MIC related studies. Antibacterial tests showed that the copper alloyed stainless steel and the oxygen free copper reduced the number of active bacteria more than two factors of ten in comparison with the control; the copper alloyed stainless steel, as well as oxygen free copper, was hence force antibacterial. Yet, the antibacterial activity of the copper alloyed stainless steel was lower than that of the oxygen free copper. In short term exposure experiments, the oxygen free copper reduced the number of planktonic bacterial cells, while the copper alloyed stainless steel, as well as the type 304 stainless steel, didn't sterilize planktonic bacterial cells. The numbers of planktonic bacterial cells for the type 304 stainless steels and the copper alloyed stainless steel saturated at the same level as that for the control, indicating that the antibacterial activity of the copper alloyed stainless steel is not enough to sterilize planktonic bacterial cells. Such a copper alloyed stainless steel, to put it another way, doesn't contaminate environment. At the end of 7 days exposure period, the number of bacterial cells adhering to the copper alloyed stainless steel surfaces was more than the number for the oxygen free copper surfaces and about the same as the number for the type 304 stainless steel surfaces. The copper alloyed stainless steel however reduced formation of biofilms on its surface and sterilized about 75 % of sessile bacterial cells. Such experimental results indicate that the copper alloyed stainless steel is effective against problems resulting from activities of sessile bacterial cells and will give less impact on environment.

28-B-1-6

BIOFOULING ON EAF STAINLESS STEEL OXIDIZING SLAG IN MARINE ENVIRONMENT

¹Hideyuki Kanematsu, ¹Akiko Ogawa, ²Seiji Yokoyama, ³Toshiyuki Takahashi, ¹Hajime Ikigai, ¹Daisuke Kuroda

Suzuka National College of Technology; ²Toyohashi University of Technology; ³Miyakonojo National College of Technology <u>kanemats@mse.suzuka-ct.ac.jp</u>

Steel industries which serve our civilization as infrastructure technology produce enormous quantity of slag on a daily basis. The steel making slag can be divided into two categories mainly - Blast Furnace Slag and steel making one. As for the former, it can be recycled almost 100%. However, the latter is still difficult to be recycled due to some serious reasons. Particularly, the major chunks of steel making slag from electric furnace are buried without any reutilization. The problem to increase the recycling ratio should be solved from the viewpoint of economy, environmental protection and resource protection. As one of problem solving ideas, the application to fishing reef, seaweed bed etc. has been investigated. When one would consider the application, the environmental risk property has to be investigated. We authors have already studied it from the viewpoints of dissolution characteristics, plankton's behavior in water environment and cytotoxicity. However, the biofouling characteristics of slag is also one of the important characteristics along with those factors for the application. Therefore, we investigated the biofouling characteristics of slag from EAF stainless steel making process from the viewpoints of constituent elements. The slag used for the series of experiments was produced in a stainless steel oxidizing process by an electric furnace. The chemical components were 45.1 mass% $SiO_2 - 33.2$ mass % CaO - 7.3 mass % MgO - 5.9 mass % Al_2O_3 , 2.9 mass % CrO - 4.4 mass % MnO - 5.9 mass % Al_2O_3 , Al_2O_3 , A0.8 mass % FeO – 0.4 mass % CaS. The slag from a conventional steel making process was used as control. They were immersed in shallow water along a Ise Bay seacoast of Japan (Pacific Ocean) in a certain period. The biofouling behavior in the marine environment was observed by naked eyes, scanning electron microscopy, confocal laser microscopy etc. And at the same time, the slag was immersed in a simulated marine environment on the laboratory scale in a short period. They were also observed by various instrumental analyses mentioned above. And the biofouling characteristics of the slag were discussed from the viewpoint of industrial application possibility.

CATHODIC DELAMINATION OF CABLE CONNECTOR ASSEMBLIES: MECHANISMS, MATERIALS AND TESTING PROTOCOLS

Z. Makama, J.R Smith, I.B.Beech, M. Webb, I.Doble, D.Nicolson and S.A. Campbell

University of Portsmouth, United Kingdom zakari.makama@port.ac.uk

The very harsh environmental conditions experienced in the offshore oil and gas, submarine and telecom industries necessitates the use of autonomous underwater vehicles as well as other remotely operated systems. Examples of such equipment include electrical assemblies and harnesses, which incorporate inter alia underwater connectors, encapsulated sensors, transducer arrays and cable bend control systems. When employed in underwater or harsh environments, cable connector assemblies must be sealed, most critically at the metal connector-to-cable interface. This is normally achieved by using a polyurethane moulding which bonds between the metal connector back-shell and the cable. However, in environments where sacrificial anodes are used to provide specific corrosion protection, cable assemblies are prone to cathodic delamination, a phenomenon which can compromise polyurethane-to-metal bonds and result in cable assembly failure. In this study, cathodic delamination data on polyurethane moulded assemblies obtained from a variety of tests including exposure trials, flowing sea water tanks and laboratory experiments are described. Novel in situ testing methods for accurate and reliable predictions of long-term performance are discussed. Finally, problems related to materials selection given REACH legislation restricting future use of many substances used in the production of cable connectors and other related products are highlighted.

28-B-1-8

USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY AND MICROSCOPY FOR EVALUATION OF BALLAST TANK COATING DEGRADATION BY MICROORGANISMS

¹A. Heyer, ²F. D'Souza, ²G. Ferrari, ³J.M.C. Mol and ¹J.H.W. de Wit

¹Materials innovation institute; ¹TNO Science and Industry; ³Delft University of Technology anne.heyer@tno.nl

Current understanding of polymer degradability has made progress in recent years through the application of advanced detection techniques in both the biology of microorganisms and corrosion science. There is still a lack of information on biodeterioration of synthetic polymeric materials. By the introduction of Electrochemical Impedance Spectroscopy (EIS) for sensitive detection of polymer degradation, new insights will be gained in this process. Microorganisms and microbial biofilms are capable of degrading polymeric material and fungi seem to be more effective than bacteria which are commonly found in marine environments. For this study lab scale set-ups were developed to study the degradation of ballast tank coatings by different bacterial strains (pure cultures as well as mixed natural samples obtained from practical ballast tank). EIS data were recorded over the period of time. During the experiments, EIS data gave an indication of degradation by microbial attack underneath the coating which was still visually intact. To evaluate the coating degradation due to microbial activity, ballast tank coating samples were exposed in liquid cultures of bacteria. Fluorescent staining was performed to show bacterial attachment on the surface. Furthermore, AFM imaging was used to characterize the changes in the surface properties of the coating over the period of time. These techniques allow understanding of the early biodegradation of the coating in a more detailed way leading to a more advanced and sensitive detection method for microbial attack in the future.

28-B-2-1

BIODETERIORATION OF THE RMS TITANIC, MICROBIOLOGICAL ASSESSMENT, 1996 TO 2010

Cullimore, D. R and L. Johnston

Droycon Bioconcepts Inc., Saskatchewan, Canada S4N 0E7 drc@dbi.ca

RMS Titanic sank on her maiden voyage in 1912 after collision with an iceberg. Since the discovery of the ship wreck site in 1985 there has been interest in the forensic aspects of the sinking and collision with the sea floor. Since 1996 there has been an ongoing investigation not only of the cause of the sinking but also the biodeterioration of the ship structures. Microbiological investigations started in that year with an initial evaluation of the role microorganisms have played in the corrosive and fouling aspects. Initial investigations concentrated on the fouling of the ship steels with bioconcretious growths (rusticles). Recovered rusticles were found to contain at least five bacterial communities that were culturable. In 1998 four steel test platforms were deployed at the site to obtain a better understanding of microbiologically influenced corrosion occurring on the steels. Three of these platforms A, B and C were recovered in 2004 and 2005 and the rate of corrosion of the steel coupons determined to average 0.031±0.005, 0.031±0.006 and 0.031±0.004gFe/cm²/year respectively. One platform (D) remains on site at port side well deck and the other platforms were replaced. One similar platform installed on the HMHS Britannic in 2003, a sister ship of RMS Titanic, which sank in the Mediterranean Sea in 1917. The platform was recovered in 2009 and found to collectively have lost 6.9g per month for a total loss of 662g or 29% of the total steel coupons deployed within the platform. This was a fourfold faster rate of corrosion observed for RMS Titanic platforms. This loss of iron from the steel coupons was found to be a combination of lateral dishing over the large surfaces, penetrative pitting into the edges of the steel coupon, and then through perforation. In all cases the corrosion observed was associated with rusticle growths and the dominant bacteria (using the BART™ technology) was found to include communities of sulfate reducing, iron related, acid producing, heterotrophically active, and denitrifying bacteria. These communities were isolated from each other and jointly occupied no more than 5% of the void volume in the bioconcretious rusticles. Biodeterioration in RMS Titanic appears to be driven, in part, by the embrittled steels generated during the collision and sinking process, partly by the indigenous microflora at site, and by the natural environment within which the ship now rests. It can be projected, particularly for the bow section of the hull which remains intact, that there will be an ongoing biodeterioration over the next few hundred years.

28-B-2-2

MICROBIALLY INDUCED LOCALIZED CORROSION OF TYPE 316L STAINLESS STEEL IN A RECIRCULATING SEAWATER SYSTEM

T.S.Rao, P.S. Murthy, Y.V. Harinath, V.P. Venugopalan, S.V.Narasimhan

Water & Steam Chemistry Division, BARC Facilities, Kalpakkam, India subbarao@igcar.gov.in

Austenitic steels like SS-316 show considerable corrosion resistance due to passive protective film on its surface. However, under unfavourable conditions, the passive film can break down leading to localized corrosion. In this study the microbially induced localized corrosion of SS-316 pipeline was investigated. The SS- 316L pipeline was exposed in a recirculating seawater system to monitor biofilm formation at a temperature of 40-45 °C. Biofilm development on industrial surfaces is influenced by substratum and bulk fluid properties. Temperature of the bulk fluid is a primary factor influencing biofilm development on heat transfer surfaces. Condenser slime is a major problem in the process water heat exchangers of the Madras Atomic Power Station (MAPS) where temperatures around 40 oC are encountered. The various experiments carried out were designed to quantify biofilm grown at different time intervals. However, within 6 sets of experimental runs amounting to 165 days of operation the SS pipeline developed leaks with pitting corrosion. The various analyses include biofilm quantification, microbial load of the biofilm, stereo zoom and scanning electron microscopy of the metal specimens. A sample was also processed for metallurgical observations. Biofilm analyses showed significant increase in protein (34 - 81 mg ml⁻¹ of biofilm volume); dissolved carbohydrates (6 - 25 mg ml⁻¹); particulate organic carbon (154 – 415 mg Γ^{-1}) and total suspended solids (1.5-2.2 mg Γ^{-1}). Live biomass estimated by esterase activity using fluorescein diacetate showed increase in biomass with increase in biofilm age. Bacterial population ranged from 105 -106 cfu cm⁻², a number of diatoms were also seen in the biofilm. Microscopic observation showed significant localized corrosion in the form of micro and macro pits. Crack initiation was noticed around the pits, propagating into the base metal. Metallographic observation after polishing showed decrease in chromium and iron concentration within the pit region. Microbial investigation confirmed the presence of iron bacteria, sulfate reducing bacteria (SRB) and heterotrophs. The consequence of events point out that the microbial biofilm with an assortment of microbiota resulted in differential ionic and oxygen concentration cells, which could have developed potentials to break down the passive film of the SS- 316 pipeline. The presence of SRB and the EDAX peak of sulfur indicate that substantial sulfide concentrations at the metal biofilm interface resulting in localized pitting corrosion of the pipeline. The microbial biofilm growth and the putative presence of corrosion bacteria could have caused the failure of the SS – 316 pipelines.

28-B-2-3

ELECTROCHEMICAL AND MICROBIOLOGICAL CONTRIBUTIONS TO THE CORROSION OF 70/30 CUNI ALLOYS IN SEAWATER

I.B.Beech, Z.Makama, J.Sunner and S.A.Campbell

University of Portsmouth, United Kingdom sheelagh.campbell@port.ac.uk

In marine habitats the activity of microorganisms in biofilms formed on metallic materials such as Cu, Fe, Sn and Al, and their alloys can result in severe deterioration of metal, a phenomenon known as microbiologically-influenced corrosion (MIC). Biofilms comprising diverse microbial population are recognised to be more aggressive towards metallic material than biofilms of single species. It has been proposed that corrosion rates observed in the presence of microbial consortia are related to cooperative metabolic activities of biofilm microorganisms as well as the chemical properties of the colonised surface. As a result of their corrosion resistance, thermal conductivity and reported anti-fouling properties, CuNi alloys find many applications in marine environments and are used extensively as heat-exchangers, pipelines and cladding materials. The stability of these alloys in chloride-containing media has been attributed to the presence of a duplex oxide layer on the alloy surface. However, contrary to accepted belief, protective oxide structure on CuNi alloys only delay the onset of macrofouling and these alloys are indeed susceptible to MIC with bacteria, fungi and marine organisms readily colonising their surfaces. This communication discusses the stability of both the duplex oxide film on the 70-30 CuNi alloy surface and the underlying metal in the presence of bacterial colonising community comprising marine acid and slime producing, Copper-resistant and hydrogen sulphide generating bacteria, co-exisiting within biofilms on surfaces of this alloy. Advanced microscopy, surface science and molecular ecology techniques have been used to elucidate biotic and abiotic components associated with observed localised corrosion in the form of pitting attack. Remedial strategies for biocorrosion control of CuNi alloys are critically evaluated.

28-B-2-4

THE EFFECT OF STERILISATION ON THE CORRODING OF MILD STEEL IN COASTAL SEAWATER

Robert Jeffrey and Robert E Melchers

The University of Newcastle, Australia 2308 robert@pacifictesting.com.au

Few successful medium term trials have been carried out to quantify the effect of micro-organisms on the surface of steel exposed to seawater, although the result of their presence has been known for many decades. Presented herein are the results of a three year investigation in which natural sea-water was taken from a Port Stephens tributary (approximately 200 km north of Sydney) on the Eastern Australian seaboard and split into two streams. One stream (natural water) was pumped directly into a tank in which 25 mm x 25 mm polished steel coupons were suspended. The natural water passed over the coupons and was returned to the estuary. The second stream was passed through a series of filters and sterilized using ultra-violet (UV) lamps prior to entering a similar but sealed tank, also fitted with UV sterilization, where identical coupons were suspended, before being returned to the waterway. Bacterial identification tests were carried out on a regular basis on the water from both tanks and during the whole three years no evidence was found of sulphate reducing bacteria (SRB) or iron related bacteria (IRB) in the sterile water tank. However, evidence of bacterial spores was found in the natural water on a regular basis. Coupons were removed from each of the tanks at various intervals and examined in detail. Of particular interest was the surface of the steel when viewed using an optical microscope and with a scanning electron microscope (SEM). The images presented in all cases show a difference in topography between coupons recovered from natural and sterile water streams where the only difference was the removal of microbiological matter. Pitting was observed on both sets of coupons but was considerably more severe on those from the natural water tank. Additionally the appearance of the corrosion product on the two sets of recoveries differed significantly with tubercles eventually presenting on all coupons recovered from the natural water tank and only generally even corrosion product on those recovered from the sterile water. It seems most likely that the increased pitting and occurrence of tubercles observed on the natural water coupons is attributable to bacterial activity. The reasonfor these differences is the subject of ongoing investigations.

CORROSION MECHANISM DRIVEN BY MARINE ELECTRO-ACTIVE BIOFILM

¹Jizhou Duan, ¹Lin Yu, ¹Fengling Xu,J ²un Zhao, ¹Baorong Hou

¹Institute of Oceanology, Chinese Academy of Sciences; ²Marine Chemical Research Institute, China duanjz@qdio.ac.cn

Corrosion is a key issue resulting in the deterioration of metal and concrete reinforcing bar materials in marine environments, related to bridges, docks, ship and petroleum platforms, pipelines and other important infrastructures. Marine corrosion environment could be divided into atmospheric, splash, tidal, immersion and seamud zones. There are different corrosion rules in different corrosion zones. Seawater is strong corrosive medium with a very high conductivity due to dissolved chloride salts, a plenty of dissolved oxygen and especially, its bioactive characters. Microbiologically influenced corrosion (MIC) is one of key characteristics of marine corrosion. MIC could be totally divided into anaerobic corrosion and aerobic corrosion. Whether anaerobic or aerobic corrosion, it has been found there are all some examples that microorganism can induce corrosion acceleration or inhibit corrosion in some conditions. Many different corrosion mechanisms have been suggested. Microorganism can attach and form the biofilm on the surface of metals. It has been found that some anaerobic or aerobic biofilms are electroactive, and electron transfer can occur between biofilm and metals. In this study, the electroactive characteristics of sulfate-reducing bacteria and marine aerobic biofilm were studied, and an accelerated corrosion and decreased corrosion phenomena were observed, individually. Based on the interaction of marine electroactive biofilm and metals, corrosion acceleration or inhibition mechanism was suggested and discussed.

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28-B-2-6

THE STUDY OF BIOFILM FORMATION AND THE ELECTROCHEMICAL BEHAVIOR OF SOME METALS IN NATURAL MARINE WATER

¹Yasuyuki Miyano, ²Hideyuki Kanematsu, ³Nobumitsu Hirai, ¹Takeyuki Hirai, ¹Osamu Kamiya

¹Akita Univeristy; ²Suzuka National College of Technology, ³Osaka University <u>v.miyano@gipc.akita-u.ac.jp</u>

When practical material is in contact with natural seawater, a biofilm will grow on the materials surface. A well known effect of the biofilm adhesion is an ennoblement of the open circuit potential (OCP). This can be considered as one of the main causes of microbiologically influenced corrosion (MIC). To elucidate the relationship of biofim formation and the corrosion starting, lab scale exposure test were carried out using natural marine water sampled around the coast of Suzuka. Eight types materials i.e. AISI 304 stainless steel, SS400 steel and metal coated 400 steel (coating: Cr, Zn, Sn, Ni, Cu and Ag) were tested in the glass vessel. The time dependence of the open circuit potential (OCP) was measured for all coupons. Ennoblement of the OCP, similar to that reported from investigations in seawater, was found in some experimental set up. Anodic polarization, cathodic polarization and Liner polarization resistance (LPR) were also measured to investigate the environmental characteristics of these materials in natural marine water. Biofilm formation on the surface of exposed materials was observed by a fluorescent microscopy and an atomic force microscope to discuss the anti-bacterial effect of some materials. From these experiments, the relationship of biofilm formation, the behavior of the potential ennoblement and the corrosion effect on some metals were investigated. Moreover the mechanism of microbiologically influenced corrosion induced by biofilm formation and the anti-bacterial effect for MIC were discussed from the viewpoint of materials.

28-B-2-7

ETCHING INITIATED CORROSION OF STAINLESS STEEL 316L BY THE CEMENT OF THE BARNACLE, AMPHIBALANUS RETICULATUS

¹R. Sangeetha, ¹R. Kumar, ¹M. Doble, ²R. Venkatesan

¹IIT Madras, Chennai-600036, India; ²National Institute of Ocean Technology, Chennai-600100, India nvrk@iitm.ac.in

The barnacle, Amphibalanus reticulatus, is a common fouler in the Indian marine waters and is found to adhere to a wide range of natural and man-made solid surfaces. Localized corrosion under barnacle basal region on ferrous materials has been known for a long time. The decomposition of barnacle flesh by bacteria, perforation of the base-plate, initiation of crevice corrosion followed by deep pit formation was considered to be the mechanism of such localized corrosion. The influence of barnacle cement on the corrosion process has not been taken into consideration till date. In the present work, we concentrate on the effect of barnacle cement on the corrosion and rusting of stainless steel 316L substrate. We clearly bring out for the first time the role of the barnacle cement in acting as an etchant, preferentially etching the grain boundaries, and initiating the corrosion process in stainless steel 316L. The adhesion interface, which consists of base-plate, cement and the substrate, is systematically studied from a materials perspective. The X-ray diffractogram (XRD) and atomic force microscopy (AFM) shows that the barnacle base-plate is found to be composed of nano-calcite crystals. Other characterization techniques like scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) are carried out to understand the corrosion mechanism taking place under the barnacle-base. SEM reveals the morphological changes in the cement structure across the interface of the base-plate and the substrate, modification of the steel surface by the cement as well as the corrosion pattern beneath the barnacle-base. FTIR of the corrosion products show that they are composed of mainly oxides of iron thereby implying that the corrosion is aerobic in nature. AFM helps in elucidating the variation in the roughness and morphology of the substrate before and after barnacle adhesion. A model for the etching and corrosion mechanism is proposed based on our observations. Sensitization study of SS316L is included so as to understand whether the corrosion is intergranular in nature.

28-B-2-8

NOVEL MIC MECHANISMS ASSOCIATED WITH STORAGE OF ALTERNATIVE FUELS IN MARINE ENVIRONMENTS

Jason S. Lee, Richard I. Ray, Brenda J. Little

U.S. Naval Research Laboratory jlee@nrlssc.navy.mil

The U.S. Navy will begin supplanting traditional high sulfur petroleum diesel with alternative fuels. Changing from traditional petroleum diesel to alternative fuels such as biodiesel may increase the risk of microbiologically influenced corrosion. Since Naval assets employ seawater as ballast in fuel storage tanks, addition of biodiesel may result in corrosion problems not anticipated based on the use of traditional petroleum diesel. Experiments were designed to evaluate the corrosion-related consequences of storing biodiesel in contact with natural seawater. Results indicated microbial sulfide production was stimulated in seawater by the presence of biodiesel. Biodiesel provided a carbon source for the production of sulfides by sulfate-reducing bacteria in seawater. The presence of seawater altered the chemistry of the biodiesel by contributing water, sulfur and chloride. Exposure of fuel tank alloys to these conditions resulted in elevated corrosion rates, raising questions about storage and transportation of biodiesel in the presence of seawater.

28-B-2-9

APPLICATION OF ATOMIC FORCE MICROSCOPY IN THE STUDY OF SULFATE-REDUCING BACTERIA BIOFILM

Duan Dong-Xia, Sui Xiong-Qiang, Lin Cun-Guo, Liu Guang-Zhou

College of Marine Life Science, Ocean University of China; State Key Lab for Marine Corrosion and Protection; Luoyang Ship Material Research Institute

duandx@sunrui.net

Structure in marine are often been covered by biofilm. The biofilm are made of bacteria, extracellular polymeric substances and water. The biofilm can drastically modify the corrosion behavior of structural metals and alloys enhancing localized alterations in the type and concentrations of ions, pH, and oxygen levels. However, biofilms also facilitate the formation of diffusion barriers to the exchange of chemical species from and towards the metal/solution interface. Problems due to biocorrosion and biofouling of industrial systems range from heavy microbiological contamination with consequent energy and efficiency losses to structural failures owing to corrosion. Sulfate-reducing bacteria are abundant in marine environment. And it is well known for microbiologically influenced corrosion. This study demonstrated that atomic force microscopy (AFM) can be used to obtain high-resolution topographical images of bacteria, and to quantify the tip–cell interaction force and the surface elasticity. Results showed that the adhesion force between the Si_3N_4 tip and the bacteria surface was 3.0nN and those at the periphery of the cell was 3.6nN. Results also showed that the adhesion force between the Si_3N_4 tip and the bacteria surface was different according to the substratum. The adhesion force at the glass was 8.4nN, while the adhesion force at the polymethyl methacrylate was 2.4nN. The elasticity varied on the cell surface and the substratum.

29-H2-P: Plenary

BIOFOULING AS A MODERN VECTOR OF INVASIONS: RISKY BEHAVIOURS AND MANAGEMENT OPPORTUNITIES

Chad L. Hewitt

National Centre for Marine Conservation and Resource Sustainability, University of Tasmania c.hewitt@amc.edu.au

The human mediated transport of species from one region to another has become a global phenomenon of import. No region of the world is pristine, making biological invasions one of the most pervasive threats to environmental, economic and social values and a leading cause of global change. This holds true across terrestrial and aquatic (freshwater and marine) environments, however our understanding and abilities to manage aquatic invasions remains poor. In these environments, management needs have recently highlighted the importance of understanding the relative roles of various transport mechanisms (vectors) and connectedness between biologically relevant provinces (pathways). The roles that various transport vectors play in the transfer and establishment of new marine and estuarine invasions have variously been discussed and analysed in numerous regions, by multiple researchers. The changing patterns of trading activities, coupled with alterations in both donor and receiving environments, influence the potential for species invasions. More than 1780 marine and estuarine species are reported as introduced to at least one region of the world. Using life-history characteristics and the time of invasion, likely vector associations have been reconstructed indicating that ship related transport, particularly biofouling and ballast water, represent the greatest global means of species invasion, although relative contributions vary across regions. The need to manage biological invasions in the face of significant uncertainty has led manager and scientists to develop appropriate analysis frameworks to identify risks. Here I present a framework for marine biofouling risk assessment at both species, vessel and pathway levels. Likelihood (the probability of an invasion event occurring) are derived from the opportunities for transfer based on a combination of species characteristics, vessel characteristics and behaviours (including voyage characteristics) and pathway strengths. In contrast, consequence (probability of impact) is determined by species level information alone. The product of these two elements results in assignment of risk. The development of the risk framework relied on the suite of perceived elements contributing to biofouling risk for consideration. These perceived risks include elements that would limit or restrict species settlement on a vessel (duration in port, type and age of antifouling paint, time since dry-docking or in service period), transit survival (vessel speed, type and age of antifouling paint) and establishment in the recipient location (duration in port, species-environment matching). These elements of risk are evaluated with an eye towards precaution and opportunities for management.

SURVEY OF SESSILE MARINE FOULING ORGANISMS FOUND ON NAVIGATIONAL BUOYS IN SINGAPORE'S COASTAL WATERS

Lee S-C Serina, Tan K-S, Ong J-L, Tan S-H, Sin T-M & Teo S. L-M

National University of Singapore tmsteolm@nus.edu.sq

There are over a hundred navigational buoys distributed around Singapore island. With some 140,000 vessels passing through Singapore annually, these buoys may be a potential means to monitor for alien species introductions into Singapore Port waters. The buoys are coated with a non-toxic epoxy coating and cleaned every 2-3 years. Although Singapore is a small island less than 60km wide but marked variation in the composition of fouling communities was observed and species diversity was high, often exceeding 50 species on each buoy. This paper will present an overview of the marine fouling communities found on navigational buoys from Singapore, and discuss some of the hurdles for biosecurity management in tropical Southeast Asia.

29-H2-1-2

INVASIVE BRYOZOANS TRANSPORTED VIA HULL FOULING INITIATED A PHASE SHIFT IN A SMALL CALIFORNIA (USA) ESTUARY

Lisa A. Needles and Dean E. Wendt

University of California, Santa Barbara and Cal Poly State University, San Luis Obispo, USA dwendt@calpoly.edu

Invasive species are commonly cited as one of the leading threats to communities and ecosystems worldwide, yet relatively few studies have demonstrated invader impacts at these scales. The lack of baseline data prior to an invasion event makes documenting the impacts of invasive species at the community and ecosystem level problematic. To understand the impact of invasive species on a community, we compared a current survey of a small estuary (Morro Bay, CA) to historic surveys. In addition, we compared the invasion of Morro Bay to larger more actively used harbors (San Francisco Bay and Los Angeles/San Diego harbors). Although Morro Bay has proportionally fewer exotic species than larger bays, the changes in community composition and abundance have been striking. There has also been a change in the richness of taxa; notably a decrease in Mollusc species and an increase in Bryozoan species. Most strikingly, the historic dominant space occupiers (the mussel species, *Mytilus californianus* and *Mytilus galloprovincialis/trossolus*) have been replaced by an exotic bryozoan, Watersipora subtorquata. We use the results from our study to address the importance of hull fouling as a vector of invasion in estuaries and to evaluate the metrics commonly used to measure community invasion. We also propose that the Southern Sea Otter (*Enhydra lutris nereis*) may have facilitated this invasion by creating a disturbance (through predation on mussels) necessary for W. subtorquata to get established. We also suggest that, once established, W. subtorquata may limit recruitment of mussels back to the community. This shift may represent an alternative stable state, as removal of *W. subtorquata* did not shift the community back to a preinvasion assemblage. Instead, another exotic bryozoan (*Schizoporella unicornis*) replaced *W. subtorquata*.

COMMERCIAL SHIP BIOFOULING AS A TRANSFER MECHANISM FOR SPECIES INOCULATIONS OF THE US PACIFIC COAST

Ian Davidson, Gail Ashton, Greg Ruiz

Portland State University & Smithsonian Environmental Research Center <u>idavidso@pdx.edu</u>

Biofouling of ships continues to act as a dominant vector for re-distributing nonindigenous species around the world. A recent global analysis of vectors associated with 1781 nonindigenous species reported that 43% were initially introduced via ship biofouling, the highest for any vector category. While the efficacy of modern antifouling paints has reduced the cover of biofouling across hull surfaces, the rate of biofouling-mediated introductions does not appear to be diminishing. Our sampling in recent years on the US West Coast has focused on containerships, barges and cruise ships. Consistent with other studies, we have recorded a wide range of organisms associated with protected and heterogeneous (non-hull) niche areas, including rudders, stern tubes, ladder-holes, sea-chests and thruster gratings. In some instances, we have estimated in the order of 104 organisms at these locations on certainer ships. These niche-area hotspots of fouling also support diverse assemblages of species, including common biofouling organisms such as barnacles, polychaetes, bryozoans and mussels. Other mobile organisms, such as amphipods, nemerteans and flatworms, have also been sampled within biofouling matrices. In association with other vectors, it is likely that ship biofouling continues to transfer new species to the NE Pacific and act as an important vector for the coastwise regional spread of species after initial introduction.

29-H2-1-4

INTEGRATING ANTIFOULING STRATEGIES TO MINIMIZE TRANSPORT OF MARINE INVASIVE SPECIES BY RECREATIONAL BOATS

Leigh T. Johnson, Carolynn S. Culver Henry M. Page, Jenifer E. Dugan

University of California Sea Grant Extension Program and University of California, Santa Barbara <a href="https://linear.org/linear.

California's recreational-boat, hull-cleaning industry uses best management practices (BMPs) on antifoulant and other hull coatings to control recruitment of marine fouling species, including non-indigenous invasive species (NIS). To investigate concerns that this approach may stimulate new growth by disturbing the fouling community and altering the hull surface, we experimentally assessed recruitment responses of NIS and other fouling species to hull cleaning BMPs at Santa Barbara Harbor and San Diego Bay. Hull cleaning practices were applied for 3 months during peak recruitment season to fiberglass tiles coated with copper-based antifouling paint, nontoxic epoxy or nontoxic siliconized epoxy. Then, tiles were cleaned and redeployed and new tiles were deployed for one month. Accumulated biomass was measured at the experiment's end. We evaluated type and level of fouling when BMPs were applied (every 2-3 weeks) and at the end. California hull cleaning BMPs did not stimulate fouling. Fouling amounts did not differ significantly among tiles that had been cleaned once, continually cleaned or never cleaned. Cleaning treatment affected tool type and effort required to remove fouling. More abrasive tools and effort were needed to remove growth from previously cleaned tiles than from tiles that had never been cleaned. Hull coating type influenced fouling and cleaning practices. Tiles with copper-based antifouling paint had significantly less fouling - lacking calcareous species and algae altogether - and required less abrasive tools and effort to clean. Location did not influence type of fouling, nor tools and effort required to remove it, yet dramatically less fouling accumulated on experimental tiles at Santa Barbara (northern location). Our results have implications for policies to control NIS and other fouling while protecting water quality. Copper-based antifouling paints were highly effective at reducing fouling, but negative impacts on water quality and movement of copper-tolerant NIS make them far less ecologically sound. Copper antifoulants are under increased regulatory scrutiny in California and are restricted in some areas. Our findings indicate: 1) California's hull-cleaning BMPs are effective for controlling NIS and other fouling species on recreational boats and 2) California BMPs could be adapted for differences in fouling rates among locations in California and elsewhere.

THE GHOST OF FOULING COMMUNITIES PAST: EVIDENCE FOR CARRY-ON EFFECTS ON TRANSPLANTED PANELS

Emily Ralston and Geoffrey Swain

Florida Institute of Technology eralston@fit.edu

Biofouling of boats and ships creates operational problems and has also been linked to the spread of invasive species. Previous research suggests that fouling community composition and quantity will be modified by prior fouling settlement and for ships and boats traveling between different ports this may have significant impact on the recruitment of organisms. This experiment was designed to determine how preconditioning affects the rate and composition of re-fouling after a transplant is performed. A series of 10.16 x 20.32 cm panels were placed at three locations in Florida (Ponce Inlet, Sebastian Inlet and Port of Miami) which were characterized by distinct fouling communities. Panels were immersed for six months and then cleaned and transplanted among the three sites. Fouling community composition and coverage was characterized at bimonthly intervals both before and after transplantation. The data showed that community structure at Sebastian and Ponce Inlets were affected by surface conditioning from different exposure sites, however no effects were observed in Miami.

29-H2-1-6

THE RELATIVE RISK OF ANTIFOULING TECHNOLOGIES FOR THE TRANSPORT OF INVASIVE SPECIES

Jeremy C Thomason

International Paint Ltd <u>Jeremy.Thomason@Akzonobel.com</u>

There is no doubt that ships act as vectors for invasive species. Evidence for translocation comes from the widespread distribution of some organisms and from surveys of fouling on relatively small samples of vessels. The proportional contribution of antifouling coatings in this diasporic process is not entirely clear as ships also release propagules in ballast water and a few organisms with planktonic larvae will expand their distributions naturally. Additionally there is no evidence to differentiate between risk of translocation on biocidal (traditional, controlled depletion polymers and self polishing coatings) and non-biocidal foul release coatings. Furthermore there is also the need to differentiate between the translocation of larger fouling organisms, which are an immediate source of propagules and the translocation of slime films which may incorporate both sources of propagules and entrapped propagules of larger organisms. This study uses data from over 250,000 records of fouling on the global maritime fleet to assess such risks, comparing between biocidal and non-biocidal technologies. It also analyses separately the risk of translocation between macro and microfouling and hence provides a strong empirical theoretical framework upon which to base further study.

SLOW MOVING BARGES: A RISK ASSESSMENT ACROSS DOMESTIC AUSTRALIAN BORDERS

Marnie L. Campbell and Chad L. Hewitt

National Centre for Marine Conservation and Resource Sustainability, University of Tasmania m.campbell@amc.edu.au

Protecting a country from introduced species requires vigilance at both international and domestic borders. Many countries are developing stringent controls on international vessel entries to reduce the risks of introductions from ballast water and biofouling. For many countries however, the translocation of primary introductions from the point of first entry to other locations, or the movement of native species from one bioprovince to another within domestic boundaries requires the development of internal borders. Slow moving vessels are considered an ideal vector for the movement of introduced marine species. The slow speed of these vessels suggests that biofouling species are exposed to reduced transit stress resulting in increased survival rates. In Australia, slow moving vessels transit vast distances to reach our international borders (eg Europe, or Singapore). Once in Australia these vessels are utilised across many projects, in different states, to defray their international transit costs and to maximise the vessel's utility. Couple these factors creates a potentially highrisk vector. As such, it is believed that these vessels pose a threat of spreading both international and domestic species. To ascertain what level of biofouling risk these vessels pose to different state locations within Australia, we undertook a risk assessment that assessed three domestic voyages of a slow moving dredger barge. This barge originated from Europe, but was cleaned in Singapore prior to the first assessed domestic voyage. This mitigated the international threat, which is not considered within this risk assessment (ie we focus on the domestic borders). The risk assessment utilised a standard risk evaluation process: determining end points, identifying hazards, assessing the likelihood that a hazard species will be moved, assessing the impacts this species may have in the recipient location and determining the level of risk. The attractiveness of this risk assessment approach is the speed with which the analysis can occur and the pragmatic approach that it takes. A vessel is not laid-up in port while divers collect samples that are subsequently taxonomically analysed and verified. Also, the data requirements are not onerous, especially if the ports in question have undertaken port surveys for introduced species.

29-B-1-1

THE EFFECT OF OCEAN ACIDIFICATION UPON MACROFOULING IN A TEMPERATE MARINA

Mr Tom Vance, Dr Roy Sanderson, Dr Jeremy Thomason

Plymouth Marine Laboratory, Newcastle University thva@pml.ac.uk

Global industrialisation has lead to the anthropogenic raising of global CO₂ concentration from 280 pp to over 380 ppm in the last 200 years causing oceanic pH to drop by 0.1 unit. It is expected to further drop by between 0.3 and 0.4 units over the next 100 years. Quantifying the impact of such a pH shift has to date relied on laboratory studies of model organisms or simple assemblages in mesocosms. Conversely, we undertook a field experiment to examine the effect of 100 yr predicted pH on a robust marina fouling assemblage through the manipulation of local CO₂ concentration. CO₂ was delivered and controlled above replicated settlement panels that were freely accessible to normal propagule supply. Over 4 months recruitment and development was shown to be largely unaffected by low pH. We could conclude that ocean acidification will have minimal affect on fouling but we offer several caveats to temper this view.

29-B-1-2

HOW DO CRABS KEEP THEIR EYES CLEAN? THE SYNERGISTIC ANTIFOULING APPROACH OF CARCINUS MAENAS

¹Greco G., ²Torrassa S, Svaldo Lanero T, ³Young R, ⁴Vassalli M, ²Rolandi R, ³Pelucchi E., ⁵Faimali M, ¹Davenport J.

¹ZEPS- UCC, Cork, Ireland; ²DIFI- University of Genoa, Genoa, Italy, ³Tyndall Institute, Cork, Ireland, ⁴IBF- CNR, Genoa, Italy, ⁵ISMAR- CNR, Genoa, Italy greco.giuliano@gmail.com

Marine technologies to monitor the marine environment are becoming more and more sophisticated and accurate; monitoring the sea increasingly requires use of optical, electrochemical and bio-sensors. Performance of these is degraded by biofouling, often within a few days. Several antifouling technologies have been applied to marine sensors, but these methodologies are often not environmentally friendly and potentially damage the marine environment being monitored. The requirement for new antifouling methods (partly in response to recent International Maritime Organisation (IMO) regulations) has led the scientific community to look for a source of inspiration from nature to find out new environmentally and economically acceptable methods to control the problem. In this study, the decapod crustacean Carcinus maenas (green crab) was selected as model organism and its antifouling (anti-epibiosis) techniques investigated. C. maenas employs several antifouling strategies to keep surfaces clean, particularly in the case of sensors such as the eyes. It thus represents a valuable model for developing new antifouling methods for environmental monitoring devices. A behavioural study on the eye cleaning techniques in the green crab was performed by means of video recording with a high speed camera. Four different eye cleaning behaviours were identified and characterized. The structures and the appendages involved in the cleaning techniques were observed with a scanning electron microscope and the performance of the identified cleaning techniques was evaluated with field experiments. Furthermore atomic force microscope (AFM) studies to characterize the crab eye surface microtopography, and to evaluate its antifouling potential, were performed. The eye surface microtopography revealed two scales of roughness, one at the micro- and one on the nano-scale; RMS values at the nanoscale indicate a potential approach to microfouling control. Data obtained on C. maenas eye cleaning behaviour suggest a well developed mechanical defence, a potential physical protection and a possible chemical strategy to protect the eyes' surfaces against the settlement of organisms, thus demonstrating a multiple, synergic approach by the crab to the biofouling problem. Results of this study represent a new insight into Carcinus maenas behaviour and morphology and provided a starting point for antifouling-biomimetic studies derived from this crab species.

29-B-1-3

UNDERSTANDING THE SETTLEMENT OF *BALANUS AMPHITRITE* THOUGH THE CHARACTERISATION OF GLYCANS INVOLVED IN GREGARIOUSNESS

Helen E Pagett

Newcastle University, United Kingdom h.pagett@nvl.ac.uk

Before settling, barnacle cypris larvae asses the suitability of a substratum for settlement through surface exploratory behaviour. The cuticular tissue of adult barnacles contains a glycoprotein-based contact cue referred to as settlement-inducing protein complex (SIPC). This cue is key to the gregarious settlement of barnacles and represents an attractive target for custom synthesis of antagonistic surfaces. Despite decades of research into marine fouling and the development of anti-fouling/fouling-release systems, detailed knowledge of the biochemical and structural composition of marine bioadhesives remains poor. Using the tropical acorn barnacle *Balanus amphitrite*, this project has fully characterised the carbohydrate moiety of SIPC, illustrating the importance of glycan based structures in conspecific identification. The SIPC active fraction has been purified by ion exchange chromatography and gel filtration and detected through SDS-PAGE gel antibody immunoblotting. The carbohydrate structure has been characterised using a combination of high performance liquid chromatography (HPLC) and exoglycosidase digestions. Current work is continuing to create develop carbohydrate-functionalised polymers that act as SIPC mimics to cue settlement on contact with barnacle cypris larvae. This will lead to a greater understanding of the contribution of glycans to gregarious mechanisms and the success of fouling organisms, and with further research it may be possible to develop surfaces that are antagonistic to the barnacle settlement cue.

29-B-1-4

INFLUENCE OF PHYSICOCHEMICAL SURFACE PROPERTIES ON THE SETTLEMENT OF SPORES OF THE GREEN ALGA *ULVA* STUDIED BY THREE DIMENSIONAL HOLOGRAPHIC TRACKING

^{1, 2}A. Rosenhahn, ¹M. Heydt, ¹S. Schilp, ³M.E. Pettitt, ³M.E. Callow, ³J.A. Callow, ^{1, 2}M. Grunze

¹University of Heidelberg, Germany; ²Karlsruhe Institute of Technology, Germany; ³ University of Birmingham, UK rosenhahn@uni-heidelberg.de

The settlement of *Ulva linza* zoospores is a three dimensional process and involves swimming in solution, exploration of surfaces and eventually settlement. To acquire and analyze the complex, three dimensional swimming and exploration patterns, we apply digital in-line laser holography. The advantage of using holography is its intrinsic three-dimensionality which allows tracking multiple organisms within a given volume simultaneously with only one camera. The influence of surface properties on the exploration patterns and surface recognition has been studied and set into correlation with settlement and adhesion strength data. Functionalization of the surfaces is carried out by immobilization of polymers, mostly via self assembled monolayers (SAMs). Such SAMs are increasingly being used in biofouling research as they allow the adjustment and characterization of surface properties. For the holography study, the focus has been the influence of wetting on the settlement behavior, which has been found to significantly affect both, exploration and settlement. It turns out that the interaction of the spores close to the surface is also connected with the additional properties of the used chemistries, such as hydration. Especially non-protein resistant chemistries show a time dependence of the motion patterns, which points towards an additional contribution of conditioning molecules on the surface.

EXPLORATORY RESPONSE OF A. AMPHITRITE CYPRIDS ON MICRO PILLARS

¹K. C. Chaw, ²G. H. Dickinson, ¹K. Y. Ang and ¹W. R. Birch

¹Institute of Materials Research and Engineering, Agency for Science, Technology and Research, Singapore; ²Tropical Marine Science Institute, National University of Singapore, Singapore

w-birch@imre.a-star.edu.sg

Surface microtopography is one of the various defenses that marine organisms have evolved against colonization by macrofoulers. Although artificial replicates of these natural microtextures have shown promise against the settlement of marine foulers, a detailed understanding of mechanism leading to their effectiveness is lacking. The larval bio-response to surface microtopography will provide valuable insights for developing materials with a broad effectiveness against marine fouling. The present study quantifies the behaviour of A. Amphitrite cyprids on micro pillars with heights of 5 and 30 μ m and diameters ranging from 5 to 100 μ m. Close range microscopy is used to observe the active response to microstructures during their exploration walk and their final selection of a settling location. On 5 um-high pillars, cyprids prefer to form temporary anchoring points in the voids between the pillars. On 30 μ m-high pillars, this preference is reduced, indicating the influence of steric hindrance on their attachment. Cyprids exhibit a preference for forming anchoring points in voids when pillars have diameters of 20 and 30 μ m. This decreases for pillars with larger diameters. Cyprids exhibit shorter lengths between temporary anchoring points on microtextured surfaces, as compared to a smooth surface. Micro pillars with 5 μ m diameter represent a special case, where the solid surface area for cyprid adhesion is reduced, resulting in significantly shorter step lengths and longer step duration. This reveals the interaction of cyprids with microstructured surfaces, leading to an understanding of settlement preferences and the design and engineering of anti-fouling surface properties.

29-B-1-6

A PREDICTIVE MODEL FOR THE ATTACHMENT OF MARINE ORGANISMS TO MICROTOPOGRAPHIES

¹Chelsea M. Magin, ²John A. Finlay, ³Linnea K. Ista, ²Maureen E. Callow, ²James A. Callow, ³Gabriel P. López and ¹Anthony B. Brennan

¹University of Florida; ²University of Birmingham; ³University of New Mexico <u>cmagin@ufl.edu</u>

A predictive model for the attachment of marine organisms to microtopographies created in poly(dimethylsiloxane) elastomer (PDMSe) was evaluated. Previously, a negative linear relationship was demonstrated between the transformed, normalized attachment density of the algal spores of Ulva and the Engineered Roughness Index (ERIII). ERIII is a dimensionless ratio of variables associated with the size and geometry of microtopographical features. It relates Wenzel's roughness factor (r) and the number of distinct features in each pattern (n) to the surface solid fraction (1- Φs). This model was further developed by evaluating the attachment of the marine bacterium *Cobetia marina* under flow conditions to microtopographies that cover a range of ERIII values. A negative linear correlation was also shown to exist between the transformed, normalized attachment density of *C. marina* in both the stationary and logarithmic growth phases and ERIII. The accuracy of the attachment model as a predictor for stationary phase *C. marina* attachment under flow conditions was tested by evaluating a new surface, Recessed Sharklet AF™ (ERIII=24), with a higher ERIII value. A 95% prediction interval was determined for Recessed Sharklet AF™ using the attachment model equation and previously obtained stationary phase attachment data. For an ERIII value of 24 the prediction interval is 0 to 48 cells/mm². The percent reduction versus smooth is predicted to be between 88% to 100% for the recessed Sharklet AF™. The attachment model is also expected to predict the attachment of *C. marina* and the cells of the diatom *Navicula perminuta*. A model that predicts attachment of marine fouling organisms to microtopographies is an extremely valuable tool for designing non-toxic antifouling surfaces.

29-B-1-7

FUNCTIONAL AMYLOID IN THE ADHESIVE OF THE BARNACLE BALANUS AMPHITRITE

¹Daniel E. Barlow, ¹John L. Kulp, ¹Kathryn J. Wahl, ²Gary H. Dickinson, ³Daniel Rittschof and ³Beatriz Orihuela

¹U.S. Naval Research Laboratory, USA; ²Tropical Marine Science Institute, National University of Singapore; ³Duke University Marine Laboratory USA daniel.barlow@nrl.navy.mil

Amyloids are fibrillar proteins with a unique cross beta-sheet structure that have outstanding biomaterial properties, including high strength and resistance to degradation. Historically, amyloids have been associated with disease, however, it is becoming increasingly evident that amyloids with beneficial functions, referred to as functional amyloid, also have roles in biology. Barnacles secret a durable, permanent, proteinaceous adhesive that has been previously shown to contain a nanofibrillar matrix (1),(2). However, until now, the protein structure of these nanofibrils has never been specifically addressed. Through atomic force microscopy (AFM), we verify that both primary and secondary cements (original adhesive and cement used for reattachment, respectively) of the barnacle *Balanus amphitrite* are primarily composed of nanofibrillar matrices. Analysis of these cements by Fourier transform infrared (FTIR) spectroscopy, far-UV circular dichroism (CD) spectroscopy, and Thioflavin T staining shows that the nanofibrils are indeed consistent with amyloid, with globular protein components also identified. Potential properties, functions, and formation mechanisms of the amyloid-like nanofibrils within the adhesive interface are discussed. These results provide a new basis from which a more focused effort can be conducted to better understand the strong, robust adhesion of barnacles.

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EVALUATION OF HEAVY METAL AND TBT CONTAMINATION ASSOCIATED WITH SHIPPING IN MUSSELS AND SEDIMENT ALONG THE WEST COAST OF THE UK

V Cumbor, P Riby, W Hartley, S Bonsall, A Wall & S Dürr

Liverpool John Moores University, UK. v.cumbor@2008.ljmu.ac.uk

In September 2008 the IMO imposed legislation banning the use of Tributyltin (TBT) because of its deleterious effects on the environment. There are still problems associated with the removal of old paints; some of the heavy metal replacements can also impact non-target species just as widely. The aim of this study was to assess the load of TBT and heavy metals in marine surface sediments and mussel tissue. Samples were collected from various sites along the West coast of the UK over July and August 2009 where little or no surveys had previously been conducted. Sediment samples were collected from Holyhead, Maryport, Seaforth Dock, Hornby Cut (Liverpool), and Huskisson Dock (Liverpool). Mussel and sediment samples were gathered from Birkenhead, Dartmouth, Padstow, Pwllheli, and the Liverpool docks Brunswick, Salthouse Quay and Albert Dock. Five replicate samples were taken at meter intervals for both sediment and mussels at each site. Sediments were obtained using an Eckman grab and mussels were size selected for adult size, 45± 10 mm. Samples were dried and ground to get a homogenous sample. The samples then underwent acid digestion and the heavy metals; As, Cd, Cr, Cu, Fe, Ni, Pb and Sn were tested for using inductively coupled plasma optical emission spectroscopy (ICP-OES) for sediment and inductively coupled plasma mass spectroscopy (ICP-MS) for mussels. TBT contamination was screened for using a gas chromatograph (GC) coupled with ICP-MS. Many studies into TBT look at total tin; here tin has undergone speciation so TBT can be seen as a proportion of total tin. Certified reference materials obtained from European Reference Materials (EUR- CE477 & EUR- CE278) for mussels and the National Research Centre Canada (PACS II) for sediment were used to verify machinery performance. Data have been analysed using standard statistical approaches. The levels of contamination found for both heavy metals and TBT will be presented and the load in mussels will be discussed.

P2

AN ANTIFOULING-PAINTS PROJECT IN CHINA AND CHINA GREEN LABELING STANDARD FOR ANTIFOULING PAINTS

Zhang Xiaodan

Foreign Economic Cooperation Office, Ministry of Environmental Protection of the People's Republic of China Zhang.xiaodan@mepfeco.org.cn

The Ministry of Environmental Protection of China (MEP), through its Stockholm Convention implementation agency (FECO/MEP), and the UNDP had developed a joint project titled Alternatives to DDT Usage in the Production of Antifouling Paint. The binding objective of the project is to eliminate the use of 250 MT/year of DDT as additives in the production of antifouling paint by conversion to non-toxic and environmentally friendly alternatives. In addition, the prospective objective of the project is to establish a long-term mechanism to protect marine environment and human health from pollution of harmful antifouling systems. In association with China Environmental Product Certification and Labeling Center, a standard titled China Green Labeling Standard for Antifouling Paints has been developed under the project, the standard is to encourage eco-design and promote compliance of antifouling paint products with relevant technical and environmental requirements.

COMPLEX INTERACTIONS BETWEEN ABIOTIC DISTURBANCE AND SURFACE REFUGE AND SHAPE DETERMINE THE SETTLEMENT OF MARINE PROPAGULES

Heather Sugden, Roy Sanderson, Jeremy Thomason

Natural England and Newcastle University heather.sugden@naturalengland.org.uk

Surface complexity is one of the most important abiotic factors in determining which species are able to co-exist in a particular area. This study investigates the settlement of species in intertidal and subtidal rocky shore habitats to discover whether the topographical features provided by four levels of surface complexity provided a refuge against the common types of abiotic disturbance; desiccation stress, physical impaction and hydrodynamic shear. Field experiments were carried out in both subtidal and intertidal areas using artificial panels that were cast from natural rocks. It was found that there was more settlement of species on the more complex surfaces that provided a greater range of refuges, and it was also discovered that certain species always preferred to settle in certain types of refuges. It was also found that the settlement of a species in a particular topographical feature was dependant upon the type of disturbance suggesting that they do provide some refuge value to the settling species. This work suggests that by creating artificial surfaces which contain specific types of topographical features, it could be possible to manipulate the settlement of certain species into certain refuges on artificial structures, therefore maintaining the natural diversity of the surrounding areas.

P4

VARIABILITY AND SUCCESSION OF FOULING AND CORROSION ON COATINGS AND ADHESIVES AT DIFFERENT TEST SITES IN THE GERMAN NORTH SEA

Tim Heusinger von Waldegge

Alfred-Wegener Institute for Polar and Marine Research. Germany <u>Tim.Heusinger@imare.de</u>

For the technical reliability of offshore wind farms biofouling is a series problem due to increased frictional drag by waves, corrosion and damages from boring organisms such barnacles and molluscs. It is in debate if lab tests and single-site deployment fulfil the requirements to forecast fouling and corrosion at future offshore wind farms. One way to increase evidence might derive from the increase in test sites. In order to contribute to this discussion, 14 products used in the marine energy industry as coating or adhesive were deployed for long-term exposure at four test sites along a north-south gradient in the German North Sea (Wilhelmshaven, Lighthouse "Alte Weser", Helgoland, Sylt). Focusing on the first 6 months of deployment, it was evident that the mussel-aquaculture of Mytilus edulis influenced the fouling community at the test site in Wilhelmshaven located in the Jade estuary. Sessile macrofauna communities are dominated by blue mussels (Mytilus edulis), barnacles (Semibalanus sp.) and hydroids (Leptomedusae and Anthomedusae) which interact in a specific succession scheme. These site specific communities showed the deterioration potential indicated by increasing weight load (up to 375%), especially during the summer months. Furthermore surface damages, indentions on soft siloxanes and sub-surface migration in a continuum with a physical displacement up to the removal of materials due to biofouling could be detected within the first six month of the climax-studies. Especially barnacles caused damages on softer materials by boring. The site lighthouse "Alte Weser" exhibiting the highest wave force was affected by macrofouling as well. Sylt was influenced by highly abundances of the pacific oysters (Crassostrea gigas). The biofouling community of the samples at Helgoland was dominated by biofilms. The results obtained show that the matrix of test sites chosen was suitable to increase the variability of fouling communities and therefore provide options to model biofouling at offshore sites where new hard substrates will be placed to substrate-free environments in future. The variability in succession is helpful to continue the study in regard to the deterioration potential of fouling and corrosion.

FOULING CONTROL: MAKING THE ECO-EFFICIENT CHOICE

Trevor Solomon

International Paint Ltd. trevor.solomon@akzonobel.com

In the past, for many ship operators there were two parameters that influenced the choice of which fouling control coating to use (1) Ability of the coating to keep the hull clean of fouling and (2) Cost of the coating. With growing public and political awareness of both the immediate and long-term environmental impact of the shipping industry it is clear that there will be a requirement to increase the influence that those other properties of the coating will have in making that choice. Fouling control coatings in use today not only give the benefit of maintaining the underwater hull of vessels clean of fouling organisms but they are proven to influence the operational efficiency of those vessels helping to reduce fuel and natural resource consumption as well as significantly cutting emissions to the environment. Today, rather than making the choice of which fouling control coating to use based on almost purely economic factors, it is now possible to make it with a balanced economic and ecological view; this is the eco-efficient choice.

P6

EFFECT OF INHIBITING WASHES ON COATING CHARACTERS BASED ON ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Yanlei Peng, Cunguo Lin, Dongxia Duan and Jiyong Zheng

State Key Laboratory for Marine Corrosion and Protection pengyl@sunrui.net

This paper tries to make comments on coating characters of modified mastic epoxy anticorrosion paint affected by using of inhibiting washes and their washing process based on Electrochemical Impedance Spectroscopy (EIS). It is proved that the impedance of coating is increased by one order when immersed in the seawater with inhibiting washes, and the adhesion of coating is also improved. After immersed in the seawater with 5% (v/v) inhibiting washes for eight weeks, the coating is still in good adhesion to the metal surface. And the washing process has nearly no effect on the characters of the coating, which can maintain the coating resistance at a high level and changes little even after eight weeks test.

STUDY ON THE ANTI-CORROSION PERFORMANCE OF ORGANIC COATINGS UNDER SIMULATED DEEP SEA ENVIRONMENT

Liu Bin, Fang Zhi-gang, Wang Hong-bin

Naval Arming Academy, Beijing, P.R. China. liubindr@163.com

Deep sea exploitation represents the future direction for its abundant resources, while organic coatings can play a very important role in the ocean engineering protection. However, the corrosion condition is extremely complicated and the anti-corrosion performance of coatings is not clear in deep sea environment because factors such as soluble oxygen content, temperature, salt content, flow velocity and water pressure change with depth of sea. In this paper, the influence of sea-water pressure on the protective property of three different types of organic coatings under simulated deep sea environment was studied in the lab using electrochemical impedance spectroscopy (EIS), infrared spectrum (IR), differential scanning calorimetric (DSC) and thermo-gravimetric analysis (TGA) techniques. The results showed that the impedance resistance (Rp) and electrochemical reaction resistance (Rct) of the coatings under 3.5MPa were far less than that of ordinary pressure sea-water, which indicated the degradation of coating performance for corrosion prevention. At the same time, the increase of coating capacitance (Cp) and sea-water absorption proved that high sea-water pressure accelerated the failure process of the coatings.

P8

THE INFLUENCE OF MARINE MICROFOULING COMMUNITY ON THE OPEN CIRCUIT POTENTIAL BEHAVIOR OF A DUPLEX STAINLESS STEEL UNDER FIELD AND LABORATORY CONDITIONS

¹Messano, Luciana V R; ^{1,2,3} Ignacio, Barbara L; ² Coutinho, Ricardo

¹ (FAPERJ); ²Instituto de Estudos do Mar Almirante Paulo Moreira; ³Instituto de Bioquímica Médica (UFRJ) <u>lvicentebm@gmail.com</u>

Open circuit potential (OCP) behavior of stainless steels exposed to microfouling effects often shows a sharp increase in its values. This phenomenon is called ennoblement and its causes are not well understood. To evaluate the OCP variation of a duplex stainless steel under different microfouling communities, a field experiment was performed at two sites with distinct environmental conditions in Arraial do Cabo, Brazil: Forno Harbor and Cabo Frio Island. The harbor area is under anthropogenic influence. Coupons of UNS 32760 duplex steel (70x50x2 mm) were placed into 100 µm nylon mesh boxes to avoid macrofouling colonization. These boxes were placed at 1.5 meter deep in both sites. During 18 days, daily measurements of OCP in relation to an Ag/AgCl electrode were made in situ. After this period, coupons were brought to laboratory where microfouling was removed and the coupons immersed in sterile seawater under UV light. Then daily measurements of OCP were made for the next 10 days. Ennoblement was detected in coupons exposed at Forno harbor (OCP range: -260 to +250 mV), but not at Cabo Frio Island (OCP range: -256 to -110 mV). After the transference of coupons to laboratory, OCP behaviors remained different until the 6th day. In the 2nd day, coupons from Cabo Frio Island showed an increase in OCP values to +40 mV, remaining in this range until the end of the experiment. On the other hand, Forno Harbor coupons showed a sharp decrease in 2nd day (from +260 mV to -99 mV), increasing to +50 mV in the 6th day, remaining in this range until the end. It was possible to verify that coupons showed different OCP behaviors at field conditions and ennoblement phenomenon occurrence was site-specific as already described in literature. Present results suggest that microfouling composition may have a decisive influence in OCP variation and thus for ennoblement phenomenon. Besides, inthe conditions provided in this study, its influence could be noticed until five days after microfouling removal when OCP behaviors from both sites progressed in a similar way.

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pq

IRON-OXIDIZING ZETAPROTEOBACTERIA ASSOCIATED WITH STEEL CORROSION IN NEARSHORE MARINE ENVIRONMENTS

¹JM McBeth, ¹Katherine Farrar, ¹EJ Fleming, ²RI Ray, ²JS Lee, ²BJ Little, ¹D Emerson

¹Bigelow Lab for Ocean Sciences, ME; ²Naval Research Laboratory, Stennis Space Center, MS <u>imcbeth@bigelow.org</u>

An association between stalk-forming iron-oxidizing bacteria (FeOB) and steel corrosion in marine environments have been observed on numerous occasions. Formation of iron oxide stalks by FeOB in sediments and associated with corrosion of steel have led observers to presume the organisms responsible were Gallionellaceae, since the morphology of the iron oxide stalks and bean shaped cells are so similar to those produced by members of this family (Hanert, 1981). However, the identity of stalk-forming FeOB associated with marine steel corrosion has not been confirmed with molecular microbiological tools such as 16S ribosomal RNA gene sequencing. Here, data is presented from enrichment studies of FeOB associated with mild steel corrosion. A novel iron stalk-forming FeOB of the candidatus phylum zetaproteobacteria has been isolated from an estuarine salt marsh environment (strain GSB2), and the organism is capable of growing on a mild steel substrate. Growth of iron stalk-forming microorganisms has also been observed on mild steel coupons incubated in nearshore environments, suggesting that these organisms are able to use the steel as a source of Fe(II) for lithotrophic growth. Sequences falling within the zetaproteobacteria based on 16S rRNA gene sequencing have been identified from enrichments and directly from marine steel coupons incubations. This work illustrates that bacteria of the candidatus phyllum zetaproteobacteria may be associated with mild steel corrosion in the marine environment, though it is not yet clear if they act to enhance or inhibit this corrosion in any way.

P10

FEASIBILITY STUDY OF AN AUTOMATED ONLINE CLEANING SYSTEM FOR SEAWATER HEAT EXCHANGERS

¹K.C. Chaw, ¹K.Y. Ang, ²W. Birch, ¹A.K.H. Chow and ¹B.H. Hui

¹HVS Engineering Pte. Ltd.; ²Institute of Materials Research and Engineering, A*STAR hvs.alexchow@gmail.com

The fouling generated by marine organisms in seawater heat exchanger tubes is a persistent problem with no satisfactory solution to date. It reduces the operational efficiency, leading to higher energy consumption and unscheduled outages. Present techniques consist of manual cleaning, with an associated downtime, or the addition of biocides to the seawater coolant. The latter have limited kill efficacy, due to the large volumes of seawater passing through the heat exchanger. They are also costly and toxic to the environment. The present study explores the feasibility of an automated system that cleans tubes without using chemicals or taking the heat exchanger offline. This solution circulates specially-designed balls through the heat exchanger using a closed-loop system of ball injection and retrieval. The balls generate a continuous scrubbing and brushing action on the inner walls of the tubes. This action is expected to maintain the tubes free of biofilms and macrofoulers. The balls are expected to dislodge exploring macrofouler larvae before they have a chance to settle or metamorphose into juvenile adults. The objective is to maximize the operational uptime of the heat exchanger and ensure a high operational efficiency, with a significant reduction in energy consumption. The trial of this cleaning system is run by pumping untreated seawater through two model heat exchangers, one of which implements the cleaning solution. Differences in fouling rates (if any) between the two models will be monitored over a one-year period. This variation is correlated with fouling pressure, as measured by the colonization of model surfaces in quasi-stagnant seawater flow.

SILICONE COATINGS AND CLEANING - ANTIFOULING STRATEGY FOR FISH NETS AND OYSTER TRAYS

^{1, 2}S Dürr, ²D I Watson, ²E Bergtun, ²J Davenport, ²D Fowler, ²J Icely, ²J Maguire, ²J Murphy, ²J Power, ²P Willemsen and ²J C

Thomason

¹Liverpool John Moores University, UK; ²Newcastle University, UK <u>s.t.durr@ljmu.ac.uk</u>

Antifouling strategies used in European aquaculture consist predominantly of husbandry, cleaning and the use of antifouling coatings. Coatings currently in use in aquaculture are copper-based. With changes in regulations and the increase in demand for organic food products non-toxic antifouling solutions are on the rise in aquaculture. The aim of this study was to determine the efficiency and feasibility of silicone coatings combined with low pressure washing as a replacement for copper coatings in aquaculture. This was part of the CRAB (Collective Research on Aquaculture Biofouling) European tests of non-toxic antifouling strategies. Silicone coatings in combination with cleaning were tested at 3 aquaculture sites for up to 28 months. The sites were Bømlo Skjell AS (S-Norway), Fastnet Mussels Ltd (SW-Ireland) and Sagremarisco-Viveiros de Marisco Lda (S-Portugal). As the field component was to be undertaken by aquaculture workers, standardisation of the survey was achieved through central coordination of the survey design, equipment used and analytical procedures undertaken. Small scale testing was done in Norway and Portugal using 20x20 cm2 net and oyster tray samples coated with up to 5 different silicone coatings. A large-scale test with full netting coated with silicone and controls including life stock (Salmon salar) was conducted in Ireland. Development of the biofouling community was assessed on the net and tray samples using carefully standardised digital photography plus measurement of wet weight and duration of low pressure washing. Digital images were analysed using semi-automated image analysis with a stereological approach. Data have been analysed using standard statistical approaches, and fouling load as well as cleaning efficiency with a pan-European perspective will be presented. Possible problems with the coatings and impact on stock will be discussed.

P12

ANTIFOULING COATINGS FOR WAR SHIPS (ACWS)

Claire Martin

Laboratoire Matériaux, Polymères, Interfaces et Environnement Marin, Université du Sud Toulon-Var <u>claire.martin@univ-tln.fr</u>

This European Defence Agency (EDA) framework project is targeted at British and French Naval requirements concerning the use of antifouling paints. The aim is to attain high performance antifouling coatings in accordance with present and future environmental, health and safety regulations. It should also afford dry-docking intervals greater than 5 years. To achieve this goal within the project timescale (3 years), only self-polishing coatings are studied. Two major areas are addressed: (a) Evaluation of emerging technologies to obtain environmentally friendly antifouling coatings with projected long term performance (6-10 years); (b) Development of advanced accelerated test methods for assessing new products, including biocide free coatings, in a short period (<1 year) but representative of long term "in service" conditions. The knowledge gained forms the basis for guideline development that will describe approved specific requirements for navy vessel antifouling coatings and dedicated test methods for evaluation and selection of suitable products. During the three-year programme, an industrial consortium (comprising British – the Defence Science and Technology Laboratory and the University of Southampton - and French entities - the MAPIEM laboratory, the Centre d'Expertise Parisien of the Direction Générale de l'Armement (DGA), the DGA Naval systems (ex-CTSN) and DCNS) carries out the scheduled Work Packages (WP). The first WP assesses the naval requirements for antifouling coatings, the systems to be studied and the strategies to be followed over the course of the project. WP 2 evaluates emerging technologies, focusing on the screening of binders, biocides and complete antifouling systems. WP 3 suggests innovative ways to accelerate the ageing process of antifouling coatings by varying specified environmental parameters. WP 4 focuses on field experimentation and correlation with accelerated testing and WP 5 ends by supplying guidelines on Self-Polishing Coatings use and evaluation (on ships or with an accelerated ageing system). Partnership with the Netherlands (especially TNO) during this project allows extension of the work to Foul Release Coatings (FRC). The same objectives of emerging products evaluation and setting up accelerated ageing methodologies are developed on FRC systems. SPC and FRC studies allow a general overview of the efficiency of the antifouling systems available on the market and under development. Accelerated ageing methodologies for both SPC and FRC coatings will allow testing future systems.

EFFICACY OF SOFT CORAL CRUDE EXTRACTS AGAINST THE FOULER - AN ATIFOULING APPROACH

Marimuthu N., Kumaraguru A.K.

School of Energy, Environment and Natural Resources, Madurai Kamaraj University, Madurai, India marinemari@hotmail.com

Protection against biofouling organisms calls for a knowledge of the study of marine bioactive molecules. With reference from previous studies related to biofouling (presented at 14th ICMCF, Kobe, Japan) from an Underwater Biofouling Panel (UWBFP) system was erected at Pudhumadam coast in the Gulf of Mannar, Cirriepedes were observed as the predominant macrofouling organisms. For antifouling study, soft corals extracts were prepared and tested against the predominant foulers. Antibiosis test against the fouling bacterial forms and bioactivity assay followed by EPA-probit analysis to check the soft coral extracts were done and presented in this study.

P14

EFFICACY OF AN ISOTHIAZOLIN COMPOUND AS A FOULING DETERRENT: RESPONSE OF A PENNATE DIATOM

¹Lucie Maranda, ²Thomas Ramotowski, ²Wayne Tucker, ²Matthew Rice

¹University of Rhode Island; ²Naval Undersea Warfare Center Newport Division <u>Imaranda@gso.uri.edu</u>

Synthetic rubbers impregnated with the non-persistent biocide 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Dow Chemical Company) remained free of any significant biofouling for more than one year when submerged in temperate estuarine waters, while control panels harbored a rich succession of communities, primarily solitary and colonial tunicates, barnacles, calcareous tube-forming worms, mussels, hydrozoans, bryozoans, sponges, and seaweeds. Within one month of immersion, a light and uneven organic matrix of mostly detritus and empty pennate diatom frustules appeared on ethylene propylene diene monomer (EPDM) panels containing either 3 or 6 % DCOIT, with only a few live pennates noted. In subsequent months, the composition of the organic matrix was gradually enriched with the live pennate diatom Entomoneis sp. One year after treatment, a few other pennate species and some microflagellates joinedthe community, but Entomoneis sp. remained by far the dominant organism. Polyurethane panels containing 0, 3 or 6 % DCOIT, immersed in April 2009, so far display patterns of community composition and succession similar to those observed on the EPDM panels. The 'green' biocide DCOIT provides an excellent deterrent to the settlement by incipient fouling and macrofouling, but pennate diatoms, especially Entomoneis sp., still present a challenge. Mechanisms specific to this tolerance should be investigated; muciferous exudate formation is strongly suspected to be involved, as it is known to help protect pennate diatoms from the action of heavy metals. Nevertheless, given that the organic matrix containing Entomoneis sp. is easily removed and that the tested surfaces remain otherwise free of macrofouling organisms for many months, DCOIT could become an efficacious antifouling treatment on sensors and special surfaces not impaired by a light organic coating.

LARVAL METAMORPHOSIS OF THE MUSSEL *MYTILUS GALLOPROVINCIALIS* LAMARCK, 1819 IN RESPONSE TO NEUROTRANSMITTER BLOCKERS AND TETRAETHYLAMMONIUM

Jin-Long Yang, Yi-Feng Li, He-Ding Shen, Cyril Glenn Satuito, Hitoshi Kitamura

Shanghai Ocean University and Nagasaki University ilyang@shou.edu.cn

The mussel, *Mytilus galloprovincialis*, is the dominant species in intertidal zones of most of Japan. It is mostly viewed as a macrofouling organism because it colonizes ship's hulls, cooling water systems of power plants and fish cages. Research to understand the mechanism of mussel larval settlement and metamorphosis is being carried out because this is important in the development of effective antifouling technologies. In the present study, metamorphic responses of pediveliger larvae of *M. galloprovincialis* to neurotransmitter blockers and tetratethylammonium chloride (TEA) were investigated through a series of bioassays. The neurotransmitter blockers chlorpromazine and amitriptyline inhibited *M. galloprovincialis* larval metamorphosis induced by epinephrine. IC50 of chlorpromazine was 4.0×10^{-8} M, and this was 600-times more effective than amitriptyline. The IC50s of rauwolscine and idazoxan were 5.1×10^{-4} M and >100 M, respectively. By contrast, atenolol and butoxamine did not inhibit larval metamorphosis. Excess K+ ions induced larval metamorphosis at 10^{-3} M to 5×10^{-2} M in 24-h exposure assays but not in continuous exposure assays. Longer exposure time to excess K+ ions yielded higher larval metamorphosis and maximum metamorphosis was observed after larvae were exposed for 24 h. Larval responses to K+ were inhibited by TEA at 10^{-3} M. These compounds can be useful inhibitors of larval metamorphosis for antifouling studies using larvae and juvenile of *M. galloprovincialis*.

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CHEMISTRY-DEPENDENT SURFACE CONDITIONING AND ITS IMPLICATION FOR SETTLEMENT OF SPORES OF THE GREEN ALGA *ULVA*

¹I. Thomé, ²M.E. Pettitt, ¹A. Rosenhahn, ²M.E. Callow, ²J.A. Callow, ¹M. Grunze

¹Karlsruhe Institute of Technology, Germany; ²Birmingham University, UK <u>isabel.thome@pci.uni-heidelberg.de</u>

Changing the surface chemistry and the composition of a coating changes not only its properties, but also the formation and composition of the conditioning layer that rapidly forms on the surface. In order to correlate colonization by spores of the green alga Ulva with surface conditioning, we varied surface chemistry and thus wetting properties. Self-assembled monolayers (SAMs) on gold provide access to highly controlled surface chemistries and allow the physicochemical surface properties to be fine-tuned. Modification of the terminal groups of SAMs affects the initial settlement kinetics of spores of *Ulva* [1]. However, the settlement density of spores an all surfaces tended to saturate at a similar level after approximately 24 hours. As different SAMs have different affinities towards the adsorption of conditioning macromolecules, the rate of spore settlement is presumably a convolution effect of conditioning and settlement kinetics. To disentangle both effects, formation of conditioning layers on a range of surface chemistries was investigated in detail by spectral ellipsometry, XPS and IRRAS. Spore settlement was significantly changed if the conditioning films were pre-formed. Thus we have demonstrated that fouling kinetics are a delicate convolution of surface conditioning and settlement kinetics.

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IN SITU ATR-IR SPECTROSCOPIC AND ELECTRON MICROSCOPIC ANALYSES OF *UNDARIA*PINNATIFIDA SPORE SETTLEMENT

Luigi Petrone, Mike F. Barker, A. James McQuillan

University of Otago, Dunedin, New Zealand luipe@ifm.liu.se

Knowledge about the settlement of marine organisms on substrates is important for the development of new environmentally benign methods for control of marine biofouling. The adhesion to substrates by spores of Undaria pinnatifida, a kelp species that is invasive to several countries, was studied by scanning electron and transmission electron microscopies as well as by in situ attenuated total reflection infrared spectroscopy. The infrared spectra showed that spore adhesive material contained protein and anionic polysaccharides with carboxylated, sulphorylated and phosphorylated groups. Energy dispersive X-ray microanalysis of the adhesive identified sulphur and phosphorus as well as calcium and magnesium which would facilitate the gelation of the anionic polysaccharides in seawater. The adhesive is thought to be secreted from electron-dense Golgi bodies located in proximity of the spore cell wall, which were imaged by transmission electron microscopy of spore thin sections. The presence of anionic groups revealed by ATR-IR spectroscopy in the spore adhesive suggests that inhibition of spore adhesion will be favoured by negatively-charged surfaces.

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OUTER SHIP HULL CHARACTERIZATION USING PHOTOMETRIC ANALYSIS

Kathleen McMonagle

Florida Institute of Technology, Department of Marine and Environmental Systems kmcmonaq@fit.edu

At present there are no simple and accurate methods to assess the condition and measure roughness of in-water ship hull coatings. Ship hull roughness and biofouling are known to increase drag, costs, and exhaust gas emissions. Monitoring and measurement of ship hull condition are critical to the efficient management of ship operations. We proposed an underwater smart camera which uses algorithms from computer vision to aid in hull coating assessments and measure coating roughness. The prototype camera uses photometric stereo to generate a three dimensional model of the coating surface on which roughness is measured. The first step toward future automation of the camera uses textons (illumination invariant, statistically representative textural elements of an image) to classify "good" and "bad" images based on generalized coating type, fouling, damage, and image noise from scattering or bubbles. Data are presented to show the potential application of this method.

MACROFOULING COMMUNITIES ON FOULING RELEASE COATINGS FROM THREE STATIC IMMERSION TEST SITES IN FLORIDA

Jeff Coogan and Geoffrey Swain

Department of Marine and Environmental Systems, Florida Institute of Technology <u>jcoogan@fit.edu</u>

Fouling release paint technology is a subject of increasing interest to the shipping industry as the possible solution to minimize biofouling. This interest has resulted in new commercial paints entering the market, which makes the field evaluation of these expensive systems of high importance. The intent of this study is to assess the performance of three commercial fouling release coatings. Three replicates of each paint type were placed at three static immersion sites on the east coast of Florida (Daytona, Sebastian Inlet, and Miami). Comparisons are made between the percent cover of fouling, diversity, and adhesion strength. These comparisons are made with respect to paint type, time, and location. At the Sebastian site the fouling release panels and a set of PVC control panels are inspected every 30 days. After inspection the fouling on the panels is cleaned back and the panels are placed back in the water. This same procedure is performed at Miami and Daytona, every 60 days for a total of 300 days. The three coatings tested in this study showed significant differences in fouling throughout the exposure period, both among paint type and location.

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WATERBORNE POLYSILOXANE-URETHANE-UREA FOR POTENTIAL MARINE COATINGS

Mohammad Mizanur Rahman, Ho-Hwan Chun and Hyun Park

The marine paint mainly consists of polymer resins, pigments, additives and organic solvents. These organic solvents which sometimes referred to as volatile organic compounds (VOCs), are employed in the coating formulation to dissolve resins and to control the coating viscosity at various stages of drying. After the coating has been applied onto a substrate, a solid film forms as the VOCs evaporate into the atmosphere. The emitted VOCs are harmful to the environment and health. Today, regulations of VOC emission from various coating systems have reached EU, US federal and international levels. Thus, the paint industry has forced on developing waterborne, VOC-free or high solid products. We synthesized such kind of waterborne polysiloxane-urethane-urea (WBPSUU) as an environmentally friendly coating by using water as a solvent. Waterborne polysiloxane-urethane-ureas (WBPSUU) were prepared through a pre polymer process using siloxane polyol, namely polydimethylsiloxane (PDMS) and polyether polyol, namely poly(tetramethyleneoxide glycol) (PTMG) as the soft segments. The adhesion, erosion and foul release properties of the resins were examined during exposure to a marine environment after immersion for a certain time. The significant improvement to combat marine biofouling was observed using the synthesized resin.

EFFECTS OF SURFACE TEXTURE ON THE ATTACHMENT STRENGTH OF BARNACLES AND THEIR LARVAE

¹Nick Aldred, ²Andrew Scardino, ²Rocky de Nys and ¹Anthony S. Clare

¹Newcastle University, UK; ²James Cook University, Australia nicholas.aldred@ncl.ac.uk

Although surface texture modulation has been demonstrated to effect biofouling resistance for a variety of materials, the mechanisms underpinning this process have yet to be established. For barnacles particularly, studies of the effects of surface texturing on settlement rate have been purely observational with no indication of the mode of action. This study relates the settlement rate of barnacle larvae to the rate of their removal under hydrodynamic stress for a range of linear sinusoidal textures, varying in scale between 4 and 512 micrometers. Settlement and subsequent removal of larvae are shown to correlate closely, suggesting that larvae have a tendency to settle in larger numbers on surfaces to which their attachment is more secure and, therefore, subsequent removal is less likely. This effect was observed for two different base materials - polycarbonate and Sylgard 184 elastomer. Barnacles grown to adulthood on textured surfaces exhibited identical critical removal stresses, with the exception of those settled on a 64 micrometer textured surface. Barnacles grown on the 64 micrometer texture attached with significantly higher tenacity than those grown on any other texture. Despite this, it appears that removal as a cyprid/young juvenile is the principle driver of selectivity on the basis of surface texture for barnacle larvae. Textures in the 128-256 micrometer range received the lowest settlement and highest removal rate for larvae and, when cast from Sylgard, proved almost entirely refractory to larval settlement.

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THE MAPPING OF ALGAL ATTACHMENT SITES ON MICRO-PATTERNED SURFACES

¹Finlay JA, ²Long CJ, ¹Clay GA, ²Brennan AB, ¹Callow ME, ¹Callow JA.

¹University of Birmingham, Birmingham, UK; ²University of Florida, Gainesville, USA. <u>J.A.Finlay@bham.ac.uk</u>

The green macroalga, *Ulva* and slimes dominated by diatoms (unicellular algae) are found worldwide in fouling communities. The methods by which these organisms colonise surfaces are very different. The spores of Ulva actively swim and are sensitive to many surface-related cues which play a large role in site-selection. In contrast, diatoms are transported to surfaces passively, by gravity and water currents, but once in contact, the cells can attach and glide to locate favourable positions. Colonisation can be reduced if either of these algae is presented with an unfavourable set of surface conditions, such as micro-topographical patterns. Previous studies on Ulva have shown that settlement of spores is strongly influenced by the presence of ridges a few μm in height and length. If the spacing between the ridges exceeded the body length of a spore (5 μm) settlement density increased, below this it decreased, with a minimum at approximately 2μm. Attempts to understand more about the surface sensing mechanism of spores and how this information may be used to achieve a non-fouling surface have led to various patterned designs. Of these, a bioinspired structure called Sharklet AFTM which consists of a series of ridges arranged in a diamond shaped pattern, has shown marked success. In the current study spores of Ulva and cells of the diatom Navicula were allowed to attach to a range of Sharklet AFTM patterns varying in the number of features making up each repeating diamond-shaped unit. In each pattern the dimensions of the features and their size remained constant (2.8μm high x 2μm wide x 2μm space). Spore settlement density decreased as the number of features increased, but diatom attachment was little affected. The location of individual algae has been mapped and compared to the distribution of glass microspheres of similar dimensions.

KINETIC ATTACHMENT OF ULVA ZOOSPORES TO TOPOGRAPHICALLY MODIFIED SURFACES

¹Scott P. Cooper, ²John A. Finlay, ²Maureen E. Callow, ²James A. Callow and ¹Anthony B. Brennan

¹University of Florida, Gainesville, USA, ²University of Birmingham, UK scottcooper@ufl.edu

The zoospores of the green alga *Ulva* is known to settle on surfaces in a gregarious manner. During early stages of settlement, the zoospore may attempt to adhere at different spots before finally attaching. Engineered topographies of a polydimethylsiloxane elastomer (PDMSe), such as Sharklet AFTM, have been shown to inhibit settlement of Ulva zoospores up to 86% over smooth PDMSe after 1 hour. However, the settlement of zoospores over time has not been fully characterized for these surfaces. The goal of this study is to compare the settlement of Ulva on smooth PDMSe and PDMSe with the Sharklet AFTM topography at time points of 15, 30, 45, 60, 120, and 180, minutes. Microscope slides with a test area of 3 inches x 1 inch are tested with varying degrees of coverage of the Sharklet AFTM topography. The test areas are either completely smooth, completely covered with Sharklet AFTM topography, or covered with Sharklet AFTM over a 1 inch x 1 inch region (surrounded by smooth regions). Results from samples which have partial coverage of the Sharklet AFTM topography show that the topography reduces settlement by approximately 70% over completely smooth slides over all times tested. Samples with a complete coverage of Sharklet AFTM topography tests whether the zoospores selectively settle in the adjacent smooth regions. Further analysis is done by mapping the preferential locations of zoospores on the Sharklet AFTM geometry throughout time. Settlement maps demonstrate whether the organism prefers certain locations on the topography at various time points. By quantifying the early stages of colonization on topographies, surfaces can be designed which further resist biofouling.

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EVIDENCE FOR THE ANTIFOULING ACTIVITY OF SELECTED MANGROVES

R. Ramasubburayan, P. Iyapparaj, A. Palavesam and G. Immanuel

Manonmaniam Sundaranar University, Rajakkamangalam - 629 502, Tamilnadu, India vramanj@gmail.com

Any substrata deployed in seawater are rapidly colonized by microbial biofilms that in turn significantly induces settlement of invertebrates and adversely lead to huge economic loss. Conventional antifouling paints have been restricted due to its non targeted toxic threat to marine livings. Hence there is an urgent need to develop novel and green antifouling compounds to combat the fouling related issues. Marine halophyte mangroves have been used so long as traditional medicine and proved to be a rich source of novel bioactive molecules. But research related to antifouling strategy of mangroves is too scarce, hence the present study was aimed to evaluate the antifouling potentials of representative mangroves such as Rhizophora apiculata, Rhizophora annamalayana (Kathir) and Avicennia marina. The methanolic extract of all the three mangroves exhibited higher level of antibacterial (antimicrofouling) activity (8 \pm 0.24 to 15.5 \pm 0.24 mm) than chloroform and hexane extracts against the tested biofilm bacterial strains. Similarly, the antimacrofouling activity of methanolic extract of R. apiculata was high with the EC50 value of 642 \pm 8.46 µg/ml, followed by methanolic extracts of R. annamalayana (Kathir) and A. marina with the EC50 value of 712 \pm 6.20 and 926 \pm 8.12 µg/ml, respectively. The TLC fractions of respective extracts were subjected to TLC bioautography assay for tracking active bands and the results inferred wide variation in bacterial growth inhibitory activity. Phytochemcial analysis and FT-IR results of methanolic extracts of candidate mangroves were documented and found much variation in the presence of basic functional groups.

POTENTIAL OF MICROALGAE EXTRACTS FOR ANTIFOULING APPLICATION: PRELIMINARY RESULTS

P. Hayes, B. Veron, C. Hellio

University of Portsmouth ghezlane.iddaoud@port.ac.uk

Fouling has economic and environmental impacts that justify the need to develop novel preventive treatments. Biocides and heavy metal-based antifouling paints are widely used, but their toxicity against non-target-organisms is driving the search for environmentally friendly antifouling compounds. There is a growing interest in screening marine organisms for the production of biogenic compounds that have potential for use in antifouling applications. Microalgae have attracted attention in this area as they have high growth rate and can be cultivated on a large scale under controlled conditions in a sustainable way. In this project we are investigating the antifouling activity of secondary metabolites produced by three marine strains of microalgae: Cylindrotheca cloisterium (Bacillariophyceae, Pennales), Exanthemachrysis gayraliae (Pavlovales, Pavlovophyceae) and Thalassiosira pseudonana (Coscinodiscophyceae, Thalassiosirales). These strains have been grown under different conditions and bioactive compounds have been extracted at different growth phases using organic solvents (Acetone, Methanol, Dichloromethane and Hexane) and then screened for their antifouling activity. Bioassays were used to assess the growth inhibition of organisms involved in micro- and macrofouling process: the bioassays utilised five marine bacteria (Shewanella putrefaciens, Vibrio estuarians, Pseudoalteromonas elyakovii, Polibacter irgensi and Pseudomonas fluorescens), five terrestrial bacteria (Escherichia coli, Salmonella typhimurium, Staphylococcus aureus, Alcaligenes faecalis and Acinetobacter baumanii), four freshwater microalgae (Scenedesmus armatus, Dictyosphaerium ehrenbergianum, Pediastrum sp., Fragilaria crotonensis), four marine microalgae (Cylindrotheca cloisterium, Exanthemachrysis gayraliae, Chlorarachnion globosum, Thalassiosira pseudonana), two marine macroalgae (Undaria pinnatifida and Ulva lactuca) and one barnacle species (Balanus amphitrite). Inhibition assays were performed using six concentrations of the extracts (0.05, 0.5, 5, 10, 30 and 100µg/mL) in order to determine the minimum inhibitory concentration (MIC). The preliminary results of this work will be presented during the congress.

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AN ENVIRONMENTALLY BENIGN METHOD FOR PREVENTING FOULING

Tom Vance, Jeremy Thomason

Plymouth Marine Laboratory and Newcastle University thva@pml.ac.uk

The goal of the maritime industry is for an effective solution to prevent fouling that works under static or dynamic conditions, that lasts a minimum of five years, and yet is environmentally benign. We present an answer to this goal that prevents accumulation of biofilm and macroalgae and animals by using the dissociation of CO_2 to form carbonic acid. By allowing CO_2 to diffuse through a suitable membrane the pH within the boundary layer can be kept at pH 5 which is inhospitable to most marine life. Data from static immersion trials against a robust marina flora and fauna will be presented. By capturing the CO_2 from the ship's engine exhaust gas, the net addition of CO_2 to the environment is zero.

ZWITTERIONIC-BASED MATERIALS AS ENVIRONMENTALLY BENIGN, DURABLE AND EFFECTIVE ULTRA LOW FOULING MARINE COATINGS

Hong Xue, Shaoyi Jiang

Department of Chemical Engineering, University of Washington, USA. xueh@u.washinqton.edu

Biofouling on ship hulls and other marine surfaces has become a global environmental and economic issue. Currently, the majority of marine coating products are based on antifouling coatings (i.e., release of biocides to kill marine microorganisms). Due to increased environmental concerns, the International Maritime Organizations (IMO) suggested a TBT (tributyltin) application ban by summer 2008. The TBT-free antifouling paint in the current market is based on non-tin biocides, such as copper particles or cuprous oxide. As these biocides are still harmful to the marine environment, their application is limited. Non-toxic, foulingrelease coatings (i.e., biofoulants are attached on ship hulls and removed at high ship speeds) based on silicone or fluorinated compounds are under development. However, these coatings are only effective on vessels moving at high speeds (> 14 knots). As fouling occurs most readily on static structures or ships moving slowly in seawater close to land, the application of these coatings is also limited. We have been developing a new type of zwitterionic-based ultra low fouling marine coatings, to which marine microorganisms cannot attach. These nonfouling coatings are as effective as anti-fouling coatings, but do not contain or leach any biocides while they are much more effectively in both performance and cost than environmentally benign fouling-release coatings, particularly for low ship moving speeds. Under support from the Office of Naval Research (ONR), we have developed several nontoxic and stable ultra low fouling coatings based on zwitterionic materials. Marine laboratory tests have confirmed the outstanding performance of our coatings against a variety of marine microorganisms. Field tests of these coatings clearly demonstrated that our coatings are very effective to defer the settlement of biofoulants. Our current focus is on the development of long-lasting coatings that are capable of effectively deferring biofouling under static conditions over a long period of time.

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NOVEL DUALLY FUNCTIONAL ZWITTERIONIC POLYMERS AND THEIR ANTI-BIOFOULING PROPERTIES

Semra Colak and Gregory N. Tew

Silvio O. Conte National Center for Polymer Research, Amherst, MA 01003, USA scolak@mail.pse.umass.edu

Biofouling remains a challenging problem for various fields ranging from biomedical applications and marine coatings technology, to water purification, transport, and storage systems. In this work, we are introducing a new polymeric system which carries dual functionality at the repeat unit level, a zwitterionic functionality coupled with an alkyl moiety that can be varied to adjust the amphiphilicity of the overall system. The alkyl group is varied to include PEG based, hydrocarbon, and fluorinated chains. Using these ring-opening metathesis polymerization (ROMP) based zwitterionic polymers as the foundation for non-fouling coatings, we are trying to understand what role the overall hydrophilicity/amphiphilicity of the materials play in fouling prevention.

SURFACE CHARACTERISTICS OF MULTI-COMPONENT XEROGELS WITH AND WITHOUT SEQUESTERED SELENOXIDE CATALYST AND THEIR EFFECTS ON BIOFOULING

Amber L. Bryant, Stephanie M. Bennett, Anastasiya Sokolova, Frank V. Bright, Michael R. Detty

University of Buffalo, USA <u>albryant@buffalo.edu</u>

Three component hybrid xerogels can be prepared by the sol-gel method. By changing the mole ratio of the components of the xerogel you can change the surface characteristics and the effects of biofouling. The three components used in the series of coatings being studied were (tridecafluoro-1,1,2,2-tetrahydroctyl)triethoxysilane (TDF), n-octyltriethoxysilane (C8), and tetraethoxysilane (TEOS). In the original series of coatings the amount of TEOS was left constant at 50% in each xerogel and the percent of TDF was incorporated at 0%, 10%, 20%, 30%, 40%, and 50%. The contact angle, and the critical removal force and amount of basal plate remaining from Barnacles were analyzed for this series. In a second set of coatings the mole percent of TEOS was again held constant while the percent by mole of TDF was incorporated at amounts from 1% to 5%. The surface angles of these coatings were analyzed. Both series of coatings will also be sent for testing with tubeworms and Ulva. As a means of delaying the onset of biofouling, selenoxide catalysts with alcohol functionality can be sequestered in the xerogels which act as a co-oxidant with hydrogen peroxide. The selenoxide works with the hydrogen peroxide to oxidize halides found in sea water. The result is the creation of a hypohalous acid at the surface of the coating, which will slow the process of microfouling. By adding different functionality to the selenoxide catalysts the rate of oxidation can be altered. The xerogel-sequestered selenoxides catalyze the bromination of organic substrates (4-pentenoic acid, 3,5-dihydroxybenzoic acid, 1,3,5-trimethoxybenzene, Nphenylmorpholine, and N,N-dimethylaniline) with NaBr and H2O2, and can be monitered by NMR as a means to determine the catalyst performance (reaction rate). Six different catalysts were tested in a 1:9 N, N-dimethylaminopropyltrimethoxysilane (DMAPTES)/TEOS xerogel.

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ALKYL CHAIN LENGTHS AND RATIOS: FACTORS IN CREATING A XEROGEL WITH SURFACE CHARACTERISTICS SUITABLE FOR BARNACLE REMOVAL

Anastasiya Sokolova, Amber L. Bryant, Stephanie M. Bennett, Frank V. Bright, Dean Wendt, Lenor Brewer, Michael R. Detty

State University of New York, University at Buffalo; California Polytechnic State University, San Luis Obispo <u>as94@buffalo.edu</u>

Biofouling costs the U.S. Navy approximately \$1 billion a year in extra fuel and maintenance costs due to friction and drag. Barnacles can account for up to 40 of the 60 percent of drag increase caused by all biofouling organisms. By creating surfaces with an organized surface protrusion pattern on the nanometer-scale, one can hope to deter the attachment of adhesion proteins produced by barnacles. In order to create this organized nanopost pattern, varying mixtures of n-octadecyltrimethoxysilane (C18), n-octyltriethoxysilane (C8), or n-propyltrimethoxysilane (C3) were used along with tetraethoxysilane (TEOS). By adding 1-5% of a longer alkyl chain to a shorter one, a pattern can be formed wherein the longer alkyl chains extend above the shorter alkyl chain 'canopy'. These longer chains would be spread far enough away from each other that they would not be touching, thus resembling a 'bed-of-nails'. Removal force testing of barnacles revealed that 1%C18/49%C8/50%TEOS was similar to a standard siloxane, Silastic T2, with respect to complete removal of barnacles (79% vs 87% for T2) and with respect to partial base plate remaining for the few barnacles that were not completely removed. Contact angles were taken to determine the hydrophobicity of 1-5%C18/C8/TEOS and it was found that the 1%C18 was the most hydrophobic with a contact angle of 111°. Subsequent studies are being done to determine the perfect percentage needed for maximal hydrophobicity, as well as, if these coatings also deter adhesion of tubeworms. The tubeworm (H. elegans) studies will be done by Michael Hadfield at the University of Hawaii, and the Ulva sporelings studies by Maureen E. Callow, John A. Finlay, and James A. Callow at the University of Birmingham.

INHIBITION OF BYSSAL THREAD FORMATION OF LIMNOPERNA FORTUNEI BY NATURAL PRODUCTS ISOLATED FROM THE BROWN ALGA *DICTYOTA DICHOTOMA*

¹García M., ²Siless G., ¹Pérez M., ¹Stupak M., ²Palermo J.

¹CIC-CONICET, La Plata, Argentina; Universidad de Buenos Aires, Argentina biofouling@cidepint.gov.ar

The Asiatic freshwater mollusk, Limnoperna fortunei (golden mussel), is an introduced species of bivalve. Since their discovery in 1991, they have spread rapidly throughout Río de la Plata basin, colonizing Paraná, Paraguay and Uruguay rivers, and Pantanal (Central West Brazil). The golden mussels attach using their glue-like byssal threads to almost any hard surface and can form thick mats of several hundred thousand individuals per square meter. These mussels spend their adult lives attached to hard substratum such as rock and cobble, as well as concrete, iron, polyvinyl chloride, plastic, and fiberglass. Piping systems at public and private facilities that use raw water are particularly susceptible to golden mussel infestations. For this reason, there is great interest in devising non-toxic methods to control mussel settlement. It is well known that many marine algae and invertebrates remain remarkably free from settlement by fouling organisms. It has been suggested that they have biologically active compounds that prevent other marine organisms from settling and attaching to their bodies. Some investigations showed that secondary metabolites of seaweed Dictyota dichotoma are responsible of the antifouling activity on marine organisms. We hypothesized that three pure compounds, pachydictyol, dictyotadiol and dictyoxide, isolated from the alga Dictyota dichotoma could be employed against the establishment of the mussel Limnoperna fortunei. For this purpose, a laboratory screening method for the evaluation of byssal thread formation was used [1]. Briefly, the number of byssal thread attached inside a circle embedded of the test compound vs a control at the end of 24 hours was recorded. Experiments indicated that pachydictyol and dityoxide have strong inhibition activity on byssal thread production in concentrations as low as 6.7µg/cm². In contrast, dictyotadiol is not a good candidate for new antifouling treatment because golden mussels were not affected on byssal threads production. These findings represent the first report of the use of secondary metabolites from a marine alga to avoid Limnoperna fortunei settlement. Results suggest the potential utility of these compounds for the development of antifouling technology.

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APPROACHES TO MARINE BIOFOULING CONTROL BY THYMOL BASED PAINTS

Miriam Pérez, Mónica García, Beatriz del Amo, Guillermo Blustein, Mirta Stupak

CIDEPINT (Centro de Investigación y Desarrollo en Tecnología de Pinturas) (CIC-CONICET), La Plata – Argentina biofouling@cidepint.gov.ar

A great quantity of natural products, most of which are found in marine organisms, has been extensively tested to assess their antifouling properties. Comparatively, little attention has been given to terrestrial plants in the search for natural products antifoulant. Essential oils of herbs and their components (secondary metabolism products) have many applications in ethnomedicine, food preservation as well as in the fragrance and pharmaceutical industries. Thymol, a natural compound isolated from essential oils of many plants (Thymus spp., Origanum spp., etc.), has been described as having useful pharmacological properties, with antifungal, antibacterial and antioxidative activities. In view of this, it was hypothesized that thymol would be potential inhibitor of the complex process of settlement of marine biofouling. The aim of this study is to evaluate the potential antifouling activity of a commercially available thymol on larval survival of Balanus amphitrite through laboratory antifouling bioassays and field trials. In the lab, it was evaluated the effect of thymol solutions ranged between 3.5 and 55μ M. Toxicity test was conducted using nauplii II and results were recorded after 24 h incubation. Larval bioassays demonstrated a marked inhibitory and reversible effect. The values obtained for LC50 were 3.7 μ M. For field trials, thymol was incorporated into a non-toxic soluble matrix paint. Acrylic panels coated with this paint were exposed in Mar del Plata harbour, Argentina. After six months exposure in the sea, thymol-based paint was effective in inhibiting settlement (p< 0.05 by ANOVA test using STATISTICA program). A great decrease in micro and macro-fouling density and diversity was observed in relation to controls (p<0.05 through ANOVA and contrast LSD test). The present study suggests that thymol could be employed as bioactive compound for antifouling paints.

EFFECT OF THYMOL ON INVASIVE GOLDEN MUSSEL LIMNOPERNA FORTUNEI

Mirta Stupak, Mónica García, Miriam Pérez, Guillermo Blustein

CIDEPINT (Centro de Investigación y Desarrollo en Tecnología de Pinturas) (CIC-CONICET), La Plata – Argentina biofouling@cidepint.gov.ar

The studies on freshwater biofouling in Argentina gained importance in the last two decades, due to the invasion of Limnoperna fortunei (Bivalvia, Mytilidae), an Asiatic mollusk that colonized rapidly hard substrates of Rio de La Plata basin generating a diversity of inconveniences not recorded before. Recently, the use of natural products with antibacterial properties has been applied to interrupt the first stages of fouling sequences. In this study, we evaluate the effect of thymol, a major component of thyme essential oil, on the settlement of *Limnoperna fortunei* in the laboratory. Adult mussels were exposed to solutions of thymol ranged between 1 and 250 μ M. Both, byssus number formation and mussel survival for 48 hours were recorded. Recovery tests were carried out in order to determine whether thymol acts through a temporary or a permanent mechanism. Finally, toxicity tests were conducted on a non-target organism, the native gastropod Heleobia piscium. The results indicate that thymol significantly reduces the formation of byssal thread number at concentrations over 10 μ M (p <0.05). The concentration that inhibits the activity of 50% of the population (LC50) was 22 μ M. However, treated organisms recovered their ability to produce byssus when they were transferred to clean freshwater. No effects on survival and/or behavior of the gastropod Heleobia piscium were registered. In conclusion thymol inhibits reattachment of mussels by a temporary mechanism. Therefore, it is a promising compound to control *Limnoperna fortunei* settlement.

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NOVEL BORON CONTAINING ANTIFOULING PAINTS

Kenan Yunlu, Duygu Kulaç, Fatma Yetim, Fatih Çelikel

TÜBITAK, Marmara Research Center, Turkey kenan.yunlu@mam.gov.tr

Novel boron containing antifouling paints were synthesized, characterized and tested in the Sea of Marmara. Biocides are based on triphenylboron complexed with N containing heterocycles (Ph3B . R; R = 4-chloro-pyridine, 4-vinylpyridine, 1,3,5-triazine, 4-(1-pyrrolidino) pyridine, quinoline, quinoxaline, 1-(2-pyrimidyl) piperazine, phenazine, 1,2,3-benzotriazole) and are combined with inorganic boron compounds like zinc borate, sodium borate (borax pentahydrate), calcium borate (colemanite) or calcium sodium borate (ulexite), which act as co-biocides. The Ph3B . R complexes are easily obtained as air-stable white precipitates by reacting a Ph3B / NaOH solution with the heterocycle. Combinations of these Ph3B . R complexes with the above mentioned inorganic boron compounds in different ratios give highly active antifouling paints. Results covering a 9 month test period from two different (static and dynamic) tests in the Sea of Marmara will be discussed.

ANTI-MICROFOULING ACTIVITY FROM MARINE SPONGE-ASSOCIATED BACTERIA

Daniela Blihoghe and Micha Ilan

Tel Aviv University, Israel dblihoghe@yahoo.com

Marine biofouling is the result of a colonization process of benthic organisms (microorganisms, invertebrates and algae) on any natural or man-made structure immersed in seawater. The environmental problems caused by metal-based antifouling coatings (in particular organotins and booster biocides) led to the increased interest in the search for non-toxic alternatives. The present research focused on isolating anti-microfouling active sponges-associated marine bacteria, and evaluating their potential use for the development of antifouling paints. The steps towards achieving the objective were: selection of sources for the isolation of microorganisms, strains isolation and purification, identification of the genus and possibly the species of the isolates, and performing antibacterial and antifungal assays with the isolates. Irciniid sponges are known to harbor a large number of bacteria, but yet, are unfouled in nature. Approximately 250 bacteria were isolated from three Irciniid sponges using various solid media cultures supplied with antibiotics. Among the isolates, 92 bacterial strains were chosen as "unique" strains based on PCR, RFLP and sequencing. These strains were assayed for anti-microfouling activity by antibacterial and antifungal activity against 17 marine microorganisms. The isolated bacteria belonged to the gram positive phyla Actinobacteria and Firmicutes and the gram negative phylum Proteobacteria (Gamma- and Alpha-Proteobacteria), altogether 13 families and 25 genera. Most of the isolated bacteria (66 %) inhibited the growth of at least one of the targeted bacteria, showing the great antibacterial potential of these strains. Between the active bacteria cultured from sponges, 8 showed potent anti-microfouling activity, since they inhibited the growth of at least 6 out of 12 tested marine environmental bacteria, and concomitantly, at least 3 out of 5 tested marine fungi. These 8 potent anti-microfouling bacteria are propos ed for further development of environmental-friendly antifouling paints. These bacteria can either be further developed for the incorporation in "living paints", or cultivated, extracted for the bioactive compounds, and perform further testing for the development of biocide-based antifouling paints.

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ANTIFOULING ACTIVITY OF TERPENES ISOLATED FROM MARINE INVERTEBRATES

^{1, 2}Daniela Blihoghe, ¹Marianna Carbone, ¹Margherita Gavanin and ²Marco Faimali

¹CNR - Istituto di Chimica Biolomeculare, Pozzuoli, Italy: ²CNR - Istituto di Scienze Marine, Genova, Italy <u>dblihoghe@yahoo.com</u>

Organotin compounds (OTC) from antifouling (AF) paints are described as the most toxic substances ever introduced into the marine environment. Recently, an increasing number of countries have ratified the international ban, imposed by International Maritime Organization (IMO), for the usage of OTC in AF coatings. Presently, the marine biocide-based AF coatings rely on copper as primary biocide, together with various synthetic biocides also known as "booster" biocides, that have a negative environmental impact and they must, eventually, be replaced by new, effective and more environmental friendly AF compounds. The natural products that inhibit settlement of potential epibionts (chemical defense), produced by marine organisms, could be studied as natural product antifoulants (NPAs), one of the most promising alternatives to toxic heavy metal-based paints. The ideal candidates as NAPs would be the compounds showing similar potent anti-settlement activity with currently used booster biocides (EC50 CuSO₄=0.30 μg/mL, EC50 copper pyrihtione <0.01μg/mL, EC50 zinc pyrithione 0.02 μg/mL), but without their high toxicity (LC50 <0.01 μg/mL). In the present study we evaluated the AF potential of four terpenes, known for various biological activities, but never reported for AF activity: aplyroseol-2, scalaradial, heteronemin and puupehenone. The tested compounds were isolated from molluscs and sponges. The AF activity (settlement inhibition) and toxicity (mortality) was determined using larvae of barnacle Amphibalanus amphitrite as model organism. The results show good AF activity, with EC50 values ranging from 0.58 to 8.95 µg/mL and variable toxicity with LC50 ranging from 2.45 to 13.82 µg/mL. One important aspect in the development of the natural product based antifouling paint is the supply issue. In the case of the studied terpenes, a successful synthesis has been reported for some compounds, while for others, the necessary steps towards their total synthesis have been taken. Our research encourages further studies of these terpenes with other fouling organisms, for a future industrial development of new environmental friendly antifoulants alternatives to the recently banned toxic biocides.

ANTI-DIATOM ACTIVITIES OF RESIN BASED COATINGS CONTAINING CRUDE EXTRACT OF GREEN ALGAL ULVA PERTUSA

Zheng Jiyong, Lin Cunguo, Liu Chao, Zhou Juan, Duan Dongxia, Wang Li, Zhang Jinwei, Peng Yanlei, Liu Huihui

State Key Laboratory for Marine Corrosion and Protection, Luoyang Ship Material Research Institute zhengjy@sunrui.net

Marine biofouling on the artificial surface causes large penalties and higher costs. In this case antifouling paints are introduced to protect the submerged surface. Since toxic anfoulants in traditional antifouling paints have been banned due to their severe environmental pollution. Novel environmental friendly antifouling method are our research focus, and among them, active substances from marine organism are studied for antifouling application. In the paper, crude extracts was isolated from green algae Ulva pertusa with four solvents, petroleum ether, ethyl acetate, ethyl hydrate and aqueous. The antifouling activities of them were screened by bioassays with marine diatoms. The crude extract of ethyl acetate was found to be most active, and the minimum inhibitory concentrations (MIC) is 1.0 mg/ml. The crude extract was blended into acrylic paint resin. Five coatings with different concentrations of the extract were prepared and painted on the glass microscope slides. All the slides were immerged in the seawater containing marine diatom. The diatom cells adhering to the surface of coating was quantified by microscope count and fluorescence spectrometer. Results demonstrated that there are antifouling active substances among extracts of Ulva pertusa, which would be a potentially natural antifouling material. It was found that coating formulation affected the leaching of bioactive compounds. In addition, the method of fluorescence recording was consistent with counting, which was found useful to test algal fouling on coating surface.

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ARE ALKYLPYRIDINE-BASED COMPOUNDS SUITABLE BIOCIDES FOR ANTIFOULING PAINTS?

^{1, 2}Daniela Blihoghe, ²Marco Faimali, ¹Emiliano Manzo, ¹Alexandre Villela, ¹Adele Cutignano, ¹Angelo Fontana

¹CNR Istituto di Chimica Biomolecolare, Pozzuoli, Italy; ²CNR - Istituto di Scienze Marine, Genova, Italy dblihoghe@yahoo.com

Marine biofouling leads to undesired consequences on artificial surfaces. In the case of ships for example, a fouled hull reduces the navigation speed, increases fuel consumption, increases the corrosion process and the risk of introduction of non-native species to new environments. Given that more than 90% of the world trade is carried out by sea transportation, and biofouling can increase the overall costs of ships operation up to 77%, there is a huge demand for antifouling technologies. Therefore, many submerged man-made structures are protected by toxic antifouling paints in order to minimize the biofouling impact. Marine organisms are potential sources of environmental friendly antifoulants. Poly-alkylpyridinium salts from marine sponge Reniera sarai have been previously reported as promising non-toxic NAP candidates for antifouling paints. In the present study, we evaluated the antifouling potential of other five alkylpyridins: two polymeric and three monomeric compounds. Three of the compounds have been purified from marine organisms, and two has been synthesized in laboratory conditions. The antifouling and toxicity bioassays were performed with larvae of barnacle Amphibalanus amphitrite, and were expressed as percentage of cyprid settlement inhibition and percentage of nauplii II mortality, respectively, compared with the controls. The toxicity assays were performed also with larvae of a non-target organism, the marine copepod Tigriopus fulvus. The results showed generally a good antifouling activity against barnacles, with EC50 ranging between 0.19 and 3.61 µg/mL. The toxicity results showed a variable response between the two tested species, with LC50 ranging between 2.04 and over 100 μg/mL. The obtained results will be discussed from the point of view of compounds application as non-toxic antifouling biocides, as well as the possibility to obtain large amounts of alkylpyridins throughout synthesis. The final goal of the work will be to stimulate the industrial development of alkylpyridins as new environmental friendly antifoulants.

ECOPAINT PACA PROJECT: NEW TECHNOLOGIES OF NON-TOXIC ANTIFOULING PAINTS

¹Charlène Anton, ¹Christine Bressy, ²Philippe Allex, ³Chantal Compere, ³Françoise Quiniou, ⁴Philippe le Calve

¹Laboratoire Matériaux Polymères Interfaces Environnement Marin, Université du Sud Toulon-Var, France; ²Blancolor S.A., France; ³IFREMER Centre de Brest, France; ⁴DCNS, France

charlene.anton@univ-tln.fr

In the history of the antifouling paint industry, the most successful products were the tributyltin (TBT)-based coatings. Their performance was due to their specific mechanism of action. Unfortunately, TBT-based compounds had caused severe damages on non-target marine species. The recognition of the dangers at the early 80's led to the ban of such compounds and forced the manufacturers to find tin-free alternatives. At the present time, the antifouling efficiency of the commercialised tin-free systems comes mainly from additional biocides which are under the European Biocidal Products Directive (Directive 98/8/EC). Furthermore, a growing concern for environmental issues such as the problem of the use of volatile organic solvent has been observed. In this context, the Ecopaint PACA project aims at developing a new generation of environment-friendlier marine antifouling paints able to match the long-time efficiency (5 years) of tributyltin (TBT)-based paints and to enhance drag reduction. The consortium provides an association of basic and applied scientific and industrial knowledge, which will significantly strengthen the current collaboration and the outcomes of the project to end to the commercialisation of competitive products, compatible existing means of production and answering the environmental and industrial requirements. The strategy is based on various aspects: (a) the decrease or the complete removal of organic solvents by developing water-borne antifouling paints, (b) the inhibition of the settlement of marine organisms by incorporating new non-toxic active molecules extracted from Mediterranean Sea's marine species and by developing nano-structured binders which enable the control of the erosion properties of the paint, (c) the evaluation of the toxicity on non-target species of the active substances and the coatings, (d) the improvement of the coating durability by combining self-polishing and drag reduction properties. At the present time, several formulations have been performed and various tests have been set up. The antifouling efficiency of the coatings is investigated through in situ ships and raft experimentations. Erosion test and biocide release rate measurement are performed to classify the new generation of paints. Moreover, the ecotoxicity of the active molecule itself or incorporated in the coating is assessed.

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COMBINED EFFECTS OF ANTIFOULANTS - SYNERGISTIC, ADDITIVE OR ANTAGONISTIC EFFECTS?

¹Åsa Arrhenius, ¹Thomas Backhaus, ¹Hans Blanck, ¹Åke Granmo, ¹Annelie Hilvarsson, ²Katherine Langford, ¹Ida Wendt

¹University of Gothenburg, Sweden; ²Norwegian Institute for Water Research (NIVA), Norway asa.arrhenius@dpes.gu.se

Antifoulants are often used in combinations in paints. A survey of the scientific literatures shows that the effects of such antifoulant combinations are often predictable with a reasonable accuracy by the classical mixture toxicity concepts of Concentration Addition (CA) and Independent Action (IA). However, some studies also reported mixture effects that were substantially higher (synergistic) or lower (antagonistic) than predicted by either CA or IA. We therefore systematically explored the frequency and quantitative importance of such interactions within a group of 6 antifoulants using settling and growth of marine periphytic communities as the endpoint. All 15 possible 2-compound combinations that can be composed from the pool of six antifoulants were experimentally tested in three different ratios per mixture and their observed toxicity was compared to the predictions by CA and IA. The results show that the toxicities of the mixtures in most cases are at least roughly in agreement with the predictions, but that in several cases antagonistic effects occurred, which were related to the mixture-ratio and concentrations applied. No cases of synergism were observed for any of the investigated combinations. Implications for paint production as well as for the environment will be discussed. This study is part of the Marine Paint research programme funded by MISTRA, the Swedish Foundation for Strategic Environmental Research.

THE EFFICACY OF ANTIFOULING BIOCIDES: A SYSTEMATIC APPROACH

Ida Wendt, Annelie Hilvarsson, Åsa Arrhenius, Thomas Backhaus, Åke Granmo, Hans Blanck

Kristineberg, University of Gothenberg, Sweden ida.wendt@dpes.qu.se

In the Marine Paint Optimization project a broad range of settling tests are used to assess the efficacy of antifoulants, in order to provide a basis for the subsequent development of optimized antifoulant mixtures. Since the fouling community is very complex, and composed of a large number of different species with vastly different sensitivities to the different antifoulants, the test approach has been to select key organisms from all the main fouling groups. By doing so the whole sensitivity range of the fouling community is captured. The "test battery" includes invertebrate larvae (barnacles (Amphibalanus improvisus), sea squirt (Ciona intestinalis) and bryozoans (Buqula neritina)) macro algae (sea lettuce (Ulva lactuca)) and biofilms (periphyton community, also referred to as slime). The sensitivity range for each individual species has been tested for a list of antifouling compounds, either in use today or likely to be registered and approved by the European Biocidal Product Directive, including Medetomedine, Copper Pyrithione, Zinc Pyrithione, Tolylfluanid, Sea-Nine (DCOIT), Copper, Borocide (TPBP) and Irgarol. EC99 for all tested species and biocides will be presented.

This study is a part of the Marine Paint research programme funded by MISTRA.

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MEASUREMENTS OF ROUGHNESS OF NEW ANTIFOULING COATINGS FOR SHIPBUILDING INDUSTRY ELABORATED WITHIN THE AMBIO PROJECT

Cezary Kania, Jan Kanar

Ship Design and Research Centre, Gdansk, Poland cezary.kania@cto.qda.pl

The paper presents the problem of the measurement of roughness of antifouling coatings applied to the flat plates, prepared for hydrodynamic tests, carried out by CTO within AMBIO project. Antifouling paints are produced and applied on ships since many years. Antifouling coatings prevent covering of a vessel's bottom part with a layer of animal and plant micro- and macroorganisms. These organisms settle on each surface submerged in sea water. Nature of antifouling coatings is briefly described in the paper. There are also presented preparation and applying of coatings with automatic work station, measuring instrument, method of roughness measurements conducting and method of data analysis. These measurements were necessary for determine hydrodynamics performance because the shipping industry puts very high requirements in scope of coating properties and ship hull drag reduction, the measurements were important part of the work. Roughness measurements of coated plates were performed with MARK III analyser produced by British Maritime Technology. This analyser is accepted by shipbuilding industry and in fact becomes standard instrument used for hulls' roughness measurements. An influence of various coating application methods (brush, roller and airless spray) on surface roughness of one reference coating is described. Perspectives of further development of antifouling systems are briefly discussed. No other green way of developing antifouling coatings is currently better than technology based on fluorinated compounds and silicones with low surface energy and low roughness. The AMBIO (Advanced Nanostructured Surfaces for the Control of Biofouling) project was founded by the European Commission under its Sixth Framework Programme. The project is at the crossroads between nanosciences and marine biology, environment and high technology and is devoted to the knowledge-based development of antifouling coatings that function through their

nanoscale physico-chemical properties, without the release of biocides.

PHOTOSYNTHETIC SYMBIONTS OF SPONGE : CHARACTERISATION AND IMPLICATION IN THE PREVENTION OF FOULING

¹Amina Bendaoud, ¹Jean François Briand, ¹Annick Ortalo-Magné, ¹Linda Dombrowsky, ²Aude Barani, ^{2.3}Gérald Gregori, ⁴Thierry Perez & ¹Yves Blache

¹MAPIEM-EA, Univ. Sud Toulon-Var, La Valette-du-Var, France; ²PRECYM, Marseille, Fr; ³UMR CNRS, Marseille Fr ⁴UMR, Marseille, Fr briand@univ-tln.fr

Marine biofouling is a complex phenomenon of colonisation of submerged natural or artificial surfaces. Pioneer stages are characterised by biofilm formation implicating microorganisms (bacteria, microalgae...) and followed by the settlement of macroscopic algae or invertebrates (barnacles). However, some marine invertebrates, which could be themselves fouled, have developed physical and/or chemical defences to keep a low level of settlement. Some sponge compounds were showed to be involved in natural antifouling process. In some particular case of sponge species, active metabolites could be produced by heterotrophic (bacteria) or autotrophic (microalgae and cyanobacteria) endosymbionts. The present research is focused on a common Mediterranean sponge (Petrosia ficiformis) which hosts cyanobacteria belonging to a sponge-specific clade of 'Candidatus Synechococcus spongiarum'. Both characterisation and isolation experiments will be described. In order to assess the implication of the symbionts in the antifouling activity, freeze-dried sponge (with and without cyanobacteria) extraction have been analysed by LC-MS chromatography. Then, the bioguided isolation of active secondary metabolites has been performed with an antiadhesion assay based on the use of marine pioneer bacteria (Pseudoalteromonas sp. and Polaribacter sp.).

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BIOFOULING STUDIES DURING WRECK DIVING AT GRANDE ISLAND OF GOA, WESTCOAST OF INDIA

Marimuthu N

National Institute of Ocean Technology, Pallikaranai, Chennai 600100, India <u>marinemari@hotmail.com</u>

Wreck diving is one of the part of recreational activities in SCUBA diving. The biofouling monitoring was carried out at Suzys wreck, Grande island of Goa. During this study, the barnacles Balanus amphitrite and the oysters were found dominantly. Density and biomass estimation per square area were calculated. Reef fishes used this wreck point as an artificial reef environment. Encrusting form of corals, Montipora sp. were settled in vertical manner on the wreck. Unidentified seafans and sponges were also found. All recorded organisms were photographed and classified as hard and soft foulers. The impacts due to recreational diving activities were also studied.

VISUALIZING ADRENERGIC RECEPTORS ON THE SENSORY ORGANS OF OYSTER AND BARNACLE SETTLEMENT STAGE LARVAE

¹Neeraj V. Gohad, ²Nicholas Aldred, ³Beatriz Orihueladiaz, ²Anthony S. Clare, ³Dan Rittschof, ¹Andrew S. Mount

¹Clemson University,USA., ²Newcastle University,UK., ³Duke University Marine Laboratory, USA <u>neerajg@clemson.edu</u>

Majority of marine invertebrate larvae explore surfaces prior to settlement and metamorphosis to juveniles. Oyster pediveliger larvae and barnacle cyprid larvae explore surfaces using an array of sensory cells. This process defined as the 'tactile chemical sense', is the ability to recognize molecular moieties present on a surface. The choice to attach and metamorphose is contingent upon receiving specific cues through the exploratory organs, such as the foot of the oyster pediveliger larvae and setae on the 4th antennular segment of the barnacle cyprid larvae. Interfering with this process of surface exploration is believed to be a promising avenue for developing effective yet environmentally friendly antifouling coatings. For development of such bioactive coatings it is important to first understand the nature of the receptors present on the larval exploratory organs. Adrenergic receptor agonists and antagonists have been shown to inhibit larval settlement in four disparate phyla Mollusca, Arthropoda, Bryozoa and Annelida. With the use of fluorescent agonists, antagonists and antibodies we have visualized adrenergic receptors using confocal laser scanning microscopy. Our findings suggest that these receptors are present on the foot of the Eastern Oyster (*Crassostrea virginica*) pediveliger larvae and the setae on the 4th antennular segment of barnacle (*Balanus amphitrite*) cyprid larvae. Engineering a bioactive coating targeting the larval adrenergic receptors is discussed.

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PRESENCE OF NMDAR1 RECEPTOR IN THE CYPRID OF *BALANUS AMPHITRITE* (=*AMPHIBALANUS AMPHITRITE*) (CRUSTACEA, CIRRIPEDIA)

¹Lorenzo Gallus, ¹Sara Ferrando, ²Chiara Gambardella, ³Alberto Diaspro, ⁴Paolo Bianchini, ⁵Marco Faimali, ¹Giuliano Greco; ⁶Paola Ramoino; ⁷Grazia Tagliafierro

¹LIBIOM, DIBIO, Univ. of Genoa, Italy; ²Univ. of Messina, Italy; ³IIT Genoa, Italy. ⁴DIFI, Univ. of Genoa, Italy; ⁵ISMAR, CNR, Genoa, Italy; ⁶ZEPS, UCC ,Cork, Ireland; ⁷DIPTERIS, Univ. of Genoa, Italy.

greco.giuliano@gmail.com

We studied by immunohistochemistry the occurrence of a NMDA ionotropic glutamate receptor (NMDAR1) in the cyprid of the barnacle Balanus amphitrite, one of the most dangerous component of biofouling. The life cycle of B. amphitrite comprises a cyprid that binds submerged surfaces by its antennulae and the secretion of a cement gland, metamorphosing into a sessile adult. In previous works γ-aminobutyric acid (GABA) and GABAergic receptors have been localized in the thoracic muscular. According to literature both GABA and Glutamate receptors might be distributed in nerve terminals (excitatory and inhibitory). Since the occurrence of NMDA-type glutamatergic receptors in crayfish neuromuscular junction has been reported in literature, we have investigated their presence in the B. amphitrite cyprid. Cyprids were embedded, sectioned, immunostained with a polyclonal rabbit antiNMDA receptor 1 (NR1-pan) (Millipore, USA) and observed. Controls: preabsorption of the I Ab with cyprids crude extract and omission of I Ab. No immunoreactivity (IR) was detected in controls. NMDAR1 IR was seen in neuromuscular junctions of thoracic appendages, as previously demonstrated in crustaceans, near the nuclei, and in antennules. IR was also detected in ommatidum cells, and in the tegumentary system, probably with non visual/neural functions. In ommatidia, IR appears in the cytoplasmic granules. These neuromuscular junctions should posses NMDAR1 receptors together to GABAergic receptors, as suggested for crustacean muscular innervations. Nerve fibers probably originate from GAD65/67 immunoreactive neurons in the posterior ganglion. The occurrence of NMDA receptors indicates a role for glutamate in the neuromuscular control in B. amphitrite cyprids. Occurrence of NMDAR1 IR in the eyes agree with the hypothesis that GABA play a role in non visual eye functions, since the photoreception neurotransmitter appears to be histamine.

NO STICKING! NITRIC OXIDE REDUCES THE ADHESION OF FOULING ALGAE

Thompson SEM, Taylor AR, Brownlee C, Callow ME, Callow JA

University of Birmingham and Marine Biological Association,UK s.e.y.thompson@bham.ac.uk

Elevated nitric oxide (NO) in animal and bacterial cells has been found to reduce adhesion, but only recently has the role of NO been studied in algal cell adhesion. NO is produced as a stress response and has also recently been found to transmit a wide range of signals in plants, including algae. Diatoms and spores of Ulva are two examples of algal cells which both selectively adhere to surfaces, however they differ in that *Ulva* attaches permanently whereas diatoms can detach when conditions are unfavourable. Diatoms and spores also differ in their attachment to the fouling-release coatings based on poludimethyl siloxane elastomers (PDMSE). PDMSE is effective at reducing attachment strength in spores of Ulva, but not against diatoms which stick more strongly to PDMSE than a hydrophilic coating such as glass. We were therefore interested to know how diatoms and spores of Ulva detect the properties of a substratum as this may provide an insight into the improved design of antifouling surfaces. Surface-normalised values of NO were measured using the fluorescent indicator DAF-FM DA and parallel hydrodynamic measurements of adhesion strength were made for both spores of Ulva and the diatom Seminavis robusta. Elevated levels of NO caused by the addition of the exogenous NO donor SNAP reduced spore settlement and resulted in lower adhesion strength for both Seminavis and Ulva spores. The strength of attachment and NO production by spores in response to four PDMSE coatings (Silastic T2; Intersleek 700; Intersleek 900 and polyurethane) shows that reduced adhesion is correlated with an increase in NO production. In Seminavis, NO was higher on a surface that it weakly attached to (glass) than on a surface it strongly attached to (PDMSE). It is proposed that NO is used as an intracellular signalling molecule to detect how conducive a surface is for settlement and adhesion. The effect of NO on a range of organisms suggests that NO-releasing coatings could have the potential to control fouling.

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EFFECT OF REPEATED CLEANINGS USING MULTIPLE TOOLS ON CONDITION OF A FOULING-RELEASE COATING

Eric R. Holm, Elizabeth G. Haslbeck

Naval Surface Warfare Center - Carderock Division eric.holm@navy.mil

The US Navy is currently investigating the potential employment of next-generation fouling-release hull coatings throughout the fleet. Operators of commercial vessels have claimed significant fuel savings from use of these coatings. In contrast to commercial vessels, however, Navy vessels tend to be inactive for long periods of time, and when active operate at relatively slow speeds. Under these conditions fouling-release coatings can experience heavy encrustations of organisms requiring frequent or aggressive cleanings in order to ensure efficient ship operations. Multiple or aggressive cleanings may impact the surface characteristics or integrity of the coatings, compromising subsequent performance. We are examining the effects of multiple applications of five hull cleaning tools on the surface characteristics of a fouling-release coating. Tools include SCAMP (two brush types), Mini-Pamper, a handheld brush unit, and two types of water jets. Before exposure all test panels were characterized for surface roughness and adhesion strength of epoxy pseudobarnacles. Panels were then exposed from a raft at Port Canaveral, FL. Exposed test panels typically acquired heavy fouling by serpulid polychaetes Hydroides spp. within 6 weeks of exposure. After each cleaning test the panels were photographed for measurement of spatial extent of macroscopic and microscopic damage, then re-immersed for accumulation of fouling before the next trial. Three rounds of cleaning will be carried out, after which the painted surfaces will be returned to the laboratory for a final measurement of roughness and pseudobarnacle adhesion. The initial test suggests that contact cleaning methods (for example, rotating brushes) can cause some microscopic and macroscopic damage to the coating surface, while waterjets appear to have no effect on coating integrity. Results will be discussed in the context of prospective husbandry strategies for fleet-wide hull maintenance. Funded by the Naval Sea Systems Command and Office of Naval Research.

TESTING METHODS TO ASSESS BOTH THE EFFICACY AND ECOTOXICITY OF ANTIFOULING COATINGS

Françoise Quiniou, Régis Delesmont, Florence Mazeas, Xavier Caisey, Romain Davy, Marcel Matarere, Michel Peleau and Chantal Compère

Ifremer and IPL santé, environnement durables Nord (France) chantal.compere@ifremer.fr

Since 1998, the European Biocidal Products Directive (BPD; 98/8/EC), applied to 23 product types (PT) for specific uses, including PT 21 the « antifouling products », regulates biocidal products before they are placed on the market. On the one hand, the efficacy of active substances and their formulations must be demonstrated for their specific employment; on the other hand their non impact on workers neither users and environment must be proved and specifically against non target species. Standard protocols for the assessment of efficacy or ecotoxicity of antifouling substances are proposed within the framework of the Ecopaint and Paintclean projects which are founded by the french industry Ministery and labellised by the "Pôle Mer" (Paca and Brittany). The potential toxicity of actives substances as well as paints or their elutriates is assessed in vitro on six trophic levels following marine TGD recommendations (2003): bacteria, phytoplancton, crustacea, mollusc, echinoderm and fish. The potential impact of antifouling paints on the modification of the condition index of oysters (10 to 12 months exposure) is observed in situ. The efficacy of active substances and paints is also tested both in vitro and in situ. In in vitro testing, the adhesion of marine pioneer bacteria is followed in presence or not of the active substances. While the biofouling development is observed on painted surfaces exposed on rafts as well as on vessel hulls during 12 months. In situ exposure could be performed in specific and/or different environments and on different kind of vessels (geographic zone, speed, duration of exposure...).

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ANTIFOULING ACTIVITY OF THREE BACTERIAL STRAINS ASSOCIATED WITH MARINE SPONGE

C.V. Sunjaiy Shankar and S. Mary Josephine Punitha

Manonmaniam Sundaranar University,India <u>cvsunjaiyshankar@gmail.com</u>

Bacteria associated with marine invertebrates are considered to be the good source for the isolation of bioactive metabolites. Sponges are currently the most important source of biologically active natural products. Many sponge derived metabolites have striking similarities with their microbial symbionts. In the present study, three bacterial species isolated from the marine sponge was screened for their antifouling activity. *Pseudomonas sp.* and *Alteromonas sp.* isolated from the marine biofilm developed on test panels were used as test organisms. The antifouling activity was assessed by disc diffusion assay and adhesion assay methods. The crude extract of the three strains showed strong inhibitory activity against the test bacteria in the disc diffusion assay. The adhesion assay showed considerable variation between the strains. Strain A and Strain C significantly inhibited the adhesion of fouling bacteria on glass surfaces. The crude extract of these two strains also affects the extracellular polymeric substance synthesis of the fouling bacteria. The crude extract of the isolated strains were characterized using Thin-layer chromatography (TLC). All the strains showed a single compound in the TLC. The compound was resolved from the thin layer chromatogram and purified using column chromatography. These partially purified compounds were again tested against fouling bacteria using disc diffusion assay. The anti-crustacean activity of the isolated compound was tested using Artemia sp. as model organism. As the extracts of two strains showed promising results, the bacterial strains were characterized based on 16s rRNA sequencing and identified using BLAST tool. The active principle contained in the crude extract was characterized using FTIR. In general, present study indicates that bacteria associated with marine sponges could provide lead compounds for the development of natural product antifoulants.

BIOFOULING AND ITS CONTROL IN THE COOLING WATER SYSTEM OF PROTOTYPE FAST BREEDER REACTOR - A TROPICAL MARINE ENVIRONMENT CASE STUDY

K.K. Satpathy¹, G. Sahu, A. Mohanthy, S. Biswas, Gopalkrishanan*, P Sahoo# & M.V.R. Prasad

¹Environmental & Industrial Safety Section, *Safety Engineering Division, #Electronics and Instrumentation Division Indira Gandhi Center for Atomic Research, Kalpakkam - 603 102, Tamil Nadu, India.

satpathy@igcar.gov.in

Bacteria associated with marine invertebrates are considered to be the good source for the isolation of bioactive metabolites. Sponges are currently the most important source of biologically active natural products. Many sponge derived metabolites have striking similarities with their microbial symbionts. In the present study, three bacterial species isolated from the marine sponge were screened for their antifouling activity. *Pseudomonas sp.* and *Alteromonas sp.* isolated from the marine biofilm developed on test panels were used as test organisms. The antifouling activity was assessed by disc diffusion assay and adhesion assay methods. The crude extract of the three strains showed strong inhibitory activity against the test bacteria in the disc diffusion assay. The adhesion assay showed considerable variation between the strains. Strain A and Strain C significantly inhibited the adhesion of fouling bacteria on glass surfaces. The crude extract of these two strains also affects the extracellular polymeric substance synthesis of the fouling bacteria. The crude extract of the isolated strains were characterized using Thin-layer chromatography (TLC). All the strains showed a single compound in the TLC. The compound was resolved from the thin layer chromatogram and purified using column chromatography. These partially purified compounds were again tested against fouling bacteria using disc diffusion assay. The anti-crustacean activity of the isolated compound was tested using Artemia sp. as model organism. As the extracts of two strains showed promising results, the bacterial strains were characterized based on 16s rRNA sequencing and identified using BLAST tool. The active principle contained in the crude extract was characterized using FTIR. In general, present study indicates that bacteria associated with marine sponges could provide lead compounds for the development of natural product antifoulants.

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