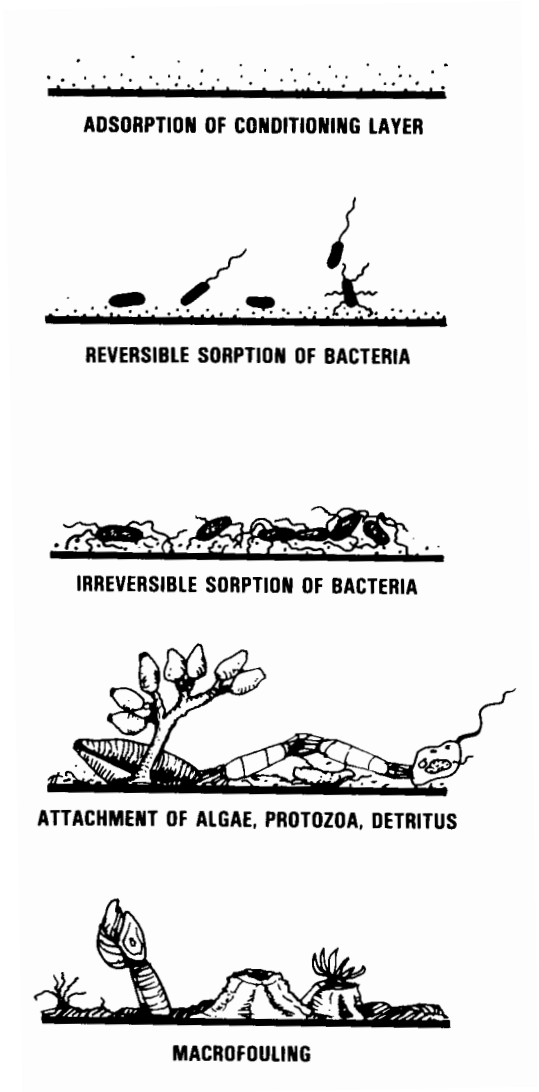
Naval Research Reviews

Office of Naval Research
Four/1997
Vol XLIX

Biofouling



Sequence of events in biofilm formation on surfaces in seawater.

Naval Research Reviews

Office of Naval Research
Four/1997
Vol XLIX

Articles

2
Introduction
K. J. Wynne and H. Guard, Guest Editors

4
Toward Minimally Adhesive Surfaces Utilizing Siloxanes
A. E. Mera, R. B. Fox, S. Bullock, G. W. Swain, M. P. Schultz, P. Gatenholm, and K. J. Wynne

9
Biofouling, Fleet Maintenance and Operational Needs
G. S. Bohlander and J. A. Montemarano

19
New Technologies for Surface Analysis to Assess Biofouling Resistance
J. A. Gardella, Jr., K. J. Wynne, T. J. McCarthy, J. F. Rabolt, and G. Belfort

35
Exterior Hull Coatings in Transition: Antifouling Paints and Fouling Release Coatings
J. R. Griffith and J. D. Bultman

39
Silicon Fouling Release Coatings
H. L. Vincent and G. G. Bausch

46
Field Evaluations of Non-Toxic Antifouling Coatings: New Field Technologies and Performance Criteria
G. W. Swain

51
Selection, Design and Delivery of Environmentally Benign Antifouling Agents
D. C. Sundberg, N. Vasishtha, R. C. Zimmerman, and C. M. Smith

60
Certification of Properties of Nontoxic Fouling-Release Coatings Exposed to Abrasion and Long-Term Immersion
R. E. Baier, A. E. Meyer, and R. L. Forsberg

Departments

18
Profiles in Science

About the cover
A panel immersed in Pearl Harbor for seven weeks shows nearly 100% cover by tubeworms (*Hydroides elegans).* Tubeworms are a problem biofouling organism in tropical and subtropical waters. Photography courtesy of Dr. Michael G. Hadfield, Celia M. Smith, Catherine R. C. Unabia, University of Hawaii.

Naval Research Reviews publishes articles about research conducted by the laboratories and contractors of the Office of Naval Research and describes important naval experimental activities. Manuscripts submitted for publication, correspondence concerning prospective articles, and changes of address, should be directed to Code 00PA, Office Naval Research, Arlington, VA 22217-5660. Requests for subscriptions should be directed to the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20403. *Naval Research Reviews* is published from appropriated funds by authority of the Office of Naval Research in accordance with Navy Publications and Printing Regulations. NAVSOP-35.

Introduction

Dr. Kenneth Wynne, Guest Editor, Physical Sciences S&T Division, Office of Naval Research

Dr. Harold Guard, Guest Editor, Biological and Biomedical S&T Division, Office of Naval Research

In this issue of *Naval Research Reviews*, there are eight articles that show the direction the Office of Naval Research (ONR) has taken to develop new and generic means of intervention to inhibit or minimize biofouling on Navy ships.

Biofouling, the growth of barnacles, seaweeds, tubeworms and other marine organisms on the hulls of ocean-going vessels, costs the international marine community billions of dollars a year. Most of this money goes for the extra fuel needed to overcome the increased drag on vessels. Some of it is spent for hull cleaning and repainting and for the upkeep on propulsion equipment. A tiny amount is invested in the search for better biofouling inhibitors.

Under certain conditions a ship with a mature biofilm (a layer of slime that forms on a wet surface due to microbial activities) of 24 months growth can require 8 percent more shaft horsepower to move as fast as a comparable ship with no biofilm. Between 18 and 22 percent of the propulsive fuel used by the Navy goes to overcome the drag caused by biofilms and organisms such as tubeworms and barnacles.

In addition to the huge financial burden, biofouling has an environmental cost as well. The use of copper-based coatings to combat biofouling over the past century and organotin-based coatings introduced in recent decades have resulted in the release of significant quantities of both metals into the marine environment. Even relatively low levels of copper and very low levels of organotin compounds have been shown to inhibit the development of fish and invertebrates. Coatings which release tributyltin oxide (TBT) are restricted in 14 states and many European countries.

The Navy operates in many seas and ports and the biofouling problems are different in each location. For example, barnacles are a major problem along the East Coast, and tubeworms cause trouble in Hawaii. Today, the Navy has domestic test sites in Hawaii, North Carolina and Florida to study antifouling strategies. Test sites were also established in the following foreign locations: Hong Kong, Singapore, India and the Mediterrranean.

In the early 1950's, the Office of Naval Research began funding basic research programs which were aimed at understanding the life cycle and biology of wood borers and hard-foulers like barnacles and mussels. It was hoped that such understanding would permit interference with the development of these organisms. Under applied research programs, the organisms were deterred through use of paints such as the TBT and copper-based coatings. These paints have been successful but function through toxicity.

Today, ONR is funding research to attack the "gluing" techniques these many organisms use to attach themselves to the hulls of ships. All the fouling creatures have one common characteristic — they adhere. Research is underway to better understand the principles that govern bioadhesion. At ONR, Dr. Harold Guard and Dr. Kenneth Wynne oversee a program to develop non-polluting antifouling coatings with an improved operational lifetime. Also, they are establishing reliable field test and evaluation systems that will hasten the transition of the new coatings to the fleet. The new studies are focused on bioadhesion, which involves exopolymers and surface polymeric properties. The focus is on the chemistries at the interface between the biofoulers and the surface. The biofoulers contain polysaccharides and glycoproteins which interact with the surface chemistries to develop the bioadhesion. In other words, the degree at bioadhesion is related to polymer surface structure morphology and energies present, and by exopolymer structure and chemistry.

Ann E. Mera, et. al. in the first article compare the surface and fouling behavior of representative coatings from two well known polydimethylsiloxane (PDMS) classes, **alkoxysilane** cured networks and **Pt** cured networks. The representative alkoxysilane-cured coating is RTV11®, the "topcoat" of the Naval Research Laboratory duplex coating. The curing chemistry is conventional RTV (Room Temperature Vulcanizing) PDMS network formation, achieved by condensing silanol-terminated PDMS chains with a multi-ethoxysilane crosslinker, in this case polydiethoxysiloxane with 40% SiO_2 content (ethylsilcate 40). Variables examined include PDMS molecular weight, tri- versus tetra- functional crosslinker, and reactant Si-H/vinyl ratio.

The second article by G. S. Bohlander and J. A. Montemarano describes a new generation of fouling control coatings that are free of heavy metals. These materials function by discouraging fouling settling, and producing a poor surface for fouling adhesion. Automated underwater vehicles offer promise providing in-water hull cleaning and maintenance monitoring for Navy ships to reduce maintenance costs. Future needs for hull maintenance include non-toxic fouling control coatings that can be applied in the industrial environment, will self-clean with low speed ship movement, and will provide 5-7 year service. These coatings should be renewable for service out to 15 years, and then be easily removable.

In the third paper, Gardella et. al. provide a review of the advances in instrumentation, measurement science and methodology which are vital to the analysis of polymer surfaces. There is also a short description of advances in methodology which are driven by problems in polymer materials surface chemistry. The use of these methods is critical in the development of model systems and standard materials. A selection of work sponsored by the ONR-Molecular Interactions at Marine Interfaces program is also mentioned. Recent ONR research in the application of these methods resulted in the development of model systems and actual candidate coating materials.

Griffith and Bultman in the fourth article outline the efforts at the Naval Research Laboratory, Washington, D.C., since 1970 to develop "fouling release coatings." Since the introduction of Teflon™, to the general public as an antistick coating for cooking utensils, inventors have dreamed of coating the exterior hulls of ships with substances so that barnacles would fall right off. Such antiadhesive coatings, in principle, have a number of very attractive features such as absolutely no environmental degradation and long, effective life. However, efforts to implement this concept in a practical manner are fraught with many difficulties.

The fifth article by Vincent and Bausch describes research in the development of silicon fouling release coatings. Since the Antifouling Paint Control Act of 1988 effectively prohibited the use of the tributyltin self-polishing copolymers for Navy use, there has been a change to less toxic copper oxide ablative coatings. However, such coatings do not provide the level of performance attained by the organotin self-polishing coatings. Research continues with fouling control coatings which are based on the PDMS backbone and offer a non-toxic approach to biofouling control. They rely upon the physical nature of the coating to retard the onset of fouling and provide easy release when fouling does occur. Additional development needs to be completed to identify commercially viable means of combining the antifouling agents and PDMS based coatings. Also, testing should continue on ideas for improving the overall toughness and fouling release properties of the PDMS coatings.

The sixth paper by Swain addresses the use of the static immersion panel evaluation methods for providing new insights into the performance of non-toxic coatings. It is now possible for researchers to quantify how modifications to their formulations alter the strength of biofouling adhesion, and for the Navy to select the coatings with the best foul release properties. Research is currently underway to relate biofouling adhesion strength to mechanical cleaning. This knowledge should help in the development of non-toxic antifouling coatings and ship hull maintenance practice that will remove the necessity for the use of biocides.

Sundberg et. al. in the seventh article describe the important ONR goal of understanding and exploiting natural agents and their analogs that promise effective biofouling control without polluting the environment. Nature has evolved a variety of strategies that prevent or minimize fouling of natural surfaces in aquatic environments without resulting in permanent environmental degradation or accumulation of refractory and toxic substances. Some organisms use physical means, including the sloughing of the outer tissue layer, the generation of an external surface that minimizes bioadhesion, and the production of secondary metabolites that can deter potential fouling organisms and predators. The chemical species employed as defensive agents are as diverse as the organisms manufacturing them. Those known agents include elemental vanadium inorganic acids, and a variety of organic compounds including saponins, terponoids and phenolic acids.

Lastly, the eighth article by Baier and Farsberg describes brush abrasion tests to sequentially evaluate fouling-release coatings after increasing numbers of wet brushing cycles. Standard tests for abrasion and wear developed for paints are not applicable to elastomeric coatings. Coatings which contain elutable oils have displayed further resistance to initial colonization by barnacles and zebra mussels, but this early benefit does not necessarily carry over to the brush-removal forces required for cleaning of the once-fouled coatings.

This research combines the efforts of Dr. Harold Guard and Dr. Kenneth Wynne, Division Directors at ONR. The cost incurred by the Navy to combat biofouling will escalate significantly with new environmental and health laws governing the use, application, and removal of environmental toxins like those present in materials used by the Navy today to coat ship hulls and submerged platforms. This ONR program will develop new and generic means of intervention to inhibit or minimize biofouling on Navy ships.

Toward Minimally Adhesive Surfaces Utilizing Siloxanes

Ann E. Mera, Robert B. Fox, and Steve Bullock, Materials Chemistry Branch, Naval Research Laboratory, Washington, DC
Geoffrey W. Swain, Division of Marine and Environmental Systems, Florida Institute of Technology, Melbourne, FL
Michael P. Schultz, Division of Marine and Environmental Systems, Florida Institute of Technology, Melbourne, FL
Paul Gatenholm, Department of Polymer Technology, Chalmers University of Technology, Göteborg, Sweden
Kenneth J. Wynne, Physical Sciences S&T Division, Office of Naval Research, Arlington, VA

Introduction

This paper is aimed at the correlation of physical surface characterization data on silicone "fouling release" polymer coatings with measurements of the tenacity of adhesion of hard fouling in the marine environment. Nontoxic coatings with minimally adhesive surfaces with respect to biofouling are of interest to Navy, from both environmental and economic standpoints.[1] The accumulation of biofouling (algae, silt, grass, barnacles, worms, etc.) on a ship's hull increases weight and drag, leading to higher fuel consumption and operating costs. Bridging of fouling on heat exchanger face plates blocks inlet water and causes inefficient cooling of power units. Currently used hull antifouling coatings contain species such as tributyltin oxide or copper oxide and function via leaching of the toxicant into the marine environment. The resulting environmental hazards of introducing such toxicants into the marine ecosystem include disruption of natural ecocycles for many commercially important shellfish and pollution of entire food chains.[2] Removal and disposal of toxicant-containing coatings from ships also pose separate environmental hazards, driving up the cost of refurbishment.

In order for a polymeric coating to function successfully as a fouling release coating, the surface must: (1) have a low surface energy to minimize chemical interactions; (2) have a low glass transition temperature, Tg, to minimize mechanical locking of a prospective fouling organism; and (3) be temporally and chemically stable in water; that is, conditions (1) and (2) must not change with immersion time in water. Poly(dimethylsiloxane) (PDMS)-based coatings have properties which meet requirement (2) and satisfy requirement (1) as well as any practical polymer developed thus far. However, there is an important challenge is in meeting requirement (3) and this is addressed in this paper.

This paper compares the surface and fouling behavior of representative coatings from two well known PDMS classes, namely ***alkoxysilane*** cured networks and ***Pt cured***

networks. The representative alkoxysilane-cured coating is RTV11®, the "topcoat" of the NRL the NRL duplex coating.[3] The curing chemistry is conventional RTV (Room Temperature Vulcanizing) poly(dimethylsiloxane) (PDMS) network formation, achieved by condensing silanol-terminated PDMS chains with a multi-ethoxysilane crosslinker, in this case polydiethoxysiloxane with 40% SiO_2 content (ethylsilicate 40). The second class of coatings is based on the well known Pt catalyzed hydrosilation of divinyl terminated PDMS chains with multifunctional silane crosslinkers. Variables examined include PDMS molecular weight, tri- versus tetra- functional crosslinker, and reactant Si-H/vinyl ratio.

One effective way to assess the temporal stability of coatings surfaces in water is dynamic contact angle (DCA) measurements.[4] We have used this method to determine the underwater surface dynamics of other coatings, poly(dimethylsiloxane-urethane-urea) segmented block copolymers[5] and poly(methyl methacrylate)-g-poly(siloxane) copolymers.[6] Other methods used to determine the chemical stability of coatings over time in water include weight loss, atomic force microscopy (AFM), and surface analysis by electron spectroscopy for chemical analysis (ESCA). Combined, these methods give insight into the mechanisms by which silicone-based surfaces change when immersed in water. Below, our surface analytical results for our representative coatings are correlated with field tests for fouling release behavior.

Experimental

Materials

GE RTV11® was obtained from Read Plastics. The Material Safety Data Sheet indicates the composition as follows: hydroxy-terminated PDMS (60- 80%)(M_w 26,000, M_w/M_n = 1.7, by GPC vs. polystyrene standard), $CaCO_3$ filler (10-30%), Ethyl Silicate 40 (1.6%). Vinyl-terminated PDMS (200 cs and 1000 cs), methyltris(dimethylsiloxy)silane (trifunctional crosslinker), tetrakis(dimethylsiloxy)silane (tetrafunctional crosslinker), and platinum divinyltetramethyl-disiloxane complex (catalyst) were obtained from United Chemical Technologies, Inc.

RTV 11® Samples

The material was mechanically stirred for five minutes prior to the addition of 0.1%, 0.25%, and 0.5 wt% dibutyltin dilaurate (DBTDL) catalyst. The mixture was stirred for an additional 10 minutes then degassed in a vacuum oven at room temperature for 10 minutes. Samples were obtained by dip coating 22 x 50 x 0.15 mm glass cover slides. Curing was accomplished in either high humidity (90% R.H.) or ambient humidity (ca. 20% R.H.). Minimal differences in wettability were observed for samples cured at high or ambient humidity utilizing 0.5 and 0.25 wt% DBTDL. Samples cured with 0.1 wt% DBTDL were cured only under high humidity conditions.

PDMS Networks Via Hydrosilation

The networks were prepared by mixing appropriate amounts of degassed vinyl-terminated PDMS and tri- or tetra-functional crosslinker with an equal volume of hexane, followed by the addition of 2-10 ppm catalyst. The reaction mixture was stirred by hand for four minutes. Samples were obtained by dip coating 22 x 50 x 0.15 mm glass cover slides. The coatings were allowed to cure 48 hr prior to measurement.

Surface Characterization

DCA measurements were performed on the polymer surfaces using a Cahn DCA Model 312 analyzer. Water for the dynamic contact angle measurements was purified to Type I with a Barnstead Nanopure Bioresearch grade system and had an average resistivity of 18 M3-cm. The surface tension of the contact angle probe water was checked daily and had a typical value of 72.6 dynes/cm. The rates of immersion and withdrawal were 100 m/s; top dwell times were three minutes and bottom dwell times ranged from zero to three minutes. Each advancing/receding contact angle data point is the average of the last three immersion/withdrawal cycles. For long term immersion testing, samples were stored in either nanopure water alone or nanopure water spiked with 200 ppm sodium azide (as a biocide[7]); solutions were replaced weekly. AFM was performed using a Nanoscope IIIa Atomic Force Microscope in tapping mode using 125 mm silicon cantilevers with typical resonance frequencies, F_o, of 271-325 Khz. The field size was 30 X 30 m. Phase contrast for AFM was performed on a Dimension 3000 large sample AFM. ESCA was performed using a Perkin Elmer PHI 5500 equipped with a Mg K X-ray source at take-off angles of 20 and 70 degrees from the plane of the sample and with 4-5 eV flood gun charge compensation. Binding energy shifts were determined by referencing the highest peak in the C_{1s} spectrum to either 292.0 eV for CF_2 groups or 285.0 eV for hydrocarbon.

Fouling Adhesion

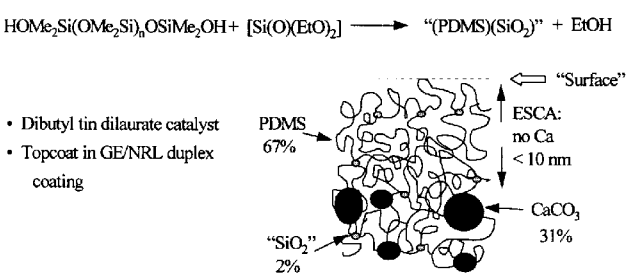
Field tests were performed at NRL, Chesapeake Beach, MD and at The Florida Institute of Technology, Melbourne, FL. Coated panels were prepared similarly to DCA slides except that only one side of each fiberglass panel was coated. Immersion tests are ongoing, results reported are those obtained after monthly withdrawal, inspection, and cleaning of the panels.

Results and Discussion

RTV 11® Surface Composition

Under the water sparse conditions of cure, hydrolysis and particularly condensation reactions which effect cure of RTV11® are relatively slow.[7] For the analytical studies described below, samples were allowed to cure a minimum of twenty-eight days, to ensure full cure throughout the entire film. X-ray spectroscopy for chemical analysis (ESCA) revealed Si, C, and O in the expected ratios, but no Ca could be detected. Figure 1 shows schematically the surface composition of RTV11® based on these and other analytical results.

Figure 1
Schematic of Near Surface Composition of RTV11®.



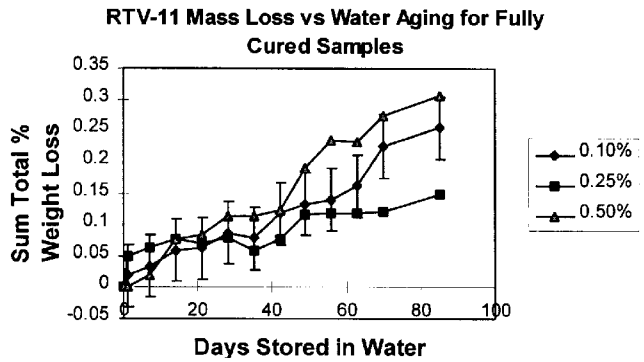
Stability of RTV11® in Water

Long-term water immersion studies were performed on fully cured samples with varying catalyst concentrations. The first indication of chemical instability of RTV11® coatings came from mass loss studies (Figure 2). Error bars are included for the 0.1 wt% catalyst samples only; similar error ranges are observed for the other samples. The total weight loss over 70-85 days is 0.1-0.3%. Differences in weight loss for different catalyst concentrations are significant only after more than two months immersion. Samples with 0.25 wt% catalyst show the lowest mass loss after this time.

To elucidate the nature of the mass loss process, tapping mode atomic force microscopy (TM-AFM) imaging was performed on samples cured with 0.25 wt% catalyst. The pristine film has a roughness coefficient of 45 nm after three months immersion in water. The roughness coefficient increased to 95 nm, with evidence of a non-uniform erosion process. Scattered pits of various size and depth appeared on the surface, indicating mass loss occurs in highly localized areas of the surface. We are currently attempting to calculate the void area from AFM and correlate this with mass loss, to determine if all of the mass is lost through pitting or if there is additional overall film erosion.

The results from TM-AFM explain why little change in the ESCA spectrum was observed in water aged samples.

Figure 2
RTV 11® immersion mass loss data for films prepared with 0.1, 0.25, and 0.50 wt% catalyst.



A relatively large area is interrogated by ESCA (ca. 4 mm^2) so the pits introduced in water-aging did not perturb a large enough area fraction to effect ESCA results. Light microscopy was not effective in identifying the presence of pits as the white pigmentation of $CaCO_3$ makes the films highly reflective. Wettability data are also not sensitive to the long term pitting-erosion process, though a dramatic short time (24 hr) increase in wettability is observed for RTV11® samples which we ascribe to diffusion of polar, near surface PDMS chain ends (terminated with Si-OH and Si-O-$Si_n(OH)_m$) to the surface.

PDMS Networks Via Hydrosilation

Two different divinyl-terminated PDMS samples (molecular weight data: 200 cs = 9400, 1000 cs = 28,000) and two different silane crosslinkers (trifunctional = XH_3; tetrafunctional = XH_4) were used to form networks with a variety of crosslink densities. Surface analysis by ESCA showed the expected ratio of Si, C, and O peaks for PDMS. The results of wettability for these PDMS networks are given in Table 1, arranged in order of highest to lowest crosslink density. Within experimental error, no measurable differences in advancing and receding contact angles are observed with varying PDMS molecular weight or crosslinker.

In each data set shown in Table 1, the Si-H/vinyl ratios were varied, from 1.1 to >2.0. Ideally, a Si-H/vinyl ratio of 1 should result in a fully cured network. In practice, this is not the case; Si-H/vinyl ratios >1 are needed to obtain non-tacky fully cured networks. Reactions other than hydrosilation occur which consume excess Si-H functionalities,[8] including reactions with water and/or oxygen to from Si-OH species which can further condense to form Si-O-Si bonds.[9] For all of our data sets there was no systematic trend of either the advancing or the receding contact angles with increasing Si-H/vinyl ratio. Therefore, the excess Si-H functionalities must react in such a way as to

Table 1
Average Water Contact Angles for PDMS Networks Via Hydrosilation

	advancing (°)	receding (°)
200 cs PDMS + XH_4	108 ± 2	87 ± 5
200 cs PDMS + XH_3	110 ± 3	87 ± 7
1000 cs PDMS + XH_4	108 ± 4	87 ± 9
1000 cs PDMS + XH_3	108 ± 3	90 ± 4

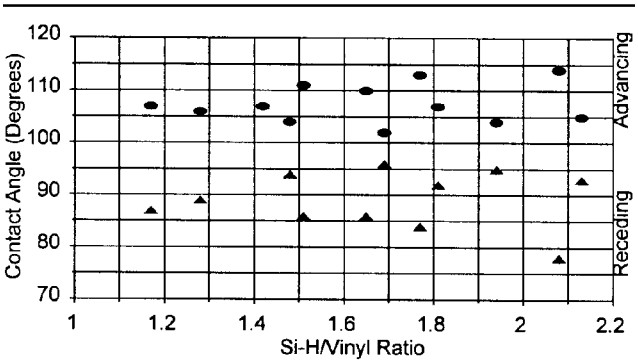
not contribute any hydrophilic nature to the surface. Formation of Si-O-Si bonds, as outlined above, is one possible route. We are currently investigating which side reactions are occurring, either during or after network formation, to explain the apparent lack of surface hydrophilicity with increasing Si-H/vinyl ratios.

Within experimental error, there is no drop in receding contact angle or measurable weight loss with time immersed in water (up to 2 months). Thus, in contrast to RTV11®, Pt- cured divinyl coatings exhibit remarkable stability in water. Figure 3 illustrates the stability of a representative sample of these networks, showing no systematic decrease in receding contact angle for 1000 cs PDMS + XH_3, over 28 days immersed in water. The Si-H/vinyl ratio was also varied in this example, from 1.18 to 3.07, and it can be seen there is no measurable trend along this axis. The stability of these coatings to acid catalyzed hydrolysis is also exceptional. We observed no changes in either the advancing or the receding contact angles over 12 hours immersion in 0.1N HCl for networks synthesized using 1000 cs PDMS with both tri- and tetra- functional crosslinkers.

Field Tests of Strength of Adhesion of Hard Fouling

Field tests have been initiated at Melbourne FL on panels coated with our PDMS networks synthesized via hydrosilation and RTV11® for comparison of fouling and fouling release behavior. Barnacle adhesion is estimated by the method of Swain.[10] This mechanical test gives a quantitative measure of barnacle adhesion to coatings. In Table 2, preliminary data is presented for 1000 cs PDMS + XH_3, along with data for RTV11® and FEP Teflon®, the best non-silicone coating for fouling release. The data show that Pt-cured divinyl silane (1000 cs PDMS + XH_3) is superior to RTV11® for ease of barnacle removal.

Figure 3
1000 cs PDMS + XH_3 ; wettability as a function of Si-H/vinyl ratio.



Conclusions

This study has shown that the surface of RTV11®, an alkoxysilane cured PDMS material, unstable when immersed in water for three months. Mass is lost, and the contact angle hysteresis undergoes substantial changes with time of immersion. TM-AFM reveals a nonuniform micron scale erosion or "pitting" phenomenon occurring at the surface. In contrast, surfaces of PDMS networks synthesized via Pt catalyzed hydrosilation exhibit remarkable stability when immersed in water No decrease in wettability and no measurable weight loss occurs for up to two months. Within the range studied, the surface properties of these Pt-cured networks are relatively insensitive to initial Si-H/vinyl ratio and to crosslink density.

The instability of RTV11® is perhaps not surprising considering the presence of $CaCO_3$ filler and the crosslinking chemistry. For RTV11®, the network is formed via condensation of Si- OH from terminal PDMS functionality and Si-OH from the hydrolyzed alkoxysilane. The PDMS chain is stable to water at ambient temperature, but the siliceous phase produced by the alkoxysilane may be susceptible to hydrolysis. While $CaCO_3$ filler is not detected by ESCA in the RTV11® surface, it may be present below detection limits which are estimated to be 1- 0.5 wt%. Any near surface $CaCO_3$ would provide a site for attack by water, as $CaCO_3$ is soluble in water. Whatever the cause of RTV11® microroughening and erosion in water, this process likely facilitates the adhesion of marine organisms.

Table 2
Barnacle Adhesion Data

Coating	Barnacle Adhesion (psi)
1000 cs PDMS + XH_3	7 ± 3
RTV11®	12 ± 2[8]
FEP Teflon	112[7]

In contrast, the surface of Pt-cured PDMS is chemically stable in water. This follows from the cure chemistry in which non-hydrolyzable C-Si and C-H bonds are formed. We believe that the better fouling release of Pt-cured PDMS

is due to the chemical stability of a surface which is principally PDMS. By its chemical nature, Pt-cured PDMS is probably the ultimate PDMS coating for fouling release and a standard by which other PDMS systems may be evaluated. It must be kept in mind that even with barnacle removal requiring only 5.4 Å 3 psi from Pt-cured PDMS, the surface of these panels readily foul but are easily cleaned.

At the present time there are a number of features of Pt-cured PDMS which make it impractical for shipyard application. Materials approaches to improve Pt-cured silicone based coatings include more robust catalysts for hydrosilation and the investigation of novel reinforcement methods to improve toughness, which is a weakness of most silicone coatings.

Materials approaches to improve alkoxysilane cured PDMS include modification of the crosslinking chemistry and improved reinforcement materials for improved stability in water. Improvements in alkoxysilane cured PDMS systems will be important because this coating chemistry is already in limited application as fouling release coatings.[11]

Acknowledgments

This research was supported by the Strategic Environmental Research and Development Program (SERDP) and the Office of Naval Research Scientific Officer Research Program (SORP). The authors thank Dr. Tai Ho for GPC data.

Biographies

Dr. Ann E. Mera earned her Ph.D. in Polymer Science from The Pennsylvania State University in 1986. She is a research chemist in the Materials Chemistry Branch at the Naval Research Laboratory (NRL), Washington, D.C. Dr. Mera's research interests include fluoropolymers, silicone-containing polymers, and low surface energy coatings for naval applications.

Dr. Robert B. Fox has over 50 years experience with the Chemistry Division at NRL, where he worked in polymer synthesis, photophysics, and sonic properties. His current interest is in hydrolytically stable silicone networks. Dr. Fox has served on the Board of Directors of the American Chemical Society and was a founding member of the Macromolecular Nomenclature Commission of the International Union of Pure and Applied Chemistry.

Steven Bullock is a master's candidate at George Mason University in Chemistry. Currently, he is working at the Naval Research Laboratory through a grant from the Office of Naval Research funded by SERDP. His research interests lie in the area of low surface energy polymers. Mr. Bullock has a B.S. from Virginia Polytechnic Institute and State University and will complete his master's in August, 1998.

Dr. Geoffrey Swain, see page 50.

Michael P. Schultz is currently a Research Engineer in the Division of Marine and Environmental Systems at Florida Institute of Technology (FIT). He received a B.S. and M.S. Degree in Ocean Engineering from FIT and is currently completing his Ph.D. (finish Spring 1998). His research interests include biofouling test method development, turbulent boundary layer flows, hydrodynamic force measurement on fouling organisms, and marine corrosion.

Dr. Paul Gatenholm is Professor of Polymer technology at Chalmers University of Technology in Gothenburg, Sweden and Adjunct Professor of Biomaterial engineering at Virginia Tech. His research interest is surface engineering of polymers and fibers and special interest is in an interface between synthetic polymers and biological environment. He has published more than 80 scientific papers and 60 conference proceedings and has several patents. He has recently been visiting scientist at NRL.

Dr. Kenneth J. Wynne, see page 32.

REFERENCES

1. R. S. Alberte, S. Snyder, B. J. Zahuranec, and M. Whetstone, *Biofouling*, **1992**, *6(2)*, 91.
2. E. W. Douglas, S. M. Evans, C. L. J. Frid, S. T. Hawkins, T. S. Mercer, and C. L. Scott, *Invert. Reprod. Develop.*, **1993**, *24*, 243.
3. J. R. Griffith, **1995**, *U. S. Patent 5,449,553*, and **1997**, *U. S. Patent 5,593,732*.
4. R. E. Johnson and R. H. Dettre, *J. Phys. Chem.*, **1964**, *68*, 1744.
5. J. K. Pike, T. Ho, and K. J. Wynne, *Chem. Materials*, **1996**, *8*, 856.
6. A. E. Mera, J. K. Pike, M. Goodwin, and K. J. Wynne, *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)*, **1996**, *37(2)*, 765.
7. A. H. Hogt, D. E. Gregonis, J. D. Andrade, S. W. Kim, J. Dankert, and J. Feijen, *J. Coll. Inter. Sci.*, **1985**, *106*, 289.
8. L. G. Britcher, D. C. Kehoe, J. G. Matisons, and A. G. Swincer, *Macromolecules*, **1995**, *28*, 3110.
9. L. Lestel, H. Cheradame, and S. Boileau, *Polymer*, **1990**, *31*, 1154.
10. G. W. Swain, J. R. Griffith, J. D. Bultman, and H. L. Vincent, Biofouling, **1990**, *6*, 105.
11. L. R. Ternoir, R. E. Foscante, and R. L. Gasmena, U. S. Patent 5,275,645 (1994).

Biofouling, Fleet Maintenance and Operational Needs

Gerard S. Bohlander and Jean A. Montemarano, Naval Surface Warfare Center, Carderock Division, West Bethesda, MD

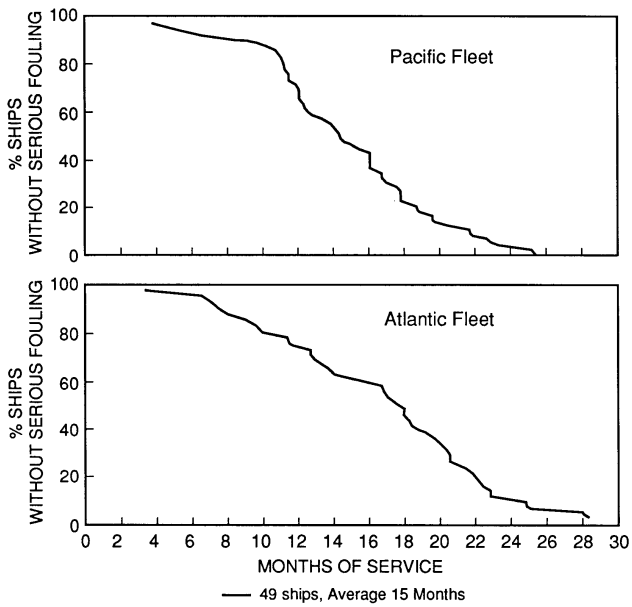
Introduction

The U.S. Navy has been searching for the ideal antifouling (AF) paint for steel hulls since the 19th century. The Navy has long term service requirements - 5 to 7 years - between drydocking and painting, and extended pierside time where the majority of marine fouling occurs. There is a severe propulsive fuel penalty and possible compromise of the ship's mission if the hull is allowed to foul. Navy Formula 121, used by the fleet until recently, is a 70% cuprous oxide by weight vinyl rosin based coating. This paint has long been known to be inadequate for the service life requirements of Navy ships. Figure 1 shows the performance of a population of both Pacific and Atlantic Fleet ships painted with F 121. All ships in the populations had serious fouling within either 24 or 28 months. The poor performance of F 121 provided incentive for research to develop improved paints. Introduction of the organotin AF paints in the late 1970's showed promise of achieving the Navy requirement of 5-7 years unattended service between repainting in drydock. Much effort was expended in research on tri-organotin toxicants and multiple paint formulations with these ingredients in the areas of performance and environmental effects. Field evaluations and ship trials were conducted on the many products that evolved from industry and Navy research. However, the organotins eventually fell into disfavor due to environmental and shipyard health concerns.

The commercial paint industry responded to the regulatory pressure on organotins by developing "tin-free" ablative AF paints containing cuprous oxide toxicant. The first Navy test ship was painted with cuprous oxide ablative AF paint in 1984. This ship, USS AINSWORTH (FF 1090) experienced 5 years of good performance from her AF paint system. The rate of application of cuprous oxide ablative AF paints to Navy ships accelerated after U.S. Navy organotin AF paint use was prohibited by the U.S. Congress in 1986. Although the ban was lifted in 1989, the U.S. Navy has chosen not to implement organotin AF paints. Instead, over 300 ships and submarines in the US fleet of 375 units have been painted with cuprous oxide ablative AF paints from two primary commercial suppliers. A new military specification[1] was issued covering AF materials.

The performance of the cuprous oxide ablative AF paints has been generally satisfactory. While some ships

Figure 1
The performance of Navy Formula 121 cuprous oxide AF paint on selected Navy ships in the Pacific and Atlantic Fleets. This shows the population of ships not requiring underwater hull cleaning. Both fleets have all ships in the population requiring cleaning due to marine fouling in 24-28 months.



have fouled before 5 years service, most have performed well, providing performance exceeding that of the Navy Formula 121. All current AF paint applications utilize the ablative AF coatings.

Cuprous Oxide Ablative AF Paint: Performance Analysis

The performance of cuprous oxide ablative AF paints on U.S. Navy ships has been analyzed by collecting ship inspection reports, conducting diver and drydock inspections, and from a diving inspection data base maintained by the Naval Sea Systems Command, Supervisor of Diving and Salvage, Code OOC. This database has been developed from inspection reports from commercial and Navy diving operations, and reports from underwater cleanings conducted on cuprous oxide ablative AF paints. Paint condition and fouling ratings observations are based on visual and written guidance contained in a Navy document[2]. Those familiar with diver observations realize the difficult environment in which divers operate. Visibility is often severely limited, and the quality of observations may be dependent on the skill of individual divers. Thus, diver observations need to be verified by photographic documentation, but are valuable for determining performance trends for these paints.

Figure 2
The age distribution of the population of US Navy ships coated with ablative cuprous oxide AF paint, as of May 1991. Both Atlantic and Pacific Fleets are shown.

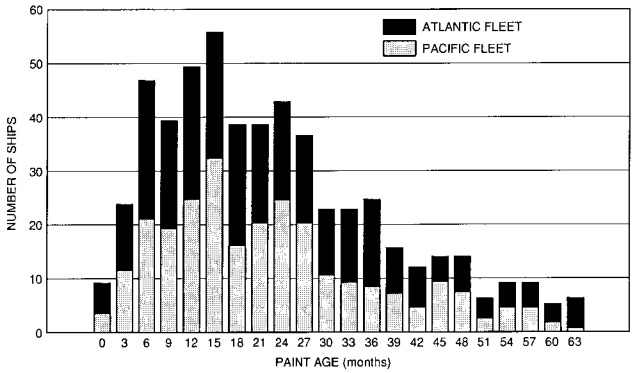


Figure 2 shows the age distribution for 170 USN Atlantic and Pacific Fleet ships painted with copper ablative AF paint The bulk of the population was between 12 and 30 months old. The age distribution of ships that have had underwater cleaning is summarized in Fig. 3. About 25% of ships painted with ablative AF paint have had underwater cleaning. The fouling rating (FR) at the time of cleaning is shown in Fig. 4. A FR of 40 or greater over 10% or more of the hull is the criterion for underwater hull cleaning. Figure 5 combines the data in Figs. 2 and 3, and demonstrates a slight increase in the number of fouled ships may be expected as the population of copper ablative painted ships ages. Note that the performance evaluation information is 4 years old, so there are more ships painted today than reflected in this analysis. Updated information is now being sought to improve this analysis.

Figure 3
Performance of the population of US Navy ships painted with ablative cuprous oxide AF paint. Graph shows number ofships with marine fouling sufficient to require hull cleaning as a function of time out of dock since painting.

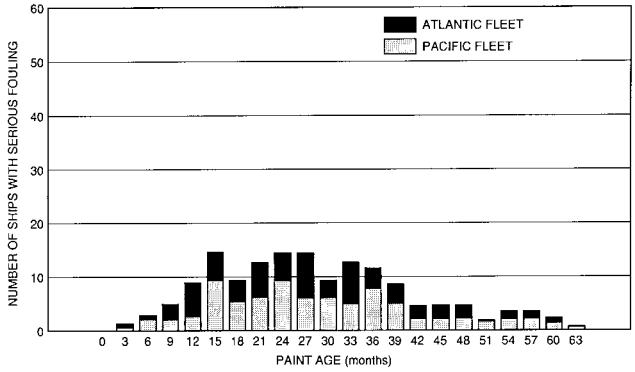


Figure 4
Observations are made on Navy ships of the marine fouling on the hull prior to underwater cleaning. The "Fouling Rating" (FR) scale runs from 10 to 100 as fouling increases in severity. This graph shows the reported FR distribution when copper ablative AF paints were cleaned.

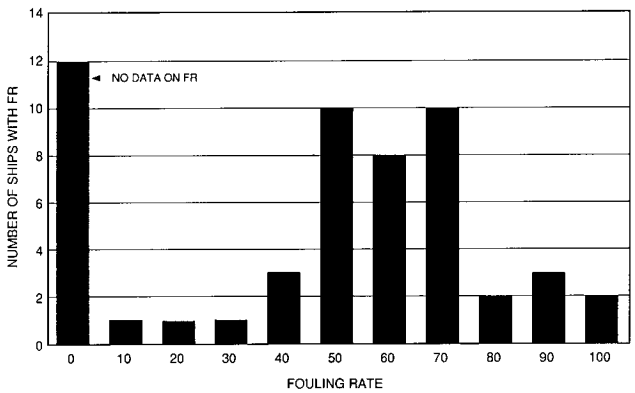
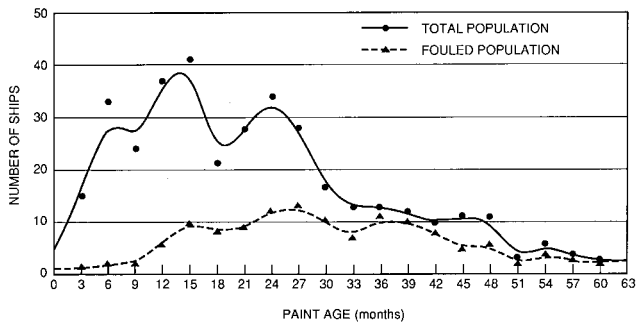


Figure 5
This is a combination of Figures 2 and 3 and shows the distribution of ages of the population of ablative cuprous oxide painted Navy ships and the population with serious marine fouling.



Perhaps the most well known benefit from the use of an effective AF paint is in the area of propulsive fuel savings. The accumulation of marine fouling on the hulls of ships increases the hydrodynamic drag, requiring the expenditure of more horsepower to move ships through the water. This increases propulsive fuel consumption. Ship trials have documented reductions of from 10 to 60 % in propulsive fuel consumption as a result of removing marine fouling from a ship hull[3]. The U.S. Navy propulsive fuel bill is approximately $500M/y, of which about $75M to $100M is expended to overcome the increased drag to marine fouling. An effective AF paint could be expected to save a substantial portion of that expense. The increasing use of ablative AF paints by the U.S. Navy is expected to recover perhaps $35M to $50M of the propulsive fuel increases due to fouling by providing better performance.

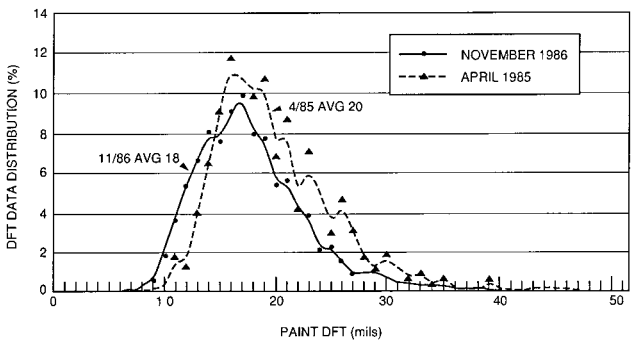
A major additional advantage to an ablative AF paint is the ability to modify the usual drydock paint maintenance procedure. Normally, the underwater hulls of U.S. Navy surface ships have been sandblasted and repainted at each overhaul dry-docking, which occurs every 5 to 7 years. This was done because the standard AF paint, F 121, becomes depleted of cuprous oxide on it's surface, accumulates a light colored layer of insoluble copper salts, and loses its AF properties. Drydock paint replacement is also done to remove and replace the anticorrosive (AC) paint, which is an epoxy material. Ideally, the ablative AF paints do not become depleted of cuprous oxide on the surface of the paint if the ship has had sea time sufficient to activate the ablation process. Even if little ablation has taken place, it is possible to wash the spent paint matrix, which is soft, from the surface of the paint after entering drydock. Additional coats of AF paint can then be applied. Thus, the option to retain the existing paint system now exists. Significant cost savings, ranging from $300K for destroyers to $1.5M for aircraft carriers, result from paint system retention. Also, this minimized the generation of hazardous waste from the paint removal operation. In addition, it is now possible to defer drydockings if they are being planned primarily for paint removal and replacement, with significant cost avoidance. It is necessary, however, to have provisions to capture and contain the washwater in drydock, since it will contain significant amounts of cuprous oxide. While most Navy drydocks cannot contain liquid waste, progress is being made to modify some major docks at naval shipyards to address this issue.

Operational Experience

Six U.S. Navy aircraft carriers have taken advantage of the ability of the ablative AF paints to be retained at drydocking. In each case, the ships had docked with a cuprous oxide ablative AF paint system on their hulls, ranging in age from 18 to 60+ months of service.

The first ship, USS AMERICA, was to undergo an overhaul in 1987 of one year in drydock followed by 5 years of service prior to the next docking. It had been painted 18 months before, in April 1985, with the ablative AF, due to severe marine fouling of the F121 AF paint. The repainting had been done with the understanding that the ship would not be blasted and repainted at the upcoming overhaul drydocking. A new maintenance procedure was established for the care of the ablative AF paint after docking. After entering dock, the hull was hydrowashed with 2500 psi fresh water to remove biofilm slimes and any surface contamination that would effect adhesion of the subsequent coats of ablative AF paint. A dry film thickness (DFT) survey was done after hydroblasting to characterize the thickness of the existing paint. The DFT survey was done with electronic DFT instruments based on magnetic induction. These instruments are capable of storing several thousand readings, and downloading them to a laptop computer in the drydock.

Figure 6
The paint dry film thickness (DFT) is measured on the hulls of Navy ships. This shows 2 populations of data taken 18 months apart on USS AMERICA. It demonstrates a slight reduction in thickness of the ablative AF paint with time in service.



The results of that survey, expressed as a histogram of frequency of occurrence, is shown in Fig. 6.

A DFT survey had been done when the ablative AF paint was applied, and that is also shown as a second data set in Fig. 6. There is a slight difference in the average and the mode of the populations, indicating that some limited ablation had probably taken place in 18 months of service.

There was, however, a problem with the hydroblast operation. Inexperienced operators had increased the pressure to 6000 psi, from the recommended 2500 psi, resulting in some scaring and removal of the existing AF paint. This necessitated the application of 3 coats of ablative AF paint to ensure that sufficient thickness of paint was present over the entire hull. Subsequent underwater surveys indicated good AF performance with some intercoat adhesion failure between the original and additional coats of ablative AF. When a survey indicated calcareous fouling was present, a hull cleaning was conducted. A cost avoidance of about $1.4M was realized from deferring the complete removal and repainting of the underwater hull paint system. The ship was subsequently drydocked in 1992 for removal and replacement of the paint system after 8 years of satisfactory service.

The second aircraft carrier, USS CARL VINSON, was docked after 42 months of service on a copper ablative AF paint. Instead of hydrowashing, this ship was given an underwater hull cleaning just prior to docking, and a fresh water wash with fire hoses immediately after docking. The paint system was in excellent condition. One coat of AF paint was applied to this ship in the fall of 1991, after all hull cuts had been repaired and paint touchup work had been completed.

An additional benefit of this process is the elimination of the consumption and disposal of between 3 and 6 million pounds of abrasive blasting material that would have been used to remove the existing paint system. This amount is for a CVN 68 class ship which has 160,000 sq. ft. of underwater hull area. This abrasive, contaminated with copper waste, costs from $25 to $650/ton to dispose of, depending on which state controls the disposal site. Thus, the retention of the existing paint system can save from $80,000 to $2,100,000 in waste disposal costs, in addition to the labor and material cost savings from avoiding the blasting and total painting operation. These costs, while quite variable, range from $750,000 to $1,400,000. The costs of touchup of the various hull cuts and paint damaged areas must be subtracted from this total.

A third ship, USS ENTERPRISE (CVN 65), painted in 1986, was docked after 37 months of service on an ablative AF paint. The paint system was also in very good condition. The paint system was hydrowashed with 2500 psi. fresh water, and the hull was overcoated with one coat of ablative AF prior to undocking. This evolution saved $1,600,000 in maintenance funds. It is expected that this paint system will operate until 1999.

A fourth ship, USS NIMITZ (CVN 68), was originally painted in 1992 with an epoxy AC and an ablative AF paint system. The ship was again docked in 1994 after having been in service 30 months with its existing ablative AF paint system. That paint application had been monitored in drydock and baseline DFT data taken. The paint was in excellent condition upon docking, and the decision was made that it was unnecessary to overcoat the AF paint, based on the comparison of the paint DFT data from the two dockings (Fig. 7). NIMITZ is expected to dock in March of 1998. A decision will be made at that time concerning retention or replacement based on the future plans for the operation and maintenance of the ship.

USS DWIGHT D EISENHOWER (CVN 69) presents a unique situation for life cycle monitoring of ablative AF paints. The ship was painted in 1985 with an ablative AF paint system. Baseline DFT data was taken on both the AC and AF applications. The ship drydocked in January 1993, where another DFT survey was done (Fig. 8). There was a

Figure 7
This shows the underwater hull paint DFT distribution on USS NIMITZ at undocking and 4 years later. It demonstrates a reduction in thickness of the ablative AF paint.

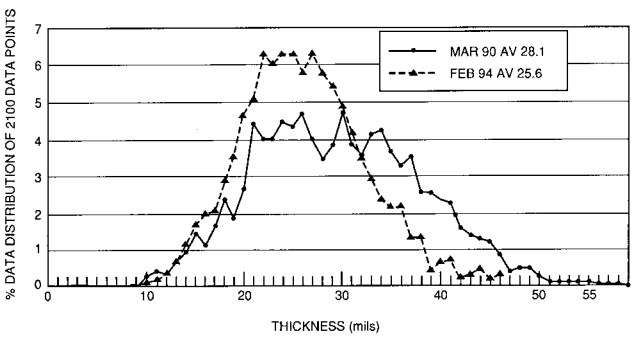
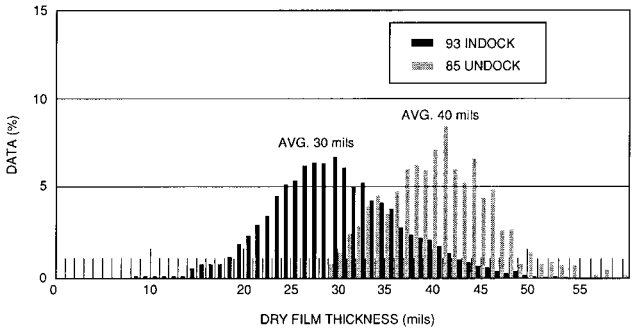


Figure 8
This is the paint DFT history of the underwater hull of USS DWIGHT D EISENHOWER. The ship was painted in 1985 with 2 coats of epoxy AC then 3 coats of ablative AF. It docked in 1993 and the DFT measured showed a 10 mil decrease in average thickness.



10 mil decrease in the average paint thickness over the 8 years of service. It is likely that a significant amount of this thickness reduction was due to two underwater hull cleanings that took place prior to docking, though the paint system was in excellent condition. The decision was made that no overcoat was necessary, since the ship was scheduled to drydock in late 1995. An additional set of DFT data will be taken at that time to document the condition of the longest paint system that has been monitored, a total of 10 years. It is likely that the paint system will be removed and replaced due to the length of time before the next planned drydock.

The life cycle of the anticorrosive paint system is also very important, since keeping the AF paint in service will also demand a service life in excess of 5 to 7 years for the AC system. The USN uses either the military specification MIL-P-24441 polyamide epoxy or several commercial epoxy paints for protection of the steel hull from corrosion. Anticorrosive paint technology has been evolving towards the use of fewer coats of paints that contain high solids materials, and thus may be applied in thicker but fewer coats. It is expected that these materials will provide lengthened service life. The new maintenance procedures that allow retention of the AF paints will take better advantage of the increased service life of these improved AC paints.

There has been a recent experience in which the retention of an ablative AF paint system was not possible. USS THEODORE ROOSEVELT docked after 5 years of service with about 3% blistering and corrosion scattered over the hull. The wide distribution of the blistering would have required significant blasting for surface preparation. It would not have been economical to touchup these scattered areas, and the decision was made to remove and replace the entire paint system at a cost of about $750,000.

Emerging New Coating Technology for Fouling Control

The use of current AF copper paints is coming under increasing regulatory pressure which may leave the Navy with no acceptable alternatives. The Navy sets the pace in AF coating technology due to long term service requirements - 5 to 7 years - in order to meet overhaul cycles and extended pierside time where the majority of fouling occurs. New emerging coating technologies must maintain the required operational service life as restrictions on application and removal of copper increase. The development of new fouling control methods has dual use applications. The military has a requirement for environmentally safe AF hull coatings which provide extended service life and increase intervals between scheduled drydockings. In addition, environmentally safe AF coatings offer tremendous potential for application to the commercial shipping and pleasure craft industry. This dual use application provides the necessary incentive and introductory technology bridge to the commercial sector in order to establish industrial preparedness for coating production for both military and commercial applications.

One approach addresses the novel concept of providing long term protection with non-polluting/biodegradable AF coatings. These coatings are based on two concepts - "easy release" technology and natural AF agents. In short term screening tests, both concepts have demonstrated their AF efficacy. Easy release coatings are based on the concept of minimal surface energy which deters or negates the attachment of fouling organisms. Underwater husbandry will be necessary for periodic removal of the fouling organisms. For the optimal easy release coating, organisms that do attach will be removed by the passage of the ship through the water. Natural antifoulants are compounds that are found indigenous to marine organisms that prevent the attachment of fouling organisms. Eelgrass and certain corals exhibit this phenomena which may be attributed to naturally occurring "chemicals", i.e. natural antifoulants. These natural antifoulants biodegrade rapidly in seawater. Therefore in order to be effectively delivered, these antifoulants may need to be incorporated into controlled release systems. Efforts are ongoing in the Navy community to develop microencapsulation based on a complex coacervation process to contain the antifoulant in capsules which are then incorporated into the coating matrix. These delivery systems will then be formulated into coatings which may couple the natural antifoulant controlled release system with the easy release coating matrix. Since some of the natural antifoulants are complex biochemical compounds, simple chemical analogues are being sought which mimic their AF efficacy. Criteria from the Environmental Protection Agency will need to be established for this new class of naturally occurring

AF compounds. Active industrial participation is anticipated in the manufacturing scale-up of both concepts as well as the commercialization of these products. The final AF coating system will be renewable so that it can be recoated without blasting to bare metal.

Easy release coating technology is the more mature of the two fouling control technologies with limited commercial products available. These products are normally silicone based elastomers which exude a silicone oil which makes the settlement of marine organisms difficult. When organisms do attach to these coatings they are easily removed. The silicone topcoat elastomer is normally bonded to a traditional epoxy anticorrosive system by a tie coat. However, silicone elastomers have poor toughness properties. The Navy requires a durable, tough coating which will be able to withstand the rigors of the operational environment. Under exploratory development funds ONR has demonstrated the feasibility of developing durable, tough materials with improved fouling release properties and a Navy patent has been awarded. The marine coating industry is geared to the commercial market which normally dock at a 2-3 year interval. Industrial participation projects will commercialize the Navy products, and increase the competitive commercial source base for these coatings. Utilizing non-toxic technical advances to biofouling control has medium to high technical risk since these are unproven technical approaches for long term operational performance.

A near term solution to provide 5-7 year unattended service for Navy hulls is the incorporation of cobiocides into copper ablative AF paint matrices. There are several cobiocides commercially available. These are organic pesticides which are effective against a wide range of fouling organisms. The cobiocides provide long term protection when used in combination with cuprous oxide or other AF agents. Once leached from the AF coating the cobiocide degrades rapidly in seawater and is not persistent in the environment. Commercial marine coating companies offer copper AF paints incorporating these cobiocides which are currently in use in the world market; however, they do not provide equivalent performance to an organotin based ablative paint[4]. Underwater hull cleaning requirements will need to be evaluated as well as environmental ramifications of cobiocides release into the water column.

Hull Maintenance

While the introduction of effective anticorrosive paints and improved ablative AF paints have contributed to increased readiness, reduced operational costs and extended the time between drydocking, often repair work is not discovered until the ship is in drydock. The planning and execution of maintenance for hull systems is difficult and expensive. Most Navy surface ships typically have docking intervals from 5 to 7 years. Periodic diver inspections are conducted for assessment of marine fouling on the hull, but diver inspections are not always able to discern deterioration of the many components on the hull. Thus, it often happens that significant additional repairs beyond what has been planned are discovered. Unplanned repair work is always very expensive to conduct, both due to potential interruptions in work already planned, and due to additional costs likely to be imposed by the shipyard for the unplanned work. Thus, it is advantageous to have as much information as possible regarding the hull condition prior to docking.

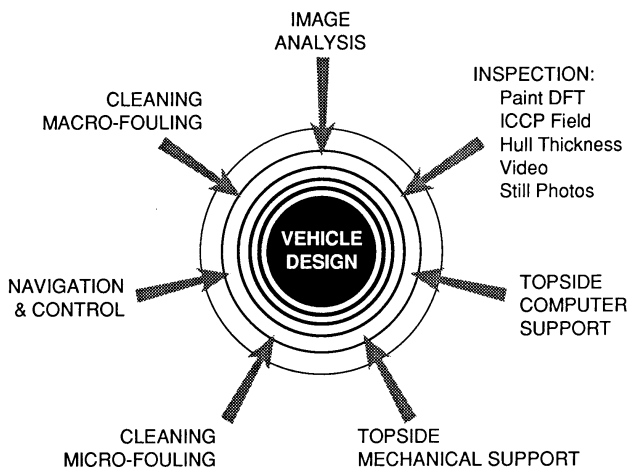
In addition, the process of underwater hull cleaning for marine fouling removal, when done on copper ablative coatings, has the potential to discharge unacceptable amounts of copper toxicant into Navy harbors. While the cleanings conducted on copper ablative painted ships have been successful in removing fouling and reducing the propulsive fuel penalty, the ablative paints are soft, and this may cause the cleaning operation to remove from 1 to 2 mils of AF paint. This does not effect the long term performance of these paints, since they are typically applied about 15 mils thick. However, the paint debris discharged during the cleaning may contain significant amounts of cuprous oxide, which then enters the harbor. The underwater cleaning of ablative AF paints was investigated by the Navy to quantify the copper release, since it is quite possible that regulatory agencies would question the cuprous oxide discharged during this operation.

An Automated Underwater Hull Vehicle Concept

The challenge of monitoring the condition of the underwater hull systems during service combined with the desire to reduce the potential discharge of copper compounds into Navy harbors has resulted in the development of a concept for a tethered automated hull maintenance vehicle (AHMV). This vehicle would be designed to perform a variety of hull inspection tasks in addition to performing hull cleaning operations that reduce the discharge of copper compounds. The AHMV is similar to a remotely operated vehicle (ROV), which is commonly used for a variety of underwater inspection and work tasks. It is planned to develop the AHMV over the next four years. The various functions of the AHMV are shown in Fig. 9.

The AHMV will have a 3 dimensional computer assisted acoustic navigation system to direct it to any location on the hull and program its movements and operations. The vehicle is planned to have both free swimming and hull crawling capability. This will enable the AHMV to move around the hull for positioning and to monitor ICCP fields, and still be able to roll over the hull with wheels to conduct the fouling removal and hull inspection functions since the navigation system will be programmed with the hull shape. A

Figure 9
This is a block diagram of the various components of the Automated Hull Maintenance Vehicle.



topside computer will control the movement and the deployment of various sensors while fouling is being detected and removed.

The ability to detect and clean marine fouling from ship hulls is a critical function of the AHMV. Optical, laser and acoustic methods of image analysis have been investigated for fouling detection. Both optical and laser imaging were found to be limited by turbidity of the water, so acoustic imaging was selected. A high frequency acoustic imaging system, now under development, will have an imaging area of about 2 x 8 feet and will detect and determine the density of the fouling, and activate a cleaning tool for fouling removal.

Three methods are being evaluated for fouling removal efficiency and copper discharge: rotary brush, high pressure waterjet, and acoustic energy. Rotary brushes on a variety of underwater cleaning machines have been used to remove fouling for over 15 years. They are effective, but will abrade the ablative AF paint causing discharge of cuprous oxide into the seawater. Rotary brushes would also release cuprous oxide into the water if used on the AHMV, but the total amount discharged would be much less, since only areas covered with calcareous fouling would be cleaned, and not the entire hull.

High pressure waterjets have been used for a variety of cleaning tasks in the ship maintenance area. Development work is underway in the Navy on high pressure waterjet paint removal[5].This method has been used underwater for cleaning fouling from propellers and sea chests. Recent work with waterjets has demonstrated the ability to improve efficiency and reduce water consumption with multiple nozzles on a rotating head. While fouling removal with waterjets has been demonstrated, the amount of cuprous oxide that would be released is a function of pressure, nozzle size and translation rate, and needs to be carefully investigated.

Recently, work has been ongoing on the use of pulsed power devices to remove marine fouling from underwater surfaces. This method uses a high voltage spark to produce a concentrated energy pulse and remove fouling. This technique is being investigated for the AHMV because it may produce minimal disruption of the ablative AF paint with reduced cuprous oxide discharge.

It is planned to contain and capture any copper containing effluent generated by the cleaning tool on the AHMV. Several preliminary designs have been generated for a variety of shrouds and pumping system to accomplish this task and transport this water topside to a pierside facility. Commercial units are available to process the water to remove particulate and dissolved copper and copper complexes from the effluent stream. Ion exchange resins, dissolved air flotation and ultraflitration are being evaluated for this process.

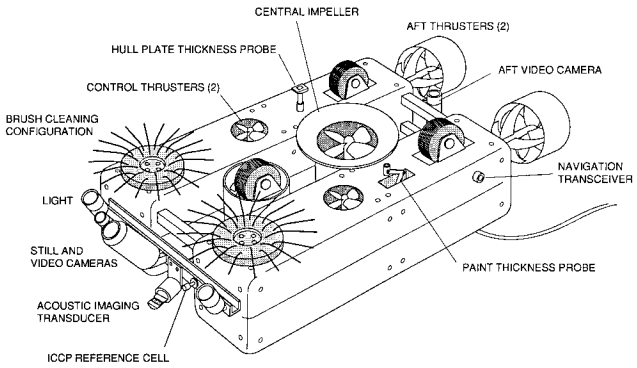
Several sensors will be incorporated into the AHMV to provide information on underwater hull systems. They include sensors for paint thickness, hull electropotential and hull plate thickness. These sensors will be deployed periodically as the vehicle transits the hull, and the data will be transmitted by the vehicle umbilical to the topside computer.

The paint thickness sensor will provide data to determine the amount of AF paint that has ablated off the hull during service. This, when compared with baseline paint thickness data taken at undocking, will allow maintenance planners to decide if the ship needs additional AF paint at upcoming dockings, and how much to apply. Figure 6 shows a histogram of the underwater hull paint system on an aircraft carrier. There are two populations of data, one at application and another taken at a drydocking 20 months later. Some decrease in total paint thickness is noted. Similar data will be generated by the AHMV.

The impressed current cathodic protection (ICCP) system, which is installed on most Navy ships, protects the underwater hull from corrosion using several permanent anodes mounted on the hull, controlled by a reference cell. It reacts to changes in the electropotential of the hull by putting electrical current into the water until the reference cell detects an acceptable potential, usually -850 millivolts. While generally effective, there are anodes failures and areas of uneven current distribution. A reference cell mounted on the AHMV is able to read hull potential and aid in determining proper anode functioning and the static electrical field distribution over the entire hull. Several ROV deployments to measure hull potential have been accomplished. Hull plate thickness can also be taken with an underwater sensor to detect thin areas of the hull that may need future maintenance.

An artist's concept of the AHMV includes brush cleaning capability and shows (Fig. 10) the various components of the vehicle, including sensors, thrusters, and cameras. A block diagram of the various systems coupled to the topside support electronics, which will provide programmed navi-

Figure 10
This is a concept of the AHMV configured with a brush cleaner and various hull sensors and an imaging system.



gation control, data analysis and video of the hull is shown in Fig. 11.

A typical vehicle deployment sequence will involve setup of an equipment van on the job site, and lowering the AHMV into the water, as shown in Fig. 12. A record of the areas cleaned and data generated by the various sensors will be maintained and be available to assist planning necessary maintenance in upcoming drydock availabilities, decreasing costs and time in dock. Ultimately, the underwater hull system data generated by the AHMV can be transferred to robotic paint removal and application systems in drydock. Finally, as shown in Fig. 13, data taken in drydock, such as paint thickness, can be transferred back to the AHMV computers, thus providing a continuity of maintenance records over the ship operating cycles, reducing costs and improving efficiency.

Figure 11
The operation of the AHMV will follow this flow diagram of events as a Navy hull is inspected and cleaned, if required.

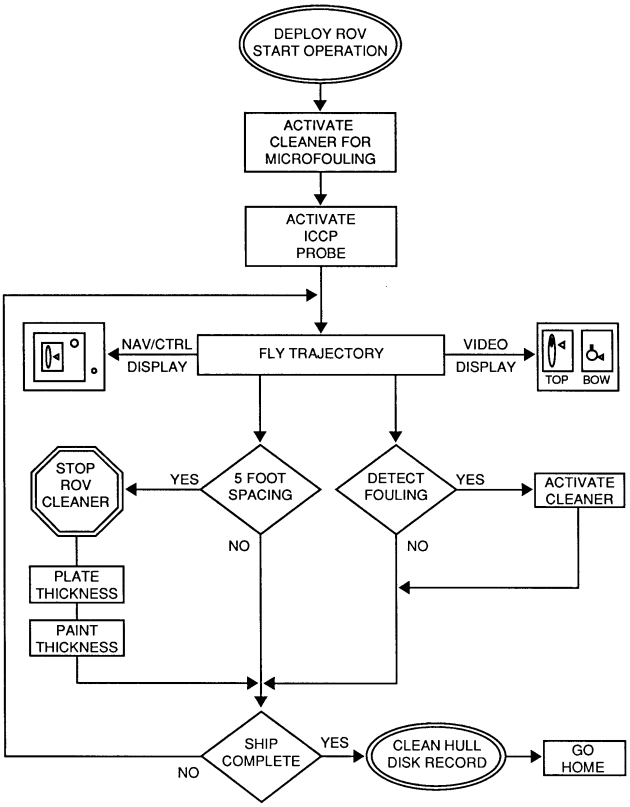
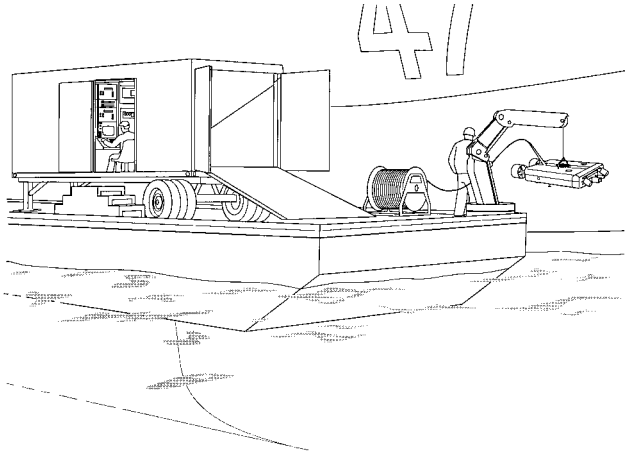


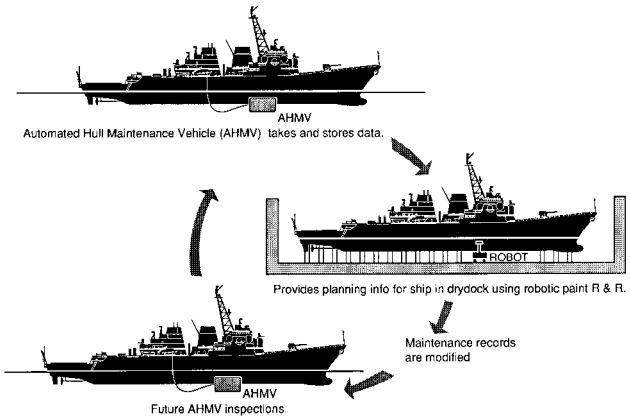
Figure 12
A concept of the deployment of the AHMV for Navy ship hull inspection and cleaning.



Conclusion

The U.S. Navy is faced with expensive maintenance requirements to maintain the underwater hulls of ships free of marine fouling and to provide fuel efficiency and mission capability. Conventional cuprous oxide containing paints did not meet performance goals, and have been superseded by ablative matrix coatings that offer improved performance. However, they still present issues of long term performance and copper containment during waterborne and drydock maintenance. A need exists to control marine fouling with minimal or no release of toxicants into the marine environment. A new generation of fouling control coatings that are free of heavy metals are now being developed. These materials function by discouraging fouling settling, and providing a poor surface for fouling adhesion. Automated underwater vehicles offer promise in providing in-water hull cleaning and maintenance monitoring for Navy ships to reduce maintenance costs. Future needs for hull maintenance include non-toxic fouling control coatings that can be applied in the industrial environment and that will self-clean with low speed ship movement, and will provide 5-7 year service. These coating should be renewable for service out to 15 years, and then be easily removable.

Figure 13
The flow diagram of information to be collected on Navy hull condition during underwater and drydock maintenance. The information will assist automated inspection and paint removal and application processes.



Biographies

Mr. Gerard S. Bohlander is a senior engineer in the Paints & Processes Branch of the Naval Surface Warfare Center Carderock Division where he spearheads the development of hull husbandry technology in order to extend the service life of Navy coatings and to improve the overall performance of Navy ships. In particular, his experience and expertise in coatings technology are utilized in transitioning research and development to Fleet usage, which has been recognized by his receipt of the Meritorious Civilian Service Award. Mr. Bohlander directs efforts to reduce underway fuel consumption of Navy ships by minimizing the increase in the hydrodynamic drag of combatants due to service induced hull roughness. Currently, he leads an advanced development program to automate hull husbandry.

Mrs. Jean A. Montemarano heads the Paints & Processes Branch of the Naval Surface Warfare Center Carderock Division where she is responsible for coatings RDT&E for navy surface combatants and submarines. Current focus of the branch's programs is extension of maintenance periodicities with environmental compliance specifically in the areas of preservation technology and underwater hull husbandry. Her numerous technical accomplishments have been acknowledged by the Center in her receiving the George W. Melville Award for her efforts on water repellent coating for submarine periscope headwindows. She has also received the Navy Civilian Meritorious Award, primarily for her work on the development of controlled release polymeric AF paints. Her efforts in this area included technological feasibility and advanced development including industrial scale-up.

REFERENCES

1. MIL-P-24647B. April 2 1991. Paint System, Anticorrosive and Antifouling, Ship Hull.
2. Naval Ships' Technical Manual, Chapter 081. April 15, 1986. Waterborne Underwater Hull Cleaning of Navy Ships.
3. Hundley, L. and Tsai, S-J. October 1991. The Use of Propulsion Shaft Torque and Speed Measurements to Improve Life Cycle Performance of U.S. Navy Ships, In: Fleet Maintenance in the 21st Century, Joint Symposium of Commander in Chief, U.S Atlantic Fleet and American Society of Naval Engineers.
4. Kjaer E.B. 1992. Bioactive Materials for Antifouling Coatings. Progress in Organic Coatings, 20: 339-352.
5. Bohlander, G.S. and Wheeler, R. April 1992. Reducing Underwater Hull Paint Maintenance Costs by Using Ablative Antifouling Coatings. Presented at the 9th Inter-Naval Corrosion Conference, Monterey, Ca.
6. Bohlander, G.S. October 1991. Biofilm Effects on Drag: Measurements on Ships. Presented at the 3rd International Conference on Polymers in a Marine Environment, Institute of Marine Engineers, London.
7. Williams, J. and Rice, R., "Navy High-Pressure Waterjet Closed-Loop Paint Stripping System", Presented at the 1995 Ship Production Symposium, Society of Naval Architects and Marine Engineers, Jan. 1995.

Profiles in Science

James R. Griffith

Dr. James R. Griffith retired recently from the position of supervisory research chemist at the Naval Research Laboratory in Washington, D.C., which he joined in 1955. His research has emphasized polymer synthesis related to materials of Navy interest, especially long-term programs in fluoropolymers and fuel resistant elastomers. He is well known for using polymeric materials as linings for large fuel storage tanks. Nearly all of the land-based Navy tanks worldwide are lined with materials he and his group produced. He has been named on 42 Navy-owned patents: the most recent being the NRL Edison Patent Award of non-toxic antifouling systems in 1996. He has won eight major awards highlighted by the NRL Sigma Xi Award in Applied Research in 1976, the Hillebrand Award of the Chemical Society of Washington in 1979, the Federal Laboratory Consortium Award in 1984 and the Secretary of the Navy's Award for Distinguished Achievement in Science in 1991.

New Technologies for Surface Analysis to Assess Biofouling Resistance

Joseph A. Gardella, Jr., Department of Chemistry, SUNY Buffalo, Buffalo, NY
Kenneth J. Wynne, Office of Naval Research, Arlington, VA
Thomas J. McCarthy, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA
John F. Rabolt, Department of Materials Science and Engineering, University of Delaware, Newark, DE
Georges Belfort, Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY

I. Overview

A. Overview and Goals: Issues in Materials for Biofouling Resistance

The development of new materials for designed uses is one seminal example of modern science and engineering; it involves orchestrating a complex symphony of multidisciplinary team members who can bring specialized expertise to the problem. In the development of materials which can inhibit or control bioadhesion, the understanding of fundamentals of biofouling, key concepts in polymer materials science and molecular biology must all be integrated for the successful development of a new generation of minimal fouling or fouling resistant coatings. A basic premise in such development is the understanding of the surface chemistry of the material which could minimize and control adhesion of marine organisms to surfaces. The design of such coating materials must utilize the state of the art in materials surface chemical analysis, and is in fact a critical determinant in the ***development*** of new methods to define the surface structure and composition of the coating interface.

Of particular interests are developing and utilizing methods which can quantitatively describe:

- the surface of the material in contact with its environment to understand and predict long term usage and degradation mechanisms
- the interactions of materials with adsorbed polysaccharide and protein films which form the basis for bioadhesives
- developing standard materials for testing and comparison

and then:

- the synthetic design and analysis of new materials based on concepts learned from these studies.

This paper will provide a short review and overview

of the advances in instrumentation, measurement science and methodology which are driving the analysis of polymer surfaces and present a short description of advances in methodology which are driven by problems in polymer materials surface chemistry. The use of these methods is critical in the development of model systems and standard materials; a selection of work sponsored by the ONR-MIMI program will be described. Finally, recent ONR sponsored results in the application of these methods towards the development of model systems and actual candidate coating materials will be highlighted.

B. Specific Problems in Polymer Materials Surface Science

In response to the challenges outlined above, rapid development of new spectroscopic and microscopic probes and continuing evolution of more established methods **[1-4]** are advancing the ***surface*** analysis of polymer materials and their interactions in biological environments. A good example of how instrumentation development has led to better applications in polymer surface science is to follow the growth of studies using X-Ray Photoelectron Spectroscopy (XPS) aka Electron Spectroscopy for Chemical Analysis (ESCA). Of common surface science related methods, the inherent analytical aspects of the method, e.g., chemical bonding information, high surface sensitivity, low damage and relative insensitivity to the insulating properties of the sample have made especially useful for the analysis of polymeric materials. The quantitative analysis of surface species and the detection of impurities or modifications at the surface have been heavily traversed areas of ESCA application for polymer surfaces. It is now rather routine to use ESCA to obtain surface composition of polymers, to follow processing steps and degradation chemistry. Many of these more sophisticated applications **[1]** have been driven by advances in instrumentation **[3]**. These developments also mean the method can be used to study systems of greater complexity.

Despite the power of ESCA, to improve the understanding of polymer surface chemistry, more information is desired about **surface structure** with further sophistication, at a higher level of precision. For example, detecting the **presence and concentration of surface active functional groups** is desirable, indeed achievable routinely with ESCA (especially in concert with infrared or Raman vibrational spectroscopy). Yet more desirable for applications in interfacial bonding important in coatings is the knowledge of **orientation and subsequent reactive availability** of these functional groups. Beyond functional group information,

Table 1
Characteristics of some spectroscopic techniques suitable for studying polymeric materials.

	XPS (ESCA)	IR and Raman	SIMS	ISS	HREELS
Analysis Environment	High Vacuum	Ambient	UHV	UHV	UHV
Resolution	0.6 eV	≈ 1 cm^{-1}	0.1 - 1 amu	variable	25-200 cm^{-1}
Elemental/ Molecular Information	no H detection Chemical Shifts	??? functional group id	all + isotopes MW molecules fragmentation	no H or He resolution limited	functional group id
Detection limit	% of monolayer	% in volume 0.01 monolayer*	ppm/ppb element 0.01 monolayer molecular	% monolayer	%monolayer
Lateral Resolution	5 µm	≈ 10 µm	10 nm (atomic) ??? molecular (ions)	none	none
Depth Sensitivity	>50 Å	µm range	10Å?	3-5Å	3-60Å?
Sample Damage	small sometimes with unmonochromatized X-rays	none	high (needs study) lower with static conditions	high (needs study)	none
Major Outcomes	elemental & chemical analysis electronic structure	molecular vibrations- functional groups bulk	low detection limits, molecular ions/fragmentation ions-bonding	elemental atomic orientation	surface sensitive molecular vibrations

monomer arrangement along a chain in copolymers, and **intrachain interactions**, again, as they are exemplified at the surface, would be important information not easily available. In addition, **macromolecular chain arrangement, termination, branching and micromorphological information** (i.e. domain size and distribution) are important in determining sophisticated surface structure property relationships. Further, **isotopic sensitivity** for detection of labeling experiments and diffusion between interfaces is very desirable. **Molecular weight distributions** at or near the surface (in comparison with the average, bulk distribution) would have major impact in many problems. Higher degrees of **spatial resolution** are required, in all three dimensions, so that buried interfaces may be precisely determined. Speed of data acquisition for **kinetic studies** is a general desirable characteristic of analytical methodology which is very limited in UHV surface analysis of polymers.

To approach this level of structural and reactivity information at surfaces and interfaces, evolution in methodology of established methods and development of new methods must both be accomplished. It is unlikely that any single surface analytical method can answer all questions about any system, and this is especially true for the complexity of macromolecular materials.

Table 1 shows a comparison of the analytical characteristics of surface sensitive spectroscopic measurements for polymer analysis. Of course, other spectroscopic methods not accomplished in UHV and other analytical methods play a continuing and increasing role in determining **surface** structure - property relationships for polymers.

In particular, measurements of surface forces have been valuable in describing the fundamental interactions at materials interfaces. Thus, this review will attempt to provide an overview of six methods being utilized for polymer surface interactions, ESCA, Secondary Ion Mass Spectrometry (SIMS), High Resolution Electron Energy Loss Spectrometry (HREELS), accomplished in UHV, optical vibrational spectroscopic methods (infrared and Raman) and the surface forces measurement. Specific examples of how these have been developed and applied will be presented, with a final section highlighting recent advances in polymer synthesis, design and characterization utilizing the methods.

II. Introduction to the Techniques

A. Spectroscopy in UltraHighVacuum: ESCA, SIMS, HREELS

One common characteristic of several of the surface sensitive spectroscopies described below is that they all **require** a UHV environment. This is mandatory for the electron or ion beam used either to probe or analyze the surface, and to keep the surface clean of any contamination from the environment. The level of vacuum necessary is extreme, typically 10^{-7} to 10^{-10} millibar pressure must be maintained.

i. Electron Spectroscopy for Chemical Analysis (ESCA)

Recent reviews have stressed the basic instrumentation **[2]** and advances **[3]** which have allowed great strides in this technique. The basic ESCA experiment requires a source of X-Rays, a lens system to collect and focus photoemitted electrons, and energy analyzer and a detector. This equipment, within vacuum, is generally interfaced to data acquisition and analysis software on an operating computer. The desirable characteristics of the X-Ray source involve narrow line width, high intensity and minimal damage. The lens system serves to allow collection of electrons from a sample distanced away from the entrance of the analyzer. This means other techniques can be focussed at the same surface position. Further, the lens system usually retards the energy of the incoming electrons, to provide higher energy resolution. The energy analyzer operates as a filter to pass specific energies of electrons to the detector. The detector serves to amplify the electron signal and produce a counting rate. Data acquisition using common interfaces allows for signal averaging needed to provide acceptable signal/noise ratios. In addition, the scanning and control of other parameters is possible with the computer.

Experimentally, a sample is introduced into the vacuum chamber, illuminated by X-Rays and the electrons energy analyzed. Commonly, it is thought that the vacuum will have some effect on the sample, making the relevance to a "real" environment questionable. Certainly, physically adsorbed gases or liquids (e.g. water) are desorbed under UHV. Thus, "wet" samples are difficult to analyze without special precautions. The use of freeze drying and low temperature sample handling can mediate some of this problem **[5]** and has been important in the development of methods for the analysis of nonfouling coatings. Never the less, the UHV can affect the sample in ways which prevent analysis of samples in the ambient environment. It is notable that both air and vacuum are very high energy environments, encouraging low energy species to segregate at the interface. Vacuum effects, themselves are not always deleterious. In many older ESCA instruments, for instance, sample heating from secondary electron emission of the source causes sample damage sometimes ascribed to vacuum alone. It is in the best interest of the analyst to evaluate the range of damage under any type of UHV analysis.

Typically, a low energy resolution survey scan allows for determination of detectable elements. These signals are then scanned at higher resolution conditions to provide information on binding energy and intensity. The binding en-

ergy of the electron gives chemical information, the intensity allows for quantitative analysis. Experimentally, it is desirable to vary the angle of the sample plane with respect to the analyzer. This allows analysis at different sampling depths (known as angle dependent ESCA). The view of composition as a function of sampling depth is important in understanding the phase or compositional separation of microstructures near surfaces. Further, the use of several X-Ray energies also produces different sampling depths. The range of depths probed by the technique using the angle and energy dependent experiments ranges from 10 to 200 ≈ in polymers **[2]**.

The most recent advances have been in three areas **[2]**. These are higher energy resolution for finer ability to distinguish chemical states, higher spatial resolution for lateral analysis, and speed of data acquisition for studies requiring low damage or kinetics. Also, the latter characteristic has allowed for development of more dependable quantitative information from polymers. Damage **[4]** has been a major concern under the X-Ray, making quantitative analysis less precise. Precision, accuracy and speed are now such that polymer surfaces can be **quantitatively** analyzed in a few moments of exposure. This allows more signal intensive experiments to be accomplished. For instance, the analysis of the topmost surface with a very shallow sampling depth can be achieved by analyzing at very shallow angles. But, this involves more signal to noise since very small signal levels result. Modern instrumentation allows this to be done without concern for sample damage. Alternatively, more sensitive polymers like PVC can be probed and radiation damage can be limited **[4b]**.

The lower damage rates, the higher speed and the better signal/noise in modern ESCA machines have opened up a better understanding of the limitations of previous applications of ESCA toward polymers.

ii. Secondary Ion Mass Spectrometry (SIMS)

Secondary ion mass spectrometry (SIMS) describes a "family" of very powerful surface analytical techniques **[6]**. Experimentally the SIMS technique involves focusing a primary ion beam of 0.5-30 keV energy onto a sample surface and then extracting the secondary ions that are generated. These secondary ions are separated, according to mass to charge ratio, in a mass analyzer **[7]**. After being mass separated, secondary ions come in contact with an ion multiplier where a signal is generated. In SIMS the primary ions usually consist of ionized Ar, Xe, Kr, O, Cs, or Ga atoms. Provisions are usually made for focussing /defocussing and rastering the primary ion beam, and the secondary ions are extracted by an electrostatic focussing lens arrangement. Ultra high vacuum conditions (pressures less than $1x10^{-8}$ torr) are necessary to ensure the efficient generation and detection of secondary ion species. In some instances, focussing lenses are set up to provide a kinetic energy filter so that organic secondary ions may be collected more efficiently. Mass analysis is commonly accomplished using quadruple mass filter (QMF), time of flight (TOF), or magnetic sector mass analyzers. Instrumentally, the development and application of TOF-SIMS is an area of great current interest, since TOF mass analysis gives the ability to detect ions of very high mass, and therefore analyze high molecular weight samples (10,000 to 20,000 amu) **[8]**. TOF-SIMS also has very low limits of detection due to the quasi- simultaneous detection of all masses.

The SIMS experiment can be performed with two different modes, namely "dynamic" and "static" **[6]**. In the dynamic mode, high primary ion current densities, greater than $1\mu a/cm^2$, are used to gain elemental information as a function of sputter erosion depth into the bulk. In addition, elemental maps or images can be obtained by focusing the ion beam to small (1-3μm) spot sizes (the so-called ion microprobe) or by illuminating the sample with a large- diameter ion beam and using ion optics to preserve the spatial resolution (the ion microscope). In the dynamic mode, virtually all molecular information is lost due to the high current densities used. In the static mode, low (primary ion) current densities and ion dosages (less than 1 nA/cm^2 and $1x10^{12}$ $ions/cm^2$, respectively) yield a very small probability that a primary ion will strike the same molecule or surface region twice in a typical analysis time. Therefore, molecular structure and bonding information can be preserved.

"Static" SIMS was first described in 1970 by Benninghoven **[9]**. With current density lowered to less than 10 nA/cm^2, and defocussed ion beams, molecular secondary ions were obtained for organic carboxylic acid compounds. In 1976-1977 static SIMS spectra of 15 amino acids **[10,11]** displaying parentlike molecular ions were published, causing increased interest in the technique. From that time, static SIMS has been used to analyze a wide variety of synthetic polymers **[8, 12-17]**, biomolecules **[18]**, and pharmaceuticals **[19]**. The focus of a majority of these studies was to investigate secondary ion emission mechanisms and/or show the capability of static SIMS to provide mass spectra of large, thermally labile, organic compounds.

As larger molecules are probed from surfaces, the problems of predicting molecular ion formation mechanisms complicate spectral interpretation. The understanding of SIMS generation of molecular ions from surfaces and **[20]** in biomolecular mass spectrometry **[21,22]** is based on the close relationship of the SIMS experiment to fast atom bombardment mass spectrometry [FAB or liquid SIMS] **[23]**, plasma desorption mass spectrometry (PDMS) **[24]** and laser desorption mass spectrometry **[25]**. These methods have been particularly useful for the mass spectrometry of high molecular weight biological molecules, allowing molecular weight determination, identification, and attempts at nucleotide and protein sequencing within the mass spectrometer.

It is important to note that a major difference between

SIMS and the other mass spectrometric experiments noted is the *surface sensitivity* of SIMS. Thus, these other "desorption /ionization" **[26]** methods, while having distinct advantages in signal/noise and ability to generate high mass ions over SIMS **[24b]**, are not appropriate for much research in surface science.

In SIMS, the basic principles of ion formation for atomic species have now been recognized as the same for **molecular** secondary ions. This allows the derivation of molecular structure information based on molecular ion and fragmentation information similar to that inherent in traditional mass spectrometry. Along with such surface specific molecular structure analysis, the excellent detection limits and ability to simultaneously detect signals from multiple species at very different concentrations, which is inherent to mass spectrometry, has allowed sophisticated methods and applications to mixture analysis. For organic and polymeric materials analysis, this could include analysis of additives, residual monomers, and other smaller molecular species, with low detection limits.

iii. High Resolution Electron Energy Loss Spectrometry (HREELS) for Vibrational Analysis

Low energy electrons (1 - 15 eV) impinging on a solid may excite electronic transitions or vibrational modes within chemical bonds near or at the surface. This interaction causes the electrons to lose energy in discrete amounts corresponding to the energy of the transition or excitation involved. This is the basis of high resolution electron energy loss spectrometry (HREELS) **[27]**. As HREELS experiments have been applied to molecular and polymeric surfaces with increased chemical complexity **[28-33]**, the ***sampling*** depth [the depth of excitation] and the ***information*** depth (the depth from which signals originate] have become important issues. Various empirical results have suggested the information depth may be as shallow as 2-5D to as deep as 20 D **[28-31]**. A critical aspect is the burgeoning understanding of vibrational excitation mechanisms in HREELS

The interactions between the primary electrons and the surface species leading to vibrational energy losses can occur by three mechanisms: dipole scattering, impact scattering and negative ion resonance **[34]**. These mechanisms determine the selection rules operating in the HREELS experiment. ***Dipole scattering*** is a long range interaction between the primary electron and the sample, on the order of 60 - 100 ≈. This mechanism is dominant when the experiment is run in the specular geometry. This selection rule is the same as for infrared external reflection spectroscopies **[32]**. When a dipole active mode is excited there is a change in dipole moment, and the vibrational mode is observed. In optical reflection spectroscopies with polarized radiation, when the dipole moment in a species is parallel to a metallic substrate, local electric fields are cancelled and vibrational excitation is not observed. Where the dipole moment is perpendicular to the substrate, the local electric fields are strengthened and the excitation is observed **[27,32]**. This "surface selection rule", common for optical vibrational spectroscopies at metal interfaces, also applies to HREELS used to study adsorbates on a metal **[27]**.

So called ***impact scattering*** is more prevalent when the experiment is run off specular or when higher energy primary electrons are used **[27]**. This mechanism is short range, on the order of a few ≈'s. In this event, all vibrations in a molecule can be excited. The cross section for scattering changes with the geometry of the experiment (specular vs off specular] **[27]**. The electrons inelastically scattered by this mechanism are broadly scattered such that fewer electrons are collected in the small acceptance angle of the analyzer. This diminishes the intensity of features due to impact scattering, as compared to the higher intensity of the dipole excited vibrations in the specular direction.

Resonance mechanisms were not reported in studies of small molecules adsorbed onto single crystal metals previous to 1982 **[27,p.10]**. Resonance or negative ion resonance occurs when the primary electron energy corresponds to the energy of an unoccupied molecular orbital (MO) (e.g. the Lowest Unoccupied Molecular Orbital (LUMO)) of the adsorbed or surface molecules. This allows primary electrons to be temporarily trapped in the MO. The captured electron can remain in resonance for 10^{-14} to 10^{-12} seconds. The exit of the electron from the MO causes excitation of vibrations which enhances the loss features due to that vibration **[27,33]**. Vibrational enhancement by resonance only occurs if the symmetry of the resonant state is compatible with the vibrational mode **[35]**: the shape of the intermolecular bond which captures the electron is changed as the electron leaves. When this shape change corresponds to a vibrational mode, enhancement occurs. Vibrational modes which already result from dipole scattering may be enhanced by this mechanism. Changing the primary electron energy, so as to be in resonance with the unoccupied MO, will affect the loss features if they are enhanced by negative ion resonance.

While resonance enhancement of adsorbed molecules and thin films has been reported **[31, 33,36]**, many questions are still unanswered regarding this mechanism. When resonance will occur is not firmly understood. Resonance enhancement of vibrations from functional groups such as CH_3 and CH_2 has been observed in different materials **[31,33,35,37]**. Whether the observation of enhancement of the same functionalities in several different compounds indicates that resonance enhancement can be predicted in similar cases is not known for certain. How resonance is affected by a material with many and various types of functional groups (for example: polymers or organic thin films) is a related concern. The extent or degree of enhancement for any given functional group or material is also not well understood. Resonance enhancement in adsorbed films is an

open research area with several groups working on the issues of concern **[29,31,33-37]**.

If a firm understanding of the contributions of these mechanisms to band intensity can be developed with predictive capability, the sensitivity and selectivity of HREELS for *organic, or polymer thin film analysis* would be improved. For instance, the ability to selectively excite particular functional groups through resonance enhancement would allow less complication for identifying structures within a complex spectrum comprised of signals from functional groups of less interest (e.g. CH_3 and CH_2). This high sensitivity for the topmost surface may be exploited, for example, in the analysis of polymeric **endgroup** effects at surfaces **[38]**.

B. Optical Vibrational Spectroscopy: FT-IR and Raman Methods

Vibrational spectroscopy has made an enormous leap in sensitivity over the last decade driven mainly by users who demanded the capabilities to investigate thinner and thinner films **[39]**. Polarized FTIR spectra using grazing incidence reflection from metallic surfaces can now be routinely obtained on films as thin as 15 angstroms with exceptionally good signal to noise ratios. With this kind of sensitivity it now becomes plausible to investigate the orientation and order of an adlayer of protein on the surface of a molecularly designed organic surface. Using the polarized nature of the infrared light it should be possible to assess the nature of the orientation of particular molecular groups and then determine their role in the adhesive process.

In a similar way Raman spectroscopy could be utilized to investigate proteins adsorbed on organic surfaces but, as yet, the sensitivity is somewhat lacking due to the fact that the Raman scattering cross section of a molecule is 8-10 orders of magnitude weaker than its absorption cross-section for the same normal mode. Recently however with the introduction of CCD Raman detectors which have quantum efficiencies approaching 80%, it should now be possible to investigate thin films and adlayers with this powerful technique which has been used very effectively to study protein conformation in both the solid state and in solution. The inherent advantage of Raman over FTIR is the non-destructive nature of the former and the lack of specific sample preparation required. In the future the increased sensitivity of CCDs in the red will provide the ability to use near IR lasers for Raman excitation thereby providing a means to avoid the fluorescence usually associated with small amounts of impurities which are found in native proteins. Hence fluorescent free Raman will then be routinely obtained. All in all, the future for the role of vibrational spectroscopy in unraveling the physics of protein adsorption and adhesion is exceptionally promising.

C. Surface Forces Measurements

Recent instrumental developments have allowed the measurement of the noncontact forces between molecules with the surface forces apparatus (SFA) and with an atomic force microscope (AFM). The SFA is a method which allows the direct measure of the molecular or atomic forces between surfaces **[40]**. With the SFA, the forces between the molecules on two opposing macroscopic surfaces are measured as a function of their separation distance; consequently, the full force law governing the material interactions is obtained directly **[40]**. The intersurface spacing is determined with single angstrom resolution by optical interferometry, and the force is measured with 0.01 nN resolution by measurement of the deflection in a sensitive spring supporting one of the surfaces. Thus, this resolution in both the force and distance measurements make possible the direct determination of the molecular forces governing molecular and surface interactions.

Atomic Force Microscopy (AFM) can be used to measure intermolecular forces between a silica sphere (attached to a cantilever tip) and a polished silica plate in aqueous electrolyte solutions **[41].** In recent developments related to the general problems associated with adsorbed polymeric species, Biggs and coworkers **[42,43]** have also studied the steric and bridging forces between surfaces bearing adsorbed polyacrylic acid. A silinized silica sphere and plate have also been used with AFM to obtain hydrophobic forces **[44].** Gaub et. al.**[45]** have measured the intermolecular forces and energies between ligands and receptors. Besides intermolecular forces, the predominant use of AFM is for imaging surfaces to obtain information about topology **[46].**

III. Advances in Methodology

A. ESCA

Three aspects of ESCA make it a desirable surface analytical technique for polymers. Qualitative information from chemical shifts allows the identification of surface functionality in a polymer. Quantitative analysis of the surface allows the determination of elemental and functional group concentrations. Finally, angle and energy dependent measurements allow this information to be determined for an in-depth profile; albeit with great difficulty due to the attenuation of signals from deeper depths. All of these aspects have been discussed in great detail for polymers previously **[2,3,5,7,8]**. However, the speed of newer instrumentation increases confidence in the measurement because of the lower amount of experimentally induced sample damage **[7]**. This allows extension to more complex samples. Further, this

lower damage allows for higher accuracy in the measurement.

A major advance sponsored by ONR work **[47-49]**, is the development of a method to extract the structure of polymer microdomains as a function of depth. In particular, it involves the transformation of concentration measurements taken as a function of sampling angle, from different depths, into a concentration depth profile. It is important to understand that the typical angle dependent ESCA results **[50-53]** allow for a quantitative analysis of the weight percentage of siloxane material (or any other component save trace impurities) at the topmost surface. The angle dependent experiments also give an indirect view of the change in composition as a function of depth over the topmost 100 D. This result is not a direct "in depth profile" of composition as a function of depth because of the effects of attenuation of the ESCA signal which confounds the result into an integral measurement. To recover the "in depth profile", deconvolution of the signal must be accomplished; previous work of this sort on polymers has suffered from the lack of knowledge of copolymer structure. The recent ONR sponsored work utilized a new approach to numerical solution of the deconvolution problem and resulted in depth profile data to be recovered. Typical examples are given in the final section on applications.

B. SIMS

Advances in SIMS methodology have been greatly accelerated by the interplay of the use of rational model systems and the development of new instrumentation. For the analysis of potential minimal fouling coatings, three specific foci can be examined which impact on the development of SIMS methodology. These constitute i) the model systems for the conditioning film or a simulation of the polymer surface using structured well prepared thin organic films, ii) the analysis of the "base" polymer materials themselves, and iii) analysis using spatial information in two or three (depth profile) dimensions. These will be reviewed separately.

i. The Study of Thin Organic Films

A critical factor to further use and understanding of SIMS is improved ability to predict the results of analysis using known features of ion formation mechanisms. Obviously, knowlege of both the presence and probability of ion formation would be helpful in qualitative and quantitative analysis. Prediction of the presence of particular ions from molecular species has been complicated by the matrix sensitivity. Put in simple terms, this means that the presence of a molecule in a particular environment does not guarantee the formation of a particular kind of molecular ion. Thus, much work is being accomplished to learn the surface chemistry which leads to the generation of simple molecular ion species. Of the huge body of work on ion formation mechanisms in molecular static SIMS, much is focussed on model systems using organic thin films on polycrystalline metal foils.

Langmuir-Blodgett (LB) films have been now extensively used as model system to study the SIMS sampling process for large organic molecules, to investigate secondary molecular ion formation mechanisms, and to develop a quantitative method for static SIMS **[53-62]**. The use of LB films as well-characterized model systems for SIMS analysis provides several advantages: (i) a highly regular and pure model system can be prepared, (ii) molecular orientations for large molecules are precisely determined, and (iii) modifications such as substrate changes, added cations, and most importantly the "physical state" of the monolayer can be changed by varying the applied surface tension during film production **[63, 64]**. In addition, techniques such as optical ellipsometry and reflection-adsorption infrared spectroscopy can corroborate the nature of the film **[64]**. The detection of molecular ions from a single (quantified) monomolecular layer demonstrates the promise of the LB technique for producing a homogeneous system of large molecules. These experiments illustrate the sensitivity of static SIMS to the chemistry of the molecular species and substrate, the "preionized state", and the final emitted molecular ion. Some of the studies have focussed on multilayer films produced by LB methods, which is a distinct advantage of the LB approach over adsorption or self assembly, mainly to address sampling depth issues **[54, 55, 59, 60]**. Methods to obtain quantitative molecular ion data from static SIMS analysis of LB films have also been published **[57, 58]**. The applications of SIMS to study self assembled monolayer (SAM) films have been more recent, and have focussed on applying SIMS to solve the chemistry of the films, rather than the use of the films as model systems **[65, 66]**. This series of studies illustrates the sensitivity of molecular ion formation to surface complexation and acid base chemistry, both seminal issues in adsorption of biological macromolecules.

ii. The Study of Polymers and Polymer Surfaces

The first applications of the static SIMS to the analysis of polymer surfaces, low mass (0-150 amu) fragment ions **[12]** were used to distinguish structure and isomerism (butyl methacrylates) in a series of methacrylate polymers with different side chain structures via fragmentation pattern from the sidechain, within a common pattern characteristic of the backbone, primarily from positive ion spectra. A significant result from these early studies was the differentiation of isomeric structures of butyl methacrylate, which could not be distinguished by ESCA core level analysis and the analysis of slight reactive surface degradations of the t-butyl methacrylate **[67]**.

Subsequent improvement in SIMS experimental conditions, to lower surface damage induced by the primary ion

bombardment, has allowed for the analysis of higher mass fragments that are related to the original structure of the polymer **[14-16]**.

Applications of the TOF-SIMS experiment to study high mass ions from nylons, polystyrenes, polydimethyl siloxanes and surface modified polymers **[8,17,68,69]** has presented information beyond characterization of the monomer identity. For instance, high mass oligomeric ions generating an accurate molecular weight distribution have been demonstrated **[8,68]**. The potential here is great; a **surface** sensitive molecular weight distribution would be extremely important for many polymer processing problems. High mass fragmentation patterns have been postulated to be sensitive to intrachain bonding in nylons **[8b]** and composition in complex polyurethanes **[70]**. Differentiation of isomeric differences is evident from high mass ions also **[8,68]**.

At masses in between the molecular weight distribution and the low mass fragmentation patterns from the monomer, ions generated from fragmentation along the chain into charge stabilized ions can be detected. These are termed "n-mer ions" **[13]**. These potentially have a great deal of information about intrachain bonding and chemical reaction sites. N-mer ions have been observed from a variety of polymers: teflon **[17]**, homopolymer and copolymer Nylons, and segmented poly(ether urethanes) **[15,71]**.

Focus on the mechanisms of formation of these three types of ions involves different considerations, as the information content of the ion increases with mass. However, the most current attention to the simple ability of static SIMS to differentiate the surfaces of polymer materials with equivalent atomic compositions and difficult ESCA chemical shift information has meant even great excitement about fragmentation pattern analysis.

Dynamic SIMS depth profile work has studied diffusion between isotopically labeled polymers **[72]**. In addition, a series of very exciting papers using dynamic SIMS depth profiling on block copolymer thin films by Russell et. al was recently described in overview **[73]**. From the monitoring of hydrogen vs. deuterium ion signals as a function of sputter time, a regular series of domain structures was measured where one domain was deuterated. This study employed highly controlled block length block copolymers. This work shows the power of focussing strictly on elemental ions in determining profiles; where unique isotopic tags can be used to identify one component, complex different ion formation mechanisms can be ignored. One nice aspect of the work by Russell, et al., is the correlation to ESCA and light and x-ray scattering. However, with these advances, much work remains to be done to identify exact conditions which describe sampling depth issues for ions other than atomic ions, and instrumental advances to further enhance the probability of formation and detection of high mass ions.

iii. Imaging Static SIMS of Organic Surface Chemistry

A recent application **[74]** was the use of imaging TOF-SIMS to demonstrate the selective surface chemistry on lithographically modified fluoropolymers using silane self assembly monolayer chemistry **[75]**. In this application, the chemically sensitive ion imaging provided the only means to contrast micron level modifications to the surface of a fluoropolymer. The surface modification was accomplished using masking techniques and plasma surface chemistry, followed by direct silane reaction, which was then limited to the lithographically modified regions. No electron microscopic or x-ray methods had the sensitivity to detect these chemical changes, yet neural cell biological model systems were quite sensitive to the spatial limitations. These results demonstrate that the micron level spatially restricted monolayer surface chemical modification could be directly visualized by imaging unique ion signals from the fluoropolymer and siloxane backbones. These materials provide wonderful test templates for examining biological adhesion to two common surface chemistries: fluoropolymers and siloxanes! These materials are being further developed under the ONR program to test bacterial and marine organism attachment in realistic environmental exposures.

This application of imaging for molecular species is just beginning, but where spatially restricted surface chemistry is necessary, static SIMS promises to provide one of the few chemically sensitive methods to complement scanning tunneling or atomic force microscopy of such films.

C. Surface Forces Apparatus

Within the laboratories of Professor Georges Belfort at Rensselaer Polytechnic Institute, SFA measurements are being applied to study the adsorption of exopolysaccharides to polymer surfaces. The technique involves the direct measurements of the intermolecular forces between two separate layers; one, an adsorbed protein or exopolysaccharide layer and the other a polymeric film. Each layer is deposited onto a smooth mica half-cylinder. The forces are obtained as a function of separation distance which is measured with an interferometry technique **[40].** Approaches are being implemented similar to that utilized to elucidate the intermolecular forces and conformation of adsorbed molecules between mica surfaces covered with surfactant **[76],** polymers **[e.g. 77]**, lipid mono and bilayers **[e.g. 78]**, and proteins **[79-82]** and glycolipids **[83]**. The thicknesses of these films can be determined from the *in-situ* inteferometry. The forces between the mica surfaces are obtained from a knowledge of the spring constant and the null distance without forces between the two surfaces.

IV. Development of Model Systems Sponsored by ONR

A number of approaches have been supported by ONR-MIMI towards the synthesis of model systems for polymer surfaces with specific properties in the control of structure in adsorbed biological macromolecules. A particular interest in several research groups is to develop surfaces with multiple chemical environments. These systems are also projected as potential coatings in contact with the entire marine biological environment. Most of this work relies on the development of polymer surface chemistry ***in concert with*** the development of measurements which can describe the particular structure and composition which effects particular macromolecular or marine biological outcomes.

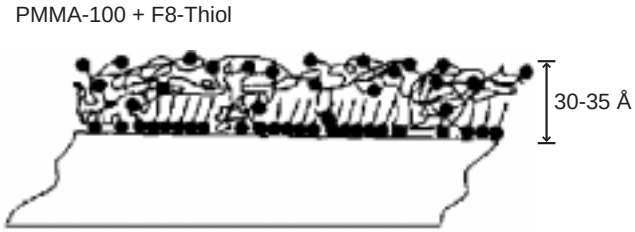
Research led by Professor Thomas McCarthy at the University of Massachusetts, Amherst, Department of Polymer Science and Engineering is part of fundamental work on organic chemistry at polymer surfaces and interfaces (particularly aqueous solution – organic polymer interfaces). The McCarthy group has developed (and continues to develop) new techniques for introducing specific organic functionality onto the surfaces of chemically resistant polymers – poly(chlorotrifluoroethylene), poly(tetrafluoroethylene), poly(vinylidene fluoride), poly(ether ether ketone), polyethylene – particularly in manners that the depth of the modifications can be controlled. The techniques are normally designed to place versatile and reactive centers in the outer few tens of angstroms of the polymer samples. The McCarthy research group studies the chemical reactivity of the surface-confined functionality and prepare series of samples with known structure and measure properties (adhesion, adsorption, coefficient of fraction, wettability) and draw structure-property correlations. Major current emphases are on (1) the preparation of surface mixtures of functionality (both random and patchy), (2) the adsorption of model polysaccharides (positively and negatively charged polyelectrolytes) from aqueous solutions to surfaces of known structure and (3) the modification of solid polymers by polymerization of supercritical solution-infused monomers. The overall goal of the research is to simultaneously understand the structure, properties and reactivity of polymer interfaces.

One approach to controlling the depth of incorporation of chemically reactive functional groups is to utilize heterogeneous (solid/supercritical fluid solution) free radical polymerization of styrene in supercritical carbon dioxide - swollen polymer films with the objective of preparing one polymer within another matrix polymer. This method may allow the control of the depth (into the film) of modification and the gradient structure of the interface, however thus far the conditions utilized (surprisingly) modify the entire polymer sample. Decompression followed by thermal initiation using AIBN or *tert*-butyl perbenzoate yields polymer blends with the polystyrene trapped inside the matrix polymer. Polymerization prior to decompression yields more extensively modified products. Conditions have been studied that render different concentrations of polystyrene throughout the thickness of film samples of poly(chloro trifluoroethylene), high density polyethylene, poly(4-methyl-1-pentene), nylon 66, poly(oxymethylene) and bisphenol A polycarbonate.

In the laboratories of Dr. John Rabolt of IBM Almaden Research Laboratories, new thin film materials are being synthesized to construct model polymer surfaces with various mixtures of controlled surface structure; the intent is to provide these surfaces for challenges by adsorbed biological macromolecules. Recently the synthesis of chemically derivatized polymers which contain side chain functionalized groups that promote chemisorption to metallic surfaces has provided the motivation to investigate both the adsorption kinetics from solution and topography produced during the self-assembling process. Initial studies on sulfur derivatized PMMA and poly(dimethyl siloxane) (PDMS) indicated that the effect of side chain modification on the diffusion coefficient in solution was minimal and independent of the "sticker" concentration. The surface morphology of the 30≈ films produced was either glassy (PMMA) or rubbery (PDMS) and quite porous raising the possibility of incorporating a second component through either a co-deposition or sequential deposition process.

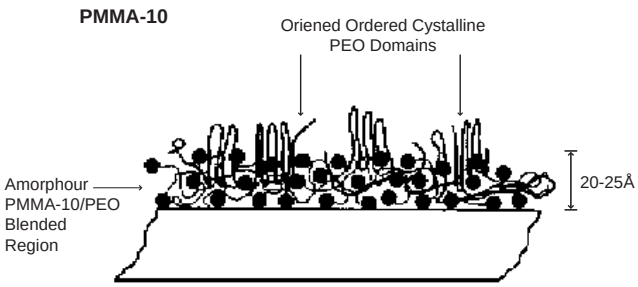
Using angular dependent XPS, contact angle, ellipsometry and FTIR it has been possible to investigate the deposition of a PMMA/PEO blend on a gold surface and the sequential deposition of PMMA and F8-thiol on gold. Both films are in the 20-30≈ range in thickness providing unique heterogeneous surface domain structures. Shown in Figure 1 is the morphology that results after a PMMA-100 self-assembled film is immersed in an F8-thiol/ethanol solution and then dried. This unique structure comes about due to the porosity of the PMMA-100 film, the relatively short length (17≈) of the F8-thiol and the tendency of F8-thiol to form domains with its molecular axis oriented normal to the surface.

Figure 1
Schematic diagram of the morphology formed by sequential deposition of PMMA-100 followed by dipping in a F8-thiol/ethanol solution.



In a somewhat analogous fashion, Figure 2 shows the resulting surface morphology when a PMMA-10/PEO blend is co-assembled on gold.

Figure 2
Schematic diagram of oriented crystalline PEO domains embedded in an amosphoase PMMA-10/PEO matrix.



Working in a relative concentration regime of the two polymers such that a semicrystalline blend results, it is interesting to note that not only do crystalline PEO domains form in this constrained geometry but that they are highly oriented with the PEO helical backbones normal to the substrate. Further co-deposition studies with other polymers compatible with PMMA are in progress in order to determine whether this observation is a more general occurrence in confined geometries.

In a related study, rubbery films of PDMS having various thiol side chain concentrations (1-3%, 5-10% and 100%) were also self assembled on gold in order to access the role of backbone mobility on surface topography. Preliminary results indicate that due to the low T_g., PDMS films are rubbery and still contain significant porosity. Angular dependent XPS indicates that nor all thiol groups are attached to the surface as was found in the case of sulfur derivatized PMMA. Studies of sequential deposition of F8-thiol in PDMS films is currently in progress so as to further ascertain the role of surface heterogeneity on protein adhesion.

The modeling of charged adsorbed macromolecules is under study in the McCarthy laboratory at Umass. This group is undertaking controlled adsorption studies of polyelectrolytes to a range of surfaces using the layer-by-layer adsorption method pioneered by G. Decher. A range of uronic acid-rich polysaccharides are adhesive to surfaces containing amines, but non-adhesive to other surfaces. Three model amine-containing surfaces and control experiments indicated that basic functionality is required for the adsorption of acidic polysaccharides. Poly(allyl amine hydrochloride) adsorbs spontaneously from aqueous solution to surfaces containing carboxylic acids or even esters – poly(ethylene terephthalate) functions well as a substrate. Poly(sodium styrenesulfonate) then can be adsorbed to the nascent poly(allyl amine hydrochloride) layer and this surface functions as an adsorption substrate for poly(sodium styrenesulfonate) then can be adsorbed to the nascent poly(allyl amine hydrochloride) layer and this surface functions as an adsorption substrate for poly(sodium styrenesulfonate) adsorption. This system provides two model substrates (positively and negatively charged) for adhesion experiments and that poly(allyl amine hydrochloride) and poly(sodium styrenesulfonate) are two useful model adsorbers for substrate testing. Additionally early experiments indicate that the mechanical integrity of these multilayers is high and may be the basis for an antifouling coating.

V. Applications of Analysis towards Candidate Non-Fouling Coatings

A. Assessing the near surface structure and dynamics of new multicomponent polymers

In the laboratories at SUNY Buffalo and the Naval Research Laboratory, collaborations between research groups headed by Professor J. Gardella and Drs. K. Wynne and T. Ho, ongoing ONR sponsored work involves both application and development of ESCA and ToF-SIMS. Results from the analysis of new polymer surfaces have lead to major breakthroughs in the development of these methods. These new experimental results have provided insight into fundamentals of phase separation and control of surface structure and composition through synthetic polymer design. The development of the new methods to quantitative analysis of polymer composition ***in depth*** using data recovered from angle dependent ESCA has been critical to the understanding of the structure and projected stability of the films toward degradation or aging effects. A centerpiece to this work was the systematic variation of bulk structure of the materials introduced in rational synthetic design. This provided a critical impetus for the work.

The synthesis **[47]** of the series of structurally controlled siloxanes shown here, the variation of the siloxane

(the so-called soft block) block length and the composition of the urea-urethane segmental block (the so-called hard block) gives a rich field of materials to evaluate to learn what structural or processing conditions controls success in surface properties (i.e. minimal fouling and stability). Both

composition and dimensional data of ***both*** the siloxane and urea-urethane components can now be determined, allowing for a three dimensional picture of the composition of the material near the surface. This means four characteristic parameters can be recovered from ESCA data to describe the surface chemistry of these materials. These are: i.) the surface composition (which, in comparison to the bulk composition yields the surface excess concentration of siloxane), ii.) the thickness of the surface excess layer, iii.) the composition of the subsurface urea-urethane rich region and iv.) the thickness of the subsurface layer. The urethane rich phase is simply the result of balancing the surface excess region of pDMS.

The significance of the detection and quantitative description of the in-depth profile can be seen in Figures 3 and 4. Both the structure, for example the block length of the siloxane, and processing, for example, annealing conditions, affect the resultant surface composition, and the in-depth profile.

For example, comparing a series of polymers with similar composition but different average siloxane block lengths, a pure siloxane surface (i.e. 100 weight % siloxane at the surface) over the topmost 10 D only occurs with the longest siloxane block lengths. This was a surprise, in that most of the materials contain large amounts of siloxane (between 70-96 weight %), yet shorter block lengths bring urea-urethane to the surface. The role of the amount of urea-urethane in the initial adhesive properties and the long term stability is of concern. However, it was interesting to note that extreme siloxane compositions and block lengths were necessary to produce a pure surface, which is only one initial consideration for utility of the material.

Encouraging results were obtained when, rather than annealing, more common coating processing conditions, differential solvent effects, were evaluated. It was shown that materials with shorter block lengths of siloxane (and better mechanical properties (*vide infra*)) would yield a pure siloxane surface after processing by annealing or more importantly, by judicious choice of solvent casting **[48]**. This portends very well for the development of these materials as potential coatings.

In related work on the same materials, Time of Flight SIMS has offered a new approach to the extraction of segment length distributions near the surface. As mentioned in the introduction, the ability to differentiate the molecular weight of species at the surface would explain a number of surface properties not predicted by compositional differences. The approach used, as references, thin submonolayer preparations of the difunctional prepolymer pDMS and the resulting segmented PU-PDMS copolymer, using silver as a substrate. This work shows that reasonable molecular weight distribution data can be obtained. Figure 5 shows a comparison of the high mass results from ToF-SIMS analysis of thin, submonolayer solution deposited films on silver. The resulting peaks originate from series of ions (sometimes up to four types of ions in series) in a pattern; the data must be assigned a structural series, and then converted to intensity values ***for one ion series which can represent the molecular weight distribution***. In the case of the pDMS prepolymer shown, with nominal average molecular weight of 1000 Da,

Figure 3
The Effect of Sample Processing on Depth Profile of Hard and Soft Segments: Recovered In Depth Profiles obtained from Angle Dependent ESCA Analysis of pU-pDMS Segmented Copolymers. The volume fraction of N containing polymer (i.e. the pU segment) is plotted versus the distance from the surface, one escape depth is approximately 25D. Curve A is for the pU-pDMS polymer with a 2400 nominal molecular weight for the pDMS segment, as cast from THF; curve B is for the same polymer after annealing at 120 EC for 15 minutes. Curve C is for the same polymer after annealing at 120 EC for 2 hours.

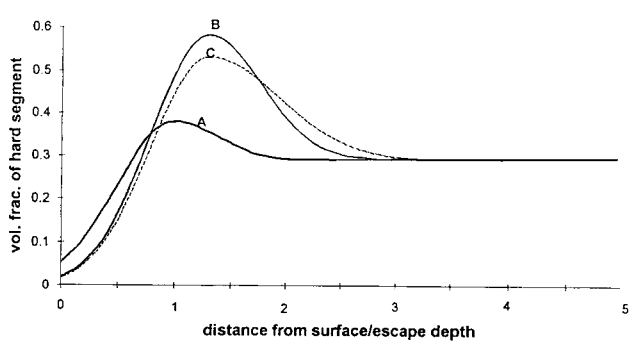


Figure 4
The Effect of Hard Segment Structure on the Surface Structure of pU-pDMS segmented Copolymers: Recovered In Depth Profiles obtained from Angle Dependent ESCA Analysis of pU-pDMS Segmented Copolymers. The volume fraction of N containing polymer (i.e. the pU segment) is plotted versus the distance from the surface, one escape depth is approximately 25D. Curve A is for the pU-pDMS polymer with a 10,000 nominal molecular weight for the pDMS segment, as cast from THF; curve B is for the same polymer after annealing. Curve C is for the 10, 000 MW pDMS copolymerized with a longer pU hard segment cast from THF, curve D for the same polymer after annealing.

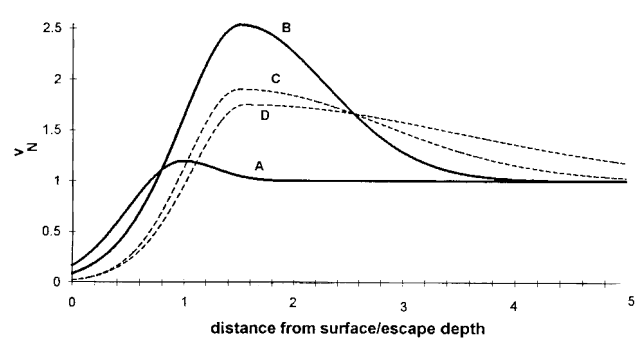


Figure 5
Comparison of ToF-SIMS High Mass Results from thin film preparations of A) 1000 MW pDMS prepolymer and B) pU-pDMS segmented copolymer with nominal 1000 MW pDMS segments.

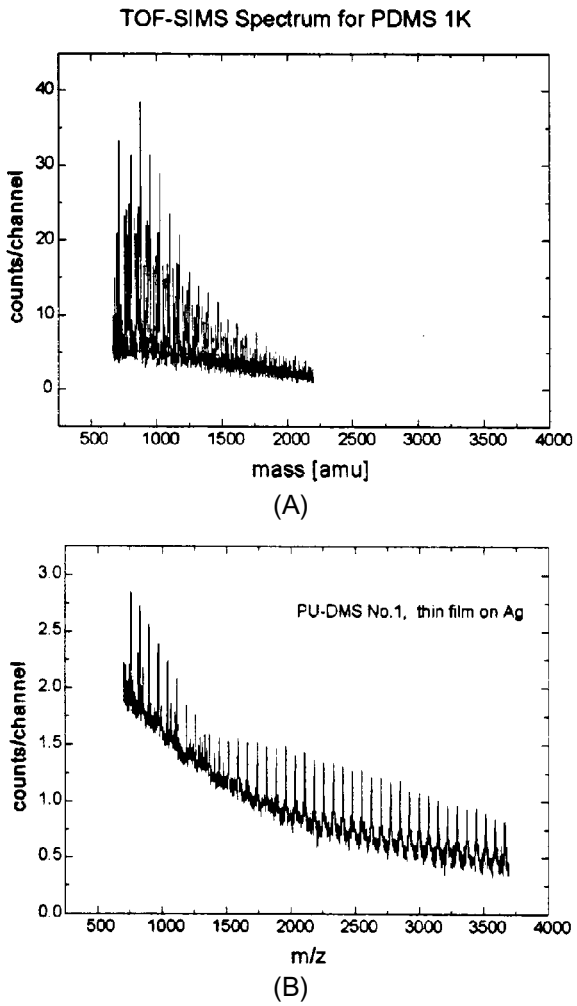
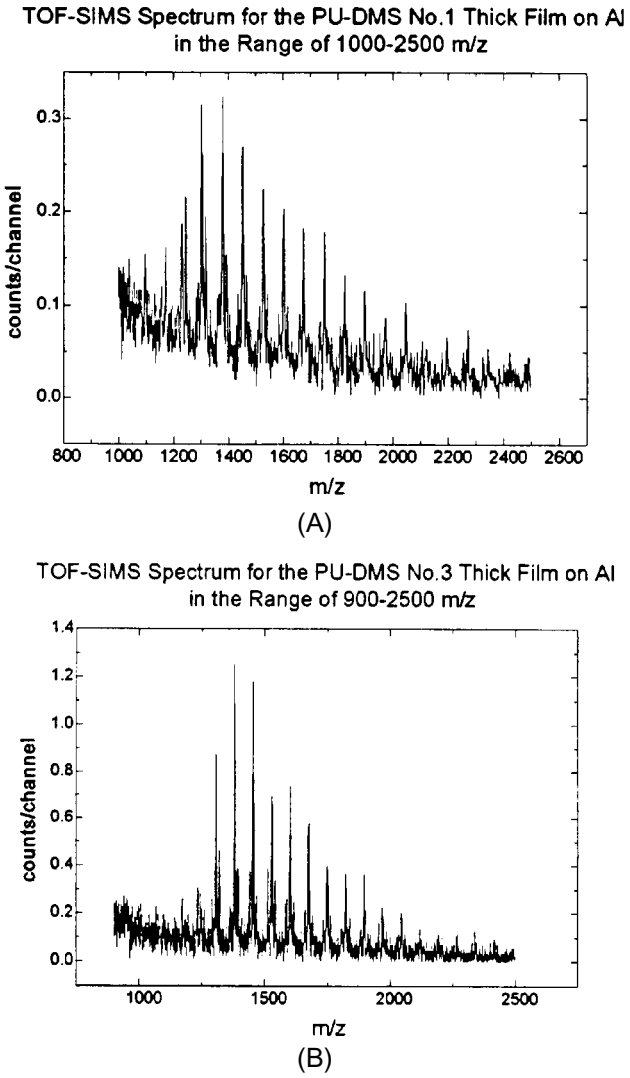


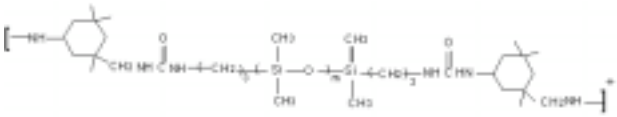
Figure 6
High Mass ToF-SIMS Results from thick films of pU-pDMS copolymers: A) pDMS MW = 1000; B) pDMS MW = 2400.



the entire molecular weight distribution should be available within the mass range presented. However, for the segmented pU-pDMS copolymer shown in the lower trace, the ion series shown are ***ions due to fragmentation processes***. Thus, these cannot represent a molecular weight distribution; in any case, the molecular weight of the copolymer is much higher than the region scanned.

However, what is important is not the molecular weight distribution of species in the copolymer, but the distribution of siloxane segments near the surface.

Normally, the analysis of thick, continuous polymer films, more representative of coatings involves sufficient chain entanglement and intrachain interactions so as to mediate against high mass ions being generated **[17]**. In this case, however, the volatility of the siloxane segment makes it a prime candidate for generation of fragment ions from the surface, despite solid state effects. High mass distributions from two different pU-pDMS copolymers were successfully measured where the segment length distribution of the siloxanes was varied by using different pDMS prepolymers **[47]**. In particular, polymers with average pDMS molecular weights of 1000 and 2400 were subjected to analysis, in the form of a solvent cast thick (ca. 100 um) films. High mass ToF-SIMS results are shown in Figure 6. Data was analyzed and the peak series assigned to the ion series represented by the structure shown below. Since it



contains the entire DMS segment, thus it can represent the DMS segment length distribution at the surface.

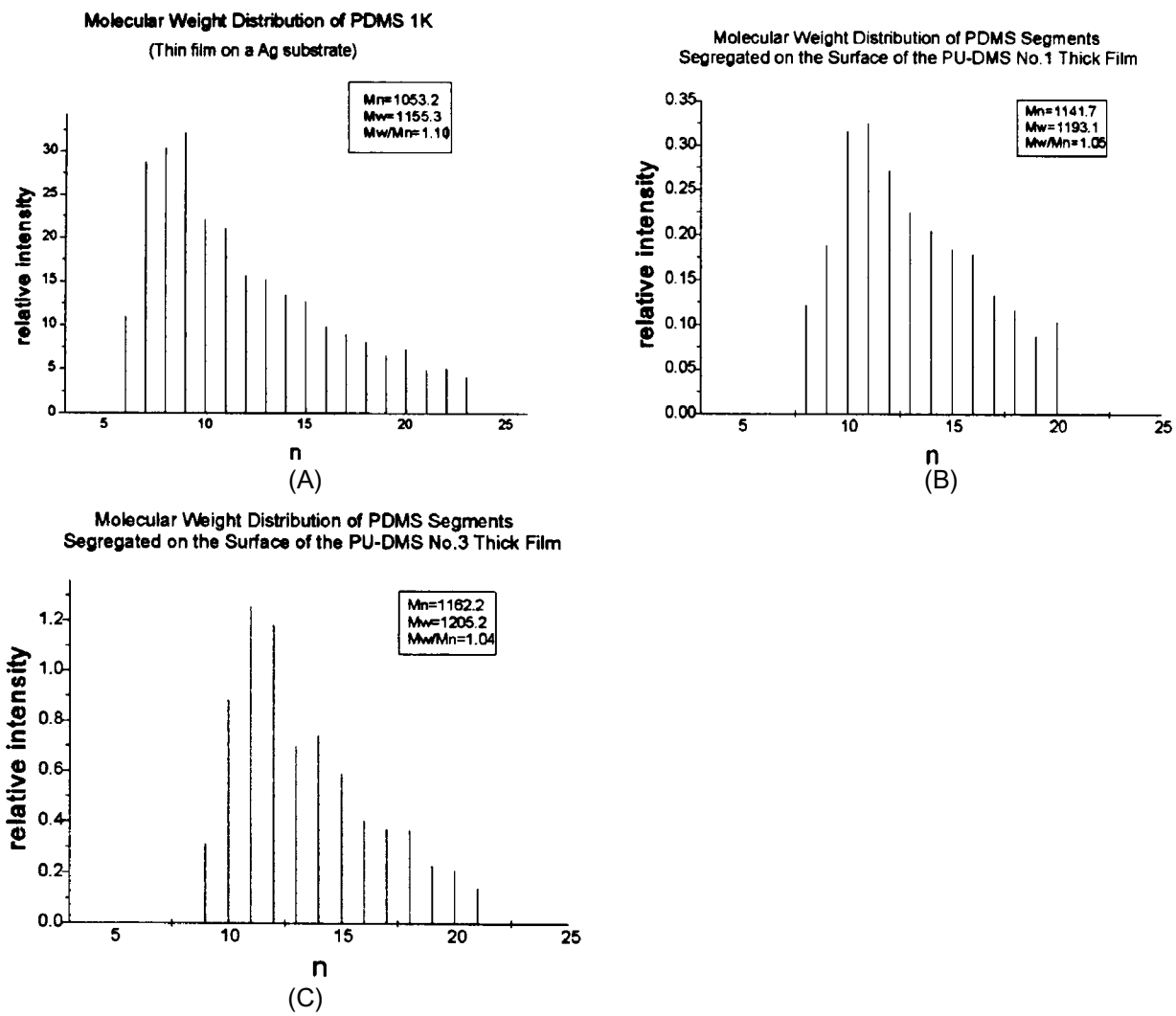
These ions were assigned to the structure series shown above. The resulting pDMS segment length distribution can be obtained because these fragments ***contain*** the intact DMS chain.

Figure 7 shows a comparison of the MW distribution obtained from the pDMS oligomer analysis on the thin films on silver (from spectrum in Figure 5a) to the segment length distributions obtained from analysis of data in Figure 6. It is evident that the change in molecular weight of the DMS ***does not*** change the distribution of pDMS segment lengths at the surface of the material. This means that the surface of the polymer synthesized with nominal molecular weight 2400 should not have different properties expected from the longer pDMS segments.

For the future of these applications there are numerous continuing challenges for the application of ESCA analytical methodology. Of course, the extension of this methodology to other polymer materials, chosen as candidate coatings and synthesized by ONR sponsored researchers is underway, in particular, fluorocarbon urethane polymers **[49, 83, 84]**. In addition, the ONR sponsored team has worked to extend the measurement to evaluate the surface compositional changes which may be due to marine exposure. To do this, recent efforts from SUNY Buffalo, sponsored by ONR-MIMI, have resulted in the development **[5]** of a sample handling probe which allows polymer samples in aqueous environments to be frozen below the glass transition temperature of the material, preserving the surface structure induced by the environment, for subsequent ESCA analysis. This can allow ESCA data to be measured for simu-

Figure 7

Comparison of MW Distributions obtained from ToF-SIMS Data: A) MWD calculated for pDMS MW =1000 thin film analysis; B) MWD calculated for pU-pDMS copolymer from thick film analysis pDMS MW = 1000; C) MWD calculated for pU-pDMS copolymer from thick film analysis pDMS MW = 2400.



lated marine exposures, to examine the long term structural stability and allow a fundamental description of environmentally induced changes in these materials. Only two research group in the world have developed such capability, and the Buffalo group is the first to apply this to study simulated marine exposures.

VI. Summary and Conclusion

In this paper, a short overview of recent developments in surface analysis of polymers is highlighted by the applications of these technologies to the development of minimal fouling coatings. The challenges presented by the design and synthesis of these new materials is a major driving force in new approaches to the use of the data and its interpretation. These demands also are supported by advances in new instrumentation and the design of model systems which are relevant to polymer surface chemistry.

VII. Acknowledgments

The authors acknowledge support from the Office of Naval Research Molecular Interactions at Marine Interfaces program and the contributions of postdoctoral fellows and graduate students who are supported by these funds.

Biographies

Dr. Joseph A. Gardella, Jr. was born and raised in Detroit, MI and graduated with a dual degree in Chemistry and Philosophy from Oakland University in Michigan, then matriculating for graduate studies in Analytical Chemistry at the University of Pittsburgh, where he received the Ph.D. with Professor David Hercules. After postdoctoral research with Professor E. M. Eyring at the University of Utah, he moved to SUNY Buffalo where he has been since. He spent one year as a program manager/visiting scientist at the National Science Foundation. He is currently Professor of Chemistry and Biomaterials and Director of the Materials Research Instrumentation Facility (MRIF) at SUNY Buffalo. His research efforts focus on the surface chemistry of polymer materials, especially those designed for contact with the environment and complex biological systems.

Dr. Kenneth J. Wynne, who earned his Ph.D. from the University of Massachusetts in 1965, is Program Manager, Organic and Polymeric Materials at the Office of Naval Research. Dr. Wynne's research interests include polymer surface design and characterization, polymers with novel optical properties, electronically conducting polymers and preceramic polymers. He has published over 80 papers, has co-edited three books, and has 10 patents. He is a member of the Editorial Advisory Boards of *Macromolecules*, *Journal of Applied Polymer Science*, *Journal of Inorganic and Organometallic Polymers*, and *Polymers for Advanced Technologies*.

Dr. Thomas J. McCarthy is currently Professor of Polymer Science & Engineering, Coprincipal Investigator for Center for University of Massachusetts Industry Research on Polymers (CUMIRP). Professor McCarthy received his B.S. in Chemistry from the University of Massachusetts at Amherst and the Ph.D. in Organic Chemistry from Massachusetts Institute of Technology, under the direction of George Whitesides. He has been at UMass in Polymer Science and Engineering since 1982. His research interests include polymer surface science, polymer synthesis and modification, reactions in supercritical fluid-swollen polymers, adsorption of polymers at interfaces, plasma polymerization, and the development of asymmetric gas separation membranes.

Dr. John F. Rabolt is currently Professor Chair of the Materials Science Program, at the University of Delaware. Previously, he was associated with IBM as a Research Staff Member at the IBM Almaden Research Center, where he was also Co-Director of the NSF Center on Polymer Interfaces and Macromolecular Assemblies, a collaboration between Stanford University, IBM and the University of California, Davis. Dr. Rabolt received his B.S. in Physics from SUNY Oneonta, and the Ph.D from Southern Illinois University in Molecular Physics. His research interests include polymer and molecular thin films, vibrational spectroscopy, polymer surface chemistry, physics and engineering.

Dr. Georges Belfort, Professor of Chemical Engineering and Director of the Bioseparations Research Center, received his Ph.D. degree in 1972 and his M.S. degree in 1969 from the University of California at Irvine in Engineering, his B.Sc. (Chemical Engineering) in 1963 from the University of Cape Town, Cape Town, South Africa. He has recently received the 1995 American Chemical Society Award in Separation Science and Technology, sponsored by Rohm and Haas Co. He is President of the North American Membrane Society, and was elected a fellow of the American Institute for Medical and Biological Engineering in 1994. Professor Belfort is an active consultant to industry in the USA, Europe and Japan on membrane technology and bioseparations. He has edited and coedited three books and written with colleagues and students 18 book chapters and over 90 reviewed papers.

REFERENCES

1a. Pireaux, J. J. *J. Elec. Spec. Rel. Phen.*, **1990**, 52, 423-45.
b. Dilks, A. *Anal. Chem*. **1981,** 53, 802A.
2. Nebesney, K. W.; Masschoff, B. L.; Armstrong; N. R. *Anal. Chem*. **1989,** 61, 469A.
3. Gardella, J. A., Jr. *Anal. Chem*. **1989,** 61, 589A.

4a. Gardella, J. A., Jr; Pireaux, J. J. *Anal. Chem*. **1990**, 62(11) 645A.
b. Schmitt, J. J.; Gardella, J. A., Jr.; Salvati, L., Jr. *Macromolecules*, **1989**, 22, 4489.
c. Vargo, T. G.; Gardella, J. A., Jr.; Meyer, A. E.; Baier, R. E., J. Polym. Sci., Part A: Polymer Chemistry, **1991**,29, 555-70.
5. Schamberger, P. S., Gardella, J. A. Jr., Grobe, G. L., III and Valint, P. L., Jr. "Optimization of Low Temperature Vitrification for Surface Analysis of Hydrated Hydrogel Polymers" *J. Vacuum Sci. and Technol. Part A*, submitted September, 1994.
6. Benninghoven,A.; Rudenauer, F.G.; Werner, H. W. In *Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications and Trends;* Elving, P.J., Wineforder, JD., Kolthoff, I.M., Eds.; John Wiley & Sons: New York, **1987**.
7a. Steffens, P.; Niehuis, E.; Friese, D.; Greifendorf, D.; Benninghoven, A. *J. Vac. Sci. Technol. A* **1985**, 3(3), 1322.
b. Benninghoven, A.; Niehuis, E.; Heller, T.; Feld, H. *J. Vac. Sci. Tech. A* **1987**, 5(4), 1243-1246.
8a. Bletsos, I.; Hercules, D. M.; van Leyen, D.; Benninghoven, A. *Macromolecules* **1987**, 20, 407.
b. Fowler, D.; Johnson, R.; van Leyen, D.; Benninghoven, A. *Anal. Chem.* **1990**, 62, 2088-2092.
9. Benninghoven, A. *Z. Phys.* **1970** 230, 403.
10. Benninghoven, A.; Jaspers, D.; Sichtermann, W. *Appl. Phys.* **1976** 11, 35.
11. Benninghoven, A.; Sithermann, W. K. *Int. J. Mass Spec. Ion Phys.* **1977** 12, 595
12a. Gardella, J. A., Jr.; Hercules, D. M. *Anal. Chem*., **1981**, 53(12), 1879-1884.
b. Gardella, J. A., Jr.; Hercules, D. M., *Anal. Chem*., **1980**, 52(2), 226-232.
13. Hook, K. J.; Hook, T. J.; Wandass, J. H.; Gardella, J. A., Jr., *Applied Surface Science*, **1990**, 44, 29-41.
14. Briggs, D. SIA, *Surf. Interface Anal*. **1986**, 9, 391.
15. Briggs, D. *Org. Mass Spectrom.* **1987**, 22, 91.
16. Brown, A.; Vickerman, J.C. *SIA, Surf. Interface Anal.* **1986** 8, 75.
17. Bletsos, I. V.; Hercules, D. M.; Magill, J. H.; van Leyen, D.; Niehuis, E.; Benninghoven, A. *Anal. Chem.* **1988**, 60, 938.
18. Benninghoven, A.; Sichtermann, W. M. *Anal. Chem.* **1978**, 50, 1180.
19. Benninghoven, A.; Sichtermann, W. *Int. J. Mass Spectrom. Ion Phys.* **1981**, 38 **351.**
20. Colton, R. J., J. E. Campana, D. A. Kidwell, M. M. Ross and J. R. Wyatt, *Appl. Surf. Sci.*, **1985**, 21, 168.
21. Chait, B. T. and K. G. Standing, *Int. J. Mass Spectrom. Ion Phys.* **1981**, 40, 185.
22. Demirev, J. K. Olthoff, C. Fenselau and R. J. Cotter, *Analytical Chemistry*, **1987**, 59, 1951.
23. Barber, M., R. J. Bordoli, R. D. Sedgwick and A. N. Tyler, *Nature*, **1981**, 293, 270.
24a. Macfarlane, R. D. and D. F. Torgerson, *Science*, **1976**, 191, 920.
b. Macfarlane, R. D., *Accounts of Chemical Research*, **1982**, 15, 268.
25. Hillenkamp, F., M. Karas, D. Holtkamp and P. Klusener, *Int. J. Mass Spec. Ion Phys.* **1986**, 69, 265.
26. Pachuta, S. J. and R. G. Cooks, *Chem. Rev*., **1987**, 87, 647.
27. Ibach, H.; Mills, D.L. *Electron Energy Loss Spectroscopy and Surface Vibrations;* Academic Press: NY 1982.
28. Wandass, J.H.; Gardella, J.A., Jr. *Surface Science Letters*, 150, **1985**, L107-L114.
29. Pireaux, J.J.; Gregoire, Ch.; Vermeersch, M.; Thiry, P.A.; Caudano, R. *Surface Science*, , **1987**, 189/190, 903 - 912.
30. Wandass, J.H.; Gardella, J.A., Jr. *Langmuir*, **1986**, 2, 543 - 548.
31. Wandass, J.H.; Gardella, J.A., Jr. *Langmuir*, **1987**, 3, 183 - 188.
32. Debe, M.K. *Progress in Surf. Sci.*, **1987**, 24(1-4), 1 - 282.
33. Apai, G.; McKenna, W.P. *Langmuir*, **1991**, 7(10), 2266 - 2272.
34. Palmer, R.E.; Rous, P.J. "Resonances in Electron Scattering by Molecules on Surfaces" *Reviews in Modern Physics* **1991**, 1
35. Schreck, M.; Abraham, M.; Gopel, W. *Surf. Sci. Lett.*, **1990**, 237, L405 - L410.
36. McKenna, W.P., Apai, G. *J. Phys. Chem.*, **1992,** 96, 5902-7.
37. DiNardo, N.J.; Avouris, Ph.; Demuth, J.E. *J. Chem. Phys.* **1984**, 81(4), 2169-80.
38. Botelho do Rego, A. M.; Lopes da Silva, J. D.; Rei Vilar, M.; Schott, M.;. Petitjean, S.; . JÈrÙme, R. *Macromolecules*, **1993**, 26, 4986-88.
39a. Koenig, J. *Polym. Mater. Sci. Eng.* **1991** 64 27.
b. Chase, B. *Polym. Mater. Sci. Eng.* **1991** 64 189.
40a. Israelachvili, J. N.; Adams, G. E.; *J. Chem. Soc. Faraday Trans*., **1978** 74 975-1001.
b. Spinke, J.; Liley, M.;. Schmitt, F.-J ; Guder,M.;. Angermaier L ; Knoll, W. *J. Chem. Phys.* **1993** 99, 7012.
41. Ducker, W. A., Senden, J. J.;Pashley, R. M., *Nature*,**1991** 353, 239 , Ibid, *Langmuir*, **1992** 8, 1983.
42. Biggs, S.; Healy, T. W., "Electrosteric stabilization of colloidal zirconia with low MW polyacrylic acid: An AFM study", *Farad. Trans*., **1994** in press.
43. Biggs, S., "Steric and bridging forces between surfaces being adsorbed polymer: An AFM study", *Langmuir,* **1994** in press.
44. Rabinovich Ya, I.;Yoon, R. H., *Langmuir*,**1994** 10, 1903.

45. Moy, V. T., Florin, E-L. and Gaub, H. E., *Science*, **1994** 266 257-259.
46. Haggerty, L. and Lenhoff, A. M. "STM and AFM in Biotechnology", *Biotechnology Progr*., **1993** 9, 1-11.
47. Chen, X.;Gardella, J. A., Jr.,Ho, T.; Wynne, K. J. *Macromolecules*, **1995**, 28, 1635-42.
48. Ho, T.; Wynne, K. J.; Gardella, J.A., Jr.; Zhuang, H.-Z.; *J. Coll. Interf. Sci*., **1995**, in press.
49. Gribben Marra, K.; Zhuang, H.-Z.; Ho, T.; Chapman, T. M.; Gardella, J. A., Jr.; *Macromolecules*, manuscript in preparation.
50. Chen, X.; Lee, H. F.; Gardella, J. A., Jr.,. *Macromolecules*, **1993**, 26, 4601-4605.
51. Chen, X.; Gardella, J. A., Jr; Cohen, R. E.; *Macromolecules*, **1994**, 27, 2206-10.
52. Chen, X.; Gardella, J. A., Jr., *Macromolecules*, **1994**, 27, 3363.
53. Wandass, J. H.; Gardella, J. A. ,Jr. *J. Am. Chem. Soc.* **1985,** 107, 6192.
54. Wandass, J. H.; Schmitt, R. L.; Gardella, J. A., Jr., *Applied Surface Science*, **1989**, 40, 85-96.
55. Cornelio-Clark, P.; Gardella, J. A., Jr. *Langmuir* **1991**, 7, 2279.
56. Hook, K. J.; Gardella, J. A., Jr., *J. Vac. Sci. Technol.*, **1989**, A7(3), 1795.
57. Cornelio P. A.; Gardella, J. A. Jr. *J. Vac. Sci. Technol.*, **1990**, A8(3), 2283.
58. Cornelio-Clark, P. A.; Gardella, J. A., Jr. *Langmuir*, **1991**, 7, 2454.
59. Johnson, R. W., Jr.; Cornelio-Clark, P. A.; Gardella, J. A. , Jr. in "ACS Symposium Series No. 493, *Macromolecular Assemblies in Polymeric Systems*; Stroeve, P.; Balazs, A., Eds.; American Chemical Society: Washington, **1992**; p113.
60. Johnson, R. W., Jr.; Cornelio-Clark, P. A.; Li, J.-X.; Gardella, J. A., Jr. in *Secondary Ion Mass Spectrometry (SIMS) VIII*, Benninghoven, A.; Evans, C. A.; Janssen, K. T. F.; T·mpner, J.; Werner, H., Eds., John Wiley and Sons, New York, NY, **1992**, 293-6.
61. Bolbach, G.; Plissonnier, M.; Galera, R.; Blais, J.; Dufour, G.; Roulet, H., Thin Solid Films, **1992**, 211, 524.
62. Hagenhoff, B.; Deimel, M.; Benninghoven, A.; Siegmund, H.; Holtkamp, D. *J. Phys. D: Appl. Phys.* **1992**, *25*, 818.
63. Langmuir, I.; Blodgett, K. B. *Phys. Rev.* **1937,** 51, 317.
64. *A Guide to Ultrathin Organic Films*; Ulman, A., Ed.; Academic Press: Boston, **1991**.
65. Tarlov, M.; Newman, J. *Langmuir* **1992**, 8, 1398.
66. Li, Y.; Hung, J.; McIver, R.; Hemminger, J. *J. Am. Chem. Soc.* **1992**, 114, 2428.
67. Gardella, J. A. Jr.; Novak, F. P.; Hercules, D. M.; *Anal. Chem*. **1984**, 56, 1371.
68. Bletsos, I. V., D. M. Hercules, D. Greifendorf and A. Benninghoven, *Anal. Chem*., **1985**, 57, 2384.
69. Bletsos, I. V., D. M. Hercules, D. van Leyen, B. Hagenhoff, E. Niehuis and A. Benninghoven, *Anal. Chem*. **1991**, 63, 1953.
70. Bletsos, I. V., D. M. Hercules, D. vanLeyen, A. Benninghoven, C. G. Karakatsanis, J. N. Rieck, *Anal. Chem*. **1989**, 61, 2142.
71. Hearn, M. J., B. D. Ratner, D. Briggs, *Macromolecules* **1988**, 21, 2950.
72. Valenty, S. J., J. J. Chera, D. R. Olson, K. K. Webb, G. A. Smith, W. J. Katz, *J. Amer. Chem. Soc.*, **1984,** 106, 6155.
73. Russell, T. P., V. R. Deline, V. S. Wakharkar, G. Coulon, *MRS Bulletin*, **1989**, XIV(10), 33.
74. Vargo, T. G.; Thompson, P. M.; Gerenser, L. J.; Valentini, R. F.; Aebischer, P.; Hook, D. J.; Gardella, J. A., Jr., *Langmuir*, **1992**, 8, 130.
75. Hook, D. J.; Vargo, T. G.; Gardella, J. A., Jr.; Litwiler, K. S.; Bright, F. V., *Langmuir*, **1991**, 7, 142.
76. Israelachvili, J. N.; Pashley, R. M.; *Nature*,**1982**, 300, 341-343.
77. Israelachvili, J. N.; Tirrell, M.; Klein, J.; Almong, Y.; *Macromolecules*,**1984**, 17 204.
78. Chen, Y. L.; Helm C. A.; Israelachvili, J. N.; *Langmuir*,**1991**, 7 2694-2699.
79. Leckband, D. E.; Israelachvili, J. N.; Schmitt, F. J.; Knoll, W.; *Science*, **1992**, 255 1419..
80. Lee, C. S.; Belfort, G.; *Proc. Nat'l. Acad. Sci.*, **1989**, 86, 8392-8396.
81. Belfort, G.;Lee, C. S.; *Proc. Nat'l. Acad. Sci.*, **1991,** 88, 9146-9150.
82. Leckband, D. E.; Israelachvili, J. N.; *Microb. Techno.*,**1993,** 15, 450-459.
83. Luckham, P.; Wood J.; Swart, R.; *J. Coll. Intf. Sci.*, **199,** 156,173-183.
84. Chapman, T. M.; Gribben, K.L.; *Macromolecules*, **1993**, 26, 7029
85. Chapman, T. M.; Gribben Marra, K.; *Macromolecules*, **1995**, 28, 2081

Exterior Hull Coatings in Transition: Antifouling Paints and Fouling Release Coatings

James R. Griffith and John D. Bultman, Naval Research Laboratory, Washington, DC

Introduction

Some of the facts regarding the ease or difficulty with which ships move through the water are intuitively obvious while others require complex hydrodynamic insights. Among the obvious facts is that a smooth surface moving parallel to the aqueous medium presents less drag than a grossly rough surface of the same dimensions. The tendency of marine organisms to attach to surfaces and render smooth areas rapidly rough has plagued sea-faring nations throughout history. It is no exaggeration to say that modern merchant marines and navies can not afford to leave port with heavily fouled hulls.

A new factor which has caused a major perturbation in traditional methods of dealing with marine fouling organisms may be called "environmental consciousness". The established technique to prevent fouling is to supply the water near a hull surface with a sufficient concentration of a broad spectrum toxicant to prevent colonization. The toxicant has been supplied by leaching from the hull paint. As long as there were relatively few ships in vast quantities of ocean, this was a logical and rather effective technology, but with the coming of millions of pleasure boats in the harbors of the world in addition to large numbers of commercial vessels, the looming prospect of biologically dead coastal and inland waters forced new thinking.

Since the introduction of *Teflon™ to the general public as an antistick coating for cooking utensils, would-be inventors have dreamed of coating the exterior hulls of ships with substance so that "barnacles would fall right off". Such an antiadhesive coating is known as a "fouling release coating", and, in principle, it has a number of very attractive features such as absolutely no environmental degradation and long, effective life. However, efforts to implement this concept in a practical manner is fraught with many difficulties, and this paper is intended to outline such efforts at the Naval Research Laboratory since the early 1970's.

Factors Affecting Marine Adhesion

Ultimately, the strength of the bond between as adhesive and any surface depends upon constitutional factors;

*Teflon™ is a trademark of the DuPont Company

that is, the chemical compositions of the components.[1] Less basic considerations such as surface roughness which results in a mechanical locking of adhesive to adhered may be important, also. The ability of an adhesive in liquid form to wet a solid surface can have a dramatic effect upon subsequent bond strength, and this ability, or lack thereof, is also controlled by constitutional factors.[2]

Very few classes of synthetic polymers hold any promise for being sufficiently antiadhesive that all marine organisms bond with minimal tenacity. The various species of barnacles, which are arguably the most important fouling organisms, can bond with great holding power to epoxies, polyurethanes, alkyds, polyesters, polysulfides, and practically all other common coating types. Only the fluoropolymers such as Teflon™, and the silicones offer possibilities for practical coatings. Polymeric hydrocarbons such as polyethylene and polypropylene hold some promise but lack necessary convenience-of-use characteristics to be seriously considered.

The cement with which a barnacle attaches its basal plate to a substrate has been studied extensively,[3,4] and the general belief that it is some sort of miracle glue notwithstanding, it is merely a specialized polypeptide composition which owes as much to its unique manner of deposition as to its constitutional makeup. The overall process is so efficient, however, that there is no known solid substance that the barnacle can not adhere to with some degree of binding. Also, the amount of adhesive strength required to sustain a close packed field of barnacles to a surface is worrisomely small. Extensive efforts have been made to put hard numbers on barnacle adhesive values.[5,6] But the variabilities in this effort which may include the general health of the individual organism and small mechanical imperfections in the adhesive layer, among other factors, make it not so simple as it may appear upon first consideration. A barnacle lifted perpendicularly to the plane of the surface experiences a suction cup effect which is roughly proportional to the basal area and the effort to slide a barnacle laterally poses questions of force distribution and possible torque leveraging. Thus, the problem of getting at the basic data upon which to mount efforts to make ultimate fouling release coatings are sufficiently daunting before the synthetic polymer chemist starts his chore.

Fluoropolymer Fouling Release Coatings

A report published in the December 1973 issue of Naval Research Reviews discussed the basic synthesis efforts on what later became known as "functional fluoropolymers". These were heavily fluorinated epoxy and polyurethane materials which were designed to add convenience to Teflon™-like substances. Shortly after the publication of that article, NRL was requested to provide advice to the Norfolk Naval Shipyard regarding the preservation of a highly valued harbor tug of World War II vintage which was deemed to be irreplaceable. The shipyard was informed that a very heavily fluorinated paint had been developed which we were certain would provide near ultimate corrosion protection to the hull because of its extremely low equilibrium water absorption values and excellent physical properties such as toughness, adhesion, and abrasion resistance. The head of the Production Engineering Department at the shipyard sprayed the external underwater hull of this vessel, called the Sea Mule. Thus, a Teflon™-filled, fluorinated polyurethane paint intended to provide long-term corrosion protection introduced NRL to experimentation on the fouling release concept. The shipyard could easily lift the Sea Mule from the water, and a regular series of cleaning experiments were performed during the following 13 years.

Although the Sea Mule coating performed its original mission almost to perfection, it suffered drawbacks as a fouling release coating. The barnacles in Norfolk harbor were able to roughen the surface with their sharp shell edges, and the mature barnacles could adhere to the uneven paint with excessive strength, disallowing easy removal. In the case of this coating the damage was shallow and it was never breached down to the unfluorinated underlying paint. However, the ability of the barnacle to express this type of action is a serious threat to the fouling release concept and a substantial difference in the ability of various silicone coatings to resist this intrusion has been observed. At present it is not certain which physical factors such as toughness, deform ability, coefficient of friction, tear resistances, etc. determine the result. If there is a defect in the coating such that the immature barnacle can achieve a solid attachment, any silicone will be underminded at that spot.

It was found during a decade of work on fluorinated surfaces of other types that barnacles can adhere with surprising force to any such surface including that of Teflon™. Since critical surface tensions below 10 dynes/cm can be attained with such materials, the lowest known, it remains a mystery why they are not better than they are. Our best present guess is that there is a highly localized polarity to the carbon-fluorine bond which allows very polar groups in barnacle cement to develop a close association over time.

Silicone Fouling Release Coatings

Patents have been issued for silicone fouling release coatings since the early 1970's, and there is presently a substantial number of U.S. and foreign patents on this subject.[8,9] The empirical observation is that certain silicones are the most antiadhesive substances known for hard fouling organisms in general although this has not been adequately explained in basic constitutional terms and all silicones are by no means equal in this property. Generally, the silicones

that are the most effective are weak, "cheesy" materials which are easily torn and have very poor qualities to be paint-like compositions. Most of the best commercially available materials were compounded to be molding compositions, and they have excellent antiadhesive properties for all synthetic casting resins, such as epoxies. Early efforts to use them as fouling release surfaces normally involved heat-cured compositions or "wall paper" techniques in which sheets of a preformed materials were adhesively bonded to substrates. Neither method was sufficiently convenient for use as ship hull coatings.

In addition to the weak nature of the best releasing silicones, there was the nontrivial question of how an extremely antiadhesive substance could be bonded to a substrate with such tenacity that it could provide long term service as a hull coating. Several early experiments at NRL in which the hulls of small boats were coated suffered premature failure because the rubbery silicone releasing surfaces came off in sheets after brief cruising.

These inherent problems with the silicones were eventually addressed effectively with what has become known as a "duplex" approach. Certain polymeric materials which contain components in addition to silicone are exceptionally tough and tear resistant. One of the best contains a styrene-butyl acrylate copolymer which is compatible with the silicone components and which serves as a very effective reinforcing agent.[10] This composition is not a good antiadhesive top coating, but it is a near perfect transition layer because of the strength of the bonding that can be developed with epoxy substrates and with releasing silicone top coats. Its use in conjuction with the better top coats imparts a "pseudo toughness" to the entire system because the top coat can only be removed destructively.

Many secondary problems are encountered in an effort to make silicone molding compounds into practical marine paints. These include such things as flow and drip control, spray ability, gel and cure times, volatile organic component (VOC) restrictions, repair and recoat consideration of cost since the silicones are among the most expensive synthetic materials on the general market for caulks, sealants adhesives, etc.

Additives for Hull Coatings

Various materials have been added to silicone hull coatings in order to enhance the antiadhesive properties or to impart an antifouling capability to the fouling release layer. The addition of an oil which slowly exudes to the surface provides a thin, liquid layer to enhance antiadhesive properties, and methyphenyl silicone has been an effective additive.[11] Extensive efforts have been made to identify naturally antifouling agents found in various sea organisms in the hope that an analog or a portion of their unusually complex molecular structure will prove to have efficacy as a coating component.[12] This approach has the particularly attractive feature that the agents preventing fouling may not need to be generally toxic. Organic toxicants[13] usually referred to as "co-biocides" can be used effectively in silicones to provide a temporary antifouling capability which is backed up by a fouling release nature. The antiadhesive outer layer is not particularly hospitable to sea creatures by its physical nature, and the dose of an organic toxicant required to keep it clean in the sea may be minimal as a consequence. In general, an organic toxicant for this purpose needs to be "broad spectrum" in that it prevents settlement of plant or animal species, and it also needs to degrade rapidly once it is free in the sea to produce harmless products. Very favorable results have been obtained recently at NRL using this approach and test panels in Chesapeake Bay for a year have been effectively antifouling while retaining a strong fouling release nature as the active ingredients became depleted.

Laboratory Simulation of Barnacle Adhesion

The population of marine fouling organisms vary seasonally in much of the world and the numbers of a given species are not constant from season to season. When a new fouling release surface is developed, it is highly desirable to know quickly whether or not an improvement in fouling release performance has been achieved, and the prospect of waiting for months for the answer makes for slow and inefficient progress.

In an effort to address this problem, albeit not perfectly, the concept of the "pseudobarnacle" was developed at NRL. As alluded to above, the constitutional makeup of barnacle cement is rather mundane and if the creature could exude a two-component epoxy under his growing shell edge he would very likely be bonded to surfaces with greater tenacity. Because of this belief, it was thought that a two-part epoxy putty formed into a small ball and pressed onto a fouling release test surface to give a barnacle-shaped mass, may, upon curing, give an adhesive value that could correlate with field results on barnacles. A preferred material for the test is a product of the Dexter Corporation with the trade name "EPOXI-PATCH" and the "1C WHITE" version has been used most extensively. An extensive evaluation of this concept is underway at the Florida Institute of Technology and the preliminary results indicate useful correlations at the lower, more important end of the anti-adhesive scale.

Concluding Remarks

Significant progress has been made in the generation of radically new exterior hull coatings for undersea surfaces which are more "environmentally friendly" than traditional antifouling paints. Whether or not these coatings will be

operationally ready in the near future depends upon a multitude of considerations not the least of which is a reluctance to abandon established old ways for uncertain new ones. Nevertheless, the last few years have seen a determined effort by NRL, with ONR support, to make such paints long-lasting and effective.

Acknowledgments

This work was supported by the Office of Naval Research.

Biographies

Dr. James R. Griffith is a supervisory research chemist at the Naval Research Laboratory in Washington, DC. He received the Ph.D. degree at the University of Maryland where he studied polymer chemistry with Professor William J. Baily. His research interests have emphasized polymer synthesis related to materials interests of the Navy with long-term programs in fluoropolymers and fuel resistant elastomers.

Dr. John D. Bultman is a research chemist at the Naval Research Laboratory in Washington, DC. He received the Ph.D. degree at Georgetown University in physical biochemistry. His research interests have included the surface chemistry of proteinaceous materials, anti-submarine warfare problems, biodeterioration of materials in the marine and terrestrial environments, the natural resistance of tropical hardwoods destroyers, and commercial utilization of byproducts resulting from the isolation of natural rubber from guayule.

REFERENCES

1. W.A. Zisman, Ind. and Eng. Chem., **55**, 18 (1963).
2 W.A. Zisman, J. Paint Tech., **44**, 41 (1972).
3. J.R. Saroyan, E. Linder, and C.A. Dooley, Proc. 2nd Int. Congr. Marine Corrosion and Fouling, 495 (1968).
4. J.R. Saroyan, E. Linder, and C.A. Dooley, Biol. Bull., **139**, 333 (1970).
5. J.D. Bultman, J.R. Griffith, J.D. Bultman, and H.L. Vincent, Biofouling, **6**, 105 (1992).
6. G.W. Swain, J.R. Griffith, J.D. Bultman, and H.L. Vincent, Biofouling, **6**, 105 (1992).
7. J.R. Griffith, D.E. Field, Nav. Res. Reviews, **15**, (Dec. 1973).
8. W. Muller and L. Nowacki, U.S. Patent 3,702,778 (1972).
9. R.R. Brooks, U.S. Patent 5,017,322 (1991).
10. J.C. Getson, U.S. Patent 3,776,875 (1973).
11. A. Milne and M.E. Callow, Trans. I. Mar. E., 229 (1985).
12. N.M. Targett and W.R. Stochaj, *Recent Developments in Biofouling Control*, Oxford and IBH Publishing Co., New Delhi, 221 (1994).
13. J.A. Dupont, U.S. Patent 4,127,687 (1978).

Silicon Fouling Release Coatings

Harold L. Vincent, HV Enterprises, Midland, MI
Gregory G. Bausch, Dow Corning Corporation, Midland, MI

Background

Because of concerns about the toxicity of the biocides used in antifouling coatings, a need has emerged for a non-toxic approach to the control of marine fouling. Antifouling coatings based on copper oxide have been used for many years to effectively control marine fouling. As copper oxide and other biocides dissolve in the water, an exponential release rate is observed and less biocide is available over time. (1) In the mid-1970's a significant advance was made with the organotin copolymer based self-polishing coatings which provided five years or more of fouling control. These copolymers contained tributyltin chemically bound to the polymer backbone. During service, the tributyltin antifouling agent was released at a constant rate and the resulting polymer backbone would erode or polish due to the motion of the ship through the water and become progressively smoother. This offered a great economic advantage in both dry docking and fuel costs. Improved copper oxide based coatings that also ablated or polished with time appeared in the 1980's; however, they did not provide the performance level of the self-polishing tin copolymers. Because the ablative or self-polishing coatings erode during service almost to the primer, they essentially released all of their biocide to the aquatic environment.

In the early 1980's, organotins were implicated in the failure of shellfish crops occurring in northwestern France. Since all of the problems were located within a short distance from marinas containing pleasure craft where many of the hulls were painted with coatings containing tributyltins, a link between the shellfish problem and the organotins was quickly established. The control of organotin containing coatings rapidly spread to other coastal European countries, Japan, Australia and New Zealand and to the United States in 1988 (2). These regulations pertain mostly to small boats less than 83 feet (25 meters) in length and not to ocean going ships. Also, the Antifouling Paint Control Act of 1988 effectively prohibited the use of the tributyltin self-polishing

copolymers from the United States Navy fleet. The result was a change to the less toxic copper oxide ablative coatings, which do not provide the level of performance attained by the organotin self-polishing coatings.

Now even the copper oxide paints are under suspicion for causing water pollution and are banned in freshwaters in Sweden (3). Several states are regulating the amount of copper oxide in local waters. Shipyards are having difficulties in meeting these new regulations, especially when using underwater cleaning which leads to the release of high concentrations of copper oxide.(4).

Fouling control coatings that do not rely upon a biocide have been known since the early 1970's. These coatings are based upon the polydimethylsiloxane (PDMS) backbone and offer a non-toxic approach to biofouling control. They are described as "fouling release coatings" and rely upon the physical nature of the coating to retard the onset of fouling and provide easy release when fouling does occur.

History of Silicones as Release Coatings

The use of silicone materials based on polydimethylsiloxane as release agents and coatings has been known industrially for nearly 50 years. Fluid additives or coatings based on PDMS have been used in a variety of release related applications including mold release agents and coatings, bakeware coatings, paper release coatings, and anti-deposition coatings.

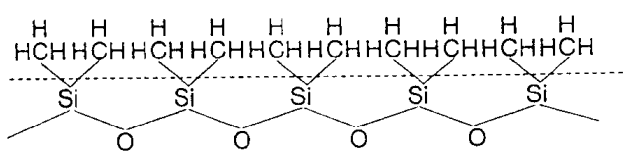
The first reported use of silicones as fouling release coatings was in 1972 when the Battelle Institute was assigned a patent (5) on the use of PDMS elastomers to prevent fouling by barnacles and other marine organisms. The silicone could be applied as a curable gum or pre-cured sheets, and room temperature curing silicone elastomers could also be employed. Immediately following this patent was another by Hempel (6) who also covered both heat and room temperature curing silicone elastomers. They compared the adhesion of the marine organisms to both heat cured silicone elastomers and a polytetrafluoroethylene surface and found that algal fouling released more easily from the silicone and that barnacles could be removed under the pressure of a water jet only from the silicone elastomer.

Early work at International Paint, now a part of Courtaulds, showed that superior results were obtained when a phenylmethylpolysiloxane fluid was added to a room temperature curing PDMS elastomer (7). Little evidence of fouling was seen after 2.5 years of immersion. A later study claimed 10 years of fouling resistance (8). However, it was reported that the poor abrasion resistance and physical properties including tear strength of these coatings limited the range of potential applications to situations where such characteristics were not of primary importance such as aquaculture, off-shore structures, piping systems and power plant water intakes(9). Since the finding that the fouling resistance of PDMS elastomeric coatings could be increased by the addition of a silicone fluid, many researchers have followed this approach using such fluids such as trimethylsilyl endblocked PDMS, PDMS/polyoxyethylene copolymers, mineral oils, petrolatum, polybutylene and others (10,11,12, 13,14,15).

Unique Properties of PDMS

The release characteristics of polydimethylsiloxane (PDMS) are derived from the unique molecular structure relative to organic polymers. PDMS is a heterogeneous molecule (Figures 1 and 2) with a very flexible backbone. As a result the polymer chain can readily adapt to the lowest surface energy configuration (16). The siloxane portion is inorganic, a silicate, has high surface energy, high intermolecular forces, and strong absorptions. The methyl groups are organic hydrocarbons with their accompanying inertness, low surface energy, low intermolecular forces and hydrophobicity. The diagrams below show the relationship between the inorganic and organic nature of the PDMS chain.

Figure 1
2-dimensional view of PDMS at interface of air and a high energy substrate.



However, while surface tension measurements show tightly packed methyl groups at the PDMS/air interface, the conformation of a PDMS monolayer may vary at other interfacial regions, such as PDMS/water. Evidence of this behavior

Figure 2
3-dimensional model of silanol ended PDMS at air/metaloxide interface.

is that PDMS has a lower interfacial tension against pure water than that of corresponding non-polar hydrocarbons.

M. Owens (17) has described five fundamental characteristics of polydimethylsiloxane as:

1. The low surface energy in air (23 mN/m2) is a direct result of the low intermolecular forces between the methyl groups. These pendent methyl groups act as close packed methyl at the PDMS/air interface with little effect from the siloxane backbone with its considerable polarity (41% ionic).

2. The siloxane backbone has a unique flexibility which results from several parameters, including Si-O bond length, flat siloxane bond angles, partially ionic (non-directional) nature of the bond, and an alternating divalent group in the backbone yielding increased spacing between corresponding Si substituent groups. PDMS with a Tg of 146K (-127 C) has the most flexible backbone among the common polymers. As a result, it can readily adapt the lowest surface energy configuration. The close packing of the pendent methyl groups at the PDMS/air interface is possible due to this flexibility. Also, this same property can allow a PDMS monolayer to have a different conformation at an interface other than PDMS/air, where the dipole of the backbone plays a more important role in the interaction. This conformation change must be driven by an overall reduction in the energy of the system.

3. The high bond energy of the siloxane bond (445 kJ Mol-1) is significantly greater than that for a carbon-carbon or carbon-oxygen bond, and is responsible for the oxidative and thermal stability of PDMS.

4. The partially ionic nature (41% ionic) of the siloxane bond results from the large difference in electronegativity of the silicon and oxygen atoms. Thus, the flexibility of the molecule can permit configurations which allow interaction of the backbone dipole with polar substrates.

5. The critical surface tension of wetting for PDMS (24 mN/m) is higher than the liquid surface tension (21.8 mN/m) which means that PDMS will spread on its own absorbed film and is not autophobic unlike many other low surface energy materials.

Fouling Control Mechanisms of Silicone Coatings

Many of the theories used to explain adhesion can be inverted to explain release. Therefore, a release coating should exhibit several features at the "release" interface, including: barrier to mechanical interlocking, prevention of interdiffusion, poor adsorption and lack of reaction, low surface tension and thermodynamic work of separation, limited or no electrostatic attraction, non-setting, and provision of a weak boundary layer (18,19). At the same time, it must exhibit at least some of the opposite properties in order to adhere to the substrate. Although the phenomena of marine biofouling is very complex and diverse, it is useful to generalize the control of fouling by PDMS coatings as a "release" application.

There are several theories relating to the mechanism by which PDMS based coatings minimize the level of or retard the on-set of biofouling, and once fouling occurs maintain an easily cleaned surface with low fouling adhesion. It is generally accepted that the lower level or inhibition of fouling is due to the low adhesion forces (easy release) of the biofouling organisms. First, it is useful to distinguish two different methods: (1) Minimum adhesion force due to coating structure (barrier coating), primarily related to surface energy to minimize wetting, and rheological properties for reduced or reversible diffusion, and (2) Improved release via use of partially incompatible additives (weak boundary layer).

Low Surface Tension

Over a decade of research resulted in the finding that the degree of biological interaction with a surface varies with its surface energy. This relationship which reflects all aspects of biofouling, depicts a minimal adhesion of biomass to surfaces that are dominated by closely-packed methyl groups or are highly hydroxylated. This minimum also varies depending on the media. but is somewhere in the range of 20-30mN/m. (20,21) Polydimethylsiloxanes with critical surface tensions ranging from 21-24 mN/m fall within this range. The Good-Girifalco-Fowkes equation is applicable to situations where all interactions at the interface are dominated by dispersion forces. Dexter (22), Schrader (23), and Baier (24) have all suggested that this is applicable to the situation of low surface energy solids in the marine environment, and thus the minimum defined experimentally correlates to the point where the dispersion component of the total interfacial energy is zero.

Mobile Molecular Interface

As mentioned, PDMS based materials have a very low Tg or very high molecular mobility even as high molecular weight elastomers. Initial data suggests that the resulting low modulus of PDMS based coatings at room temperature may be related to the ability to release hard fouling organisms. The modulus of PDMS based elastomeric coatings can be varied to provide improved release, but this is often at the expense of coating toughness.

Micromosaic Surfaces

The addition of a mixture of hydrophilic and hydrophobic fluids to room temperature cure PDMS coatings results in a cured film containing the liquids dispersed as a micro phase. These microphases of additives yield an over-

all coating of alternating hydrophilic/hydrophobic nature. A relationship between the least amount of fouling and the clearest micro phase separation was observed. No relationship between fouling performance and surface energy was observed (25,26). However, this could be due to the presence of a thin layer of these incompatible polar and non-polar fluids on the coating surface. These fluids also form a thin boundary layer at the coating/water interface and the polar fluids could be partially water soluble resulting in an ablative boundary layer.

Weak Boundary Layer-Fluid Additives

The commercial PDMS based coatings contain either a mixture of polar/non-polar fluid additives or non-polar fluid additives. These fluids are also slightly incompatible in the cured PDMS coating which provides a driving force for diffusion to the coating/water interface, and results in a thin layer of fluid. This liquid interface could act as a weak boundary layer resulting in improved release of biofouling. However, the addition of these fluids to organic coatings does not result in any long term enhancement of fouling performance such as occurs with the PDMS coatings.

Weak Boundary Layer-Polar Surface

When PDMS is exposed to a high energy surface such as water, theory suggests that a thermodynamic driving force will exist to minimize the interfacial tension between PDMS and water by having a siloxane and silanol rich PDMS/water interface. By reducing the interfacial tension to very small values the driving force for the fouling organisms to adsorb on the surface has been greatly reduced. Also, due to the weak water boundary layer on such a surface, it will be difficult for the fouling organism to displace water completely and form a strong bond.

As Zisman and co-workers first indicated (16), an electrical attraction between the siloxane backbone and water is expected because of the semi-ionic nature of the Si-0 bond. Also, some residual SiOH can remain on or migrate to the surface of the cured coating and these acidic sites can interact with counterions present in sea water. The ability of PDMS to change conformation in response to its environment has been reported elsewhere (16,27,28,29). Underwater surface tension work at Dow Corning and the Florida Institute of Technology is believed to be the first measurements of the reorientation of PDMS underwater (30). Additional data gathered at Dow Corning on commercial coatings stored underwater in a sterile environment also show a decrease in the water contact angle over time. This change could be due to siloxane backbone conformation change, silanol species migration/orientation to the interface, or some type of hydrolysis. This reorientation mechanism is not possible in organic polymers since their structure does not allow heterogeneous behavior.

Technology of PDMS Coatings

Polydimethylsiloxane coatings have their roots in room temperature curing silicone sealants such as the familiar Bathtub Caulk (R). A sealant can be dispersed in solvents such as xylene, toluene or mineral spirits and the cured coating will offer a degree of fouling resistance. However, the high molecular weight of the PDMS used in the sealants results in a high viscosity coating which must be reduced with sufficient solvent so that it does not meet VOC regulations.

A PDMS coating can be as simple as a mixture of silanol (SiOH) functional PDMS, fillers, and an endblocker or crosslinker for the silanols which is also reactive with moisture present in the atmosphere. Catalysts can be added to accelerate the moisture activated cure.

There are several types of cure systems available. The 1-part and 2-part condensation cure systems result in siloxane (Si-0-Si) bonds and release a volatile leaving group. The 2-part addition cure results in an ethylene (Si-CH2-CH2-Si) bond with no leaving group.

1-part Moisture Activated Cure

Basic 1-Component Formulation

Silanol functional PDMS	100 parts
Fumed Silica (treated or untreated)	6 - 15 parts
Crosslinker (acetoxy, oxime, methoxy)	3 - 7 parts
Catalyst	0.1-0.5 parts

Polymer

Linear PDMS terminated with silanol groups is the starting polymer. Two aspects must be balanced in order to select the best polymer. First, the modulus and toughness of the coating will partly depend on the polymer molecular weight and resulting crosslink density. Second, the coating viscosity will also be effected by choice of the polymer. The two factors should be balanced to provide a coating that will provide good application properties at a solids level that will meet Volatile Organic Content (VOC) requirements. Such polymers have a molecular weight (Mn) range of 20,000-40,000.

Filler

Fumed silica is incorporated into the PDMS polymer under high shear. This type of high surface area silica

(150-300 m2/gm) is used in almost all PDMS coatings and sealants to provide strength. The surface silanol groups interact with the siloxane bonds through hydrogen bonding and create a "mechanical" reinforcement. They also react with the crosslinkers forming a covalent bond. The tensile strength of a non-filled, crosslinked PDMS is about 20 psi. The same polymer/crosslinker mixture with 15% highly functional silica filler could have a tensile strength of more than 600 psi or a 30-fold increase (31). However, high levels of these high surface area reinforcing fillers will result in higher viscosity formulations.

The treatment of the silica surface with Me3Si0- or Me2SiO- results in a hydrophobic surface. These treated silica's are more easily dispersed in PDMS and have a lower moisture content, but provide lower reinforcement. High surface area calcium carbonates are often used in sealants to provide higher tear strengths. Other pigments can also be used to provide opacity, color or harder coatings. Titanium Dioxide, iron oxides, carbon black, and a range of other materials are typical for silicone elastomeric sealants and coatings.

Crosslinker/Catalyst

The moisture reactive crosslinker is added under anhydrous conditions at a concentration where all of the silanols on the PDMS are endblocked. A deficiency of crosslinker will result in a viscosity increase or even gelation. Typical crosslinkers are methyltriacetoxysilane, methyltris-(methylethylketoximo) silane and methyltrimethoxysilane. Typical catalysts are metal carboxylates, alkylmetal carboxylates and alkylmetal alkoxides such as dibutyltindiacetate, dibutyltindilaurate, tetrabutyltitanate and tetraisopropyltitanate.

Aliphatic solvents such as mineral spirits can be used to reduce the coating to a suitable application viscosity. Several other solvents may also be used, such as methylamylketone, isoparaffinic solvents such as Isopar G, and recently use of volatile methyl siloxanes (VMS) with are low molecular weight linear or cyclic dimethylsiloxanes.

Curing

Cure is accomplished by the reaction of the crosslinkers with moisture in the air forming the stable siloxane (Si-O-Si) bond and emitting the reactive group as acetic acid, methylethylketoxime or methanol. Cure starts at the surface and by proper selection of the crosslinker and catalyst, tack free times of less than 30 minutes can be achieved. The cure rate is effected by both the relative humidity and the temperature. For example, a coating that will be tack free in 30 minutes at 25 C and 50% relative humidity may take longer than 60 minutes at 20 C and 30% relative humidity and only 15 minutes at 30 C and 90% relative humidity.

Two-component Coatings

Moisture Cure

Two component coatings consist of a Part A containing the silanol functional PDMS, fumed silica, other pigments and solvent and a Part B which contains either ethylorthosilicate or propylorthosilicate sufficient to crosslink the silanols. The catalysts normally used are stannous octoate or dibutyltindilaurate. Upon mixing, the alkoxide sites react with the silanols to form the Si-O-Si bond and the corresponding alcohol.

Two-part Addition Cure

In two-part addition cure systems, Part A usually consists of a vinyl functional PDMS with reinforcing fillers. Sometimes a vinyl functional methylsilicone resin is used in place of the silica. All of the reinforcements are treated so that the SiOH and water content are minimal. This prevents reaction with the crosslinker which creates hydrogen gas.

Part B contains SiH functional silane or siloxane which when catalyzed reacts with the vinyl sites to create the ethylene crosslink. Typically, chloroplatinic acid (H2PtCl6) is used as the catalyst.

Cure System Comparison

The following table summarizes some of the general advantages and disadvantages of different possible cure systems. Although many other types of cure systems are known, those listed are most commercially utilized. Understanding the trade-offs which are made can assist with choice of the

Table 1
Comparison of widely used commercial silicone elastomer cure systems.

Cure Type	Advantages	Disadvantages
1-Part Condensation		
Oximosilane	1-part system	May require adhesion promoter
- Ketoxime by-product	Non-corrosive to most substrates	Complexes with copper
	Adjustable cure rate	Higher oxime content required
	Easy processing	due to higher mw
	Good shelf life	Relatively strong odor
	Organotin catalyst not needed	
Acetoxysilane	1-part system	Strong acetic acid odor
- acetic acid by-prod.	Fast cure	Corrosive to many substrates
	Easy process	Fast Skin Over
	Excellent adhesion	Often require organotin catalyst
Methoxysilane	1-part system	Shelf life can be short (neat)
- MeOH by-product	Non-corrosive	Thick phase in manufacturing
	Pleasant odor	May require adhesion promoter
	Some control of cure rate	
	Organotin catalyst not needed	
2-Part Condensation	Least expensive cure system	Requires organotin catalyst
- MeOH or EtOH	Adjustable cure rate	Reversion can occur
by-product	Non-corrosive	
2-Part Addition	Fast cure is possible	More expensive than
	No volatiles/by-product from cure	condensation cure
	thus no shrink	Catalyst/cure easily inhibited
	Little or no odor	May require adhesion promoter

best possible system for a particular application, such as a fouling release coating.

Future of Silicone Fouling Release Coatings

Due to environmental regulations on toxic antifouling materials, a non-toxic solution for control of fouling is desired. Silicone elastomeric coatings based on polydimethylsiloxane (PDMS) have been identified as the best current alternative for fouling control. Silicone technology for release applications is broadly known and dominates several industries including paper coatings. The unique structure of PDMS imparts a low surface energy coating due to tightly packed methyl groups, and a low Tg material which provides a weak diffuse interphase. Although the overall mechanism for release of marine biofouling organisms is not known, it likely involves the structure and properties mentioned.

Many types of formulations can be prepared, including variations in polymer molecular weight, filler type and level, crosslinker and catalyst type and level, and solvent type and level. The specific formulation used will depend on the relative fouling control needed, the toughness necessary, and the application properties needed.

Currently, polydimethylsiloxane fouling release coatings are being evaluated for application in cooling water inlets of power plants and other stationary structures where they have been shown to be effective against marine fouling including the fresh water Zebra Mussels. In addition, practical evaluation in the form of ship test patches is being carried out by the US Navy. The purpose of this testing is to determine real world performance for control of fouling and durability of the systems, especially when cleaned via underwater scrubbing methods, and thus define whether these materials are operationally viable.

Although it is clear that the current non-toxic fouling release coatings are not as efficacious as ablative tin coatings, they do represent an environmentally friendly alternative to dealing with the problems of fouling. To obtain better performance in the short term, it may be necessary to utilize coatings with non-toxic fluid additives, or perhaps with low release rates of biodegradable organic antifouling agents. Additional development needs to be completed to identify commercially viable means of combining the antifouling agents and PDMS based coatings. Also, in the next several years, testing should continue on ideas for improving the overall toughness and fouling release properties of the PDMS coatings. Continued research to identify the fundamental mechanism for improving release should also be pursued, in order to guide future development efforts aimed at providing self cleaning vessels.

Biographies

Gregory G. Bausch received a B.S. Degree in Chemistry/Mathematics from the University of Wisconsin-LaCrosse in 1987. Mr. Bausch has worked at Dow Corning since graduation, and has led development efforts for several silicone fluids, resins, and emulsions. He is currently a Group Leader/and Development Specialist for Coatings and Additives. Mr. Bausch has 5 patents and numerous 3 publications.

Harold L. Vincent received his B.S. Degree from Michigan State University in 1954. His career in the silicone industry spans 40 years of research, development, and commercialization of silicone resins, composites and coatings at the Dow Corning Corporation. Mr. Vincent retired as an Associate Scientist in 1993 and is now active as a consultant on a variety of silicone technologies including fouling release coatings. He has published numerous papers, holds 25 patents, and has made technical presentations throughout the world.

REFERENCES

1. Kjaer E.B., Bioactive Materials for Antifouling Coatings, Progress in Organic Coatings, 20 (1992) 339-352.
2. Organotin Antifouling Paint Control Act of 1988
3. Sisson W., Bottom Paints: Getting Greener, Soundings (March 1994) A32.
4. Thorn F., Water Quality Standards, National Paint and Coatings Marine and Offshore Conference, 1993,
5. Muller, W., and Noacki, L., US3702778, 1972.
6. Kroyer K., GB1307001, 1973.
7. Milne A., US4025693, 1977.
8. Milne, A., and Callow, M., Non-Biocidal Antifouling Processes, Trans IMarE (C) Vol 97, Conf. 2, Paper 37, 1984.
9. Callow, M., Pitchers, R., and Milne, A., The Control of Fouling by Non-Biocidal Systems, Stud. Environmental Sci. 28 Algal Biofouling, 145-158, 1986.
10. Chugoku (Assignee) J58013673, 1983.
11. Ibid, GB2141436, 1984.
12. Kishihara, M., Nanishi, K., and Yonehara, Y., US5218059, 1993.
13. McLoughlin, B., et. al., GB1581727, 1980.
14. Shone, E., and Riches, K., GB2096019, 1981.
15. Riches, K., et. al., GB7942682, 1981.
16. Fox, H., Taylor, P., and Zisman, W., Polyorganosiloxanes: Surface Active Properties, Industrial and Eng. Chem., Sep. 1947, 1401-1409).
17. Owen, M.J., Low Surface Energy Inorganic Polymers, Comments, Inog. Chem., Vol. 7, No. 4, 1988, 195-213.
18. Owen, M.J., Encyclopedia of Polymer Science and Engineering, 1988, Volume 14, pg. 411- 421.

19. Jabbari, E., and Peppas, N.A., Polymer-Polymer Interdiffusion and Adhesion, J.M.S-Rev. Macromol. Chem. Phys., C34(2), 1994, pgs.205-241.
20. Goupil, W., DePalma, V., and Baier, R., Prospects for Nontoxic Fouling Resistant Paints, Proceedings 9th Annual Conference on the Marine Technology Society, Washington, D.C., 1973.
21. Goupil, W., DePalma, V., and Baier, R., Physical/ Chemical Characteristics of the Macromolecular Conditioning Film in Biological Fouling, Bio. Mar. Comun. Congr. Corros. Mar. Incrustaciones, 5th. 401-410, Ed. Garsi, Madrid, Spain.
22. Dexter, Stephen C., Influence of Substratum Critical Surface Tension on Bacterial Adhesion; Journal of Colloid and Interface Science, Vol. 70, No. 2, June 15, 1979.
23. Schrader, Malcolm E., On Adhesion of Biological Substances to Low Energy Solid Surfaces; Journal Of Colloid and Interface Science, Vol. 88, No. 1, July, 1982.
24. Baier, R., Why Zisman/NRL Critical Surface Tension Better Predicts Biological Fouling Resistance Than Do Undewater Contact Angles, ONR Seminar, Oct. 1994.
25. Murase, H., and Nanishi, K., Studies on the Adhesion Control of Marine Organisms by Means of a Heterogeneous Polymer Surface, Kobunshi Ronbunshu, 50(11), 837-45, 1993.
26. Kishihara, M., Nanishi, K., and Yonehara, Y., US5218059, 1993.
27. Chaudury, M.K., Lin, R., and Owen, M.J., Dow Corning Internal Report, 1987-I0030-6182 (1987).
28. Owen, M.J., Chemtech, 11, 288 (1981).
29. Owen, M.J., Gentle, T.M., Orbeck, T., and Williams, D.E. in “Polymer Surface Dynamics”, (J.D. Andrade, Ed.), Plenum Press, NY, p. 101 (1988).
30. Schmidt, R.G., Vincent, H.L., Swain, G., Polymer Surface Tension Dynamics in Sea Water; Influence on Marine Antifouling Performance, Unpublished Work.
31. Klosowski, J., Sealants in Construction, Marcel Dekker, Inc.,1989.

Field Evaluations of Non-Toxic Antifouling Coatings: New Field Technologies and Performance Criteria

Geoffrey W. Swain, Florida Institute of Technology, Melbourne, FL

"It is the mark of an instructed mind to rest satisfied with that degree of precision which the nature of the subject admits, and not to seek exactness where only an approximation of the truth is possible" --Aristotle.

Introduction

A key component to antifouling research is a well structured test and evaluation program. This must be tailored to provide scientific information to research groups and operational performance to the end users. The development of non-toxic antifouling coatings has provided some unique challenges with regard to selecting and developing test protocol. During the 1994 Office of Naval Research (ONR) Biofouling Contractors Workshop, a list of criteria considered important for the evaluation and understanding of such coatings was developed (Figure 1). These were categorized under four main headings: operational requirements, physical properties, chemical properties, and biofouling properties.

The operational requirements of an antifouling system are fairly well understood and reflect the needs of the US Navy to preserve the submerged portion of ship and submarine hulls in a smooth and foul free condition. The long term objective is to develop a coating which provides equal or better performance than the self polishing organotin coatings, at similar cost, but with out the adverse environmental impacts. Many of the chemical and physical properties can be found through standard test protocol[1], however, new techniques and instrumentation are being developed and these enable a more detailed understanding of coating characteristics. The biofouling properties are determined using both laboratory and field techniques. This paper focuses on biofouling tests, and in particular new methodologies that have been developed for panel testing of non-toxic surfaces under static immersion conditions.

Biofouling Evaluation

Over the years, a variety of techniques have been developed to assess the effectiveness of both natural and synthetic compounds as antifouling agents. These, traditionally, have been directed to evaluate biocidal compounds, however, the mode of action of non-toxic coatings is quite different (Figure 2). Marine organisms that settle on a toxic

Figure 1
Criteria used to evaluate the performance of antifouling coatings.

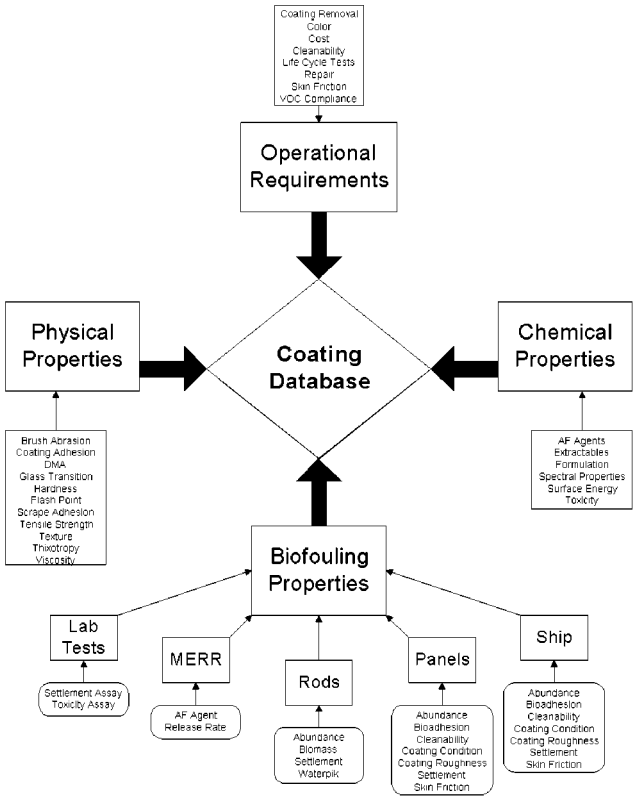
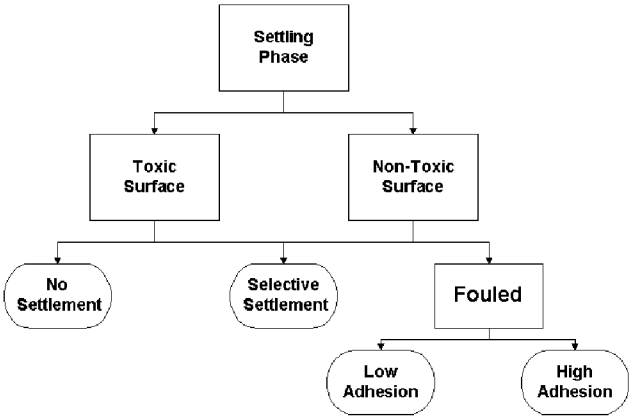


Figure 2
Settlement matrix for toxic and non-toxic surfaces.



surface may survive short periods, but providing the coating is functioning, they soon die or become detached. The coating remains free of fouling. A non-toxic surface, however, may become totally covered by fouling organisms, and its effectiveness then becomes a function of the ease with which the biofouling can be removed.

With-in the ONR biofouling program, a hierarchy of tests has been established to streamline the evaluation of formulations that are being developed. A coating or compound is first screened using short term laboratory tests. These include the use of bioluminescent bacteria[2], and barnacle in vitro assays using *Balanus amphitrite*[3]. The advantage of such tests is that they only require small quantities of the test material and this eliminates the need for large volume production of a non-proven prototype system. If the formulation shows promise, it is then subjected to rod testing[4].

The rod test is a field evaluation that was designed to bridge the gap between laboratory findings and long term panel tests. Candidate coatings are applied to fiberglass rods, 110 mm long and 7 mm diameter. These are mounted, in binary comparison, at 7.5 cm intervals in 50 cm by 50 cm square racks made of 15 mm internal diameter PVC pipe supporting Vexar 10 mm (long dimension) diamond mesh screening. For a test, 20 rods of each coating type are deployed in a blocked and randomized array. The racks are deployed in the marine environment and the rods monitored for the first signs of macrofouling. When fouling is detected, 5 rods of each type are removed and the fouling counted each week for one month. Uncoated fiberglass rods and AF 121 cuprous oxide coated rods provide a reference for the effectiveness of new formulations. Promising formulations from the rod testing are then applied to panels for long term static immersion.

Long Term Panel Testing

Panel testing provides the first opportunity to subject coatings to a broad spectrum of physical, chemical and biological action over a prolonged time period (Table 1). Candidate coatings are applied to standard 254 x 305 mm (10 in. x 12 in.) test panels with 9.5 mm (3/8 in.) holes at each corner to facilitate attachment to the test frames. These are immersed at a static exposure site with known fouling communities.

The selection and design of methods to evaluate the performance of the test panels was made on the basis of the following questions:

- What information will be useful to improve the knowledge of the research scientist?
- What information will be useful to enable the Navy to select the best system for their needs?
- How can the test results be related to performance?
- What are the limitations of the type of test selected?
- How should the precision of the work be adjusted to be in accord with the limitations of the method and yet achieve economy of effort and consistent reliable results?
- How many samples are necessary to obtain representative results?

The most obvious parameters to monitor are the rates

Table 1
Variables associated with field testing antifouling coatings.

Coating	Complexity of Product	Application Process Cure Time Edge Effect
	Changes with Time	Chemical Composition Physical Degradation Processes
Environment	Chemical	Salinity Oxygen Nutrients Pollutants
	Physical	Temperature Water Velocity
	Biological	Indigenous Communities Succession Competition Grazing and Predation

of biofouling accumulation and the physical deterioration. A test procedure for antifouling coatings containing active biocides was already available (ASTM D 3623 - 78a (1987) "Standard method for testing antifouling panels in shallow submergence"[5]) and this was adopted for the general management and observations of the test panel performance. The non-toxic systems, however, may become fully fouled and it is then the strength of biofilm adhesion to the substrate that determines the effectiveness of the coating. To quantify biofouling adhesion we designed two test methods:

- Water jet evaluation
- Barnacle adhesion measurements.

Both methods were designed to be fully portable, field friendly and economic with regard to effort and time.

It must be remembered that biofouling is a dynamic process in which community structure is for ever changing. The interpretation of results must take into account seasonal and spatial differences at individual test sites, and community differences on a global scale. In addition, the coating itself will age. It is our experience that for short term exposure (less than 12 months) of panels that do show some antifouling characteristics, only the results from panels that were placed under static immersion at the same time should be directly compared one to another. It is also important to test replicate panels at several sites world wide and that these should be calibrated to coatings of known performance. This means that forward planning of test panel exposure is of the utmost importance to get meaningful and comparative information.

Test Protocol

The following methods have been established for the test and evaluation of non-toxic antifouling coatings:

- Biofouling and physical condition of the coating.
- Biofouling adhesion measurements using a calibrated water jet.
- Barnacle adhesion measurements in shear.

The standard calibration surfaces used in the present Navy Program are F150 Epoxy, BRA Copper Ablative, Dow Corning RTV 3140, General Electric RTV 11 and International Intersleek.

Biofouling and Physical Condition of the Coating

The biofouling and physical condition of the coating are evaluated according to ASTM D 3623 [5]. This standard was developed as a method to evaluate antifouling coatings that contain biocides as their mode of action. It describes how to organize a static immersion site, how to maintain a biofouling attachment census and details methods to evaluate the surface for fouling and physical condition.

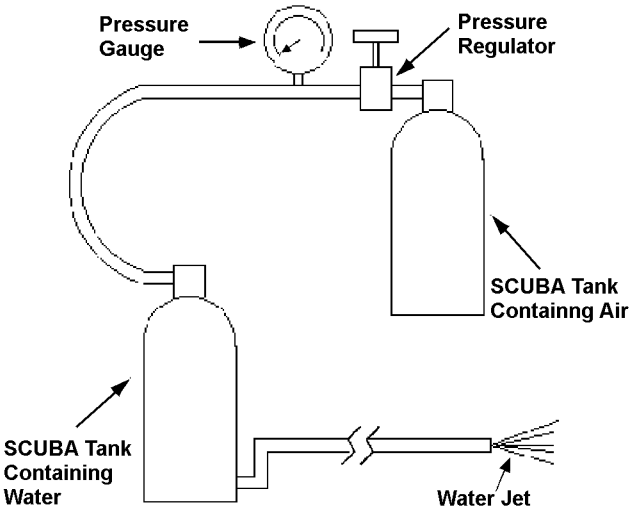
Fouling is rated according to the percentage of the intact proportion of coating or surface that is covered by a particular type of fouling organism as classified in Table 2. Fouling on portions of a panel where no test surface is present (due to coating failure, e.g. delamination) is ignored. The following definitions are made with regard to the reporting of fouling and coating condition.

- Absorbed organic and inorganic chemicals, trapped silt and detritus, should be reported as "silt".
- Diatoms, initial algal germination and low form algae should be reported as "algal slime".

Table 2
Description of fouling types according to ASTM D 3623[2].

Fouling Type	Abr.	Definition
Incipient Fouling	IF	Recently settled and juvenile forms of macrofouling
Silt	Si	Absorbed organic and inorganic chemicals, trapped silt and detritus and unidentified slimes.
Slime	Sl	Diatoms, initial algal germination and low form algae.
Algae	Al	Fully established algae types and larger forms, eg. *Ulva sp.*, *Enteromorpha sp.* and *Ectocarpus sp.*
Encrusting Bryozoans	E.B.	Colonial animals forming an encrusting layer over the surface. These layers are generally 1 - 2 mm thick and have a rough texture.
Bryozoans	Br	Colonial animals forming a turf like mat rarely exceeding 3 cm in length. They maybe mistaken for plants.
Barnacles	Barn	A hard shelled crustacean that cements itself permanently to a substrate, and is difficult to remove. The outer shell is generally whitish in color and shaped like a truncated cone. The barnacles in this area may grow to 2 cm in height and 2 cm in width at the base. The most abundant species at the FIT test site is *Balanus eburneus*.
Polychaetes	PC	Worms that may form a hard calcareous exoskeleton which becomes cemented to the substrate. The individuals rarely exceed 2 cm in length and may show some coiling of the tube.
Sponges	Sp	Soft animals with sponge like texture forming thin surface cover or thicker accumulations. Often brightly colored.
Tunicates	Tun	Soft animals that may be solitary or colonial. Solitary types may reach several centimeters in height and colonial forms tend to form a thin cover over the surface.
Molluscs	Mol	Animals with two hard shells, hinged along one edge. Typical examples are oysters and mussels

Figure 3
Water jet apparatus.



· Immature foulers should be reported as "incipient foulers".

· Mature foulers should be reported as number of individuals present or as percent cover for colonial forms.

· The physical condition of the surface should be rated according to percentage of surface affected by coating defects (Table 3), and the type of coating deterioration should be described qualitatively.

This method then awards a rating for Fouling Resistance (F.R.) and Physical Rating (P.R.). For coating surfaces free of fouling except for the presence of algal spores and other biological slimes, a F.R. rating of 100 is given. This is reduced to 95 if only incipient fouling is present, and when mature fouling is present the rating is further reduced by subtracting the percentage cover or the sum of the number of individuals present from 100 or 95. The P.R. is obtained by subtracting the percent surface affected by defects from 100. The overall performance is obtained by awarding the coating the lowest rating from the fouling resistance and physical condition.

Biofouling Adhesion Measurements Using a Calibrated Water Jet

The water jet test was developed to provide an assessment of the adhesion strength of silts, slimes, and low form fouling types to surfaces where biofouling adhesion is low. It was designed to be fully portable and self contained for field operations and this limits the maximum water jet force that can be applied.

The apparatus consists of a SCUBA tank containing compressed air and a regulator to adjust the pressure between 0 - 1.65 MPa (0 - 240 psi), a SCUBA tank containing water, and a quick change blow gun with a 1.6 mm (1/16 inch) diameter nozzle to apply the water jet (Figure 3). A 50 x 50 mm template is used to delineate the surface to be evaluated, and the test procedure is fully recorded by a video camera.

The measurements are made on an area that is defined by a 50 x 50 mm template placed over a representative part of the surface. The biofouling communities of this area are assessed and recorded using a video camera. The regulator is set to 0.138 MPa (20 psi) to pressurize the SCUBA tank containing water. The resulting water jet is applied to the area within the template in a manner so as to maximize fouling removal. The operator accomplishes this by changing the angle and distance of the water jet to the surface until the maximum amount of fouling that can be removed at that setting is achieved. The biofouling cover of the surface is reassessed and recorded by the video camera. The pressure in the system is increased by 0.138 MPa (20 psi) and the cycle repeated until all the fouling is removed or the maximum pressure setting is obtained.

For evaluation purposes, the biofilm is divided into silt, slime, soft and hard foulers. The waterjet pressure required to remove each of these groups is recorded. The maximum true force exerted by the water jet at the surface for each pressure setting was measured using a force transducer and by observing the area over which the water exerted an effect.

Barnacle Adhesion Measurements in Shear

The barnacle adhesion test was designed to enable rapid and multiple measurements of barnacle adhesion strength in shear to a coating under field conditions. It was approved as an ASTM standard in 1994 [6], and it provides quantitative data that can be used to compare the ability of surfaces to reduce biofouling adhesion. The method was based on previous research conducted on the adhesion strengths of barnacles to natural substrates [7,8,9,10, 11].

Test surfaces that are exposed to static immersion are monitored for barnacle settlement. To facilitate adult barnacle growth on silicones with low fouling adhesion strengths, it has been found necessary to enclose the test area with a 25mm (1 inch) mesh net that excludes larger fish and other predators which would otherwise remove the immature forms. When settlement is observed, the shear strength of adhesion is measured as described below. Typically live barnacles between 5-20 mm diameter at the base are selected for testing, and their species and condition are noted. They should be at least 20 mm from the edges of the test panel, be attached to undamaged areas of the test surface, and not be in direct contact with other barnacles. The barnacle base is measured with calipers in four directions (0, 45, 90, 135 degrees) to obtain an average base diameter . The barnacle base plate area, A, is then estimated using the average base

diameter, d_a and the formula $A = (\pi d_a^2)/4$. A shear force is then applied to the barnacle base using a hand held force measuring device at a rate of approximately 4.5N/s (1.0 lb/s) until the barnacle becomes detached or the maximum shear force is reached. The force measuring device used in the this experiment was a Shimpo mechanical dial force gauge. This device had a range of 0-89 N (0-20 lb), an accuracy of ±0.3%, and a resolution of 0.45 N (0.1 lb). Care must be taken to apply the force parallel to the surface. The force (F) required for detachment is noted, and observations are made as to the mode of failure. If more than 10% of the barnacle base plate is left attached to the substrate, then the test is deemed void. The strength of adhesion, τ pascals (psi), is then calculated by dividing the force required to remove the barnacle, F newtons (pounds), by the area of the barnacle base plate, A square meters (square inches).

$$\tau = F/A$$

It is recommended that, when possible, a minimum of ten measurements be made per coating, and the mean and standard deviation of the strength of adhesion, τ, are calculated. The strength of adhesion values for test surfaces are compared to control surfaces of known adhesion. Variations in barnacle adhesion strength may result from differences in species, age, time of year, and physical condition. Additionally, incomplete removal of the barnacle base plate from the surface during testing may lead to erroneous adhesion values. Care must also be taken not to dislodge the barnacle during base diameter measurements.

Summary

The use of the static immersion panel evaluation methods provides some new and interesting insights into the performance of non-toxic coatings. It is now possible for researchers to quantify how modifications to their formulations alter the strength of biofouling adhesion, and for the Navy to select the coatings with the best foul release properties. Research is currently underway to relate biofouling adhesion strength to mechanical cleaning methods and to the ship speed required for self cleaning. This knowledge should help in the development of non-toxic antifouling coatings and ship hull maintenance practice that will remove the necessity for the use of biocides.

Acknowledgments

This work was supported by the Office of Naval Research (Grant No N00014-91-J-1465). I would like to thank Dr. Randall Alberte and Captain Steven Snyder for their support of this program, Mike Schultz for helping to develop the test methods, and all the participants of the ONR Biofouling Program for their lively interest and input.

Biography

Dr. Geoffrey Swain is an Associate Professor in the Ocean Engineering Program at the Florida Institute of Technology. He has an active research group specializing in corrosion and biofouling control in marine environments.

REFERENCES

1. American Society of Testing and Materials, Paint - Tests for Formulated Products and Applied Coatings. Volume 06.01, 1996.
2. Angell, P., Arrage, A., White, D.C. “On-line, non-destructive monitoring of microfouling on painted antifouling surfaces”. Non-Polluting Biofouling Workshop, Monterey, CA Nov. 1992.
3. Rittschof, D., Clare, A.S., Gerhart, D.J., Sister Avelin Mary, Bonaventure, J. “Barnacle in vitro assays for biologically active substances using mass cultured *Balanus amphtrite amphitrite* Darwin”. Biofouling V. 6, No. 2, 1992.
4. Rittschof, D., Clare, A.S., Gerhart, D.J., Bonaventure, J., Hadfield, M.G. “Rapid field assessment of antifouling and foul-release coatings”. Biofouling V. 6, No. 2, 1992.
5. ASTM D 3623 - 78a (1987) “Standard method for testing antifouling panels in shallow submergence”, American Standard for Testing and Materials.
6. ASTM D5618 (1994) “Standard test method for measurement of barnacle adhesion strength in shear”, American Standard for Testing and Materials.
7. Becka A, Loeb G (1984) “Ease of removal of barnacles from various polymeric materials”, Biotechnology and Bioengineering, XXVI, 1245-1251.
8. Bultman J D, Griffith J R, Field D E (1981) “Fluoropolymer coatings for the marine environment”, In Proc. Symp. on Marine Biodeterioration, eds. J.D. Costlow and R.C. Tipper, pp 237-249, Naval Institute Press, Annapolis, MD.
9. Denny M W (1988) Adhesion. In Biology and the mechanics of the wave-swept environment. Princeton University Press, pp. 228-237.
10. Grenon J F, Elias J, Moorcroft J, Crisp D J (1979) “A new apparatus for force measurement in marine bioadhesion”, Marine Biology, 53, 381-388.
11. Swain G W, Griffith J R, Bultman J D, Vincent H L (1992) “The use of barnacle adhesion measurements for the field evaluation of non-toxic foul release surfaces”, Biofouling, V. 6, No. 2, 105-114.

Selection, Design and Delivery of Environmentally Benign Antifouling Agents

Donald C. Sundberg and Niraj Vasishtha, Polymer Research Group, Dept of Chemical Engineering, University of New Hampshire, Durham, NH
Richard C. Zimmerman, Dept of Biology, University of California at Los Angeles, CA
Celia M. Smith, Dept of Botany, University of Hawaii at Manoa, Honolulu HI

Introduction

The search for effective means to control biofouling accumulation on manmade surfaces in aquatic environments began with the first attempts to explore and exploit the sea. Today, the need for materials that prevent biofouling in aquatic environments is approaching a crisis. Since the 1970's organometallic compounds such as tributyl-tin (TBT) have become the industry standard because they produce economical, highly effective and long-lasting antifouling (AF) coatings. Unfortunately, these highly effective materials are also extremely toxic and environmentally recalcitrant, which has led to serious problems of environmental pollution associated with their application, use and disposal. The gradual abandonment of organo-tin based antifoulants has resulted in a significant increase in the use of less effective copper-based coatings in the last 10 years. Not surprisingly, the increased use of copper-based AF coatings has been blamed for recent but dramatic increases in levels of copper found in marine sediments[1] and in mussels (*Mytilus californianus*) used as indicators of marine pollution[15], suggesting that copper-based coatings may also present unacceptable environmental hazards. In Europe, the triazine herbicide Iragol 1051 has been added to Cu-based AF coatings for more effectiveness in the wake of the ban on TBT. This compound accumulates in fish and decomposes very slowly in seawater, raising concerns about the potential environmental hazard associated with its use in AF coatings[10].

Nature has evolved a variety of strategies that prevent or minimize fouling of natural surfaces in aquatic environments without resulting in permanent environmental degradation or accumulation of refractory and toxic substances. Some organisms use physical means, including the sloughing of the outer tissue layer[4,9,13] the generation of an external surface that minimizes bioadhesion (Vroilick et al. 1990), and the production of secondary metabolites that can deter potential fouling organisms[14] and predators[6]. The chemical species employed as defensive agents are as diverse as the

organisms manufacturing them. Those known agents include elemental vanadium, inorganic acids, and a variety of organic compounds including saponins, terpenoids and phenolic acids[3]. An important goal of the non-toxic antifouling research program supported by the U.S. Navy, Office of Naval Research (ONR) has been to understand and exploit natural agents and their analogs that promise effective biofouling control without polluting the environment.

New Antifouling Agents

U.S. patents for natural antifouling agents were first awarded in the 1880's for the use of relatively crude tannic substances extracted from terrestrial and aquatic plants[14]. The relatively low effectiveness of these tannins, however, has precluded their practical use in AF coatings. In recent years, sophisticated chemical techniques have been used to identify a number of specific secondary metabolites from invertebrates and plants that show promising AF activity[11,16,17,18,22]. In order to be considered for the next generation of non-polluting AF coatings for use by the U.S. Navy, candidate agents must be:

(i) effective at concentrations that do not present a toxic hazard to non-target organisms,

(ii) short-lived in the environment and decompose to prevent food-web bio-accumulation or accumulation to toxic levels through sediment deposition,

(iii) economical to produce without exploiting or endangering natural populations,

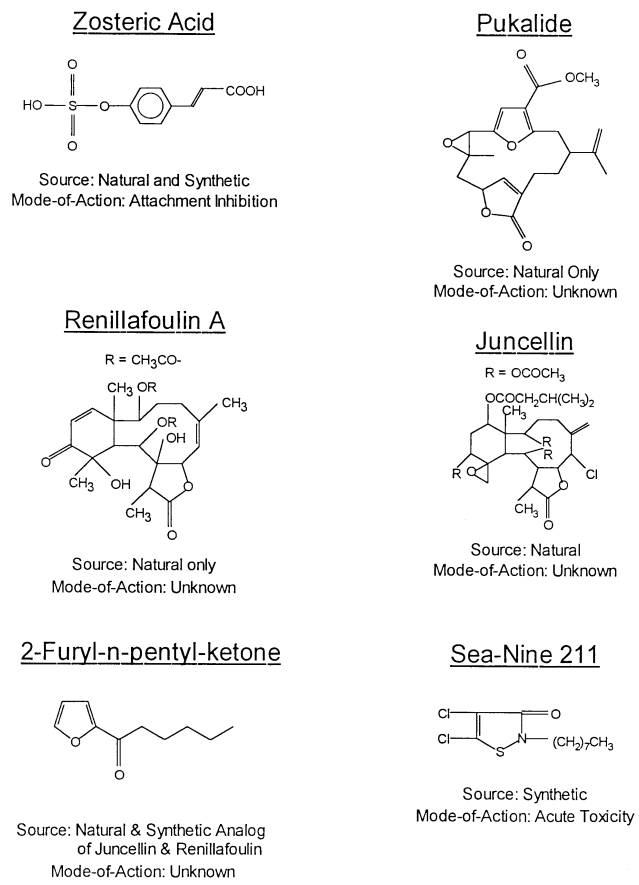
(iv) safe to apply and remove in coatings, and

(v) compliant with federal regulations for minimizing air/water pollution (EPA) and worker exposure (OSHA). In essence, our objective is to exploit natural methods of biofouling control to produce effective and environmentally-safe protection of manmade structures.

The natural agents currently under investigation include terpenoids and a sulfated phenolic acid (Fig. 1). The terpenoids renillafoulin and pukalide were isolated from marine coelenterates[11,16], while juncellin was isolated from a terrestrial angiosperm native to tropical India (Sister Mary Avelin pers comm). The sulfated phenolic acid (zosteric acid) was isolated from the marine angiosperm *Zostera marina* (eelgrass[18]).

Synthetic routes for generating these compounds and/or their derivatives were explored because their isolation from organisms represents prohibitive production costs and unacceptable impacts on natural populations. It was possible to synthesize zosteric acid faithfully from readily available precursors, but structural complexity prevented *de novo* synthesis of the terpenoids in the laboratory. Consequently, smaller chemical analogs were employed that reproduced enough of the original chemical structure to maintain biological activity (Fig. 1). The chlorinated isothiazolone, Sea-Nine 211 (Rohm & Haas Co.), was also evaluated in this program. Unlike Iragol 1051, Sea-Nine 211 appears to have a very short half-life in seawater, reducing the potential for it to accumulate to toxic levels in the environment.

Figure 1
Candidate antifouling agents and their structures, sources of these products and their modes-of-action.



Initial screening of AF effectiveness of individual compounds involved static laboratory assays in which agents were dissolved or dispersed in seawater containing marine bacteria, diatoms or invertebrate larvae and a suitable substrate for attachment, such as a glass slide. The assays generally produce a concentration-dependent attachment response from the target organism that can be used as an initial indicator of AF effectiveness (Fig. 2), but the static nature of these tests can make it difficult to extrapolate the potential effectiveness to real-world conditions.

Mode-of-Action Studies

In addition to being classified as natural agents, natural analogs of natural agents or synthetic agents, candidate AF compounds can also be categorized by their mode-of-action in preventing biofouling. Potential AF mechanisms involve (i) acute toxicity, (ii) avoidance or repellence and (iii) non-toxic inhibition of attachment.

Figure 2
Dose-response curve for the ability of zosteric acid to inhibit settlement by the calcareous polychaete Hydroides elegans *in static laboratory experiments, plotted as a percentage of larvae set in control dishes that contained no zosteric acid. Error bars represent 1 sd of the mean.*

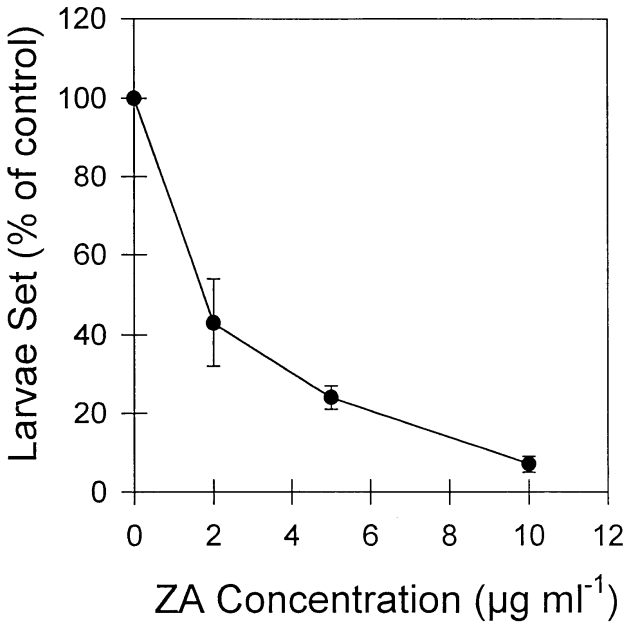
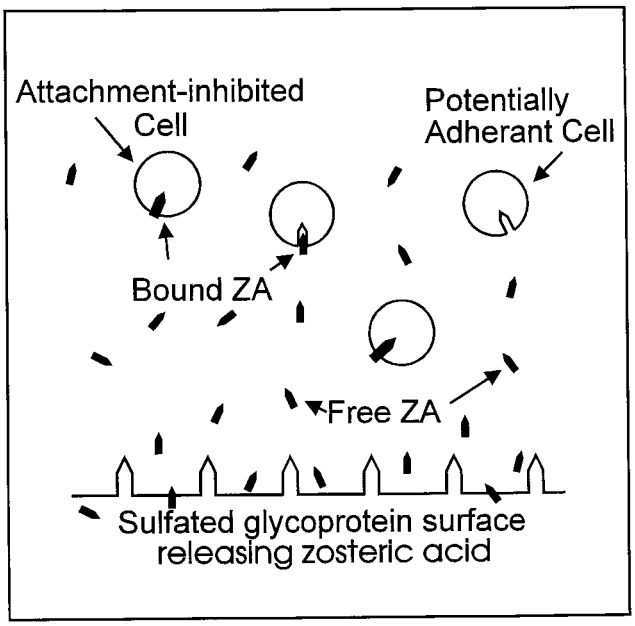


Figure 3
Compounds that inhibit attachment such as zosteric acid interact with surface moieties on target organisms to prevent adhesion of cells to the protected surface. Such inhibitors are non-toxic and dissociate from the organisms at low concentration.



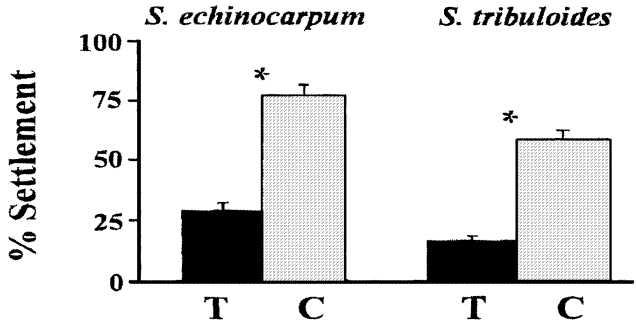
Acute toxicity is the highly effective mode-of-action of organo-tins, copper and the synthetic biocides (Iragol 1051 and Sea-Nine 211). These compounds do not prevent attachment, but chronic exposure is fatal to the developing organisms after attachment. Unfortunately, the indiscriminate nature of this mechanism can affect non-target organisms as well. Repellence involves chemosensation and avoidance behavior, causing organisms to move away from the protected surface. Although repellents may be toxic in high concentration, the elicitation of escape behaviors at low concentrations suggests that repellents can be engineered to be effective close to the protected surface at concentrations that do not threaten non-target organisms. A repellent mode-of-action will not, however, be effective against unresponsive organisms.

A novel approach to biofouling control that can prevent attachment through non-toxic means involves compounds that bind to cell membranes or cell walls/extracellular matrices, thereby altering cell surface properties and affecting the ability of organisms to attach to surfaces. Zosteric acid appears to fall into this category of antifouling agents. The specific mechanism can involve changes in cell surface hydrophobicity that prevent cells such as bacteria from interacting with filmed surfaces that may themselves possess cues for settlement[8], interaction with specific receptor molecules (e.g. lectin binding sites) on the surfaces of bacteria and algal spores that prevent binding to molecules present on the target surfaces (Fig. 3), or blocking the polymerization or "curing" of proteinaceous adhesives secreted by invertebrates.

The search for new AF agents that are broadly effective at low flux rates and even more benign to the marine environment continues. An important breakthrough for the Pacific Test site and our understanding of fouling by tropical organisms was the development of a settlement bioassay with larvae of *Hydroides elegans*, a polychaete tubeworm and the principal fouler of Pearl Harbor. This single advance substantially accelerated ONR testing from one month in the field to one week in the laboratory[5] with full statistical rigor. Our strategy has been two-fold:

(i) focus on those tropical organisms that appear to have solved the biofouling problem without shedding their surfaces[4] and (ii) assay their surfaces as well as possible compounds that they may release into surrounding waters. Using *H. elegans* larvae as a biological probe, we have identified other marine organisms that can (i) inhibit settlement, (ii) increase settlement or (iii) result in the same extents of settlement by *H. elegans* as if the larvae were exposed to only filtered seawater. In all trials, we discriminate those compounds that clearly deter settlement (solid bars Fig. 4) from concurrent experiments for settlement under control conditions (patterned bars, with nested ANOVA, * = $p < 0.05$). Findings of this study[21] (Fig. 4) indicate that settlement can be delayed without longer term effects on vi-

Figure 4
Inhibition of settlement by Hydroides elegans *when exposed to seawater conditioned by two marine algae,* Sargassum echinocarpum *and* Sphacelaria tribuloides*. Within each pair of bars, solid bars represent the percentage of larvae that settled within one day of exposure to treated water (T); patterned bars represent the percentage of larvae that settled within one day under control conditions (C). (* = p<0.05 nested ANOVA[21]).*

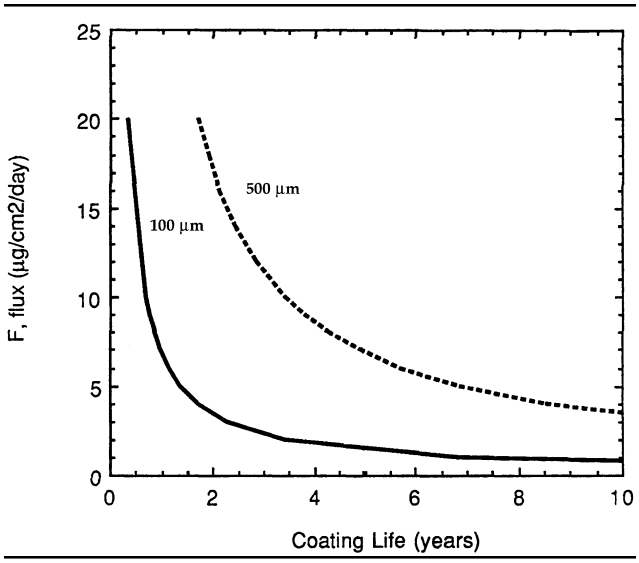


ability of larvae; future research into the identity of these compounds will likely be fruitful.

Delivery of AF Agents From Coatings

To be effective, an AF agent must be delivered to the coating surface at a desired rate. This release rate, or flux, is traditionally expressed in units of micrograms per square centimeter of surface area per day ($\mu g\ cm^{-2}\ d^{-1}$). Depending upon the type of coating being evaluated, this release rate may or may not be constant. It goes without saying that constant release rates are preferable in that they yield efficient use of the AF agent throughout the lifetime of the coating. Figure 5 displays the relationship between the expected useful life of a constant release rate coating and the flux necessary to be effective against fouling. The two curves in the figure represent the results for coatings of different thicknesses, both containing 25 wt % AF agent at the time of application. Here it is clear that in order for a coating to last for 5 years, the release rate required for effective control of biofouling cannot be larger than 5 to 10 $\mu g\ cm^{-2}d^{-1}$. This provides a useful basis upon which to select among candidate AF agents. Unfortunately, developing a coating which yields a constant release rate over a sustained period of time (5 to 7 y for Naval applications) is not a trivial task.

Figure 5
Release rate, or flux, necessary to prevent biofouling as a function of the expected coating life when the AF agent is released at a constant rate for coating thicknesses of 100 and 500 μm. Coatings initially contained 25 wt% AF agent, independent of coating thickness.



There are several distinctively different types of marine coatings that need to be considered because coatings typically fall in two categories, each with unique characteristics that influence release rate properties. The first type of coating has polymers that constitute the matrix phase of the coating and can be made to dissolve slowly, or ablate, into sea water. The dissolution rate of the matrix phase controls the rate at which AF agents are delivered to the marine environment. A second, non-ablative type of coating, also contains AF agents but relies on diffusion processes within the coating to deliver an AF agent to the marine interface. These non-ablative coatings can be porous or non-porous. For porous coatings, sea water penetrates somewhat into the coating to dissolve an AF agent and to provide a pore through which the agent is delivered to the surface. For non-porous coatings, molecular diffusion through the polymer results in delivery of the AF agent to the surface. Because future coatings are likely to be non-porous and perhaps non-ablative, we will discuss these in somewhat greater detail.

Monolithic Coatings

When an AF agent is freely dispersed in a polymer binder, the coating is described as monolithic. Molecular diffusion is responsible for the transport of the AF agent through the coating and diffusional characteristics will depend on the concentration of the agent relative to its saturation limit in a particular polymer. Mathematical descriptions of the release rate can be obtained and such expressions show that release rates depend on the diffusion coefficient in the polymer and the concentration of the agent. Concentration gradients develop within the coating during the release period and the diffusion coefficient will often be dependent upon the local concentration. This results in an often complex quantitative expression for the release rate, but analyses are available. Higuchi[7] has described the flux through coatings in which the agent is initially present above its saturation limit. For unsaturated conditions the analysis is somewhat simpler and diffusional analyses are available[2].

For the simpler case where the concentration of an AF agent is below its saturation limits in a particular polymer, the release rate will always be variable because the concentration of the AF agent decreases with time. Evaluating the time dependent release rates from such simple coatings allows us to characterize a diffusion coefficient of an agent in the polymer. Here we use an approximate form of the flux equation from Crank[2] as shown in equation 1.

$$M_t / M_0 = 4\{\pi\}^{1/2}[Dt / a^2]^{1/2} \qquad (1)$$

where M_t is the total amount of the agent that has diffused out of the coating at time t, M_0 is the amount of agent in the coating, D is the diffusion coefficient, and a is the radius of the cylinder (we have taken the case of a cylindrical coating). The amount released per unit area of the coating, Q, is related to M_t as :

$$Q = M_t / \{2 \pi a L\} \qquad (2)$$

where L is the height of the cylinder. With data for the value of Q as a function of time, we can characterize the release rate profile for the coating and determine the apparent diffusion coefficient by evaluating the slope of a Q versus $t^{1/2}$ plot. Figures 6 and 7 show some data for the release of Sea-Nine 211 (isothiazolone $C_{11}H_{17}NSOCl_2$). From such data, the diffusion coefficient calculates to be 10^{-13} cm^2 s^{-1} when the polymer matrix is a copolymer of vinyl chloride and vinyl acetate (VYHH from Union Carbide). Such data provide a useful model system that allows us to test theory based on simple manipulations in the laboratory. This approach is invaluable in the preparation of other coatings which display constant release rate characteristics.

Constant Release Rate Coatings

Clearly one cannot expect constant long term release from monolithic coatings such as those described above. There are ways to achieve such fluxes, but each requires manipulation of the coating in some fashion. For non-ablative coatings, the requirement is that the driving forces for molecular diffusion and the resistances to diffusion are constant with time. Constant release rates can be achieved by keeping the local concentration of agent at a steady value throughout the lifetime of the coating and simultaneously restricting the diffusional pathway to a constant length. This effort gives rise to two concepts, both involving the creation of a domain of very high concentration of agent that is surrounded by a layer of material to control flux of the AF agent. The first of these ideas is the so called "reservoir membrane". A reservoir membrane is a two-layer coating where the base layer is composed of pure or nearly pure AF agent. The base layer has a top coat applied applied in the form of a polymer which creates a membrane over the AF agent and acts to control the diffusion of the agent to the surface. As long as the agent remains near its initial concentration value, the overall flux will be constant because the diffusional pathway is a constant length. Figure 8 shows a "Q vs time" plot

Figure 6
Quantity of Sea Nine 211 released as a function of time for a monolithic coating initially containing Sea Nine 211 at 20-35 wt %.

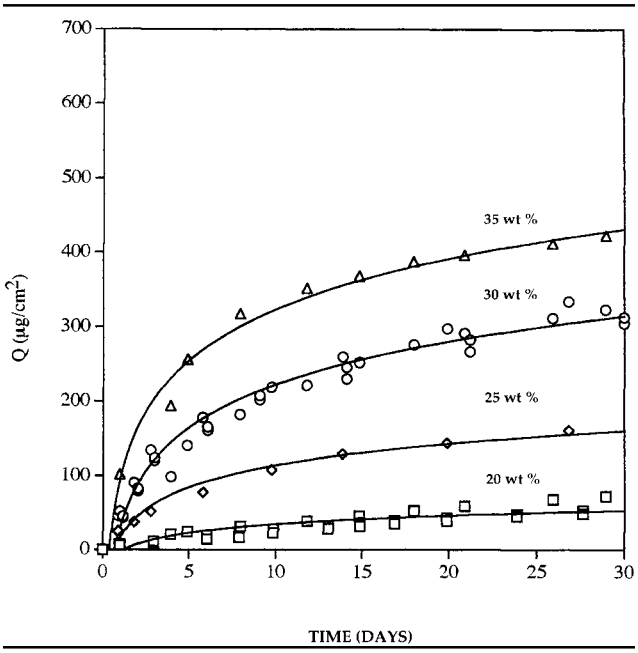


Figure 7
Quantity of Sea Nine 211 released versus square root of time for a monolithic coating initially containing Sea Nine 211 at 20-35 wt %.

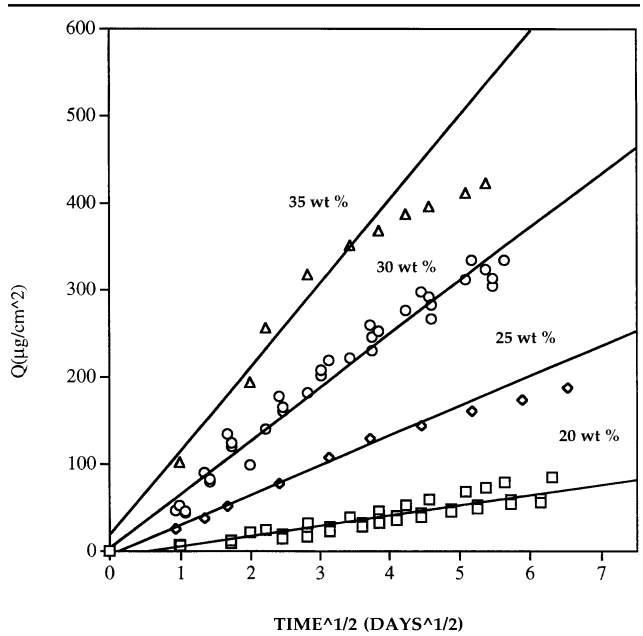


Figure 8
Quantity of Sea Nine 211 released versus time for a reservoir membrane coating.

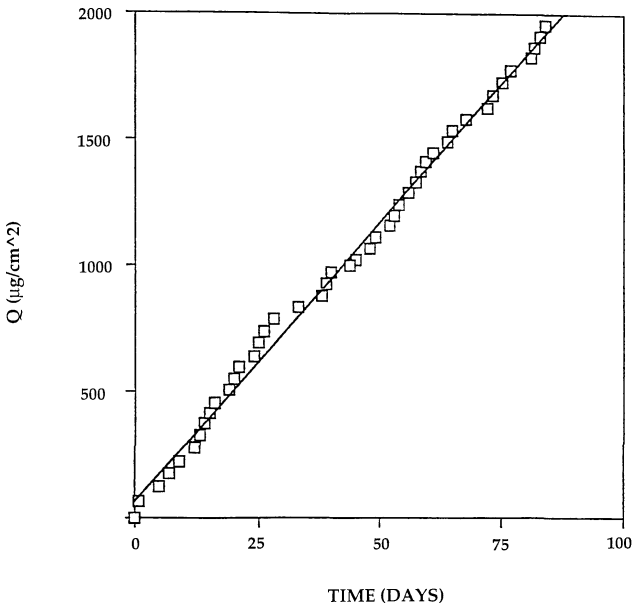
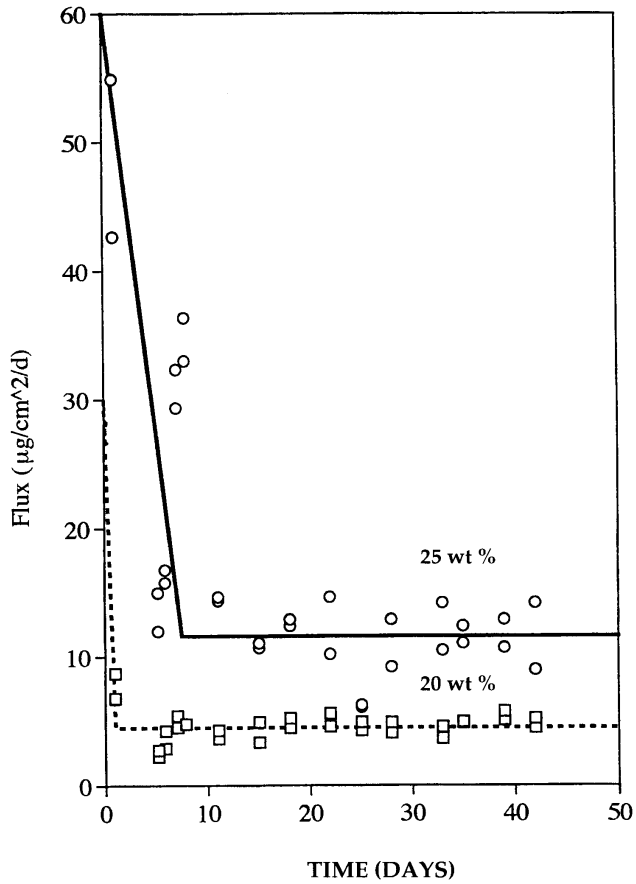


Figure 9
Release rate of Sea Nine 211 at 20 and 25 wt % loading versus time for a microcapsule based coating.



for such a coating in which the base layer was composed of a highly concentrated phase of Sea-Nine 211 dissolved and dispersed in a plasticizer (Santicizer™ from Monsanto Co.). The top layer was a room temperature vulcanized silicone coating (RTV3140 from Dow Corning Co.). From these data, the release rate, as judged by the slope of the line fit to the data, is quite constant over the nearly 90 days of the test. In this case the flux was 22 $\mu g\ cm^{-2}\ d^{-1}$.

A second technique to achieve steady release rates is microencapsulation of an AF agent prior to its addition to the polymer matrix. Microencapsulation can be achieved using a pure agent or a highly concentrated solution of agent and a polymer capsule that is insoluble with the matrix polymer. In this case, the release rate will depend on control of the slowed or controlled diffusion through the capsule wall and much more rapid diffusion through the polymer matrix. Another controlling parameter is the size distribution of the microcapsules. In contrast to the concentration-dependent release kinetics from the monolithic coatings containing Sea-Nine 211 in VYHH resin (Fig. 6), microencapsulation provides an effective means for achieving constant release rates over moderate periods of time (Fig. 9). The AF agent was dissolved in tricresyl phosphate at 45 weight % prior to encapsulation and the coating was prepared to contain 20 weight % AF agent in the final coating. After the first few days, the release of Sea-Nine 211 was quite steady at about 5 $\mu g\ cm^{-2}\ d^{-1}$ for a 100 day period. When time scales expand well beyond 100 d, release rates will likely decline as the concentration of the AF agent within the microcapsules diminishes. One step to alleviate this decline somewhat is to encapsulate pure AF agent.

Evaluation of Antifouling Performance

As with any coating containing one or more AF agents, it is critical to know the minimum release rate needed for that agent to be effective in real world settings. Experience teaches us that such rates may differ among the diversity of marine organisms known to be troublesome foulers in coastal regions worldwide. The diversity in minimum effective release rates must be related in part to the mode of action of a particular AF agent, as described earlier for zosteric acid. While steady release rates from coatings are a final goal, when we evaluate long term effectiveness of a coating-AF agent complex, the use of variable release rate coatings can be extremely valuable in determining the minimum release rate that is effective for problematic fouling species.

Minimum Release Rate Studies

We have taken advantage of the variable release rate characteristics of monolithic coatings to establish the minimum flux of Sea Nine 211 necessary to control settlement by a variety of fouling species by conducting field trials in both Atlantic and Pacific Test sites. Here we prepared a variety of coatings based on VYHH polymer matrix with different loadings of Sea-Nine 211 dissolved in them. The test materials were produced by coating cylindrical rods of glass filled epoxy with the various coating formulations. The rods were then placed in the marine environment and tested weekly for the extent and nature of fouling over a 28 day period following Rittschof et al.[12]. This length of time is sufficient to determine the minimum effective flux necessary to minimize fouling of particular target organisms. Simultaneously, we measured release rates in the laboratory and have been able to establish substantial correlation between the release rate for Sea-Nine 211 in VYHH resin and the extent of fouling for a diverse group of temperate and tropical species[19]. Because the polymer matrix of the coating may have an effect upon the minimum release rate determination, we normalize the fouling data to a control sample of the same resin without any AF agent. Figure 10 shows the type of results that can be obtained from such a manipulation. These data represent results for arborescent hydrozoans obtained from field trials conducted in different oceans over different seasons of the year. The various data points represent samples analyzed at 7, 14, 21, and 28 days. A flux above 5 to 7 $\mu g\ cm^{-2}\ d^{-1}$ keeps the hydrozoan from fouling the AF + VYHH coating. Similar data are available for diatoms, barnacles, amphipods and polychaete worms, including *H. elegans* and colonial tunicates.[19] Interestingly, the minimum effective release rates for all of these species excepting diatoms and barnacles were also in the 5 to 7 $\mu g\ cm^{-2}\ d^{-1}$. Both diatoms and barnacles required greater fluxes, estimated at this point to be in the 15 to 25 $\mu g\ cm^{-2}\ d^{-1}$ range. The strength of this approach comes from the ease with which effective concentrations can be determined for a variety of troublesome fouling organisms in their real world habitats but with an accelerated timeframe for data acquisition. This approach is new but appears very powerful in being able to diagnose minimum effective release rates for the study of any other AF agent and/or another matrix resin.

Constant Release Rate Studies

Results from minimum release rate determinations can be very helpful to formulate and rapidly test new coatings which deliver the agent at constant rates. We extended these studies by preparing Sea-Nine 211 microcapsule based coatings (with VYHH matrix polymer) to deliver Sea-Nine 211 at fluxes significantly above and just below the 5 to

Figure 10
Normalized extent of fouling of arborescent hydrozoans versus release rate of Sea Nine 211 for a monolithic coating.

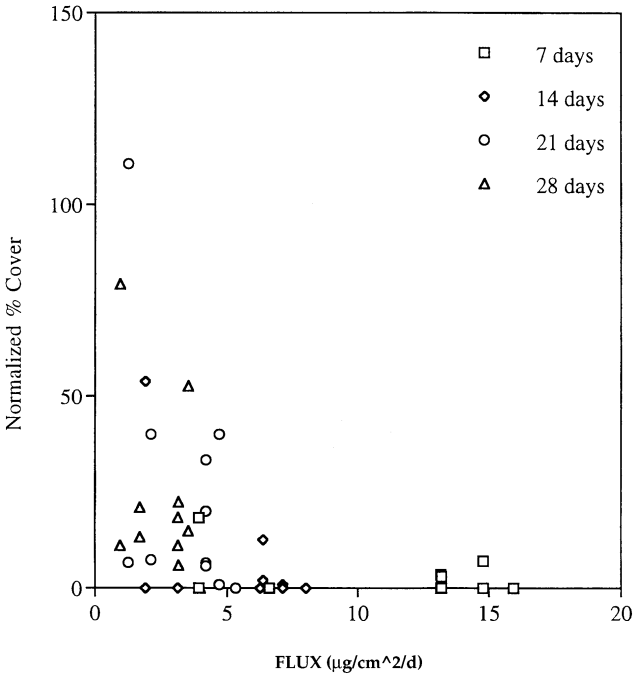


Figure 11
Normalized extent of fouling of arborescent hydrozoans versus time for a microcapsule based coating at two different release rates of Sea Nine 211.

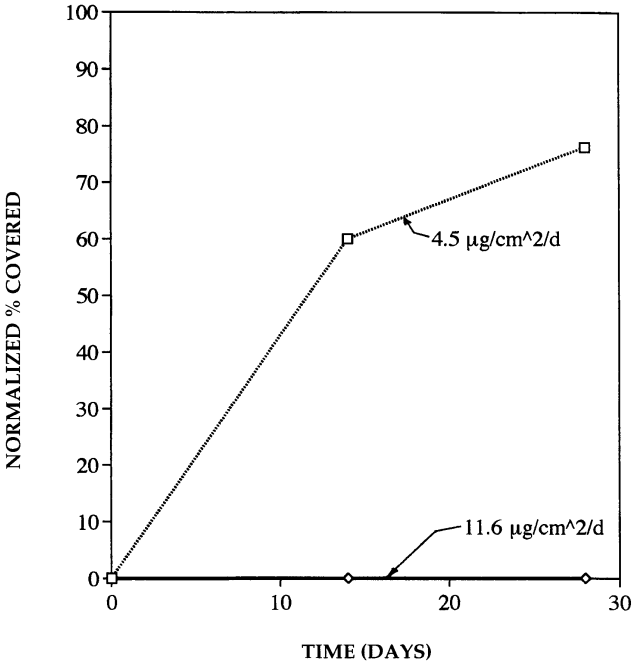
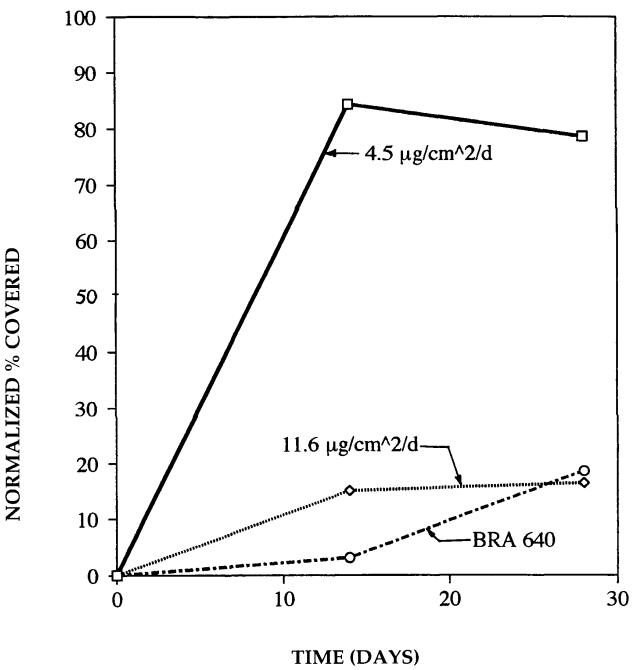


Figure 12
Normalized extent of fouling of diatoms versus time for a microcapsule based coating at two different release rates of Sea Nine 211. Extent of fouling for copper oxide control coating (BRA 640) included for comparison.



7 µg cm^{-2} d^{-1} values determined as above. These samples were tested in Pearl Harbor waters for a period of 60 days and the results for arborescent hydrozoans are shown in Figure 11. Clearly at a flux of 11 to 12 µg cm^{-2} d^{-1}, the fouling of this species has been well controlled, while a flux of 4 to 5 µg cm^{-2} d^{-1} resulted in only partial control. As expected from the minimum release rate study, these two microcapsule-based coatings performed poorly against diatoms. In Figure 12, the test coatings demonstrate different partial levels of control. The standard ablative copper-based marine paint (BRA 640) did not control diatom fouling any better than the higher releasing (i.e. 11-12 µg cm^{-2} d^{-1}) Sea-Nine 211 coating (Fig. 12). All of these results demonstrate the utility of the minimum release rate procedure described above as well as the practicality of microcapsule based coatings. Further it demonstrates that copper ablative coatings with the addition of an AF agent such as Sea-Nine 211 may not offer significant AF advantages over formulations containing just copper.

Future Directions

The directions outlined here point out new arenas that result from novel combinations of polymer chemistry, natural products chemistry with marine biology and ecology to solve the age-old problems associated with biofouling. There will likely always be a need to search for new AF agents that will both be (i) broadly effective at low flux rates and (ii) even more benign to the marine environment because the settling organisms themselves may evolve to new fouling strategies. In this kind of ecological arms race, we have accelerated testing and other innovations to identify new sources of non-toxic natural products from diverse classes of marine organisms screened with larval settlement as a rapid, powerful bioassay. Future environmental concerns will also focus on safety associated with painting and drydock operations. Future complex multicomponent coatings may payoff in novel ways by minimizing fouling among complex biological communities world-wide. Finally, other matrix polymers will have to be examined or even created as we take advantage of materials with lower surface energy, easy release characteristics and other technological breakthroughs brought about for the coatings of the next century.

Acknowledgments

This work has been supported by the Office of Naval Research under contract numbers N00014-91-J-1536 and N00014-92-J-1516 to DCS, N00014-92-J-1687 and N00014-95-I-G007 to RCZ, and N00014-91-J-1932 and N00014-94-I-0196to CMS for which the authors are grateful. The collaboration among academic, US Navy and industrial scientists and engineers involved in this program has been critical to the advancements described in this article.

Biographies

Dr. Donald Sundberg is the Vice President of Research and Public Service at the University of New Hampshire. He is also the Director of the Polymer Research Group within the Department of Chemical Engineering. His research interests are in controlled release technology, surface science, and in polymer reaction kinetics and composite particle morphology of emulsion polymers.

Dr. Niraj Vasishtha is the Manager of the Microencapsulation and Process Research Section in the Chemistry and Chemical Engineering Division at Southwest Research Institute. His primary research focus is in the microencapsulation of food, pharmaceutical, agricultural, and consumer products. His other interests are in controlled release technology, polymer coatings and blends.

Dr. Richard C. Zimmerman is Associate Research Scientist at Moss Landing Marine Laboratories, San Jose State University. His research interests are in the ecological physiology of marine autotrophs, particularly with regard to environmental influences on photosynthesis, nutrient uptake, chemical composition, resource partitioning and growth of seagrasses and seaweeds.

Dr. Celia M. Smith is Associate Professor of Botany, Botany Department of the University of Hawaii and active in the field of biofouling research with emphases on algal

recognition of potential fouling surfaces via settlement cues and identification of new non-toxic antifouling agents from algae.

REFERENCES

1. Brady, S.A., Johns, R.B., & Smith, J.D. 1994. *Mar. Poll. Bull*. 28:230-4.
2. Crank, J. 1975. *The Mathematics of Diffusion.* Oxford Clarendon Press. 2nd ed., pp 77-9.
3. Davis, A.R., Targett, N.M., McConnell, O.J. & Young, C.M. 1989. *Bioorg. Mar. Chem.* 3:85-114.
4. Filion-Myklebust, C. & Norton, T.A. 1981. *Mar. Biol. Let.* 2:45-51.
5. Hadfield, M. G., Unabia, C. C., Smith, C. M., Michael, T. M. 1994. Settlement preferences of the ubiquitous fouler *Hydroides elegans*. In: Thompson, M. F., Nagabhushanam, R., Sarojini, R., Fingerman, M. (eds.) Recent developments in biofouling control. Oxford and IBH Publishing Co. New Delhi, pp 67-74.
6. Hay, M. E. & Fenical, W. 1988. *Ann. Rev. Ecol. Syst*. 19:111-145.
7. Higuchi, T. 1963. *J. Pharm. Sci.* 52: 1145-9
8. Michael, T. & Smith, C. M. 1995. *Mar. Ecol. Prog. Ser.* 119:229-236.
9. Patton, W.K. 1972. *Bull. Mar. Sci*. 22:419-31.
10. Pearce, F. 1995. *New Scientist* 45:7.
11. Rittschof, D., Hooper, I.R., Branscomb, E.S., & Costlow, J. D. 1985. *J. Chem. Ecol.* 11:551-64.
12. Rittschof D., Clare, A. S., Gerhart, D. J., Boneventura, J., Smith C. M., & Hadfield, M.G. 1992. *Biofouling* 6: 181-92.
13. Rublee, P.A., Lasker, H.R., Gottfried M. & Roman, M.R. 1980. *Bull. Mar. Sci*. 30:888-93.
14. Sieburth, J.M. & Conover J.T. 1965. Nature 208:52-3.
15. Stephenson, M.D. & Leonard, G.H. 1994. *Mar. Poll. Bull*. 28:148-53.
16. Targett, N.M. 1988. Allelochemistry in marine organisms: Chemical fouling and antifouling strategies. In: Thompson, M. F., Sarojini, R., Nagabhushanam, R. (eds*) Marine Biodeterioration*. Oxford and IBH Publ. Co. Pvt. Ltd., New Delhi, pp. 609-18.
17. Targett, N. M., Bishop, S. S., McConnell, 0. J. & Yoder, J. A. 1983. *J. Chem. Ecol*. 9:817-29.
18. Todd, J.S., Zimmerman, R.C., Crews P. & Alberte R.S. 1993. *Phytochem*. 34:401-4.
19. Vasishtha N., Sundberg D., & Rittschof D. 1995. *Biofouling* 9:1-16.
20. Vrolijk, N.H., Targett, N.M., Baier, R. E. & Meyer A. E. 1990. *Biofouling* 2:39-54.
21. Walters, L.J., Hadfield M.G., & Smith, C.M. 1996. *Marine Biology* 126:383-93.
22. Yamashita, N., Etoh, H., Sakata, K., Ina, H. Ina, K. 1989. *Agric. Biol. Chem*. 53:2827-2830.

Certification of Properties of Nontoxic Fouling-Release Coatings Exposed to Abrasion and Long-Term Immersion

Robert E. Baier, Anne E. Meyer, and Robert L. Forsberg, Industry/University Center for Biosurfaces, State University of New York at Buffalo, Buffalo, NY

Introduction

Laboratory and field trials have demonstrated that methylsilicone-based coatings having critical surface tensions between 20 and 25 mN/m allow the easiest mechanical detachment of biofouling from coated test panels.[1] Continuing evaluations of such coated panels and trash racks at test sites in Western New York State have confirmed and extended these findings more than 5 years in zebra mussel-infested fresh waters.[2] Coatings which, in addition, contain elutable oils have displayed an apparent further resistance to initial colonization by barnacles and zebra mussels, but this early benefit does not necessarily carry over to the brush-removal forces required for cleaning of the once-fouled coatings. Some of the elastomeric methysilicone coatings are prone to cutting and abrasion damage, limiting their suitability for heavy-duty use and/or situations requiring periodic cleaning. Since standard tests for abrasion and wear (e.g. falling sand test) developed for paints are not applicable to elastomeric coatings, we developed a brush abrasion test to sequentially evaluate fouling-release coatings after increasing numbers of wet brushing cycles. Both laboratory and field-deployed devices are in routine use for this purpose.

The Test Protocol

Table 1 lists the series of analyses included in our protocol for evaluation of fouling-release coatings.

Comprehensive contact angle analyses (Figure 1) are used to determine the critical surface tensions and the composite surface free energies of all samples, as well as the "polar" (including acid and base descriptors) and "disper-

Table 1
Coating Evaluation Methods.

PRE-EXPOSURE EVALUATION	- Comprehensive Contact Angle Analysis - MAIR-IR Spectroscopy - Rotating Brush Abrasion and Wear Test - Oil Uptake/Swelling Test
FIELD TESTS	- Fouling Resistance and Physical Condition Ratings [ASTM] - Swab Test [for MAIR-IR spectroscopy in laboratory] - Delamination Test [finger rub]
POST-EXPOSURE EVALUATION	- Brush Shear Tests [fouling removal] - Comprehensive Contact Angle Analysis - MAIR-IR Spectroscopy

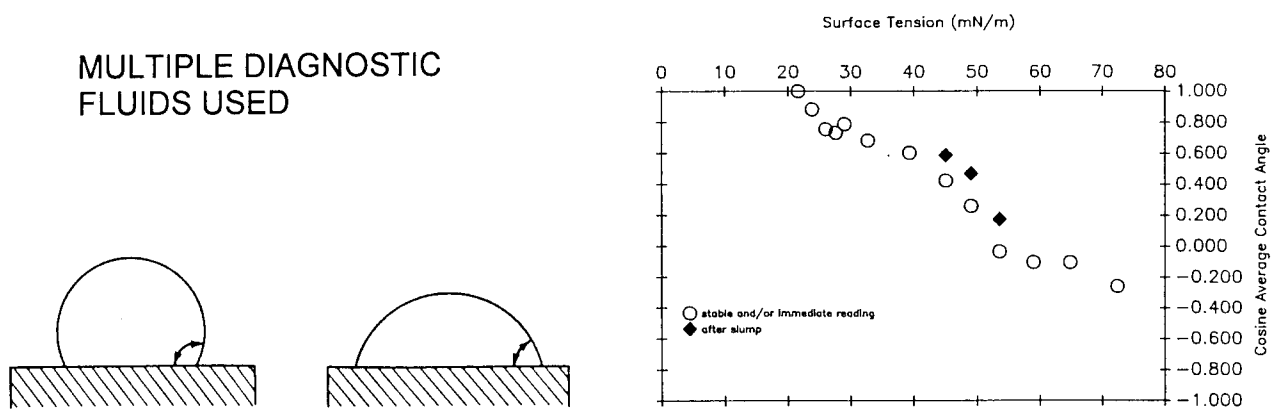
sion" components of the surface energies.[5,6] Contact angle measurements are sensitive to the outermost atomic layers of the sample surfaces, so this technique is most pertinent to characterization of coatings both before immersion (pre-exposure) and after removal of replicates from test sites at various evaluation intervals.

Multiple-attenuated-internal-reflection infrared (MAIR-IR) spectroscopy is applied for the evaluation of the chemical composition of the outermost, approximately, 1000 Angstroms of each coating's surface zone. Methyl, methylene, silicone, epoxy, carbonyl, amide, and other covalently bound moieties are easily detected by this method (Figure 2). Coating or environmental compounds transferred from the samples to internal reflection test plates (e.g. elutable oils, diatomaceous slimes) are easily detected. MAIR-IR spectroscopy, used for characterization of both pre- and post-exposure coatings, generally has revealed biofilm buildup on all the latter specimens.

The rotating brush abrasion and wear test was developed in our laboratory to overcome shortcomings of other accepted paint film test methods.[8] Falling sand (or other abrasive material) tests do not provide meaningful data for the easy-release, elastomeric silicone-based coatings; prior test procedures that utilize brushes evaluate only the outermost aspects of coating surfaces, indicating whether the surface finish dulls within a specific test interval (the brush is unloaded in these procedures).

The rotating brush abrasion and wear test discussed here is customized for foul-release coatings. Standardized nylon bristle brushes are fixed to a rotating wheel, which is positioned against a surface bearing the test coating (Figure 3). The contact pressure (normal to the direction of the brush stroke), is controlled to be approximately 40 psi. This brush load was selected on the basis of numerous laboratory trials to determine the minimum forces required to remove all visible biofouling (including slime films) from coatings that showed consistent easy-release properties in the field.[9] Thus, our tests provide realistic predictions for coating wear

Figure 1
Comprehensive contact angle analysis, as originally described by Young[3], is an affordable, sensitive, and reliable method of monitoring the adhesive properties of any coating. Contact angle measurements characterize the outermost 4-5 Angstroms of a sample. The "critical surface tension" is derived from a graph [Zisman plot], which relates the surface tensions of a variety of diagnostic liquids to the cosines of the angles the liquid droplets make with a given coating surface.[4] Water contact angles, alone, are insufficient, and often misleading, with regard to fouling performance over the long term.



Results reported as

γc - critical surface tension
γd - dispersion component
γp - polar component
γs - composite surface free energy

γLW - London/van der Waals energy
$\gamma +$ - acid component
$\gamma -$ - base component
γAB - combined acid/base
γtot - total surface energy

Figure 2

Internal reflection infrared (IR) spectroscopy[7] is a simple and powerful technique for learning the chemical composition of coatings and their transferrable residues. For thick-layer materials, the sampling depth of the technique ranges from approximately 1 micrometer (for nonabsorbing materials), to as little as 1000 Angstroms for absorbers. Superficial residues, as little as 10-15 Angstroms in thickness, are easily detected by re-analysis of the internal reflection test plate after removal of the primary coating sample. For fouling-release coatings, the amounts of silicone (or other materials) transferred to the test surface via pressure-contact is an excellent indicator of the presence of elutable or releasable components in the sample.

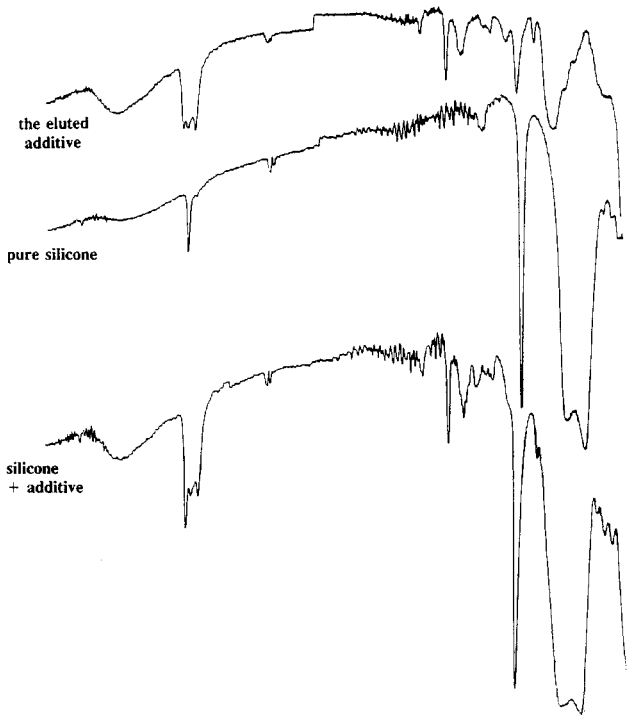
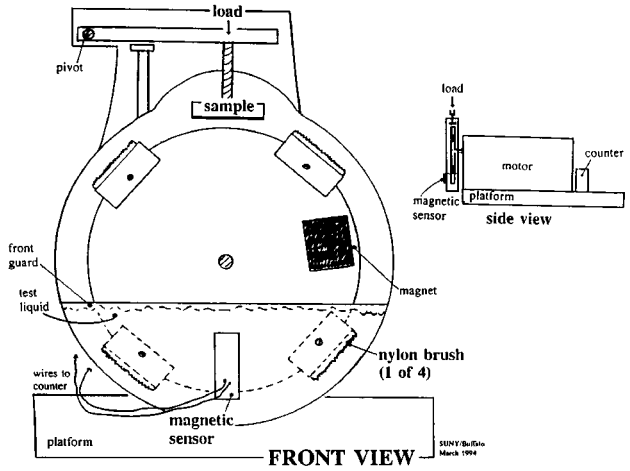


Figure 3

Schematic of the rotating brush abrasion unit, used to evaluate a coating's resistance to cleaning-related damage. Determination of the worn coating's new operational critical surface tension is key to determining whether the coating will maintain its fouling-release character after being abraded.



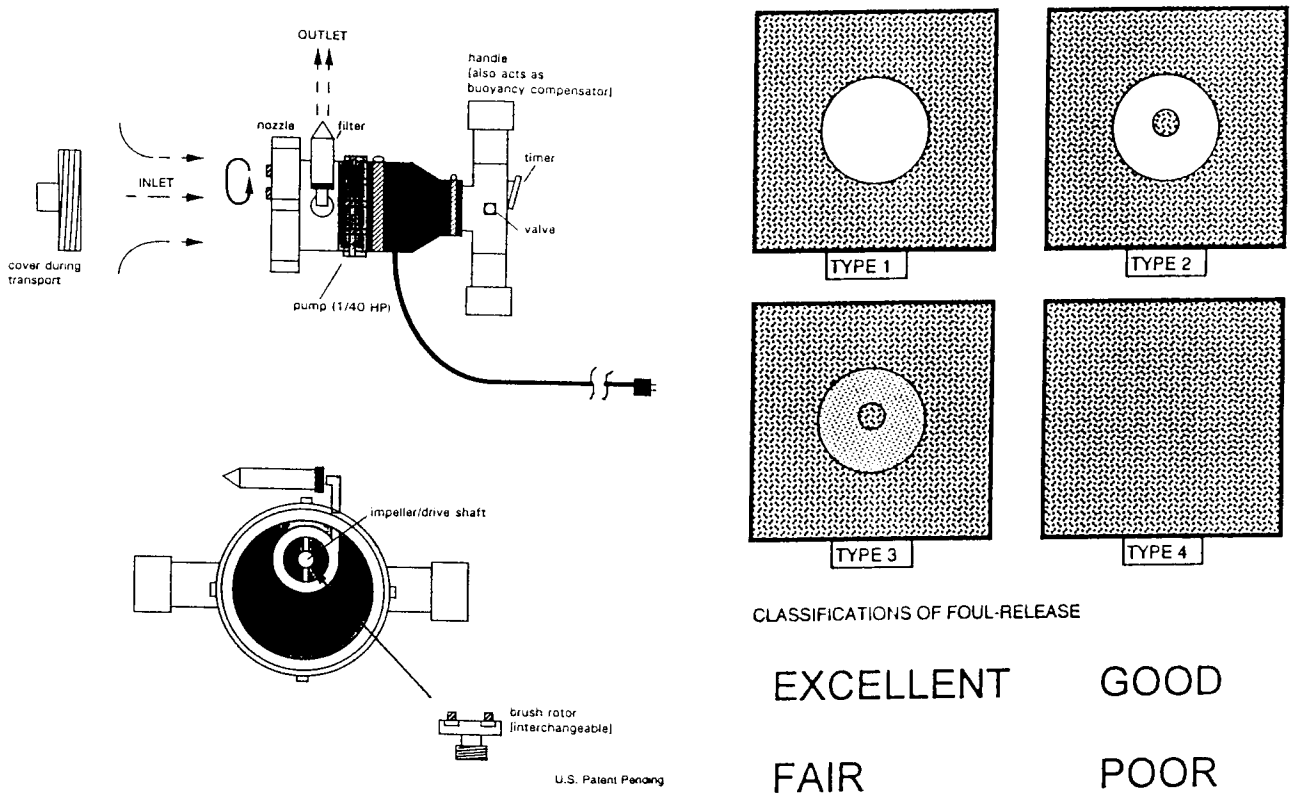
from sequential brush-based cleaning events. In our laboratory device, the brushes move through the top of a reservoir of either freshwater or seawater (depending on the requirements of the study), carrying up clean water before moving across the surface of the coated coupon at a rate of approximately 200 brush strokes per minute. Removed coating fragments collect at the bottom of the water reservoir for later analysis. The coupons, water, debris, and brushes, all, can be saved for a complete evaluation of the wear process. In the field-deployed device (Figure 4), the brushes trace a circular path that leaves behind an annular "ring" pattern in the fouling layer.[10] Pre-exposure brushing of coated panels results in easily recognized "wear rings" on the coating surfaces, to allow later inspection of differences in fouling attachment to the abraded *v.* as-coated regions of the panels.

In the lab test, the coatings are characterized by comprehensive contact angle analyses (to determine sample critical surface tension, which indicates retention or loss of fouling-release character), MAIR-IR spectroscopy (for the chemical signature of exudates and pressure-transferred residues), and depth of wear measurements after each of four intervals of rotating brush abrasion and wear: 20,000 brush strokes, 50,000 strokes, 90,000 strokes, and 145,000 strokes. Exemplary results reported here are for coatings prepared either by the manufacturer or by experienced applicators, in the identical manner employed for coatings exposed in the field.

The oil uptake/swelling test is in the preliminary stages of development in our laboratory. Due to the relatively open, elastomeric structure of most fouling-release coatings, it is possible that dimensional changes due to oil-uptake (recall the fundamental "rule of thumb" in chemistry: "like likes like") or exudation will affect the long-term stabilities of the coatings. Coated coupons are immersed at the waterline (i.e. partial immersion) in a deep container of water into which #2 fuel oil is vortexed in sufficient quantity to saturate the water and allow a thin (iridescent) oil film to remain on its surface. This simulates harbor situations, where coated ships might be on station for extended periods between operational assignments. Some of the fuel remains suspended in the water column. Observations are made for coating dimension changes and any delamination from base coats or the original substratum.

Figure 4

Schematic of the underwater unit used in field brush shear tests to evaluate ease of fouling removal. Brush loading is similar to that in the lab unit (see Figure 3). A simple scoring system is used to evaluate the extent of fouling removed in the test. An "excellent" (Type 1pattern) score indicates that all visible fouling was removed from both the brush path and from the central area, which is untouched by the brushes and is affected only by turbulent water action.



Coatings Wear Differently

The following bar charts illustrate the types of differences found during rotating brush abrasion and wear tests performed with pre-exposure coatings. Figures 5-7 summarize the average depths of wear and post-abrasion results from comprehensive contact angle analyses after each test interval. Table 2 gives a general description of each of the 16 coatings represented in Figures 5-7.

Similar Wear Depths Reveal Different Chemistries

Brush abrasion and wear does remove the fouling-release layers of some coatings, resulting in loss of performance in the field. Among the coatings tested in this group, oil-free and low-oil-content coatings tended to be more abrasion-resistant than oil-laden coatings in the test procedures reported here. Depth of wear does not simply correlate directly with loss of fouling-release properties, due to the variations of topcoat thicknesses and tiecoat compositions from coating to coating. This is an important observation, since it shows that measurements of abrasion resistance, alone, are not sufficient to judge retention of fouling-release qualities.

Continuing field inspections demonstrate that coatings having initial critical surface tensions between 20 and 25 mN/m have better fouling-release properties than coatings with critical surface tensions outside of this range.[1,11] Within the optimal range, however, some coatings perform consistently better than others.[8] Current studies focus on the effects of surface "polarity" and surface "compliance" on the organization of vicinal water that may influence biological adhesion strengths and drag phenomena.[12,13]

Some fouling-release coatings tend to release oils, and others to imbibe floating and suspended oils. Whether these events significantly affect field performance is not yet known. Retention of easy-release properties has been observed for many such coatings over 5-year observation periods, and most are still performing well at this writing. Previously reported observations note that some coatings actually seem

Table 2
Description of Coatings Evaluated by Rotating Brush Abrasion and Wear Test.

A - a toxic (copper-laden) antifouling control coating
B - a commercial silicone with oils
C - a commercial silicone with less oil than B
D - same as "C", but applied to rubber
E - a commercial silicone coating containing styrene
F - a silicone in the R&D stage
G - formulation "F" with oils
H - another silicone in R&D stage
I - another silicone in R&D stage
J - another silicone in R&D stage
K - "RTV" silicone control
L - another silicone in R&D stage, with oils
M - same as "L", but without oils
N - another silicone in R&D stage, with oils
O - a fluorinated polyurethane in R&D stage
P - a methylated polyurethane in R&D stage

to improve in fouling-release character with exposure in the field. Others that do degrade generally fail a "rub test", in which coatings exposed for more than 2 years in the field reveal easy delamination (topcoat from tiecoat). Delamination from steel or concrete substrata has been rare. The occurrence of release-layer delamination is not surprising, given the difficulty of binding such low-energy materials to anticorrosion undercoats. Manufacturers have continued to work on and improve this aspect of their coating systems, since it is now clear that a balanced evaluation of fouling-release coatings must include abrasion resistance (with maintenance of surface chemical integrity), resistance to oil-uptake and swelling, and resistance to delamination as a function of exposure time, as well as minimization of the relative strengths of fouling adhesion.

Figure 5
Results of rotating brush abrasion and wear test for Coatings A-E [see Table 2]. Stars indicate that the average depth of wear was less than 0.3 thousandths of an inch. Solid circles indicate that the abraded coating no longer has a critical surface tension in the "fouling-release zone". Coating A was not designed as a fouling-release material.

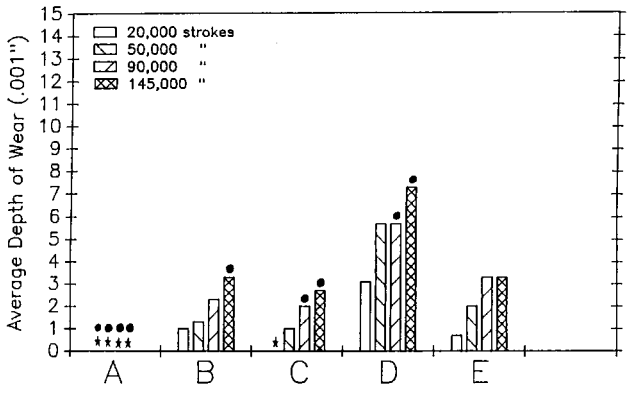


Figure 6
Results of rotating brush abrasion and wear test for Coatings F-J [see Table 2]. Symbols are defined in Figure 1 caption.

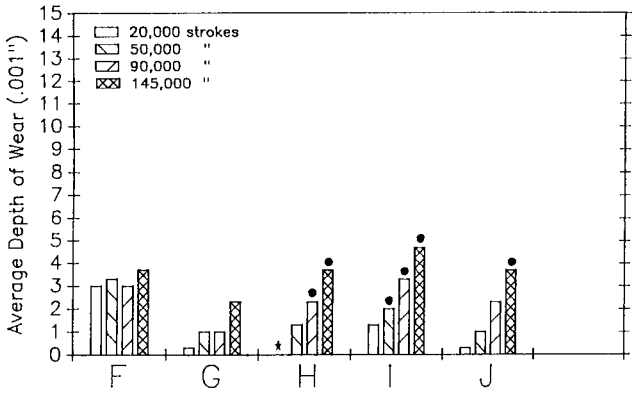
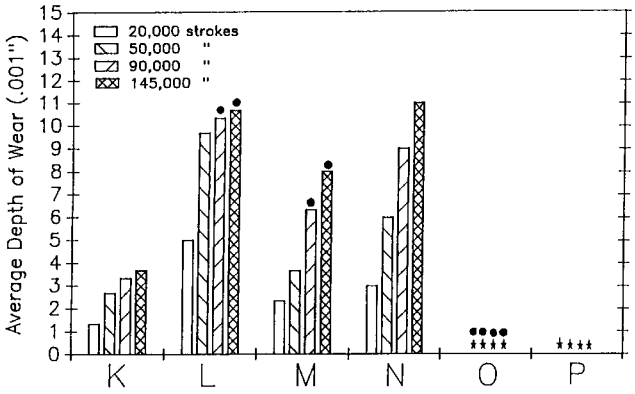


Figure 7
Results of rotating brush abrasion and wear test for Coatings K-P [see Table 2]. Symbols are defined in Figure 1 caption. Note that the critical surface tension of Coating O was not in the "fouling-release zone", even before the first cycle of abrasion testing.



Acknowledgments

Different aspects of the work reported here have been sponsored by ONR Grant #N00014-89-J-3101, the Environmental Security Technology Certification Program, Niagara Mohawk Power Corporation (Syracuse, NY), and Parsons Power (Reading, PA). The authors thank Lawler, Matusky & Skelly Engineers (Pearl River, NY) for their contributions to the field studies.

Biographies

The authors are with the National Science Foundation-sponsored Industry/University Cooperative Research Center for Biosurfaces (IUCB), of which ONR was a founding member. Dr. Robert Baier trained in Engineering Physics (B.E.S., Cleveland State University, 1962), Biophysics (Ph.D., State University of New York at Buffalo, 1966), and Surface Chemistry (NRC/NAS Postdoctoral at NRL, 1966-68) before joining Cornell Aeronautical Laboratory (1968-84). He joined the faculty of State University of New York at Buffalo on a full-time basis in 1984. Dr. Baier is the Executive Director of IUCB, which involves research activities at 4 different universities in the U.S. Dr. Anne Meyer, Director and Principal Research Scientist at the Center's University at Buffalo site, received her B.S. in Chemistry from SUNY College at Potsdam in 1973 and her doctorate in prosthetic materials from Lund University, Sweden, in 1990. She joined the technical staff of SUNY/Buffalo in 1986, after twelve years with Calspan Corporation (formerly Cornell Aeronautical Laboratory). She was Principal Chemist and Head of Calspan's Surface Science Section during 1983-1986. Mr. Robert Forsberg was originally trained in avionics in the U.S.Marine Corps, completed a B.S. in Biology at State University of New York at Buffalo in 1986, and worked in the materials fabrication industry before joining IUCB as a Research Support Specialist in 1987.

REFERENCES

1. Meyer, A.E., Baier, R.E., and King, R.W. 1988. Initial fouling of nontoxic coatings in fresh, brackish, and sea water. Can. J. Chem. Eng. 66:55-62.
2. Evaluation of nontoxic fouling-release coatings as a means of reducing the attachment of zebra mussels (*Dreissena polymorpha*) at Great Lakes generating stations. 1997. Final project report prepared by Lawler, Matusky & Skelly Engineers LLP and the Industry/University Center for Biosurfaces, SUNY/Buffalo for Niagara Mohawk Power Corporation, Syracuse, NY.
3. Young, T. 1805. An essay on the cohesion of fluids. Philos. Trans. Roy. Soc. Lond. 95:65-87.
4. Zisman, W.A. 1964. Relation of the equilibrium contact angle to liquid and solid constitution. in *Contact Angle: Wettability and Adhesion*. Adv. Chem. Ser. Vol. 43, Amer. Chem. Soc., Washington, D.C., pp 1-51.
5. Baier, R.E. and Meyer, A.E. 1992. Surface analysis of fouling-resistant marine coatings. Biofouling, 6:165-180.
6. Good, R.J., Islam, M., Baier, R.E., and Meyer, A.E. [in press] The effect of surface hydrogen bonding (acid-base interaction) on the hydrophobicity and hydrophilicity of copolymers: Variation of contact angles and cell adhesion and growth with composition. J. Dispersion Sci. and Tech.
7. Harrick, N.J. 1960. Surface chemistry from spectral analysis of totally internal reflected radiation. J. Phys. Chem. 64:1110-1114.
8. Meyer, A., Baier, R., Kohl, J., Singer, I.L., Griffith, J., Haslbeck, E., Montemarano, J.A., Ross, A., Schultz, M., and Swain, G. 1997. Duplex foul-release coatings; Environmental Security Technology Certification Program: Advanced non-toxic antifouling coatings technology demonstration. NSWCCD-TR-64-96/15.
9. Meyer, A.E., Baier, R.E., and Forsberg, R.L. 1994. Field trials of nontoxic fouling-release coatings. Proceedings, 4th International Zebra Mussel Conference. Electric Power Research Institute Report #TR-104029, pp 273-290.
10. White, J.A., Baier, R.E., Forsberg, R.L., and Meyer, A.E. 1995. Abrasion tester. Research Foundation of State University of New York (Buffalo) Patent Disclosure #R5325.
11. Wells, A.W., Meyer, A.E., Matousek, J.A., Baier, R.E., and Neuhauser, E.F. 1997. Nontoxic foul-release coatings for zebra mussel control. Waterpower '97, Proceedings of the International Conference on Hydropower. American Society of Civil Engineers, Vol. 1, pp 451-460.
12. Fruci, V. 1997. Use of nuclear magnetic resonance to characterize liquids structured from various liquid-solid interfaces. Masters thesis, State University of New York at Buffalo.
13. Baier, R.E., Meyer, A.E., Forsberg, R.L., and Ricotta, M.S. 1997. Intrinsic drag reduction of biofouling-resistant coatings. Proceedings, Emerging Nonmetallic Materials for the Marine Environment; U.S.-Pacific Rim Workshop sponsored by U.S. Office of Naval Research, March 18-20, 1997. pp 1.35-1.40.