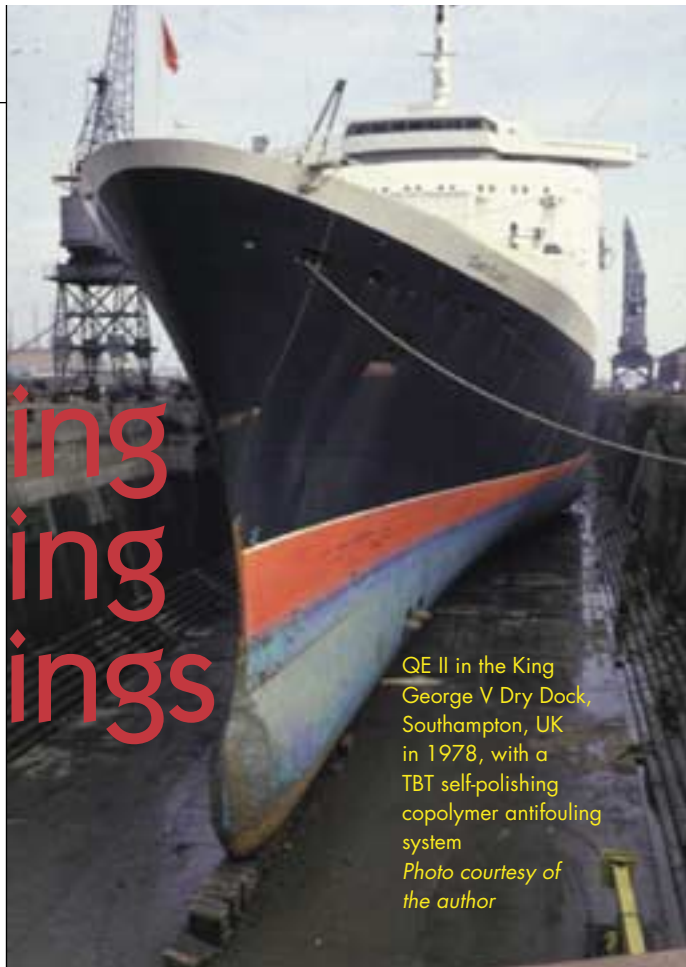


Redefining Antifouling Coatings

by Dr. Geoffrey Swain,
*Oceanography and Ocean Engineering,
Florida Institute of Technology,
Melbourne, FL, U.S.*



QE II in the King George V Dry Dock, Southampton, UK in 1978, with a TBT self-polishing copolymer antifouling system
Photo courtesy of the author

This article describes alternatives to antifouling formulations formulated with tributyltin.

For nearly a quarter century, tributyltin-based self-polishing copolymer antifouling paints have provided an efficient and economic method of ship hull protection. Yet as we enter the 21st century, this important technology is likely to be eliminated by new regulations proposed by the International Maritime Organization.¹ This has created a major challenge for the scientific community and the marine paint industry. The challenge is to formulate replacement systems that meet or exceed the performance standards of tributyltin (TBT) self-polishing copolymer coatings and that comply with present and future environmental regulations.

To redefine antifouling (AF) coatings, it is useful at the outset to understand the properties that made TBT self-polishing coatings so successful and at the same time environmentally unacceptable (Fig. 1).

TBT self-polishing copolymer technol-

ogy, first patented by Milne and Hale in 1974², revolutionized the way the shipping industry does business. A cost/benefit analysis made by Milne and Abel³ compared TBT self-polishing coatings to the next best non-tin alternatives that were available prior to 1982. They estimated that these coatings saved the world's commercial fleet approximately \$2.4 million in direct fuel costs, extended dry-docking, improved ship availability, and capital savings. In addition, there have been unspecified reductions in fossil fuel emissions and the generation of wastes during repainting.

One of the first ships coated with this system was the prestigious liner QE II (shown above). The TBT self-polishing system was so successful that it was soon applied to much of the world's commercial fleets, navies, and recreational craft. Recent estimates suggest that about 70% of the world's commercial fleet is protected by TBT self-polishing coatings.⁴ These systems are able to provide in excess of five years

protection, an average hull roughness of about 100 microns and complete protection against biofouling.⁵

Their success is due to many factors. First of all, tributyltin is an extremely active biocide, about 10 times more toxic than copper.⁶ This means less biocide is required to maintain a fouling-free coating. Secondly, TBT is chemically attached to the methyl methacrylate polymer backbone via an organotin-ester linkage. On immersion in sea water, the copolymer at the paint surface reacts to release the TBT. This causes the copolymer to become brittle and hydrophilic. Removal of the copolymer chain causes a self-polishing action and provides for a new supply of biocide. The coating remains stable because the reaction is confined to an extremely narrow surface layer due to the hydrophobic properties of the unreacted paint film.

TBT self-polishing copolymer paints are usually formulated with cuprous oxide pigments and other organic co-biocides. These combinations enable paint manufacturers to formulate coatings that comply with the most stringent current regulations that limit the maximum release rate to 4 $\mu\text{g}/\text{sq cm}/\text{day}$ TBT (Fig. 2).

Problems

The success of TBT has been overshadowed by its impact on non-target organisms. Ships, boats, and structures coated with AF paints act as a point source input of fouling-control biocides into the marine environment. For example, a 65,000 Gross Registered Ton container ship that is 260 m long has an approximate wetted surface area of 13,000 m^2 . If it is coated with a TBT self-polishing copolymer-based system with a biocide output of 4 $\mu\text{g}/\text{sq cm}/\text{day}$, then the TBT input into the environment would be about 190 kg/year. If a copper-based AF system was used with a minimum biocide output of 20 $\mu\text{g}/\text{sq cm}/\text{day}$, then the copper input into the environment would be about 950 kg/year.

By the late 1970s, a link between the use of TBT in AF paints and damage to the

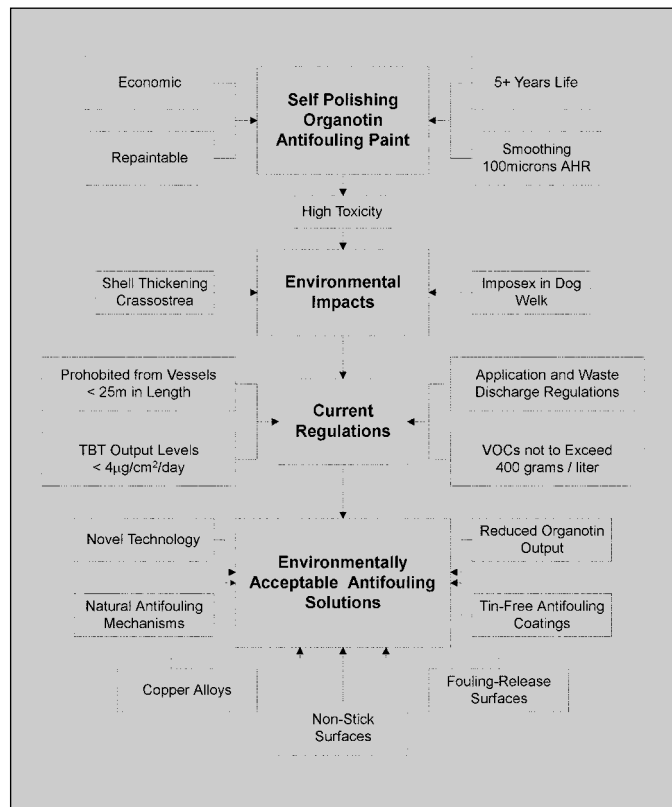


Fig. 1 - Performance and environmental criteria of TBT self-polishing copolymer systems and the development of environmentally friendly antifouling technology

pacific oyster *Crassostrea gigas* was observed along the northwest coast of France. Subsequent research in other parts of the world demonstrated that organotins were indeed impacting non-target organisms. It was shown that TBT concentrations in sea-water as low as 20 nanograms per liter will cause defective shell growth in the oyster, *Crassostrea gigas*⁷ and that concentrations of 1 nanogram per liter are sufficient to disrupt the reproductive capabilities of the female dog-whelk, *Nucella* sp., by causing a condition known as imposex.⁸ More recently, TBT has been implicated in the deaths of bottle-nosed dolphins (*Tursiops truncatus*)⁹ and other marine mammals.

Regulations

The first country to regulate against TBT was France in 1982. These regulations prohibited the use of organotins from recreational boats less than 25 m in length, except for aluminum-hulled vessels.

Antifoulings on U.S. Navy Ships to Require Pollution Controls

The U.S. Navy is an exception to most large ship operators inasmuch that it has chosen not to use organotin-based paints on its ships.¹

Furthermore, it has a goal to develop environmentally sound ships that are capable of operating in compliance with applicable state, federal, and international environmental regulations and that cause no significant adverse environmental impacts.

Section 325 of the 1996 National Defense Authorization Act² amended Section 312 of the Clean Water Act to provide the Department of Defense and Environmental Protection Agency authority to jointly establish Uniform National Discharge Standards for incidental liquid discharges from vessels of the Armed Forces.

Antifouling coatings have been identified as a discharge that will require some sort of

marine pollution control device (MPCD) by December 2000. An MPCD is any equipment or management practice designed to treat, retain, or control discharges incidental to the normal operation of an Armed Forces vessel.

This policy is indicative of future practices and regulations that may affect the worldwide fleet. ○

References

1. R. Alberte, et al., "Biofouling Research Needs for the United States Navy: Program History and Goals," *Biofouling*, Vol. 6, pp. 91-95, 1992.
2. U.S. Environmental Protection Agency, *Uniform National Discharge Standards for Vessels of the Armed Forces; Final Rule*, *Federal Register*: Vol. 63, No. 176, September 11, 1998.

Other countries soon followed, and by the early 1990s, similar regulations were in force throughout the industrialized nations. In addition to the ban on vessels less than 25 m, some countries also required that TBT output not exceed 4 µg/sq cm/day.

It appears that these regulations have had their desired effects, and there has been a decline in TBT concentrations in water, sediment, and aquatic life.¹⁰ However, there is still concern that the use of TBT antifoulings on commercial ships is having adverse impact on the marine environment.

At the 42nd session of the Marine Environment Protection Committee of the International Maritime Organization (2-6 November 1998),¹ a draft resolution was approved that includes a deadline of 2008

for the complete prohibition of organotins acting as biocides in antifouling systems on ships and a prohibition of the application of such systems by 1 January 2003. This draft resolution was again debated at the 43rd session of the MEPC, and it will be submitted to the 21st IMO Assembly in November 1999 to be considered for adoption.

In addition to regulations restricting the use of biocides, paint manufacturers may also have to comply with the amount of hazardous air pollutants (HAP) that can be released. In the U.S., the Environmental Protection Agency has national emission standards for HAP for shipbuilding and ship repair.¹¹ The present regulations stipulate that the amount of permissible volatile organic HAP content for antifouling coatings be 400 g/L or less, and it is likely that the permissible HAP will be further reduced in California.

Alternative Technologies

There are many patents and ideas relating to biofouling control, but so far, few have been found to be practical, economic, or effective.¹²⁻¹⁴ The environmental problems associated with organotin-based systems has forced a move to "environmentally friendly antifouling" systems. This term is not yet fully defined. In its purest sense, it can be interpreted as meaning a system that has no toxic components. In its broadest sense, it may be defined as lessening the impact of TBT self-polishing coatings or the return of copper and other biocides (Fig. 1).

Return of Copper

The most common alternative biocide to organotin is copper. This is usually added to a paint matrix in the form of cuprous oxide.

There are three general categories of copper-based paints: conventional, ablative, and self-polishing. The active life expectancy of a conventional copper paint is 12-18

months. This is due to inefficient leaching characteristics, loss of copper from the surface layer, and build-up of insoluble copper salts (Fig. 2). Ablative systems are formulated so the paint matrix saponifies at about the same rate as the copper is released into the sea water. These systems may achieve an active life of three or more years. Self-polishing copper-based systems have recently been developed¹⁵⁻¹⁷ with claims of five years' protection.

Copper on its own is vulnerable to diatom and algae fouling, and therefore, biocides that act synergistically to enhance the performance are required. The most commonly found additions are diuron, triazine, isothiazolin, and zinc omidine. These compounds, however, may prove to be environmentally undesirable. Diuron and triazine have been shown to be long-lasting in the environment,¹⁸⁻²⁰ and even copper itself has come under scrutiny.^{21,22} Potential environmental problems and regulations associated with copper-based paints coupled with the high cost of biocide registration (more than \$10 million to register a new compound in the U.S.) increase the need to find a non-toxic alternative for AF protection.

Non-Stick and Fouling-Release Surfaces

From an environmental perspective, the non-stick and fouling-release technologies offer the most attractive options for biofouling control.

Interest in the use of non-stick surfaces was stimulated by the synthesis of polytetrafluoroethylene and other hydrophobic plastics in the late 1950s. It took the scientific studies of Baier²³ and Dexter²⁴ to explain the mechanism for the non-stick phenomenon. They demonstrated that settlement and attachment by microorganisms could be related to the surface-free energy of the substrate. They further identified a surface-free energy of 22-24 dynes/cm that produced a minimum of biological adhesive strength. These observations increased interest in the development

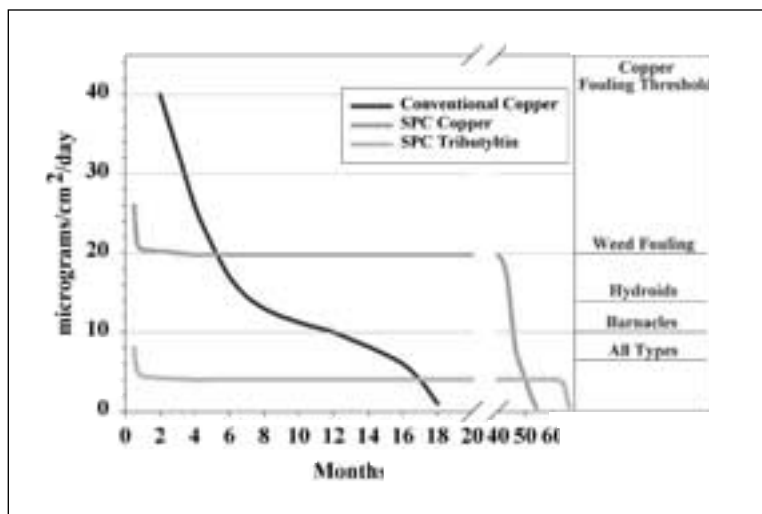


Fig. 2 - Typical performance curves for conventional and self-polishing copolymer antifouling paints

of non-stick surfaces, and a number of fluorinated coatings were developed with superior non-stick characteristics.^{25,26} However, these coatings were unable to provide sufficient non-stick characteristics to prevent attachment by macrofouling organisms. Research continues to investigate the non-stick phenomenon, but to date, no material has been identified that can prevent adhesion by fouling organisms.

The only alternatives to fluorinated compounds identified as having non-stick and fouling-release properties are silicones. In addition to low surface energy and low micro-roughness, which impart non-stick characteristics, these materials have other properties that promote fouling release. Silicones have low glass transition temperatures and low modulus of elasticity. These properties minimize mechanical locking of biological glues, thereby increasing slippage and fouling release.^{27,28} Also, most commercial poly (dimethylsiloxane)-based coatings contain fluid additives. It has been suggested that these additives create weak surface layers and macromosaic surfaces that further promote fouling release.²⁹

Silicone was first reported as a fouling-release coating in 1972 in a patent registered to the Battelle Institution.³⁰ During the 1970s and 1980s, there was only limited interest in these coatings due to the success of TBT self-polishing systems and to some practical limitations of existing silicone for-

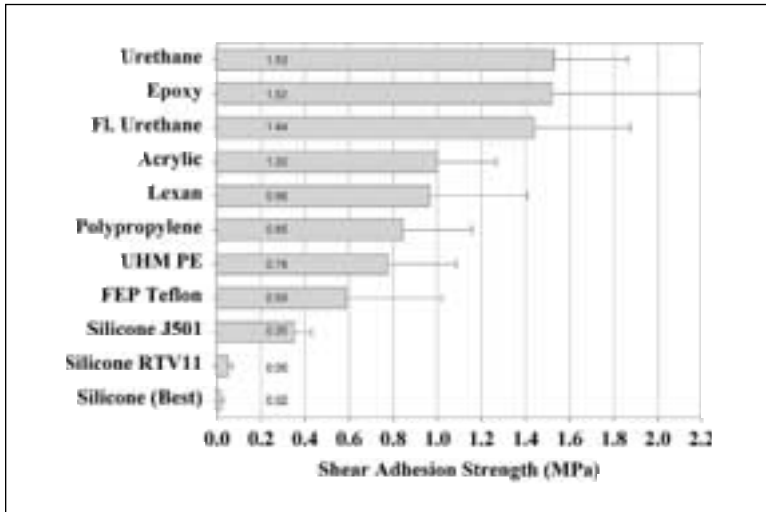


Fig. 3 - Barnacle adhesion strength in shear

mulations.^{31,32} It was only when the biocide-containing coatings came under pressure from environmental regulations that a concerted effort was made to better understand the mechanisms by which silicone formulations function and to improve their performance.

The antifouling properties of these coatings are different from biocide-containing systems. As such, their adoption for use may require a change in operating procedures. Because they are non-toxic, they may become fouled. This is most likely to occur on vessels that spend extended times in port, and under such circumstances the coatings will require some form of in-water hull cleaning. However, for vessels that are continually operating at high speeds, hydrodynamic forces will tend to maintain the hull in a fouling free condition.

The effectiveness of fouling-release coatings can be measured by the ease with which the organisms become detached. In 1994, an ASTM standard for measuring the shear adhesion strength of barnacles was approved.³³ There is now a significant database of barnacle adhesion strength measurements for different species and different substrates (Fig. 3).

From research at Florida Institute of Technology,^{34,35} a model was developed to predict the ship speed required for self-cleaning of individual barnacles (Fig. 4). Assuming free stream velocity and no boundary layer, it was predicted that indi-

vidual barnacles growing on the best performing silicone shown in Figure 3 would self-clean at about 10 knots. This has been confirmed during speed trials on a variety of silicone formulations.

Although the hydrodynamic forces experienced by individual barnacles are easily calculated, at present there is insufficient information to predict the water velocities required to remove other fouling types and communities. This is due to differences in the adhesion strengths and the drag and lift coefficients for different fouling types as well as the variable hydrodynamic characteristics of boundary layer thickness and flow patterns along a ship hull. The Florida Institute of Technology data suggests that hydrodynamic lift and drag forces will be insufficient to remove all the fouling on the best present-day formulations.

Full-scale ship and boat trials have demonstrated that, under optimum operating conditions, the present generation of silicone fouling-release coatings can provide satisfactory biofouling control. The major advantage of these systems are that they are non-toxic, and in addition, there is preliminary evidence to suggest that they provide a smoother surface, reducing skin friction drag thus providing improved performance. Disadvantages of silicones are that they are expensive, exhibit poor adhesion to the substrate, are easily damaged, and require some form of hull cleaning. These drawbacks can partly be addressed by improved coating application and dock yard practice, improved fendering and hull care, and new technology for in-water cleaning.

Future Technology

One possible source of new technology involves natural antifouling processes. In recent years, much research has been devoted to this area, mainly focused on chemical inhibition.

It has long been known that the settling phases of marine organisms respond to a diversity of chemical cues.^{36,37} This has generated interest in identifying com-

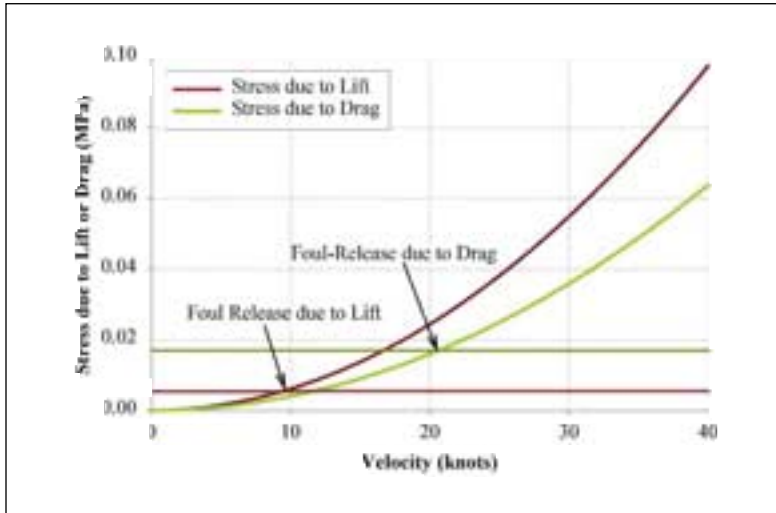


Fig. 4 - Theoretical fouling release velocities for the barnacle *Balanus eburneus* from the best silicone

pounds that might repel or inhibit fouling organisms.³⁸ For a compound to be considered effective, it must satisfy certain conditions, including the following:

- a non-toxic mode of action;
- activity at low concentrations;
- rapid breakdown to non-polluting substances;
- effectiveness over a broad spectrum of biofouling organisms; and
- compatibility with coating systems.

Much of the research has investigated substances derived from organisms that are known to remain free from fouling. For example, extracts from bacteria,^{39,40} algae,^{41,42} sea grasses,⁴³ corals,⁴⁴ sponges,^{45,46} and even terrestrial plants⁴⁷ have been identified as active antifouling agents.

The identification of active compounds is just one of the steps required before they can be incorporated in AF coatings. A mechanism must be found by which they can be combined with the coating matrix and supplied to the surface at a rate sufficient to prevent fouling but without wasting the compound.⁴⁸ Natural sources or synthetic analogues must be identified to ensure supply at a reasonable cost. In addition, the compounds must pass rigorous scrutiny from environmental regulation agencies. No natural products have been commercialized for antifouling yet, but researchers are hopeful of identifying

compounds that can deter fouling without compromising the environment.

Physiological responses that reduce biofouling are also known. For example, all arthropods undergo periodic molts, which will inevitably result in the shedding of old fouled surfaces.⁴⁹ Tissue sloughing in the sponge *Halichondria panicea* has also been associated with antifouling activity.⁵⁰ Antifouling systems comprising a multi-layered surface from which the top layer could periodically be peeled have been proposed, but no practical system has successfully been engineered.

Several studies have investigated the surface properties of marine organisms (e.g., dogfish egg cases⁵¹ and the epidermis of sea urchins⁵²) with respect to biofouling control. These studies identified a variety of interesting mechanisms, but none has been developed into practical solutions.

From a hydrodynamic standpoint, the three groups of greatest interest are the cetaceans (whales and porpoises), teleosts (bony fish), and elasmobranchs (cartilaginous fish). The no-foul condition of porpoise and killer whale skin has been attributed to the outermost surface being composed of a glycoproteinaceous material with low surface energy.^{53,54}

Finally, it should be remembered that behavioral activities frequently associated with biofouling control include spending extended periods of time out of the water (seals, sea lions, sea otters, etc.), migrating into fresh water, or attending cleaning stations (shrimp on coral reefs). Parallel behaviors (dry boat storage, freshwater soaks, and hull cleaning) are often practiced to control biofouling on ships and boats.

Other Technology

It is well known that the 90:10 copper-nickel alloys provide excellent mechanical, corrosion, and AF properties.⁵⁵ They have been successfully used as the hull plate material on several boats⁵⁶ and recently as cladding material. With the use of modern adhesives and polymers, copper alloys can be applied to steel hulls and structures

without creating bimetallic corrosion problems. In unpolluted sea water, this alloy exhibits relatively low homogeneous corrosion rates, which prevent fouling, and yet it maintains a relatively smooth surface. It is interesting to note that a 1 millimeter-thick copper foil homogeneously corroding at 20 $\mu\text{g}/\text{sq cm}/\text{day}$ would theoretically last about 120 years.

In some ways it is surprising that these materials have not received wider use. However, higher capital cost compared to AF paints, the possibility of galvanic interactions with other metal components and cathodic protection systems, and unpredictable performance in polluted waters have prevented their widespread adoption.

The use of electricity, through conductive coatings, has been proposed by many researchers.⁵⁷⁻⁵⁹ By creating anodic (halogen evolution) or cathodic (high pH) conditions at the paint surface, organisms can be deterred or even killed. However, neither has been made to work for extended periods due to voltage drop across the surface, cathodic chalk formation, and possible corrosion of the underlying steel.

Smooth surfaces generally foul less than rough surfaces. However, no topographical surface condition has been identified that will prevent biofouling. One recent idea has been the use of microfibers,⁶⁰ but this has yet to be verified by long-term field testing.

Thermal control of biofouling is well known and practiced at some power utilities.⁶¹ However, heat or cryogenic treatments of ship hulls and structures are impractical.

Summary

Unless there is a last-minute reprieve for TBT self-polishing copolymer materials, the marine industry is going to be looking for antifouling coatings with equal or better performance.

In the short term, it would appear that copper-based systems will re-emerge. The most promising of these are the new generation of copper self-polishing copoly-

mer paints. However, at present their long-term performance is unsubstantiated, and it is possible that the increased use of copper in combination with co-biocides will prove as equally environmentally undesirable as TBT.

The other technology vying for market share is fouling-release silicone. Its non-toxic mode of action and the possibility of reduced skin friction characteristics compared to the TBT self-polishing paints makes it extremely attractive. However, there are technological and operational problems to be overcome. Improvements are needed in coating toughness, abrasion and cut resistance, and adhesion to the tie coat. Operationally, these coatings may require periodic in-water cleaning, and this will require the development of devices that can clean without damaging the coating. Ship operators may also have to pay greater attention to fendering and mooring to reduce damage to the systems.

The present copper- and silicone-based technologies do not provide systems that are equal to or better than TBT self-polishing paints. Therefore, research and development is still required. This may involve alternative non-stick and fouling-release materials. New ideas may be developed by studying natural AF mechanisms or by better understanding the cues that determine the settlement of the dispersal phases. The idea of discovering a non-toxic compound that deters settlement is indeed attractive.

Many novel ideas have been proposed for biofouling control. Several are not considered environmentally acceptable; others are not feasible with present technology; and many do not work. However, it is important that new ideas continue to be promoted and evaluated through peer review and trial and error.

Finally, it should be remembered that the development of new AF technology requires a multi-disciplinary approach. Knowledge of biological, chemical, and physical properties as well as an understanding of operational requirements of the system are all necessary to solve the age-old problems of biofouling control. □

References

1. International Maritime Organization, Marine Environment Protection Committee, 42nd session, 2-6 November 1998.
2. A. Milne and G. Hails, Patent GB 1 457 590, International Paint Plc, 3 April 1974.
3. A. Milne and P.D. Able, "Cost Benefit Analyses of Remediation of TBX Contamination," *Environmental Impact of Tributyl Tin (TBT) and Development of Methods for the Treatment of Contaminants by Biotechnological Means*, MEDSAP 91-1/UK/002/INT06, 1995.
4. A. Milne, "Roughness and Drag from a Marine Paint Chemist's Viewpoint," Paper 12, *International Workshop on Marine Roughness and Drag*, The Royal Institution of Naval Architects, London, March 1990.
5. C.D. Anderson, "Tin vs. Tin-Free Antifoulings," *proceedings of Protecting the Ship While Safeguarding the Environment*, London, 5-6 April 1995.
6. C.D. Anderson and R. Dalley, "Use of Organotin in Antifouling Paints," *proceedings of Oceans 86*, V. 4, Washington, DC, September 1986.
7. C. Alzieu, "TBT Detrimental Effects on Oyster Culture in France—Evolution Since Antifouling Paint Regulation," *proceedings of Oceans 86, Organotin Symposium*, Marine Technology Society, Washington, DC, V. 4: 1130-1134, 1986.
8. P.E. Gibbs and G.W. Bryan, "Reproductive Failure in Populations of Dog-Whelk *Nucella lapillus* Caused by Imposex Induced by Tributyltin from Antifouling Paints," *Journal of the Marine Biological Association UK*, Vol. 67: 507-523, 1986.
9. K. Kamman, et al., "Elevated Accumulation of Tributyltin and Its Breakdown Products in Bottlenose Dolphins (*Tursiops truncatus*) Found Stranded Along the U.S. Atlantic and Gulf Coasts," *Environ. Sci. Technol.*, 31, 296-301, 1997.
10. S.M. Evans, et al., "An Assessment of Tributyltin Contamination in the North Atlantic Using Imposex in the Dogwhelk *Nucella lapillus* as a Biological Indicator of TBT Pollution," in *Invertebrate Reproduction and Development*, 34: 2-3, 277-287, 1998.
11. U.S. Environmental Protection Agency, National Emission Standards for Hazardous Air Pollutants: Proposed Standards for Shipbuilding and Ship Repair, 40 CFR Part 63, December 6, 1994.
12. "Marine Fouling and Its Prevention," Woods Hole Oceanographic Institution, 1952.
13. E.C. Fischer et al., "Technology for Control of Marine Biofouling—A Review," *Marine Biodeterioration: An Interdisciplinary Study*, Naval Institute Press, 1981.
14. G.W. Swain, "Biofouling Control: A Critical Component of Drag Reduction," *International Symposium on Seawater Drag Reduction*, Newport, RI, USA, 22-24 July 1998.
15. Yoshibiro Honda, "Quantum Leap Technology After Ban of TBT in Japan," *proceedings of Emerging Nonmetallic Materials for the Marine Environment*, Honolulu, HI, USA, 18-20 March 1997.
16. Ping-Lin Kuo, et al., "Interface-Crashed Self-Polishing Type of Tin-Free Antifouling Coating," *proceedings of Emerging Nonmetallic Materials for the Marine Environment*, Honolulu, HI, USA, 18-20 March 1997.
17. Anon., "Five-Year Japanese TBT-free SPC System—But at a Price!" *Ship Repair and Corrosion Technology*, 1st Quarter, pp. 24-31, 1997.
18. Anon., "Review of Current and Future Marine Anti-Fouling Coatings," *Marine Safety Agency, UK, Report 93/TIPEE/4787*, 1993.
19. M. Callow and G.L. Willingham, "Degradation of Antifouling Biocides," *Biofouling*, V. 10, pp. 239-249, 1996.
20. F. Pearce, "Alternative Antifouling Widespread in Europe," *New Scientist*, p. 7, 14 January 1995.
21. D. Claisse and C. Alzieu, "Copper Contamination as a Result of Antifouling Paint Regulation?" *Marine Pollution Bulletin*, V. 26, No. 7, pp. 395-397, 1993.
22. J.J. Molnar, "Copper Storage in the Liver of the Wild Mute Swan (*Cygnus olor*). Its Possible Relation to Pollution of Harbor Waters by Antifouling Paints," *Archives of Pathology and Laboratory Medicine*, V. 107, No. 12, pp. 629-632, 1983.
23. R.E. Baier, "Influence of the Initial Surface Condition of Materials on Bioadhesion," *proceedings of the 3rd International Congress on Marine Corrosion and Fouling*, pp. 633-639, October 1972.
24. S.C. Dexter, "Influence of Substrate Wettability on the Formation of Bacterial Slime Films on Solid Surfaces Immersed in Natural Sea Water," *proceedings of the 4th International Congress on Marine Corrosion and Fouling*, pp. 137-144, June 1976.
25. J.R. Griffith and J.D. Bultman, "Fouling Release Coatings," *Naval Engineers Journal*, pp. 129-132, April 1980.
26. R.F. Brady, et al., "Nontoxic Alternatives to Antifouling Paints," *Journal of Coatings Technology*, Vol. 59, pp. 113-119, 1987.
27. B.Z. Newby, M.K. Chaudbury, H.R. Brown, "Macroscopic Evidence of the Effect of Interfacial Slippage on Adhesion," *Science*, Vol. 269, pp. 1407-1409, 8 September 1995.
28. A.E. Mera, et al., "Toward Minimally Adhesive Surfaces Utilizing Siloxanes," *Naval Research Reviews*, Vol. XLIX, pp. 4-8, 1997.
29. W.A. Finzel and H.L. Vincent, "Silicones in Coatings," *Federation Series on Coating Technology*, March 1996.
30. K. Kroyer, Great Britain Patent 1,397,001, 1973.
31. A. Milne and M. Callow, "Non-Biocidal Antifouling Processes," *Transaction of the Institute of Marine Engineers*, Conf. 2, Paper 37, 1984.
32. A. Milne, M. Callow, and R. Pitchers, "The Control of Marine Fouling by Non-Biocidal Systems" in *Algal Biofouling*, L.V. Evans and K.D. Hoagland (eds.) Elsevier, Amsterdam, 1986.
33. ASTM D5618, *Standard Test Method for Measurement of Barnacle Adhesion Strength in Shear*, American Society for Testing & Materials, 1994.
34. G.W. Swain and M.P. Schultz, "The Testing and Evaluation of Non-Toxic Antifouling Coatings," *Biofouling*, Vol. 10, p. 187-197, 1996.
35. M.P. Schultz, C.J. Kavanagh, and G.W. Swain, "Hydrodynamic Forces on Barnacles: Implications on the Detachment from Fouling-Release Surfaces," *Biofouling*, 1999.
36. J.R. Paulik, "Chemical Ecology of the Settlement of Benthic Marine Invertebrates," *Oceanography and Marine Biology Annual Review*, 30: 273-335, 1992.
37. M.G. Hadfield, "Research on Settlement and Metamorphosis of Marine Invertebrate Larvae: Past, Present and Future," *Biofouling*, Vol. 12 (1-3), pp. 9-30, 1998.
38. A.S. Clare, "Marine Natural Product Antifoulants: Status and Potential," *Biofouling*, Vol. 9, pp. 211-229, 1996.
39. C. Holmstrom, et al., "Regulation of Activity and Settlement of Marine Organisms by Bacterial Extracellular Components," *proceedings of Emerging Nonmetallic Materials for the Marine Environment*, Honolulu, HI, USA, 18-20 March 1997.
40. S. James, et al., "Marine Bacteria Immobilized in Hydrogel Prevent Settlement of Larvae," *3rd International Marine Biotechnology Conference*, Tromsø, Norway, 1994.
41. N.G.M. Nadal, "Process for Producing Antibiotic, Antifungal and Antifouling Substances by Solvent Extraction of *Sargassum natans*, *Chondria littoralis* and *Cymopolis barbata* and the resulting products," U.S. Patent No. 3,415,928, 10 December 1968.
42. P.D. Steinberg, R. de Nys, S. Kjelleberg, "Chemical Inhibition of Epibiota by Australian Seaweeds," *Biofouling*, Vol. 12 (1-3), pp. 227-244, 1998.
43. J.S. Todd et al., "The Antifouling Activity of Natural and Synthetic Phenolic Acid Sulfate Esters," *Phytochemistry*, Vol. 34, No. 2, pp. 401-404, 1993.
44. D. Rittschoff, et al., "Barnacle In Vitro Assays for Biologically Active Substances: Toxicity and Settlement Inhibition Assays Using Mass Cultured *Balanus amphitrite* amphitrite Darwin," *Biofouling*, Vol. 6 (2), pp. 115-123, 1992.
45. C. Unabia and M. Hadfield, "Bioactive Marine Isonitrile Compounds from Hawaiian Sponges as Models for Synthetic Nontoxic Antifouling and Antibiotic Agents," *proceedings of Emerging Nonmetallic Materials for the Marine Environment*, Honolulu, HI, USA, 18-20 March 1997.
46. P.R. Willemssen, "The Screening of Sponge Extracts for Antifouling Activity Using a Bioassay with Laboratory Reared Cyprid Larvae of the Barnacle *Balanus amphitrite*," *International Biodeterioration and Biodegradation*, 1995.
47. S.S. Sawant and A. Wagh, "Terrestrial Plants: A Potential Source for Isolation of Eco-Friendly Antifouling Compounds," *proceedings of Emerging Nonmetallic Materials for the Marine Environment*, Honolulu, HI, USA, 18-20 March 1997.
48. G.R. Weisman, et al., "Controlled Release Antifouling Coatings. 1. Approaches for Controlled Release of 2,4-Dinitrophenolate and Benzoate into Seawater," *Biofouling*, Vol. 6 (2), pp. 123-147, 1992.
49. K. Becker and M. Whal, "Behaviour Patterns as Natural Antifouling Mechanisms of Tropical Marine Crabs," *Journal of Experimental Marine Biology and Ecology*, Vol. 203, No. 2, pp. 245-258.
50. D. Barthel and B. Wolfrath, "Tissue Sloughing in the Sponge *Haliclondria panicea*: A Fouling Organism Prevents Being Fouled," *Oecologia*, Vol. 78, No. 3, pp. 357-360, 1989.
51. J.C. Thompson, et al., "Antifouling Performance of the Embryo and Eggcase of the Dogfish *Scyliorhinus canicula*," *Journal of the Marine Biological Association UK*, Vol. 74, pp. 823-836, 1994.
52. J.D. McKenzie and I.V. Grigolava, "How Do Marine Invertebrates Keep Their Surfaces Free from Microfouling," *9th International Congress on Marine Corrosion and Fouling*, Portsmouth, UK, 17-21 July 1995.
53. R. Baier, et al., "Porpoise and Killer Whale Skin as Natural Examples of Low-Drag, Low Adhesion Biomaterial Surfaces," *Transactions of the 2nd World Congress on Biomaterials, 10th Annual Meeting for the Society for Biomaterials*, Minneapolis, MN, USA, p.190, 1984.
54. H. Gucinski and R. Baier, "Surface Properties of Porpoise and Killer Whale Skin In Vivo," *American Zoologist*, Vol. 23, No. 4, p. 506, 1983.
55. "Marine Engineering with Copper-Nickel," *The Institute of Metals*, London, 19-20 April 1988.
56. D.W. Czinnmek and L.W. Saundor, "Economic and Technical Feasibility of Copper-Nickel Sheathing of Ship Hulls," *Marine Technology*, Vol. 22, No. 2, pp. 142-154, April 1995.
57. T. Matsunaga, "Electrochemical Prevention of Biofouling," *proceedings of Emerging Nonmetallic Materials for the Marine Environment*, Honolulu, HI, USA, 18-20 March 1997.
58. J. Shibata, et al., "Ship Hull Anti-Fouling System Utilizing Electrolyzed Sea Water," *proceedings of 3rd International Congress on Marine Corrosion and Fouling*, 1972.
59. E.S. Castle, "Electrochemical Control of Marine Fouling," *Industrial and Engineering Chemistry Research*, Vol. 43, No. 4, pp. 901-904, 1951.
60. G. Forsberg, "Fiberflock—A Biomimicking Nonfouling Concept," *proceedings of an International Workshop, Biofouling: Problems and Solutions*, University of New South Wales, Eds. S. Kjelleberg and P. Steinberg, p. 77, April 1994.
61. D.C. Sommerville, "Heat Treatment Optimization Studies at the Diablo Canyon Power Plant," *proceedings of Condenser Biofouling Control—State-of-the-Art Symposium*, EPRO CS-4339, November 1985.