COATINGS, ANTIFOULINGS

1. Introduction

When living organisms attach and grow on the underwater surfaces of ships there is either a loss of speed or an increase in propulsive energy required to counteract the speed loss: This presents an enormous economic problem. For example, if a large Container vessel succumbs to fouling it can add an extra $250,000/year to the fuel bill. The U.S. Navy (1) has estimated that they would have an increased annual fuel bill of $75–100 million if fouling was allowed to grow unchecked on all of the U.S. Fleets. The cost of removal of fouling in dry-dock, and reapplying a new antifouling coating system, can also be substantial (2).

Apart from the bottoms of commercial ships and boats, there are also other submerged surfaces on which fouling can create problems. Offshore oil platforms (which are designed to stay for long periods of time in the world's oceans), can become more susceptible to damage from the added weight that fouling contributes to the structure and from the increased resistance to tidal and water flow. Fouling growth in conduits for conveying cooling water to Power Stations can lead to serious and costly downtime for cleaning if fouling is allowed to build up. On yachts and pleasure craft, fouling is not only unsightly but also reduces the manoeuvrability and speed.

One of the most important fouling organisms is the barnacle. As barnacles grow they exert pressure on the surface to which they are attached and their basal edges, growing outward and downward, can penetrate and undermine protective coatings leading to premature corrosion and loss of structural integrity.

There are also marine organisms that can bore into underwater structures of wood, such as the pilings used for habor piers. The “shipworm” Teredo is a notorious example, which bores it way through the wood in which it lives thus weakening it considerably, and this has lead to the demise of many wooden ships (3).

2. Marine Biofouling

Many organisms can contribute to marine fouling communities; from microscopic bacteria and diatoms, through shelled invertebrates such as barnacles and tubeworms, to kelps >10 m long (2). Microfouling includes microbial organisms such as bacteria, fungi and microalgae (notably diatoms), and their secretions. Microfouling organisms are able to form tenacious films of exuded extracellular polymeric materials, which chelate inorganic ions (4). A wide range of factors affects the fouling rate and composition of microfouling communities, including water chemistry, water temperature, pressure, shear stress, and substratum composition and structure (4).

Although the number of species reported as fouling organisms is large and extremely diverse, with >4000 species recorded, this actually represents only a very small proportion of known species, even with dominant fouling groups such as barnacles, tubeworms, and algae (4). The Cirripedian barnacles are perhaps the best-adapted group of organisms, with >20% of known species recorded in fouling communities (5). However, the number of fouling species within a group may also belie the importance of those representatives. For example, although only a very small number of bivalve molluscs are known as foulers, mussels and oysters are among the most important fouling species worldwide.

On a worldwide scale, there is often similarity in a structure, and sometimes specific composition, of fouling communities. This is particularly the case in harbors and on vessel hulls, and is most likely due to biological adaptations of fouling species that facilitates their growth and survival in a range of environments and their ability to be transported around the world on vessel hulls. Examples can be seen in catalogues of marine fouling species (6) with many species identifiable in geographically disparate regions. In more pristine environments, such as encountered with offshore structures, the fouling community is likely to more closely reflect local biodiversity as seen on reefs and other natural hard substrates.

From studies on fouling composition and development at a number of sites scattered through the world’s oceans, some general guidelines have been developed to enable the prediction of fouling severity in coastal and offshore environments (7). Coastal and open-sea fouling communities could be distinguished from each other, as could warm and cold water growth forms. Cold water fouling communities tend to be dominated by bulky growth forms, (mussels and kelps) near the surface and low profile, cementing calcareous growth forming near the bottom. In contrast, warm water fouling communities tend to have constantly low profile, hard shell growth forms from surface to bottom. In coastal areas, maximum fouling attachment is generally found close to shore, diminishing seaward and with increasing depth.

Within harbors and estuaries, although there are frequently structural similarities between fouling communities in different locations, the composition and severity of a fouling growth can vary immensely with latitude (largely due to variation in water temperatures), between seasons, from year to year, and site to site (8). Many factors contribute to this, including water temperature, depth, clarity, salinity, pollution levels and movement, and the proximity of brood sites. Even on a scale of several metres, variation in the distribution of larvae and spores in the water column can significantly affect the density or even presence of the adult form on a submerged surface (8).

3. The Biofouling Process

Three stages can be identified in the formation of the microbial film: conditioning colonization by "pioneer species", colonization by other microorganisms, and accumulation (2,4). Conditioning commences within seconds of the surface being immersed, with the formation of a film of both organic and inorganic matter adsorbed from the aquatic phase (9). This effectively generates a new substratum interface with altered physicochemical properties. Subsequent microbial colonization of this film is influenced by the composition of the conditioning film, the nature of the substratum, the nature of the aquatic phase, and the species composition of the microbial community in the aquatic phase.

The "pioneer" species are often very small; rod-shaped bacteria, that attach within several hours. Initial attachment is weak and reversible (adsorption), until the bacteria are able to secrete extracellular adhesive polysaccharide and secure nonreversible attachment (adhesion) (10). Once attached, these primary colonizers assimilate nutrients and synthesise new cellular and extracellular material that accumulates in the surface deposit (4). Attachment of secondary colonizers, including stalked or filamentous bacteria, diatoms, other microalgae, and protozoa, then proceed quite rapidly. Diatoms, that contribute much of the biomass in biofilms on illuminated surfaces in the sea (11), reach a surface by purely hydrodynamic means, then attach by a secretion of an adhesive polymer (12).

The biofilm surface is highly adsorptive and, although microorganisms and their remains make up the most conspicuous components in the deposit, varying amounts of organic secretions, trapped detritus, inorganic precipitates, and corrosion products, compose the bulk of the fouling layer. Formation of natural surface films and especially bacterial films can significantly change the adhesion force and interfacial energy of surfaces immersed in seawater (13). Measurements have shown that adhesion force is reduced by adsorption of natural conditioning films and enhanced by bacterial film formation.

Several days to weeks after a surface is first exposed, the last and longest phase of fouling colonization begins with the settlement, attachment, and growth of multicellular organisms (10). In the absence of any antifouling agent, the buildup of organisms will proceed until most of the bare surface is occupied (8). The major organizing factors influencing the department of fouling communities are recruitment of species onto a surface, competition between resident organisms, and disturbance by predation and/or environmental factors. Pioneering macrofoulers tend to be small, fast growing, and maturing species with extended periods of recruitment. In contrast, later spatial dominants within the community, such as solitary and colonial ascidians (sea squirts), are generally poor recruiters due to the short duration of their larval stage, but are competitively successful due to their large body size and extended longevity (8). Interactions between organisms that can influence the composition and structure of the biofouling community can include facilitation, in which resident species enhance the chances of subsequent colonizing species, inhibition, in which established species resist invasion, and tolerance, in which there is interaction between resident and colonizing species (8,10,14).

Algal spores generally rely on passive, random hydrological, and physical processes to deposit them on a surface and the surface texture of a substratum can be important in physically restraining the spores and allowing them to attach (8,14). Recruitment of fouling invertebrates onto a surface is a more complex process, in which several physical, chemical and biological factors interact (15). Recruitment requires temporal and spatial availability of larvae and appropriate chemical and physical cues to stimulate attachment and metamorphosis. Larvae seek a surface to which they can adhere, which is within appropriate environmental gradients, and that will allow the juveniles to grow to maturity and reproduce (8). Positioning in relation to food sources, light, water, velocity and temperature, turbulence, gravity, and hydrostatic pressure are major considerations. Some larvae show a strong response to settle near established individuals of the same species, particularly species such as barnacles, which rely on proximity of other adults for fertilization (8). Before permanently attaching to a surface, many invertebrate larvae explore a surface to determine its acceptability (16,17). During this phase, the larva need to maintain a hold on the surface, yet, if they find that the surface is unacceptable, they must be able to be released and carried to alternative settlement sites. Temporary attachment is by either a suction apparatus or a secreted sticky substance; permanent attachment by hardened or cured adhesive cement sometimes reinforced with calcareous deposits.

4. Historical Development of Antifoulings

Coatings to prevent fouling have been applied since antiquity (18). A very early record on the use of some form of paint on ship's hulls can be found in the translation from the Aramaic of a papyrus of ~412 BC concerning the repairs of a boat of that date (19, p. 48):

> "And that the arsenic and sulphur have been well mixed with Chian oil thou broughtest back on thy last voyage and the mixture evenly applied to the vessel's sides that she may speed through the blue waters freely and without impediment?"

In the third century BC, the ancient Greeks used tar and wax to coat ship bottoms. From the thirteenth to the fifteenth century, pitch, oil, resin, and tallow were used to protect ships. For his remarkable travels between 1405 and 1433, the Chinese Admiral Cheng Ho had the hulls of his junks coated with lime mixed with poisonous oil from the seed of *sryandra cordifolia* to protect the wood from worms (20,21). In his life of Columbus, Morison (22, p. 124) mentions that:

> “All ships” bottoms were covered with a mixture of tallow and pitch in the hope of discouraging barnacles and teredos, and every few months a vessel had to be hove-down and graved on some convenient beach. This was done by careening her alternately on each side, cleaning off the marine growth, repitching the bottom and paying the seams.”

During the following centuries, the main form of protection for wooden ships was copper sheathing or the use of a mixture containing sulfur and arsenic. It was not until the development of iron hulls that copper sheathing was abandoned because of serious galvanic problems (23).

In 1625, William Beale was the first to file a patent for a paint composition containing iron powder, copper, and cement. In 1670, Philip Howard and Francis Watson patented a paint consisting of tar, resin, and beeswax. In 1791, William Murdock patented a varnish mixed with iron sulfide and zinc powder, using arsenic as antifoulant (23).

The number of patents proliferated in the second half of the nineteenth century—more than 300 patents were registered by 1870—but all these paints had little to no effect over a very limited time. Mallet (24, p.129) stated:

> “. . . it is probable that under no other head in the whole range of the Patent Office Records is such a mass of ignorance, absurdity and charlatanry exhibited, as in these antifouling patents. One or two of the best have proved palliatives (no more can be said for any of them), and are for want as yet of anything better, more or less in practical use. The writer refrains from particularizing those that to his observation seem best or next best; but the vast mass of these “compositions” are worthless or hurtful – several are more worthy of the name of “impositions”; and some even of the most recently patented are grotesque in their ignorant absurdity, – as for instance, one in which a farrago of the soluble drastic purgatives (such as colocynth) of the apothecary’s shop is mixed up with incompatible resinous fluids, to scare away the unhappy zoöphytes.”

The basic principle of these toxic antifouling paints, however, still holds today: A toxic substance is mixed into a resinous substance or binder to kill off fouling organisms by some kind of leaching mechanism (25,26). The latter is the key factor in the success of antifoulings and has always been the focus of the efforts of antifouling formulators. As Mallet (24, p. 120) put it:

> “The necessary balance between adhesion and slow diffusion or washing away through the water of the poisonous soap is too delicate for practice. Either the soap adheres firmly and does not wash away enough to keep off fouling or it washes away so fast as soon to be all gone.”

Salts of copper, arsenic, or mercury were popular biocides. Linseed oil, shellac, tar, and various kinds of resin were used as matrix and solvents included turpentine oil, naphtha, and benzene. In 1854, James McInnes patented the first practical composition to come into widespread general use. It used copper sulfate as toxin in a metallic soap composition, which was applied hot over a quick-drying priming paint of rosin varnish and iron oxide pigment. Soon after, a similar hot plastic paint known as "Italian Moravian" was developed that was a rosin and copper compound. It was one of the best paints of that time and was used well into the twentieth century. In 1863, James Tarr and Augustus Wonson were given a U.S. patent for antifouling paint using copper oxide and tar (23). In 1885, Zuisho Hotta was given the first Japanese patent for an antifouling paint made of lacquer, powdered iron, red lead, persimmon tannin, and other ingredients (27). These paints, although reasonably successful, were expensive and had a short life-span.

In 1906, the U.S. Navy decided to manufacture its own antifouling coatings and tested shellac and hot plastic paints at Norfolk Navy Yard (23). From 1911 to 1921, more experiments were performed both to find substitutes for scarce materials such as mercuric oxide and to improve the paints (23,28). In 1926, the U.S. Navy developed a hot plastic paint using coal tar or rosin as binder and copper or mercuric oxides as toxins. Hot plastic paint required some heating facility that made application difficult (23). Consequently, cold plastic paints were developed that dry by evaporation of the solvent and that were easier to apply (29). These paints effectively decreased fouling and the time between dry-docking for repainting was extended to 18 months.

It was only after the Second World War that major advances in antifouling coatings took place, leading to the currently used technologies.

5. Current Antifouling Technologies

There are currently only two principal ways that marine fouling is controlled on underwater hulls. The first of these is based on the historical method of dispersing a biocide in a binder system that is then released slowly from the coating surface once it is immersed in seawater. The second type does not use biocides, but relies on the surface being "nonstick". This is referred to as "foul release" technology.

5.1. Biocidal Antifoulings.

There are two key factors in the development of a successful biocidal antifouling:

- The *toxicity* of the biocide, or biocide combinations.
- The *delivery mechanism* of the biocide(s) to the marine environment.

Biocide Toxicity. Following on from the historical use of copper as sheathing, copper compounds were the first biocides used in the large scale industrial production of antifouling paints, and they are still the most common biocides employed in antifoulings. The most commonly used copper compounds are cuprous oxide (Cu_2O), which is red, cuprous thiocyanate (CuSCN), a pale cream compound used for making brightly colored antifoulings, and metallic copper, either in the traditional sheet form or as a powder.

Copper by itself is, however, limited in its effectiveness. It tends to work well as a biocide against animal (shell) fouling, but algal (weed) fouling is more resistant to copper and therefore antifouling chemists have spent much time and effort searching for additional biocides that can be added to the copper to boost performance. These are referred to as boosting biocides. A key characteristic of these is that they should have very low seawater solubility (ideally <10 ppm) so that they are not released too quickly from the antifouling paint film. In the 1950s, mercury and arsenic compounds were commonly used as boosting biocides, but these were largely replaced in the 1960s by organotin compounds that came from the agricultural industry, where they were used as pesticides (30). The organotin compounds were found to be extremely effective against a very wide range of marine fouling species at very low concentrations. Since the discovery of organotin compounds there have been very few other boosting biocides developed. Not only has it proven to be very difficult to improve on the efficiency and effectiveness of the organotin boosters, but also the relatively small size of the overall antifouling market ($\sim$50 million liters of paint worldwide, annually) makes it difficult to justify the very high cost of developing and registering new biocides. It can now cost in excess of $ 4 million to undertake all the human and environmental toxicity testing required for registration purposes. No return on this investment can occur until the product containing the biocide is itself registered, which can take many years to accomplish.

Some commonly used booster biocides currently in use are as follows (31):

- 2-methylthio-4-*tert*-butylamino-6-cycloproylamino-*s*-triazine (eg, Irgarol 1051 ex Ciba Speciality Chemicals).
- Dichlorophenyl dimethyl urea (eg, Diuron).
- Zinc hydroxypyridmethione (eg, Zinc Omadine from Arch Chemicals).
- Copper hydroxypyridmethione (eg, Copper Omadine from Arch Chemicals).
- 4,5-Dichloro-2*N*-octyl-4-isothiazol-3-one (eg, SeaNine 211 ex Rohm and Haas).
- *N*-Dimethyl-*N*-phenyl-*N*-fluorodicholoro-methylthiosulphamide (eg, Prevetol A4 ex Bayer).
- Tolylfluanid (eg, Preventol A5S ex Bayer).
- Zinc ethylene-1,2-bisdithiocarbamate (Zineb).

From the above, only those that show rapid degradation in sea water, and in sediments, will be likely to survive the close regulatory scrutiny to which they are being increasingly subjected.

Given the limited availability of new biocides, research and development in antifouling coatings is now focused on maximizing the efficiency of the few biocides that are available. This involves studies on both the synergies between the biocides, to get the maximum toxic effect from the minimum quantities, and studies on the best mechanism to control the release of the biocides, to maximize the lifetimes.

Biocide Release Mechanisms. The standard method for measuring the biocide release from antifoulings is the leaching rate. This rate is defined as the amount of biocide released from a given surface area in a given time, and this is expressed as μg/cm^2/day.

The release mechanism itself depends on the technology of the coating system employed. There are three main technologies:

- Rosin based.
- Self-polishing copolymer (SPC).
- Hybrid SPC/rosin systems.

Rosin-Based Technologies. Rosin, or rosin derivatives, are used to enable seawater to penetrate the antifouling coating and as it does so it allows release of the biocides by a diffusion process. This results in the pseudo-exponential leaching rate of biocides, with an excessive release in the early days of immersion that gradually falls over the following months to a level below which fouling will start to occur. This is shown in Figure 1.

Rosin comes from trees and is also commonly referred to as Gum Rosin or Wood Rosin or Tall Oil Rosin. It is widely used in the adhesives industry, and has a complex chemical makeup, which varies depending on the trees where it is grown and from which it is harvested. The major constituent of Rosin is abietic acid, which is slightly soluble in seawater (pH ~8.2). It is this slight solubility that makes it suitable for use in antifouling coatings, since as it dissolves it enables the biocides to be released from the paint matrix. Modification of rosin can be carried out in a number of ways, such as hydrogenation or esterification.

Rosin by itself does not form durable films and it has to have other film-forming binder components (referred to as resins and plasticizers) added to give films of good mechanical strength. However, these added components are generally insoluble in seawater and their use has to be limited or the release of the biocides will be impaired. There is thus a careful balance needed between the amount of rosin necessary to get sufficient biocide release and the quantity of the other film-forming components needed to form tough and durable films.

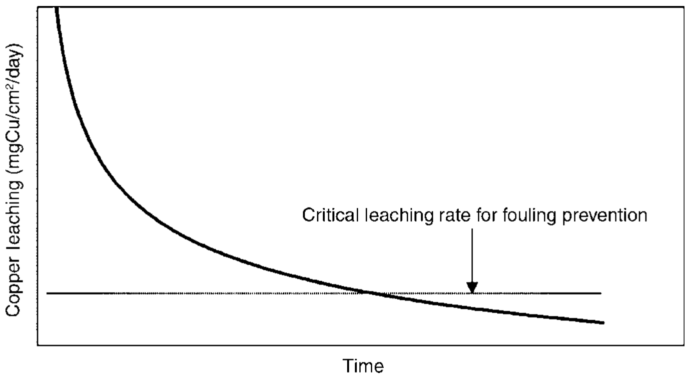

Fig. 1. Exponential biocide release (rosin-based antifoulings).

Achieving the right balance has been a conundrum that has challenged antifouling chemists for >100 years (24, p. 120, 32).

A high rosin content means that the binder system is more soluble in seawater, whereas a low rosin content makes the binder system hard and very insoluble. The former types of antifouling are known as "soluble matrix" antifoulings, whereas the hard, insoluble types are known as "contact leaching" antifoulings.

(*1*) *Soluble matrix antifoulings*. Prior to the Second World War almost all antifouling paints were of the Soluble Matrix type. After this time, major improvements came about with the advent of a wide range of new industrial chemicals such as the synthetic petroleum-based polymers. As the chemical companies developed new synthetic polymers they were used to upgrade and improve Soluble Matrix antifoulings, a process that continues to this day. All Marine paint companies now market modern versions of the traditional Soluble Matrix antifoulings, with a wide variety of confusing nomenclatures to describe them, such as "Controlled Depletion Polymer" antifoulings, "Eroding" antifoulings, "Ablative" antifoulings, "Polishing" antifouling, "Self-polishing" antifoulings, and "Hydration" antifoulings (33). These all refer to the physical dissolution of the rosin-based antifouling systems, and should not be confused with the chemically controlled dissolution of SPC antifoulings, which are described in the section Self-Polishing Copolymer. Copper oxide is the biocide most commonly used in these Soluble Matrix paints, along with boosting biocides.

Although in theory these paints could dissolve fully over time releasing all the biocides contained in them, they do in fact become increasingly less soluble due to the build up of insoluble copper salts and other inert species (such as rosin impurities) at the surface. This results in the formation of a "spent" layer at the surface, free of biocide, which is commonly referred to as the "leached layer". Biocides from the depth of the film have to diffuse through this leached layer to reach the surface. The size of this leached layer increases with time, resulting in a decrease in the release rate of biocide according to Fick's laws of diffusion. This limits performance lifetime to a maximum 36 months between dry-dockings. In high fouling areas, Soluble Matrix antifoulings can succumb to fouling well before this time, especially if the copper leaching rate falls below the critical level, which is generally acknowledged to be $\sim 10\ \mu g/cm^2/day$ (23).

(*2*) *Contact leaching antifoulings*. In the 1950s, attempts were made to increase the lifetime of soluble matrix antifouling coatings by increasing the biocide content. Such highly pigmented coatings required larger quantities of the inert resin and plasticizer film-forming components, with less rosin, thus making these coatings insoluble in seawater and hard. They became known as Contact Leaching antifoulings since the biocide particles were all in close contact with each other.

As with the Soluble Matrix antifoulings, it was recognized that the major barrier to extended lifetimes was the development of the leached layer at the surface, which acted as the rate-controlling and lifetime limiting step (30). As a way around this, it was found that the leached layer could be removed by in-water cleaning, without damaging the paint surface too extensively since Contact Leaching antifoulings form tough and hard films. These paints could thus be "reactivated" to extend their lifetime. Without the reactivation process in-service life was limited to 24 months.

Self-Polishing Copolymer. The desirability of chemical mechanisms to control the release of biocides from antifouling coatings, rather than relying on a physical dissolution and diffusion process, long predates the means of their achievements. It was only in 1974 that the technology and opportunity finally came together with the introduction of tributyltin (TBT) and SPC antifoulings (30). Hydrolysis or ion exchange of an acrylic polymer at the surface of the antifouling makes the polymer soluble, resulting in biocide release without the use of Rosin. The control of surface solubility by this chemical reaction gives controlled, pseudo-zero-order release of the biocides, until all the paint is dissolved away. This results in a much more efficient use of the biocides, as shown in Figure 2.

The main improvements that TBT SPC antifoulings bought compared to the previously available rosin-based products were as follows:

- Improved antifouling performance.
- Extended in-service periods (up to 60 months).
- Reduced fuel consumption due to hull smoothness.
- Easier maintenance and repair.
- Bright and clean colors.

These benefits were rapidly recognized by yacht and ship owners and operators and SPC products soon came to dominate the market (34). Their biocidal effectiveness was the key to their success, but it also proved in the end to be their undoing since nontarget organisms (those not fouling the vessels) were found to be affected (35). In the early 1980s in France, a link between the use of TBT antifoulings on Yachts and the poor growth of oysters nearby was suggested (36). Subsequent research in other parts of the world demonstrated that the TBT from antifoulings was relatively persistent in seawater and therefore could have an impact on nontarget organisms. These findings resulted in government action to restrict their use. Initially, in many countries the use of TBT antifoulings

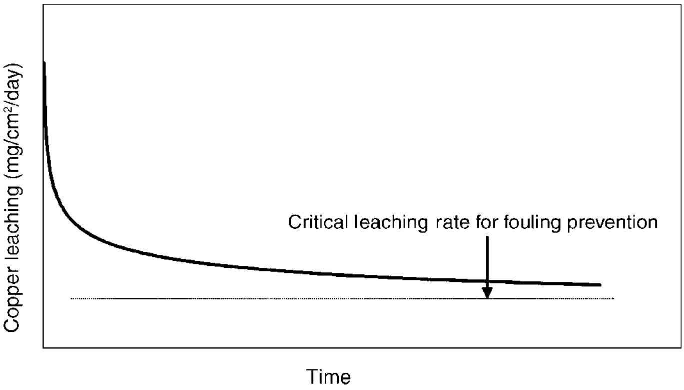

Fig. 2. Controlled biocide release (self-polishing copolymer antifoulings).

was banned on vessels <25 m in length. This was targeted at the Yacht and Pleasure boat industry since TBT becomes the antifoulings used on these boats in marinas in enclosed waters was deemed to be the most damaging to nontarget organisms

The International Maritime Organisation (IMO), which was set up by the United Nations in 1958 to deal with maritime affairs on a global basis, established a Antifouling Working Group in 1990 to study the problem more widely. In 1997, the Marine Environment Protection Committee (MEPC) of IMO agreed a draft resolution calling for a worldwide ban on TBT antifoulings. This eventually resulted in the passing of an Antifouling Systems Convention at a Diplomatic Conference of the IMO in October 2001. This Convention calls for a worldwide ban on the application of organotins that are used as biocides in antifoulings on all vessels begining January 1, 2003, to be followed by a ban on the presence of organotins that are used as biocides in antifoulings on ships by January 1, 2008. Full details of this Convention can be found on the IMO website “http://www.imo.org” (37).

TBT SPC Antifoulings. The chemistry of the organotins goes back as far as 1939 (38) and their antifouling possibilities to 1958 (39). The first TBT antifouling was introduced in 1968, in the Yacht market, with the TBT being added in pigment form as tributyltin fluoride (TBTF). Its use in this form, however, resulted in a concern for the health and safety of those handling the material, both at the manufacture stage and during application by the end-user. This concern led directly to the development of polymer-bound TBT, which greatly reduced this health risk.

It was discovered that when these TBT polymers were immersed in seawater, hydrolysis or ion exchange occurred at the surface, resulting in the polymer becoming soluble in seawater. As this process was repeated, the coating slowly dissolved away, without the need to use rosin, with the rate of dissolution being controlled by the quantity of TBT in the polymer.

This seawater reaction is confined to the top surface only, with the underlying bulk of the film remaining insoluble. This means that water is unable to penetrate into the depth of the film, and the biocide-depleted leached layer of an SPC coating is very thin and is generally $<20\ \mu$, even after several years of immersion. This is in marked contrast to the rosin-based soluble matrix and contact leaching antifoulings, that can have leached layer wells in excess of $50\ \mu$.

It is the character of the Sn−O bond that is the key to the success of these TBT SPC antifoulings. In certain instances, this bond exhibits covalent behavior, as evidenced by a low dipole moment, but in other reactions, such as hydrolysis rate, it behaves as a characteristically ionic bond (40). In a low dielectric constant medium, it behaves covalently but in a high dielectric constant medium such as water it behaves ionically. This change in behavior with polarity is thought to be a consequence of the change in molecular shape from planar alkyl groups to trigonal pyramidal alkyl groups. The first ship trials with TBT SPC antifoulings were not very successful since the dissolution rate of the coatings, commonly referred to as the “Polishing Rate”, was much too fast. It was found that the test patches dissolved away within 6 months, resulting in heavy fouling. However, it was soon realized (41) that the polishing rate could be controlled by varying either the polymer composition or some of the other key ingredients in the paint formulation, and therefore so long as enough paint was applied it would provide the necessary antifouling protection. For example, 100 μ at a low polishing rate was sufficient to provide fouling protection for up to 24 months, depending on in-service conditions (such as vessel speed, water temperature, vessel activity etc).

Initially, the main biocide used (in addition to the TBT polymers) in these SPC antifoulings was DDT, but this was soon replaced for environmental reasons by cuprous thiocyanate (CuSCN) and eventually by cuprous oxide (Cu_2O)—the latter only when in-can stability problems had been overcome. In the 1980s some manufaturers then replaced part of the cuprous oxide with a boosting biocide, Zineb (Zinc ethylene-1,2-bisdithiocarbamate), to improve slime control. This resulted in a formidable biocide "cocktail" with unparalleled fouling control, and so it was no surprise that these coatings came to dominate the antifouling market: >80% of all Marine antifouling sales were of the SPC type by the mid-1990s. This was helped by the fact that, as the technologies matured and competitive market forces were bought to bear, the costs were also significantly reduced.

As well as the superb ability to control fouling, TBT SPC antifoulings also kept surface roughness to a minimum by the polishing process. Asperities on the paint surface acquired during the painting process (such as runs and sags) were rapidly removed once the vessel was underway at sea, and this reduced the drag. Lowered fuel consumption resulted and this was just at the time when fuel prices rose dramatically following the 1973 Middle East war. Another major advance with TBT SPC antifoulings was the extension of in-service periods between dry-dockings from 36 to 60 months, which was possible since there was no decrease in biocide release rate over time since there was no leached layer build up. The in-service lifetime was determined solely by the original thickness applied. This gave ship owners the opportunity to keep their vessels at sea longer, thus increasing earning capacity.

The costs of maintaining and repairing SPC systems was also found to be lower than with traditional antifoulings since there was less detachment, and minimal deterioration due to weathering.

TBT-Free SPC Antifoulings. With the anticipated demise of TBT SPC antifoulings for environmental reasons, much R&D effort in the 1990s was directed at finding suitable alternatives. The first country to fully ban the use of antifoulings containing TBT was Japan, in 1991, and consequently most of the early TBT-free SPC systems came from the Japanese marine paint companies.

Three principal chemistry types have emerged, all based on acrylic copolymers, and with pendant groups that potentially undergo hydrolysis or ion exchange in seawater. These are all attempts to mimic the reaction of TBT acrylate copolymers in seawater:

TBT Acrylate: $\text{Polymer–COO–Sn (Bu)}_3 + \text{NaCl} \Leftrightarrow \text{Polymer–COO–Na} + \text{Sn (Bu)}_3\text{–Cl}$

Copper Acrylate: $\text{Polymer–COO–Cu–R} + \text{NaCl} \Leftrightarrow \text{Polymer–COO–Na} + \text{R–Cu–Cl}$

Zinc Acrylate: $\text{Polymer–COO–Zn–R} + \text{NaCl} \Leftrightarrow \text{Polymer–COO–Na} + \text{R–Zn–Cl}$

Silyl Acrylate: $\text{Polymer–COO–Si (R)}_3 + \text{NaCl} \Leftrightarrow \text{Polymer–COO–Na} + \text{(R)}_3\text{ Si–Cl}$

These TBT-free SPC systems are at varying degrees of technical and commercial development, and there is some uncertainty regarding the claims made by their respective manufacturers that they have exactly the same benefits as can be obtained with TBT SPC systems (such as extended dry-docking intervals, self-polishing smoothness, and tough and durable films). However, the copper acrylate system has been proven to work on ships for the full 60 month in-service period required (42) and since the technology was first introduced in 1990 it has a large track record, of >6,000 vessel applications.

The main biocide used in all these TBT-free SPC systems is cuprous oxide (Cu_2O), which is added as a pigment during paint manufacture. In addition, boosting biocides are used to provide the necessary biocidal activity replacing that previously obtained from TBT. These boosting biocides are nonpersistent, and degrade rapidly once they leave the surface of the coating. Their rapid degradability means that they do not build up in the environment and therefore they should not affect nontarget organisms (43,44). Once the biocides have diffused away from the paint surface, they can degrade in the presence of light and/or bacteria into substances with very low toxicity and persistence, thus giving these systems a better environmental profile than the TBT SPC systems they replaced.

Hybrid SPC/Rosin Systems. With some of the TBT-free SPC systems it was found that the hydrolysis or ion exchange reaction of the TBT-free acrylate copolymers is not as easily controlled as with the previous TBT SPC systems. The reaction is either too fast or too slow and so rosin has been added to provide a "backup" mechanism for the biocide release. This combination is a new technology type, and is referred to as a "Hybrid" technology. The use of rosin with these TBT-free SPC systems has the advantages of lowering cost, increasing the volume solids, giving improved overcoatability, and surface tolerance. However, the release of the biocides from these Hybrid SPC/rosin systems is not as well controlled as with the "pure" SPC systems and they do not have the same extended life time capability.

The price and performance of these Hybrid SPC/rosin systems is midway between that of the SPC and rosin-based "parent" systems. The higher the SPC polymer content the more SPC-like is the behavior of the product, and vice versa with the rosin content.

5.2. Foul Release Antifoulings. From an environmental perspective, the most desirable approach to fouling control is one that does not rely on the release of biocides to achieve its effect. A plethora of ideas for how this can be achieved have been proposed, and numerous patents have appeared (30), but only the foul release or low adherence systems have been commercialised successfully. These operate by a "nonstick" principle, having surface characteristics that minimize the adhesion strength of fouling organisms, and any fouling that does settle is removed by hydrodynamic forces that are present on the hull when it moves through water.

The concept of low adherence to deter fouling was first considered in the nineteenth century (23, pp. 226–227), but it was not until the discovery of the fouling control properties of silicones (45) that commercial systems started to appear. These have been improved and refined since then and the majority of foul release systems currently available are silicone materials based on polydimethysiloxane (PDMS). The only other chemistry types to have been considered to any great extent have been fluorinated polymers (46,47), but they have not been commercialized to the same extent as the silicone systems.

The PDMS polymer has an extremely flexible backbone, with rotation around the [−O−Si−O] bond being very easy, resulting in a very low glass transition temperature (T_g). This allows the polymer chain to readily adapt the lowest surface energy configuration (48). Low surface energy alone, however, is not the only important criteria for success in deterrence of fouling settlement: coating thickness and elastic modulus (49,50) have also been shown to be important variables.

Smoothness is also a very important feature for an effective foul release coating. Surface energy, and the area available for adsorption, increases with roughness and it is well-known that fouling species prefer rough surfaces (51), an effect that is known as the *thigmotactic* nature of fouling settlement. It has been shown that the topography and texture of foul release silicone coatings is completely different from that of SPC antifoulings (18). Whereas typical SPC antifoulings have a “closed texture” with frequent peaks and troughs akin to a steep mountain range (Fig. 3), the foul release systems have a long wavelength “open texture” surface, similar to well-rounded hills and shallow valleys (Fig. 4).

In addition to surface topography, it has been demonstrated that enhancement of silicone foul release coatings can be accomplished by the incorporation of low molecular weight polymers or oils (45,52). It has been postulated that the surface structure of silicone foul release coatings is changed when the nonbonded oils migrate to the coating surface and increase the “slipperiness”. Radio labeled studies on the fate of these oils has shown that they do not migrate from the coating surface to any great extent (53) and this is also confirmed by the successful in-service performance results of over 5 years (42).

Quantification of the foul release properties of coatings is done using the American Standard for Testing and Materials (ASTM) test D5618-94. This measures the force with which it is necessary to remove barnacles from the surface in

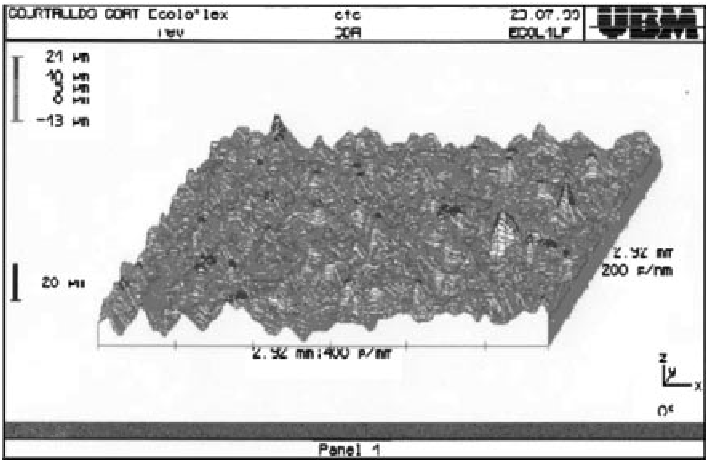

Fig. 3. Surface profile of an SPC antifouling.

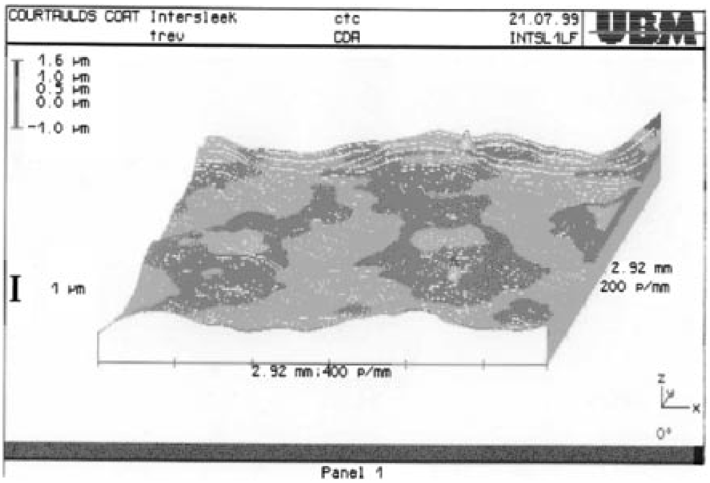

Fig. 4. Surface profile of foul release antifouling.

shear (54). From this measurement of the shear adhesion strength, it is possible to predict the speed at which barnacles will release from surface of a vessel. Towing experiments to verify these predictions have been carried out (55) and these tests show that there is a good correlation between the predicted and observed velocities at which fouling will release. It has been found that most fouling species are removed at 15 knots or above (56), although slime fouling, which stays close to the surface, can still remain even at speeds in excess of 30 knots.

Despite their beneficial environmental profile the market penetration of foul release coatings has been limited. In part, this is due to the increased initial cost of installation, but it also due to the fact that the majority of the world's fleet (Crude Oil Tankers and Bulk Carriers) do not operate at high enough speeds or activity for foul release coatings to perform at their best. As the technology matures it is very likely that products will emerge that both work at lower ship speeds, and are also less expensive to install.

6. The Future

As a result of the expected ban on the use of TBT antifoulings, there has been increasing interest from innovators and academic institutions in solving the challenge of fouling control (35). The use of "natural product" antifoulants has received wide attention, along with attempts to mimic the surfaces of marine animals such as seals, dolphins, and whales. The successful commercial development of any such novel approach will require knowledge of biological, chemical, and physical processes involved as well as an understanding of the operational requirements of the end-users.

In the meantime, copper-based systems are certain to dominate the antifouling coatings market for the foreseeable future, but it is anticipated that foul release systems will become increasingly important as the environmental pressure on the use of biocides increases.

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COLIN ANDERSON
International Coatings, Ltd.