

REVIEW PAPER

Fouling-release Coatings for Warships

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ABSTRACT

The International Maritime Organisation, a unit of the United Nations, has approved a resolution to phase out and eventually prohibit the worldwide use of toxic organotin antifouling paints. Thus, there is a compelling need to develop, test, and market eco-friendly hull coatings, which effectively keep ships free of fouling. The replacement for tin coatings will likely be low-toxicity copper-based paints, and various toxin-free fouling-release coatings. This paper reviews the composition and mechanism of action of these coatings and gives the strengths and weaknesses of each coating, with the aim of clarifying the impact of these coatings on the operation of warships.

Keywords: Antifouling paints, organotin antifouling paints, antifouling biocides, copper-based paints, fouling-release coatings, tin-based paints, hull coatings, toxin-free fouling-release coatings

1. INTRODUCTION

The problem of marine organisms adhering to structures in the sea is as old as time. This problem is acute for ships, especially the warships. A layer of marine organisms on a ship's hull decreases its speed, manoeuvrability and range, and raises propulsive fuel consumption as much as 30 per cent. To prevent the formation of a fouling layer, antifouling paints typically incorporate compounds, such as cuprous oxide or organotins, which are toxic at low concentrations to most forms of fouling. However, these compounds persist in the water and cause deformations in some kinds of sea life. The Marine Environment Protection Committee (MEPC) of the International Maritime Organisation (IMO), a unit of the United Nations, has approved a resolution to phase out and eventually prohibit the use of toxic organotin derivatives in antifouling paints. In the 21st Session of the IMO Assembly in London in November

1999, it adopted a resolution which includes a deadline of 01 January 2003 for the application of organotins acting as biocides in antifouling systems on ships, and a second deadline of 01 January 2008 for the complete prohibition of antifouling paints containing organotins. The MEPC has proposed to the IMO Council, a conference in the 2000-01 biennium to adopt a legal instrument for the international regulation of the use of shipboard antifouling systems, in particular, to phase out those containing organotins. Several countries, including France and Japan, and some states in the United States of America, have already banned organotins in antifouling paints for most ships.

Alternatives to the current generation of tin-based antifouling paints include low-leach rate copper-based paints and non-toxic fouling-release paints. A successful replacement for the tin-based coatings is not a simple challenge, however, there are 12

well-defined zones in the oceans of the world that differ in temperature, salinity, clarity, the nature, amount of micronutrients and other factors. Thus, the types and numbers of native fouling organisms differ from zone-to-zone, and the adhesives used by these organisms to adhere to the structures in the sea are equally varied. Formulators of antifouling coatings need to realise that nature does not rely on one mechanism for adhesion, but uses many, and all of these must be defeated, at the same time.

2. TOXIC FOULING-RELEASE COATINGS

2.1 Copper-based Coatings

The copper-based antifouling coatings have been used in the marine industry for the last 200 years. The current generation of copper-based paints relies on three factors for their effectiveness: (i) toxicity of copper, (ii) secondary biocides, which are effective against organisms not harmed by copper, and (iii) an abrasive resin system which slowly but constantly dissolves, taking with it early stages of fouling.

2.1.1 Copper

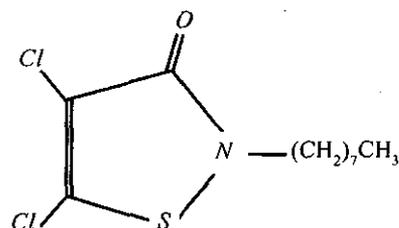
The copper has been used since antiquity as an antifouling agent. Copper sheathing was first used on ships of the British Navy² in 1779. It is widely distributed in animal and plant tissues. For human beings, copper is an essential trace element and is comparatively non-toxic compared to other trace elements. It is also an effective control agent, for many but not all forms of marine life.

2.1.2 Secondary Biocides

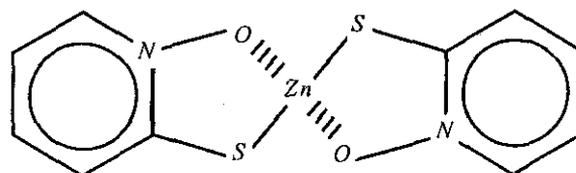
When used alone, cuprous oxide is not effective against some forms of sea life, such as diatoms and algae. Secondary biocides must be incorporated into the paint to control these organisms and to provide protection against fouling under stagnant water or low-water velocity conditions. Two important examples of secondary biocides are 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one or DCOI (sea-nine ® 211, a product of Rohm and Haas Co, Spring House, PA, USA) and the zinc complex of

2-pyridinethiol-1-oxide (zinc omadine ®, a product of Arch Chemicals, Norwalk, CT, USA). Both the biocides are registered with the US Environmental Protection Administration for use in marine paints

The DCOI has broad spectrum activity against bacterial slime, barnacles, algae, tubeworms, hydroids, bryozoans, tunicates, and diatoms. The DCOI and its metabolites remain in the environment for only a short period of time; in seawater, they bind strongly and essentially irreversibly to sediment, and subsequently are rapidly degraded³.



4, 5-Dichloro-2-*n*-octyl-4-isothiazoline-3-one



Zinc complex of 2-pyridinethiol-1-oxide

STRUCTURE I

The zinc complex of 2-pyridinethiol-1-oxide possesses broad spectrum antimicrobial activity against algae, bacterial slime, fungi, and diatoms. It is frequently used in combination with cuprous oxide to provide protection against hard and soft marine fouling organisms. The copper complex of 2-pyridinethiol-1-oxide (copper omadine⁷, Arch) is not yet registered with the US Environmental Protection Administration, but is available outside the United States.

2.1.3 Abrasive Resins

The abrasive self-polishing resins are made from polymers with labile functional groups, such as esters. On hydrolysis, these groups release a small molecule and create a hydrophilic site on the

polymer backbone. The small molecule released is sometimes toxic and may contribute to antifouling performance through its poisonous properties. When the polymer backbone accumulates a sufficient number of hydrophilic sites, it becomes water soluble and is washed away from the surface of the coating, taking with it algae, diatoms, and other marine organisms and their juvenile forms. A fresh surface is thus created, and the process is repeated.

The ablative coatings require a constant water flow past the surface and are most effective at consistently high-water velocity condition. The lifetime of these coatings is determined by the initial thickness of the coating and temperature of the seawater. In temperate waters, ablation is of the order of 75 μm per year; thus, a new coating applied at a thickness of 375 μm (15 mils) would be expected to give five years of service to the structure.

2.2 Non-toxic Fouling-release Coatings

The prospective non-toxic hull paints include fluoropolymer and siloxane-based coatings⁴. These coatings, which have been a subject of intense laboratory and field studies for the past 25 years, are called fouling-release coatings to differentiate these from their poisonous precursors. Ideally, these nonstick coatings should completely prevent the attachment of fouling, but actually these do foul, but the foul is very weak. These significantly limit the strength of the joint between the foulant and the hull, making the bond so weak that it can be broken by the weight of the fouling or by the movement of the ship through the water.

The performance of the fouling-release coatings is determined by the following properties:

- Surface Energy; a low surface energy will discourage the initial attachment of fouling.
- The modulus of the coating is important because it influences the mechanism by which the joint between the coating and a foulant will fail.
- The thickness of the coating can be an important factor in favouring peel fracture rather than shear fracture.

The fracture mechanics at an interface—in this case, the joint between the foulant and the coating—differs from that of a solid because the interface determines the direction of a crack propagation⁵. A joint is tough if a large amount of energy is expended to propagate a crack along it. The toughness of the joint is strongly influenced by the deformation of the adherends near the crack tip. Elastomeric coatings, such as silicones, deform readily and failure of the joint occurs by peel, a mechanism which requires lower energy than failure by shear. As a crack moves along an interface, a polymer in the crack tip is placed in tensile stress. Newby, Chaudhury and Brown⁶ have shown that an adhesive slips on a silicone surface toward the crack tip, reducing the extension of the polymer, thus reducing its tensile stress, and reducing the energy needed to propagate the crack. Studies⁷ have shown that, in joints with one mobile side, the shear stress at the interface can be as low as 5-100 kPa. Thus, the limited amount of bio-adhesion on silicone polymers is a consequence of the ability of the fouling to slip on the polymer surface. This behaviour does not occur on fluoropolymers.

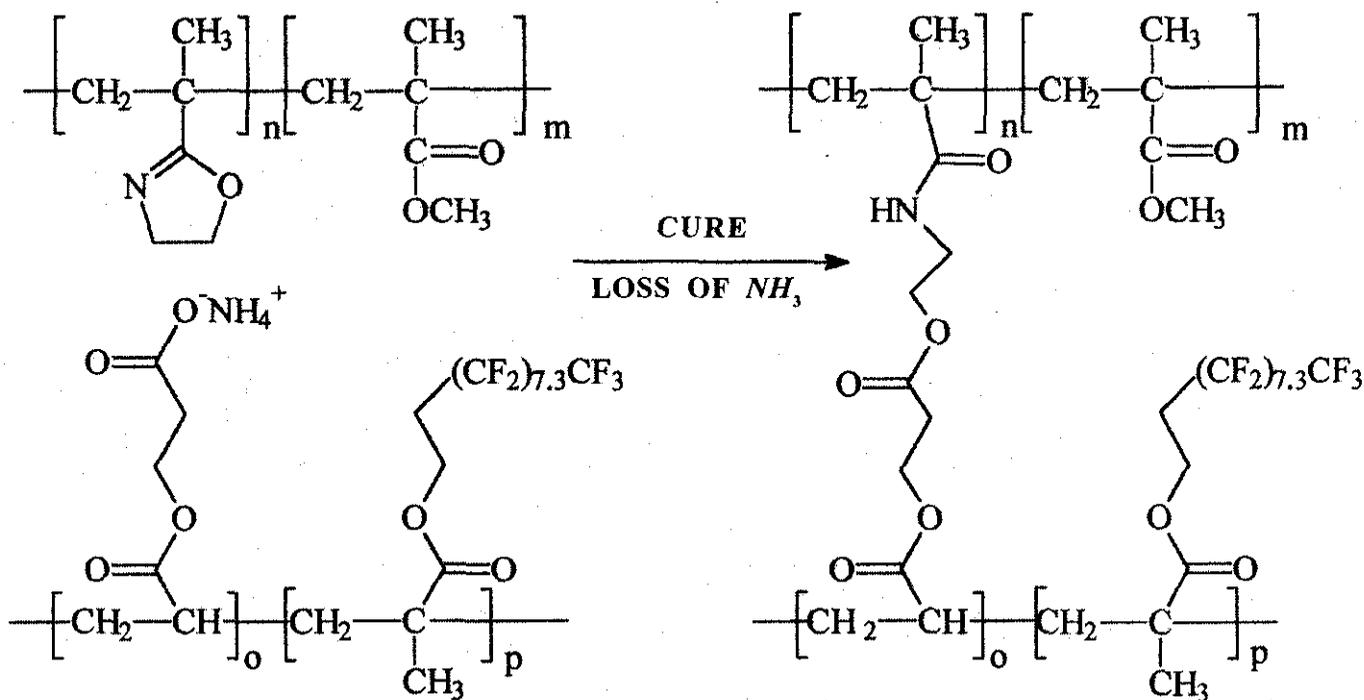
Thus, it is crucial to understand that fluoropolymers and silicone fouling-release coatings achieve their effectiveness through different mechanisms. Fluoropolymer coatings fail by shear at the joint between the foulant and the coating, but silicone coatings fail by peel. Thus, the criteria for successful coating are distinct in important ways.

2.2.1 Fluorinated Fouling-release Coatings

The fluorinated polymers were first considered attractive fouling-release candidates because of their low surface energy. Subsequent research has demonstrated that many other factors are of equal or greater importance than the surface energy. The most productive route to fouling-free performance is to discourage the initial bonding of marine organisms. This is accomplished by constructing a well-organised surface of closely-packed fluorinated groups, driving its surface energy as low as possible, and crosslinking or otherwise stabilising the surface so that it resists rearrangement and penetration of marine adhesives. The fouling is minimised when:

- The surface is very smooth. Teflon® (polytetrafluoroethylene) accumulates marine fouling rapidly because it is a porous material. Marine adhesives invade cavities on the surface and cure inside these, creating a secure mechanical interlock even when the chemical compatibility does not exist⁸.
- The surface is composed exclusively of fluorinated groups. CF_3 groups are more effective than CF_2 groups, which, in turn, are more effective than CF groups, in reducing the energy of the surface⁹.
- There is sufficient fluorine in the bulk of the coating to effectively control the organisation of fluorine at the surface.
- Dipoles, such as $-CF_2-CH_2-$ are located well beneath the surface¹⁰.
- The surface is crosslinked to hold fluorine in place, resist rearrangement and infiltration of marine adhesives, and maintain stability in the marine environment.

The fluorinated coating which best accomplishes these goals, was developed by Brady¹¹, *et al.* They obtained a coating with a surface composed of oriented, immobilised perfluoroalkyl groups by crosslinking the two reactive perfluoroalkyl polymeric surfactants with a copolymer of 2-isopropenyl-2-oxazoline, as illustrated in Structure II. The fluorinated moieties self-assemble at the air-liquid interface from a water medium to produce an array of closely-packed, oriented CF_3 -terminated perfluoroalkyl groups on their surface. Upon loss of solvent and heating, the reactants polymerise, form covalent crosslinks, and lose ionic charge. Because of the high crosslink density in the coating, the oriented perfluoroalkyl groups are strictly immobilised and tend to resist both the infiltration of adhesive molecules and adhesive-induced molecular rearrangement. By virtue of the low energy of the surface, its interface with the adhesive is not strong, and by virtue of the high resistance of the surface to molecular interdiffusion and rearrangement, its interface to the marine adhesive is sharp, well-defined, and easily-cleaved. These coatings resist attachment of marine fouling more effectively than any fluoropolymer tested so far¹².



STRUCTURE II

2.2.2 Silicone Fouling-release Coatings

The coatings based on silicones have also been extensively tested for resistance to marine fouling. Kohl and Singer¹² made the critical discovery that fouling release does not correlate with surface energy alone, but with the square root of the product of surface energy (γ) and elastic modulus (E), as shown in Fig. 1. The minimum in adhesion coincides with the lowest value of elastic modulus tested, although this does not correspond to the lowest surface energy tested, demonstrating that elastic

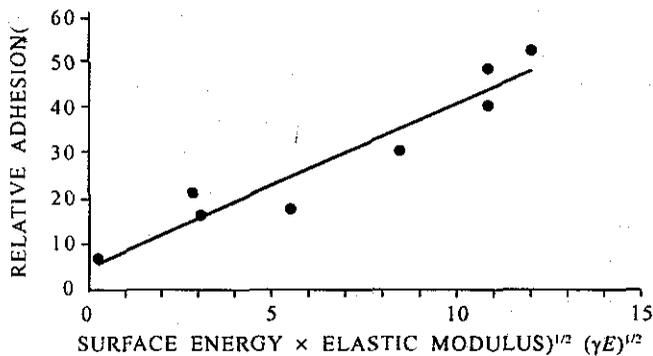


Figure 1. Correlation between fouling release and surface energy and elastic modulus.

modulus is, at least, as important as surface energy in determining the performance of silicone fouling-release coatings. Therefore, the most effective route to fouling-free performance is to encourage the release of fouling organisms from the surface by predisposing the adhesive joint between the foulant and the coating to quick and easy failure by peeling. This is accomplished by judicious control of the thickness and the elastic modulus of the silicone coating. Fouling release from silicone coatings is best enabled when:

- The silicone resin has a linear, highly flexible backbone substituted by a sufficient number of groups to diminish surface energy while preserving backbone mobility.
- The silicone resin has the lowest elastic modulus consistent with physical toughness.
- The silicone resin is stable in the marine environment and is resistant to hydrolysis which causes loss of mass and development of surface roughness.

- The coating is applied at a thickness that favours failure by peel rather than failure by shear at the coating-foulant joint.
- The coating is very smooth.

Some commercial non-toxic silicone coatings contain silicone oil which migrates from the bulk of the coating to the surface and into the water. Fouling settles on the oil rather than on the surface of the coating. The joint between the oil and the coating is weak and fails readily; the oil migrates into the water taking early stages of fouling with it. The oil also plasticises the coating. Despite the encouraging performance of commercial coatings based on this technology, there are the following drawbacks to this approach:

- The silicone oils are lost, usually within two years in temperate waters, with several consequences. The mechanical properties of the coating deteriorate significantly and sharply, and the coating becomes brittle and cracks. The weak boundary layer is no longer formed, fouling settles and adheres with tenacity, and the coating must be replaced.
- The silicone oils are released into the environment. Although there is no toxicity associated with these compounds in seawater, one believes that a policy of absolutely no release to the environment will prove best in the long run.

3. ENVIRONMENTAL IMPACT ON VESSEL OPERATIONS

The current generation of ablative copper paints is providing good service on commercial vessels and warships. An ablative copper coating installed on the aircraft carrier, USS DWIGHT D EISENHOWER in 1988 continues to provide effective service even today. It is important to consider the waters in which a vessel will be operating and to apply a thickness of coating which will give the desired service life at the anticipated ablation rate. Periodic hull cleaning is also beneficial. Although, the environmental impact of long-term use of the required secondary biocides in copper paints is unknown, these coatings will be a favoured alternative to tin-based paints as long as copper-based paints are legally accepted by the major maritime nations of the world.

Several non-toxic fouling-release coatings are now in the market, and it is safe to say that every major marine coatings house is actively developing and testing improved versions of these coatings. All of the present commercial products are based on fugitive oils and have, at least, the potential for environmental impact while these oils leach from the coating. The service life limit of the present coatings is approximately two years.

More importantly, a decision to use a non-toxic coating is also a decision to accept a responsibility for routine hull maintenance. The interval between the cleaning hull depends on the waters in which a ship is operating and the length of time a ship lies at pierside, for most fouling takes place when a ship is still. The speed, which a ship with a fouled hull might attain is also an important consideration. Water velocities in excess of 22 knot (37 foot/s) effectively remove attached fouling organisms from the surfaces of these coatings¹⁴, so certain high-performance craft, which are infrequently idle, may never require hull cleaning. Initial material costs for silicone coatings are high, but life-cycle costs are low. Adhesion to the substrate requires careful attention, and the low-modulus coatings may suffer mechanical damage, but procedures to relieve these factors are well-established.

4. FUTURE STUDIES

The development and testing of fouling-release coatings will focus on non-toxic coatings. Copper-based coatings seem to have reached their limits, and further improvements are likely to come through secondary biocides. However, how long copper and the secondary biocides will continue to be acceptable to environmental authorities, is unknown. Products based on natural poisons found in sea creatures, such as grasses, corals, sponges, and algae may be another avenue to antifouling technology, but wide-spectrum toxicity testing of a paint containing one or more of these will be lengthy and prohibitively costly (\$10 million in the US alone).

Presently, silicone coatings have an edge over the fluoropolymer coatings. However, there is a great need to improve the mechanical strength of silicones to obviate current problems with cutting,

tearing, and puncturing. Improvements are also needed in the chemistry of bonding silicones to the hull. In some cases, the ship does not adhere to the coating any better than the barnacles!

There is a need for a new generation of hull-cleaning equipment which will remove marine fouling from complex hull shapes without excessive damage to the coating. In the case of copper paints, this equipment will not scrape away as much paint as the present devices, and thus, will extend the life of a paint system which relies on its thickness, and will release far less copper into the environment. For non-toxic coatings, the new equipment will be designed to take advantage of the unique ways in which fouling is released from the coating. The hard, tough fluoropolymers, which release fouling by shear fracture at the coating-fouling joint, will be cleaned by devices which apply shear force parallel to the coating surface at high speed. The softer, lower-modulus silicone coatings are much more susceptible to cuts, tears, and other mechanical damage, and release fouling by letting it peel away from the surface. These coatings will be cleaned by a machine which will apply a weak force to the fouling at low frequency and will maintain the force on the fouling until the joint with the coating peels apart.

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Dr Robert F. Brady (Jr) received his BS and PhD in Chemistry from the University of Virginia, USA. During 1982-2001, he was on the staff of the US Naval Research Laboratory, where he directed and conducted basic research in polymer chemistry and coatings science, formulated and tested advanced marine coatings, and developed and validated test methods for coatings. His main interests include: High solids epoxy and polyurethane coatings, solar heat-reflecting coatings, non-toxic anti-fouling coatings, and the composition, structure, and production of low-energy surfaces. He has published 60 papers and holds 12 patents.

He received the *Roon Award* (1992) and *Mattiello Award* (1999) from the Federation of Societies for Coatings Technology, the *Meritorious Civilian Service Award* (1997) and the *NRL Sigma Xi Award for Applied Research* (1994) from the Naval Research Laboratory, and the *Vice Admiral Harold G Bowen Invention Award* (2000) from the Office of the Naval Research. He was Technical Editor of the *Journal of Coatings Technology* from 1992-97. He is a member of the American Chemical Society, the Federation of Societies for Coatings Technology, Alpha Chi Sigma, and is a fellow of the Royal Society of Chemistry, London.