BIOCIDES FOR ANTIFOULING MARINE COATINGS – ISSUES IN REACTIVITY, PERFORMANCE, AND ECOTOXICITY

S.H. Lawrence, A.W. Webb, and R.L. Foster

Naval Research Lab, Code 6130,
Center for Corrosion Science & Engineering,
Washington, DC 20375

For centuries, owners of private, commercial and military sea vessels have attempted, with varying degrees of success, to surface treat their underwater hulls with coatings to prevent the adhesion and/or growth of large fouling organisms that cause severe drag, reducing vessel speed and maneuverability, and increasing fuel consumption. Two major approaches are currently under development: (1) "easy release" coatings, usually employing silicones or fluoropolymers designed to prevent strong adhesion of foulants, and (2) "ablative/self-polishing" coatings, which typically contain a rapidly ecodegradable biocide which is toxic to foulants upon release, and is slowly but continuously released from the coating during its ablative process. Critical performance issues currently limit use of the easy release coatings to a relatively small number of vessels. For large commercial and military vessels, the more mature ablative antifouling coatings with biocides are necessary to maintain adequate operability.

Based on its excellent performance, the biocide of choice in the latter half of the last century was tributyltin (TBT) oxide. In addition to its biocidal properties, it can be incorporated directly into the resin polymer structure (as an ester linkage), and is therefore released evenly and continuously as the resin itself ablates. However, these coatings are currently being phased out internationally, because of the mutations TBT causes in certain marine organisms. As a result, research into antifouling coatings is concentrated on both well-established biocides having known performance (e.g., Cu_2O, CuSCN), and newer metal-free organic and reduced metal metallo-organic biocides. These compounds are designed to be highly reactive upon exposure to seawater, then to rapidly decompose to nontoxic byproducts upon release into the nearby open water.

This presentation will address the mechanisms of activity of a few of these biocides, and some of the advantages and challenges posed by their use. The "classic" inorganic pigments, for example, while offering known behavior and relative ease of formulation, do not perform as well as the TBT coatings. One reason is their presence in the coatings matrix as a (relatively large) second phase, leading to their uneven release rate with time – see *figure 1*, which shows the microstructure of an inorganic pigmented system. In addition, organic and metallo-organic biocides of current interest will also be discussed. These tend to offer advantages of more rapid dispersibility and more intimate mixing into the coating system. Two such compounds are shown in *figure 2* (DCOI) and *figure 3* (CuPT/ZnPT); the former is a metal-free organic which undergoes rapid ecodegradation once it enters open water, and the latter is characterized by an anion which is also ecodegradable, as well as photochemically reactive. This latter feature provides both enhanced biocidal efficacy and more rapid ecodegradation to byproducts having low toxicity.

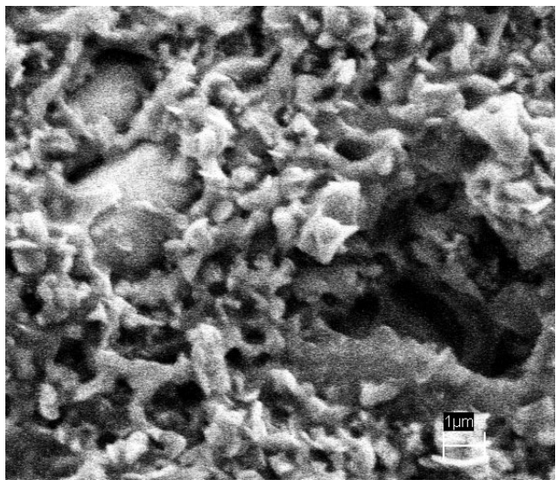

Fig. 1. Partially ablated antifouling coating with inorganic biocide (pigment particles at upper left; scale bar represents 1µm length)

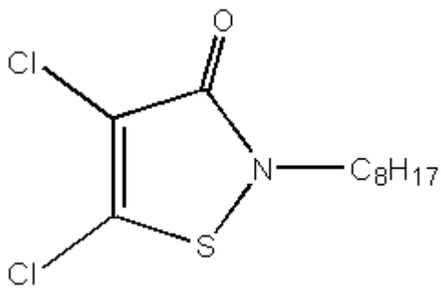

Fig. 2. 4,5-dichloro-2-n-octyl-3(2H)-isothiazolone ("DCOI")

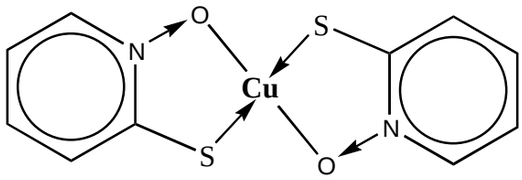

Fig. 3. 2-pyridinethiol-1-oxide, copper complex ("copper pyrithione"; Zn complex also used)