



The use of copper-based antifouling on aluminium ship hulls



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ARTICLE INFO

Article history:

Received 29 May 2015

Accepted 20 September 2015

Available online 22 October 2015

Keywords:

Marine Antifouling

Copper

Galvanic Corrosion

Aluminium

Differential Aeration

Leaching

ABSTRACT

Copper, most commonly in the form of copper oxide, is used in the majority of marine antifouling globally, but some paint companies do not allow their copper oxide based antifouling to be used on aluminium hulls. This is because aluminium is more anodic in the electrochemical series than copper and if the two are in direct contact in sea water, the aluminium will corrode away. This galvanic reaction only occurs if copper metal is in direct contact with aluminium, and since modern copper oxide based antifouling contain virtually no metallic copper there appears to be no valid reason for the ultra-cautious approach regarding the use of copper oxide based antifouling on aluminium hulls. A number of different copper-based commercial antifouling were applied on suitably prepared Marine-grade aluminium panels, along with an un-coated control panel. The panels were immersed in seawater. Furthermore a laboratory experiment was also undertaken where coated aluminium panels were submerged in a salt water solution as a controlled experiment. All the samples were then analysed using electron microscopy. Copper leaching out of copper oxide based antifouling had no effect on the corrosion of Marine-grade aluminium.

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1. Introduction

Currently most paint companies recommend that their copper oxide based marine antifouling are not to be used on aluminium ship hulls. One assumption is that the copper could be deposited on the aluminium hull from the antifouling, thus creating a galvanic cell where the copper acts as the cathode, the aluminium hull acts as the anode and seawater is the electrolyte. This would result in accelerated corrosion of the aluminium, by a pitting type attack (International Paint, 2008). Galvanic corrosion cells are formed between dissimilar metals. When two dissimilar metals in contact are placed in salt water, an electric potential is established and corrosion occurs. The more active metal (anode) will corrode at a faster rate than it would by itself. The more noble metal of the pair (cathode) is protected from corrosion by the galvanic coupling. The corrosion potentials of metals and alloys measured in seawater or salt solutions can be arranged in a galvanic series in which a metal high in the series will generally have a greater resistance to corrosion than one low in the series. Aluminium is very susceptible to galvanic corrosion because of its place in the galvanic series (Butler and Ison, 1976).

There are two potential ways by which copper from an antifouling could make contact with the aluminium hull. The first way is in places where the bare aluminium hull is exposed, and any

copper leaching from the adjacent antifouling coating deposits as copper metal on the exposed aluminium surface. The second potential way is that copper pigments or copper ions in solution could move inwards through gaps in the polymer coating matrix and deposit as copper metal on the aluminium surface. However there are no literature reports in the public domain of either of these potential events happening in practice and since modern copper oxide based antifouling contain virtually no metallic copper there appears to be no valid reason for the ultra-cautious approach regarding the use of copper oxide based antifouling on aluminium hulls. Therefore, for the above reasons and particularly the present scarcity of literature on this subject this research study was carried out. The main aim of the study was to determine whether the use of copper oxide in antifouling plays any part in the corrosion of aluminium in seawater.

In order to achieve this two sets of immersion tests were conducted, using sample aluminium plates coated with different antifouling, as described in the Section 2. The results of these experiments are presented in Section 3 while the discussions on the results are given in Section 4. The main conclusions of the paper are presented in Section 5 together with a recommendation for future work.

2. Methods and materials

In order to collect evidence whether or not copper oxide in antifouling paints contributes to the accelerated corrosion of marine grade aluminium, a set of sea water immersion tests and

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controlled laboratory experiments were carried out on flat test panels. Six panels were cut from 5083 marine grade aluminium alloy, three panels 300 mm high, 205 mm wide and 5 mm thick and three panels 100 mm high, 100 mm wide and 5 mm thick. Three of these panels were used for the sea water immersion tests while the other three panels were used for the laboratory tests, as shown in Figs. 1 and 2 respectively. The typical chemical composition of 5083 marine grade aluminium alloy is shown in Table 1. The surface of each of the aluminium test plates was prepared using a grinder to British Standards Institution (2010) BS EN ISO 8501-1:2007, St 3 Surface preparation standards for hand held tools, which states that “the surfaces shall be free from visible oil, grease and dirt, and from poorly adhering mill scale, rust, paint coatings and foreign matter” (Transocean Coatings, 2010). Using the grinder also gave the aluminium a good key to enable the paint to adhere to it.

Three commercially available antifouling paints systems were used, which had varying amounts of copper, as follows;

- *International paint Trilux 33* (red colour, “Aluminium antifouling AF”) Ingredients of Trilux 33 include; Zinc oxide, Xylene, Cuprous Thiocyanate, Rosin, Ethylbenzene, Zinc pyrithione and Triphenyl phosphate.
- *International paint Micron Extra 2* (brown colour, “Controlled depletion polymer CDP”) Ingredients of Micron Extra 2 include; Copper (1) oxide, Zinc oxide, Rosin, Xylene, Solvent naphtha, Zineb, 1,2,4-trimethylbenzene, Isopropylated triphenyl phosphate, Ethylbenzene and Triphenyl phosphate.
- *International paint Micron 77* (blue colour, “Self polishing copolymer SPC”) Ingredients of Micron 77 include; 4-methylpentan-2-one, Butan-1-ol, Copper (1) oxide, Copper Pyrithione, Ethylbenzene, Solvent naphtha, Xylene and Zinc oxide.

Both *Micron Extra 2* and *Micron 77* are not recommended for use on aluminium hulls because they contain copper oxide. *Trilux 33* is recommended for use on aluminium hulls as its active ingredient is cuprous thiocyanate, not copper oxide.

The antifouling coatings were applied directly to the aluminium panels, without any primer.

The structure of each antifouling surface is very different (Figs. 11–13). The aluminium antifouling has very few cracks and holes, it is also relatively smooth, whereas the CDP coated surface has many small holes and it can also be seen that the surface is very rough. It is well-known that CDP type antifouling generate a thick leached layer through which the biocide must travel to prevent fouling effectively (Anderson, 2007). The SPC coated surface has many holes and cracks but a fairly smooth surface.

The seawater immersion tests were carried out on the three plates cut to a size of 300 mm × 205 mm. These plates were coated with the three different antifouling paints using airless spray



Fig. 1. Sea plates before immersion. (Left AF, middle SPC and right CDP).



Fig. 2. Laboratory plates before immersion. (Left SPC, middle CDP and right AF).

Table 1

Typical chemical compositions of aluminium alloy 5083 (Aalco, 2014).

Element	% By mass
Manganese (Mn)	0.40–1.00
Iron (Fe)	0.40 max
Copper (Cu)	0.10 max
Magnesium (Mg)	4.00–4.90
Silicon (Si)	0.40 max
Zinc (Zn)	0.25 max
Chromium (Cr)	0.05–0.25
Titanium (Ti)	0.15 max
Aluminium (Al)	Balance

under ambient conditions, to the thickness recommended by the paint manufacturer (*International Paint*). The antifouling was applied directly to the bare aluminium, without any primer, which is not recommended by the manufacturer but for the experiment this would simulate the worst case scenario of the antifouling being in direct contact with the aluminium substrate, rather than scribing. Scribing without a primer applied would simply create a crevice which is susceptible to corrosion. Also scribing an antifouling coat that has a primer applied will allow water to penetrate under the coating and detach the coating system, and this would result in the experiment failing. A strip of aluminium was left uncoated at the top of the panel, 20 mm high and 205 mm wide, as shown in Fig. 1. This was intended to show if any copper leaching from the antifouling deposited on the bare aluminium substrate and would also simulate a creation of a holiday in the coating. In addition one completely bare and uncoated control plate was also used for comparison. The plates were immersed to a depth of 2–3 m and secured to the jetty in a series 2 m apart in the North Sea (*Blyth harbour, North East of England*) for a total of 88 days during December 2013–March 2014.

A controlled laboratory experiment was also set up identical to the sea water immersion experiment but with 100 mm × 100 mm size plates, and a 20 mm × 100 mm strip of bare aluminium, as shown in Fig. 2. This test was undertaken to see if similar results could be achieved in a controlled laboratory experiment. The specimens were placed in a plastic rack 100 mm apart and placed in a bath 350 mm wide 700 mm long and 200 mm deep. This was filled with 25 l of distilled water and sea salt (35 g l⁻¹) with the temperature set at 34 °C to increase the reaction time of any corrosion. A layer of polystyrene foam pieces was used to cover the water surface of the bath to reduce heat loss and to limit evaporation. The laboratory specimens were placed fully immersed in the bath for 8 days.

Various methods of analysis were deployed to determine the type of corrosion attack of the plates. All the specimens were examined visually using a low powered optical microscope (*Brunel SP1500XP*)

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