



Strathprints Institutional Repository

Bagley, Frank and Atlar, Mehmet and Charles, Alasdair and Anderson, Colin (2015) The use of copper-based antifoulings on aluminium ship hulls. Ocean Engineering, 109. 595–602. ISSN 0029-8018 , <http://dx.doi.org/10.1016/j.oceaneng.2015.09.044>

This version is available at <http://strathprints.strath.ac.uk/59417/>

Strathprints is designed to allow users to access the research output of the University of Strathclyde. Unless otherwise explicitly stated on the manuscript, Copyright © and Moral Rights for the papers on this site are retained by the individual authors and/or other copyright owners. Please check the manuscript for details of any other licences that may have been applied. You may not engage in further distribution of the material for any profitmaking activities or any commercial gain. You may freely distribute both the url (<http://strathprints.strath.ac.uk/>) and the content of this paper for research or private study, educational, or not-for-profit purposes without prior permission or charge.

Any correspondence concerning this service should be sent to Strathprints administrator: strathprints@strath.ac.uk

The Use of Copper-based Antifoulings on Aluminium Ship Hulls

By

Frank William Bagley, Mehmet Atlar, Alasdair Charles
(Newcastle University, UK)

and

Colin Anderson
(American Chemet, USA)

ABSTRACT

Copper, most commonly in the form of Cuprous Oxide (Cu_2O), is used in the majority all marine antifoulings globally, but some paint companies do not allow their Cu_2O based antifoulings to be used on aluminium hulls. This is because aluminium is more anodic in the electrochemical series than copper, and if the two are directly connected 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 Cu_2O based antifoulings contain virtually no metallic copper there appears to be no valid reason for the ultra-cautious approach regarding the use of Cu_2O based antifoulings on aluminium hulls. A number of different copper-based commercial antifoulings 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 Cu_2O based antifoulings had no affect on the corrosion of Marine-grade aluminium.

Keywords

Marine Antifouling, Copper, Galvanic Corrosion, Aluminium, Differential Aeration, Leaching

1. Introduction

Currently most paint companies recommend that their Cu_2O based marine antifoulings are not to be used on aluminium ship hulls. The 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 Technical Bulletin 05/08 "Coating of Aluminium Hulls", August 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,G. & Ison,H,C,K.1976).

There are two potential ways by which copper from an antifouling could make contact with the aluminium hull. The first is in places where bare aluminium is exposed by damage to the paint system, and any copper from the adjacent antifouling coating, leached into solution, 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 copper metal deposit 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 Cu_2O -based antifoulings contain virtually no metallic copper there appears to be no valid reason for the ultra-cautious approach regarding the use of Cu_2O -based antifoulings 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 antifoulings plays any part in the corrosion of aluminium in seawater.

In order to achieve the above aim two sets of immersion tests were conducted, using sample aluminium plates coated with different antifoulings, 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 controlled laboratory experiments were carried out on flat test panels. Six panels were cut from 5083 marine grade aluminium alloy with a 5mm thickness. 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 Figures 2 and 3 respectively. The typical chemical composition of 5083 marine grade aluminium alloy is shown in Table 1. It is noteworthy that copper is listed as one of the ingredients.

Table 1 Typical chemical compositions of aluminium alloy 5083 (percentage by mass) (Aalco 2014)

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

The surface of each of the aluminium test plates was prepared using a grinder to 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;

- Trilux 33 (red colour, “Aluminium antifouling AF”) contains an active ingredient of cuprous thiocyanate and is commonly used on aluminium boat hulls.
- Micron Extra 2 (brown colour, “Controlled Depletion Polymer CDP”) whose active ingredient is copper (I) oxide.
- Micron 77 (blue colour, “Self Polishing Copolymer SPC”) whose active ingredient is also copper (I) oxide.

Both Micron Extra 2 and Micron 77 are not recommended for use on aluminium hulls because they contain copper (I) oxide. The antifouling were applied directly to the aluminium panels, without any primer.

The seawater immersion tests were carried out on the three plates cut to a size of 300mm x 205mm. These plates were coated with the three different antifouling paints using air less spray under ambient conditions, to the thickness recommended by the paint manufacturer (International Paint). A strip of aluminium was left uncoated at the top of the panel, 20mm high and 205mm wide, as shown in Figure 2. This was intended to show if any copper leaching from the antifouling deposited on the bare aluminium substrate. In addition one completely bare and uncoated control plate was also used for comparison. The plates were immersed in the North Sea (Blyth harbour, North East of England) for a total of 88 days during December 2013 - March 2014).



Figure 2 Sea Plates before immersion
(Left AF, Middle SPC and Right CDP)

A controlled laboratory experiment was also set up identical to the sea water immersion experiment but with 100mm x 100mm size plates, and a 20mm x 100mm strip of bare aluminium, as shown in Figure 3. 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 100mm apart and placed in a bath 350mm x 700mm, the bath is shown in Figure 4. This was filled with 25 litres of distilled water and sea salt (35g per litre) with the temperature set at 34°C this was to

increase the reaction time of the corrosion. A layer of polystyrene foam pieces were used to cover the solution surface in order to reduce heat loss and to limit evaporation. The laboratory specimens were placed fully immersed in the bath for 8 days.



Figure 3 Laboratory plates before immersion
(Left SPC, Middle CDP and Right AF)

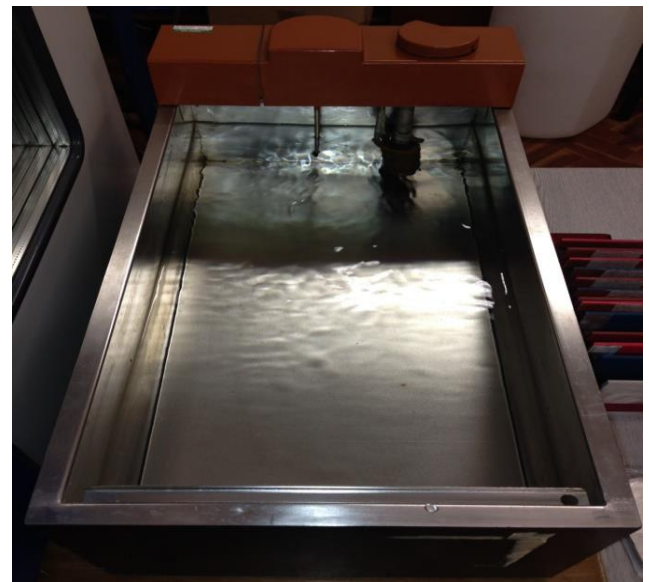


Figure 4 Solution Bath

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) and then examined using a SEM (Hitachi S2400 Scanning Electron Microscope) and analysed with the energy dispersive x-ray.

3. Results

3.1 Laboratory experiment results

The visual examination of the specimens after 8 days in the artificial seawater solution revealed a dulling of the surfaces of the aluminium and the antifouling, as seen in Figure 5. Also evident is the breakdown of the SPC.



Figure 5 Laboratory plates after artificial immersion (Left SPC, Middle CDP and Right AF)

The bare aluminium strips of each test plate plus a aluminium strip before immersion, were examined with the low powered microscope, as shown in Fig 6. The top left picture in Fig 6 show an aluminium strip before it was put in the solution. The top right picture is the view above the SPC coated strip after 8 days in the solution; the bottom left picture is the view above the Aluminium antifouling, after 8 days in solution and the bottom right is the view above the CDP coated antifouling, also after 8 days in solution. All the specimens from the solution had dark brown spots which followed the lines of the surface preparation grooves. Also pockets of aluminium oxide can be seen at random points all over the aluminium substrate.

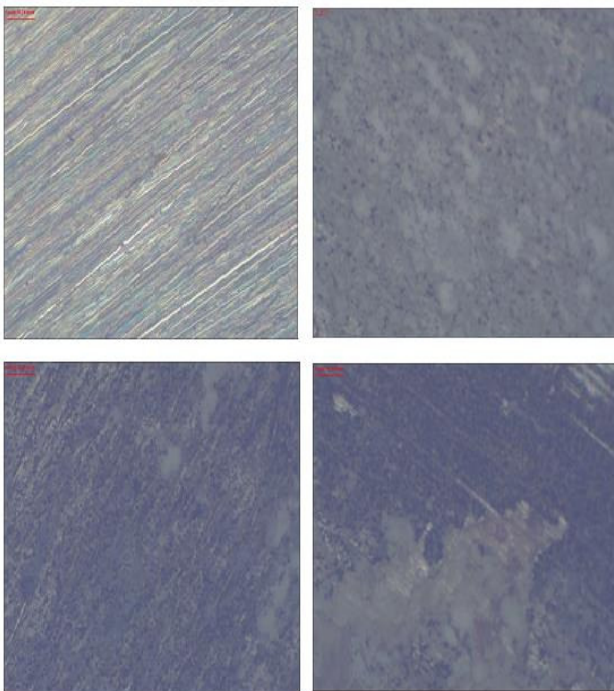


Figure 6 Laboratory specimens (aluminium strip) (x10) (Top left test plate before immersion, top right SPC after immersion, Bottom left AF after immersion and bottom right CDP after immersion)

The visual examination of the antifouling surface using the low powered microscope revealed the aluminium antifouling showed some defects, with a darkening in the centre of each defect as shown in left hand side picture in Fig 7. The CDP coating also had a minor defect at a point in the coating under the microscope it was evident some corrosion had taken place this can be seen in the middle

picture of Fig 7. The SPC coating had a complete coating breakdown, as seen in the right hand side picture of Fig 7, the exposed aluminium on all the plates showed dark brown spots in the crevices that followed the lines of the surface preparation grooves.

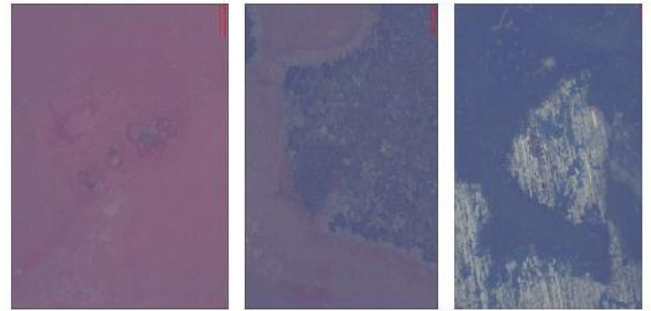


Figure 7 Laboratory samples (x10) (Left AF, Middle CDP and Right SPC)

3.2 Sea immersion results

When the three coated test plates were taken out of the sea, after 88 days of immersion it was noticed that all of the plates were free of any visible biofouling. However, all of them had blisters and obvious deposits of corrosion product, mainly where the antifouling and the bare aluminium alloy met, as shown in Fig 8.

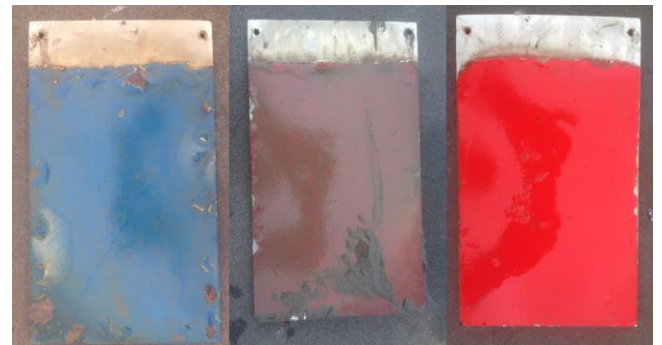


Figure 8 Plates after immersion (Left SPC, Middle CDP and Right AF)

An area of each specimen where the corrosion was at its worst was selected. The worst area was where the antifouling and the bare aluminium alloy met, and it is this area where copper deposits on the aluminium substrate, resulting from leaching, might be expected. Also the joint between the substrate and the antifouling created a crevice, hence the possibility of corrosion. Each area was examined under the microscope (x10) magnification, as seen in Figs 9 to 11. This shows ruptured corrosion blisters of various sizes on each sample. The bare aluminium strip above each antifouling showed the same dark spots in the crevices as also seen in the lab experiment, which were formed by the breakdown of the aluminium oxide film (Davis, 1999).



Figure 9 Self Polishing Copolymer (x10)

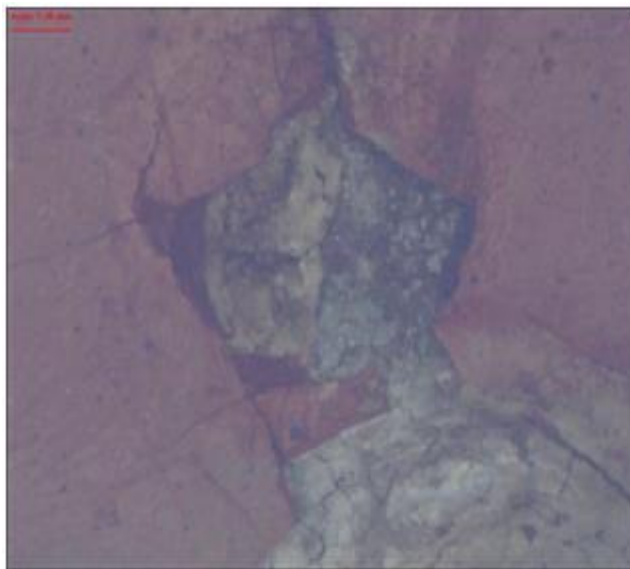


Figure 10 Controlled Depletion Polymer (x10)



Figure 11 Aluminium Antifouling (x10)

Initial inspection of the panels showed that the areas where the bare aluminium and the coated aluminium meet had suffered from corrosion. White and brown corrosion

is clearly visible in this region of the plates as seen, in Fig 9 to 11.

The specimens were examined using the Scanning Electron Microscope (SEM), and the Energy-Dispersive X-ray (EDX) as presented in Tables 2 to 9, as well as Figs 12 to 18.

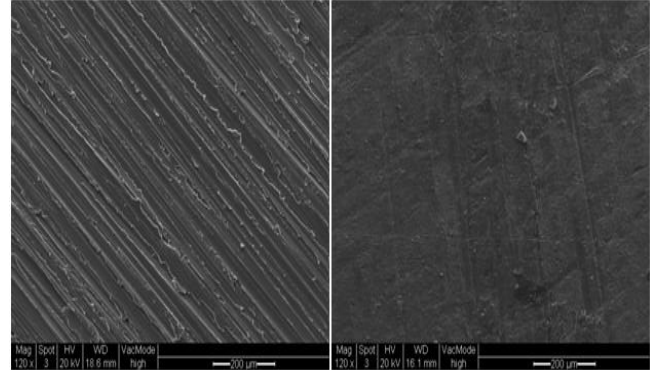


Figure 12 bare Aluminium test plate before (left) and after (right) immersion (x120)

Table 2 Aluminium before immersion (x120)
(As seen EDX results of aluminium before immersion)

Element	Atom. C [at.-%]
Aluminium	94
Magnesium	6

Any metal surface exposed to air will start to surface oxidise and so some oxygen will always be present on the surface so table 2 should show some oxygen content. The reason table 2 isn't showing any oxygen content is that the oxygen content is very low and the EDX can't pick up. Also the data is not accurate to decimal places. For this reason all the EDX results have been rounded to whole numbers.

Table 3 Aluminium after immersion (x120)
(As seen EDX results of aluminium after immersion)

Element	Atom. C [at.-%]
Aluminium	56
Magnesium	4
Oxygen	40

Typical views from the SEM for the three different coated surfaces are also presented in Figures 13 to 15, while the analysis results from the EDX for the same surfaces are tabulated in Tables 4 to 6.

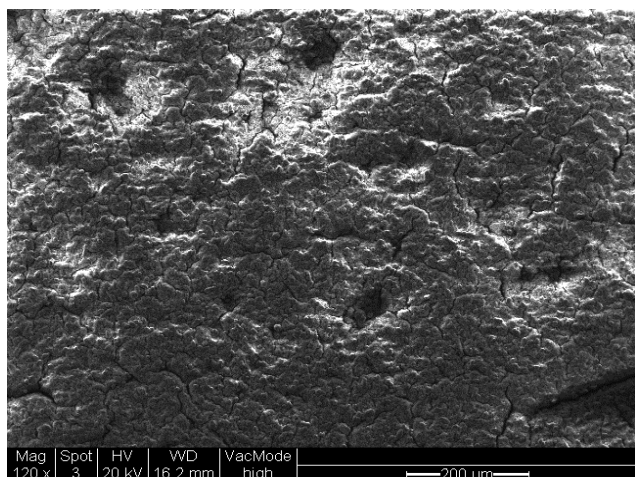


Figure 13 Aluminium Antifouling (x120)
(Surface of the AF after immersion)

Table 4 Aluminium Antifouling (x120)
(As seen EDX results of AF surface after immersion)

Element	Atom. C [at.-%]
Aluminium	1
Chlorine	5
Copper	7
Magnesium	1
Oxygen	74
Phosphorus	2
Silicon	3
Sulfur	7

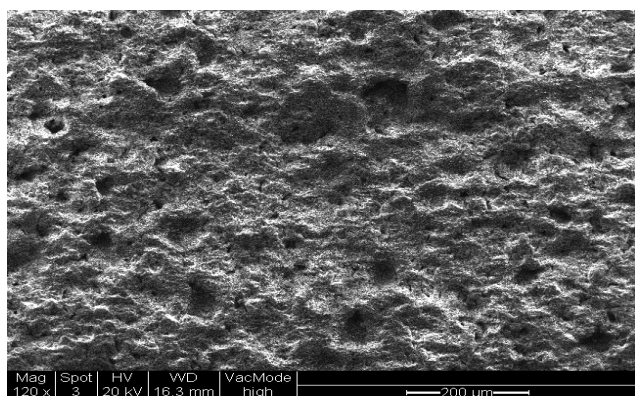


Figure 14 Controlled Depletion Polymer (x120)
(Surface of the CDP after immersion)

Table 5 Controlled Depletion Polymer (x120)
(As seen EDX results of CDP surface after immersion)

Element	Atom. C [at.-%]
Aluminium	2
Chlorine	2
Copper	4
Iron	1
Oxygen	70
Phosphorus	1
Silicon	5
Sulfur	7
Zinc	8

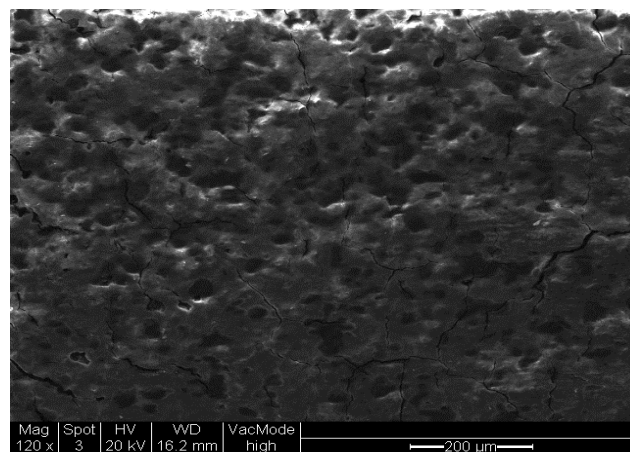


Figure 15 Self Polishing Copolymer (x120)
(Surface of the SPC after immersion)

Table 6 Self Polishing Copolymer (x120)
(As seen EDX results of SPC surface after immersion)

Element	Atom. C [at.-%]
Aluminium	7
Calcium	1
Chlorine	14
Copper	13
Iron	1
Magnesium	3
Oxygen	38
Phosphorus	2
Potassium	1
Sulfur	7
Silicon	6
Titanium	7

As can be seen in Figs 13 to 15, the structure of the each coated surface is very different. 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). This layer has affected the EDX results given in Table 5, which show a low copper content on the surface. The SPC coated surface has many holes and cracks but a fairly smooth surface. The EDX results showed all three antifouling had high oxygen contents after immersion, as seen in Tables 4 to 6.

After first investigations and analyses, the three test plates were washed in deionised water and placed in a sonic bath to remove the loose material (blisters) and examined under the electron microscope. The typical views of the three substrate surfaces from the SEM are presented in Figs 16, 17 and 18 while the analysis results from the EDX are given in Tables 7, 8 and 9 for the same surfaces. Corrosion pits were found where the loose material was removed from the Aluminium antifouling coated plate as shown in Fig 16 and the CDP coated plate in Fig 17. These areas were examined by the EDX and traces of the antifouling elements were present on the surface as seen in Tables 7 to 9. The results of the analysis for the SPC coating show a brown layer of

corrosion product covering the metal surface, as shown in Figures 18. The pits seen in Fig 16 with the Aluminium antifouling coated plate could also suggest some intergranular attack, again high amounts of oxygen were also present on all three samples as seen in Table's 7 to 9.

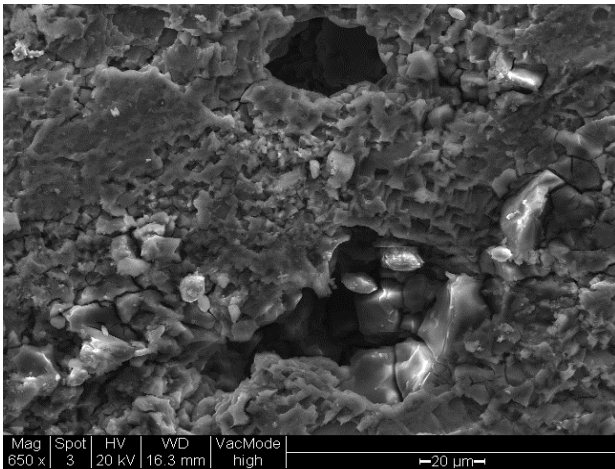


Figure 16 Aluminium Antifouling pits (x650)
(aluminium surface under blister after immersion)

Table 7 Aluminium Antifouling pits (x650)
(As seen EDX results of AF surface after immersion)

Element	Atom. C [at.-%]
Aluminium	49
Copper	1
Chloride	1
Magnesium	3
Oxygen	45
Sulfur	1

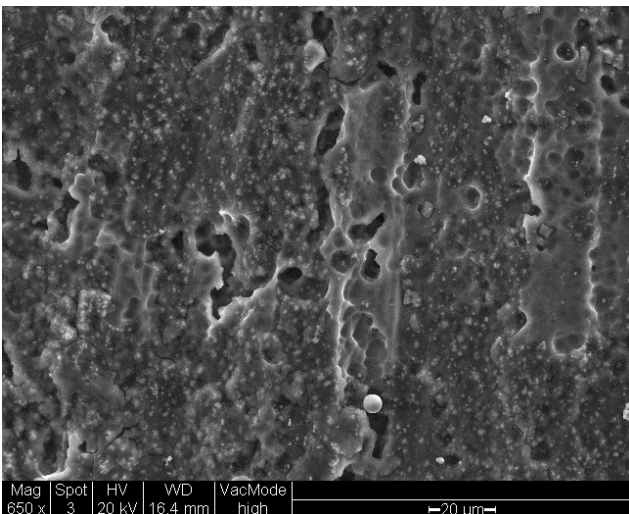


Figure 17 Controlled Depletion Polymer pits (x650)
(aluminium surface under blister after immersion)

Table 8 Controlled Depletion Polymer (x650)
(As seen EDX results of CDP surface after immersion)

Element	Atom. C [at.-%]
Aluminium	53
Copper	2
Magnesium	6
Oxygen	38
Sulfur	1

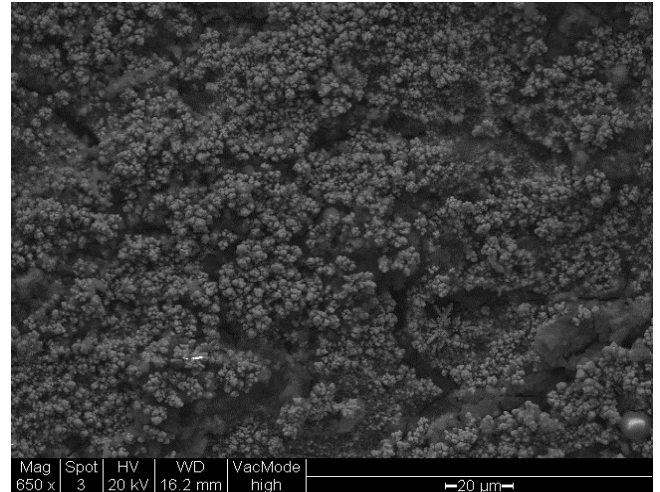


Figure 18 Self Polishing Copolymer (x650) (aluminium surface under blister after immersion)

Table 9 Self Polishing Copolymer (x650)
(As seen EDX results of SPC surface after immersion)

Element	Atom. C [at.-%]
Aluminium	47
Calcium	1
Copper	1
Magnesium	3
Oxygen	48

4. Discussion

This work was carried out in order to determine whether copper oxide in some antifouling paints can accelerate corrosion rates when applied to aluminium alloy immersed in sea water. Aluminium has a tough protective oxide film which forms when the bare metal is exposed to air. It is generally known that metals that form oxide films tend to pit in seawater if the film breaks down for any reason. This action can be seen in the natural immersion experiment, where the antifouling is at the edge touching the bare aluminium strip. The breakdown of the film has initiated because of variations in the environment over the surface of the material.

Differences in oxygen levels, temperatures and flow rates initiate the corrosion attack. The small area where the breakdown occurs becomes the anode of a galvanic cell, where the large intact film areas being the cathode. Once started the action tends to accelerate so deep pits occur (Winston & Herbert 2008). The propagation stage of pitting on aluminium involves formation of blisters

beneath the oxide film due to continuing localised reactions which lead to an acidic localised environment. The blisters subsequently rupture (McCafferty 2002). Antifouling coatings are designed to be permeable (W.H.O.I.1952). The varying permeability in the samples allows water to flow through the coating and act as an electrolyte in crevices left by the surface preparation, thus creating a good place for localised corrosion to occur. The oxygen content of the liquid in the crevice is consumed by the film formation reaction with the aluminium surface, and corrosion stops when the replenishment of oxygen by diffusion into the crevice is slow. At the mouth of the crevice oxygen is more plentiful. This creates a local cell between the oxygenated water and deoxygenated water and the corrosion potentials are such that localised corrosion occurs in the oxygen depleted crevice, which becomes the anode, and the oxygen rich peak which becomes the cathode. This is called a concentration cell or a differential aeration cell (Davis,1999) and (Nace)

Intergranular corrosion may have had an influence on the corrosion as seen in many aluminium base alloys that are susceptible to intergranular corrosion. This corrosion can occur on account of either phases of the alloy being anodic to aluminium and being present along grain boundaries. This could also be due to depleted zones of copper adjacent to grain boundaries in copper-containing alloys. Intergranular corrosion is a form of galvanic corrosion that can occur on a microscopic level. It is a form of localised surface attack in which a narrow path is corroded preferentially along the grain boundaries of a metal; this can be seen in Fig 16. The driving force is a difference in corrosion potential that develops between a thin grain boundary zone and the bulk of the immediately adjacent grains. In the 5xxx series aluminium alloys, magnesium is anodic to aluminium and is preferentially dissolved when the constituent forms a continuous path along grain boundaries (Vereecken,1994) and (Muller, & Galvele, 1977)

Within the above framework it was noticed that the corrosion was present on all samples, in varying amounts. This was of a localised nature which formed at the edge of the coating where the differing amounts of oxygen created an oxygen differential accelerating the corrosion forming blisters. In the meantime, as seen in Tables 4 to 6, the surface of the antifouling had relatively high amounts of copper which were detected on the areas where blisters had formed. In contrast Tables 7 to 9 had a relatively low concentration of copper suggesting that the copper was unable to leach through the paint to the aluminium substrate. Modern antifouling coatings have relatively low copper leach rates of <10 ppm (Anderson, 2007). It has been seen that in a NaCl solution the presence of Cu²⁺ ions at levels of >100 ppm greatly increases the corrosion on aluminium in the form of pitting (Kane, 1995).

Furthermore traces of other elements, such as Sulphur, copper, Chloride from the AF, Sulphur and copper from the CDP and Calcium and Copper from the SPC, which were present in the antifouling, were also found on the surfaces of the aluminium in trace amounts, where the antifouling coatings had been. This indicated that some

part of the antifouling coating was still present on the samples after the antifouling had been removed. Moreover no trace of copper was found on the bare aluminium immediately above the antifouling coatings, demonstrating that the copper leaching out of the coating did not deposit on the aluminium surface.

Furthermore copper has an electro potential which is larger than the electro potential of copper oxide and the difference between aluminium and copper oxide, will be much smaller than between metallic copper and aluminium. This will reduce the corrosion rates of any galvanic action.

5. Conclusions

The antifouling coatings tested performed very differently depending on their permeability. The Controlled Depletion Polymer (CDP) antifouling is semi permeable, the self-polishing copolymer antifouling (SPC) is fully permeable and the Aluminium antifouling had a very low permeability. The higher permeability suggests in such cases more rapid oxygen and water passage through to the aluminium alloy, resulting in under-film corrosion and subsequent coating detachment.

The evidence presented in this study shows copper from the antifouling plays no part in the corrosion process. As corrosion only occurred at areas where crevices had formed, and since there was no corrosion where the antifouling was intact, in the centre of the plate, this shows the corrosion attack was a crevice corrosion attack, with the differing amounts of oxygen in the samples driving the corrosion. This being the case there is no reason why the Cu₂O-containing CDP or the SPC type antifouling coatings could not be used on aluminium hulls, particularly when part of a complete coating system that includes a primer underneath the antifouling.

It would be beneficial to do some further work in order to understand in greater detail the cause of the pitting found on the samples, by using metallographic analysis. Metallographic examination will show any intergranular corrosion between the different alloying elements. This will also show if the alloying elements are distributed evenly, free from inclusions and the material is completely homogeneous.

Acknowledgements

The Authors wishes to thank Alnmaritec Ltd, UK, in particular Mr Chris Millman and Ron Bonallie for their collaboration and help during the preparation and conduct of the sea immersion tests.

References

Aalco (2014) Aluminium and its Properties [online] Available from: <http://www.azom.com/article.aspx?ArticleID=2804> [Accessed 14th April 2014]

Anderson, C. (2007) Kirk-othmer encyclopaedia of chemical technology: Vol 7,Coatings Antifoulings. 5 ed. USA: Wiley & Sons, pages 150-167

Butler, G. & Ison, H,C,K. (1976) Corrosion, Design and Materials: General and Pitting, Philosophical Transactions of the Royal Society of London. Series A. A Mathematical and Physical Sciences p.225-234

Coastal Engineering Manual, part 6. (2002) Materials and Construction, USA: U.S Army Corps of Engineers

Davis, J,R. (1999) Corrosion of Aluminium and Aluminium Alloys. USA: ASMI

Winston, R, Revie and Herbert, H, Uhlig, (2008), Corrosion and corrosion control, An introduction to corrosion science and engineering, 4th edition, Wiley & sons, page 14.

Kane, P.(1995).The effects of antifouling paints on the corrosion of aluminium and its alloys. MSc Thesis. Victoria University Manchester. Ch7, p.2.

McCafferty. E. (2002) Sequence of steps in the pitting of aluminium by chloride ions, Corrosion Science ,45. p.1421–1438.

Muller, I.L. & Galvele, J.R. (1977) Corrosion Science (17) p.179

NACE. Crevice Corrosion [online] Available from: <http://www.nace.org/Corrosion-Central/Corrosion-101/Crevice-Corrosion/> [Accessed 14th April 2014]

Vereecken, J. (1994) Corrosion Control of Aluminium – Forms of Corrosion and protection- Talat lecture 5013, EEA. Belgium: University Brussels, p.13.

Transocean coatings, Surface Preparation (www.transocean-coatings.com/static/.../2010/04/surfacepreparation-0.pdf) [Accessed 01/09/2014] p1-11

Woods Hole Oceanographic Institution (WHOI) (1952). Marine Fouling and its Prevention. USA: US Naval Institute p.283