Evaluation of Barrier Properties of Antifouling Coatings on Naval Steel

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The barrier properties of two antifouling coatings, namely a silicone foul-release coat and an epoxy self-polishing coat, were examined through accelerated and natural weathering methods. The accelerated aging included exposure of intact coatings for 1.5 month in a UV chamber and for 3 months in a salt spray cabinet. Moreover, scribed specimens were tested into the salt spray chamber for 2 months. Natural exposure included immersion of intact coatings for 4 months in the laboratory at room temperature and in 2.5m depth in Elefsis Gulf, correspondingly. Periodic evaluation of the intact coatings was made through electrochemical impedance spectroscopy, 60° gloss, colorimetry, König pendulum hardness measurements and visual examination. Analysis of the experimental results revealed that the silicone foul-release coating exhibits superior performance than its epoxy self-polishing counterpart, since it provides better antifouling protection, satisfactory barrier properties in both intact and flawed conditions, while retaining the color and gloss during the whole testing period.

1. Introduction

Antifouling marine paints have long been used for the protection of the ship hull from fouling and corrosion. Their aim is to maintain the hull smooth for longer periods of time, thus, reducing fuel consumption and CO_2 emissions, which generally increase when the hull is fouled and becomes roughened. Until recently, self-polishing copolymers, which release the biocide compound in a controlled rate, have been widely applied. The biocide compound is often cuprous oxide, while the paint itself is commonly based on polyurethane formulations. However, latest antifouling advances suggest the use of foul release coatings, which include polysiloxane formulations and do not repel the foulers with biocides, but they make the hull surface extremely slick for the organisms to attach and grow.

In order to examine the efficacy of an antifouling product, accelerated and natural aging methods can be applied (Loveday et al., 2004c; Skerry et al., 1987). Salt spray and UV exposure are the common practice among the accelerated aging techniques. Intact and scribed coated specimens are often examined, in order to investigate the protection a coating can provide as a barrier when it is intact and when flawed, correspondingly (Bierwagen, 1996). However, since accelerated aging tests can intensify only a certain number of parameters (e.g. salt-fog, temperature, humidity, UV light) at a time, natural aging tests are considered as giving more realistic, but rather time consuming, results, because they represent better the real service conditions an antifouling paint will possibly encounter throughout its lifetime. Laboratory immersion test gives a good estimate of the water changes that the leaching products cause and the deterioration of an antifouling system when continuously immersed in artificial sea water. However, in order to examine an antifouling product's resistance to fouling attachment, field tests should be performed. These include immersion of coated specimens in the sea for long periods of time (often a year). It becomes clear that each test provides information with regard to an antifouling system's efficiency against the deteriorating parameters that this specific test induces. Finally, EIS measurements have been extensively applied for evaluation of organic coatings (Loveday et al., 2004a; 2004b) and for description of their failure modes (Hinderliter et al., 2006), together with 60° gloss, thickness, weight, colour, König hardness measurements and visual examination (Bierwagen, 1987). Hence, it seems that a spherical

evaluation of an antifouling coat would include all the aforementioned tests, in order to come to a safer conclusion.

For this reason, two antifouling coatings, namely a silicone foul-release coat (Coat 1) and an epoxy self-polishing coat (Coat 2) were investigated regarding their barrier and antifouling properties, using the aforementioned experimental methods. More specifically, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) methods were implemented for the evaluation of the barrier properties and corrosion of coated naval steel specimens, along with visual characterization (colour, gloss, deterioration effects on surface), hardness and antifouling properties. The above measurements were performed on coated specimens after natural and accelerated aging.

2. Experimental setup

A silicone, red colour, of oily and slippery surface foul-release antifouling was Coat 1 and an epoxy, red colour, of matte surface, with chalking, self-polishing antifouling was Coat 2. Both antifouling systems were applied onto a Grade A naval steel substrate and consisted of four layers, making a total dry film thickness of around 650 μm, which is representative of a freshly painted ship hull. All the specimens used were of dimensions 100 X 100 X 6 mm^3, except for the specimens used for the laboratory immersion test which had dimensions 50 X 50 X 6 mm^3. Each test was performed on duplicate specimens for each antifouling paint, except for the Elefsis test, during which 6 pairs of Coat 1 and Coat 2 specimens were immersed in 2.5 m depth (each pair consisted of one sample coated with Coat 1 and one sample coated with Coat 2, both hung vertically from nylon ropes) at the same time, and every 2 months a pair was removed, in order to be assessed in the laboratory. Until now, 2 pairs have been removed making a total duration of 4 months.

The salt spray tests were performed into a QFOG® CCT1100 chamber, according to the ISO 14993-1 standard with 5 % NaCl solution. The back and edges of the specimens were covered with a sealing tape. As regards the scribed specimens, one specimen per reference paint was used for this test, with dimensions similar to the corresponding of the intact specimens. The specimens were scribed manually with a sharp cutter. On each specimen, two diagonal scribes, perpendicular to each other, were made. The length of each scribe was 9 cm and the width was 0.45 mm, while a 2 cm distance from the specimens' edges was kept. According to the ISO 14993-1 standard, the scribe marks penetrated the coating until the metallic substrate was exposed.

The UV tests were conducted into an Angelantoni® GTS 600 global test system climatic chamber, according to the ASTM G 154-06 standard. The conditions of the experiment were: a) 4 h with the UV lamp on at 60 ^{o}C (dry day) and b) 4 h with the UV lamp off at 50 ^{o}C and relative humidity 98 % (humid night).

The laboratory immersion test was conducted at room conditions. Each duplicate was immersed in separate containers filled with 400 mL of 3.5 % NaCl solution. The water was not entirely renewed, only refilled when necessary, in order to measure the monthly pH and conductivity variations of the solution, due to the leaching product release.

The quality of the coatings was evaluated by EIS and LPR methods. The electrochemical measurements were performed at room temperature in a three electrode flat cell using the coated specimen as a working electrode, a platinum mesh as counter electrode and a saturated calomel electrode (SCE) as a reference. The electrolytic solution consisted of 3.5 % NaCl in naturally aerated deionized water. The exposed area was 12.56 cm^2 for all specimens except the ones tested in laboratory immersion, which had an exposed area of 3.14 cm^2. A Solartron 1260 phase/gain analyzer was used combined with a PAR 263A potentiostat. The perturbation amplitude was 10 mV and was applied versus reference at the early stages of immersion and versus open circuit potential when applicable. The coatings' characterization included, also, 60° gloss, CIELab discoloration index (dE) and König pendulum hardness measurements, as well as, visual examination.

3. Results and discussion

3.1 Accelerated aging on intact specimens

Salt pray and UV caused an intense checking effect on Coat 2 surface. More specifically, after UV tests the topcoat presented intense checking (the shrinkage tie type according to ASTM D-660), that is, topcoat microcracking which extended from the topcoat to the immediate underneath layer (Figure 1). Specimen Coat2-(A) presented big cracks, the ASTM 3 rank, while Coat2-(B) specimen exhibited smaller and denser checking, the ASTM 2 rank, even though the specimens were placed close to each other inside the chamber. Checking was noticed, also, after 2 weeks of salt spray as individual cracks, which, gradually

interconnected and made a mosaic pattern, the ASTM 3 rank, after 3 months aging. Checking after salt spray seemed less intense than the one caused by UV exposure, verifying the destructive effect of UV radiation on epoxy polymers (Kotnarowska, 1999).

The discoloration index remained almost unaffected for Coat 1 after both accelerated aging tests. On the contrary, Coat 2 exhibited a constantly increasing discoloration, which became apparent from the first week of all the experiments. The polysiloxane groups included in Coat 1 give a very good resistance against discoloration, while the isocyanate groups of the polyurethane Coat 2 seem very prone to it (Figure 2a & d).

König hardness was originally higher for Coat 2 (around 80), possibly due to an inorganic fibre reinforcement that included, which provides mechanical strength. Coat 1 was softer in nature (around 30), since polysiloxane groups are of higher elasticity. Hardness of Coat 2 increased after accelerated aging, possibly due to both the checking and chalking effects. Hardness of Coat 1 increased after salt spray and decreased after UV test. However, since these fluctuations are very small, it can be concluded that hardness of Coat 1 remained almost unaffected, during both accelerated aging tests (Figure 2b & e).

Figure 1: Discoloration and checking effect after 6 weeks UV exposure; a) Coat 2 specimen as painted, b) Coat2-(A) with ASTM 3 shrinkage checking and c) Coat2-(B) with ASTM 2 shrinkage checking.
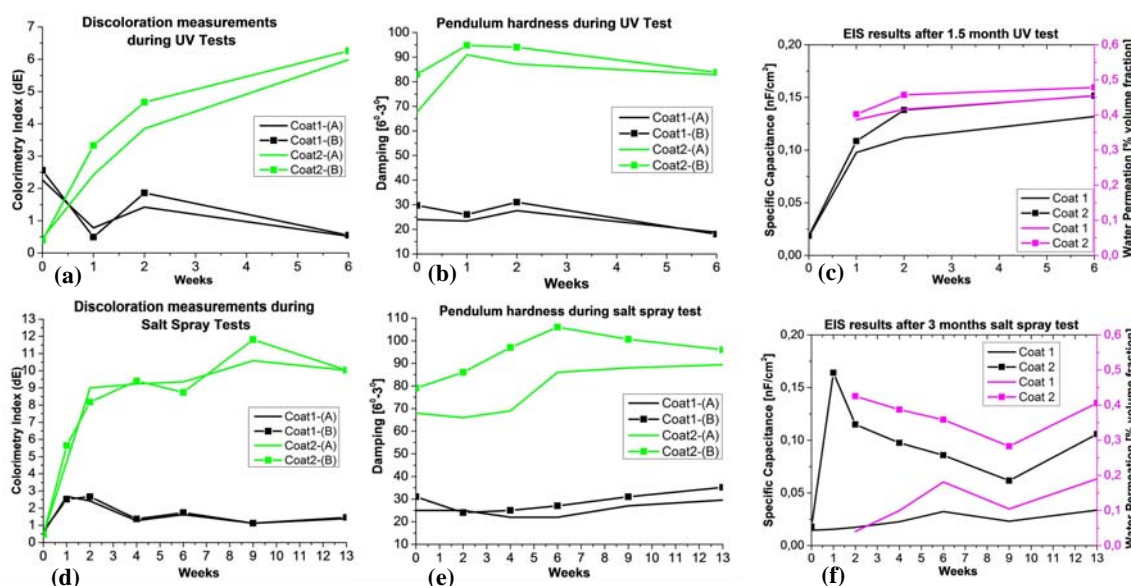

Figure 2: a) & d) Discoloration Index (dE) and d) & e) König pendulum hardness for the duplicates of both coats; c) & f) EIS results for one specimen per coat

Coat 2 was a matte, low gloss coat originally (values around 14), which retained almost no gloss after all tests (values 0-3). This is, also, attributed to the chalking effect of the epoxy groups. Coat 1 had higher initial gloss values (around 30), which, after UV test, slightly increased, verifying the good stability of the polysiloxane groups against photo aging.

EIS measurements verified the capacitive behavior of all intact specimens, since a line with slope -1 was presented between the frequencies 10^5 Hz – 10^3 Hz in the Bode plot of the impedance magnitude (|Z|). The Bode plot of the phase shift was a horizontal line at –pi/2 rad, which is the phase of an ideal capacitor.

The specific capacitance and volume fraction of water that has infiltrated the coating, which was calculated by the Brasher-Kingsbury equation, are presented in Figure 2(c) and (f) for one specimen per system. Coat 1 exhibited smaller capacitance and water permeation than Coat 2, during both tests. The average specific capacitance value for Coat 1, during salt spray test, was 0.023 nF/cm^2, while for Coat 2 was 0.092 nF/cm^2. During UV tests, the same value for Coat 1 was 0.089 nF/cm^2 and for Coat 2 was 0.104 nF/cm^2, showing an increase of 75% and 11.5 % respectively, with regard to the salt spray test. However, all the above specific capacitance values are characteristic of a good coating with satisfactory barrier properties. This was, also, verified by the amount of water that has penetrated the coatings, which was retained below 0.5 % for both systems and after both tests.

3.2 Salt spray test on scribed specimens

The scribed specimens were examined for 2 months in the salt spray chamber (Figure 3). The scribe lines of both specimens were covered with black regions of magnetite, while inside the scribes brown or orange coloured rusty layers of iron hydroxides were noticed. The same type of corrosion products has been observed, also, by Jorcin et al. (2006) after performing salt spray test on scribed epoxy coatings. However, as regards Coat 2, the corrosion products spread over the unscratched area, colouring the region brown. The width of the scribes has, also, become larger. For Coat 1 after 1 month of aging the width was around 1.1 mm, while after 2 months it was around 1.7 mm. For Coat 2, the width of 1 mm that was noticed after 1 month remained the same. A profound and dense blistering commenced on the scribe borders of Coat 2, leading to topcoat flaking and exposure of the underneath layer. However, at this stage of degradation, the blisters were restricted in this area only. Blister formation was not observed in the un-treated area of the painted specimen. The blisters were accompanied by intense checking spreading over the entire surface of the specimen. The checking effect adjacent to the scribes may be attributed to the blisters formation, while in the rest of the surface it was apparent during all the accelerated aging tests. Nevertheless, besides the blisters and the checking effect, no filiform corrosion was detected. As regards Coat 1, the behaviour was totally different. There were no apparent blisters adjacent to the scribes, but rather a slight paint swelling. No other defects were detected in the region of the scribes or in the rest of the specimen's surface. Thus, the silicon paint seems to behave better than the epoxy, even when defected. This conclusion is in agreement with Kumar et al. (2006).
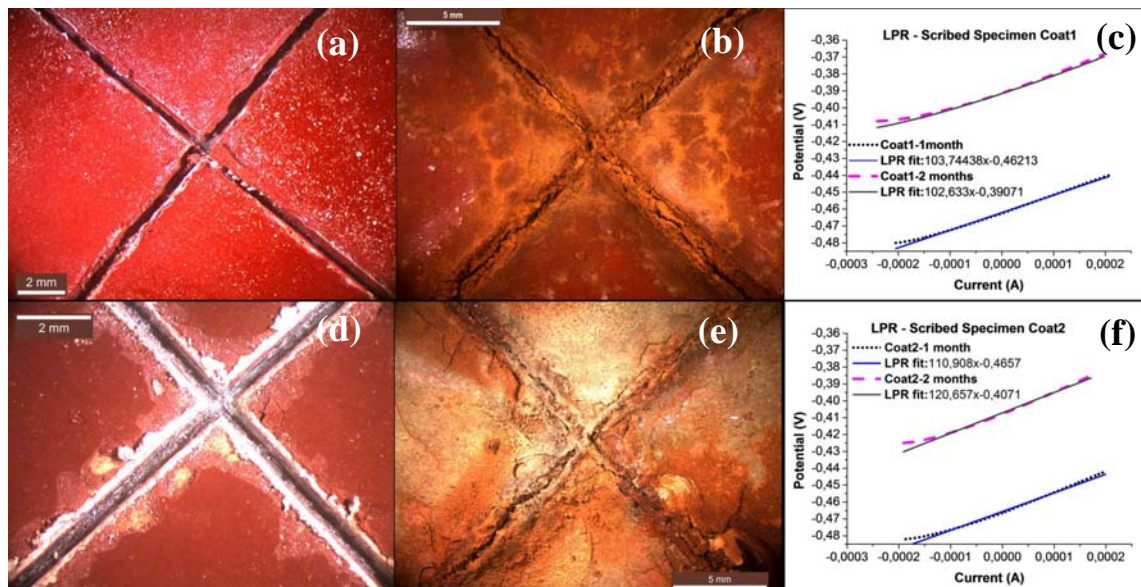

Figure 3: Up: Coat 1 a) as scribed, b) after 2 months salt spray, c) LPR after 1 and 2 months of aging. Down: similarly for Coat 2.

LPR measurements were conducted after 1 month and 2 months of salt spray. The polarization resistance (R_p) for Coat 1 was found 103.7 Ohm and 102.6 Ohm, respectively. The R_p values for Coat 2 were 110.9 Ohm and 120.6 Ohm, respectively. It can be assumed that in both cases R_p values correspond to those of a passivated metal substrate.

3.3 Laboratory Immersion test on intact specimens

Duplicates of both coatings were immersed in 3.5 % NaCl solution with pH 6.15 and conductivity 49.5 mS/cm in separate vessels. The solution where Coat 1 samples were immersed attained a pH value of 6.29 and conductivity 51.8 mS/cm, after 4 months of immersion. Thus, the electrical properties of the solution, as well as, its acidity remained constant. As regards Coat 2 solution, the leaching products that were released contain cuprous oxide which increased the pH to 7.59 and the conductivity to 54.1 mS/cm making the solution alkaline after 4 months of immersion.

The results of the EIS measurements were similar to those of the intact specimens after accelerated aging. No open circuit potential was measured, each coating behaving as a capacitor. An exception was the specimen Coat2-(B), where a plateau appeared in the Bode plot of the impedance magnitude (Figure 4a) after 3 months of immersion and for frequencies below 10 Hz. The pore resistance (R_{pore}) values after 3 and 4 months of immersion were $4.1 \cdot 10^7$ Ohm and $3.6 \cdot 10^7$ Ohm, respectively.
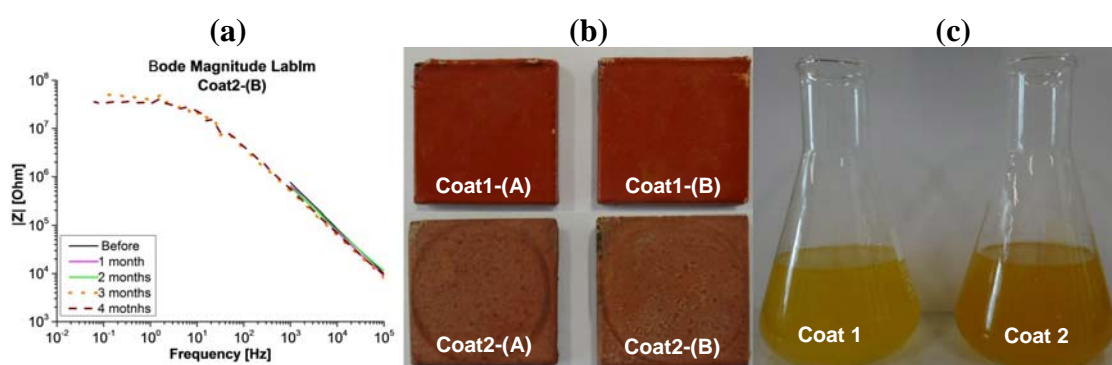

Figure 4: a) Bode plot of |Z|, b) condition of specimens and c) condition of solution after 4 months of laboratory immersion.

As can be seen from Figure 4(b), Coat 1 presented a slight discoloration (yellow colour) which can be attributed to the attachment of released products (Figure 4c). On the other hand, Coat 2 appeared heavily discoloured (dE≈13), since a great amount of leaching products was released, colouring the solution orange (Figure 4c). However, no checking effect was detected. Hardness of Coat 1 increased and Coat 2 decreased, both around 15 %. Finally, the gloss of Coat 2 was not retained, whereas for Coat 1 dropped from an initial value of ~30 to ~18.25 (decrease approximately ~40 %).

3.4 Elefsis immersion test on intact specimens

During immersion of Coat 1 in Elefsis for 4 months no slime was attached onto its surface. This observation is indicative of the self-cleaning ability of this coating in marine environment. The only foulers observed were 10 shells with a diameter of 2 mm. Moreover, Coat 1 gloss presented an increase of 9 %. Coat 2 specimen exhibited a homogenous thick layer of slime and 4 shells of the same diameter, indicating poor antifouling performance. EIS measurements showed a capacitive behaviour after 2 and 4 months of immersion for both systems. The specimens' condition is presented in Figure 5.
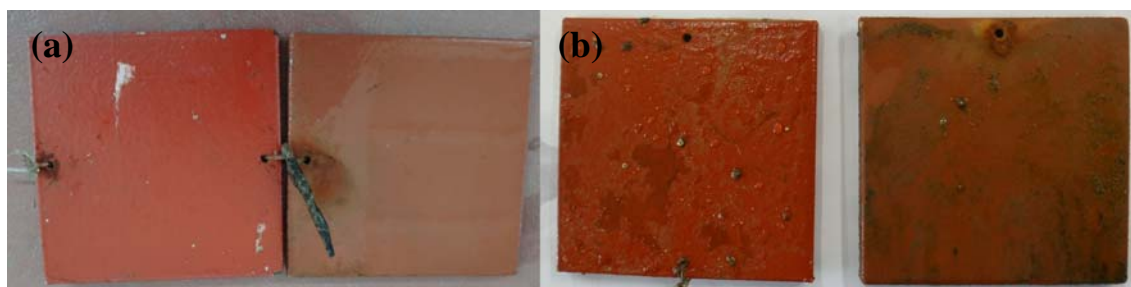

Figure 5: a) Pair 1 removed after 2 months and b) Pair 2 removed after 4 months of Elefsis immersion, in the as fouled condition. On the left side of each picture is Coat 1 and on the right side is Coat 2.

4. Conclusions

The epoxy coating exhibited a shrinkage mode checking effect after UV exposure and a mosaic type after salt spray. These effects can be attributed to the more intense thermal stresses induced during accelerated aging.

The discoloration index remained more or less constant for the silicone coating after all tests. This can be attributed to the polysiloxane content of the coating. On the contrary, the epoxy paint exhibited heavy discoloration, due to the oxidation of the isocyanate groups. The discoloration was more intense during laboratory immersion test, due to leaching, shifting the solution's pH to alkaline values.

The epoxy antifouling paint retained almost no gloss after all tests, since the surface was initially matte and prone to chalking. On the other hand, the silicone paint had higher initial gloss values, which increased slightly after UV tests and immersion in marine environment. The high gloss values verify the good stability of the polysiloxane groups against photo aging.

EIS measurements revealed that the silicone antifouling paint retained very good barrier properties after both accelerated and natural aging tests. As regards the epoxy coat, a pore resistance value was detected after 4 months of laboratory immersion test, indicating its less effective performance as a barrier.

As regards the scribed specimens, the epoxy paint suffered a more severe degradation than the silicone one, having a larger amount of corrosion products into and adjacent to the scribes along with blistering, flaking and checking along the scribe lines. The silicone paint presented only swelling.

Finally, immersion tests in marine environment revealed that the silicone antifouling coating provides a better antifouling protection, due to its self-cleaning ability.

From all the above it is concluded that the silicone foul-release system (Coat 1) exhibits superior barrier properties, visual characteristics and antifouling ability under accelerated and natural aging conditions than the epoxy self-polishing antifouling coating (Coat 2).

Acknowledgement

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