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## Corrosion resistance of epoxy primer, polyurethane, and silyl acrylate anti-fouling on carbon steel

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# Corrosion resistance of epoxy primer, polyurethane, and silyl acrylate anti-fouling on carbon steel

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**Abstract.** Anti-fouling paint is commonly applied as a protective coating on steel structures in the marine environment; one of the anti-fouling paint materials is silyl acrylate copolymer which can hydrolyse with seawater and form leaching layers to release biocide pigments. This study evaluates a three-layer paint comprised of epoxy primer, polyurethane, and silyl acrylate anti-fouling on carbon steel plates through polarization measurements and a salt spray test. Linear polarization measurements are carried out on an unscribed specimen with a potential range of -1.0 to 1.0 Volts. The salt spray test is conducted on scribed specimens, lasts 168 hours, and involves periodic visual observation. The polarization analysis shows pseudo-passive behavior in a system that represents, first, the less protective passive layer of primer and, second, the progressive erosion of a leaching layer of the anti-fouling paint which exposes a new layer beneath. The salt spray test shows that the three-layer paint has poor corrosion resistance in the atmospheric environment indicated by peeled layers and the occurrence of underfilm corrosion since the 48-hour test period.

## 1. Introduction

Seawater generally contains about 3.4% salt and is somewhat alkaline with a pH of 8. Seawater is a good electrolyte and can cause galvanic and crevice corrosion that is also affected by oxygen contents, speed, temperature, and biological organisms [1]. The largest marine organisms that lead to corrosion, such as barnacles, mollusks, and related species, are mostly attached to structures around the sea such as docks, bridge posts, and ship bodies. This fouling inhibits the speed of the ship, reduces the flow of seawater in pipes and tubing, and even damages the wood structure. Products produced by the growth of organisms or metabolic processes are often acidic and thus accelerate corrosion on metal substrates. These organisms also envelop the metal surface from dissolved oxygen and forms differential aeration cells, which contribute to the acceleration of corrosion. The oxygen-free or anaerobic environment under these macroorganism is a place for the growth of sulfate-reducing bacteria [2].

One of the ways to prevent the attachment of marine organisms bringing about corrosion is to apply an anti-fouling paint to parts that are submerged in water. The anti-fouling paint is formulated with pigments that release biocides to kill micro and macroorganisms on the surface of the structure. Based on the biocide release mechanism, the anti-fouling paint is divided into a paint with a water-insoluble matrix and that with a water-soluble matrix [3]. Tin, copper and zinc are the most widely added metal biocides in anti-fouling paint [4]. Until now, a self-polishing copolymer paint—a development of a soluble matrix paint and a substitute tin-based paint that is harmful to the environment—is still widely used since the formulation allows the release of biocide compounds at controlled rates [5].



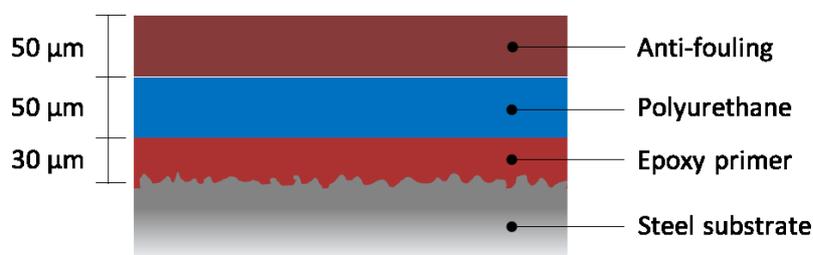
Most of the anti-fouling paints are organic coatings constructed of a primer and a final coat—both also have an anticorrosive function—, but the anti-fouling paint as a final coat is often porous [6]. The use of anti-fouling paint as a final coat in a multilayer paint is usually combined with other anticorrosive paints which have (1) a barrier function, such as epoxy, polyurethane, and acrylic, (2) a passivation function with phosphate and chromate pigments, or (3) a sacrificial function such as zinc-rich. These anticorrosive paints provide direct protection to metal substrates by forming thick and tight paint films or by galvanic protection which hinders water penetration and other aggressive species that trigger corrosion.

Prior explorations investigated a self-polishing anti-fouling paint with several matrixes such as silicon [7], epoxy [5], polyurethane and acrylic [8], and zinc-based acrylate [9]. Different approaches were also carried out to determine the rate of paint matrix degradation and biocide pigment release in water, the rust morphology formed in metals, and the development of more environmentally-friendly paint technology. However, there have not been many researches on anti-fouling paints in a multilayer-paint system.

Therefore, the investigation on the corrosion resistance of epoxy primer, polyurethane, and silyl acrylate anti-fouling on structural carbon steel is conducted. The research method includes polarization measurements of the unscribed specimen and a salt spray test on the scribed specimens. Through these two tests, the corrosion resistance of the multilayer paint, a combination of anticorrosive and anti-fouling paints, in the atmospheric environment will be revealed.

## 2. Research Procedure

A JIS SS400 carbon steel plate with dimensions of 15 cm x 10 cm x 0.2 cm was used as a metal substrate. Before being painted, the plates were sandblasted in accordance with the SSPC SP-10 standard to achieve a cleanliness level of 2½ Sa (an ISO 8501-1 standard). The multilayer paint was comprised of three types of commercial paint applied through manual spraying with dry film thickness (DFT) as shown on Figure 1. The drying process of each layer took approximately 4 hours followed by a final curing taking 7 days in an open space.



**Figure 1.** The three-layer paint.

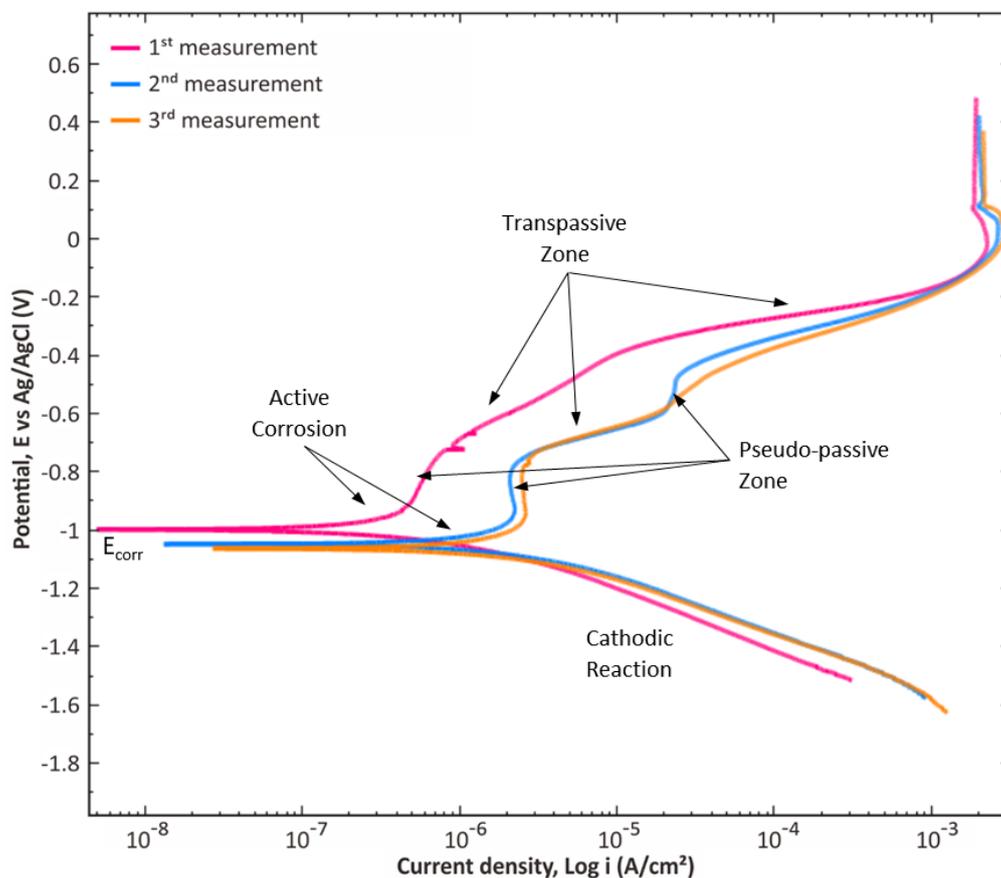
In the process of polarization measurements, the painted specimens were cut to 1 x 1 cm, soldered with a copper wire, and mounted with resin. These specimens functioned as the working electrode, the platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. All the electrodes were immersed in 3.5% NaCl solution and connected to a PGSTAT-302N Autolab potentiostat controlled by Nova 1.11 software. Electrochemical cells were put in a Faraday cage to minimize the capture of external noise that may interfere with the measurement process. The polarization measurements were conducted at a potential of -1.0 to 1.0 Volts and repeated for 3 times to ensure the accuracy.

Meanwhile, other specimens were scribed across until the scribe penetrated the entire layer and revealed a steel substrate. The specimens were then exposed to 5% NaCl solution in a 168-hour salt spray cabinet based on an ASTM B 177/ISO 9227 standard. Visual observations were done periodically at 48, 96 and 168 hours to assess rust, blisters, and other kinds of damage inside and outside the scribes.

### 3. Result and Discussion

#### 3.1. Polarization measurements

The polarization measurements, carried out 3 times on the same specimen, produce a potential curve  $E$  (V) and a current density  $i$  ( $A/cm^2$ ) as shown on Figure 2. This curve informs anodic and cathodic reactions, corrosion potential ( $E_{corr}$ ), and passive conditions that may occur in the system. On the other hand, the Tafel extrapolation of the curve shows the corrosion current density ( $i_{corr}$ ) to calculate the corrosion rate. The result of these polarization measurements shows that the layer is actively corroded after -0.9 and -1.05 V vs Ag/AgCl ( $E_{corr}$ ) potential while the current density is relatively constant or only increases slightly as the passivation potential rises. In the 1<sup>st</sup> measurement, passivation looks quite clear at a potential of about -0.92 V vs. Ag/AgCl. Whereas in the 2<sup>nd</sup> and 3<sup>rd</sup> measurements, the passivation curve is formed twice at the potential around -0.95 V and -0.60 V vs. Ag/AgCl.



**Figure 2.** The polarization curve of specimens in 3.5% NaCl.

**Table 1.** The results of Tafel extrapolation.

Measurement	$E_{corr}$ (V)	$i_{corr}$ ( $\mu A/cm^2$ )	$\beta_a$ (mV/dec)	$\beta_c$ (mV/dec)	$R_p$ (k $\Omega$ )	CR (mm/year)
1 <sup>st</sup>	-0.998	1.107	165.25	-624.17	88.1260	0.01287
2 <sup>nd</sup>	-1.040	1.167	124.30	299.99	32.7070	0.01356
3 <sup>rd</sup>	-1.057	1.021	193.57	112.29	30.2070	0.01187

This passivation is linked to zinc phosphate contents,  $Zn_3(PO_4)_2$ , as an anti-corrosion pigment in the epoxy primer paint. According to a study by Hao et al. [10], zinc phosphate pigment has an inhibitory mechanism in the form of a shielding effect combination of zinc phosphate and the formation of a passive phosphate layer consisting of  $FePO_4$ ,  $Fe_2O_3$ , and  $FeO$  on the metal surface that covers corrosion products and prevents further corrosion. However, the pseudo-passive behaviour of the system shows that the passive layer of phosphate formed at the steel paint-substrate interface is weak, unstable, and not tight.

Another factor that influences the occurrence of pseudo-passive condition is the characteristic of the anti-fouling paint materials that can start chemical hydrolysis with seawater, forming a thin leaching layer—which then eroded by the flow of seawater—and releasing the biocides. Silyl acrylate polymers are relatively difficult to be permeated so that the cycle of both formation and erosion of the leaching layer takes place at a relatively constant rate. In other words, passivation occurs when the leaching layer forms and erodes, leading to a decrease in the thickness of the paint. This also explains a bit more about the difference of the curve shape from the first run of polarization measurement with the next two, where during the initial immersion the paint is still intact or the process of forming and erosion of the leaching layer has not yet occurred. As the measurement took place and the specimen has been immersed for some time, the leaching layer is formed and eroded thus affects the passivation curves on subsequent measurements.

### 3.2. Salt spray test

The rating of specimen condition after the salt spray test is shown in Table 2. The average scribe width of the specimens before the test (0 hour) is around 0.5 mm while after the 168-hour test, the rate becomes 3.8 mm or rises by approximately 3.3 mm. This indicates that the paint film loses adhesion in the scribes. Even so, in areas that are not scribed there are almost no visible signs of paint damage such as rust, flaking, and blisters.

**Table 2.** The results of salt spray test.

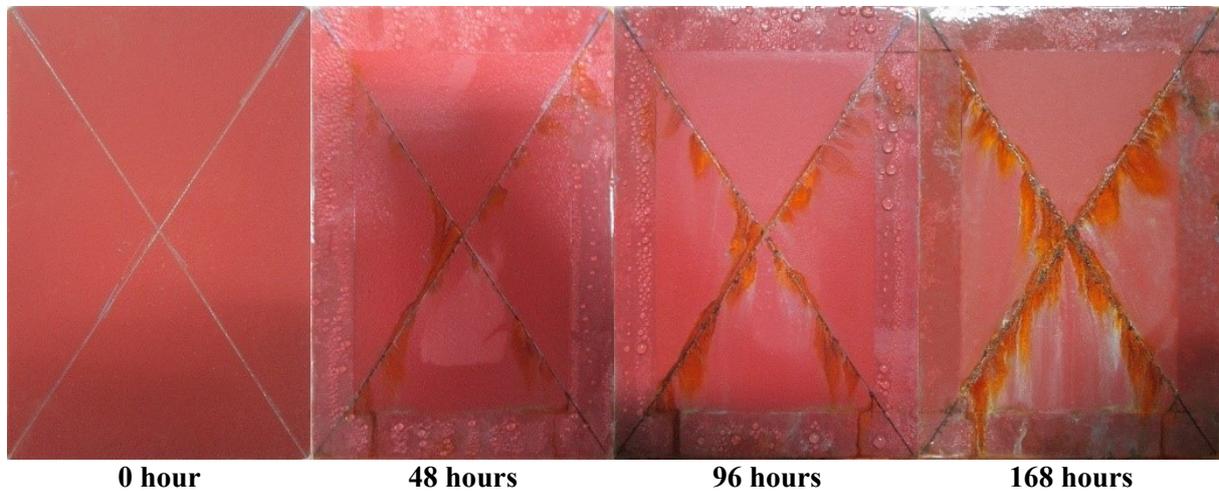
Test Periods (hours)	Specimen Code	Rating of Failure at Scribe		Rating of Unscribed Areas	
		Mean Creepage from Scribe (mm)	Rating Numbers <sup>(*)</sup>	Area Failed (%)	Blister Rating <sup>(**)</sup>
0	A	-	10/10	-	10/10
	B	-	10/10	-	10/10
	C	-	10/10	-	10/10
48	A	0.2	9/10	-	10/10
	B	0.3	9/10	-	10/10
	C	0.1	9/10	-	10/10
96	A	1.0	8/10	-	10/10
	B	0.8	8/10	-	10/10
	C	1.0	8/10	-	10/10
168	A	2.5	6/10	0.1	8F/10
	B	2.5	6/10	0.1	8F/10
	C	5.5	4/10	0.1	8F/10

(\*) Rating based on an ASTM D 1654 standard on a scale of 10 – 0.

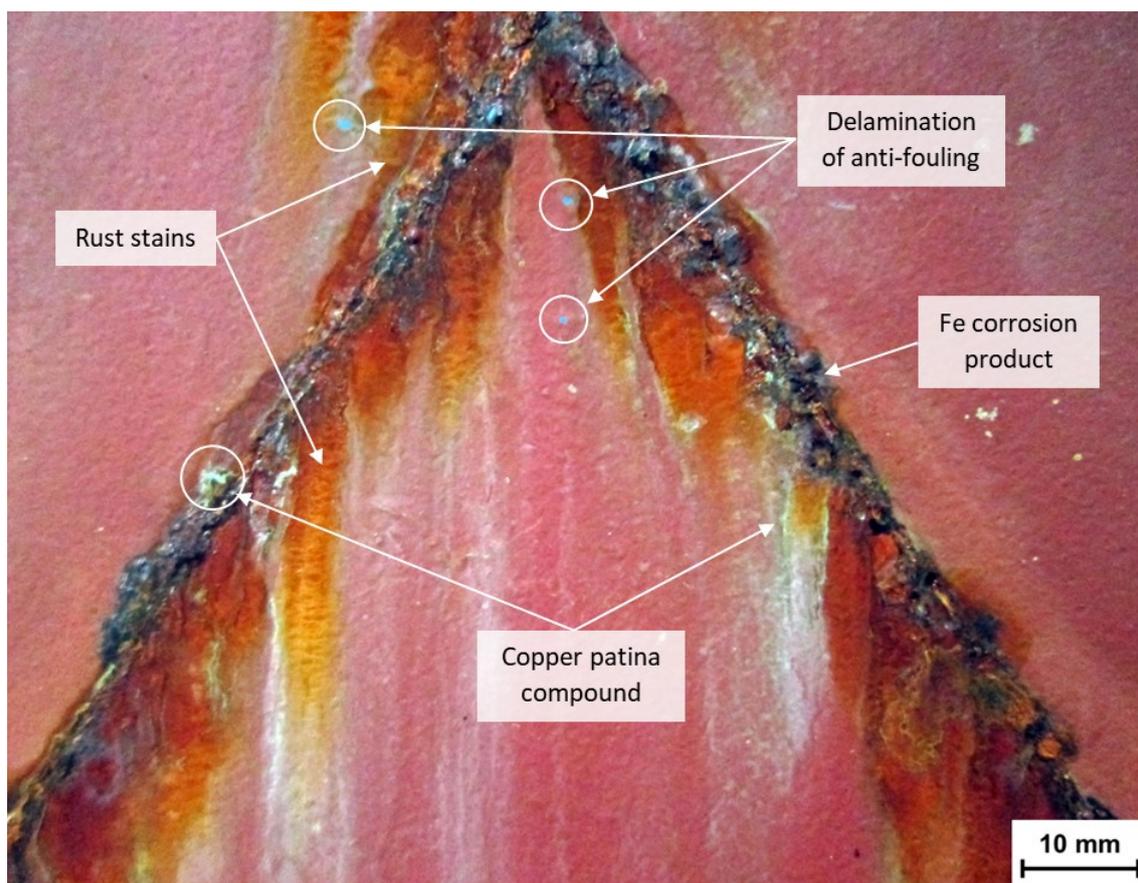
(\*\*) Rating based on an ASTM D 714 standard on a scale of 10 – 0.

Figure 3 shows the visual condition of the specimens before and after salt spray test. All the specimens suffer a severe damage to the scribes and the formation of rust has clearly been visible from the 48-hour test period. Most of the corrosion products are brown-orange-reddish and black which are the characteristics of iron oxide rust. The iron rust seems to decay until it comes out of the scribed areas, leaving rust-brown stain on the specimen surface. In addition, there are also white patches

around the scribes which are salt deposits from NaCl solution that dissolve in the anti-fouling paint and then dry.



**Figure 3.** The condition of specimens before and after salt spray test.



**Figure 4.** The detailed rust in the middle of scribe.

A number of greenish products appear in several locations around the scribes, which are suspected as copper hydroxy chloride compounds. If the paint is in its actual service condition, which is

seawater, the pigments released by the anti-fouling paint should be carried away by the flow of seawater. However, in this salt spray test, the drops of electrolyte solution actually remain attached to the surface of the paint and seep into the paint film instead of flowing down. The reason is that the self-polishing anti-fouling paint formulated to hydrolyze with water forms a leaching layer. Therefore, the copper (I) oxide ( $\text{Cu}_2\text{O}$ ) pigment released remains attached to the specimen surface and reacts with NaCl and oxygen solution to form the following copper hydroxy chloride compounds ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) [11]:



However,  $\text{Cu}_2\text{O}$  is said to be a semiconductor with relatively weak electrochemical activity [12]. Another study also reveals that the existence of  $\text{Cu}_2\text{O}$  in the anti-fouling paint does not have any role in the corrosion process of metal underneath, as corrosion only occurred at areas where crevices or paint damage had formed [13]. While in this study, no corrosion was seen in which anti-fouling paint was intact, proving that corrosion attacks occurred due to differential aeration cells in the paint crevice or scribe. Polyurethane and epoxy primer paint also act as insulation layers between anti-fouling paint layer and steel substrate, so that neither copper nor seawater can rapidly penetrate through coating pores. Moreover the  $\text{Cu}_2\text{O}$  anti-fouling paint contains virtually no metallic copper. Hence, the presence of  $\text{Cu}_2\text{O}$  as a paint pigment has no significant effect on the corrosion rate of carbon steel.

In short, the system of the three-layer paint has poor corrosion resistance especially when the paint has defects such as scribes and other types of mechanical damage. The blisters and the peeled parts around the scribes indicate that low adhesion reduces the paint protection. Electrolyte solutions that are absorbed horizontally into the paint film through the edge of the scribe also get the steel substrate to corrode. Corrosion products formed at the paint-steel interface push the layer until it blisters and is peeled. The lifting of the layer from the steel substrate allows corrosion products to be eroded by the flow of water and thus the steel surface is exposed to electrolyte attacks and forms new corrosion products.

In addition, anticorrosive zinc phosphate pigments contained in the epoxy primer also work less effectively due to the amount of rust formed in the scribes. As a result, the specimens experience a significant increase in the scribe width. This strengthens the analysis of pseudo-passive behavior on the polarization curve, that a protective passive layer that should be formed from phosphate and iron reaction with oxygen cannot protect the steel substrate, especially, in the defective or non-coated parts.

Several studies suggest that salinity has an effect on the rise in the diffusion of biocide pigments such as  $\text{Cu}_2\text{O}$  and the solubility of rosin in water, in addition to the thickness of the leaching layer which is the result of the pigment dissolution at the water-paint interface and of the polishing of the paint binder [14,15]. Therefore, the biocide release in seawater is higher than in brackish and fresh water, especially in the rosin-based anti-fouling paint or the self-polishing paint [16]. Based on this theory, high NaCl concentration in the test medium (5% NaCl) makes the anti-fouling paint degrade so fast that the thickness of the layer decreases. The thinning of the paint layer—the paint barrier function reduces—causes the water to enter the paint layer more quickly and attack the steel substrate.

#### 4. Conclusion

Polarization measurements and a salt spray test on epoxy primer, polyurethane, and silyl acrylate anti-fouling coated on carbon steel plates show that, first, the pseudo-passive condition on the polarization curve indicates a passive layer of the phosphate pigment reactions on the epoxy primer which is both less protective and affected by (a) the formation cycle and (b) the erosion of the leaching layer of the anti-fouling paint system. Second, in atmospheric condition, the paint corrosion resistance on the scribed specimens is low since they are not protected by a passive phosphate layer. The corrosion process occurs when the electrolyte solution enters the paint layer horizontally and weakens its adhesion. The loss of adhesion then has the layer easily lifted and triggers underfilm corrosion and blisters.

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