The corrosivity and performance evaluation of antifouling paint exposed in seawater Muara Baru port, Jakarta

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Abstract. Antifouling paints were applied on a wide range of the under seawater structures in order to protect them from the growth of fouling organisms. The performance investigation of two commercial anticorrosion and antifouling paints was conducted in Muara Baru port, Jakarta. The specimens were coated by anticorrosion and/or antifouling paint. Blank specimen (without exposed) were also prepared as a control. On the other hand, bare mild steel was prepared for measure the corrosion rate through weight loss method. The test panels containing specimens were exposed up to 3 months for immersion depths of 0, 1, 2, 3 meters from sea level. Sea water parameters such as temperature, pH, salinity, conductivity and dissolved oxygen (DO) were also measured. The evaluation of coating performance was carried out such as thickness, glossy, hardness and adhesion strength. The results showed that both surfaces of anticorrosion paint and bare mild steel specimen covered by fouling organisms, whereas no fouling took place on the surface of antifouling paint. The corrosion rate of bare mild steel in the depths of 0, 1, 2, 3 meters were 12.5; 11.6; 8.3; 10.4 mpy, respectively.

1. Introduction

Corrosion and biofouling have been driving force for investigating interactions between microorganisms and solid surfaces [1]. Corrosion is the deterioration of a metal as a result of chemical reactions between it and the surrounding environment. Whereas, Biological fouling, also called biofouling, is the undesirable formation of organisms on a surface immersed in water [2]. Corrosion and fouling causes severe problems on both dynamic and static structures. Fouling on many static structures may compromise safety by reducing stability and concealing structural defects [3]. The fouling process has been considered to consist of four general stages, from the attachment of microfouling organisms to macrofouling organisms [4]. The influence of various sea water characteristics such as salinity, temperature, pH, dissolved salts and oxygen concentration on the fouling of immersed solid surfaces will also play a significant role in the growing of the fouling organism [5].

Antifouling paints have been proved as the primary method for combating biofouling in the marine industry [6, 7]. Due to the restrictions on tributyltin (TBT) compounds usage in antifouling paints since 2003 and its complete ban on all vessels in 2008 (IMO 2001), copper (Cu) has been widely used as the main biocide ingredient in antifouling paint coatings. Copper exhibits antifouling activity against organisms such as barnacles, tube worms and the majority of alga fouling species [8]. Copper(I) oxide (Cu2O) is still being used as an antifouling pigment in marine paints [9]. However,
copper has harmful effects not only on the fouling community but also on non-target species [10]. Therefore it is important to find the new environment friendly antifoulants [11] due to no similar studies in Indonesia. The objectives of this preliminary study are to evaluate the performance of two commercial anticorrosion and antifouling paints in Muara Baru port, Jakarta. The effect of different depth of exposure and evaluation on the corrosion rate of bare mild steel using weight loss method will be comprehensively discussed. The result of the present investigation can be used for further work in order to compare the performance of coating with commercial paint and friendly antifouling paint.

2. Materials and Methods

2.1. Specimen and application of coatings
A commercial metal sheet of mild steel (C=0.13%, Si=0.11%, P=0.02%, Mn=0.29, Ni=0.01, Cr=0.30, Cu=0.01, Ti=0.01, Ti=0.01, Fe=99%) with the thickness of 0.3 cm were used in this study. Sheets of mild steel were cut into required number of specimens of sizes, 20 cm width x 25 cm height for the immersion studies. The specimens were sandblasted according to the standard of ISO 8501-1 and coated by two commercial paints (specimen code “A and B”) for anticorrosion and/or antifouling. Blank specimen (without exposed) were also prepared as a control. In contrast, bare mild steel with dimension of 7.5 cm wide x 15 cm high x 0.3 cm thick was prepared to measure the corrosion rate (specimen code “b”).

2.2. Location and exposure time
The performance investigation of two commercial anticorrosion and antifouling paints was conducted in Muara Baru port, Jakarta. The test panels containing specimens were exposed up to 3 months for immersion depths of 0, 1, 2, 3 meters (specimen code “A0, A1, A2, A3; B0, B1, B2, B3; b0, b1, b2, b3”) from sea level.

2.3. Evaluation of coatings for anticorrosion and antifouling properties
After immersion of specimens, the evaluation of coating properties was carried out as follow:

a. Specular gloss was determined at 60° using Horiba Gloss Checker IG-331 according to ASTM D 523
b. Thickness was measured using coating thickness gauge Elcometer 456 according to ASTM B 499
c. Hardness was tested using pencil hardness tester Elcometer 501 according to ASTM D 3363
d. Adhesion measurements were carried out using automatic adhesion tester Elcometer 510 according to ASTM D 4541 standard specification, the adhesive was a 2-pack epoxy system (Araldite 2011), the dolly diameter was 20 mm. After the dollys were glued, the adhesive cured for 24 h at 30°C and 50% RH.

Sea water parameters, i.e, temperature, pH, salinity, conductivity and dissolved oxygen (DO) were also measured.

2.4. Weight loss and corrosion rate determination
In the laboratory, fouling on the specimens was gently removed followed by cleaning the specimens to remove corrosion products on the surface of the coupons according to ASTM G1. Further, the weight of the specimens after cleaning was compared to the initial weight of the specimens. The difference of weight indicated the metal loss during the expose period.

The corrosion rate in mils per year (mpy) was calculated from the weight loss using the equation:

\[ CR \text{ (mpy)} = \frac{W \times T}{D \times A \times t} \]  \hspace{1cm} (1)

Where \( W \) = weight loss in grams; \( K \) = constant; \( D \) = metal density in g/cm\(^3\); \( A \) = coupon area (cm\(^2\)); \( t \) = exposure time (days)
3. Results and discussion

3.1. Evaluation of coatings for anticorrosion and antifouling properties

3.1.1 Gloss property

Gloss is a very important property of a paint to show the capacity of surfaces for the reflection of directed light. According to ASTM D 523, the geometry of 60° was used to measure the specular gloss on paint films which do not have a very high gloss or a very low one. The range of gloss levels was calculated from 2 to 7 units as shown in table 1. The results show that none of 10 gloss units or higher and under 5, which is a typical measurement of gloss for flat paints. The analysis level of gloss specimen A and B compared each other for the condition before and after exposure. It revealed that no significant changes on gloss level in the specimen A and B in all depth at 3 months after exposure.

| Specimen code | Gloss at 60° (Gloss units) | Hardness | Thickness (µm) | Adhesion (MPa) |
|---------------|-----------------------------|----------|----------------|----------------|
| A0            | 7.0                         | B        | 710.2          | 2.22           |
| A1            | 4.5                         | B        | 767.2          | 1.82           |
| A2            | 5.5                         | B        | 650.8          | 1.96           |
| A3            | 4.8                         | B        | 730.0          | 1.93           |
| B0            | 3.1                         | 2B       | 506.8          | 2.28           |
| B1            | 2.9                         | 2B       | 517.8          | 2.35           |
| B2            | 2.6                         | 2B       | 502.6          | 2.00           |
| B3            | 2.0                         | 2B       | 433.0          | 1.99           |

3.1.2 Hardness

The pencil scratch hardness test showed that all of specimen A are type B and all of specimen B are type 2B. Both of them are classified in soft type of hardness test and no significant differences.

3.1.3 Thickness

The physical performance of the paint thickness after exposures shows that paints A has the higher value of thickness than paint B. The antifouling topcoat paints will took place the process of surface polish (erosion or ablation) under water flow conditions to provide a biofouling free.

3.1.4 Adhesion test

The range of average adhesion strength test values for the antifouling coatings A and B are between 1.82 MPa and 2.35 MPa. There is no trend for particular coating system. In table 1, the same values of the pull-off strength and the type of failure indicate that the systems of coating tends to 100% cohesive antifouling, where both of coating A and B occurs fractures inside antifouling coating layer.

3.2. Weight loss and corrosion rate

Figure 1 shows the visual observation of coating A and B compared with blank specimen (without exposed) in Muara Baru seawater for 3 months. The results shows that the surface of anticorrosion coating was not undergo discolouration and fading on specimens A and B in various depth, where the surface of antifouling coating occurred a discolouration or the colour change on the surface paint from red to pink. In table 2, the phenomena of fading tend to increase due to the presence of moisture from 3 month of exposure and the growing of fouling organism.

After 3 month of exposure, the growth of marine organisms (benthos) created a dense fouling ecosystem on all surface of both anticorrosion paints for type A and B at various depth of seawater. Antifouling paints of type A and B showed that antifouling paints could minimize the attachment of
marine organisms for 3 month as observed that no fouling attached in the surface on paint A. In contrast, a little of fouling organism was found in antifouling side of paint B. Therefore, the anticorrosion and antifouling paint A has better performance than paint B. This indicated that the anticorrosion and antifouling paint A has the ability to work in preventing the existence of fouling than the anticorrosion paint B. It is also implied that the antifouling paints could work well in preventing the existence of fouling with the release of some biocidal compounds, which are bound or integrated in the organic polymer matrix paint.

Figure 1. Photographs of specimen (a) blank (without expose) of coating A, (b) blank (without expose) of coating B and (c) without coating.

Table 2. Specimen of coating A and coating B after 3 month of exposure.

| Specimen Code | Anticorrosion paint | Anticorrosion and Antifouling paint | Specimen Code | Anticorrosion paint | Anticorrosion and Antifouling paint |
|---------------|---------------------|-------------------------------------|---------------|---------------------|-------------------------------------|
| A0            |                     |                                     | B0            |                     |                                     |
| A1            |                     |                                     | B1            |                     |                                     |
| A2            |                     |                                     | B2            |                     |                                     |
| A3            |                     |                                     | B3            |                     |                                     |

Table 3 shows the weight loss of the bare steel after exposure. The weight loss in all specimens occurred because the activity of fouling organism on the surface of specimens. The weight of the bare steels decreases due to the presence of fouling organism on the surface of the steel plates. Figure 2
shows the corrosion rate of bare specimen at various depths of 0, 1, 2, 3 meters are 12.5, 11.6, 8.3, 10.4 mpy, respectively. Furthermore, the seawater depth of 0 meter has the highest value of corrosion rate due to the location of between splash zones.

**Table 2.** The weight loss of specimen in various depth of seawater.

| Specimen code | Weight loss (gram) |
|---------------|--------------------|
| b0            | 13.90              |
| b1            | 12.87              |
| b2            | 9.18               |
| b3            | 11.51              |

**Figure 2.** Corrosion rate of bare specimen at various depths of seawater.

Generally, all paints contain the same constituents of polymeric binder, pigments, solvent, and additives. The polymer or binder is the most important component in a successful hydrolyzing antifouling paint. From material safety data sheet (MSDS) of the paint, this two paints (A and B) work based on a silyl acrylate polymer, which is hydrolysed upon exposure to seawater. These copolymers blended with cuprus oxide as biocides confer a smooth surface on the copolymer and an ability of controlling/regulating biocide leaching rates [12]. However, they exhibited poor marine antifouling performance on static conditions. This is because the self-renewed ability of such polymers with nonreactive main chain which determined by the hydrolysis of the side groups and the shear force which generated by seawater flow [13]. Together with copper, other booster biocides were used to increase the efficiency of antifouling coatings [14]. 18 compounds are currently used as antifouling paint booster biocides with various degrees of regulation [15]. There is not specific information of MSDS paint A and B about the booster biocide used in both paint because there is no significant difference from the main component in paint A and B. The difference in result that paint A better than paint B in prevent the biofouling effect in this research might comes from the difference of booster biocide or the concentration of biocide. However, further experiment is required to clarify this hypothesis.

As explained that antifouling paint systems A and B containing copper as main fouling biocide were applied as topcoats on metal substrates. The mechanism for the release of copper compound is well known and described with the following reactions:

\[
\frac{1}{2} \text{CuO}_{(s)} + \text{H}^+ + 2\text{Cl}^- \rightarrow 2\text{CuCl}_2^- + \frac{1}{2} \text{H}_2\text{O} \quad (2)
\]

\[
\text{CuCl}_2^- + \text{Cl}^- \leftrightarrow 2\text{CuCl}_3^{2-} \quad (3)
\]
Where reaction (1) is reversible but kinetically constrained and reaction (2) is reversible and instantaneous. In the presence of dissolved oxygen, univalent copper is rapidly oxidised to the biocidal form, Cu$^{2+}$, in each layer. The dissolution of copper (I) oxide involved the formation of copper chloride complexes ($\text{CuCl}_2^-$, $\text{CuCl}_3^{2-}$) in two reversible reactions [16, 17]. Variation between its species depends on pH, salinity and the presence of dissolved organic matter. It shown that Cu$^{2+}$ ions were more toxic than Cu$^+$ and high concentrations of Cu$^{2+}$ ions in seawater had deleterious effects on marine ecosystem [18].

Chen et al. [19] explained that the fouling layer formation begins with an attack of bacterial cells, which later developed into a small colony and subsequently increased the amount thus forming a biofilm layer. This promotes the development of complex layers of bacteria and extracellular polysaccharides. Nutrient-rich layer (biofilm) were formed followed by colonization of invertebrates and macroalgae [20]. The growth of fouling depends on many parameters, i.e., pH value, temperature, salinity and dissolve oxygen (DO) [5]. In this research, the physical condition of the sea waters of Muara Baru, Jakarta was described and shown in table 3. Based on temperature, pH, salinity and DO, there is not much different between each depth of sea water, where the same of fouling species observed on the surface.

Table 3. Site-specific environmental conditions at Muara Baru Port, Jakarta.

| Depth (meters) | Temperature(°C) | pH | Salinity (ppt) | Dissolve Oxygen (mg/L) | Conductivity |
|---------------|-----------------|----|----------------|------------------------|--------------|
| 0             | 30.45           | 8.35 | 28.15         | 5.06                   | 48.45        |
| 1             | 30.35           | 8.38 | 28.15         | 4.937                  | 48.38        |
| 2             | 30.25           | 8.41 | 28.15         | 4.814                  | 48.31        |
| 3             | 30.15           | 8.44 | 28.15         | 4.691                  | 48.24        |

4. Conclusion
The results showed that both surfaces of anticorrosion paint A and B, and uncoated specimen were covered by dense fouling organisms. Further, there was no fouling took place on the surface of antifouling side of paint A, although the little of fouling organism was found in the antifouling side paint B. Therefore, from visual observation, we can conclude that the anticorrosion and antifouling paint A has better performance than paint B. Whereas, the corrosion rate result of uncoated specimen at the depths of 0, 1, 2, 3 meters were 12.5, 11.6, 8.3, 10.4 mpy, respectively.

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