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Case Study in Evaluation and Performance of Metallic and Polymer Coating as Corrosion Protection in Marine Environment

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Abstract: Marine corrosion damaged will cause loss of huge cost to the industries. As a preventive method, the coating of a substrate is required to sustain the damaged due to corrosion damaged. The marine corrosion will affect the industries such as oil and gas industries and maritime industries. Therefore, this study is relating to the evaluation of the metallic coating and paint coating performance as corrosion protection in the marine environment. The numerical study had been carried out by using different parameter and type of coating. Each coating has its own method and technique used for applying the coating to metal. For examples, the metallic coating can be applied via electroplating, hot-dip galvanizing and thermal spray and for polymer or paint coating can be applied via brushing or air compressed spray. However, the main focus of this researched is a concern about how it performs under corrosion test in the marine environment such as the immersion test and salt spray test. The corrosion behavior of the coating can be measured via electrochemical impedance spectroscopy (EIS) test. The x-ray diffraction (XRD) and scanning electron microscope (SEM) were used to analyze the phases and microstructure of the coating.

Keywords: Marine corrosion, Metallic coating, Polymer coating

1. Introduction

The marine environment is considered to be a harsh environment for metal materials which are commonly used for shipbuilding, piping or tubing for offshore structures. Also, the marine atmosphere has a high level of salinity and humidity which is very corrosive and the effect of corrosion are allegedly responsible for 30% of failures on ships and other marine equipment. The cost produce by corrosion damaged are expensive to be repaired or maintenance to vessels, structural and equipment operations due to financial on breakdown outages and repair [1]. The marine environment is considered to be a severe environment for metal materials which are commonly used for shipbuilding, piping or tubing for offshore structures. Also, the marine atmosphere has a high level of salinity and humidity which is very corrosive and the effect of corrosion are allegedly responsible for 30% of failures on ships and other marine equipment.

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Corrosion is an electrochemical process that requires simultaneously with the presence of moisture and oxygen. In the process, the presence of moisture and oxygen will react to the iron in the steel is oxidized to produce rust. The process takes place on a piece of uncoated steel. The factors such as variations in the composition of steel and the presence of impurities due to the higher of the instance of recycled steel. Metal corrosion defined as the deterioration of desired metals properties on interaction with certain elements that are presented in the spontaneously and avoidable process. The deposition of salt particles on metallic surface accelerates corrosion especially, the influence of chloride which effects to raise to soluble corrosion products rather than the only slightly soluble product formed in pure water. The Chloride ions (Cl^-) are high content in the marine atmosphere which is basis source of mineralization that consists of saltwater particles that carried along by air masses which pass oversea, ocean and salt lakes whereas, only salt particles and droplets of more than 10 µm are able to influence corrosion deposited on a metallic surface [2].

As for salt to accelerate corrosion the metallic surface needs to be wet. The relative humidity that marks the point which salt start to absorb water from the atmosphere whereas, the effect of chloride ions on metal (substrate) affect the corrosion mechanism which a high chloride concentration in the aqueous add layer on the metal and high rate of moisture retention in very deteriorated area rust give rise to the formation of ferrous chloride (FeCl2), which hydrolyses the water: The metallic coatings can be applied to a substrate such as via electroplating, electroless plating, hot dipping, clad, pack cementation, vapour deposition, thermal spray, laser processing and ion implantation. [3]. Metal coating can be divided into two groups which are more active than base metal and those that are nobler. As for the protection of steel, the first group which includes coatings such as aluminium, zinc and cadmium. These coatings will act as sacrificial anodes at sites of discontinuity and acted as cathodic protection to the metal. As for the lifetime of a coated structure which related to coating thickness will determine the amount of sacrificial material [4]

Generally, organic coatings counter-reaction of corrosion for protection of metal to prevent it from corroded. In other words, it is stated that the most efficient methods for the protection against corrosion of metal used for many years involve the use of polymer and paint coatings [5]. The purpose of this study is to compare the outcomes and result of primer-based coating on the marine environment as corrosion protection on the substrate which on the marine environment. Also, the variables on coating which is the relationship to the substrate such as the thickness of coating applied.

2. Materials and Methods

The materials used are carbon steel and which was cut into pieces following the guidelines from ASTM E-3. The coating needed to be cleaned out before undergoes coating process on it. In this case study, there were a few types of coating method used on the specimen, which is a metallic coating and paint coating. Each method has its own procedure that needed to be followed. Therefore, the investigation of the outcomes through the researched in corrosion behaviour method and microstructure analysis.

2.1 Electroplating of Nickel

One of the examples of metallic coating is electroplating where specimen will undergo plating of metal coating. In this case, the substrate and nickel-plating process. At the anode terminal is nickel base plate while at the cathode terminal is the substrate. The composition of Watt's bath used for this experiment includes Nickel Chloride ($NiCl_2H_2O$), Nickel Sulfate ($NiSO_4H_2O$) and Boric Acid, (H_3BO_3). The mixture of Watt's bath needed to stir before the experiment begin which acquire the mixture of nickel sulfate and boric acid completely dissolved. Figure 1 shows the examples set up of apparatus for electroplating.

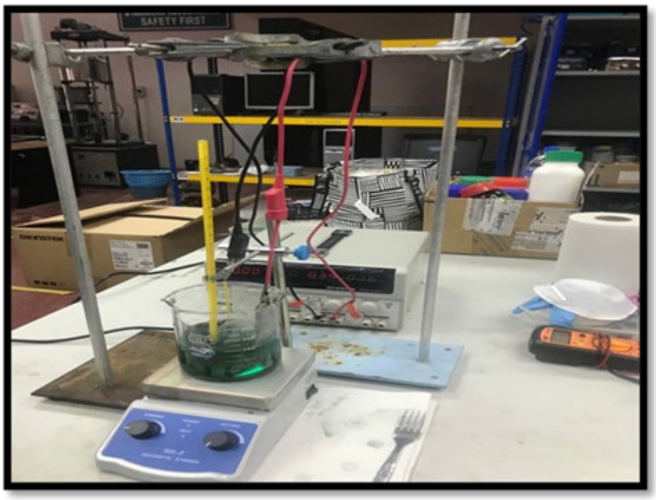


Figure 1: Apparatus set up of electroplating

Specifications and properties of materials, equipment, and other resources used in the current study should be described in this section.

2.2 Paint Coating

For paint coating, the substrate or specimen will be coated by using organic coating or paint. One of the examples is the commercial type of polyurethane paint (PU 5015) which brands came from Nippon Paint. This type of paint required to be mix with a hardener with a ratio of 4:1.

2.3 Immersion Test

In this study, using an immersion of corrosion test where the specimen was immersed into a solution of 5 wt% of sodium chloride or seawater. The immersion standard that is applied to this research is ASTM G-1 where it provides an alternative method to determine the corrosion rate in an aqueous condition [6]. Also, the specimen with a different type of coating is applied to the immersion testing especially to paint coating. The requirement for this immersion testing to be done is from 24 hours until to several months. To ensure the result gained in weight loss, there was a standard procedure that needs to be followed. The initial weight of the specimen was taken and recorded. As for the final weight of the specimen, the specimen needed to be cleaning before weight recorded.

$$Corrosion\ rate = (K\ x\ W)(A\ x\ T\ x\ D) \qquad \text{Eq. 1}$$

Where,

K= a constant,

T= time of exposure in hours,

A = area in cm^2,

W= mass loss in grams,

D = density in g/cm^3

2.4 Salt spray test

For salt spray test or salt fog, the standard will be followed is B117 where the standard procedure and preparation of specimen before and after conducted natural salt spray test [7]. The specimen must be placed between 15° and 30° from the vertical and preferably parallel to the principal direction of flow of fog through chambers. Meanwhile, the pH of the salt solution must be in between 6.5 to 7.2. After that, the salt spray test is conducted in a closed tested chamber where a saltwater solution is applied to spray nozzle and dense saltwater fog is used to imitate a corrosive experiment.

2.5 Electrochemical Impedance (EIS) Test

The aim of the current work was to evaluate whether electrochemical impedance spectroscopy (EIS) testing of a series of coated but non-exposed metal (substrate) capable of predicting the corrosion results of other parts of the same coated metal subject to continuous and cyclic corrosion testing. Metal, pretreatment, priming, and topcoat featured variables.

2.6 Microstructure analysis by scanning electron microscopy (SEM)

Scanning electron microscope (SEM) uses electron to produce images by recording different types of signal that caused from the interactivity of electron beam as it is scanned in a raster pattern across the sample surface [8]. Through the signals, all the details about the specimen comprising the chemical composition and crystalline structure, external morphology and the orientation of material making up the specimen.

2.7X-ray Diffraction (XRD) analysis of phase

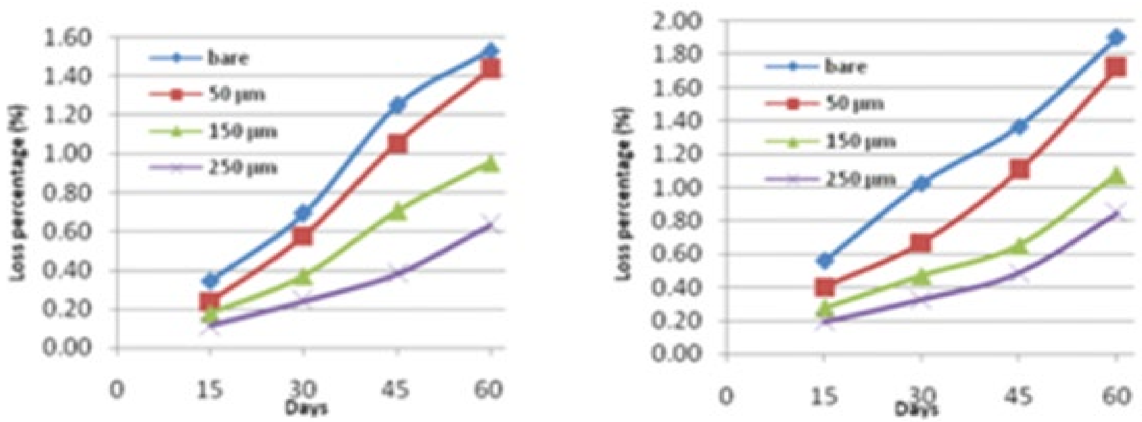
X-ray powder diffraction is a rapid analytical technique mainly used to classify a crystalline substance in phases and to provide details on the unit cell measurements. The average composition of bulk is defined whereas the material evaluated finely ground and homogenized. X-rays are relatively a short wavelength, high-energy electromagnetic radiation which is required in diffraction experiments which are required x-ray wavelength of the order of the interatomic spacing to produce interface. The typical wavelength rages between 0.07 to 0.2 nm and the common radiation used is λ=0.15406 nm. Also, this technique is used to identify the composition of the specimen.

3. Results and Discussion

The result based on previous researched which are evaluations is being made on certain coating and substrate used. The evaluations and results of coating will be compared based on surrounding or test that being conducted.

3.1 Analysis of coating thickness

In this context, the comparison between the thickness of coating towards corrosion rate. The corrosion rate is indicating the speed at which substrate in a specific environment. Also, it can define as the amount of corrosion loss per time in thickness. The lower the value of the corrosion rate, the higher the coating performance. Figure 2 shows the relationship of the thickness of the coating and weight loss in seawater immersion test and salt spray test for zinc-rich primer.



(a) (b)

Figure 2: The weight loss of specimen against time a) immersion salt test, b) salt spray test [9]

Figure 2 states that increasing of thickness of the coating will affect the weight loss of specimen which is the corrosion rate become decrease. Also, the time or duration was set up from 15 days, 30 days, 45 days and 60 days. The highest thickness of the coating will be $250\mu m$ which have the lowest weight loss percentage compare to others [9].

3.2 Analysis of inhibitor corrosion influenced corrosion rate

For this analysis, the henna act as corrosion inhibitor towards alkyd paint which acts as a coating agent towards aluminium alloy. The extraction concentrations were different which at 0%, 5% and 10% of henna extract. Figure 3 shows the relationship between weight loss and time with the different henna extract. Figure 4 shows the corrosion rate and time with the different henna extract.

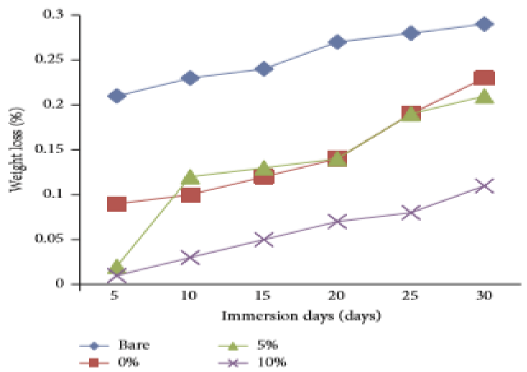


Figure 3: Result of weight loss and time with different henna extract [10]

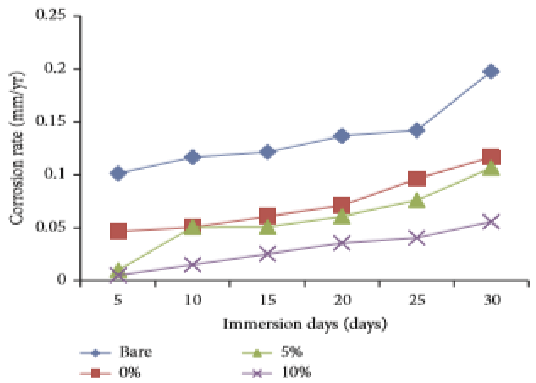


Figure 4: Result of corrosion rate and time with different henna extract [10]

Figure 3 show that 10% of extraction of henna had the lowest weight loss. This is because the henna extract contained in the coating used is in the highest percentage. It affects the coating by ensuring the adhesion between the coating and substrate, but also providing a thin barrier with efficient effect against oxygen diffusion on the metal interface. The highest percentage of henna extract had caused the decrease of weight loss due to the inhibitive effect of lawsone by the formation of insoluble complex compounds combined with metal cations. Figure 4 shows that the lowest corrosion rate is the paint with 10% of the henna extract. The weight loss will affect the corrosion rate calculated which based on the calculated formula. As the concentration of the matrix increase, the corrosion rate is decreased. Upon incorporation of henna, the inhibitive action of lawsonia extract could be due to the adsorption of its molecules on the substrate surface making a barrier in order to protect the substrate surface [10].

3.3 Electrochemical Impedance Spectroscopy (EIS)

EIS reaction of all coatings showed just one depressive loop across the entire frequency spectrum. It indicated the potential of the electrochemical system under review electrical double layer (EDL) and responsible for improved deposit corrosion resistance. Figure 5 shows the Nyquist plot which shows the relationship of corrosion resistance

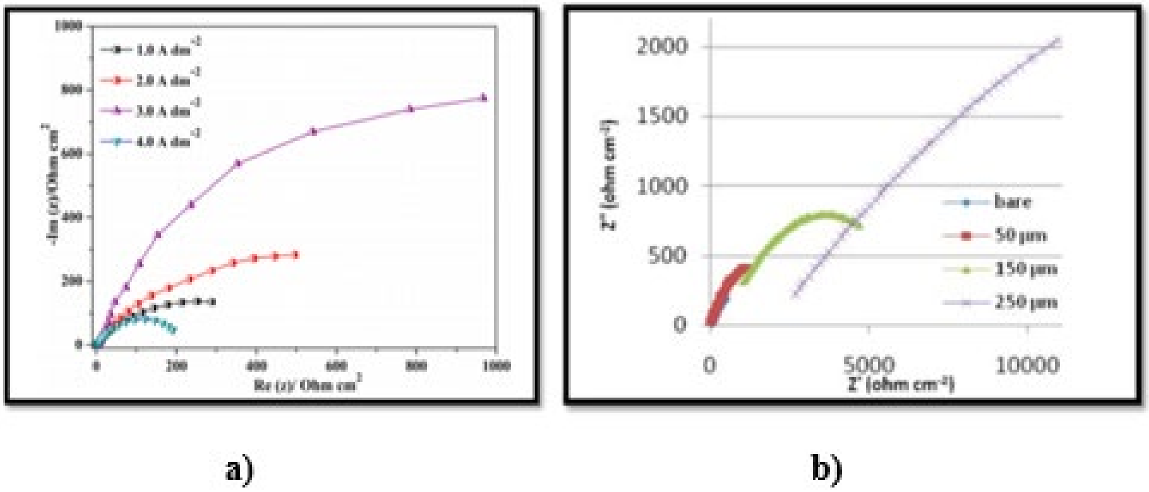


Figure 5: The Nyquist plot a) Nyquist plot of Cu-Ni alloy coating with different current density, b) Nyquist plot of Zinc rich-primer with different thickness [11]

The plot Nyquist shows that the data illustrated that increasing in coating thickness which influence the result to higher semicircles formed. The larger loop capacitive loop via a larger radius, the radius corresponding indicates the greater resistance to corrosion [11].

3.4 Microstructure analysis (SEM)

For morphology analysis, the surface morphology was observed and analyze for mild steel before and after the test. The surface morphology for coated steel is almost the same for all thickness due to the same type and content of paint used which act as a coating agent to mild steel. Figure 6 shows the morphological of coated mild steel before and after the test.

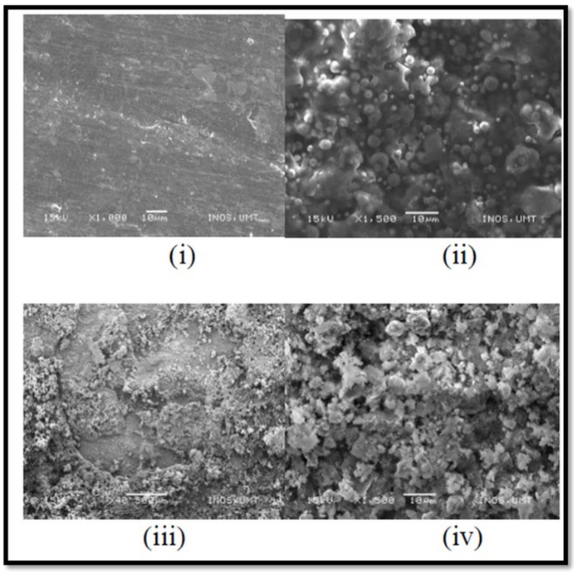


Figure 6: (i) Uncoated mild steel (ii) Coated steel before the immersion test (iii) Uncoated steel after 60 days immersion (iv) Coated steel after the immersion test

From Figure 6(i), it is indicated that the clear surface of uncoated mild steel before tested without any morphology. After that, Figure 6(ii) shows the surface morphology of coated mild steel before the test. The bubble formed is from the uneven spraying of paint during the coating process. Figure 6(iii), it shows the morphology of uncoated mild steel after immersion period of 60 days. There are many cracks produced since the metal was not protected by any coating agent. Moreover, one of the mild steel properties is that it can easily crack when exposed to harsh environments such as marine environments. The last figure which is Figure 6(iv), it is shown that morphology for coated mild steel after the test. The morphology of coated mild steel after the immersion test and salt spray test are similar. Although, Figure 6(iv) are clearly seen of round shapes particles are produced which is particles shows is the salt content at the surface of mild steel.

4. Conclusion

Based on the result, it is showed that metallic coating is more effective to act as corrosion protection compared to organic coating in harsh environments such as marine environments. From the result, for paint zinc rich-primer paint coating show that the parameter of increasing of thickness of coating optimizes the maximum performance of coating towards protection towards corrosion damaged in marine environments. As for metallic coating, the parameter such as the thickness of the coating fluctuates which is not fully rely on the thickness of the coating. The parameter used in the electrodeposition of copper-nickel alloy as coating agent shown that the increase of current density will increase the thickness of the coating. However, based on data and microstructure analyses, it stated the most effective coating are used of 3.0 A dm^{-2} which are the second highest of current density used in the experiment. Also, according to morphological analyses, the used of 4.0 A dm^{-2} which have the highest thickness in the experiment shown that the crystallinity of the deposit is decreased and the particle cluster is found to be soft edge because of thick, brittle and porous deposit.

Acknowledgement

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