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Development of anti-corrosive paint incorporated with henna extract as a natural inhibitor

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ABSTRACT

Metallic materials are the most applicable materials in various industries. They are useful due to their excellent mechanical properties. However, they are exposed to corrosion because the environment contains oxygen, humidity and some other factors. This paper describes about a paint incorporated with organic inhibitor, i.e., henna extract. This paint was produced to enhance its anticorrosive property. Henna extract was chosen as the corrosion inhibitor as it is organic, environmentally acceptable, readily available and a renewable source of material for a wide range of corrosion problems. The extractions were characterised by using Fourier Transform Infrared. Meanwhile, the inhibitive action of henna extract was investigated through an electrochemical technique. The inhibitive effects of henna extract were investigated with percentages of 0%, 4%, 8% and 10% incorporated into a rosin (epoxy)-based matrix. The specimens were characterised by electrochemical impedance spectroscopy measurement. The morphology study was investigated through surface analysis by using scanning electron microscopy. The inhibition efficiency increased as the concentration of henna extract was increased. The results showed that Paint 3 has the lowest corrosion rate of 0.001767 mm/yr as compared to Paint 1 with 0.005148 mm/yr. The inhibitive action of the henna extract is discussed. Paint 3 was proposed as the most effective paint that contains a natural inhibitor for aluminium alloy.

Keywords: Coating; EIS; organic inhibitor.

INTRODUCTION

The application of metals and alloys in most industries is very important, especially in construction. Industries that are involved are the automotive, building construction and marine sectors. However, the marine industry is the most affected industry due to the exposure of metals towards seawater and humidity. Marine environment is very synonymous with the aggressive environment and causes the deterioration of metals or alloys. Marine structures, such as jetties, oil and gas platforms and parts of a ship body, are the most affected parts of the corrosion problem [1]. Corrosion is the biggest contributing factor of marine structural failures through loss of structural strength at a local and global level [2].Historically, traditional paints use tributyltin (TBT) as an ingredient in marine paint due to its excellent performance. However, it was strictly restricted since 1982 to protect oyster growth [3]. Nowadays, great attention is focused on the use of natural corrosion inhibitors to reduce metals and alloys deterioration. This method is very practical for corrosion protection and it also decreases hydrogen evolution [4]. Inhibitors are substances or mixtures that are applied in low concentration and used in an aggressive environment to inhibit, prevent or minimise pitting or localised corrosion [5]. Corrosion inhibitors can be organic or inorganic and are classified by the mechanism of action as anodic, cathodic or an anodic-cathodic mix and by adsorption action or act as oxidants or anti-oxidants (Figure 1) [6].

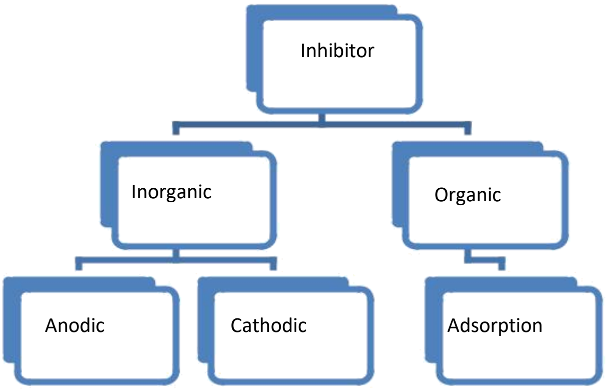

Figure 1. Inhibitors classification.

The addition of inhibitors helps metals or alloys to maintain their resistance against corrosion. This phenomenon occurs due to various inhibition mechanisms produced [7]. The application of a corrosion inhibitor is not only limited by incorporating into the paint but it may also be added during the production process, such as drilling for offshore work [8]. Recent research were focused on the plant extracts as natural sources of corrosion inhibitor due to their potential in corrosion inhibition. Other than that, natural sources are readily available, ecologically acceptable, cheap, renewable and also environmental friendly [9, 10]. In this study henna plant extract was chosen in an attempt to investigate its potential as a corrosion inhibitor. In previous studies, researchers investigated about the corrosion inhibition of henna extract with different metals and solutions. Some researchers improved the corrosion protection properties by incorporating active corrosion inhibitors into coatings. Henna extract was incorporated into rosin-based paint. Rosin is a gum derived from the exudation of pine trees, which acts as a binder in a coating matrix [11]. In addition, the incorporation of inhibitors into paint is for self-healing effect in the coatings [12]. The inhibitive actions of henna extract were investigated in present studies due to their cheap, eco-friendly and natural occurring substance [13]. The aim of this study is to evaluate the inhibition corrosion potential of henna extract, incorporated into paint, to produce an anticorrosive paint. Inhibited aluminium surfaces were examined with scanning electron microscopy (SEM) while the protective film was subjected to Fourier Transform Infrared Spectroscopy (FTIR) analysis. The weight loss study and electrochemical impedance spectroscopy (EIS) were performed to investigate the inhibitive action of henna extract.

MATERIALS AND METHODS

Preparation of Specimens

Aluminium alloy (AA5083) specimens were used for this study due to their extensive usage in marine industry, particularly as a plate for ship building. The specimen were cut into square shapes with dimension of 25 mm x 25 mm x 3 mm. The AA5083 has percentage composition of 0.40% Si, 0.40% Fe, 0.10% Cu, 0.40-1.0% Mn, 4.0-4.9% Mg, 0.05-0.25% Cr, 0.25% Zn and 0.15% Ti. The specimens were polished with 400, 800 and 1200 grit of abrasive paper. The polished specimens were cleaned by using acetone (according to SSPC-SP1 Standard) to remove all visible oil, grease, soil, drawing and cutting compounds, and other soluble contaminants. To provide good adhesion between the primer and metallic substrate, the cleaning process is very important. The specimens were then coated with epoxy-based paint. There are four types of paints used in this study, in which Paint 1 (without henna extract) acts as the control paint. Besides that, there are Paint 2, Paint 3, and Paint 4. The paints were diluted with 4%, 8%, and 10% of henna extract, respectively. The experiment was conducted for 60 days.

Extraction Preparation

The commercial henna powders were purchased at a local market and it was mixed with ethanol solution. Then it was left for 7-day daily agitation. The ethanol extract was filtered by Whatman filter paper, The remaining filtrates were collected and heated in a water bath at 48°C to evaporate its liquids content. Ethanol was removed from the henna extractions by using rotary evaporations (ROTAVAP). The remaining residues were stored at room temperature [14] until it was ready for use.

Paint Preparation

WW rosin type resin (colophony) was used as a binder and oleic acid as the plasticiser. The paint was prepared by using a magnetic stirrer to blend all the ingredients together and also to achieve an efficient dispersion. WW rosin and oleic acid were dissolute in a xylene/white spirit mixture (1:1) by using a high speed disperser. The ingredients were then mixed with the pigments and additives (zinc oxide and calcium carbonate), and dispersed for 24 hours [15]. For the anticorrosion paints (Paint 2, Paint 3 and Paint 4), the henna extract was incorporated into the matrix paint and dispersed for 5 hours. After 5 hours, the paint was ready for coating. The coated samples were scratched with 'X' mark to assess the paint coatings resistance towards separation from substrates [16] since the immersion period was only 60 days and this method was referred to the ASTM D7187-15.

Weight Loss Measurement

The coated specimens with different % of henna extract were weighed and suspended in seawater solution. The experiments were carried out at ambient temperature and they were immersed for 60 days [14]. Every 12 days, the specimens were withdrawn and washed by using nitric acid for 2-3 minutes and cleaned with distilled water, dried and weighed again to obtain the final weight. The experiment was conducted in a fume cupboard at room temperature.

Fourier Transform Infrared

Fourier Transform Infrared (FTIR) was carried out by using Thermo Nicolet 380 FTIR spectrometer at the Organic Chemistry Laboratory, in Universiti Malaysia Terengganu. A drop of henna extract was placed on the sample holder with the sample cap of diffused reflectance accessory. The extract was exposed under a range of infrared rays beams and the sensor below the platform would sense the frequency, either reflected or absorbed. The liquid transmittance and reflectance of the infrared rays at different frequencies were translated into an IR absorption plot consisting of reverse peaks.

Electrochemical Measurement

For electrochemical measurement, the test was conducted to measure the impedance of a system over a range of frequencies according to the ASTM STP 1188. The Autolab software was used by conducting Autolab PGSTAT 302N. This device was connected to a computer to obtain useful data. Frequency Response Analyser (FRA) was used for analysing data. A scanning rate $0.0101 Vs^{-1}$ was set and the electrode potential was automatically changed from -0.5 mV to +0.5 mV and it was then represented in Nyquist plot.

Scanning Electron Microscopy

The effect of inhibitor on corrosion process of AA5083 was investigated by using scanning electron microscope (SEM) technique according to the ASTM F1877-16, a standard practice for particles characterisation. The images were recorded by using JSM-6390LA SEM, after the exposure test. The specimens need to be coated with gold powder to aid in the specimen's surface conductivity.

RESULTS AND DISCUSSION

Fourier Transform Infrared

The results in Figure 1 were confirmed by Fourier Transform Infrared (FTIR) spectra of henna extract. The main constituent of henna extract is lawsone (Figure 2), which contains benzene unit, p- benzoquinone unit and phenolic group [13]. Other than that, the three major functional groups that can be derived from the structure were phenols O-H, ketone C=O and alkenes C=C [17]. These three groups were also known as flavanoids [18]. The phenolic group (O-H) stretch appeared at 3353.5 cm^{-1}. The peaks at 2855.3 cm^{-1} and 819.6 cm^{-1} can be considered as aliphatic and aromatic C-H. The aromatic C=C stretching frequency appeared at 1656.1 cm^{-1}. The ketone group (C=O) stretching frequency appeared at 1711.9 cm^{-1} and 1696.7 cm^{-1}. The presence of phenol group of lawsone contributed to the electron donation to the metal to achieve its noble state of orbit. The metal becomes more stable as it received the electron [12]. The double carbon bond indicated good corrosion resistance in the henna extracts [19]. Previous work has reported that the main components of henna extract were hydroxyl aromatic compounds such as tannin and lawsone, and they were attributed to the formation of passivating layer tannates on the metal surface and due to these reasons they were used in the manufacturing of anti-rusting paints and coating [20].

Weight Loss Measurement

The weight loss measurements for Paint 1, Paint 2, Paint 3 and Paint 4 for 60 days immersion are given in Figure 3. The presence of inhibitor shows a decreasing value of weight loss against time of immersion. It is indicated that the increase of henna extract incorporated into paint led to a decrease in specimen weight loss. This finding can be related from the FTIR result obtained, which is the amount of lawsone structure present in the paint composition [13]. Table 1 shows the readings of weight losses and the corrosion rate of specimens after 60 days immersion in seawater. Paint 3 shows the smallest value of the weight loss of about 0.69% as compared to the Paint 1(without inhibitor) which is 2.10%. On the other hand, corrosion rate for Paint 1 is 0.005148 mm/yr and the reading shows a subsequent decrease to 0.001767 mm/yr with increasing henna extraction.

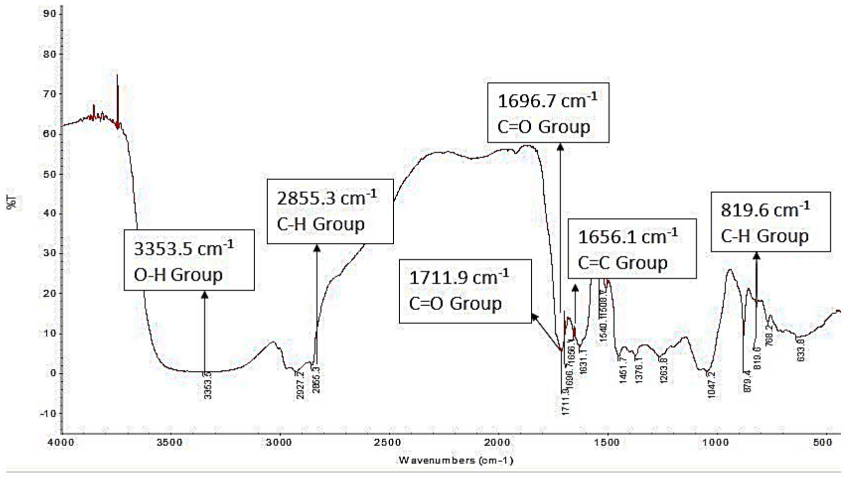

Figure 2. IR spectra for henna extraction by using FTIR analysis.

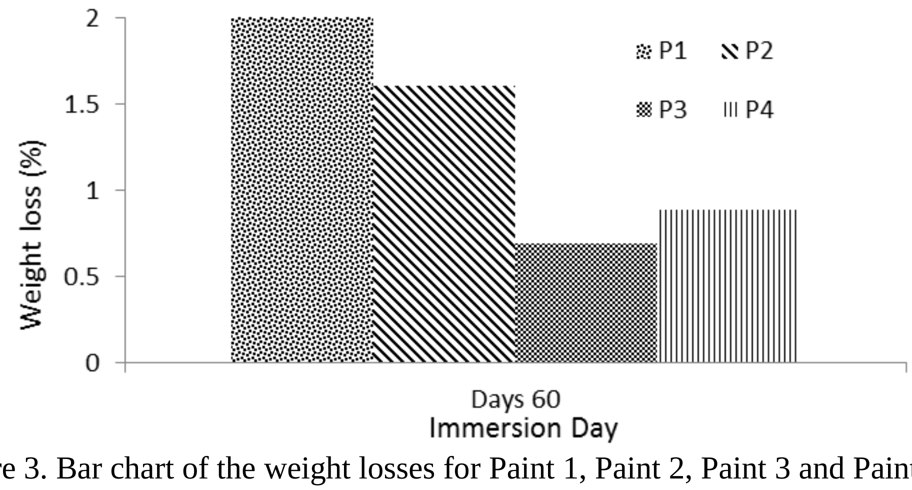

Figure 3. Bar chart of the weight losses for Paint 1, Paint 2, Paint 3 and Paint 4 for 60 days immersion.

Table 1. Parameter of weight loss (%) and corrosion rate of specimens after 60 days of immersion.

Type of paint	Weight loss (%)	Corrosion rate (mm/yr)
Paint 1 (P1)	2.10	0.005148
Paint 2 (P2)	1.60	0.003846
Paint 3 (P3)	0.69	0.001767
Paint 4 (P4)	0.88	0.002129

Inhibition Efficiency

The values of the inhibition efficiency, IE (%) from the weight loss test were calculated by using Equation (1):

$$IE\ (\%) = 100\ (1 - W/W_0) \tag{1}$$

where W_0 and W are the weight loss in the absence and the presence of inhibitor.

The analyses of the IE (%) values are given in Table 2. The IE increases with the increasing of the henna extract incorporated into paint. The value of the IE (%) increases due to the adsorption of the inhibitor molecules on the specimen/solution interface where the adsorbed molecules mechanically screen the coated part of the metal surface from the action of the corrodent [21]. For EIS measurements, the percentage of inhibition efficiency was calculated using *Rp* values through Equation (2):

$$IE\ (\%) = 100\ (1 - R_{p\,(0)} / R_p) \tag{2}$$

where $R_{p\,(0)}$ and R_p are the polarisation resistance values in the absence and presence of inhibitor.

Table 2. IE (%) values from weight loss and EIS technique.

Types of paint	IE (%)	
	Weight loss	EIS
P1	-	-
P2	31.63	79.51
P3	77.75	96.25
P4	69.39	53.69

IE from EIS method shows that P3 is the most efficient paint as compared to others. This occurrence maybe due to the limitation of henna extract itself. This may be explained by the presence of more ions which hinders the absorption of dye to fibre where rare ions favour it and it has mentioned that due to the increment of henna concentration, the absolute quantity is diminished [22]. On the other hand, there is a report about the limitation of the henna extract can be incorporated into paint matrix where the presence of more inhibitor ions hinders the adsorption to the metal surface. This is related to the inhibition performance of henna extract decreases when it reaches a certain amount in a paint system due to the shift of a certain functional group present in lawsone structure [23].

Electrochemical Impedance Spectroscopy

The corrosion behaviours of the specimens with four different percentages of henna extracts immersed in seawater were investigated by using Electrochemical Impedance Spectroscopy. The data obtained were represented in Nyquist plots (Figure 4). The features of all impedance spectra exhibit a similar shape. The single capacitive semi-circle shows the corrosion process was mainly charge transfer controlled [24]. The results show that the presence of henna extract increases polarisation resistance (R_p) value from 1792.2 $\Omega.cm^2$ to 47 783 $\Omega.cm^2$ and decreases to 3870.4 $\Omega.cm^2$ when 10% of henna extract was added into matrix paint. The increment in the R_p value leads to an increase in inhibition efficiency. As the percentage of henna extract increases, the value of R_p increases as well due to the formation of passive films. Double layer capacitance (C_{dl}) decreases from 0.003793 F to 0.000283 F.

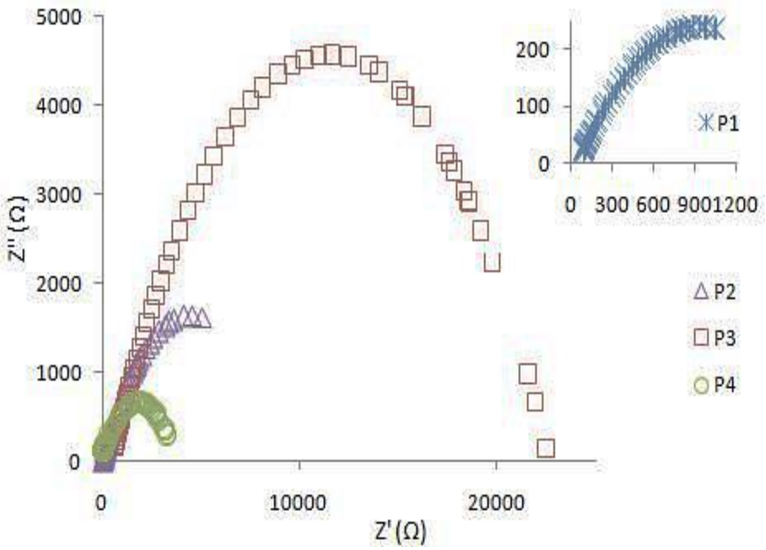

Figure 4. Nyquist plot of specimen immersed in seawater for 60 days.

Paint 1 (without inhibitor) was observed to have a small semi-circle as compared to others with the R_p value was only 1792.20 Ω. This indicates that the inhibition is mainly affected by charge transfer and once the surface is covered by inhibitor molecules, some competitive diffusion resistance is taking place between the molecules to reach metal surface [6]. Other than that, as the value of C_{dl} decreased, it resulted in a decrease in local dielectric constant and/or an increase in the thickness of the double layer capacitance.

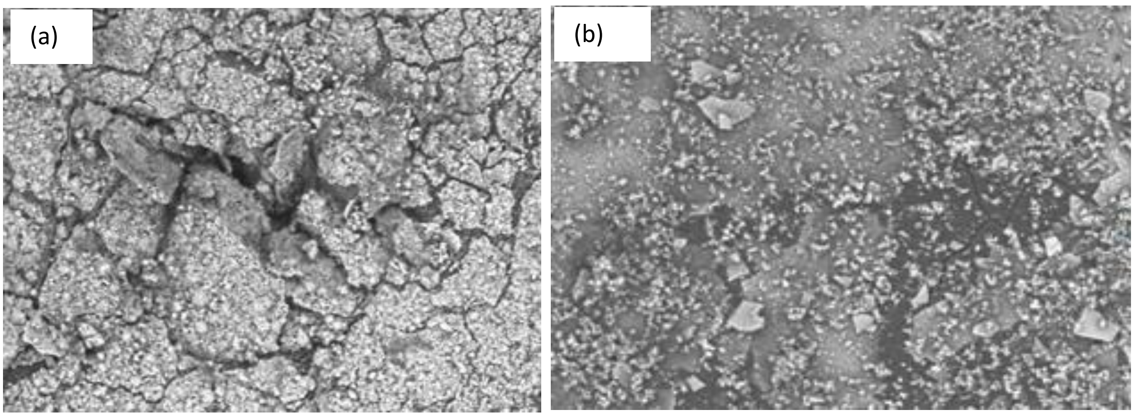

Figure 5. (a) Paint 1 and (b) Paint 3 after 60 days of immersion in seawater.

Scanning Electron Microscope

In order to study the corrosion phenomena on the specimen's surface, Scanning Electron Microscope (SEM) analysis was carried out. Figure 5 shows the SEM analysis after 60 days of immersion in seawater. Other than that, corrosion was produced due to the exposure of the substrate after electrochemical testing [25]. By comparing the SEM images at the same magnification, it was observed that the surface was very rough and severely damage as shown in Figure 5, which represents the surface of specimen without inhibitor. The surface is smoother and with more uniform deposits with the addition of 4% of henna extract. Therefore, it can be assumed that the formation of inhibitors in paint system also had contributed to the inhibitive action by forming a protective film on the substrate surface [26].

CONCLUSIONS

Based on the investigation, henna extract acts as a good inhibitor for the corrosion of aluminium alloy 5083 in seawater. This is due to the high inhibition efficiency produced. From the EIS study, the incorporation of henna extract into matrix paint had provided a barrier with the inhibition efficiency recorded to be 96.25%. Based on the observations, the inhibition efficiency of inhibitor increased with increasing of henna extract. In the presence of henna extract, the value of R_p increases and the value of C_{dl} decreases. P3 is shown to be the most efficient paint due to the inhomogeneity in coating sample as the henna percentage increased. The FTIR shows that the compounds present in the henna extract form a corrosion inhibitive layer and the inhibitor can be adsorbed on the metal surface through oxygen atom of lawsone, which is the main constituent present in henna extract. In the absence of henna extract, the surface of specimen is very rough and damages could be observed on its surface whereas the surface gets smoother and more uniform in the presence of henna extract.

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