

DEVELOPMENT OF BIO-BASED PAINT BY USING METHYL ESTERS FROM PALM OIL FOR CORROSION INHIBITOR

(Pembangunan Cat Berasaskan Bio Menggunakan Metil Ester Dari Minyak Sawit Untuk Mengawal Pembentukan Karat)

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Abstract

Paint is used as a means of protection to prevent surfaces from being corroded over time. This research is focused on the development of a Bio-based paint made from palm oil methyl ester (POME) which originated from crude palm oil (CPO). New formulation paint has been developed to protect the pipeline from corrosion thus reducing the cost of the operation. Bio-based paint is made up of four components which are solvent, binder, additives, and pigment. The solvent in the bio-based paint is POME. The additives used are wetting and dispersing agent. The pigment used in the bio-based paint is TiO_2 . The formulation was developed by using a constant amount of additives and binder but varying the amount of POME at 10 ml, 15 ml, 20 ml, 25 ml and 30 ml with addition of water. The Standard Testing Methods for measuring the corrosion rate (ASTM G5-94(2011)) was carried out for each sample. In conclusion, it is proven that in the making of bio-based paint formulation for better corrosion inhibitor; the best amount of binder, additives and de-foam that should be used is 20 ml, 10 ml and 10 ml, respectively.

Keywords: bio-based paint, additives, crude palm oil, palm oil methyl ester

Abstrak

Cat digunakan sebagai satu cara perlindungan dengan mencegah permukaan daripada berkarat dari masa ke masa. Kajian ini memberi tumpuan pada pembangunan cat berasaskan Bio-dibuat dari minyak metil ester sawit (POME) yang berasal dari minyak sawit mentah (MSM). Cat formulasi baru telah dibangunkan untuk melindungi saluran paip dari kakisan sekali gus mengurangkan kos operasi. Berasaskan Bio-cat terdiri daripada empat komponen yang pelarut, pengikat, bahan tambahan, dan pigmen. Pelarut cat berasaskan bio adalah satu POME. Aditif yang digunakan membasahkan dan ejen bersurai. Pigmen digunakan dalam cat berasaskan bio adalah TiO_2 . Penggubalan telah dibangunkan dengan menggunakan jumlah berterusan tambahan dan pengikat tetapi mengubah jumlah POME di 10 ml, 15 ml, 20 ml, 25 ml dan 30 ml dengan penambahan air. Kaedah Ujian Standard untuk mengukur kadar kakisan (ASTM G5-94 (2011)) telah dijalankan bagi setiap sampel. Kesimpulannya, ia membuktikan bahawa dalam membuat perumusan cat berasaskan bio bagi perencat kakisan yang lebih baik; jumlah terbaik pengikat, aditif dan penyahbuih yang harus digunakan adalah 20 ml, 10 ml dan 10 ml, masing-masing.

Kata kunci: cat berasaskan bio, bahan tambahan, minyak sawit mentah, minyak metil ester sawit

Introduction

Mild steel has been used widely in industry as a material for reaction vessels, storage tanks, etc. However, corrosion damage on mild steel causes heavy losses on the economy and potential problems in safety at work place [1, 2]. Recently, environmental regulations on industrial consumption and development of new corrosion inhibitors have been tightened up. Thus, natural products (e.g. vegetable oil), non-toxic and environmental-friendly products, have gained much attention in regard to the development of "green corrosion inhibitors" that have high inhibition efficiency [3]. Conducting polymers properties of the bio-based paint have recently been studied as a new class of materials for the corrosion protection of metals. These polymers are non-toxic and it is anticipated that they could replace harmful anticorrosion additives based on transition metal oxides [4]. In contrast to other macromolecular

compounds used in the corrosion protection due to their barrier properties, conducting polymers have a porous structure and are highly permeable to liquids and gases [5].

Corrosion of materials continues to receive interest in the technological world. In the field of corrosion inhibition, scientists are persistent in seeking better and more efficient ways of combating the corrosion of metals. Addition of corrosion inhibitors to the corrosion environment with respect to the other methods of corrosion inhibition has been employed [6]. Corrosion inhibition of materials has been the focus of research for centuries and in many cases has been well analyzed and understood [7 - 9].

Organic compounds are well known as acid inhibitors used in industry. These organic compounds have multiple bonds in their molecules that mainly contain nitrogen, sulphur, oxygen atoms through which they are adsorbed on the metal surface [10 - 12]. In order to solve the corrosion problem, development of bio-based paint as a corrosion inhibitor is a brilliant idea, instead of use as a product colour. Basic formulation of paint consists of a pigment, binder, solvent and additives that serve different purposes to the application of paint [13 - 15]. Nowadays, all of the components in paint are made from hazardous chemicals which are harmful to the environment and the society. In 2002, paint and coatings manufacturers released 7,000 tons of volatile organic compounds (VOCs) such as formaldehyde and methane [16]. In 2003, 420 facilities in the paint and coatings manufacturing sector reported air toxics releases of 4.7 million pounds [17].

The emissions of volatile organic compounds (VOCs) and odor problem are the result from evaporation of organic solvents that are used as one of the constituents of paint ingredients. Solvent is important because it is the ingredient responsible to carry the solid components of paint which allows consistency when applying by brush, roller, and spray or dipping. The flow of the paint after it has been applied is also affected by the choice of solvent since the film develops the correct surface appearance. The paint film wets the substrate to which it has been applied thus maximizing adhesion to the surface. Most commonly used solvents are ketone and esters. However, the pitfall of using these solvents is that these solvents contain hazardous constituents that can cause serious health problem to human and environmental effects as air toxics [18]. Organic solvent based coatings are still a serious problem in the construction sector and that there are no general indications, that the problems are going to be solved. With concerns to these issues, production of bio-based paint from palm oil methyl ester (POME) is developed to overcome the emission of volatile organic compounds (VOCs) and odor problem [19].

Methodology

Polarization Curves

According to ASTM G3 and G5 reported by Najmiddin (2007) [20], Potentiostat / galvanostat Voltalab 21 was used to determine current density under steady state conditions as a function of potential. Polarization curves were obtained according to corrosion Testing Standard ASTM G3 and G5. Electrochemical tests were performed with sample coupon immersed in 1 M HCL. All potential were measured versus a saturated Calomel Electrode (SCE). For Tafel analysis, the corrosion current density, I_{corr} is calculated by the exploration of the anodic and cathodic Tafel line. The efficiency was calculated using the following equation:

$$E=100[1-(i_{add}/i_{free})]$$

where:

$$\begin{aligned} i_{add} &= I_{corr} \text{ iron electrode in the presence of coating} \\ i_{free} &= I_{corr} \text{ iron electrode in the absence of coating} \end{aligned}$$

The main parameters for the polarization curve include the scan rate and the potential (mV). The suitable scan rate which was used in the testing was 1 mV/s. The value of potential is between -700mV to 200mV, depending on the corrosion media. In order to determine the current density (mA/cm^2), the potential that is applied to the mild steel in 1 M HCL ranges from -700 to 200mV. A current density (mA/cm^2) versus potential (mV) curve is plotted. In order to determine the E_{corr} and I_{corr} , extrapolation from Tafel curve was done.

Cell Design

According to ASTM Standard, the electrochemical cell for the corrosion measurement consists of a working electrode, reference electrode, counter electrode and electrolyte. The working electrode needs to be reproducible, representative, free from crevices free from edge effects and free from water line effect. In this work, mild steel is used as the working electrode. The reference electrode was platinum wire mesh. The auxiliary is saturated calomel electrode (SCE). The electrolyte is 1 M HCl. To complete the arrangement of the cell design, platinum wire mesh is used as the counter electrode which allows current to pass with tolerable polarization. Figure 1 shows the cell design and Figure 2 shows the equipment for corrosion test. Table 1 below indicates the sample specimen for this study.



Figure 1. Cell design



Figure 2. Equipment for corrosion test

Table 1. Sample specimen for corrosion test

Sample	Binder Volume (ml)	Sample	Additives Volume (ml)	Sample	De-foamer Volume (ml)
5A	20	6A	2.0	7A	2.0
5B	30	6B	4.0	7B	4.0
5C	40	6C	6.0	7C	6.0
5D	50	6D	8.0	7D	8.0
5E	60	6E	10.0	7E	10.0

Results and Discussion

Effect of Binder to Corrosion Rate

Corrosion test with 1 M HCl and varying quantity of binder, the corrosion rate was determined in mm/y. It was found that the corrosion rate for sample 5A is 1.95 mm/y. This amount was found to be the smallest rate, thus showing that this sample is the least corrosive. As for control sample, the corrosion rate was 6.716 mm/y. The results show the differences in the corrosion rate between control sample and the sample 5A. These differences are observed due to the successful coating of sample 5A on the surface of mild steel. For sample 5E, the result was 6.008 mm/y. This result shows that sample 5E has the highest corrosion rate as compared to other samples. This higher corrosion rate was due to the unsuccessful coating of this sample on the surface of mild steel. It was found that by increasing the binder quantity, the corrosion rate increases due to less adhesion. This was concluded by observing the coating on the mild steel. The success of the coating affects the corrosion rate. For the optimum sample that was obtained by varying amount of binder, the results concluded that the sample 5A is the optimum sample for the corrosion test because of the smallest value in corrosion rate and since it adhered onto the mild steel plat. Figure 3 shows the graph of Corrosion Rate for different concentrations of paint binder.

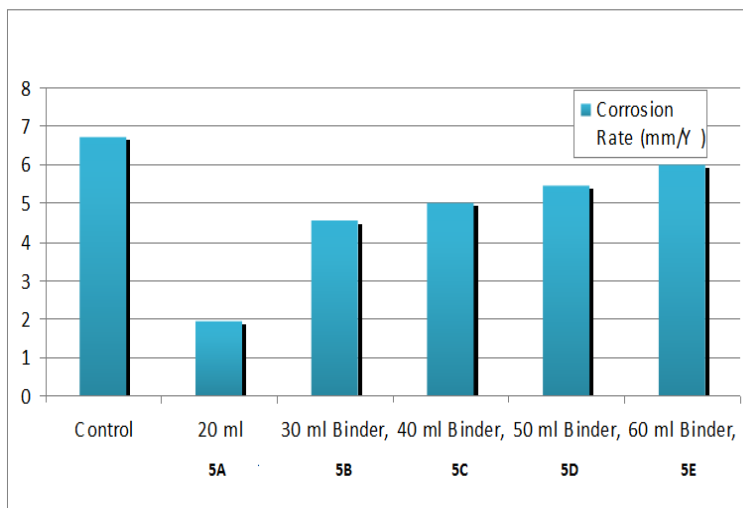


Figure 3. Corrosion Rate for different concentrations of binder

Table 2. Electrochemical corrosion parameters of mild steel in 1 M HCl various in binder

Sample	E_{corr} (mV)	I_{corr} (mA/cm ²)	R_p (ohm.cm ²)	E_1 (%)
Control	-443.4	0.7887	278.81	-
20 ml Binder, 5A	-367.2	0.2291	11.3	70.95
30 ml Binder, 5B	-357.5	0.6121	80.45	22.39
40 ml Binder, 5C	-348.9	0.5865	72.84	25.64
50 ml Binder, 5D	-348.7	0.5225	78.55	33.75
60 ml Binder, 5E	-347.1	0.7055	53.77	10.55

At constant temperature and variation in binder quantity, more electrons were released where higher dissolution of iron (Fe) was determined when higher corrosion current density (I_{corr}) was obtained. High corrosion current density would result in a high corrosion rate. This can be seen in Table 1 for control sample. The five various samples are compared in Table 2. The higher efficiency was obtained from sample 5A at 70.95% while the lowest efficiency was obtained from sample 5E at 10.55%. The lowest corrosion current density was determined from sample 5A which justified that the dissolution of Fe was retarded since fewer electrons were transferred due to the coating. Besides that, 5A sample shifted to the lowest corrosion current density (I_{corr}) which was the main criteria in determine the corrosion rate. The sample 5A adsorbed onto the surface of the mild steel plat which created a protective layer preventing corrosion due to higher polarization resistance which was determined as compared to the other samples. The formula of calculation showed in earlier equation.

Effect of Additive to Corrosion Rate

Figure 4 shows the graph of Corrosion Rate for the different amount of additives use in bio-paint development. In corrosion test of 1 M HCl with variation in additives, the corrosion rate was determined in mm/y. In this test, the corrosion rate for sample 6E was 1.941mm/y, the least corrosive sample as compared to all the other samples. The control sample has a corrosion rate of 6.716 mm/y. The results show the different of the corrosion rate between control sample and the sample 6E. These differences happened because of the successful coating of sample 6E on the surface of mild steel. For sample 6A, the result was 5.611mm/y which is the highest corrosion rate out of all samples. Higher corrosion rate was because of the unsuccessful coating on the surface of mild steel plat which is also shown in Figure 4. It was found that by increasing the amount of additives, there is a decrease in corrosion rate.

The successful coating affects the corrosion rate. As for the optimum sample with variation in additives, the results concluded that sample 6E is the optimum sample for the corrosion test rather than other samples because of the lesser corrosion rate in the corrosion test and it was adhered on the mild steel.

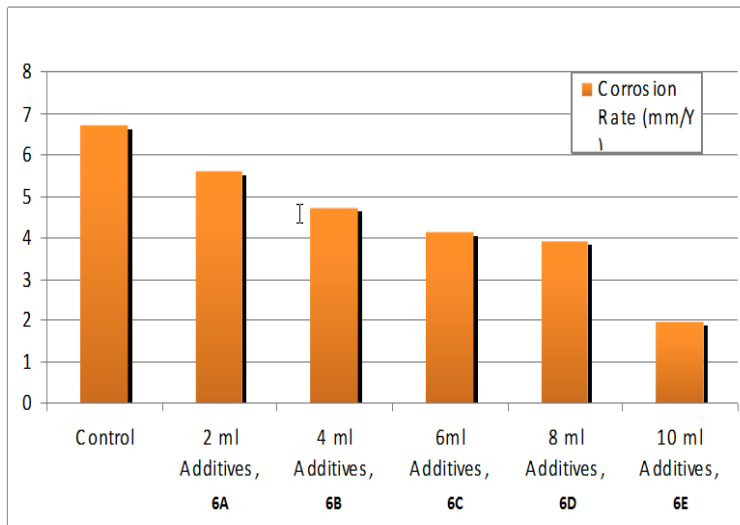


Figure 4. Corrosion Rate for Additives

Table 3. The effect of additive on electrochemical corrosion parameters of mild steel in 1 M HCl

Sample	E_{corr} (mV)	I_{corr} (mA/cm ²)	R_p (ohm.cm ²)	E_1 (%)
Control	-443.4	0.7887	278.81	-
2 ml additives, 6A	-365.2	0.711	80.51	$[1-(0.711/0.7887)]100=9.85$
4ml additives, 6B	-350.3	0.637	65.74	19.23
6 ml additives, 6C	-350.6	0.539	66.74	31.66
8 ml additives, 6D	-346.8	0.4608	140.63	41.57
10 ml additives, 6E	-379.5	0.1105	373.65	85.99

At constant temperature and varying amount of binder, more electrons were released where higher dissolution of Iron (Fe) was determined when higher corrosion current density (I_{corr}) was obtained. High corrosion current density would result in a high corrosion rate. This can be seen in Table 2 for control sample. The five various samples are compared in Table 3. The highest efficiency was obtained from sample 6E at 85.99%, lowest efficiency was obtained from sample 6A at 9.85% and lowest corrosion current density was determined from sample 6E which justified that dissolution of Fe was retarded since fewer electrons were transferred. According to high efficiency of sample 6E, it showed shifts to the lowest corrosion current density (I_{corr}) which was the main criterion to determine the corrosion rate. Sample 6E adsorbed onto the surface of the mild steel plat which creates a protective layer that prevents corrosion due to higher polarization resistance which was determined in sample 6E.

Effect of De-foam to Corrosion Rate

In the corrosion test of 1 M HCL with variation in de-foam composition; the corrosion rate was determined in mm/y. According to this test, the corrosion rate of sample 7E with 10 ml de-foam was 1.18mm/y. This shows that this sample has the smallest corrosion rate as compared to all other samples. As for the control sample, the corrosion rate was 6.716 mm/y. Different rates obtained due to the successful coating on the mild steel plat which is shown in Plate 4.3. In sample 7A, the result was 6.145mm/y and showed that sample 7A has the highest corrosion rate

between all five samples. The higher corrosion rate is due to the unsuccessful coating of this sample on the mild steel plat. It was found that increasing amount of de-foam can cause a decrease in the corrosion rate. This is due to coating on the mild steel where successful coating affects the corrosion rate. Optimum sample is obtained by varying the amount of de-foam, this sample identified to be sample 7E which has the smallest corrosion rate because this sample adheres lightly on the mild steel plat. The entire sample 7 did not adhere well onto the mild steel because lacks of de-foam in the compositions. Further studies must be conducted to improve on this shortcoming. Table 4.9 shows the corrosion rate of the mild steel plats in 1 M HCL with the different samples. Figure 3 shows the graph of Corrosion Rate for different concentrations of Defoamer.

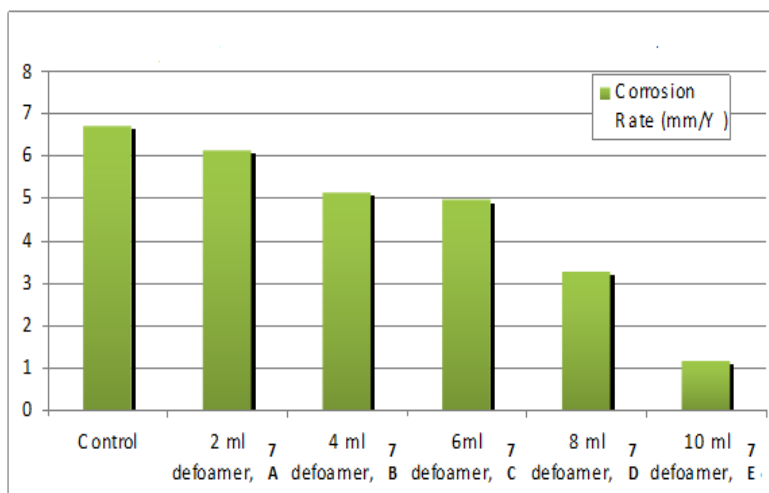


Figure 5. Corrosion Rate for different concentrations of Defoamer

Table 4. The effect of de-foam on electrochemical corrosion parameters of mild steel in 1 M HCl

Sample	E_{corr} (mV)	I_{corr} (mA/cm ²)	R_p (ohm.cm ²)	E_1 (%)
Control	-443.4	0.7887	278.81	-
2 ml de-foam , 7A	-347.4	0.7215	73.26	$[1-(0.7215/0.7887)]100=8.52$
4 ml de-foam, 7B	-346.0	0.6481	208.87	17.83
6 ml de-foam, 7C	-349.1	0.5131	69.05	34.94
8 ml de-foam, 7D	-345.3	0.2197	503.76	72.14
10 ml de-foam, 7E	-363.5	0.0387	372.84	95.1

At constant temperature and various amount of de-foam, more electrons were released where higher dissolution of Iron (Fe) was determined when high corrosion current density (I_{corr}) was obtained. High corrosion current density would result in a high corrosion rate. This can be seen in Table 3 for control sample. The five various de-foam samples are compared in Table 4. The highest efficiency was obtained from sample C₅ at 95.1 %. The 7E sample shifts to the lowest corrosion current density (I_{corr}) which is the main criterion in determining corrosion rate. The lowest efficiency was obtained from sample 7A at 8.525%, lowest corrosion current density was determined from sample 7E which justified that the dissolution of Fe was retarded since fewer electrons were transferred. Sample 7E coated the mild steel plat which creates a protective layer to prevent corrosion since high polarization resistance was determined compared to other various defoamer samples. The overall efficiency of the variation in de-foam composition from the polarization analysis with concentration 1 M HCl at constant temperature is shown in Table 3.

Conclusion

Based on Tafel analysis, the sample A₁, B₅ and C₅, performed well in 1 M HCL at room temperature when this sample recorded high value in coating efficiency as compared to other samples. The above findings are supported by the result from the Tafel analysis which showed that corrosion rate measured in mm/year in the 20 ml binders, 10 ml additives and 10 ml sample has the lowest rate as compared to all other samples.

Acknowledgement

The authors gratefully acknowledge to the Research Management Institute (RMI), Faculty of Chemical Engineering, Universiti Teknologi MARA Malaysia for providing the necessary budget, facilities and equipments to this research.

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