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Oil as Corrosion Inhibitor for Aluminium Alloy in Aggressive Environment

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ABSTRACT. Corrosion processes are responsible for huge losses in industry. This deterioration of components results in loss of plant efficiency, total shutdown and aggressive damage in a number of industries. Though organic, inorganic and mixed material inhibitors were used for a long time to combat corrosion, the environmental toxicity of inorganic corrosion inhibitors has prompted the search for organic corrosion inhibitors. In search for this, the use of organic inhibitors is one of the best options of protecting metals and alloys against corrosion as it is environmentally acceptable, inexpensive and readily available. In this regards, silicon oil was used as inhibitor in this study. Weight loss, corrosion rate, inhibition efficiency and potentiodynamic polarization techniques were used in this study. The aluminium alloy samples exposed to the inhibitor showed a lower corrosion rate values and excellent polarization resistance as compared with the corrosion rate samples without inhibitor. The corrosion inhibition rate increases with increasing the concentration of the silicone oil. The adsorption isotherm was confirmed by Langmuir adsorption isotherm.
Keywords: Corrosion; Silicone oil; Inhibition; and Corrosion rate

1. INTRODUCTION

Aluminum comprises eight percent of the earth’s crust. The annual market of aluminium is 25 million tons which makes it one of the principal nonferrous metals in the metallurgy industry [1]. The applications of aluminium and its alloys varied from household to electrical engineering, packaging, transport and building [2-6]. Also, it demonstrates a good fatigue resistance as well as high strength to weight ratio. Aluminium resistance to corrosion in aqueous media can be attributed to a rapidly formed surface oxide film. Because the aluminium oxide layer is very thin, it is easily degraded by physical or chemical methods. On the contrary, this alloy is highly susceptible to corrosion because of the presence of inter metallic particles at the surface resulting in need for the development of several methods in order to enhance its resistance against corrosion [7, 8]. Efforts have been made to protect the corrosion of aluminium surface in different corrosive environments. Recently, the addition of inhibitors has been considered to be one of the most common approaches to hinder the corrosion of aluminium [9-13]. Aliphatic, aromatic amines and nitrogen heterocyclic molecules compounds have been widely reported as corrosion inhibitors of aluminum in aggressive media [14-16]. However, some of these compounds are costly and not environmentally friendly. In search for an alternative, environmentally friendly, protection for alluminium alloy, the present study aims to investigate the inhibition action of silicone oil and their protective performance for aluminium alloy in 3.5% NaCl solution using a variety of electrochemical tests; weight loss, corrosion rate, inhibition efficiency and potentiodynamic polarization techniques. Adsorption mechanism was also investigated.

2. MATERIALS AND METHODS

2.1. Materials and Sample Preparation

The aluminum alloy sheet with chemical composition shown in Table 1 below was mechanically press-cut into specimens of dimension 30 mm by 30mm by 0.3mm. All test plates of aluminium alloy samples were ultrasonically degreased in acetone for 15 min. After that, the aluminum alloy specimens were washed thoroughly with distilled water and dried. The specimens with an exposed area of 1 cm^2 were used for potentiodynamic polarization tests. Analytical reagent grade of sodium chloride and double distilled water were used to prepare the corrosive medium. Molecular structures of silicone oil are shown in Figure1.

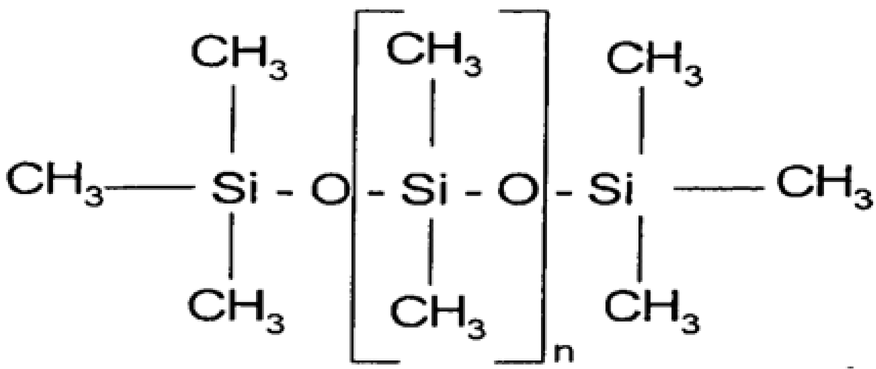

Figure 1. Molecular structure of silicone oil

2.2. Weight Loss Test

The aluminum alloy specimens in triplicate were immersed in a 3.5 % NaCl solution with and without different concentration (0.1–0.5 g/L) of silicone oil for 168 hours. The temperature was controlled by a thermostat aqueous bath at 304K. For all weight loss tests, the volume of prepared solution was 250 mL. After the immersion, all specimens were brought out from the solution, scrubbed with bristle brush under running water, then washed thoroughly with distilled water, dried in acetone, and weighed accurately. Minimum of three samples were tested and the average value was obtained. The corrosion rates and inhibition efficiency were determined from equations previously reported by [13].

Table 1: Chemical composition of aluminium alloy (%wt)

Element	Compositions
Si	0.157
Fe	0.282
Cu	0.0025

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Mn	0.024
Mg	0.51
Cr	0.023
Ti	0.006
Ca	0.0011
Zr	0.002
V	0.0035
Al	Balance

2.3. Electrochemical Measurements

The potentiodynamic polarization tests were carried out in a three-electrode cell system with a non-aqueous Ag/Ag electrode used as reference electrode, and a platinum wire used as counter electrode. The working electrode was mounted aluminium alloy sample. For each sample, measurements were performed in at least triplicate. The following electrochemical parameters were determined: corrosion current density (icorr), corrosion potential (Ecorr), and corrosion rate (CR). The corrosion inhibition effectiveness, IE, was calculated accordingly using equation reported elsewhere. All specimens were embedded in Teflon using epoxy resin and were prepared as rotating disc electrodes. Before the electrochemical measurements, all samples were mechanically polished with 1,200 grit emery paper, washed with double distilled water and put into the cell containing the studied solutions. There was an immersion in the solution for 1 h for the open circuit potential to reach a steady state. The polarization curves were obtained by changing potential from -250 mV to +250 mV with a scan rate of 0.5mV/s. The electrochemical experiments were performed using a Potentiostat/Galvanostat with NOVA software, Version 1.8. Each experiment was repeated at least three times to ensure the reproducibility.

2.4 Adsorption Isotherm

To understand the adsorption mechanism of the corrosion resistance of aluminium alloy surface, the data obtained from the corrosion study were tested with several adsorption isotherms models including Langmuir, Frumkin, and Temkin. The surface coverage, 8, was calculated using equation 1 below where 1 is the inhibition efficiency:

$$8 = \frac{n(\%)}{100(\%)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

3. RESULTS AND DISCUSSION

With the silicone oil concentration varying from 0.1 to 0.5 g/L in saline solution, the weight loss by the aluminium alloy in various concentration of silicone oil took the order of Control < 0.1 < 0.2 < 0.3 < 0.4 < 0.5.

3.1. Adsorption Characteristics
Inhibition efficiency of silicone oil falls within the first 96 hour but becomes linear after 120 hours. For the period of 96 hours the inhibition efficiency of silicone oil was averagely maintained at 70% and 83% respectively at 0.4 and 0.5g/L of silicone oil as indicated in Figures 2, 3 and 4. Corrosion rate of aluminum in various concentrations of silicone oil in the studied medium are in the order control > 0.1 > 0.2 > 0.3 > 0.4 > 0.5 as shown in Figure 4. As corrosion of aluminum alloy increases with time that of inhibitor decreases with inhibitor concentration. It was observed that out of the five concentrations of silicone oil that were tested for weight loss, 0.5g/L gave the highest efficiency. This implies that 0.5g/L concentration of silicone oil inhibited the aluminum alloy most and followed by 0.4g/L. The silicone oil contents are expected to have affinity to bind with the aluminum alloy surface. Therefore elements contained in this oil are required to be attracted to aluminum alloy coupon and adhered to its surface by chemical reactions thereby preventing direct attack by the medium.

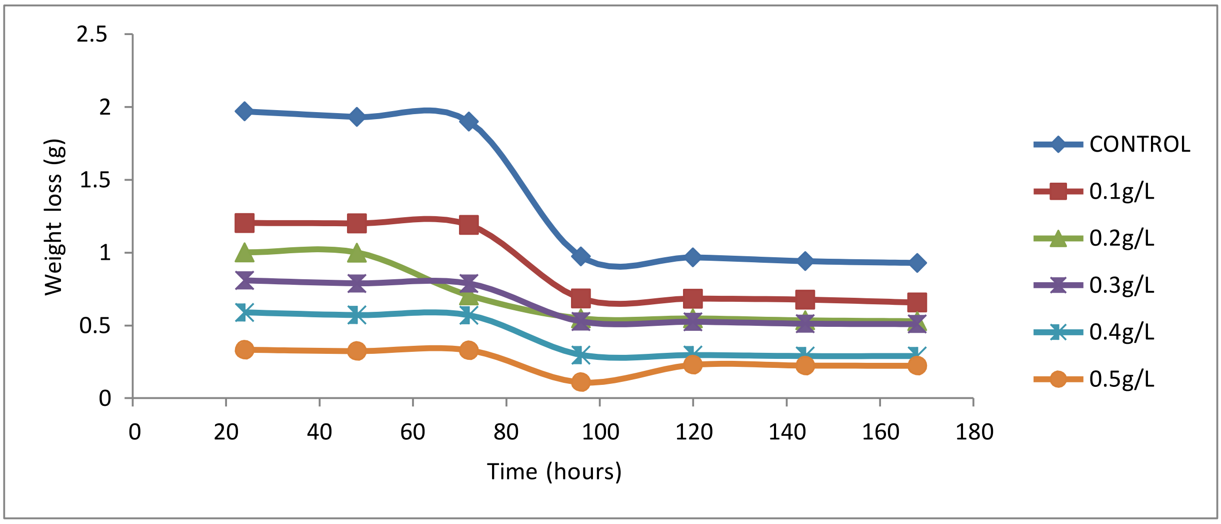

Figure 2: Weight loss of aluminium alloy with time of immersion in 3.5% NaCl at 304K at different inhibitor concentration

Figure 4 indicated the higher inhibition efficiency potential of silicone oil to be higher with increase in its concentration. In Figure 3, corrosion rate of the samples with inhibitor decreased above the control at all the concentrations studied. The adsorption of this oil on the aluminium alloy surface reduces the rate of corrosion. It shows aluminium alloy has affinity for elements that made up its ore rather than organic constituents of silicone oil. The addition of the oil hindered the affinity of the aluminium alloy for the elemental components of the oil thereby reduced the adsorption of the components on the metal. Different oil has been reported to inhibit corrosion of metals [18-23]. Due to interaction between the metal and the oil there could be formation of a soluble compound which may stimulate corrosion rather than favor inhibition. Also the properties responsible for effective inhibition such as the number of adsorption active centers in the molecule, their charge density, the molecular size and the mode of adsorption may have been restructured. The ability of the silicone oil to reduce aluminium corrosion is shown in Figures 2, 3 and 4

This confirms that pure metals are ready to return to their ore or oxide state in the presence of required substances and in the absence of organic substance from oil with significant sodium content will retard adsorption of inhibitors on the metal surface.

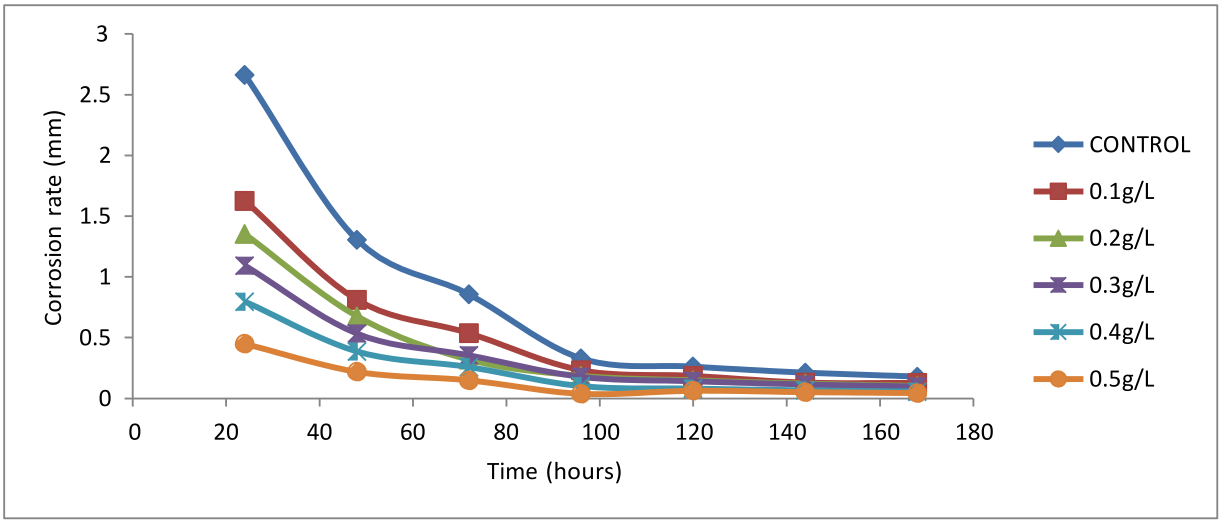

Figure 3: Corrosion rates of aluminium in 3.5% NaCl at 304K at different inhibitor concentration

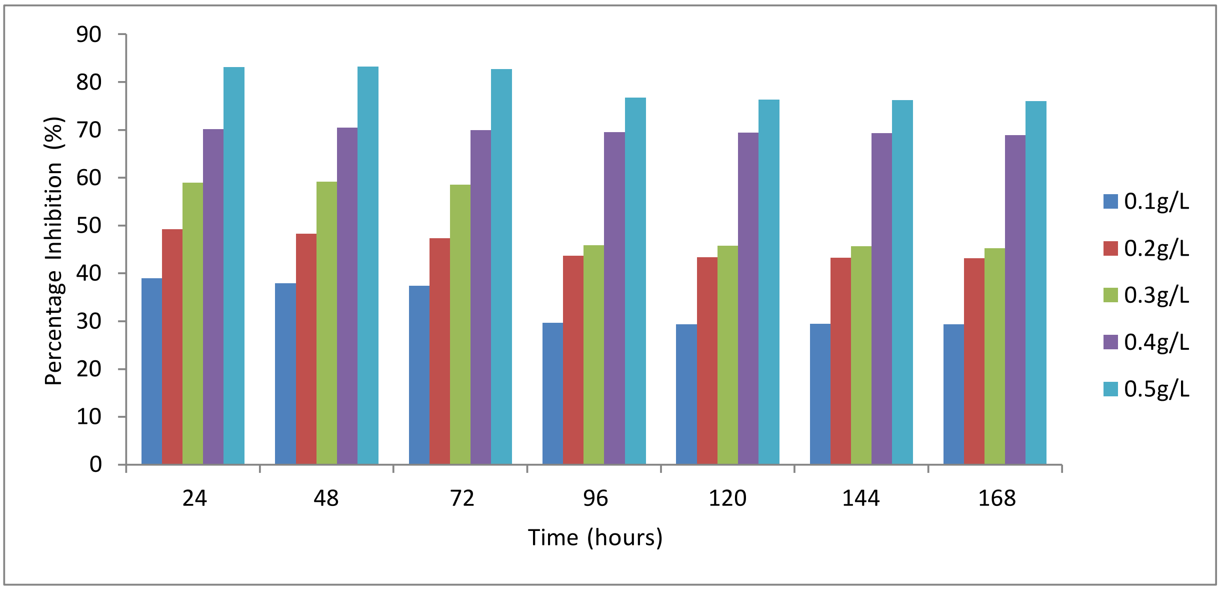

Figure 4: Percentage inhibition efficiency of aluminium in 3.5% NaCl at 304K at different inhibitor concentration

Table 2. Data obtained from Tafel plot curves of aluminium alloy in 3.5%NaCl solution at different concentrations of silicone oil

S/N	C (g/L)	Icorr (A/cm2)	βc (V/dec)	βa (V/dec)	LPR Rp (Ωcm2)	-Ecorr (V)	CR (mm/yr)
1	Control	0.000802	0.60085	1.3086	175.96	-0.92732	3.7570
2	0.1	0.000235	0.27822	0.64902	359.87	-0.92732	2.7309
3	0.2	0.000164	0.02582	0.1081	86.79	-0.92732	1.9011
4	0.3	0.000156	0.20144	0.094419	178.57	-0.92732	1.8168
5	0.4	5.75E-05	0.24695	0.352	196.4	-0.92732	0.6679
6	0.5	4.28E-05	0.16668	0.15949	55.324	-0.92732	0.4974

Current density-potential curves were recorded to obtain information on the effectiveness of the silicone oil on the corrosion processes and its effect on the anodic and cathodic reactions. Figure 5 represent the anodic and cathodic polarization curves for the aluminium alloy immersed in 3.5% NaCl in the absence and presence of different concentrations of silicone oil at 304K. From these polarization curves the corrosion kinetic parameters such as corrosion current density (icorr), corrosion potential (Ecorr), anodic and cathodic Tafel slopes (ba, bc) were deduced by extrapolating Tafel's lines.

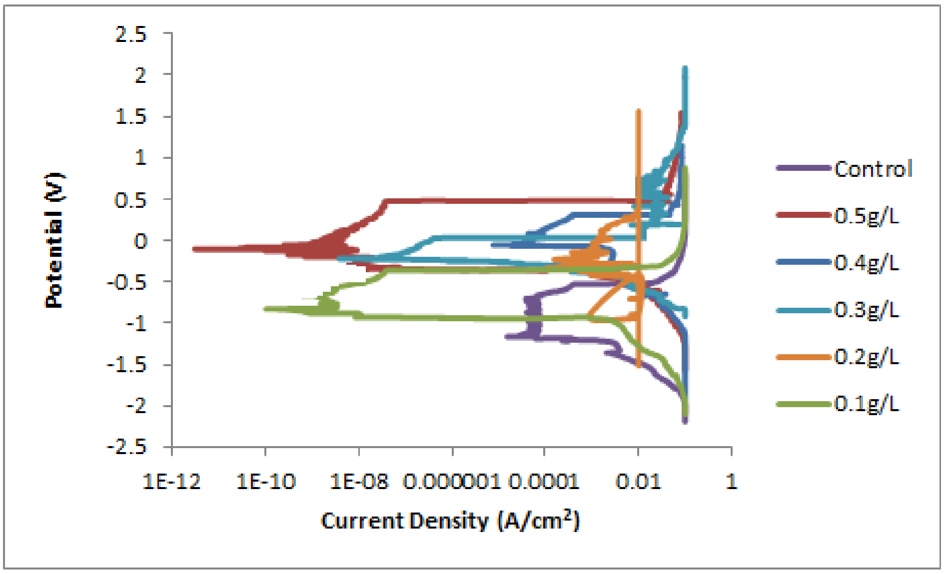

Figure 5. Tafel polarization curves of aluminium alloy in 3.5% NaCl solution in the absence and presence of different concentrations of silicone oil

The changes observed in the polarization curves in the presence of the inhibitor are usually used as criteria to classify inhibitors as anodic, cathodic or mixed. Figure 4 shows the shifting of corrosion potential (Ecorr) as dependent on inhibitor concentrations, while the general shape of anodic and cathodic curves in the absence and presence of the inhibitor is comparable. The curves are shifted towards lower current density values compared to that of the control solution, indicating the inhibition of the aluminium alloy. The decrease in corrosion rate associated with a shift of both cathodic and anodic plots of the polarization curves toward lower current densities, and a positive shift in corrosion potential, indicates that this oil acts as a mixed-type inhibitor. When the concentration of oil increases, the anodic branches make a sudden shift to more positive potential direction. The data in Table 2 show that the bc values are almost constant at different concentrations of inhibitor. This observation indicates that the mechanism of proton discharge reaction is not affected in the presence of silicone oil. Likewise, the constancy of the cathodic slope may have indicated that the hydrogen evolution reaction is activation controlled and that the inhibitor is absorbed by simply blocking the active sites of the aluminium surface [17]. In the anodic area, as the inhibitor concentration increases, there is a shift towards positive values of corrosion potential. However, the slight variation of ba near the shift of Ecorr toward anodic potentials may be attributed to the modification of the anodic process due to the formation of a protective film on the electrode surface rather than a simple adsorption on the active sites. The analysis of these results shows that the increase of silicone oil concentration decreases icorr, and consequently there is an increase of inhibition efficiency. The increase in efficiency may be due to the blocking effect on the surface by both adsorption and film formation mechanism, which decreases the effective area of attack.

Adsorption Isotherm

Adsorption characteristics are helpful in understanding the nature of corrosion inhibition and it can be deduced in the term of adsorption isotherm. By fitting the various adsorption isotherms into Freundlich, Temkin, Langmuir and Frumkin isotherms, the data were tested graphically. The process of adsorption occur when liquid or gas accumulates on the surface of a solid or liquid, forming a molecular or atomic film. In general, adsorption isotherm can be divided into two categories. First category occurs when the molecules adsorb but their chemical originality remains unchanged. In this state, the adsorption bond between inhibitor molecule and surface is fairly weak. The best fitted isotherm that describes the adsorption behavior of silicone oil on aluminium surface was Langmuir adsorption isotherm and it can be expressed by using the equation as described by [23].

It was found that the Langmuir adsorption model was the best fit with correlation coefficients above 0.858 for the temperature studied (Figure 6) while the others correlated are less than 0.602.

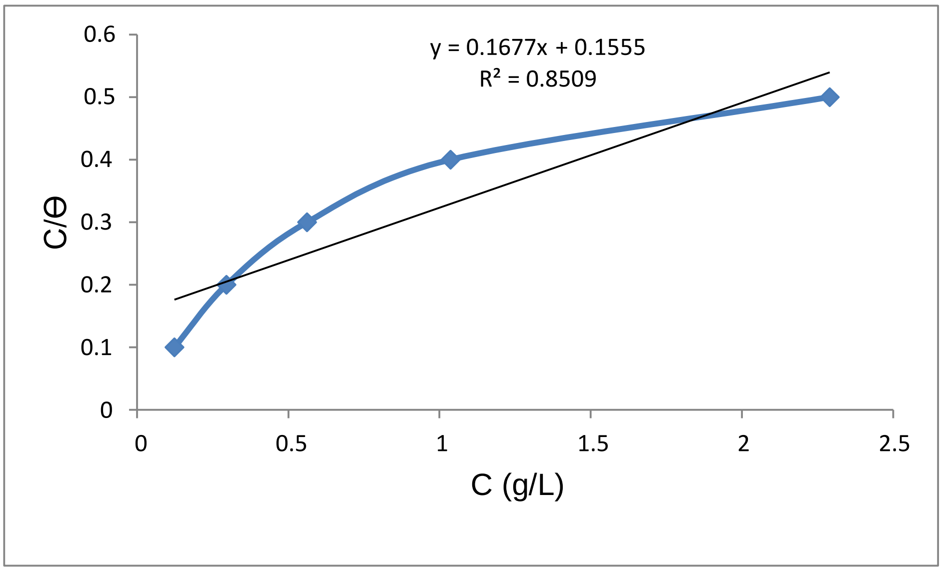

Figure 6. Langmuir adsorption isotherm model for silicone oil in 3.5% NaCl medium

4. CONCLUSION

Our study indicates that silicone oil acts as an effective corrosion inhibitor for aluminium alloy in 3.5% NaCl solution. The inhibition efficiency of the inhibitor concentration is in the order 0.5 > 0.4 > 0.3 > 0.2 > 0.1 > Control. Polarization tests indicated that this oil behaves as a mixed-inhibitor type with a predominant anodic effectiveness at higher concentration. The results obtained from weight loss measurements and electrochemical techniques were in reasonable agreement.

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