AN INVESTIGATION OF AGANOERION POLYMORPHUM LEAF EXTRACT AS A COPPER WORKING FLUIDS' ADDITIVE

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ABSTRACT

This work presents the Aganonerion Polymorphum leaf extract as an additive for metals working fluids (MWF). The results indicated that the Aganonerion Polymorphum leaf extract additive shows high corrosion resistance and very small changes of the MWF composition as well as its properties. These benefits are attributed to the forming protective inhibiting deposits on the copper surface that control the electrochemical corrosion reactions. In addition, the study also compared the Aganonerion Polymorphum leaf extract with a commercial inhibitor, imidazolines, in investigated solution at the same experimental conditions.

Keywords: metalworking fluids, corrosion, corrosion inhibitors, Aganonerion Polymorphum leaf extract, imidazolines.

1. INTRODUCTION

Metalworking fluids (MWFs) have been addressed in several works published in CIRP Annals - Manufacturing Technology in the past played a significant role in manufacturing processes such as cutting, forming, rolling, and grinding, as well as equal-channel angular pressing [1-3]. They influence heat generation in metalworking processes by reducing friction between workpiece and tool. Cooling is furthermore achieved by dissipating and conducting the generated heat by their lubricating and cooling properties to avoid thermal damage of the workpiece material as well as reduce wear of the tool. Therefore, MWFs should be applied to ensure workpiece quality, to reduce tool wear, and to improve process productivity and corrosion resistance. The specific chemical composition of an applied MWF should be strongly dependent on the scope of application, particularly corrosion. So far, corrosion inhibitors play a key role in these systems by reducing the cost and make the in-situ changes without disrupting the processes. The performance of oil-based MWFs was improved by adding further additives which contained nitrogen, phosphor, sulfur, chlorine, or boron. It was found that these substances are suitable to increase the lubricating ability under high pressure and furthermore prevent corrosion. However, it has been found that these additives are toxic and affect to environment, human health, and aggravated localized corrosion. Numerous studies have shown that high-performance corrosion inhibitors are organic compound which their molecular structure contains heteroatoms with high electron density, such as nitrogen, sulfur, oxygen, with double bonds or aromatic. Through the mechanism of adsorption of organic molecules to the metal surface, forming the film on the surface of the metal, that protects the metal from corrosive agents [4,5]. However, they have some disadvantages related to environment, aquatic, animal life, human health because they are toxic, furthermore, they are quite expensive as well [6]. Literature review reveals that corrosion inhibiting compounds from plants and natural product extracts have many outstanding benefits, they were environmentally- friendly, non-toxic, cheaper, diversity source and readily available and effective molecules having a very high inhibition efficiency. From the forging viewpoints in the consideration that leaf-extract from Aganonerion Polymorphum, a non- toxic plant that is Aganonerion Polymorphum can be used as a vegetable or medicine [7]. Some organic substances such as tannin, saponin, etc. are present in Aganonerion Polymorphum these contain heterozygous compounds, hydroxyl groups and nitrogenous elements, which have the possible interaction with empty d-orbits of the surface copper atoms, that forming the film on the copper metal to reducing the corrosion rate [8,9]. Considerable studies have been employed to anticorrosion from plants and natural-source. In particular, there have been no studies to develop corrosion inhibitor additives from natural sources for metalworking, which is an important issue in the metalworking industry. Therefore, the present study focuses on evaluation of corrosion inhibition performance of an Aganonerion Polymorphum leaf extract as an additive for copper working fluids. In addition, the study also compared the Aganonerion Polymorphum leaf extract with a commercial inhibitor, imidazolines, in investigating a solution.

2. EXPERIMENTAL

Flash point and pour point are vital parameters for lubricants. Flash point of lubricants is the lowest temperature of the atmospheric pressure (101.3 kPa or 760 mmHg) which vapors of the sample burns with ignition under conditions of test. The pour point is the lowest temperature, which a liquid becomes semi solid and we can observe the movement of the test specimen under test conditions. In this study, measuring flash point of metal working fluids with the concentration of 0, 100, 300 and 500 ppm Aganonerion Polymorphum leaf extract by the one cup method is detailed in ASTM D92 [10]. While, ASTM D97 method for pour point of metal working fluids with the same corrosion inhibitor concentration in flash point test [11]. The material used in the present study was copper with chemical compositions, which were checked via optical emission spectroscopy, as shown in Table 1. Copper was manufactured to controlling 10 mm × 10 mm × 3 mm as an exposed surface area. All copper specimens for the corrosion test will be surface treated by grinding with silicon carbide (SiC) paper abrasives at the roughness of 500, 1000 and 2000, then washed with ethanol, and then dried before immersion in the solution. All the experiments of electrochemical were performed at room temperature and used Aganonerion Polymorphum leaf extract and imidazoline in 0.6 M NaCl solution. A 0.6 M NaCl solution is a strong electrolyte solution and similar to sea water for use in corrosion assessment in the laboratory, therefore the solution was chosen as a corrosive environmental.

Table 1. Chemical compositions of the base metals examined by optical emission spectroscopy.

Sample	Composition (wt.%)							
	C	Fe	Sn	Zn	P	Ni	Al	Cu
Copper	0.0369	0.0029	0.0039	0.0338	0.0066	0.0125	0.0016	Bal.

In this study, the evaluation concentrations of Aganonerion Polymorphum leaf extracts were 0, 100, 300 and 500 ppm and 0, 10, 30 and 50 ppm of imidazoline. Electrochemical experiments were carried out using a SP300 system. The electrodes used to reference and counter in the measurement were silver/silver chloride (Ag/AgCl) and titanium, respectively. In this test, all of copper samples were immersed in solution with and without anti-corrosion compound in open-circuit for 24 hours. The potentiodynamic polarization test was used to evaluate the effects of the corrosion inhibitors on the corrosion resistance of copper in 0.6 NaCl solution with distinct concentrations of corrosion inhibitors through the current density. The scan rate was 0.166 mV/s with an initial potential of -250 mV and a final potential is anodic potential. The electrochemical impedance spectroscopy (EIS) test showed the resistance of the protective film and the impedance of the double layer of charge between the protective layer and the substrate surface and then determined the efficiency of inhibitor. The EIS has carried out the performance of the copper from 10 kHz to 10 mHz with a peak-to-peak amplitude at 10 mV. Scanning electron microscopy (SEM) was used to evaluate the effect of inhibiting the copper surface after immersion for 24 hours in 0.6 M NaCl solution, especially the appearance of the pits in uninhibited system. The method used JOEL mechanic at 20 kV and with a magnification of 500 times. In addition, the surface film was also examined by X-ray diffraction using X'Pert Powder at the voltage of 45 kV and the current of 40 mA. The range of 2θ angle is from 10 to 100º at a rate of 0.02º.

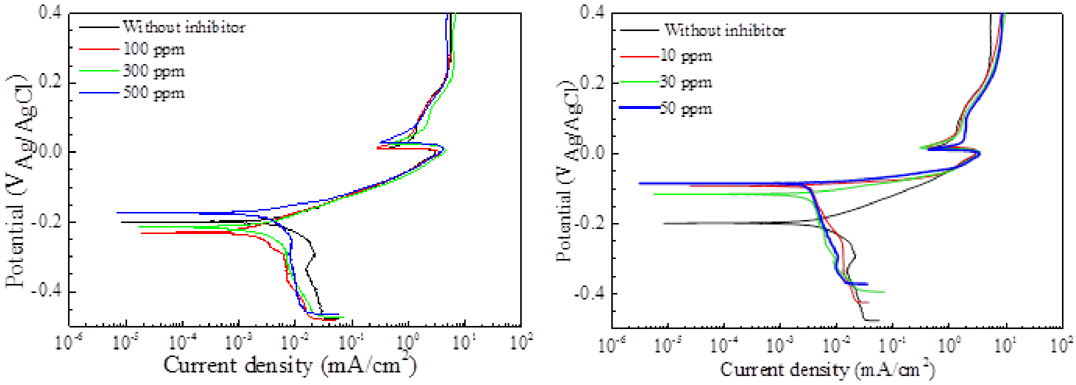
Table 2. The results of the flash and pour points of metal working fluids containing Aganonerion Polymorphum leaf extract.

Concentrations (ppm)		Flash point (°C)	Pour point (°C)
0	1st	220	-22.30
	2nd	222	-22.50
	3rd	220	-22.50
	Average	220.67	-22.43
100	1st	220	-22.80
	2nd	219	-22.50
	3rd	220	-22.50
	Average	219.67	-22.60
300	1st	218	-22.90
	2nd	220	-22.80
	3rd	220	-23.00
	Average	219.33	-22.80
500	1st	220	-23.10
	2nd	221	-23.00
	3rd	220	-23.00
	Average	220.33	-23.33

3. RESULTS AND DISCUSSION

Table 2 describes the results of flash point and pour point experiments of metal working fluid with concentration of Aganonerion Polymorphum leaf extract between 0 and 500 ppm. Overall, flash point and pour point of metal working fluid contain corrosion inhibitors with different concentration had slight fluctuation. Particularly, the average of flash point of three measurements without inhibitor was 220.67 ºC and for metalworking fluid with corrosion inhibitor concentrations of 100, 300 and 500 ppm had figures respectively 219.67, 219.33 and 220.33 ºC. Similarly, the pour point of metal working fluid with corrosion inhibitor concentrations of 0, 100, 300 and 500 ppm had average results are -22.30, -22.60, -23.00 and -23.30 ºC, respectively. Therefore, it can be concluded that the properties of metal working fluid performed an insignificant changes when APLE was added.

Figure 1 shows the potentiodynamic polarization curves of copper without and with corrosion inhibition performance with Aganonerion Polymorphum leaf extract and the imidazoline addition in 0.6 M NaCl solution with different concentrations. The shape of potentiodynamic polarization curves in Figure 1(a) demonstrated that the Aganonerion Polymorphum leaf extract had an effect on both anode and cathode curves when concentrations increased from 0 ppm to 500 ppm, that the inhibitor exhibited mixed inhibition with a copper electrode in the investigated solution. While, the figure for the potential tended to rise when concentration imidazoline increased from 0 ppm to 50 ppm and showed anode inhibitory activity (Fig. 1(b)). However, cathode polarization was also affected by the decreasing current density of the cathode, which was also polarized.



(a) (b)

Figure 1. Potentiodynamic polarization curves of copper after 24 h immersion in solutions containing (a) Aganonerion Polymorphum leaf extract and (b) Imidazoline.

The Tafel extrapolation method has been used to determine the parameters of corrosion. Current density, corrosion potential and Tafel coefficients of the anode and cathode obtained by moving the Tafel branch around the corrosion potential about 100 mV with all relative error and iterations were e^{-20} and 1000, respectively. Electrochemical parameters are summarized in Table 3. It can be seen the significant effects of Aganonerion Polymorphum leaf extracts and imidazoline on the electrochemical parameters of copper electrodes in research solution. There was a dramatic reduction in corrosion current density when increasing the concentration of both inhibitors. For Aganonerion Polymorphum leaf extract, the corrosion inhibition effects trended to grow when increasing concentration and reached the peak at 300 ppm (80.21 %). Whereas, the highest inhibition efficient of imidazoline at 50 ppm could be reached at 60.81 %. The corrosion inhibition effect of imidazoline was lower than that of the Aganonerion Polymorphum leaf extract, it can be explained that the lack of concentration to form a protective layer of the copper surface, meaning that concentration of imidazoline needs to be increased for improving inhibition performance.

Table 3. Corrosion properties from the potentiodynamic polarization curves of copper after 24 h immersion in solutions.

Concentration (ppm)		E_{corr} ($mV_{Ag/AgCl}$)	i_{corr} ($\mu A/cm^2$)	β_a (mV/decade)	$-\beta_c$ (mV/decade)	η (%)
Aganonerion Polymorphum leaf extract						
0	1st	-226	6.70	96	573	-
	2nd	-227	6.33	89	586	-
	3rd	-228	7.12	110	559	-
	Average	-230	6.72			
100	1st	-229	3.00	70	312	55.22
	2nd	-234	2.90	72	299	54.19
	3rd	-227	3.41	73	331	52.11
	Average	-230	3.10			53.87
300	1st	-214	1.31	35	69	80.45
	2nd	-214	1.32	38	73	78.15
	3rd	-215	1.35	39	74	81.04
	Average	-214	1.33			80.21
500	1st	-186	3.09	25	88	53.88
	2nd	-186	3.12	29	101	50.71
	3rd	-189	3.34	30	109	53.09
	Average	-187	3.18			52.68
Imidazoline						
10	1st	-100	3.31	17	293	50.59
	2nd	-101	3.21	22	421	54.91
	3rd	-101	3.20	19	271	55.10
	Average	-100	3.24			53.53
30	1st	-121	2.84	46	358	57.61
	2nd	-118	2.79	41	358	60.82
	3rd	-120	2.83	45	357	60.25
	Average	-120	2.82			59.21
50	1st	-82	2.72	48	367	59.40
	2nd	-80	2.69	47	367	62.22
	3rd	-81	2.73	48	367	62.08
	Average	-81	2.71			61.23

Figure 2 depicts the results of EIS obtained after embedding a copper samples in 0.6 M NaCl solution containing Aganonerion Polymorphum leaf extract and imidazoline. The Nyquist plots (Figure 2(a)) presented that the semi-circular curves of the total impedance increased when corrosion inhibitor concentration increased from 0 ppm to 300 ppm, then decreased. It can be seen in this case, the corrosive inhibition effect at a concentration of 500 ppm was lower than that of the concentration of 300 ppm. The reason could be that the high inhibitor concentration has slowed down the ion movement in the solution and prevented the adsorption of inhibitor onto the copper surface. In addition, the local surface defects at the high frequency spectra, while the medium and low frequency spectra discover the processes occurring within the film and at the metal/film interface, respectively. Figure 2(b) illustrates the EIS results obtained after embedding a copper samples in 0.6 M NaCl solution containing imidazoline with concentrations of 0, 10, 30 and 50 ppm. Similar to the results shown in Figure 3(a), when the imidazoline concentration was increased, the curvature of the curve increased, suggesting corrosion inhibition increased.

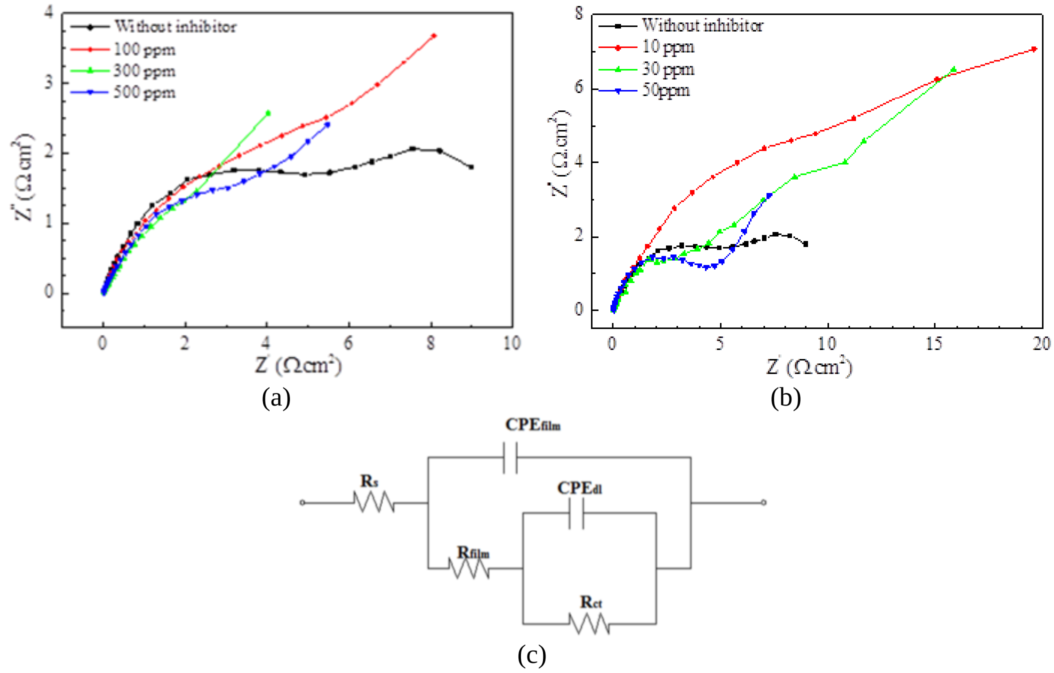


Figure 2. EIS results of copper after 24 h immersion in solutions containing (a) Aganonerion Polymorphum leaf extract and (b) Imidazoline, and (c) equivalent circuit for fitting EIS data.

Based on the electrochemical results and surface analysis, the equivalent circuit is establish and using Zsimpwin program. The equivalent circuit in Figure 2(c) for copper immersed in 0.6 M NaCl solution with and without corrosion inhibitors consists of the following factors: the solution resistance R_s of the test electrolyte between the working electrode and the reference electrode, the protective film resistance R_{film} of the protective film formed on the copper surface, the charge transfer resistance R_{ct} of the substrate/protective film interface, the constant phase element of the double layer CPE_{dl} and the charge transfer resistance R_{ct} of the eqsubstrate/protective interface and the constant phase element CPE_{film} of the protective film/electrolyte interface. The information for electrochemical parameters by equivalent circuit is given in Table 4.

The results shown in Table 4 demonstrated that a slight decrease in solution resistance was obtained when the Aganonerion Polymorphum leaf extract concentration increased, while both the protective film resistance (R_{film}) and the charge transfer resistance (R_{ct}) increased dramatically with the increasing of inhibitor concentration from 0 ppm to 300 ppm, and they slightly fell when inhibitor concentration was 500 ppm. In addition, the double layer capacitances (CPEdl) had an opposite trend of both the R_{film} and R_{ct} in the evaluated concentrations of the inhibitor. For imidazoline inhibitor, there was an upward trend on all resistances of solution, protective film and charge transfer, while there was a downward trend in the figure of both capacitances of two layers when an increase in an inhibitor concentration. Both R_{film} and R_{ct} increased and the reduction of the double layer capacitances due to the formation of a strong protective layer and it attached firmly to the copper surface.

Table 4. Electrochemical impedance parameters of copper immersed in 0.6 M NaCl solution containing distinct inhibitor concentrations.

Concentration (ppm)	R_s ($\Omega.cm^2$)	CPE_{film}		R_{film} ($\Omega.cm^2$)	CPE_{dl}		R_{ct} ($\Omega.cm^2$)
		C ($\mu F/cm^2$)	n (0~1)		C ($\mu F/cm^2$)	n (0~1)	
Aganonerion Polymorphum leaf extract							
0	8.9	0.629	0.725	2125	148	0.812	7132
100	10.3	0.255	0.804	4625	66	0.832	16001
300	11.5	0.126	0.841	5432	30	0.887	35660
500	13.7	0.301	0.751	3987	74	0.815	15264
Imidazoline							
10	10.3	0.322	0.733	3541	78	0.822	14206
30	12.6	0.270	0.735	4163	63	0.816	15686
50	13.0	0.252	0.754	4793	59	0.831	17830

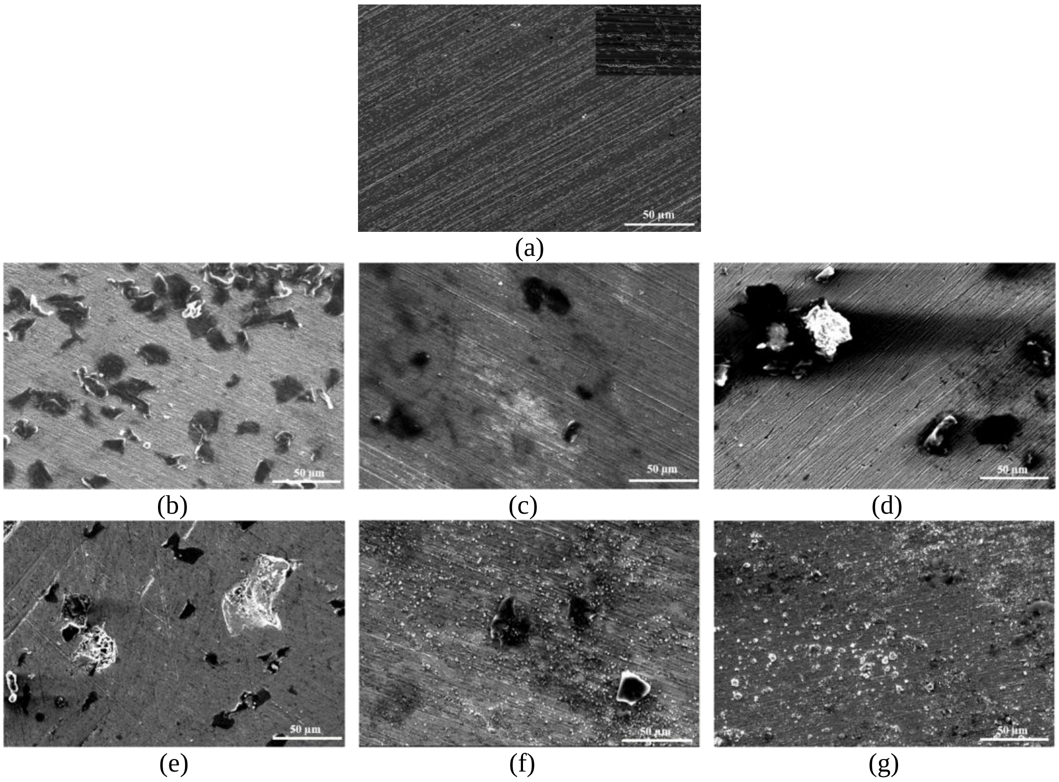
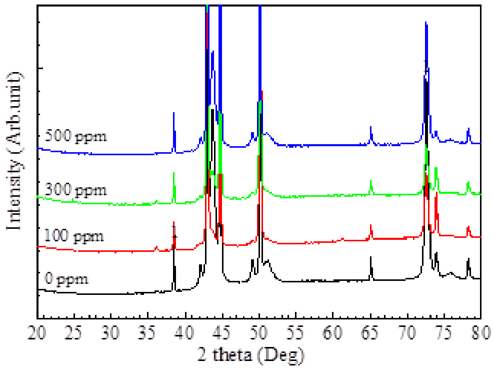
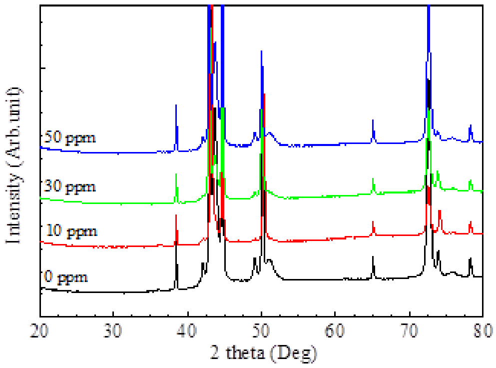


Figure 3. SEM images of copper surfaces after 24 h immersion in 0.6 M NaCl solutions (a) without inhibitor addition, with (b) 100, (c) 300 and (d) 500 ppm Aganonerion Polymorphum leaf extract and (e) 10, (f) 300, and (g) 50 ppm imidazoline additions.

SEM pictures shown in Fig. 3 expressed a considerable difference of surface morphologies on copper surfaces after 24 h-immersion in distinct inhibitor concentration solution due to the pit on the copper surface which were accelerated by the inward penetration of Cl^- ions. Pitting corrosion was clearly observed on copper surfaces immersed in 0.6 NaCl solution without inhibitor addition. This phenomenon occured more slowly on copper surface in situations of low inhibitor concentration as shown in Fig. 3(b-g). It indicated that copper surface was still corroded due to the lack of protective layer on the surface in low inhibitor concentration. The results of X-ray diffraction analysis of copper sample after immersion in 0.6 M NaCl solution with the presence and absence of the inhibitor were shown in Figure 4. The Joint Committee on Powder Diffraction International Centre for Diffraction Data used to analyze results. The results expressed the local around the positions as 38, 44, 65 and 73-74º correspond to corrosion products Cu_2O (or protective layer), while the local around position of 50º correspond to substrate Cu was found [12]. Corrosion products Cu_2O and substrate Cu in the XRD results indicated that these products combined with the product of adsorption inhibitor on copper surface. This phenomenon leaded to copper corrosion resistance in research solution.



(a)



(b)

Figure 4. XRD analysis for copper surface after 24-hour immersed in NaCl 0.1 M without and with (a) Aganonerion Polymorphum leaf extract and (b) imidazoline additions.

From the electrochemical tests and surface analysis results, the mechanism of copper corrosion in the presence of chloride ions was proposed through the following reactions [13, 14]:

$$CuCl + Cl^- \leftrightarrow CuCl_2^- \quad (1)$$

$$Cu^+ + Cl^- \rightarrow CuCl \quad (2)$$

$$CuCl + Cl^- \rightarrow CuCl_2^- \quad (3)$$

$$Cu^{2+} + Cu + 2Cl^- \rightarrow 2CuCl \quad (4)$$

$$2CuCl_2^- + 2OH^- \rightarrow Cu_2O + H_2O + 4Cl^- \quad (5)$$

$$Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^- \quad (6)$$

In addition, the corrosion products containing Cu_2O were formed as shown in XRD analysis in Figure 4. The Cu^{n+} ion beared on the copper surface would combine with the organic radicals containing the negative charge and it combines with corrosion product Cu_2O forms a protective layer on the copper surface, preventing the dissolution of the copper. Therefore, the oxidation reaction was controlled by the inhibitor in the corrosive solution, which increased the polarization of anode and cathode and significantly diminished corrosion current density. Both inhibitors protected copper avoid corrosion through adsorption mechanism. Particularly, in the molecular structure of imidazoline containing two nitrogenous elements at position 1 and 3 in their ring structure with very high electron density, suggesting an adsorbent capacity with positive ions on the copper surface. Therefore, ion Cu^{n+} would attract with imidazoline molecular in solution contain an inhibitor of imidazoline. Likewise, ions Cu^{n+} would also attract organic heterocyclic compounds containing hydroxide and nitrogenous elements such as tannin and saponin… in the Aganonerion Polymorphum leaf extract when copper immersed solution with this inhibitor. As for imidazoline inhibitor, the more positive potential and low corrosion current density at higher at higher inhibitor concentration have been observed. However, the obtained results in this study showed that the inhibitor effectiveness of Aganonerion Polymorphum leaf extract was higher than that of imidazoline. SEM and XRD results showed the surface of metal forming a film interacting with corrosion products and organic components.

4. CONCLUSIONS

The study has shown that metal working fluids still retained the necessary properties such as flash point and pour point when add an inhibitor performance of an Aganonerion Polymorphum leaf extract. Both Aganonerion Polymorphum leaf extract and imidazoline had a good inhibitory effect on copper corrosion on the investigate solution. The corrosion inhibitory efficacy of both cases increased with increased inhibitory concentrations and, the inhibitor effectiveness of an Aganonerion Polymorphum leaf extract was higher than that of imidazoline. Inhibitor performance of an Aganonerion Polymorphum leaf extract expressed mixed inhibition with efficacy was over 80% at a concentration of 300 ppm, due to the formation of a protective layer on the copper surface after 24 hours immersion in a solution containing the inhibitor via adsorption mechanism. Imidazoline expressed anode inhibition, the results showed that the protective efficacy was 61.23% at a concentration of 50 ppm, it can be proposed that the protective efficacy will continuously increase when the concentration of imidazoline increase.

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