Effect of Palm Oil as Corrosion Inhibitor on Ductile Iron and Mild Steel.

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ABSTRACT

This work has investigated the effect of palm oil as a corrosion inhibitor on ductile iron and mild steel. The weight loss technique was employed. Palm oil was applied on each coupon before exposing it to various media representing possible applications in society.

The results showed that in 1M NaOH, no noticeable corrosion occurred both on the ductile iron and mild steel samples, even throughout the 1,344 hrs (7 wks) of the experiment. When the coupons were exposed to fresh water inhibited by palm oil, the corrosion rate of DI coupons was initially high and later dropped sharply. However, for mild steel coupons, there was an initially low corrosion rate which later shot up. There was little or no corrosion loss on impregnated DI exposed to air while the impregnated mild steel exposed in air initially corroded. For simulated seawater inhibited by palm oil, there was little initial corrosion attack followed by a sharp rise in corrosion attack.

It can be concluded from this research that palm oil can be a good raw material for preparation of "environmentally friendly" corrosion inhibitors. It has been proved that palm oil has demonstrated high inhibition efficiency especially on corrosion of ductile iron in 1M NaOH and air. It has also shown to be a reliable protective shield against the corrosion of mild steel in 1M NaOH.

(Keywords: corrosion inhibitor, ductile iron, mild steel, sodium hydroxide, NaOH, simulated seawater)

INTRODUCTION

Corrosion can be defined as the destructive and unintentional attack of metals. It is extractive

metallurgy in reverse (Fontana and Green, 1987); that is, it serves to return metals back to their ore (MP, 2007). In corrosion inhibition, additions of certain chemicals are made to the environment, although it should be noted that the environment can, in some cases, be made less aggressive by other methods (e.g., removal of dissolved oxygen or adjustment of pH). Inhibitors are substances added in small concentrations to particular environments with the aim of slowing down the rate of corrosion at such sites.

It is well established that inhibitors function in one or more ways to control corrosion: by adsorption of a thin film onto the surface of a corroding material, by inducing the characteristics of the environment resulting in reduced aggressiveness (Hackerman and Hurad, 1962). Inhibitors slow the corrosion processes by increasing the anodic or cathodic polarization behavior, reducing the movement or diffusion of ions to the metallic surface and increasing the electrical resistances of the metallic surface. The corrosion inhibition of metals may involve either physiosorption or chemisorption of inhibitors onto the metal surface and subsequent interference with either cathodic, or anodic, or both reactions occurring at the adsorption sites.

Continued growing environmental concerns are providing the impetus for increased demand and usage of vegetable oils in lubricants for many applications. Vegetable oils can offer significant environmental advantages with respect to resource renewability, biodegradability, and adequate performance in a variety of applications (Gawrilow, 2003).

It has been discovered that improved oil field corrosion inhibition may be achieved by employing the inhibitor formulation of the products obtained from fatty acid (Knox and Fischer, 2008). Therefore, the fatty acids present in palm oil may be used be as an inhibitor.

Palmitic acid, or hexadecanoic acid in IUPAC nomenclature, is one of the most common saturated fatty acids found in animals and plants (Beare-Rogers et al., 2001). Its molecular formula is $CH_3(CH_2)_{14}COOH$ or $C_{16}H_{32}O_2$. As its name indicates, it is a major component of the oil from palm trees (palm oil, palm kernel oil, and coconut oil).

Fatty acids and fatty acid methyl esters are probably the most important basic oleochemicals in the oleochemical industry. Fatty acids are used as starting materials for soaps, medium-chain triglycerides, polyol esters, alkanolamides, and many more products. They are derivatives of oleochemicals. Oleochemicals, by their very name, may be defined as chemicals from oil. These could be natural fats and oils, or oils of petrochemical origin. To have a clear distinction, oleochemicals derived from natural oils are termed natural oleochemicals, whereas those derived from petrochemicals are termed synthetic oleochemicals (Richtler, 1983).

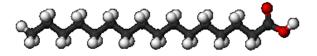


Figure 1: Molecular Structure of Palmitic Acid (courtesy Wikipedia).

Fatty Acid	Soybean	Palm	Rape*	Sunflower	Cotton	Peanut	Maize	Olive	Palmkernel	Coconut	Butter**	Lard	Tallow
Butiric (4:0)* **	-	-	-	-	-	-	-	-	-	-	17	-	-
Caproic (6:0)	-	-	-	-	-	-	-	-	0.2	-	6.4	-	-
Caprylic (8:0)	-	-	-	-	-	0.1	-	-	4	7.1	1.7	-	-
Capric (10:0)	-	-	0.6	0.2	-	-	3.9	7.3	4.3	-	-	-	-
Lauric (12:0)	0.1	-	-	-	0.5	0.7	-	-	50.4	54.1	4	-	-
Myristic (14:0)	0.3	2.5	0.1	-	0.9	0.4	-	-	17.3	17.4	12.8	1.7	3
Palmitic (16:0)	10.9	40.8	5.1	6.5	20	13.7	11.2	11	7.9	6.1	26.6	27.9	33
Stearic (18:0)	3.2	3.6	2.1	4.5	3	2.3	1.8	2.2	2.3	1.6	8.5	13.5	- 24
Oleic (18:1)	24	45.2	57.9	21	25.9	-	25.4	77	11.9	5.1	17	46.7	36
Linoleic (18:2)	54.5	7.9	24.7	68	48.8	47.8	60.3	8.9	2.1	1.3	1.5	10.2	2
Linolenic (18:3)	6.8	-	7.9	-	0.3	29.2	1.1	0.6	-	-	-	-	1
Arachidic (20:0)	0.1	-	0.2	-	-	1.3	0.	-	-	-	-	-	-
Gadoleic (20:1)	-	-	1.0	-	-	1.2	-	0.3	-	-	-	-	-
Behenic (22:0)	0.1	-	0.2	-	-	3	-	-	-	-	-	-	-
Erucic (22:1)	-	-	0.2	-	-	0.1	-	-	-	-	-	-	-
Saturated	14.7	46.9	8.3	11	25	21.7	13.2	13.2	86	93.6	81.5	43.1	- 39
Unsaturated	85.3	53.1	91.7	89	75	78.3	86.8	86.8	14	6.4	18.5	56.9	61

Table 1: Typical Fatty Acid Profiles of Various Oils and Fats (weight percent).

Iso-fatty acids were added to the fatty acids with the same number of carbon atom:

••• -(nn:x) means a fatty acid with nn carbon atoms and x double bonds.

The natural oleochemicals are obtained from natural oils with the least change in the structure of the carbon chain fraction. In contrast, synthetic oleochemicals are built up from ethylene to the desired carbon chain fraction or from oxidation of petroleum waxes.

The advantages of natural oils as base fluids in lubricants and inhibitors are perceived to be the following:

- 1. Non-toxicity
- 2. Biodegradability
- 3. Resource renewable
- 4. Affordable application cost
- 5. Good lubricity
- 6. High viscosity index

Chemistry of Palm Oil

Like all oils, triacylglycerols (TGs) are the major constituents of palm oil. Over 95% of palm oil consists of mixtures of TGs, that is, glycerol molecules, each esterified with three fatty acids. During oil extraction from the mesocarp, the hydrophobic TGs attract other fat- or oil-soluble cellular components. These are the minor components of palm oil such as phosphatides, sterols,pigments, tocopherols, tocotrienols, and trace metals. Other components in palm oil are the metabolites in the biosynthesis of TGs and products from lipolytic activity. These include the monoglycerols (MGs), diglycerols (DGs) and free fatty acids (FFAs).

The fatty acids are any of a class of aliphatic acids, such as palmitic (16:0), stearic (18:0) and oleic (18:1) in animal and vegetable fats and oils. The major fatty acids in palm oil are myristic (14:0), palmitic, stearic, oleic and linoleic (18:2).5 The typical fatty acid composition of palm oil from Malaysia is presented in Table 2. Palm oil has saturated and unsaturated fatty acids in approximately equal amounts (Kalyana Sundram, 2010).

Crude palm oil has a rich orange-red color due its high content of carotene (700 – 800 ppm). Carotenoids are the precursors of vitamin A, with -carotene having the highest provitamin A activity. Most of the minor components found in the unsaponifiable fraction of palm oil are sterols, higher aliphatic alcohols, pigments and hydrocarbons.

The aim of this work is to evaluate the suitability and credibility of palm oil as one of the major inhibitor formulations against ductile iron and mild steel corrosion. This is part of the major efforts to synthesize effective corrosion inhibitors for oil and gas fittings, equipment and pipelines transporting multiple-phase systems.

Fatty acid	Mean	Range	Standard
chain length		observed	deviation
12:0	0.3	0 - 1	0.12
14:0	1.1	0.9 – 1.5	0.08
16:0	43.5	39.2 – 45.8	0.95
16:1	0.2	0 – 0.4	0.05
18:0	4.3	3.7 – 5.1	0.18
18:1	39.8	37.4 – 44.1	0.94

Table 2: Typical Fatty Acid Composition (%) of Palm Oil.

Element	Fe	Cr	Ni	V	Mn	Мо
%Wt	81.83	0.77	15.43	0.34	1.51	0.02

Table 4: Chemical Composition of Mild Steel.

Element	Fe	Cr	Ni	V	Mn	Мо
%Wt	91.90	0.69	6.84	0.20	0.00	0.35

MATERIALS AND METHODS

The ductile iron used for this research work was produced at EMDI Akure Nigeria from rotary furnace by using by using green sand moulds and spectrometrically analyzed using EDX-XRF at EMDI Akure.

Thirty two rectangular coupons of 100mm x90mm x 90mm were cut from ductile iron and same numbers of coupon were cut from the Mild steel of 200mm x 200mm x 0.5mm using cutting saw and thread was tied to each of them for easy suspension in the various media. Equal proportion of water was used to prepare the fresh water, salt water and the basic media.

Each coupon was mechanically polished using emery papers with 240, 320, 400, and 600 grits to remove scaling, surface contaminants and oxide film on the surface of the coupons. This was followed by degreasing with acetone to remove grease, dirt or dust to avoid error in experimentation and subsequent corrosion rate measurement. The degreased coupons were then air-dried and stored in a dessicator prior to exposure to avoid reaction with the environment.

For salt solution, 1500cm³ of water was weighed in sensitive digital balance and the equivalent weight was recorded. This is done to know the percentage of salt to be added in order to simulate the seawater environment (i.e., 3.5%wt).

For the basic environment, 1M NaOH solution was prepared. After the corrosive media have been set up, palm oil was applied to each of the tied coupon and then lowered into each medium. At the interval of seven days, each coupon was removed and weight loss was determined. The experimentation lasted for a period of fifty six (56) days. The microstructure of each coupon before and after exposure was examined using software – driven optical microscope. The procedure was in accordance with ASTM standards (1993). The corrosion rate of each coupon was calculated. The formula used for calculating corrosion rate in mils per year is:

Corrosion Rate (mpy) = $\frac{534 \text{ W}}{\text{D}^{*}\text{A}^{*}\text{T}}$

where W is weight loss in milligrams, D is the density of the coupon in grams/cm³, A is the exposed area in square inches, and T is the exposure time in hours (Fontana, 1987).

One extra coupon was cut out from the ductile iron and mild steel to serve as control.

RESULTS AND DISCUSSION

Figures 2 and 3 show the corrosion of ductile iron and mild steel in 1M NaOH inhibited by palm oil. It was observed that there was no noticeable corrosion attack on the coupons within the period of experiment. This was due to the effective corrosion inhibitive property provided by the palm oil. Physical observation showed that, there was formation of thick stubborn protective layer around each of the coupons. This phenomenon will prevent anodic dissolution of the coupons in reacting to the medium. In other words, there was no appreciable electron loss which would have caused appreciable corrosion. This was similar to the Betaine fluid which was tested with a conventional film forming corrosion inhibitor (Jokinen, 2003).

From the micrographs, Plates 1 and 2 show the DI and mild steel coupon before to any of the media.

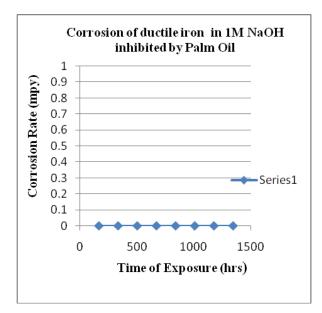


Figure 2: Corrosion of DI in 1M NaOH Inhibited by Palm Oil.

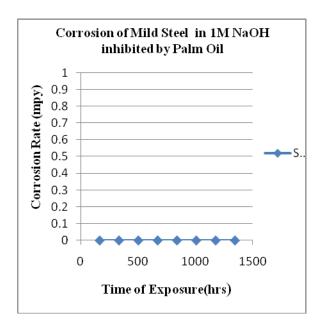


Figure 3: Corrosion of Mild Steel in NaOH Inhibited by Palm Oil.

In fresh water inhibited by palm oil, it was observed that initially high attack (5.5 mpy) on DI coupon after first 168hrs (1 wk) was followed by sharp drop to almost zero corrosion (Figure 4). This observation in Figure 4 almost remained constant until after 672 hrs (4 wks) when there was a little rise in corrosion. After this, the corrosion rate was unstable throughout the experimentation (7 wks). This may not be unconnected with inconsistency in air velocity, dissolved contaminants and constituents of the medium. The interference caused by different species individually or combined may be major player. However, for mild steel coupons (Figure 5), the initial almost zero corrosion observation suddenly rose 0.6 mpy after 672 hrs (4 wks) and followed by a sharp drop and rise. This may be attributed to the same reason highlighted above.

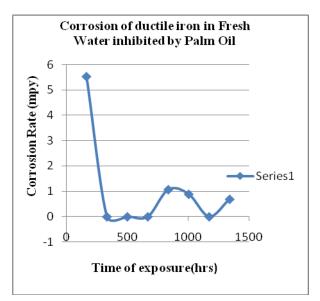


Figure 4: Corrosion of DI in Fresh Water Inhibited by Palm Oil.

With DI coupons soaked in palm oil before exposure to air (Figure 6), it was observed that there was no noticeable corrosion throughout the experiment (7wks). This was due to the thick passivating coating formed by palm oil on the coupons. Figures 7 shows the corrosion of mild steel in air inhibited by palm oil.

It was observed that there was intial sharp rise in corrosion attack (3 mpy) on the coupon followed by sharp drop to almost no noticeable corrosion attack for the rest of the experimentation period. The initial high corrosion rate could be caused by human error as a result of not applying the palm oil all over the coupon before exposure. It could also due to sudden harsh environmental condition prevalence within the first 168 hrs (1 wk), such as

The Pacific Journal of Science and Technology http://www.akamaiuniversity.us/PJST.htm heavy rainfall washing off the palm oil on the coupon.

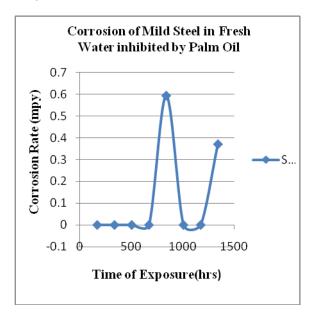


Figure 5: Corrosion of Mild Steel in Fresh Water Inhibited by Palm Oil.

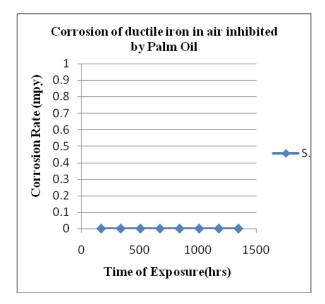
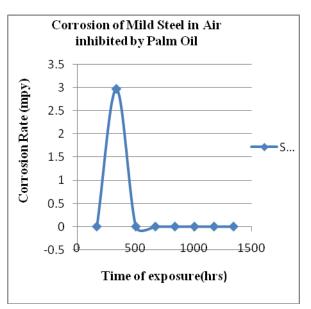
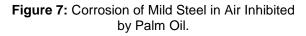


Figure 6: Corrosion of DI in Air Inhibited by Palm Oil.

Figures 8 and 9 show the corrosion of DI and mild steel in simulated seawater inhibited by palm oil. It was observed that the initial low corrosion rate suddenly shot up after 504 hrs (3 wks) to 2.2 mpy for DI and 220 mpy for mild steel; and then followed by a drop and rise.





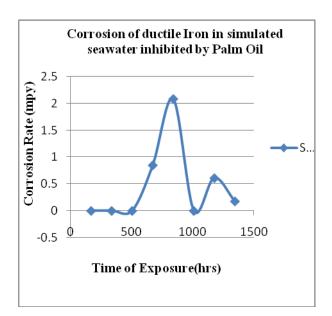


Figure 8: Corrosion of DI in Simulated Seawater Inhibited by Palm Oil.

This unstable behaviour in both DI and mild steel coupons could be due to the inhomogeneity of the medium and non-uniform coating of the palm oil on the coupons. The microstrucures are shown in the plates below.

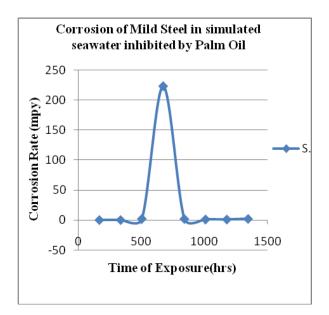


Figure 8: Corrosion of Mild Steel in Simulated Seawater Inhibited by Palm Oil.

Micrograph Plates (X200)



Plate 1: DI Before Exposure.

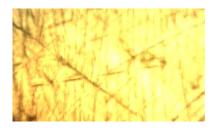


Plate 2: Mild Steel Before Exposure.

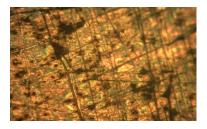


Plate 3: DI in NaOH after 7wks.

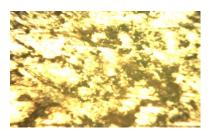


Plate 4: Mild Steel in NaOH after 7wks.

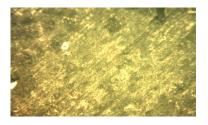


Plate 5: DI in Fresh Water after 7wks.

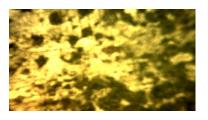


Plate 6: Mild Steel in Fresh Water after 7wks.

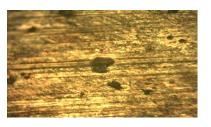


Plate 7: DI in Air after 7wks.

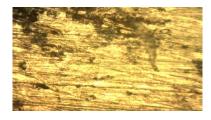


Plate 8: Mild Steel in Air after 7wks.

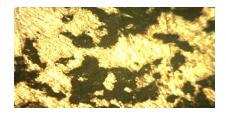


Plate 9: DI in Simulated Seawater after 7wks.

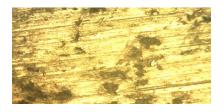


Plate 10: Mild Steel in Simulated Seawater after 7 wks.

CONCLUSION

- 1. This research indicates that the palm oil is a good raw material for preparation of "environmentally friendly" corrosion inhibitors. Also, palm oil, being non-toxic, has met one of the stringent requirements for corrosion inhibitors and its application.
- 2. Based on these experiments and performed calculations of corrosion rates, we have shown that palm oil has demonstrated high inhibition efficiency especially on corrosion of ductile iron in 1M NaOH and air. It has also shown reliable protective shield against the corrosion mild steel in 1M NaOH.

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SUGGESTED CITATION

Daniyan, A.A., O. Ogundare, B.E. AttahDaniel, and B. Babatope. 2011. "Effect of Palm Oil as Corrosion Inhibitor on Ductile Iron and Mild Steel". *Pacific Journal of Science and Technology*. 12(2):45-53.

