Maghrebian Journal of Pure and Applied Science
ISSN : 2458-715X
http://revues.imist.ma/?journal=mjpas&page=index
https://doi.org/10.48383/IMIST.PRSM/mjpas-v7i2.26742

Tribological Characterization of Lubricants Oil with Nano Concentrated Highly Ash Egyptian Petroleum Coke and Calcium Palmitate

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Received 14 October 2021, Revised 01 December 2021, Accepted 20 December 2021

Abstract. The effects of calcium palmitate (CAP) alone and in conjunction with petroleum coke were studied after flotation processes on wear and corrosion of steel in base oil. The results of the investigation demonstrated that a synergism effective as anti-wear and inhibitor of corrosion between calcium palmitate and petroleum coke. The effects of calcium palmitate (CAP) alone and in conjunction with other minerals dispersed in petroleum coke were investigated. As the results reduce the corrosion rate of steel and it's wearing. Photographic analysis of steel inhibited steel reveals that it is cleaner than blank steel. X-Ray photoelectron spectroscopy (XPS) analysis confirmed the adsorbed film and its composition. The results show that wear resistance increased by about 80% and anticorrosion performance increased by about 85%. These findings were explored in terms of the CAP's adsorption isotherm at solid-liquid interface. Also, the XPS confirm that the synergistic action of mixed CAP and petroleum coke with highly ash content after flotation processes

Key words: lubricating oil, additives, petroleum coke, flotation, antiwear, anticorrosion.

1. Introduction

The activated Si-C-Ni composite powder was mixed with base lubricating oil with different ratio 1–4% by weight in the prescience of dodecyl benzyle triethanole ammonium ethoxylate bromide with 20-unit ethylene oxide as wetting and dispersing agent was studied early by Omar [1].

Dibutyl 3,5-di-t-butyl 4-hydroxy benzyl phosphate, triphenyl phosphorothionate, sulfurized octadecanoic, sulfurized docosanoic acid, triethylenetetramine zinc dialkyldithiophosphate, and poly alkylmethacrylate are some of the most popular additives used in lubricating oil formulations [2–4]. Pour point depressants, dispersants, anti-wear agents, and anti-corrosion agents are all functions of these additives. Lubricant oil creates a fluid layer between the touching mating surfaces, separating them. Metal-to-metal interaction is reduced by the fluid film. The proper selection of lubricants is critical in order to

reduce friction and material wear. Nanoparticles have a large surface area per volume, which means they have a lot of surface energy. The rate of sedimentation is affected by agglomeration of the nanoparticles, and wear loss occurs. The nanoparticles' dispersion stability is important.

Stability implies that at a large rate, the particles do not accumulate. For an efficient nano lubricant formulation, a stable suspension is a prerequisite. Metal nanoparticle additives, Metal Oxide nanoparticle additives, Sulphide nanoparticle additive, Nitride nanoparticle additive, Carbon based nanoparticle additive, and nanocomposite based additives are all categorized by chemical composition. Au, Ag, Cu, Ni, Fe, and Zn are metal nanoparticle additives. These nanoparticles are added to base oils to improve their efficiency. To enhance the properties of polymers, various fillers such as glass and carbon fibers, kaolin, talc, and mica are widely used. Polyamide has been shown to have a higher wear resistance as compared to other polymers when sliding against a steel counterpart [5–6].

The tribological output of lubricating oil containing nanoparticles of highly concentrated heavy metal oxide of petroleum coke after flotation processes with calcium palmitate (CAP) additive is investigated in this paper under various conditions. CAP adsorption at interfaces is essential in a variety of physicochemical processes. The mechanism of such adsorption has been the subject of intense research and to determine the significant thermodynamic parameters.

Also included in this research was the preparation of CAP for use as an anti-wear and anti-corrosion coating for carbon steel. XPS were used to examine the adsorbed film. The Frumkin adsorption isothotherm was used to investigate the CAP adsorption isotherm on petroleum coke.

2. Experimental

Palmitic acid is a form of fatty acid. 1 mol of NaOH (40 g) was dissolved in hot water and added to it with stirring. After cooling, a 73.5 g aqueous CaCl2 solution was added with stirring. The result was a white precipitate that was filtered, washed, and dried. The yield was about 80% and degree of purity about 93%. The following table confirms the prepared compound.

Table 1. Elemental analysis of the prepared calcium palmitate

Calcium palmitate					
Carbon, %		Hydrogen, %		Oxygen, %	
Calc.	Found	Calc.	Found.	Calc.	Found
384	383.6	62	62	64	64.11

Mass spectroscopy is a technique for determining the chemical composition of a substance A molecular ion peak at m/z 550 was visible in the mass spectrum of the synthesized calcium palmitate.

The nuclear magnetic resonance (HNMR) confirmed the synthesized calcium palmitate in its chemical structure. While Infrared spectroscopy shows that, the absorption due to the OH group occurs in the region of 3000–50 cm^{-1}. The COO^- stretching vibration fatty acids occur in the region of 1700–1720 cm^{-1} bending of OH^- group appear near 920 cm^{-1}. The complete disappearance of the absorption bands was at 1700 cm^{-1}.

Feeds.

Table 2. The following table lists the physicochemical properties of paraffinic base oil

Physicochemical properties of the c base oil

Properties	Base oil	Test
Density (g/ml) at 15.5°C	0.8958	D. 1298
Refractive index nD^{20}	1.4955	D. 1218
ASTM color	4.5	D. 1500
Kinematic viscosity cSt		
at 40°C	15.76	D. 445
at 100°C	27.15	D. 455
Pour point, °C	16	ASTM D 97
Molecular weight	560	GPC
Total paraffinic content, wt. %	33.5	Urea adduction
Carbon residue content, wt. %	1.5	ASTM D524
Total aromatic, wt. %	45	
Nitrogen content, wt. %	4.2	

Petroleum coke after flotation and purification are separated to concentrate and tail. The optimum conditions and complete chemical analysis are published by author early [7]. In this paper we will use tail fraction which represent about 10 wt. % of feed. The complete chemical analysis of tailing fraction of the petroleum coke was shown in the following table 3 [7].

Table 3. Complete chemical analysis of residue petroleum coke after flotation processes

Constituents	Tail, wt. %
Ash	12.4
Nitrogen	2.1
Fixed carbons	71.7
Sulphur	4.1
Metal content, ppm	
Ni	1690
V	1000
Fe	2000
Si	17500
Co	Trace
Mo	Trace
Co	1060
Cu	83
Ti	Trace

Ca Cr Na	Trace Trace

Corrosion Test.

A 50 mm long carbon steel specimen was embedded in paraffin oil with and without calcium palmitate. After 24 hours, the specimens were demoded, and all samples were removed from the solution, washed with petroleum ether, and dried. Following that, the specimen was dried and measured. The efficacy of the inhibitor was estimated from the weight loss using the following equation (1).

$$\text{Percentage efficiency of inhibitor} = [(W_0 - W) / W_0] \times 100$$

Where W_0 represents the average final weight (in mg) of copper embedded in liquid, and W represents the average final weight (in mg) of copper embedded in inhibited samples.

Samples of petroleum coke (tail fraction) (1.000 g) were distributed in 50 ml of calcium palmitate dissolved in petroleum ether in small vessels that could be tightly sealed with appropriate caps. The suspension present therein was continuously stirred.

Samples of petroleum coke (tail fraction) (1.000 g) were dispersed in 50 ml of calcium palmitate dissolved in petroleum ether in small vessels that could be tightly enclosed with appropriate caps. To achieve equilibrium, the suspension stored therein was continuously stirred. After that, the suspension was filtered, and the caked precipitate was dried. The isotherm of adsorption was calculated for various concentration of additive CAP.

The chemical features of the surfaces of the experimental samples were examined by (XPS) thermo scientific (K-Alph= K_α). It was used to investigate the prepared nanomaterial as well as provides quantitative elemental identification and valuable information on the chemical state of materials, including chemical bonding.

3. Results and discussion

3.1. Adsorption isotherms.

Figure 1 shows the calcium palmitate adsorption isotherms onto petroleum coke fraction at 30, 40, and 50°C.

The isotherms shown are clearly analogous to the Frumkin adsorption isotherm. When relatively low concentrations of calcium palmitate were used in the oil process at their critical micelle concentration, equilibrium adsorption was achieved. At equilibrium, 0.2 m.mol of water is adsorbed.

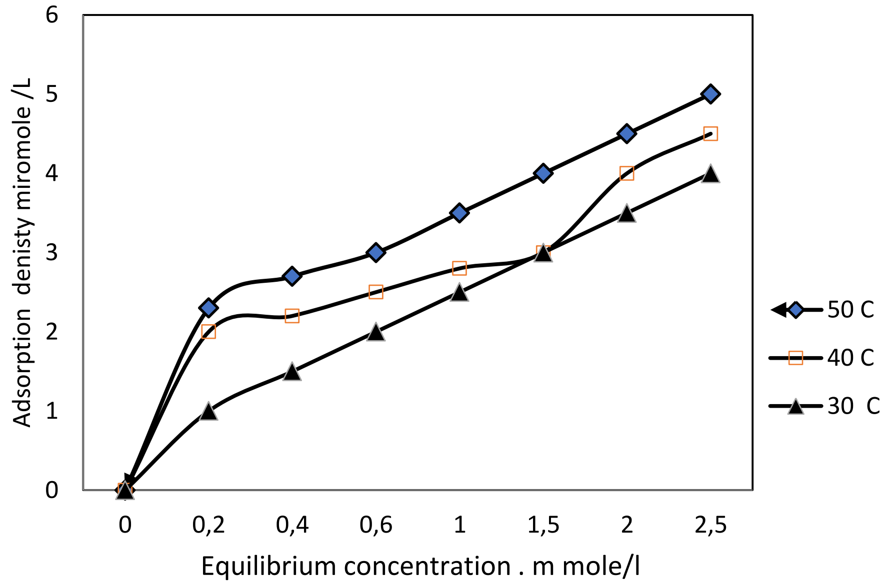

Figure 1. Adsorption isotherm for CAP on petroleum coke.

Since calcium palmitate prefers adsorption on oil phase and metal surfaces of steel or contact surfaces, the adsorbed amount did not display a continuous increase after critical micelle concentration, indicating that adsorption did not occur after the monolayer was completed.

Analysis of adsorption data gives the free energy of adsorption process at petroleum coke surface. A plot of standard free energy $-\Delta G^0$ against degree of surface coverageθ, for the petroleum coke is shown in Fig. 2.

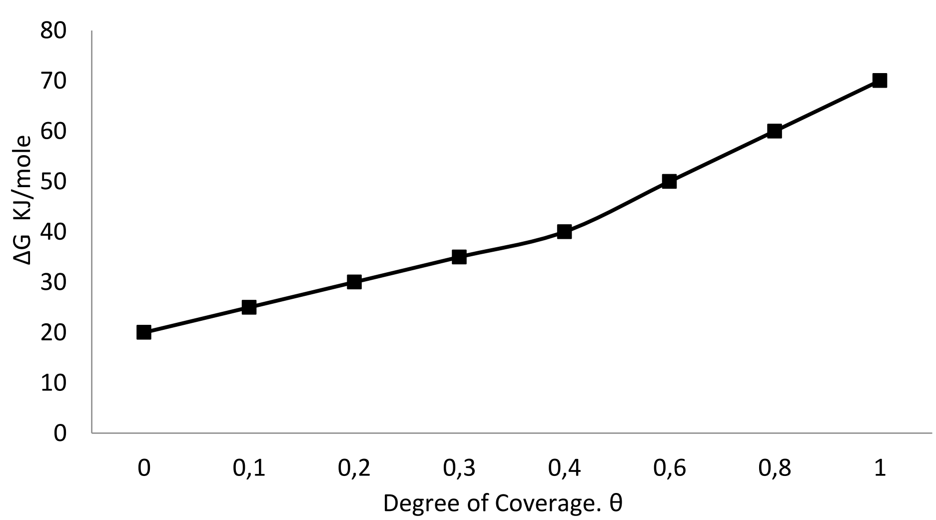

Figure 2. Effect of coverage on the adsorption free energy.

It is clear the adsorption on petroleum coke surface take place by free molecule ion and reach maximum at its critical micelle concentration of dissolved CAP which is known CMC. The molecules of CAP have heads and tail, it accumulates head with head and tail with tail forming micelle with the best reduction of the surface tension interface. This indicates that calcium palmitate adsorption onto petroleum coke is the product of physical adsorption, which is supported by the measured free energy of adsorption.

3.2. XPS analysis.

XPS is a well-known surface analysis technique that has been used to investigate changes to the surface of petroleum coke. It should be noted that after adsorption, the sample's oxygen content increased significantly while the carbon content decreased. The presence of calcium palmitate on the surface of petroleum coke may explain these changes. The spectra show a peak at 284.8 eV appears in the C1s spectrum and this may be assigned to the C–C bond. In the C1 spectrum, three peaks are assigned to the C=O bond at 290.0 eV, the C–O bond at 286.5 eV, and the C–C bond at 284.8 eV, respectively. As a result, these findings point to the presence of C–O and C=O bonds on the surface of petroleum coke. It should be noticed that the peak area of the C–O bond (55.6%) was greater than that of the C=O bond (8.0%), indicating that the calcium palmitate molecule interacts.

Figure 3 shows the wear loss/area (wear rate) of oil samples under different load and sliding time. It clears that, the wear resistance increases with increase ratio of petroleum coke with adsorbed CAP. The dispersed petroleum coke enhances degree of wear resistance to 80%. The author thinks the additive molecule and dispersed petroleum coke adsorbed on the surface to form adsorbed layer between contact surfaces.

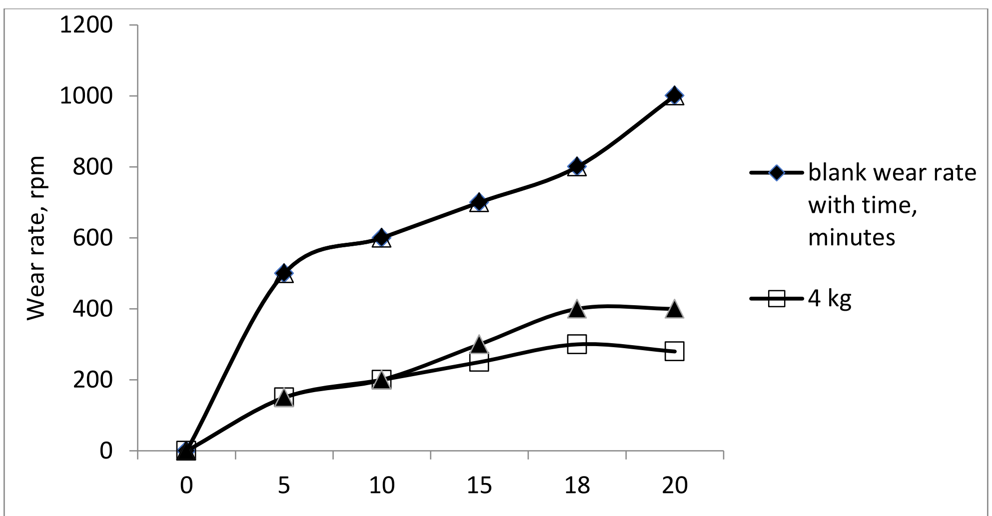

Figure 3. Effect of variation of wear rate with sliding time (min).

Figure 4 showed that CAP has inhibition efficiency 85% in oil and reach maximum near its CMC, this can have attributed to adsorption CAP on steel surface forming barrier layer. This result confirms degree of adsorption CAP and its surface coverage increase until CMC which is in agreement with above published elsewhere [8].

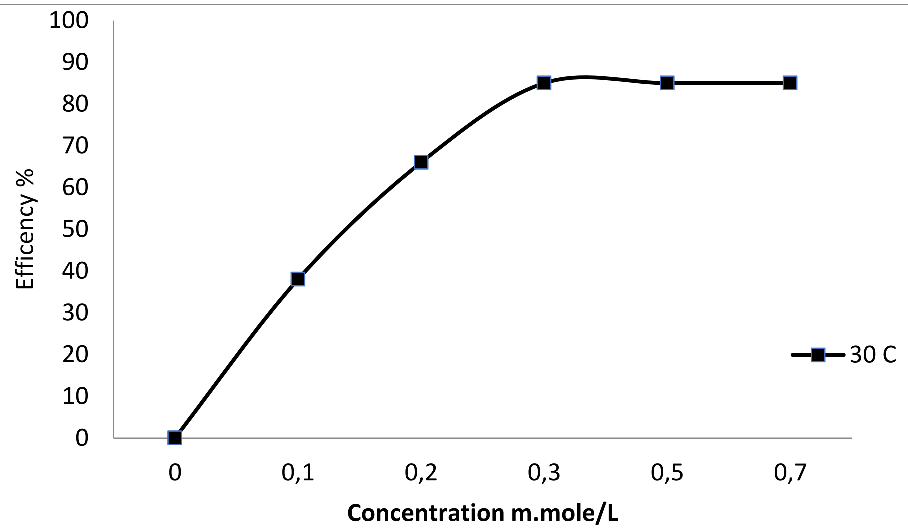

Fig. 4. Efficiency of CAP of inhibition corrosion of Carbon Steel at 30°C.

4. Conclusion

The adsorption behavior of CAP onto petroleum coke and steel increased enhance wear resistance until its CMC. Also weight loss technique was proved efficiency of calcium palmitate adsorbed onto steel surface depend on its CMC. Furthermore, XPS analysis revealed that C–C bonds were the primary connection between the calcium palmitate molecule and the surface of petroleum coke

It can be concluding that there is a synergism between CAP and petroleum coke with highly ash content as anti-wear and anti-corrosion resistance of lubricating oil toward contacting surface which forming stable film.

This study has shown that petroleum coke after flotation process and beneficiation from silica and heavy metals give two parts concentrate (90%) and tail (10%). The purity of concentrate reaches 99.8% while the residue tail contains all heavy metals and silica. (a by-product of heavy oil cracking in petroleum Suez company - Egypt about 3 million ton/year). The concentrate was used in production graphite electrode, while the tail will use in this paper to find outlet for using it instead of graphite or nano composite as anti-wear. Petroleum coke tail has a high surface area and more effective in anti-wear. The

adsorption behavior of CAP onto petroleum coke and steel increased enhance wear resistance until its CMC. Also weight loss technique was proved efficiency of CAP adsorbed onto steel surface depend on its CMC. In addition, XPS analysis established that C–C bonds provided the main linkage between CAP and the petroleum coke surface. The synergism between CAP and petroleum coke with highly ash content as anti-wear and anti-corrosion resistance of lubricating forming stable film

References

1. Omar AMA (2019). Wear Resistance of Lubricating Oil Contains Nano Composite Ni Si- C and Dodecyl Benzyl Triethanol Ammonium Bromide Ethoxylated with 20 Unit of Ethylene Oxide, *J. Miner. Met. Mater. Eng*. 5: 33–37.
2. Gurram, R, Al-Shannag, M, Knapp S, Das T, Singsaas E, and Alkasrawi M (2016) Technical possibilities of bioethanol production from coffee pulp: A renewable feedstock, *Clean Technol. Environ. Policy*18: 269–278.
3. Karmakar G, Ghosh, Sharma B K (2017) Chemically Modified Vegetable Oils to Prepare Green Lubricants, *Lubricants* 5, 4. 44: 17
4. Kalam, M.A., Masjuki, H.H., Shahabuddin, M., and Mofijur, M., Tribological characteristics of amine phosphate and octylated/butylated diphenylamine additives infused bio-lubricant, *Energy Edu. Sci. Technol. Part A: Energy Sci. Res*., 2012, vol. 30, pp. 123–136.
DOI – No.
5. Kukureka S N, Hooke C J, Rao M, Liao, P, and ChenY K (1999) The effect of fibre reinforcement on the friction and wear of polyamide 66 under dry rolling-sliding contact, *Tribology Int* 32: 107–116.
6. Yang, E L, Hirvonen J P and Toivanen RO (1991) Effect of temperature on the transfer film formation in sliding contact of PTFE with stainless steel, *Wear*146: 367–376.
7. Omar A.M.A., Ph. D. Thesis, Ain Shams University, Faculty of Science (1994)
8 Al Sabagh AM, Osman, M, Omar A M.A, and El-GamalI. M (1996) Organic corrosion inhibitors for steel pipelines in oilfields, *Anti Corrosion Methods and Materials*, 43,. 6: 11–16.

(2021);http://revues.imist.ma/?journal=mjpas&page=index