

Additive properties of saturated very long chain fatty acids in castor and jojoba oils

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Abstract

Tribological and oxidation stability properties of saturated very-long-chain-fatty acids present in castor and jojoba oils have been investigated by the four ball tribosystem, pressure differential scanning calorimetry, optical micrographs and electron probe micro-analysis (EPMA). Test results of the oils additized with eicosanoic and octadecanoic acids in the oils were compared with those of zinc dialkyldithiophosphate (ZDTP). Results showed that eicosanoic and octadecanoic acids possessed better antiwear and lubricity properties compared to the popular ZDTP, though with reduced oxidation stability. EPMA and optical micrographs of worn surface morphology showed that lubricating films formed by these acids were metallic salts whose breakdown was not associated with tribochemical wear surface modification of the mating pairs.

Keywords: Antiwear additives; Extreme pressure additives; Vegetable oils; Very-long-chain-fatty-acids

1. Introduction

Natural vegetable oils were veritable sources of lubricants before the advent of the petroleum industry. Hence, mineral oils possess some desirable lubricating properties at a relatively cheap cost. Recent demands for increased environmental protection and alternative energy have motivated enormous researches into the tribological applications of vegetable oils. Most vegetable oils are known to be composed of triglycerides molecules of fatty acids as in Fig. 1(a), though others like Jojoba oil are composed of fatty acids and fatty alcohols molecules as in Fig. 1(b). The behavior of these natural oils depends largely on the chain lengths, type of bonds, number of monounsaturated and polyunsaturated bonds, among others. Recently, vegetable oil researches have focused on three major aspects: (a) additive properties

derivable from vegetable oils, (b) utilization of vegetable oils as lubricant base-stocks, and (c) bio-diesel applications for alternative energy. Adopting the first approach, Bisht et al.[1] doped mineral oil base stocks with different concentrations (5%, 10%, 20%, 30%, 50%) of jojoba oil as an additive and compared the performance with other additives such as tricresyl phosphate and zinc dialkyldithiophosphate (ZDTP). According to their study, the use of jojoba oil as a blending component in lubricating oil formulations can enhance or impart certain desirable properties such as viscosity index improvement, antirust, anti-foam, antiwear (AW) and friction reduction properties to the blend. These properties, they explained, were derived from the straight, high polarity and longer chain molecules of jojoba which adsorb strongly to metal surfaces. Similarly, Minami and Mitsumune [2] studied the antiwear properties of phosphorus-containing compounds in vegetable oils using peroxide-value measurement and the four-ball wear method. In their study, phosphorus-containing

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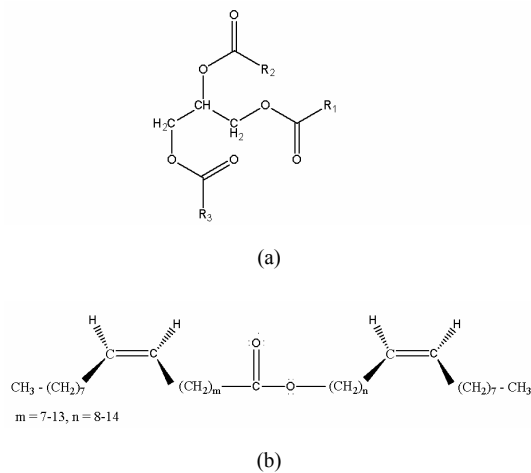


Fig. 1. Typical structure of (a) Vegetable (Castor) (b) and Jojoba oil molecules.

compounds such as ZDTP and dialkylphosphonates improve the antiwear properties of vegetable oils, a characteristic which was attributed to the peroxide value of the base stock, because peroxides decomposed the antiwear additives to less active forms.

Following the second research approach, Jayadas et al. [3] investigated the tribological properties of coconut oil as an environment-friendly lubricant using the four-ball wear tribo-tester and a two-stroke engine test-rig. Their results showed that coconut oil possessed better lubricity properties compared to commercial mineral oil (SAE 20W50), but its antiwear (AW) and extreme pressure (EP) properties were worse. However, an optimal dose of 2%wt ZDTP additive in coconut oil increased its weld load by 1217N (124kg), and reduced wear scar diameter and friction coefficient by 0.20mm and 0.02, respectively. This study adopts the second approach as the first two approaches form the basis of lubrication technology.

Trenkamp et al. [4] described very-long-chain-fatty-acids (VLCFAs) as those with carbon chains greater than C18, and Wormser [5] classified C12-C26, C6-C10, and C2-C4 as long-chain fatty acids, medium and short chain fatty acid, respectively. However, for the purpose of this study VLCFAs were considered to be C18 or more. Eicosanoic and octadecanoic acids are few saturated VLCFAs in castor (*Ricinus communis L.*) and jojoba (*Simmondsia chinensis L.*) oil, which are used as additives in this study to investigate their roles in lubrication properties of biodegradable castor and Jojoba as well as mineral oil base-stocks.

Table 1. Fatty Acid Composition of oil Samples.

Fatty Acid (FA)			Castor ^[20]	Jojoba ^[21]
Common name	Chain length	Melting point		
Palmitic	C16:0	63.1	1.0	1.08
Stearic	C18:0	69.6	1.0	< 0.3
Dihydroxystearic	C18:0 + 2(O)	133.0	0.7	-
Oleic	C18:1	13.5	3.0	10.1
Ricinoleic	C18:1 + (O)	5.5	89.5	-
Linoleic	C18:2	-5.0	4.2	-
Linolenic	C18:3	-11.0	0.3	-
Arachidic	C20:0	75.4	0.3	-
Gadoleic	C20:1	20.0	-	72.5
Erucic	C22:1	80.0	-	14.8
Nervonic	C24:1	34.0	-	1.42

Table 2. Physico-chemical Properties of Oil Samples and ZDTP.

Sample	Physico-chemical Properties				
	Viscosity (v) 40°C, cSt	Viscosity (v) 100°C, cSt	Viscosity Index (VI)	Density, (ρ) 27°C, g/cm ³	TAN, mgKOH/gm
Castor	251.49	19.01	84	0.958	1.55
Jojoba	24.94	6.67	238	0.860	0.15
Mineral	63.41	8.81	113	0.858	0.00
ZDTP	123.32	9.84	32	1.089	> 50

2. Experimental details

2.1 Samples and reagents

Non-additive castor, jojoba and paraffin-base mineral oils were used as base-stocks. Eicosanoic acid, octadecanoic acid and zinc dialkyldithiophosphate (ZDTP) were used as additives in this study. The fatty acid compositions of the base-stocks are shown in Table 1, while the physico-chemical properties of base-stocks and ZDTP were determined as shown in Table 2 by using relevant ASTM standards. The compositions in Table 1 differ slightly from some published data of Lawate et al. in Booser [6] due to the methodological differences in gas chromatography, mass spectrometry, etc., but these differences are negligible.

2.2 Equipment and materials

EN31 chrome alloy steel balls of 12.7mm diameter and 64HRC were used on the four-ball wear (*Shell*)

and four-ball extreme pressure (*Shell*) testers. Dana-Loadcell, signal conditioner (*2310 Vishay*) and Data Acquisition module were used for friction measurement in the four-ball wear tester as shown in Fig. 2. Optical microscope was used for wear scar diameter measurement. Reichert MetaPlan-2 imager with Toshiba camera logged to a computer was used to obtain wear scar optical micrographs. Viscosity tests were performed with cannon viscometers (*C300 and C450*) in a Seta KV-8 viscometer bath. Acid number tests were performed with TAN tester (*AS-KI-101, Kittiwake UK*). Pressure differential scanning calorimeter, PDSC (*DSC-204, Mettler-Germany*) was used for oxidation stability tests, while the field-emission electron probe micro-analyzer, FE-EPMA (*JXA-8500F, Jeol-Japan*) with fully automated computer controlled systems was used for worn surface analysis.

2.3 Procedures

Viscosity and viscosity index (VI) tests were performed to ASTM D445 and ASTM D2270 standards, respectively. ASTM D4172 procedure was used for four-ball wear tests except for the modification in friction force data acquisition instrumentation as in Fig. 2, and ASTM D2783 standard procedures were utilized for EP tests. All friction data were obtained at amplifier gain-1000 to give a load-cell calibration sensitivity of 2.3712mV/gf and at signal capture rate of 10s. PDSC tests were performed by adopting ASTM D6186 standard procedures with uncovered Aluminum pan under isothermal conditions at 150°C and 10°C/min heating rate.

Before each test the balls were cleaned in hexane for 20-minutes. Tests were performed at temperature $T = 75^{\circ}\text{C}$, load $W = 40\text{kg}$, duration 60-minutes and sliding velocity 0.225 or 0.465m/s. After wear scar diameter measurement, the balls were washed with hexane and stored in silica-gel dried space for optical micrograph imaging and EPMA surface analyses.

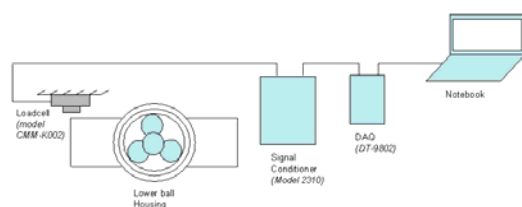


Fig. 2. Instrumentation for friction measurement.

3. Results and discussions

3.1 Wear

From Fig. 3, octadecanoic acid (C18:0) showed positive effect on wear for the mineral oil at high speed (0.465m/s) but negative effect at low speed (0.225m/s). This is considered to be due to the lower strength of adhesion of ferric stearate lubricant film molecules compared to the increased rheological forces at higher sliding speed, besides surface temperature effects. However, Kong [7] and Bos [8] showed by surface and flash temperature mapping that such speed difference could increase the surface temperatures of the mating pairs to well over 150°C, above the 145°C transition temperatures obtained by Frewings [9] and Bowden and Tabor [10] for C18-molecules in n-hexadecane base-stock. Furthermore, Lansdown [11], [12] indicated that adsorbed films have low shearing displacement. Hence, such wear transition is attributable to either desorption of adsorbed films due to increased surface temperature, shearing displacement of adsorbed films due to their poor shear resistance or both. From Fig. 4(c) eicosanoic acid (C20:0) showed better antiwear behavior compared to C18:0 and ZDTP irrespective of the sliding speed.

From Fig. 4(a), the saturated VLCFAs showed better antiwear behavior than ZDTP in castor oil base-stock, with C20:0 showing better optimal concentration of 1.0%wt compared to 2.0%wt for C18:0. Though the optimal concentration of ZDTP in castor is best (0.5%wt), its stable antiwear property and acidic corrosion observed in surface analysis beyond optimal point overrides this benefit. The increase in wear after the optimal point is due to tribochemical interaction enhancing increased acidic corrosion. Similarly, in jojoba oil (Fig. 4(b)) eicosanoic and

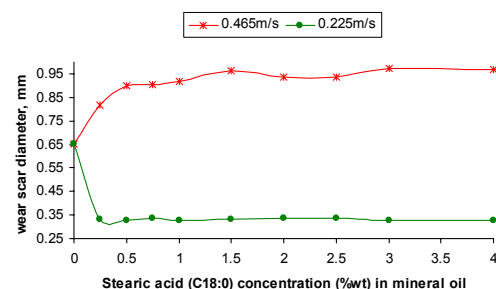


Fig. 3. Antiwear behavior of Octadecanoic acid in Mineral Oil.

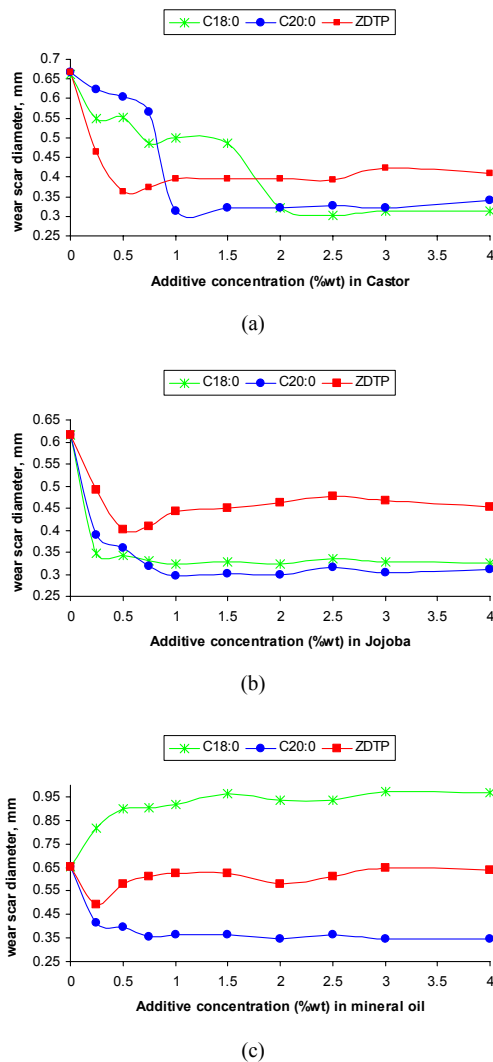


Fig. 4. Antiwear behavior of Additives in (a) Castor, (b) Jojoba and (c) Mineral Oil base-stocks.

octadecanoic acids (C20:0 and C18:0) showed superior antiwear properties compared to ZDTP, with Eicosanoic being better than octadecanoic acid.

3.2 Extreme pressure (EP) properties

Zinc dialkyldithiophosphate showed superior extreme pressure behavior compared to eicosanoic and octadecanoic acids. Whereas there was no considerable increase in the weld load (WL) of the samples with the use of eicosanoic and octadecanoic acids, zinc dialkyldithiophosphate, a renowned EP-additive showed appreciable weld load improvement. Weld load was 140, 185, 195kg with the use of 0, 2, 4%wt

ZDTP in Castor oil; and 112, 160, 176kg for 0, 2, 4%wt ZDTP in jojoba and paraffin mineral base-stocks. The initial-seizure load (ISL) showed appreciable improvement with the use of the VLCFAs. From Table 3, initial-seizure load (ISL) increased from 81–90kg, 81–100kg, 81–190kg corresponding to 11.1, 23.5, 134.6% initial-seizure load (ISL) increment with the use of octadecanoic, eicosanoic and ZDTP, respectively, in castor oil in the range of 0–4%wt additive concentration. Also, from Table 3 initial-seizure load (ISL) increment for jojoba and mineral base-stocks was 27, 27, 138.1% and 28.6, 12.5, 157.1% with the use of octadecanoic, eicosanoic and ZDTP, respectively. In their as-received states castor oil showed the best extreme pressure (EP) properties, compared to other samples. This is understood to be caused mainly by the closer packing of the long-chain-ricinoleic and dihydroxystearic acid molecules derived from their hydroxyl groups, which gives higher topological surface area (TPSA), rather than the chemical reactivity of the films with metal surfaces. Though, Jojoba oil has longer chain gadoleic and erucic acid molecules, these are monounsaturated double bonded VLCFAs that will give less thick and more loosely-packed lubricant films due to the “kink” in their molecular structure. These results corroborate those of Wang et al. [13].

Electrical resistance measurement using alternating current impedance spectroscopy (ACIS) by Wang et al. [13] indicated that metal / lubricant interfacial film thickness was greater (≈ 1000 times) with the use of acid phosphate compared to Oleic acid in mineral base-stock. In their study, (a) 2%wt alkyl acid orthophosphate (acid phosphate) blended into mineral oil, (b) 2%wt oleic acid blended in this same mineral oil and (c) a commercially available engine oil were used between two indium-tin oxide coated iron electrodes. The results showed interfacial film thicknesses of 5.74, 0.002 and 2.63 μm with acid phosphate, oleic acid and engine oil, respectively. Hence, for a lubricant containing oleic acid (VLCFA), which physically adsorbs onto the metals, the film interfacial region was quite thin. But, for lubricants containing chemically reactive additives such as engine oils or a blend containing acid phosphates additive, the film interfacial region was significantly thicker.

In the present study, the superior extreme pressure properties of lubricants blends with these chemically reactive films such as the samples with ZDTP additives could be attributed to this greater interfacial film

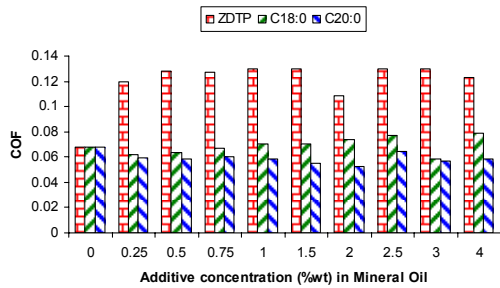


Fig. 5. Effect of Additives on the lubricity (coefficient of friction – COF) of Mineral oil base-stock.

thickness, compared to those with VLCFAs. The initial-seizure load (ISL) increment with the use of VLCFAs is due to increased surface density of the adsorbed molecules as the additive concentration increased.

3.3 Lubricity

From Fig. 5, VLCFAs showed superior lubricity (coefficient of friction - COF) compared to the popular zinc dialkyldithiophosphates additive in mineral base-stock, just like castor and jojoba base-stocks. Eicosanoic acid (C20:0) lubricity was better than that of octadecanoic acid (C18:0) for all base-stocks due to increased carbon chain length. These results agree with those of Jahanmir [14] on the effect of chain lengths on the coefficient of friction and transition temperatures in boundary lubrications. He investigated the effect of oil temperature on friction at 5×10^{-4} ms⁻¹ sliding speed for a homologous series of acids (1%) and alcohols (1%) in n-hexadecane at a constant heating rate. The results showed that below the transition temperatures, longer carbon chain additives exhibited lower friction, and the transition temperatures (thermal stability) characterized by higher friction values which increased with increase in chain length.

3.4 Oxidation stability

From Table 3, the oxidation induction time (OIT) of the oils decreased with increase in concentration of the saturated VLCFAs in all base-stocks. As the concentration of saturated VLCFAs is increased, the amount of free unsaturated acids is therefore decreased. In the as-received and additized states, OIT of paraffin mineral oil was greatest, while that of Jojoba was least due to its higher PUFA composition. Oxidation proceeds through the absorption of oxygen by the fatty acid molecules, to form peroxides.

Table 3. Initial Seizure load and Oxidation Induction Time of different additized samples.

Oil samples	C18:0 in oil			C20:0 in oil			ZDTP in oil		
	0%	2%	4%	0%	2%	4%	0%	2%	4%
Initial Seizure Load - ISL, kg									
Castor	81	90	90	81	100	100	81	170	190
Jojoba	63	72	80	63	80	80	63	150	150
Mineral	56	72	72	56	63	63	56	140	144
Oxidation Induction Time - OIT, mins									
Castor	33.2	28.0	25.6	33.2	9.2	8.7	33.2	38.5	62.6
Jojoba	11.6	7.5	7.3	11.6	8.7	8.0	11.6	51.1	> 80
Mineral	> 60	> 60	> 60	> 60	> 60	> 60	> 60	> 60	> 60

Monounsaturated fatty acid (MUFA) and polyunsaturated fatty acid (PUFA) chains in the triglyceride oil molecule easily absorb oxygen due to their unsaturated bonds, causing a decrease in OIT. These results corroborate those of Gouveia-de-Souza et al. [15] and Erhan et al. [16]. On the other hand, ZDTP has been known to be a good antioxidant additive in mineral oil base-stocks; similar to the natural biodegradable base-stocks observed in Table 3. Two studies [17], [18] reported its antioxidant mechanism to be through the decomposition of peroxides and terminating chain reactions involving peroxy-radicals formed during hydrocarbon oxidation.

3.5 Optical micrographs and worn surface electron probe micro-analysis (EPMA)

Optical micrograph (Fig. 6) of the worn surface morphology with the use of eicosanoic acid (similarly, for octadecanoic acid) in different base-stocks indicates different levels of wear reduction with additive concentration. For the eicosanoic acid additive shown in Fig. 6, the wear volume $V_w = 1.408 \times 10^{-12}$, 0.193×10^{-12} , 0.134×10^{-12} m³ and wear rates $k = 3.589 \times 10^{-15}$, 0.492×10^{-15} , 0.341×10^{-15} m³/N for 0, 0.5, 1.0%wt additive, respectively, in paraffin mineral base-stock. For castor base-stock wear volume $V_w = 1.530 \times 10^{-12}$, 1.039×10^{-12} , 0.074×10^{-12} m³ and wear rates $k = 3.898 \times 10^{-15}$, 2.648×10^{-15} , 0.188×10^{-15} m³/N for 0, 0.5, 1.0%wt C20:0 additive, respectively; while for jojoba base-stock wear volume $V_w = 0.883 \times 10^{-12}$, 0.128×10^{-12} , 0.059×10^{-12} m³ and wear rates $k = 2.250 \times 10^{-15}$, 0.326×10^{-15} , 0.152×10^{-15} m³/N for 0, 0.5, 1.0%wt C20:0 additive, respectively. However, for ZDTP in the different base-stocks, tribochemical damage was observed on the wear surface due to its high acidity (TAN > 50).

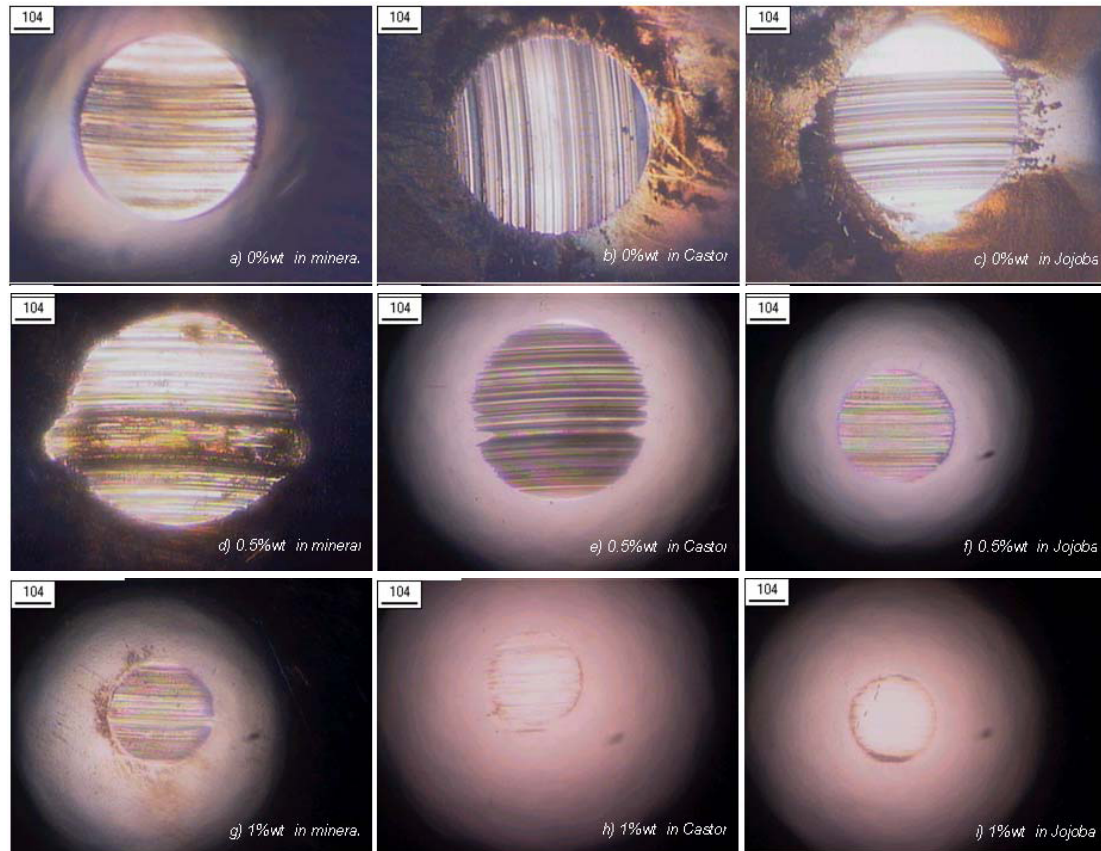


Fig. 6. Optical micrographs of worn surfaces with different concentration (%wt) of Eicosanoic acid in Castor, Jojoba and Mineral oils base-stocks (dimension scales in μm).

The field-emission electron probe micro-analysis (FE-EPMA) basically operates by bombarding a micro-volume of a sample with a focused electron beam (typical energy = 5-30keV) from a field emission electron gun and collecting the X-ray photons hence induced and emitted by the various elemental species. Because the wavelengths of these X-rays are characteristic of the emitting species, the sample composition can be easily identified by recording wavelength dispersive spectra (WDS). EPMA is a scanning electron microscopy (SEM) technique designed to perform quantitative X-ray microanalysis using WDS and energy dispersive X-ray spectrometry (EDS or EDX). Compared to EDS, the sensitivity of WDS is about 100 times more (typically 10 to 50ppm), the spectral resolution is 4-60eV (EDS is about 150eV), the peak to background ratio is as much as 100X greater and >100,000 count per second count rates are possible. These properties result in a much more di-

rect measurement of the X-ray intensities, which translates into higher precision and accuracy. The JEOL FE-EPMA used in this study has 5-WDS and an EDX with fully automated computer controlled systems.

For the quantitative elemental EPMA scanning and mapping some points in and around the wear scar were selected. These regions indicated on the SEM-images (Fig. 7(a), (b), (c), (d)) include: wear scar central point-1, the contact lubricant film inlet point-2 (outside the wear scar and parallel to the sliding direction), another point outside the wear scar but normal to the sliding direction (point-3), and any other point of interest (point-4). In the quantitative analyses, mass concentration is categorized as major in the elemental range $E_c > 10\% \text{mass}$, minor in the range $(1 \leq E_c \leq 10) \% \text{mass}$ and traces for $E_c < 1\% \text{mass}$.

From the quantitative elemental scan for eicosanoic acid in jojoba there was major- $C_c (> 36) \% \text{mass}$ with

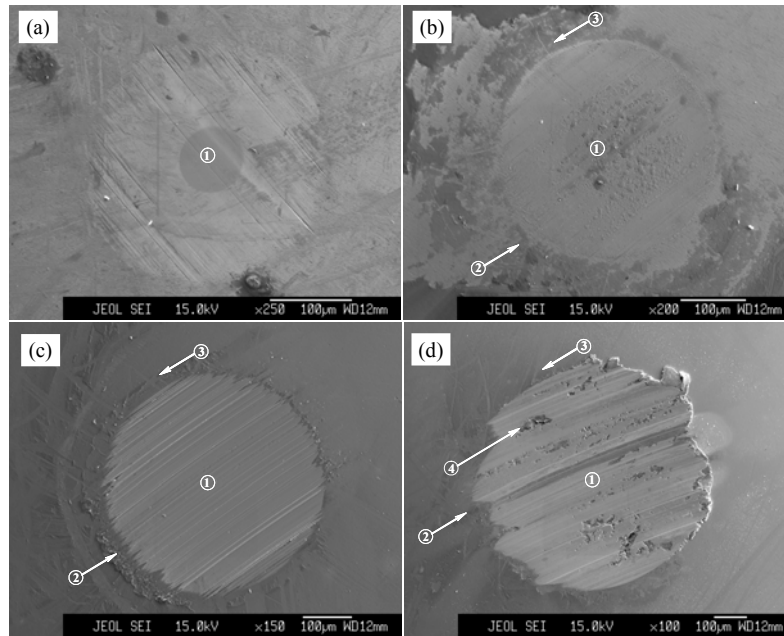


Fig. 7. EPMA-SEM Image of Worn Surface Morphology for (a) 1%wt Octadecanoic acid in Castor oil at $W = 27\text{kg}$ $T = 80^\circ\text{C}$, (b) 1%wt Zinc dialkyldithiophosphate in Castor oil at $W = 30\text{kg}$ $T = 52^\circ\text{C}$, (c) 1%wt Eicosanoic acid in Jojoba oil at $W = 40\text{kg}$ $T = 75^\circ\text{C}$, (d) 2%wt Eicosanoic acid in mineral oil at $W = 40\text{kg}$ $T = 75^\circ\text{C}$ (arabic numerals indicate EPMA-WDS elemental scan points).

minor- O_c at the contact film inlet point-2, and major- C_c with traces- O_c in point-3, but minor- C_c with traces- O_c inside the wear scar point-1. This indicates that the eicosanoic acid films did not diffuse into the mating surfaces, and film formation was not by chemical reaction in the course of wear and friction mitigation but adsorption onto the surfaces. This is further confirmed by the elemental mapping which showed an increase in C-level average of 41% outside the wear scar surface relative to the inside surface, and the EDX-spectra (Fig. 8) of the points showing higher C-counts (> 3500) for point-2 compared to points-1 (C-count ≈ 200) and 3 (C-count ≈ 650). This higher C-count is due to metallic salt deposits outside the contact region as more films converge onto a wedge at the contact inlet, as against less film which diverges from the wedge at the contact exit. Similar situation was observed with octadecanoic acid additive in castor oil base-stock and eicosanoic acid in mineral oil. However, in the case of mineral oil there was severe wear causing pitting (Figs. 9 and 7(d)) on the wear surface (point-4) characterized by highest major C_c ($>65\%$ mass), C-counts > 7000 from EDX-spectrum (Fig. 10), C-level average of 59% from elemental mapping due to films entrapment and deposition in

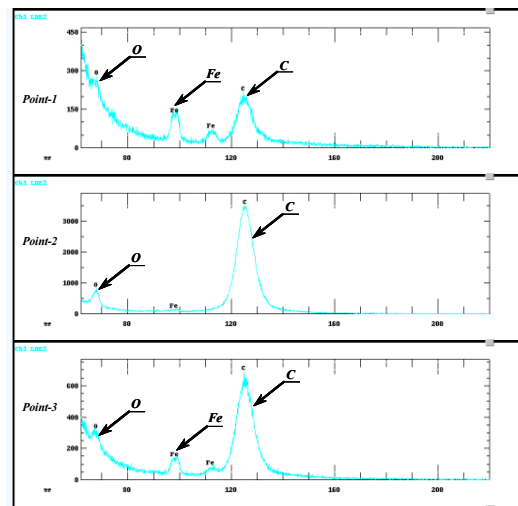


Fig. 8. Worn surface EDX spectrum for Eicosanoic acid in Jojoba oil (scan points refer to the points on Fig. 7(c)).

the wear pits. The contact exit region in Fig. 7(d) also shows gross metal displacement (material flow) due to severe wear. Similarly, in points-1, 2 and 3, there was minor- C_c , major- C_c , and major- C_c ; as well as minor- O_c , minor- O_c and traces- O_c respectively, from the quantitative analyses.

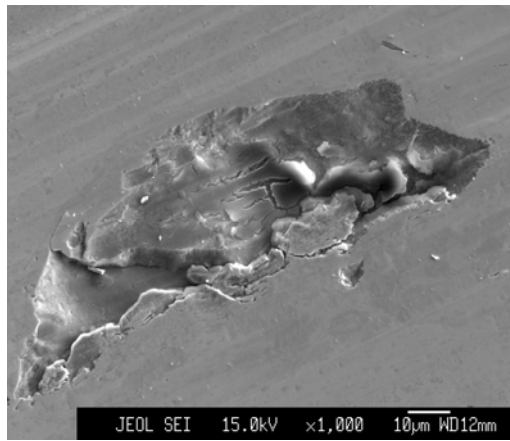


Fig. 9. EPMA-SEM image of a wear-pit (region point-4 of Fig.7(d)) on the wear surface with the use of 2%wt Eicosanoic acid in mineral oil base-stock at $W = 40\text{kg}$ $T = 75^\circ\text{C}$.

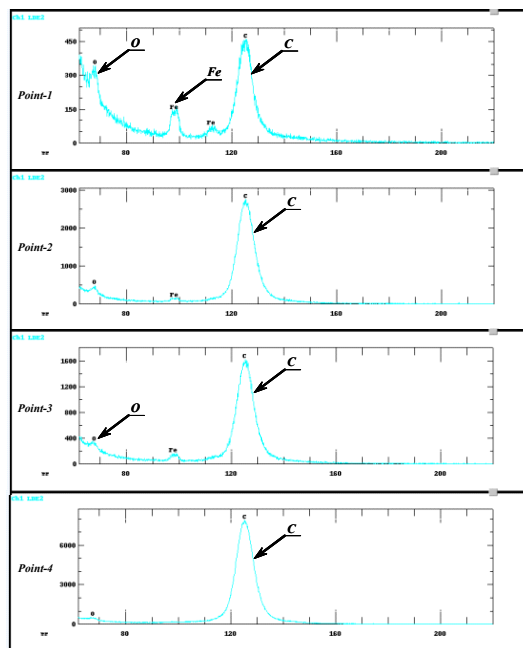


Fig. 10. Worn surface EDX spectrum for Eicosanoic acid in Mineral Oil (scan points refer to the points on Fig.7d).

However, a different mechanism of film formation was observed with the use of ZDTP additive. While the metallic salts were concentrated outside the contact region, ZDTP films consisting of Zn, P, S were diffused into the wear surface as tribochemical reaction products. From the elemental quantitative analysis, there was major- Zn_c , minor- C_c , O_c , P_c and S_c on the mating surfaces (wear surface) but minor Zn_c and O_c , P_c traces and major- C_c outside the wear surface at

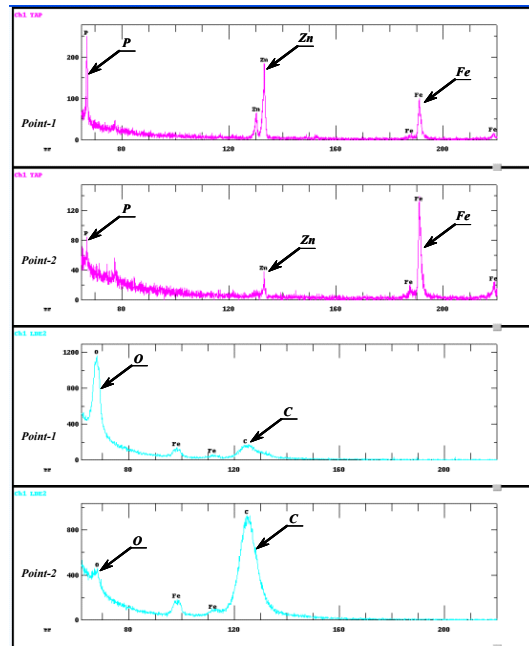


Fig. 11. Worn surface EDX spectrum for Zinc dialkyldithiophosphate (ZDTP) in Castor oil (scan points refer to the points on Fig.7b).

the contact film inlet. This corroborated the Zn, P, O, C-counts on the EDX-spectra for points-1, 2, 3, 4 (Fig. 11). The elemental mapping showed an average of 36, 5, 10, and 14% for C-level, S-level, P-level and Zn-level, respectively (Fig. 12). From the EPMA elemental maps of ZDTP additive in castor oil (Fig. 12), metallic salts (ricinoleates) can be observed as increased concentration of the carbon (C-map) outside the worn surface compared to Zn, P, S-maps). These metallic salts appear as deposits (patches) around the worn surface except in the contact film exit (bottom right point of C-map) region due to the erosive action of the film rheology as lubricant film molecules force their way out of the contact region. Carbon C in this outside point increased to about 12.268% against 2.638% by mass in the worn surface, indicating that whereas the metallic salts (ricinoleates) formed from triglyceride oil molecules reacting with the mating steel surfaces constituted the bulk lubricant film, the additive ZDTP molecules reacted with the mating surfaces to form phosphates, sulfates, etc., films that mitigated against wear. This is further confirmed by the EPMA elemental compositions of Zn, P, S, O, Fe being 11.885, 2.072, 1.389, 7.237, 72.601% on the worn surface and 2.063, 0.414, 0.0, 1.060, 82.303% outside the worn surface, respectively. Though the

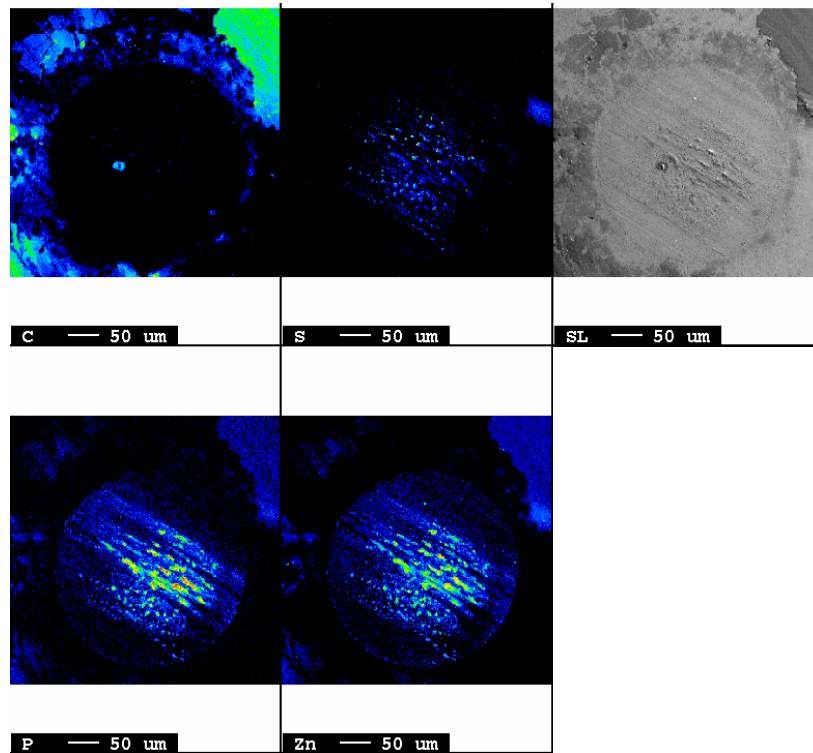


Fig. 12. EPMA elemental Mapping with key elements concentrations increasing from blue to red for Worn Surface morphology of 1%wt ZDTP in Castor oil at load $W = 30\text{kg}$ $T = 52^\circ\text{C}$.

values above are not absolute, they show significant difference compared to the EN31 steel balls composition of 1.0%C, 0.30%Mn, 0.25%Si, 1.5%Cr, 0.2%Ni, 0.05%Mo reported by Ramesh and Gnanamoorthy [19] in their studies of the fretting wear tests of EN24 mating with EN31 steels interfaces. From the EPMA mappings it can be observed that atoms of Zn, P and S modify the surface layer of the steel balls wear scar with the use of ZDTP unlike the VLCFAs additives. These results corroborate those of Tuszynski et al. [17] in which Zn, P and S observed on the wear surfaces were attributed to tribochemical conversion of ZDTP under high contact pressure. They explained that asperity contacts in the four-ball tribosystem caused high surface temperatures and high friction energy which enhanced decomposition by cleavage of the Zn-S and P-S bonds in ZDTP. Subsequently, there is surface layer modification due to the formation of phosphonates, sulfonates, sulfides, etc., and diffusion of Zn, S and P atoms into the surface of the mating pairs.

4. Conclusion

Tribological and oxidation stability properties of very-long-chain-fatty acids (VLCFA) present in the castor and jojoba oils have been investigated. Results showed that VLCFAs (eicosanoic and octadecanoic acids) possessed better antiwear and lubricity properties compared to the popular ZDTP, though with reduced oxidation induction time (OIT) of samples. The reduced OIT of Castor and Jojoba oils additized with VLCFAs could be enhanced with ZDTP. The extreme pressure property improvement of castor and jojoba oils with the use of VLCFAs was less than that of ZDTP due to differences in the lubricant film formation and adherence to the substrate. Adsorbed metallic salt films of triglyceride VLCFA-molecules exhibited lower extreme pressure properties compared to chemically modified surface layers formed with the use of ZDTP additive. Worn surface analysis by EPMA and optical micrographs showed evidence of tribochemical decomposition, conversion and hence surface layer modification with the use of ZDTP in contrast with the use of VLCFAs in differ-

ent base-stocks.

References

- [1] R. P. S. Bisht, G. A. Sivasankaran and V. K. Bhatia, Additive properties of Jojoba oil for lubricating oil formulations, *Wear*, 161, (1993) 193-197.
- [2] I. Minami and S. Mitsumune, Antiwear Properties of Phosphorus-Containing Compounds in Vegetable Oils, *Tribology Letters*, 13 (2), (2002) 95-101.
- [3] N. H. Jayadas, K. P. Nair and G. Ajithkumar, Tribological Properties of Coconut Oil as an Environment-Friendly Lubricant, *Tribology International*, 40, (2007) 350-354.
- [4] S. Trenkamp, W. Martin and K. Tietjen, Specific and Differential Inhibition of Very-Long-Chain Fatty acid Elongases from Arabidopsis Thaliana by Differential Herbicides, *Proceedings of the National Academy of Sciences of the United States of America*, *PNAS*, 101 (32), (2004) 11903-11908. Available at www.pnas.org, Accessed: 06th November 2007.
- [5] H. Wormser, Lipids – psc3110, (2007). Available at <http://wiz2.pharm.wayne.edu/biochem/lipidsc.ppt>. Accessed: 06th November 2007.
- [6] S. S. Lawate, K. Lal and C. Huang, Vegetable Oils – Structure and Performance, in E. R. Booser (Ed), *Tribology Data Handbook*, CRC Press, Chapter 11, 103-116, (1997).
- [7] H. Kong, Friction and Wear at Sliding Ceramic Surfaces, A Doctor of Philosophy (PhD) degree Dissertation submitted to the Engineering Department, Darwin College, Cambridge University, (November, 1991).
- [8] A. Bos, The Temperature at the Wear Scars of the Four-Ball Apparatus, *Wear*, 31 (1975) 17-27.
- [9] J. J. Frewing, The influence of Temperature on Boundary Lubrication, *Proceedings of the Royal Society of London, Series A, Mathematical and Physical Sciences*, 181, (984), (September 24, 1942) 23-42.
- [10] F. P. Bowden, D. Tabor, *The Friction and Lubrication of Solids*, Clarendon Press – Oxford, 200-227 (1986).
- [11] A. R. Lansdown, High Temperature Lubrication - First Edition, Mechanical Engineering Publication Limited - London, 81-94, (1994).
- [12] A. R. Lansdown, *Lubrication – A Practical Guide to Lubricant Selection - First Edition*, Pergamon Press Limited – Oxford, 1-14, (1982).
- [13] S. S. Wang, G. J. Nelson and R. Huo, Measuring Thickness of Metal / Lubricant Interfacial Regions with AC Impedance Spectroscopy, *Journal of Colloid and Interfacial Science*, 132, (1), (1989) 243-249.
- [14] S. Jahanmir, Chain Length Effects in Boundary Lubrication, *Wear*, 102, (1985) 331-349.
- [15] A. Gouveia de Souza, J. Oliveira Santos, N. M. Conceicao, M. C. Dantas Silva and S. Prasad, A Thermoanalytic and Kinetic Study of Sunflower, *Brazilian Journal of Chemical Engineering*, 21(02), (2004) 265-273.
- [16] S. Z. Erhan, B. K. Sharma and J. M. Perez, Oxidation and Low Temperature Stability of Vegetable Oil-based Lubricants, *Industrial Crops and Products*, 24, (2006) 292-299.
- [17] W. Tuszynski, J. Molenda and M. Makowska, Tribochemical Conversions of Zinc Dialkyldithiophosphate (ZDDP) under Extremely Different Pressure Conditions, *Tribology Letters*, 13 (2), (2002), 103-109.
- [18] K. L. Rhodes and P. C. Stair, The Surface Chemistry of Zinc Dialkyldithiophosphate, an antiwear additive on Oxidized Iron and Steel Foils, *Journal of Vacuum Science and Technology-A*, 6 (3), (1988) 971-974.
- [19] R. Ramesh and R. Gnanamoorthy, Effect of Post Oxidation on the Fretting Wear Behavior of Liquid Nitrided EN24 Steels, *Surface Coatings Technology*, 200 (12-13), (2006) 3926-3932.
- [20] G. R. O'Shea Company, Castor Oil and its Chemistry, (2007). Available on WWW.groshea.com/caschemchemistry.html Accessed May 3, 2007.
- [21] M. A. Perillo and D. M. Maestri, Surface Behavior of Jojoba Oil alone or in mixtures with Soybean Oil, *Colloids & Surfaces – A: Physicochem. Eng. Aspects*, 256, (2005) 199-205.