IMPROVEMENT OF LUBRICANTS TRIBOLOGICAL PROPERTIES USING SOME OXYGEN ORGANIC COMPOUNDS

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Abstract: In the current work, a number of standard tests, for several additive compounds used to improve the capability of the lubricants to reduce the friction and hence the wear, have been performed to determine the activity of these compounds. The tests, which include diameter of the wear trace, friction coefficient and the thickness of the insulating layer, have been carried out under the tribological conditions, that is, under the boundary friction conditions. Tribological analyses for the compounds were established by using the (HFRR) instrument. The pin-on-disc technique was employed. The results showed that a maximum wear was found with hexadecane; however, all the additives were active in decreasing the wear of the metallic ball. In addition, the activities were enhanced by ascending their concentrations in hexadecane. Moreover, the most active compounds at 100 ppm and 300 ppm were 16-hydroxyhexadecanoic acid and C_{36} dimer acid/ 1,6-hexanediol mono ester, respectively. Furthermore, the least friction coefficient at 100 ppm and 300 ppm was found to be 0.115 for 16-hydroxyhexadecanoic acid and 0.066 for C_{36} dimer acid/1,2-ethanediol monoester and C_{36} dimer acid/1,6-hexanediol monoester, respectively. Finally, the highest thickness of the insulating layer between the frictioned surfaces at 100 ppm and 300 ppm was found to be 48% for 16-hydroxyhexadecanoic acid and 81.3% for C_{36} dimer acid/1,6-hexanediol monoester, respectively.

1. Introduction

Because of the increasing demand on the synthetic lubricating oils throughout the world, a great deal of attention has been turned to research improving the lubricating functions of oils. The addition of different monomers to oil aims to improve the friction condition and to improve the chemical and physical properties of different types of oils. There are numerous studies including this type of work and many international companies competing to do so.

For example, Hu and Tao(1) studied the mechanism of the formation of friction polymer with 13,14-dihydroxydocosanoic acid. They concluded that the functional antiwear mechanism is the formation of a polymeric friction film on the rubbing surface. The tribochemical polymerization of 2-hydroxycarboxylic acids with straight alkyl chains, having carbon number of 14-18, was found to form an ester-metal connection and that led to an excellent improvement of oil properties (2). This phenomenon was attributed to the formation of lubrication film between the metal surface and the formed polymer.

The effect of polar compounds, on silicon nitride wear in the friction between silicon nitrides under mineral oil lubrication, was also studied [(3)]. It was found that adding polar compounds such as fatty acids and esters tended to accelerate increase in wear. However, the addition of aliphatic alcohols did not produce an accelerated increase in wear.

Fourier Transform Infrared (FTIR) Microspectroscopy [(4)] for surface profilometry resulted from the reaction of stearic acid on copper surfaces indicated that stearic acid had the capability to reduce the wear. In another study, Kramer [(5)] investigated copper surface-hardening rates as a function of stearic acid concentrations in paraffin oil, and proposed the formation of copper stearate on the surface.

In another study, the tribological behavior and lubricating mechanism of copper nanoparticles in oil was evaluated on a four-ball machine. It was found that copper nanoparticles as oil additives have an excellent friction reduction and antiwear properties [(6)].

Minami *et al.* [(7)] studied the lubricating functions of carboxylic acids in polar basic oils. It was found that monocarboxylic acids did not show much friction reduction capability; however, the addition of dicarboxylic acids with modified polar functional groups showed a superior friction reduction effect.

In a recent study [(8)], two sets of copolymers additives were prepared. The first set was based on propylene sebacate and the second one was on propylene succinate; the efficiency of the prepared copolymers for improving the viscosity index and the lowering of the pour point was found to be increased with increasing the molecular weight of the prepared copolymers.

The present work aimed to perform a comparison between the capabilities of two types of additives, to improve the efficiency of the lubricants as antifriction and antiwear materials. One may react under the friction conditions to form a protective polymeric layer, whereas the other cannot. Another object was to investigate the effect of the glycol chain length upon the activity of the monoester in order to improve the lubricants characteristics.

2. Experimental

2.1 Chemicals

The monoester organic compounds have been synthesized in the laboratories of the engineering college, University of Warsaw [(*)]. The chemical properties of these compounds were published before [(9)]. Other utilized organic compounds were purchased from FLUKA with purities > 95% and used as supplied. The compounds studied as agents, which reduce the friction and the wear, were selected according to their chemical structure, and hence, some of them could form a polymer via the step-growth mechanism, under the tribological conditions, whereas others could not react by following the same mentioned mechanism. Table 1 demonstrates the names and abbreviations of the tribologically examined compounds. All the compounds were tested in the form of their solutions in the paraffin oil, hexadecane, of concentrations 100 ppm and 300 ppm. The pure oil was considered to be the reference.

Table 1: The names and structures of the studied compounds

No.	Compound	Structure
Ia	C_{36} dimer acid /1,2-ethanediol monoester	HOOC-R-COO-$(CH_2)_2$OH
Ib	C_{36} dimer acid /1,4-butanediol monoester	HOOC-R-COO-$(CH_2)_4$OH
Ic	C_{36} dimer acid /1,6-hexanediol monoester	HOOC-R-COO-$(CH_2)_6$OH
II	16-Hydroxyhexadecanoic acid	$HOCH_2(CH_2)_{14}COOH$
III	1,16-Hexadecanedioic acid	$HOOC(CH_2)_{14}COOH$
IV	1,16-Hexadecanediol	$HOCH_2(CH_2)_{14}CH2OH$

2.2 Experimental Technique

Tribological analyses of the employed compounds have been performed by High Frequency Reciprocating Rig (HFRR), supplied by PCS instruments.

All tests were carried out under the tribological boundary friction conditions. The standards, which have been determined to establish the activity of the tribological additives, were the diameter average after the wear of the metallic ball, the friction coefficient and the insulating oil layer thickness. The first standard was found by measuring the wear trace dimensions by using a special microscope. Thereafter, the average readings were calculated. Concerning the second and the third standards, they both were recoded, periodically, every 5 seconds. Table 2 shows the tribological conditions, at which the tests were accomplished.

3. Results and Discussion

3.1 Synthesis of the Monoesters

It is well known that it is not easy to effect attack on the carbonyl carbon atom of RCO_2H (1), with nucleophiles of the general formula Y^-, because they are eliminating the proton, instead, to give RCO_2^-, which is insusceptible to nucleophilic attack. Weaker nucleophiles of the type YH, e.g. ROH, do not suffer this incapability; however, their reactions with relatively unreactive carbonyl carbon atom of RCO_2H are slow.

Nevertheless, the protonation, by acid catalysis, enhances the reactivity in, for example, esterification [10]:

$$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O \quad (1)$$

In this work, the acid, namely, C_{36} dimer acid, has been reacted with three glycols; that is, 1,2-ethanediol, 1,4-butanediol and 1,6-hexanediol, which differ in the chain length. Following a modified procedure for that mentioned by Fury [11], a toluene solution of equimolar amounts of the acid and each of the glycols, in the presence of catalytic amount of 4-methylbenzenesulphonic acid, was refluxed for 90 min. Work up was then carried out to offer the desired products, as is shown in equation [2].

$$\underset{C_{36}\text{ dimer acid}}{HOOC\text{-}R\text{-}COOH} + \underset{\text{Glycol}}{HO(CH_2)_nOH} \rightarrow \underset{C_{36}\text{ dimer acid / glycol monoester}}{HOOC\text{-}R\text{-}COO\text{-}(CH_2)_nOH} + H_2O \quad (2)$$

n=2 Ia
n=4 Ib
n=6 Ic

Table 2: The tribological conditions

Parameters			Characteristics
Material System			Steel-on-steel
Tribological Pair	Ball	Material	Steel LH 15
		Diameter, mm	6
		Manufactured by	Iskra manufactory, Warsaw, Poland
	Disc	Material	Steel LH 15
		Diameter, mm	10
		Thickness, mm	3
		Hardness, H	< 0.25
Stroke Length, mm			1.0
Frequency, Hz			50
Velocity, m/s			0.1
Load, N			1.962
Test time, min.			70
Temperature, °C			60

3.2 The Standards

Table 3 revealed the determined standards, accompanied with the standard deviation, for four tests per a solution. Regarding the diameter of the wear trace, the diameter average measurements for the metallic ball wear trace, indicated that all the additives lessened the wear of the metallic ball. In

*) The practical work has been carried out by Dr. Mohamed S. Al-Nozili

addition, the same table points out that the activities of all the compounds have been improved by increasing their concentrations in hexadecane. Moreover, the results illustrated that the maximum wear of the metallic ball occurred when using the pure hexadecane oil. At 100 ppm, (II) was the most active, whilst at 300 ppm, (Ic) was the most active one. Besides, the results have not disclosed any relation between the number of the carbon atoms composing the glycol chain in monoester compounds and the activity of these compounds in decreasing the wear average.

Concerning the friction coefficient, which is defined as the ratio of the friction force between two bodies to the normal or perpendicular force between them [12], all the utilized compounds have diminished this standard and their maximum activities were at 300 ppm. In addition, the results illustrated that at 100 ppm the least friction coefficient of 0.115 was found for (II). However, at 300 ppm the least friction coefficient of 0.066 was for (Ia) and (Ic). Moreover, it was observed that the friction coefficient had no direct relation with the wear average of the metallic ball. The evidence came from the highest activity of (Ib) in minimizing the wear of metallic ball at 300 ppm beside the greatest friction coefficient compared with rest of the monoesters.

As regards the thickness of the insulating layer between the frictioned surfaces, the measurements demonstrated that at 100 ppm the thickness of the insulating layer, was the highest when using (II), where it was of 48%. However, at 300 ppm the greatest thickness was when using (Ic) to equal 81.3%. Finally, the results disclosed the converse relation between the insulating layer and the friction coefficient.

Table 3: The standards determined under boundary friction conditions

Additive	Additive concentration [ppm]	Average film [%] ±SD	Average friction coefficient ± SD	Wear scar Average diameter $x10^{-1}$ [mm] ± SD
Hexadecane	100	32.6 ± 1.53	0.142 ± 0.0020	6.61 ± 0.0451
Ia	100	46.3 ± 1.53	0.119 ± 0.0017	5.73 ± 0.0300
Ib	100	37.3 ± 2.08	0.122 ± 0.0015	6.42 ± 0.0153
Ic	100	43.3 ± 2.52	0.123 ± 0.0010	5.93 ± 0.0306
III	100	40.0 ± 1.46	0.121 ± 0.0010	6.31 ± 0.0210
IV	100	38.7 ± 1.71	0.134 ± 0.0020	6.48 ± 0.0190
II	100	48.0 ± 2.11	0.115 ± 0.0010	5.32 ± 0.0280
Ia	300	80.3 ± 2.08	0.066 ± 0.0021	3.48 ± 0.0153
Ib	300	74.0 ± 1.00	0.078 ± 0.0010	3.43 ± 0.0351
Ic	300	81.3 ± 1. 53	0.066 ± 0.0026	3.26 ± 0.0351
III	300	53.0 ± 1.08	0.117 ± 0.0030	4.32 ± 0.0211
IV	300	65.0 ± 1.14	0.093 ± 0.0020	3.87 ± 0.0195
II	300	79.0 ± 1.62	0.076 ± 0.0010	3.34 ± 0.0163

4. Conclusion

The outcomes demonstrated the following:

1. The greater activity of the additive compounds, which may react under the friction conditions to form the polymeric protecting layer, compared with the additives, which have not the capability to react and give such a layer.
2. There is no relation between the number of carbon atoms in the glycol carbon chain and the activity of the monoester compounds in diminishing the wear and reducing the friction coefficient.
3. The absence of any relation between the diameter of the wear-scar trace and the friction coefficient.

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