Research Article

Tribochemistry and EP Activity Assessment of Mo-S Complexes in Lithium-Base Greases

Tarunendr Singh

R & D Centre, Bharat Petroleum Corporation Limited, "A" Installation, Sewree (E), Mumbai 400 015, India

Correspondence should be addressed to Tarunendr Singh, tsingh_dr@yahoo.com

Received 13 July 2007; Revised 30 March 2008; Accepted 27 April 2008

Recommended by Si-Wei Zhang

The blends of bis(1,5-diaryl-2,4-dithiomalonamido)dioxomolybdenum(VI) complexes in lithium-base grease are evaluated for their extreme pressure activity in a "four-ball test" using 12.7 mm diameter alloy steel ball specimen. The additive, bis(1,5-di-p-methoxyphenyl-2,4-dithiomalonamido)dioxomolybdenum(VI) and bis(1,5-di-p-chloro-phenyl-2,4-dithiomalonamido)dioxomolybdenum(VI) exhibited lower values of wear-scar diameter at higher load and higher values of weld load, flash temperature parameter, and pressure wear index as compared with lithium-base grease without additives. The greases fortified with the developed additives prevent rusting and corrosion of bearings while grease containing no additives did not pass these tests as per the standard tests. These greases have also better oxidation protection as compared to the grease that has no additive. The topography and tribochemistry of the wear-scar surface are carried out by means of scanning electron microscopy and Auger electron spectroscopy techniques, respectively.

Copyright © 2008 Tarunendr Singh. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. INTRODUCTION

Lubricants are employed in bearings to decrease wear and destructive heating and to increase mechanical efficiency. Under extreme pressure, the boundary film of lubricant may fail leading to deterioration of surface properties causing adhesion, seizure, and excess wear. Using an appropriate extreme pressure, lubricant additive may minimize the friction and damage, which form a chemical film with the material of the surface. Certain lubricants containing EP additives find extensive applications in hypoid gears and in metal cutting and forming operations. The use of molybdenum disulphide as an excellent solid lubricant is well known, however, its insolubility in oil prevents its use in liquid lubricants. Oil-soluble organomolybdenum compounds, for example, molybdenum dialkyldithiophosphate (MoDTP) and molybdenum dialkyldithiocarbamate (MoDTC), have been used as excellent antifriction, antiwear, and extreme pressure additives in lubricating oils and greases. These additives that are known to increase the load-carrying capacity of lubricants and reduce fuel consumption and power loss by reducing friction lubricants containing oil-soluble

organometallic compounds, sometimes referred as third-generation lubricants, have been known to show outstanding advantages over conventional lubricants in enhancing the component life, reducing operating temperatures and greatly extending lubrication intervals [1–8].

It is believed that the molybdenum and sulphur present in the additive form a low-friction surface film during operation of a machine under high loads. In view of these observations and our interest in searching for better extreme pressure additives, we are reporting, in this paper, few potential molybdenum-sulphur complexes as potential extreme pressure additives for lithium-base lubricating grease and their tribochemistry by AES and topography by SEM techniques.

Lithium-base greases are widely used in industrial machineries and automobiles [9]. These greases are formulated with various compounds with a view to optimizing the end use. In steel plant applications, lithium-12-hydroxystearate greases, formulated with extreme pressure additives, have performed well and they vary from sinter plant to coke oven. These greases have shown better performance, for example, high drop point, better antiwear and extreme

pressure properties, better oxidation stability, pumpability as well as better wheel bearing performance as compared to conventional calcium base grease. The use of certain S-P and Pb-S systems in the lithium-base grease has been on record [10–13].

2. EXPERIMENTAL

2.1. Lithium grease

Lithium-base grease (Grease A) was prepared in situ by reacting 12-hydroxystearic with lithium hydroxide monohydrate in presence of paraffinic mineral oil (see Table 1).

Whereas, Ar=*p*-Methoxyphenyl- and *p*-Chlorophenyl-groups.

2.4. Preparation of Bis(1,5-diaryl-2,4-dithiomalonamido) dioxomolybdenum (VI)

The following two Mo-S complexes were prepared and used as extreme pressure additives in the lithium-base grease.

Bis(1,5-di-p-methoxyphenyl-2,4-dithiomalonamido) dioxomolybdenum(VI)

Molecular Formula: $\text{MoO}_2\text{C}_{34}\text{H}_{36}\text{N}_4\text{S}_4\text{O}_4$.
Melting Point: $>200^\circ\text{C}$ (Dec.)

Bis(1,5-di-p-chloro-phenyl-2,4-dithiomalonamido) dioxomolybdenum (VI)

Molecular Formula: $\text{MoO}_2\text{C}_{30}\text{H}_{24}\text{N}_4\text{S}_4\text{Cl}_4$.
Melting Point: $>200^\circ\text{C}$ (Dec.)

2.5. Grease additive admixture

The optimized dosages of the above additives were blended at a temperature of 80°C with the prepared Grease 1 (without additive) and with a view to achieve the following two main properties for the extreme pressure greases.

2.2. Base oil

Typical characteristics of the base oil used in the prepared lithium-base grease are given in Table 1.

2.3. Additives

The Mo-S complex additives were prepared [14, 15] by reacting an ethanolic solution of an appropriate 1,5-di-aryl-2,4-dithiomalonamide (2 mol) with an acidic solution of ammonium molybdate (1 mol) and digesting the reaction mixture for 15 minutes on a water bath.

- (a) Timken OK load of 60 lbs minimum.
- (b) Four-ball weld load of 315 kgf minimum.

The following greases were used in this study.

Grease A: Lithium-base grease without additive.

Grease B: Grease A + bis(1,5-di-*p*-methoxyphenyl-2,4-dithiomalonamido)-dioxomolybdenum(VI).

Grease C: Grease A + bis(1,5-di-*p*-chlorophenyl-2,4-dithiomalonamido)-dioxomolybdenum(VI).

The rust and corrosion inhibitors were also incorporated in the above greases with a view to pass the following tests.

- (a) Emcor rust test, ASTM D 6138 [16].
- (b) Corrosion prevention test, ASTM D 1743 [16].

2.6. Test balls

SKF steel bearing balls of 12.7 mm diameter (type RB-12.7/111/E212) were used as the test specimen in the four-ball test.

2.7. Apparatus

(a) Extreme pressure lubricant test

- (i) *Four-ball machine*. The tests were conducted on a four-ball machine by following standard procedure [16]. The duration of the test was 60 seconds. A series of tests were performed until the welding point was reached, and the determined parameters were initial seizure load (ISL), 2.5-second seizure delay load (SDL), just before weld load (JBWL), weld load (WL), wear-scar diameter (d) at ISL and JBWL, flash temperature parameter (FTP), and pressure wear index (PWI).

(a)

(b)

(c)

FIGURE 1: Scanning electron micrographs. (a) Grease A at 140 kgf, (b) Grease B at 280 kgf, (c) Grease C at 280 kgf.

FIGURE 2: AES of Grease B at just before weld load; 280 kg.

- (ii) *Timken machine*. The measurement of load-carrying capacity of the prepared polyurea greases was carried out by Timken method by following ASTM D 2509 test method [16]. The duration of the test was ten minutes. The test results obtained with the Timken machine are recorded as Timken OK load in Table 3.

FIGURE 3: AES of Grease C at just before weld load; 280 kg.

TABLE 1

Test	Results	Methods
(1) Nature of the base oil	Paraffinic mineral base oil	—
(2) Base oil viscosity at 40°C	100.70	ASTM D 445
at 100°C	10.94	
(3) Viscosity index	92	ASTM D 2270
(4) Flash point (COC), °C	234	ASTM D 92
(5) Pour point, °C	0	ASTM D 97
(6) Aniline point, °C	104	ASTM D 611

(b) *Rust tests*. These tests were performed by following ASTM D 6138 method in SKF Emcor test rig [16] and ASTM D 1743 test rig [16]. The prepared polyurea greases (Grease 2 and Grease 3) pass the rust tests as per ASTM D 6138 and ASTM D 1743.

(c) *Oxidation stability test*. It was carried out using oxidation bomb method, ASTM D 942, [16].

(d) *Topography* of the wear-scar surface was studied by scanning electron microscopy (Phillips XL-20) technique [17]. The wear scar obtained with Grease A, Grease B, and Grease C after “four-ball” test at just before weld loads were selected for the study. The stains of sludge or varnish found on the ball surface in the vicinity of the wear scar were removed with cotton and then cleaned with acetone in an ultrasonic bath before taking the micrographs.

(e) *Tribochemistry* was performed to study the film, formed on the wear-scar surface, obtained after “four-ball” test using AES technique [18]. The presence of sulphur and molybdenum in the film, formed during lubrication, was detected. The loads selected for the investigation were just before weld loads (for Grease B and Grease C). The tested ball surface was cleaned with acetone in an ultrasonic bath before the AES analyses.

TABLE 2: Summary of the experimental results obtained with prepared Grease A, Grease B, and Grease C in the four-ball test.

Sl. No.	LUBRICANT	ISL* kgf	d^* at ISL mm	SDL* kgf	JBWL* kgf	d^* at JBWL* mm	WL* kgf	FTP* max	PWI* max
(1)	Grease A	80	0.70	100	140	1.90	160	132	9
(2)	Grease B	112	0.70	126	280	2.60	315	217	11
(3)	Grease C	112	0.50	126	280	2.50	315	270	11

d^* = wear-scar diameter, ISL* = initial seizure load, SDL* = 2.5-second seizure delay load, JBWL* = just before weld load, WL* = weld load, FTP* = flash temperature parameter, PWI* = pressure wear index.

TABLE 3: Typical test results recorded for the prepared Grease A, Grease B, and Grease C.

Sl. No.	Test	Results GREASE A	Results GREASE B	Results GREASE C	Methods ASTM
(1)	NLGI grade	2	2	2	NLGI
(2)	Penetration, 60 X	274	272	272	D 217
	Penetration, 100,000 X	299	294	295	
(3)	Drop point, °C	198	198	199	D 2265
(4)	Oil separation, % by wt at 100°C, 30 h	1.4	1.5	1.8	D 6184
(5)	Oil separation on storage, % by wt	Nil	Nil	Nil	D 1742
(6)	Oxidation stab. at 99 ± 1°C, 100 h pressure drop, psi	15	2	1.5	D 942
(7)	Water washout at 80°C, % loss by wt	4.0	4.2	4.0	D 1264
(8)	Rust test	FAILS	1	1	D 1743
(9)	EMCOR rust test	FAILS	0,0	0,0	D 6138
(10)	Copper corrosion test at 100°C, 24 h	PASS	PASS	PASS	D 4048
(11)	Deleterious particles, number of scratches	NIL	NIL	NIL	D 1404
(12)	Wheel bearing test at 105°C for 6 h, leakage by wt, gms.	1.2	1.2	1.3	D 1263
(13)	Four-ball wear test, Wear-scar dia., mm, ~1200 rpm, 40 kg at 75°C	0.85	0.45	0.42	D 2266
(14)	Four-ball weld load, kg	160	315	315	D 2596
(15)	Timken Ok Load, lbs	20	45	45	D 2509

3. RESULTS AND DISCUSSION

The prepared greases were evaluated for the extreme pressure, rust and corrosion inhibition, and oxidation stability properties, and the results are reported in Tables 2, 3.

Table 2 presents a record of the values of the initial seizure load (ISL), wear-scar diameter (d), 2.5-second seizure delay load (SDL), just before weld load (JBWL), weld load (WL), flash temperature parameter (FTP), and pressure wear index (PWI) for the prepared Grease A, Grease B, and Grease C in the four-ball test.

A series of test were conducted with the prepared greases, a “four-ball machine”, and it was found that the wear-scar diameter values increase gradually up to ISL, owing to the physisorbed/chemisorbed thin layers

of the additive/lubricant on the rubbing surfaces. On increasing the load, there is a sharp increase in the wear-scar diameter values, indicating that the adsorbed lubricant/additive film has become partially desorbed. The transition from ISL and the consequent rise in the temperature from ISL to SDL result in the chemisorption of additive film on the contacting surfaces, and ultimately a chemical film of iron-sulphide/iron-oxide/molybdenum-disulphide is believed to be formed. This mixed film separates the contact surfaces and lower the friction coefficient and wear-scar diameter values, even at much higher loads.

Table 3 records the typical test results for the prepared greases (Grease A, Grease B, and Grease C). The additive fortified greases (Grease B and Grease C) show better

oxidation stability as well as excellent rust and corrosion protection properties. The greases (Grease B and Grease C) show higher load carrying properties in four-ball test (weld loads of 315 kgf) and Timken test (Timken OK loads of 45 lbs) as compared to the Grease A (without additive).

Topography. The effectiveness of the prepared greases was examined by the technique of scanning electron microscopy [17]. The wear scar obtained with Grease A, Grease B, and Grease C after four-ball test at just before weld loads was selected for the study. The stains of sludge or oil found on the surface of the test specimens in the vicinity of the wear scar were removed with cotton. The tested specimens were then cleaned with acetone in an ultrasonic bath. The micrographs are shown in Figure 1. The micrographs of Grease B and Grease C exhibit smoother surfaces in comparison to the micrograph obtained with Grease A. The flow pattern at the leading edges indicates adhesive wear, which might be due to the junction growth and subsequent rupture. The black lines and spots are probably due to the formation of mixed chemical films of iron-sulphide/iron-oxide/molybdenum-disulphide, which provide effective lubrication at higher loads. Thus, the SEM study confirmed the wear scar obtained with Grease B and Grease C is smoother in nature as compared to the wear scar obtained with Grease A.

Tribochemistry. Auger electron spectroscopy [18] was used to explore the chemical composition of the film formed during lubrication in the wear tracks. The "Auger spectra" were obtained by plotting the derivative of electron energy distribution against energy. The Auger analyses of the used balls were analyzed using scanning electron micro-probe. The Auger spectra obtained with line analyses for Grease B (see Figure 2) and Grease C (see Figure 3) (at just before weld load) show the presence of oxygen, carbon, sulphur, nitrogen, chlorine, and molybdenum. The quantitatively detected elements are absent in the lithium grease without additive (Grease A at just before weld load). It appears that the sulphur and molybdenum are responsible for higher weld load for Grease B and Grease C, this may probably be due to the formation of iron-sulphide as well as molybdenum-disulphide at high temperature, which diffuses into the first atomic layer of the metal and forms a new alloy, which then provides effective lubrication to the bearing ball surfaces.

Thus, it can be corroborated that these elements are derived from the additives which are used in the lithium-base grease and are responsible for the smooth efficiency of the prepared greases at higher loads.

4. CONCLUSIONS

The prepared greases blended with different additives were found to be more effective in reducing friction and wear at sliding surfaces, and increasing the load carrying capacities as compared to Grease A (grease without additives), Grease B, and Grease C showed lower values of wear-scar diameter and higher values of weld loads.

The scanning electron micrographs showed that the wear scar obtained with the Grease B and Grease C is smoother in nature than Grease A. The tribochemistry by AES analyses

confirmed the presence of sulphur and molybdenum in the wear tracks of the test specimen obtained after the four-ball test with Grease B and Grease C. The prepared greases (Grease B and Grease C) also pass the rust and corrosion and oxidation stability tests.

ACKNOWLEDGMENT

The authors are thankful to the management of the Bharat Petroleum Corporation Limited for permission to publish this work.

REFERENCES

- [1] P. C. H. Mitchell, "Oil-soluble MO-S compounds as lubricant additives," *Wear*, vol. 100, no. 1-3, pp. 281-300, 1984.
- [2] E.-C. Zheng and X.-L. Qian, "Tribological properties and lubrication mechanism of molybdenum dialkylthiocarbamate and calcium compounds in greases," *Wear*, vol. 130, no. 1, pp. 233-247, 1989.
- [3] Y. Yamamoto, S. Gondo, T. Kamakura, and N. Tanaka, "Frictional characteristics of molybdenum dithiophosphates," *Wear*, vol. 112, no. 1, pp. 79-87, 1986.
- [4] E. R. Braithwaite and A. B. Greene, "Critical analysis of the performance of molybdenum compounds in motor vehicles," *Wear*, vol. 46, no. 2, pp. 405-431, 1978.
- [5] Y. Yamamoto and S. Gondo, "Friction and wear characteristics of molybdenum dithiocarbamate and molybdenum dithiophosphate," *Tribology Transactions*, vol. 32, no. 2, pp. 251-257, 1989.
- [6] K. Malsuo, *Journal of JSLE*, vol. 31, no. 4, p. 260, 1986.
- [7] T. Singh and V. K. Verma, "New organomolybdenum compounds as potential E.P. lubricant additives," *Indian Journal of Technology*, vol. 28, no. 11, pp. 649-656, 1990.
- [8] A. B. Green and T. J. Ridson, "The effect of molybdenum-containing, oil-soluble friction modifier on engine fuel economy and gear oil efficiency," SAE Technical paper 811187, 1981.
- [9] C. J. Bonor, "Manufacture and application of lubricating greases," National Lubricating Grease Institute, USA, 1994.
- [10] A. G. Izcus, "The effects of lead compounds upon the droppig points of lithium lubricating grease," *NLGI Spokesman*, vol. 44, no. 8, pp. 280-290, 1980.
- [11] J. R. Hasting, "Lithium and lithium complex greases for use in the steel industry," *Lubrication Engineering*, vol. 37, no. 2, pp. 91-94, 1981.
- [12] S. K. Sharma, P. Vasudevan, and U. S. Tewari, "High temperature lubricants-oils and greases," *Tribology International*, vol. 16, no. 4, pp. 213-219, 1983.
- [13] R.-H. Jiang, "Effects of the composition and fibrous texture of lithium soap grease on wear and friction," *Tribology International*, vol. 18, no. 2, pp. 121-124, 1985.
- [14] G. Barnikov, V. Kath, and D. Richter, "Isothiocyanate. II. N,N'-Aryl-substituierte Dithiomalonsäurediamide. I," *Journal für Praktische Chemie*, vol. 30, no. 1-2, pp. 63-66, 1965, Chemical Abstract, 64, 3411c, 1966.
- [15] T. Pal, P. Anjali, and P. K. Das, *Journal of the Indian Chemical Society*, vol. 65, p. 821, 1988.
- [16] Petroleum Products and Lubricants, Annual Book of ASTM Standards, Vol. 5.01-5.03.

-
- [17] M. Tomaru, S. Hironaka, and T. Sakurai, "Effects of oxygen on the load-carrying action of some additives," *Wear*, vol. 41, no. 1, pp. 117–140, 1977.
 - [18] T. P. Debies and W. G. Johnston, "Surface chemistry of some antiwear additives as determined by electron spectroscopy," *ASLE Transactions*, vol. 23, no. 3, pp. 289–297, 1980.