Tribological Properties of Castor Oil tris(Diphenyl Phosphate) as High-Performance Antiwear Additive in Lubricating Greases for Steel/Steel Contacts at Elevated Temperature

Xinhu Wu, Qin Zhao, Ming Zhang, Weimin Li, Gaiqing Zhao, Xiaobo Wang*

Abstract: Castor oil tris(diphenyl phosphate) (CODP) was synthesized using an environment friendly and renewable resources–castor oil, and its tribological properties were evaluated in lithium 12-hydroxystearate greases (LHG) and lithium complex greases (LCG) at 150 ^{o}C. The tribological behaviors of the additive for LHG and LCG application in steel/steel contacts were evaluated on an Optimol SRV-IV oscillating reciprocating friction and wear tester as well as on MS-10J four-ball tester. The worn steel surface was analyzed by a JSM-5600LV scanning electron microscope and a PHI-5702 multifunctional X-ray photoelectron spectrometer. The results indicated that CODP as the additive could effectively reduce friction and wear of sliding pairs in the two base greases. The tribological performances were also better than the traditional used Zinc dialkyldithiophosphate (ZDDP) based additive package in LHG and also in LCG.

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Boundary lubrication films composed of Fe(OH)O, Fe_3O_4, $FePO_4$ and compounds containing the P-O bonds were formed on the worn surface, which resulted in excellent friction reduction and antiwear performance.

1 Introduction

Lubricating greases are colloidal dispersions of a thickener in a lubricating fluid and are generally formed by heating the two components together until the thickener swells and absorbs the oil. Grease is a preferred form of lubrication in certain applications because it gives low friction, is easily confined, and has a long lubricating life at low cost.[1,2] However, technology is constantly being challenged to develop multifunctional lubricants to operate at higher temperatures and pressures and with a variety of contact surfaces, to minimize friction and increase system efficiency.[2] This has triggered a steady rise in the development and application of greases at high temperatures, eg 300-450°F (149-232°C),[3,4] or higher. To address these problems, various high-performance lubricating greases such as aluminium complex soap greases, lithium 12-hydroxystearate greases, lithium complex greases, polyurea greases, synthetic hydrocarbon greases and silicone greases, etc. were developed to meet the demand of high temperature lubricants.[5,8] However, only a minority of high temperature lubricant additives especially the anti-wear (AW) agents was commercially available, which limits the high-temperature lubricant formulation.

Previous studies have shown that aryl-phosphate exhibited excellent friction-reducing and AW performance in lubricating oils or greases at elevated temperature.[9,11] The excellent tribological performances of phosphate esters can be explained that phosphorus containing additives can be film-forming on the metal surfaces at ~200 ^{o}C,[12] and provide an extremely low friction coefficient between 250 and 550 ^{o}C.[13] The film can cause a smoothing of the metal surface that is then able to proving a low shear strength boundary layer. Consequently, phosphate esters, especially that have advantages of high molecular weight and high thermal and chemical stability as well as very low vapor pressure, could be potential candidates as high temperature lubricating additives.

Simultaneously, worldwide potential demands for replacing petroleum derived raw materials with renewable plant-based ones in production of valuable materials are quite significant from the social and environmental viewpoints. Therefore, using inexpensive renewable resources are expected to be an ideal alternative chemical feedstock to produce high temperature lubricating additives. Castor oil (CO), a renewable resource, is a relatively inexpensive plant oil obtained from the seed of ricinus communis. The oil is a viscous, pale yellow non-volatile and non-drying oil with a bland taste and is sometimes used as a purgative.[14] Additionally, castor oil exhibits more effective lubricity than other vegetable oil esters make it suitable for using as the base oil and additives of biodegradable lubricants, which have drawn considerable interest in recent times. Prasenjit et al. have investigated the tribofilms of castor oil and other three kinds of base oils.[15] Wu et al. prepared an environment friendly water-based lubricants from castor oil, organic hydramine and boric acid.[16] Li et al. developed new class of phosphorous-nitrogen-incorporated castor oil as extreme-pressure (EP) and AW lubricating additves.[17] Bisht et al. examined the potential of sulphurised castol oil for use as extreme-pressure (EP) additives for developing formulations for industrial gear oils.[18] Drown et al. analyzed the effectiveness of castor and Lesqurella oil esters as lubricity enhancers for diesel fuel and compare their performance to those for the commercial vegetable oil derivatives soybean and rapeseed methyl esters.[19]

Much less is known with respect to introduce phenyl-phosphate groups in the castor oil backbone and use it as high-performance AW additive in lubricating grease at 150^{o}C. In the present paper, castor oil tris(diphenyl phosphate) (CODP) was synthesised and its tribological properties in lithium 12-hydroxystearate greases (LHG) and lithium complex greases (LCG) for steel/steel contacts were evaluated on an Optimal SRV-IV oscillating friction and wear tester at 150 ^{o}C. The morphology and chemical composition of worn surface was studied by SEM and XPS in order to explore the lubrication mechanism of CODP under high temperature.

2 Experiment

2.1 Chemicals and Materials

The reaction scheme for the synthesis of castor oil tris(diphenyl phosphate) (CODP) is shown in Scheme 1, which was prepared according to previously reported method.[10,11] Castor oil was obtained from Shantou Xilong chemical Co., Ltd. Diphenyl chlorophosphate (≥99.0%) was purchased from J&K Chemical. Zinc dialkyldithiophosphate (ZDDP) was also commercially obtained from the Lubrizol corporation. All the chemicals were analytical grade (AR) and were used without further purification.

Synthesis of castor oil tris(diphenyl phosphate) (CODP). 5.0g (5.36 mmol) castor oil, 4.463g (16.6mmol) diphenyl chlorophosphate, 0.1g $AlCl_3$ and 50 mL toluene were introduced into a dry 100 mL four-necked flask with a thermocouple, a dip tube for N_2 purge, a product condenser and a vacuum receiver. The mixture was heated to 100 ^{o}C while keeping the flask devoid of moisture. After being stirred at this temperature for 15 hours, toluene was removed and the resultant precipitate was washed repeatedly with water and acetonitrile. A white powder 7.16g (yield of 82%) was obtained after drying under vacuum at 80 ^{o}C, until a constant weight.

Lithium 12-hydroxystearate greases (LHG) and lithium complex greases (LCG) were obtained from our laboratory. Their typical properties are listed in Table 1. The base greases and additives with different concentrations were mixed thoroughly prior to the tests and finely ground three times in a three-roller mill.

2.2 Thermal Analysis

The thermal property of the CODP was measured on an STA 449 C Jupiter simultaneous thermogravimetric-differential scanning calorimeter (TG-DSC). A total of 5 mg of sample was placed in the thermogravimetric analysis (TGA) sample holder. The temperature was set to increase from ambient temperatures to approximately 800 °C, at a heating rate of 10 °C/min in air. The weight loss was monitored in the TG-DSC analysis.

2.3 Copper Strip Corrosion Test.

The test was performed according to GB/T7326-1987 procedure. A piece of bright finish copper was immersed in 20 g of base grease containing additive and heated for 24 h at 100^{o}C. At the end of the test cycle, the copper strip was washed and compared with the copper strip corrosion standards.

2.4 Tribology Test

The friction and wear tests were carried out on an Optimol SRV-IV oscillating reciprocating friction and wear tester. The contact between the frictional pairs was achieved by pressing the upper running ball (10 mm diameter, AISI 52100 steel, hardness of approximately 58-60 HRC) against the lower stationary disc (ø 24mm×7.9 mm, AISI 52100 steel, hardness of approximately 59-61 HRC). The tribological tests were conducted at an amplitude of 1 mm and a relative humidity of 50-60%. The wear volume of the lower disc was measured by a MicroXAM 3D noncontact surface mapping profiler. Three repetitive measurements were performed for each wear of the discs, and the averaged values are reported in this paper. The morphology and chemical composition of the worn surfaces were analyzed by JSM-5600LV scanning electron microscope (SEM) and PHI-5702 multifunctional X-ray photoelectron spectrometry (XPS) using Al Kα radiation as exciting source. The binding energies of the target elements were determined at a pass energy of 29.35 eV, with a resolution of about ±0.3 eV, using the binding energy of contaminated carbon (C 1s, 284.8 eV) as reference.[20]

The four-ball wear test was carried out according to the SH/T0204-92 standard. The tester is operated with one steel ball, referred to as the ‘‘top ball’’, under a load rotating against three steel balls held stationary and clamped together for three-point contact. All of the balls (diameter 12.7 mm, HRC 64-66) are made of AISI 52100 steel. An optical microscope equipped with calibrated measuring scale and readable to an accuracy of 0.01 mm was used to measure the wear scar diameters (WSD) of the three low balls.

3 Result and Discussion

3.1 Structural Analysis

The chemical identity of CODP was evaluated by the ^{1}H nuclear magnetic resonance (^{1}H-NMR) and Fourier-transform infrared spectroscopy (FTIR). Fig. 1 shows ^{1}H-NMR spectrum of CODP. ^{1}H-NMR (DMSO-d$_6$, 400 MHz), δ (ppm) = 7.09–7.34(-P(OC$_6$**H**$_5$)$_2$), 5.38(-C**H**=C**H**-), 5.19(-CH$_2$-C**H**-CH$_2$-), 4.0–4.3 (-C**H**$_2$-CH-C**H**$_2$-), 3.58(-CH$_2$-C**H**(O-P)CH$_2$-), 2.28(-OCO-C**H**$_2$(CH$_2$)$_6$CH=CH-), 2.08(-CH=CH-C**H**$_2$-CH(O-P)CH$_2$-), 1.98(-OCO(CH$_2$)$_6$C**H**$_2$-CH=CH-), 1.50(-CH(O-P)C**H**$_2$(CH$_2$)$_4$CH$_3$), 1.24(-C**H**$_2$-), 0.85(-C**H**$_3$).

Fig. 2 shows the IR spectrum of CODP. The disappearance of absorption bands at 3670–3120cm^{-1} confirm the absence of free hydroxyl groups in CODP. The bands at 3070, 2930 and

2852 cm^{-1} can be attributed to stretching vibrations of the C-H bond in the $-CH_3$ and $-CH_2$ groups, respectively. The intensity band at 1483 cm^{-1} correspond to the bending vibrations of the -C-H bonds. The band located at 1743 cm^{-1} is due to the stretching vibration of -C=O. The additional band at 1587 cm^{-1} can be attributed to the frame vibration of benzene ring. The band at 1229 cm^{-1} is typical for -P=O compound. The bands at 1229 and 1130 cm^{-1} can be attributed to stretching vibrations of the (P)-O-benzene ring and -P-O-(benzene ring) bond in the diphenyl phosphate groups. The bands at 772, 752, 684 and 565cm^{-1} are due to the bending vibrations of the -C-H bonds in the benzene ring.

3.2 Thermal Stability

Fig. 3 shows the thermogravimetric/derivative thermogravimetric (TG/DTG) curve of CODP. The TG curve shows weight losses during the thermal decomposition of the compound. It is seen that the decomposition temperatures (T_d) of CODP is 279°C. The temperatures for 10 wt%, 20 wt% and 50 wt% weight loss of CODP are 305, 337 and 411°C, respectively. Moreover, the total decomposition temperature is about 800°C, revealing its high thermal stability. The DTG curve shows a weight loss per minute with an increase in temperature. It indicates that the rate of the weight loss for CODP is just a few percent per min in the temperature interval 100-200^{o}C. It then increases dramatically and at 338 ^{o}C reaches its maximum value of 78.6% of the total weight of the sample per min.

3.3 Friction and Wear Behavior

3.3.1 CODP as Additive for LHG and LCG

The tribological behavior of CODP as additive in LHG and LCG at 150 ^{o}C were investigated, and ZDDP was used for comparison.[21] The friction coefficient evolution at a constant load of 100N for 1-4 wt% CODP and the wear volumes after the tests are shown in Fig. 4 and 5. When the concentration of CODP reaches 3 wt % in LHG, the lubricant has very low and stable friction coefficient, more importantly, with the lowest wear volume. Further increasing the CODP concentration above 3 wt %, anti-wear (AW) property of the base grease could not be improved any more (Fig. 4a, c). It is evident that LCG plus 1-4 wt % CODP tested here all experience a running-in period (Fig. 4b). When the concentration of CODP is 3 wt %, the running-in time is dramatically shortened, concomitant with very stable friction and a lower friction coefficient. It is seen that 3 wt % CODP could improve the AW properties of the base greases by 2.5 times as compared with pure LCG (Fig. 4c). So 3 wt % CODP is the optimum concentration to provide significant friction reduction and AW properties.

Fig. 5 shows the changes in friction coefficients and wear volumes of sliding discs under lubrication of the two base greases plus 3 wt% ZDDP and 3 wt% CODP. It can be seen that the tribological properties of the two additives in LHG and LCG are different. The friction coefficients of the two additives in the two base greases increased in the following sequence: 3wt % CODP < 3wt % ZDDP < LHG (Fig. 5a); 3wt % CODP < 3wt % ZDDP < LCG (Fig. 5b). The wear volumes of the discs are in the same order with the friction coefficients (Fig. 6c). It is clearly seen that the AW properties of 3 wt % ZDDP and 3 wt % CODP increased by 9.7 and 12.5 times as compared with LHG and 1.5 times and 2.5 times as compared with LCG, respectively. Therefore, CODP as additives in LHG and LCG display dramatically better friction reduction and AW properties than ZDDP.

3.3.2 Friction at Variable Frequencies and Loads

The boundary lubricating capability of CODP was further tested by varying applied loads and sliding speeds by changing the reciprocating frequencies. Fig. 6 shows frequency ramp test from 15 Hz up to 40 Hz stepped by 5 Hz intervals. The tests were done under a steady load of 200 N for different additives in LHG and LCG at 150 ^{o}C, with 5 min test duration for each frequency. It is seen that both of LHG and LHG plus 3 wt % ZDDP also experienced a running-in time with larger friction coefficients. However, the addition of 3 wt % CODP presents a stable and lower friction coefficient compared with the others (Fig. 6a). From Fig. 6b, we can see that LCG with 3 wt % CODP exhibits smaller friction coefficient than the pure grease during a frequency ramp test from 15 to 40Hz. However, ZDDP as comparison exhibits a friction behavior that is comparable to the base grease. Fig. 6c demonstrates that wear volumes increase in the following sequence: 3 wt % CODP < 3 wt % ZDDP < LHG, and 3 wt % CODP < 3 wt % ZDDP < LCG. These are consistent with the results shown in Fig. 5. Both the friction reduction and AW capability of CODP are very prominent during the test, and the tribological properties of CODP are better than those of ZDDP under the same conditions. Furthermore, from Fig. 5 and 6, we can see that both the friction reduction and AW capability of CODP and ZDDP in LHG are better than in LCG.

Fig. 7 shows a load ramp test of 3 wt % ZDDP and 3 wt % CODP in the two base greases from 100 N up to 500 N stepped by 100 N intervals with 5 min test duration for each load at 150 ^{o}C. Besides, Table 2 clearly demonstrates that the maximum contact pressures (P_0) increased exponentially, from 2.155 GPa at 100 N up to 3.685 GPa at 500 N. From the test, it can be seen that although the friction coefficients of LHG and LCG plus 3 wt % ZDDP and 3% CODP showed surprisingly large increases in the welding load during extreme pressure test, the friction coefficients of LHG and LCG plus 3 wt % CODP decreased significantly. Whereas the two base greases plus 3 wt % ZDDP as comparison exhibited relatively high friction coefficient under the same conditions. These results verify that CODP as additive in the two base greases both in the constant load, variable load, and variable frequency tests have better tribological performance for steel/steel contacts at 150 ^oC. This may be due to the high thermal stability and the effective boundary films formed.[22,23]

3.3.3 Four-Ball Wear Test

The antiwear properties of CODP as additive in the base greases were also evaluated with a four-ball tribometer. Test conditions were as follows: rotational speed 1200 rpm, test duration time 30 min, load 196 N and temperature 150^oC. Table 3 shows the mean WSD of the lower steel balls lubricated with the base greases containing 3 wt % ZDDP and 3 wt % CODP. Both CODP and ZDDP are found to reduce WSD at the optimum concentration. The WSD increase in the following sequence: 3 wt % CODP < 3 wt % ZDDP < LHG, and 3 wt % CODP < 3 wt % ZDDP < LCG. Moreover, the AW capability of CODP and ZDDP in LHG are better than in LCG. This is consistent with the results shown in Fig. 5 and 6. The possible reason might be relevant to a corrosive action of CODP and ZDDP in LCG (the results of copper strip corrosion tests are shown in Table 3).

3.4 Surface Analysis

Fig. 8, 9 give the morphologies of worn steel surfaces lubricated by the two base greases plus 3 wt % ZDDP and 3 wt % CODP at 100 N, 25Hz and 150^oC. It is clearly seen that the worn surfaces of the steel lubricated by neat base greases display considerably wider and deeper wear scars; severe scuffing occurred in this case (LHG: Fig. 8a-b; LCG: Fig. 9a-b). However, the wear scars of steel discs lubricated by 3 wt % ZDDP is relatively narrow and shallow, and scuffing is greatly alleviated, as shown in Fig. 8c-d and Fig. 9c-d. In marked contrast, when 3 wt % CODP is added into LHG, not only is the width of wear scars smaller in size for steel discs but the abrasions is also fewer and smoother (LHG + 3 wt % CODP: Fig. 8e-f); when 3 wt % CODP is added into LCG, the wear scars obviously become narrow and the friction scratches also become thinner and more shallow (LCG + 3 wt % CODP: 9e-f). This is consistent with the previously measured wear volume results, which again proved that CODP has excellent antiwear property at elevated temperature.

In order to explore the lubricating mechanism of CODP additive, we obtained the XPS spectra of the worn steel surfaces lubricated by 3 wt % CODP in LHG (Fig. 10a) and LCG (Fig. 10b) at 150 ^{o}C. It can be seen that no obvious difference is observed in XPS spectra of Fe2p on the worn surfaces. The peaks of Fe2p appear at approximately 711.5 and 725.1 eV, which corresponds to Fe(OH)O and Fe_3O_4.[21,24] XPS peaks of O1s appear at the binding energies of 531.2-532.6 eV, which may include P-O bonds and C-O bonds.[24,25] XPS peak of P2p appearing at 133.7 eV may correspond to $FePO_4$.[24,26] Given the above explanations, it is suggested that chemical reactions occurred on the wear surface in the frictional process with the generation of a boundary lubrication film composed of Fe(OH)O, Fe_3O_4, $FePO_4$ and compounds containing the P-O bonds etc., which significantly contribute to the friction-reducing and antiwear properties of CODP in the two base greases at elevated temperature.

4 Conclusions

Castor oil tris(diphenyl phosphate) was synthesized and its tribological properties has been studied as high temperature friction-reducing and anti-wear additive in lithium 12-hydroxystearate greases (LHG) and lithium complex grease (LCG) at 150 ^{o}C. The friction and wear test results show that the additive reduces friction significantly and has excellent anti-wear properties during lubrication of steel/steel contacts. XPS analysis revealed that the good tribological properties of CODP is attributed to the formation of a surface-protective film composed of Fe(OH)O, Fe_3O_4, $FePO_4$ and compounds containing the P-O bonds. The film was generated on the worn surface, which resulted in good friction-reducing and anti-wear performance at elevated temperature.

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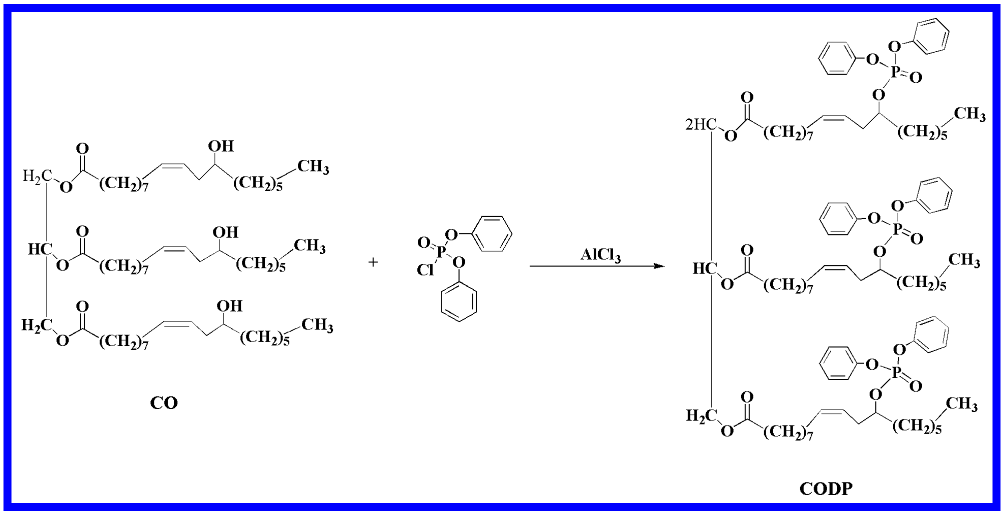
Figures



Scheme1 Synthetic route for CODP.

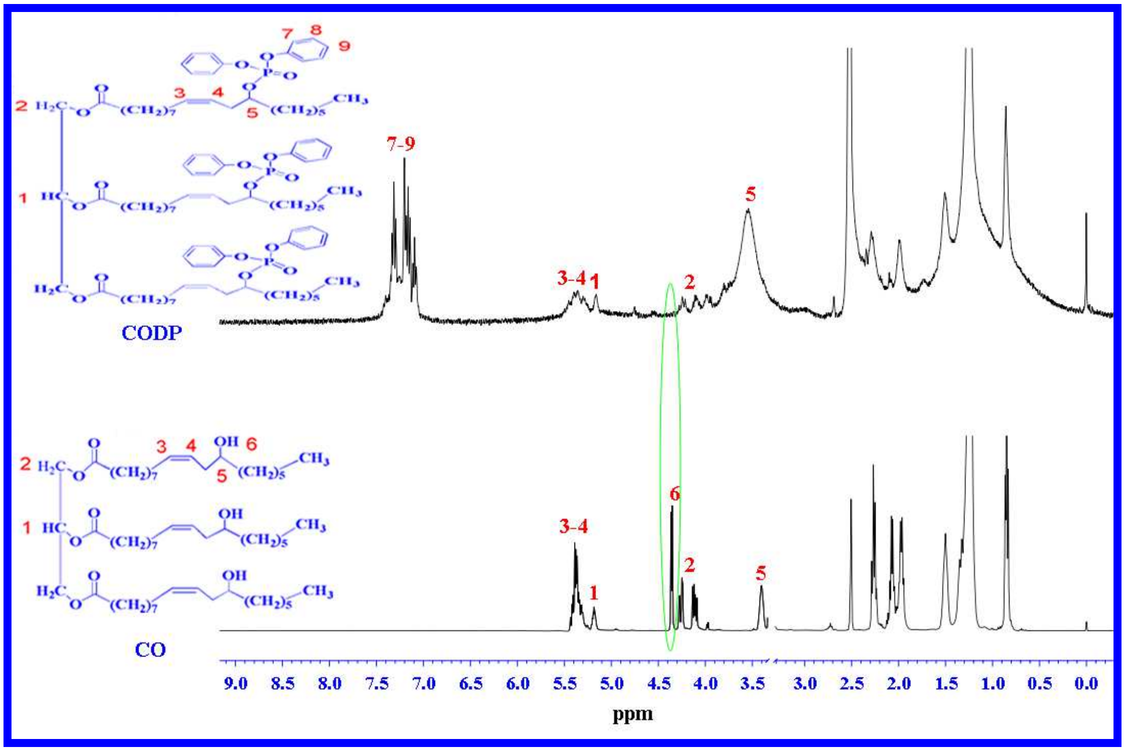


Fig. 1 ^{1}H NMR spectrum of CO and CODP.

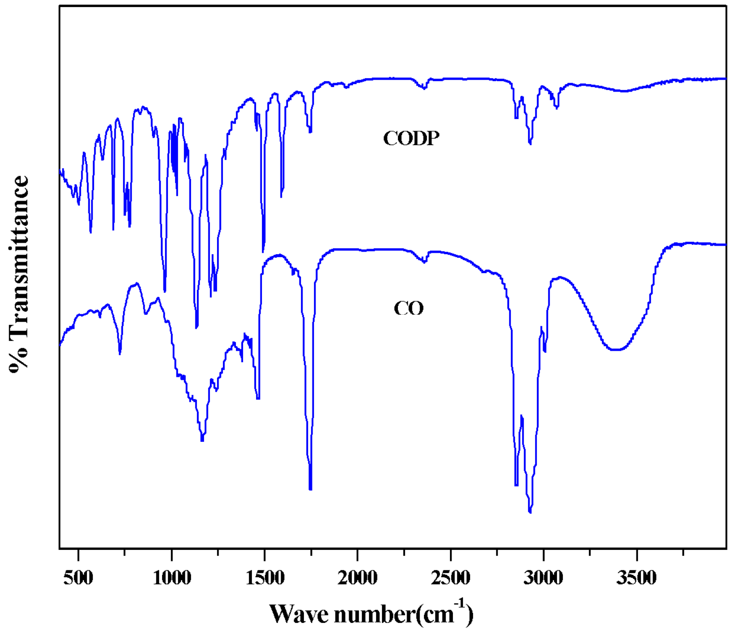


Fig. 2 FTIR spectrum of CO and CODP.

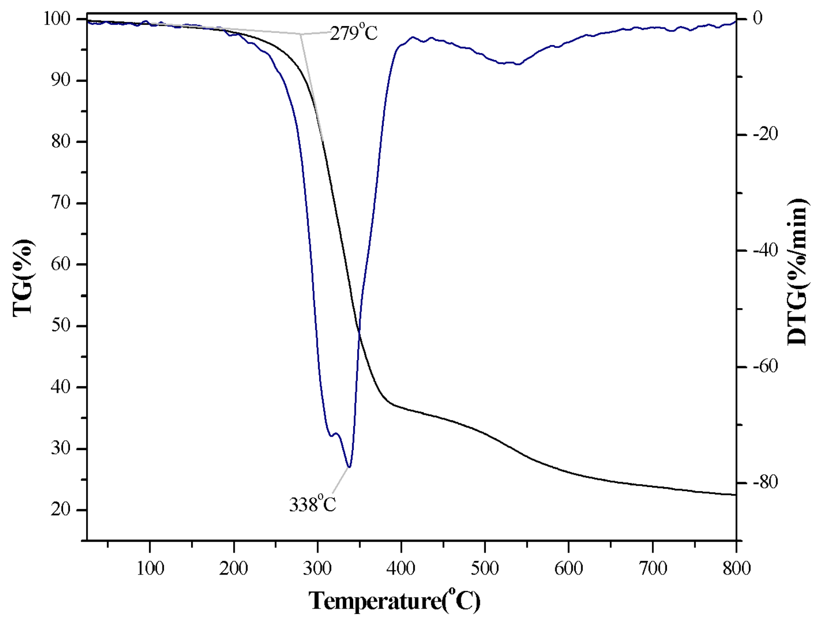


Fig. 3 TG/DTG curves of CODP in air atmosphere.

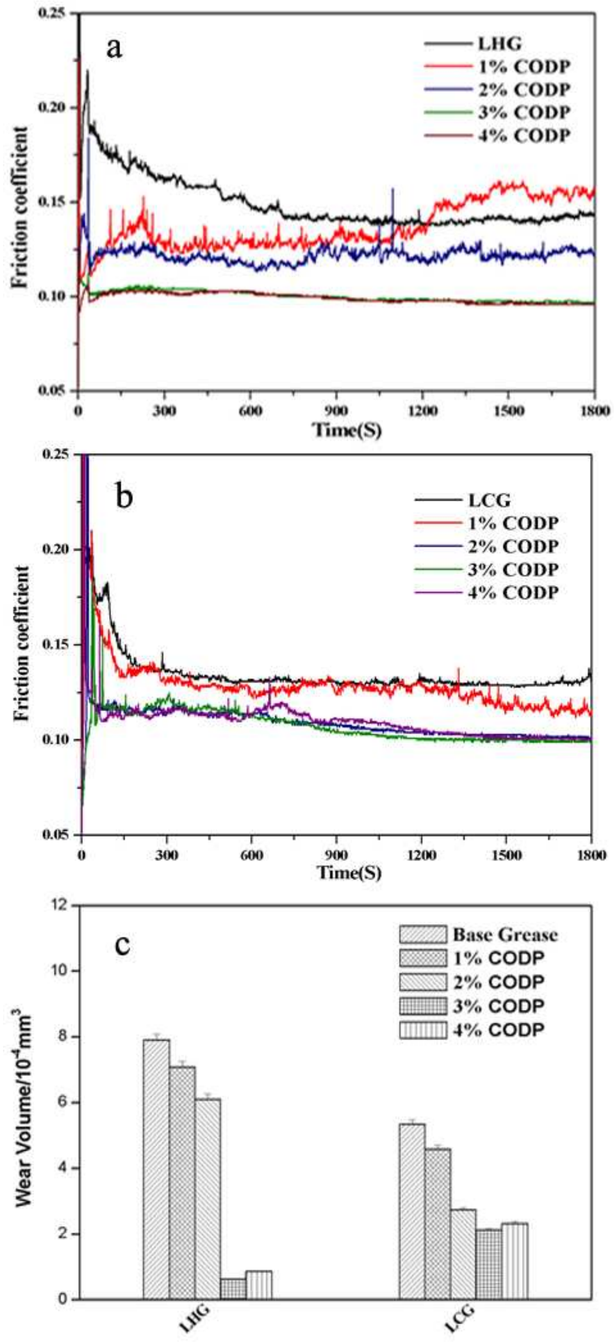


Fig. 4 (a-b) Evolution of friction coefficient with time at 100 N for the base greases plus CODP additive at different concentrations; (c) Wear volume losses of the steel discs lubricated by LHG and LCG with CODP at different concentrations after the constant load tests. (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min; temperature, 150 ^{o}C).

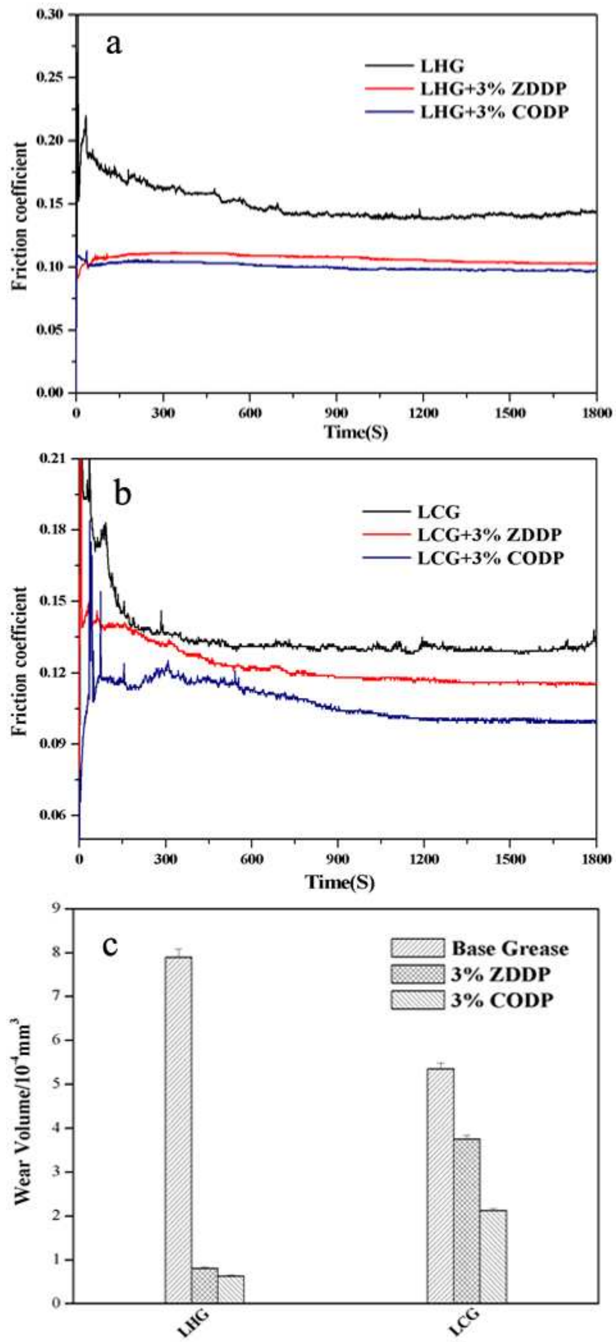


Fig. 5 (a-b) Friction coefficient curves and (c) Wear volumes of steel/steel contacts lubricated by LHG and LCG with 3 wt % ZDDP and 3 wt % CODP. (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min; temperature, 150 ^{o}C).

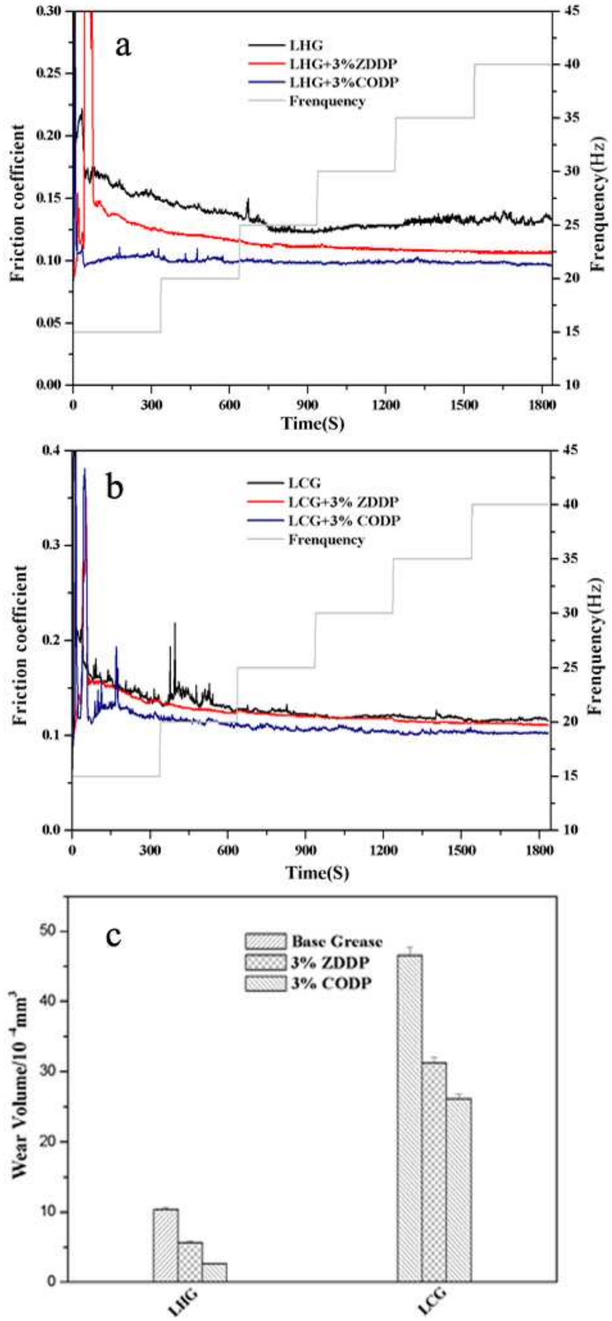


Fig. 6 (a-b) Evolution of friction coefficient with time during a frequency ramp test from 15 to 40 Hz for the base greases with CODP additive at 150 ^{o}C; (c) Wear volume losses of the steel discs lubricated by the two base greases plus 3 wt% each of ZDDP and CODP at 150 ^{o}C. (load, 200 N; stroke, 1 mm; frequency, 15-40 Hz).

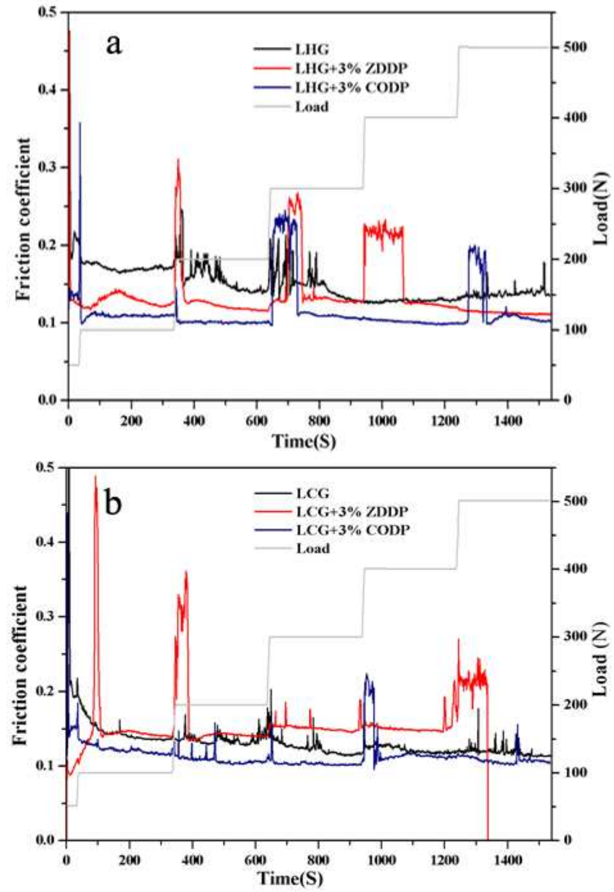


Fig. 7 (a-b) Variations of the friction coefficient with time during a load ramp test from 100 to 500N for the two base greases plus 3 wt % ZDDP and 3 wt % CODP at 150 ^{o}C. (load, 100-500 N; stroke,1 mm; frequency, 25 Hz).

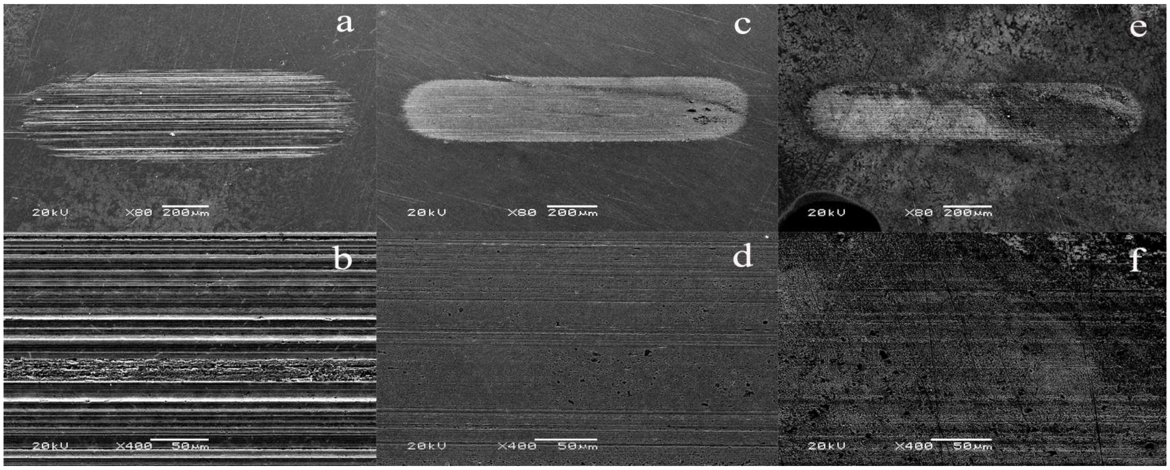


Fig. 8 SEM morphologies of worn surfaces lubricated by LHG plus CODP additive: (a, b) LHG, (c, d) 3 wt % ZDDP and (e, f) 3 wt % CODP (the magnification of the above is 80×, and that of the below is 400×; SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min; temperature, 150 °C).

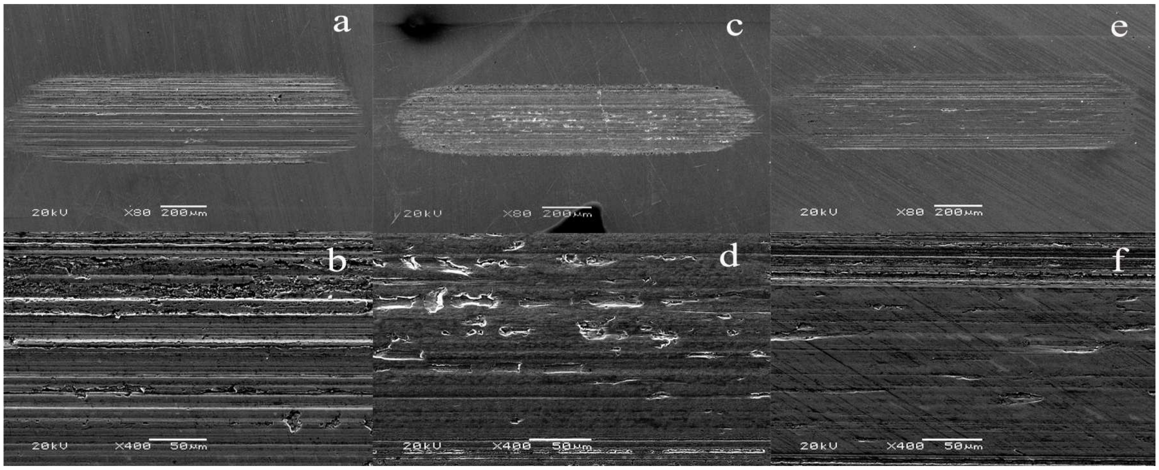


Fig. 9 SEM morphologies of worn surfaces lubricated by LCG plus CODP additive: (a, b) LCG, (c, d) 3 wt % ZDDP and (e, f) 3 wt % CODP (the magnification of the above is 80×, and that of the below is 400×; SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min; temperature, 150 °C).

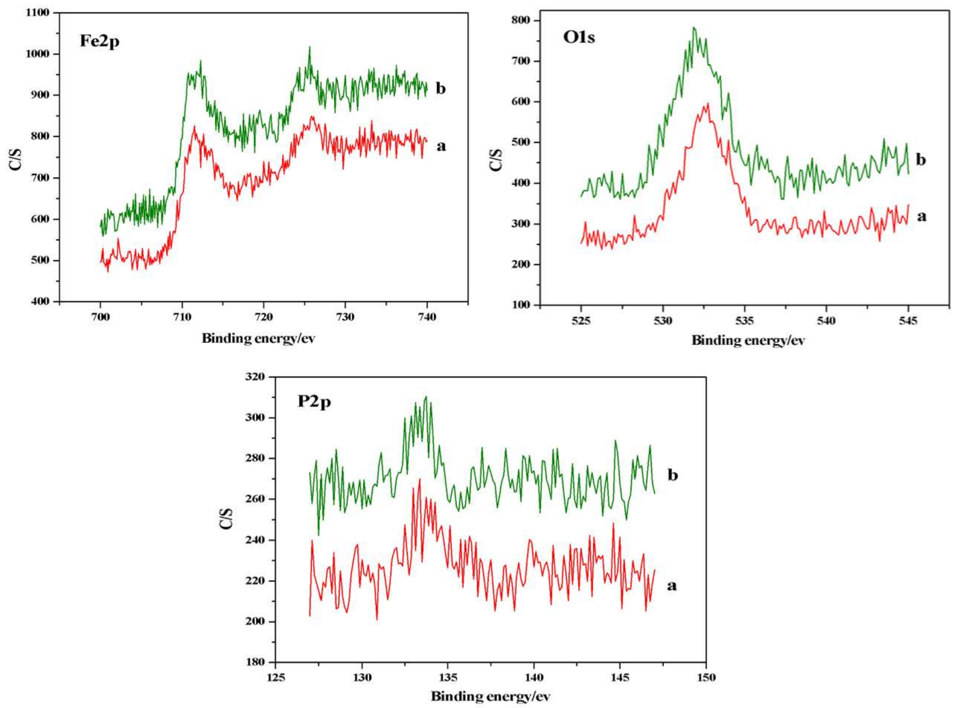


Fig. 10 XPS spectra of Fe 2p, O 1s and P 2p of the worn surfaces lubricated by (a) LHG + 3 wt % CODP and (b) LCG + 3 wt % CODP at 150 ^{o}C (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min).

Tables

Table 1 Performance parameters for Lithium12-hydroxystearate greases and lithium complex grease

item	result		test method
	lithium12-hydroxystearate greases (LHG)	lithium complex grease (LCG)	
work penetration (1/10 mm)	314	320	GB/T 269
dropping point (^{o})	210	308	GB/T 3498
copper corrosion (T2 copper, 100 ^{o}C, 24h)	1b	1b	GB/T 7326
steel mesh sub-oil (100 ^{o}C, 24h) (%)	1.7	0.3	SH-T 0324
evaporative capacity (99 ^{o}C, 22h) (%)	0.85	0.32	GB/T 7325
similar viscosity (-10 ^{o}C, 10 s^{-1}) (Pa S)	480	430	SH/T0048
water washout characteristics (38 ^{o}C, 1h) (%)	1.7	1.5	SH/T0109

Table 2 The Hertzian pressures of SRV test at various applied loads

applied load (N)	P_0 (GPa)	P_m (GPa)
100	2.155	1.437
200	2.715	1.810
300	3.108	2.072
400	3.421	2.281
500	3.685	2.457

P_m mean contact pressure, P_0 maximum contact pressure, with the P_0 being 1.5 times the P_m

Table 3 Results of copper corrosion strip and Four-ball wear tests

sample code	corrosion grade[a]	Four-ball wear test WSD (mm)[b]
LHG	1b	0.52
LHG+3 wt % CODP	1b	0.41
LHG+3 wt % ZDDP	1b	0.44
LCG	1b	0.55
LCG+3 wt % CODP	2b	0.45
LCG+3 wt % ZDDP	2c	0.48

[a]T2 copper, 100 ^{o}C, 24h; [b]196 N, 1200 r/min, 30 min.