

EVALUATION ON ANTIWEAR AND LOAD-CARRYING PROPERTIES OF ORGANIC COPPER COMPOUNDS CONTAINING SULFUR AND PHOSPHORUS IN LUBRICANTS

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Abstract

Copper dialkyl-dithiophosphyl-dithiophosphate additives with different alkyl groups were synthesized. A four-ball tester was used to evaluate the tribological performance of these additives in mineral base oil under different loads, compared with commercial additives. The results show that they exhibit excellent antiwear and load-carrying capacities and better than commercial additives. The surface analytical tools such as Auger Electron Spectrometer (AES), Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) were used to investigate the topography, the contents and the depth profile of some typical elements on the rubbing surface of worn scar. Smooth and light topography of worn scar further confirms that the additive showed good antiwear capacities, the results of Auger electron spectrometer and energy dispersive X-ray analysis indicate that tribo-chemically protective films consists of copper containing compounds, sulfides, sulphates and phosphates were formed on the rubbing surface, which contribute to improving the tribological properties of lubricants. Particularly, the results from depth profile indicate that a large number of copper atoms are rich in outer layer of surface, which play an important role in improving antiwear properties of oils.

Key words: Copper dialkyl-dithiophosphyl-dithiophosphate; additive; antiwear; load-carrying; surface analysis.

1. Introduction

Many organic metal compounds containing phosphorus and sulphur groups were used as extreme pressure (EP) and antewear (AW) additives to improve the friction and wear behaviors of mineral oils. Under boundary lubrication conditions, these chemically active compounds undergo decomposition under extreme conditions (high load and high temperature) forming protective films through the adsorption process and chemical reactions, so thin layers prevent welding of surface asperities and thus reduces adhesive wear [1,2]. Their effectiveness is determined by their ability of form a protective film on sliding contacts. This ability is related to their action mechanism, namely physical adsorption, chemisorption or chemical reaction with the metal. Their performance depends not only on the polarity due to a functional group, but also on the quantity of chemically active elements, the activity of decomposition products and the chemical activity of metal surfaces [3-5].

Metal dialkyl-dithiophosphyl-dithiophosphate are mainly used as antioxidants, antiwear, extreme pressure and anticorrosive additives for lubricating oils. They can provide particularly protection against wear similar to that achieved with other multifunctional additives, but at substantially lower concentrations, can give better protection at equal concentration, metal may be selected from zinc, molybdenum, antimony, etc [6-8].

Thin films of soft metals are generally used to reduce wear and friction between rubbing materials when the surfaces are working under severe conditions. It is discovered that soft metal compounds, such as copper, tin, cadmium can produce elemental metal atoms under tribochemical conditions, which deposit on the rubbing surfaces, and play a key role on lubrication and antiwear protection [9-12]. The addition of carbon-coated copper nanoparticles can decrease wear and increase the load-carrying capacity of the base oil [13]. In addition, copper coating as a solid lubricant exhibits better friction and wear properties than nickel and tin coatings tested under the same conditions [14].

In view of these observations, the authors have synthesized copper dialkyl-dithiophosphyl-dithiophosphate with different alkyl groups, to be used as an AW/EP additive. Its antiwear and load-carrying properties have been evaluated in mineral base oil. The quality of the wear

scar, chemical states of elements and depth profile in the reactive films has been identified by surface analysis such as AES, SEM and EDX, and the action mechanism are proposed.

2. Experimental

2.1 Oil samples and additives

Mineral oil 500SN was used as base oil. The additives were a commercial amine dialkyl-dithiophosphyl -dithiophosphate (T 307), zinc dialkyldithiophosphate (ZnDTP) and Copper dialkyldithiophosphyl-dithio -phosphate ($\text{Cu}(\text{DDP})_2$), which was prepared by four steps synthesis. In the first step, mixtures of alcohol with different alkyls are reacted with phosphorus pentasulfide at 90–110°C to yield corresponding dithiophosphoric acid. In the second step, dithiophosphoric acid is reacted with epoxy propylene at 35–40°C, the dithiophosphoric alcohol is produced. In the third step, it is reacted with phosphorus pentasulfide at 80–90°C again, the dithiophosphyl-dithiophosphoric acid is obtained, which was neutralized with alkali metal hydroxide, and filtered. Fourth step, the filtrate in distilled water were mixed with copper chloride aqueous solution at room temperature, then light blue liquid precipitate was extracted with diethyl ether, the ether extracts were dried and filtered to produce a light blue semi-liquid of $\text{Cu}(\text{DDP})_2$. The compound was characterized by element analysis and IR. Meanwhile, zinc dialkyldithiophosphyl-dithiophosphate was synthesized.

2.3 Tribological tests

Tribological performances of mineral oil containing additives were evaluated with a four-ball tester at a rotating speed 1450 rpm, test duration of 30 min, room temperature about 25 °C. The balls used in the tests were made of GCr15 steel at a diameter of 12.7mm with HRC of 59 to 61.

An optical microscope was used to determine the wear scar diameters of the three lower balls with readings as accurate as 0.01 mm, the average of the three wear scar diameters was calculated each time. Then, the average of three experiments is cited as the wear scar diameter reported in this paper.

2.4 Surface analysis

Profiles and elemental distributions of the worn surfaces were obtained using scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis. Particular attention was paid to the atomic concentration of elements on the worn scars of the steel balls. The elements present in the surface films and their depth profile were investigated using PHI 610 Auger electron spectrometer (AES). This was done in the working vacuum below 1.33×10^{-7} Pa, with an electron beam energy of 3KV. The depth profile was accomplished by sputtering through the surface layer using a 25 mA and $1 \times 1 \text{mm}^2$ Argon ion beam at an estimated rate of 30 nm/min, which was calibrated against SiO_2 .

Before analysis, all samples were ultrasonically rinsed with hexane and petroleum ether for 10 min.

3. Results and discussion

3.1 Evaluation on antiwear and load-carrying capacities of additives

Copper Dialkyl-dithiophosphyl-dithiophosphate ($\text{Cu}(\text{DDP})_2$) was added to the 500SN oil and the resultant antiwear properties were evaluated by the four-ball tester under loads of 392, 588 and 686 N for 30 min according to ASTM D4172–82. The load-carrying capacities of additive was characterized as maximum non-seizure load (P_B value) and weld load (P_D value) which was evaluated according to ASTM D2783–88. The relationships between its performances and the concentrations are also given, for comparison, the performances of T 307 and ZnDTP were also evaluated.

The wear scar diameter (WSD) of tested balls lubricated with different samples under different loads are list in Table 1, from which we can see clearly that the WSD adding $\text{Cu}(\text{DDP})_2$ was obviously smaller than base oil and additive T 307 at each experimental load, and its antiwear properties are better than ZnDTP with same alkyl group at higher loads. Accordingly, $\text{Cu}(\text{DDP})_2$ exhibits good abilities as regards antiwear properties at less concentration.

Table 1 Wear scar diameter with oils containing Cu(DDP)₂ (392, 588 and 686 N, 30 min)

Additives	Concentration wt .%	Wear scar diameter , mm		
		392 N	588 N	686 N
500SN	–	0.62	0.80	failure
T 307	1.5	0.47	0.60	0.82
ZnDTP (i-butyl)	3.0	0.35	0.56	0.80
Cu(DDP) ₂ (i-butyl)	1.5	0.31	0.40	0.55
ZnDTP (i-pentyl)	3.0	0.32	0.58	0.78
Cu(DDP) ₂ (i-pentyl)	1.5	0.32	0.46	0.59
ZnDTP (n-octyl)	3.0	0.32	0.68	0.95
Cu(DDP) ₂ (n-octyl)	1.5	0.30	0.47	0.64

Table 2 Influence of Cu(DDP)₂ concentration on load-carrying capacities of 500SN

Additive	Concentration wt , %	Maximum non seizure load P _B , N	Weld load P _D , N
500SN	-	696	1568
T307	1.5	1118	2450
ZnDTP (i-butyl)	3.0	950	2450
Cu(DDP) ₂ (i-butyl)	1.5	1329	3087
ZnDTP (i-pentyl)	3.0	980	2450
Cu(DDP) ₂ (i-pentyl)	1.5	1294	3920
ZnDTP (n-octyl)	3.0	1029	2450
Cu(DDP) ₂ (n-octyl)	1.5	1398	3920

The P_B and P_D values of oil containing different additives were organized in Table 2, the results summarized indicate that Cu(DDP)₂ could improve load-carrying properties of the base oil dramatically, the P_B and P_D value of the base oil was enhanced about two times respectively. Moreover, the P_B and P_D value of oil containing Cu(DDP)₂ additives are better than ZnDTP with same alkyl group and T 307. As a whole, They possess good antiwear and load carrying properties under the same conditions.

3.2 Surface analysis

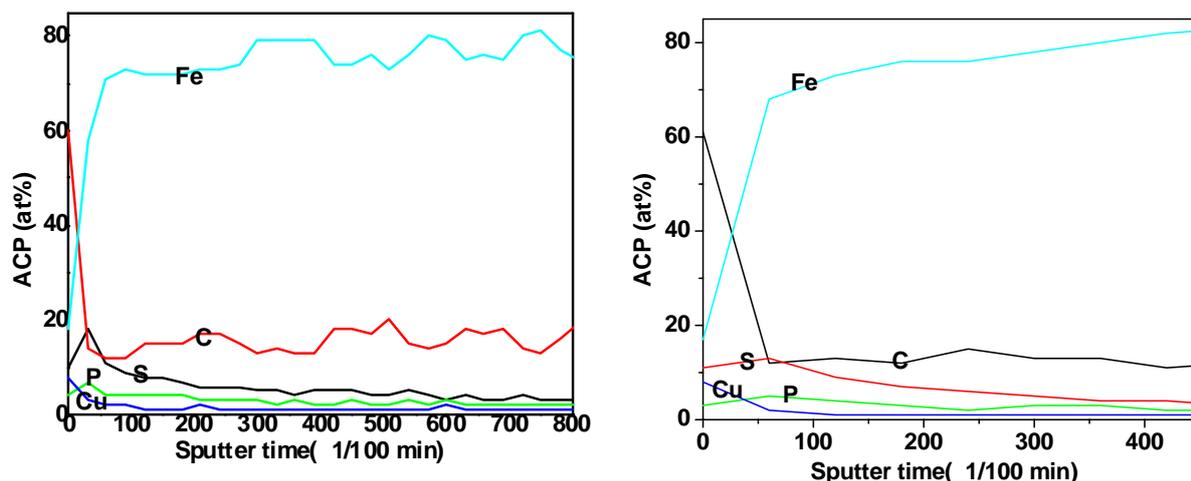
3.2.1 Auger electron spectroscopy (AES)

Table 3 give the AES analysis of a worn scar lubricated with 1.5% Cu(DDP)₂ under 588 and 686N. It can be seen that the surface films contain following elements: copper, sulfur, oxygen, phosphorus, carbon and iron. Furthermore, there are copper and sulfur-rich layers existing on the surface by analyzing the contents of elements.

Table 3 Elements contents present in worn surface lubricated with 1.5% Cu(DDP)₂ under the different loads

Elements	C	O	P	S	Fe	Cu
588 N	42.96	34.54	4.12	8.76	3.82	5.80
686 N	43.46	35.35	3.51	9.08	3.19	5.41

Fig. 2 (a) (b) give the AES spectra profiles of a wear scar lubricated with Cu(DDP)₂ under corresponding loads. Auger depth profile technique can provide the distribution of the relative atomic concentration of elements in the films. From which we can observe that there are a large number of copper atoms on the top layer of two rubbed surfaces, and with the increase of sputter time, the contents of copper atoms decreased. After sputtering for 0.5 min, copper atoms disappeared, at the same time, the atomic concentrations of sulfur, phosphorus and iron attain the maximum.



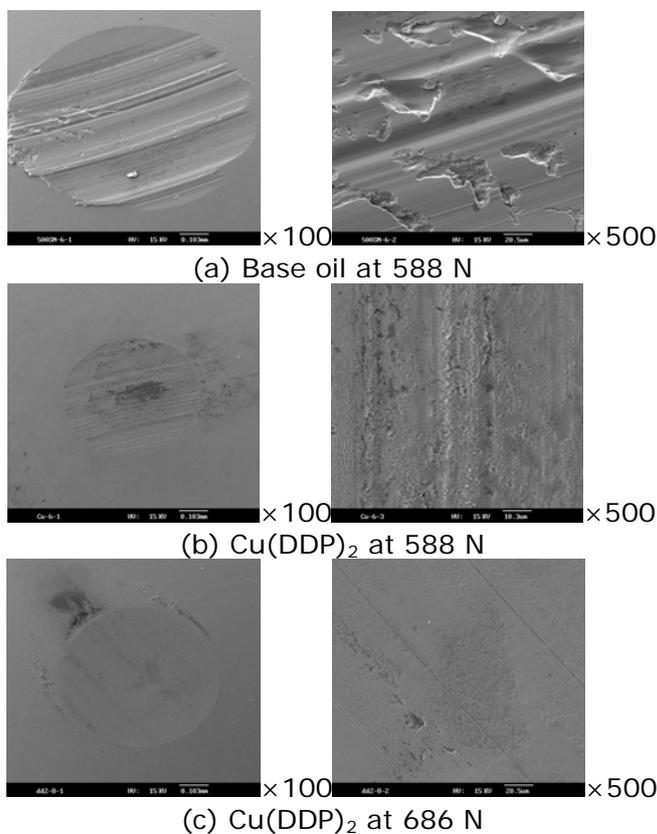
(a) AES depth profile of $\text{Cu}(\text{DDP})_2$ at a load of 588 N

(b) AES depth profile of $\text{Cu}(\text{DDP})_2$ at a load of 686 N

Fig. 2 AES depth profile of a wear scar lubricated with 1.5% $\text{Cu}(\text{DDP})_2$ under the different loads

Fig. 3 (a), (b), (c), (d) show the wear scar micrographs of the steel balls lubricated by 500SN oil under 588 N and the same with $\text{Cu}(\text{DDP})_2$ under 588, 686 and 784 N. the area of wear scar with 500SN oil was 3 times larger than oil containing $\text{Cu}(\text{DDP})_2$ under 588 N, the enlarged micrographs ($\times 500$) display that the scratched surface lubricated by $\text{Cu}(\text{DDP})_2$ is uniform and smooth. However, the one lubricated by basic oil had already been broken at the same experimental condition. Therefore, above evidences further prove that $\text{Cu}(\text{DDP})_2$ exhibits good antiwear properties as a lubricant additive.

3.2.2 Scanning electron microscopy (SEM) with energy dispersive X-ray (EDX)



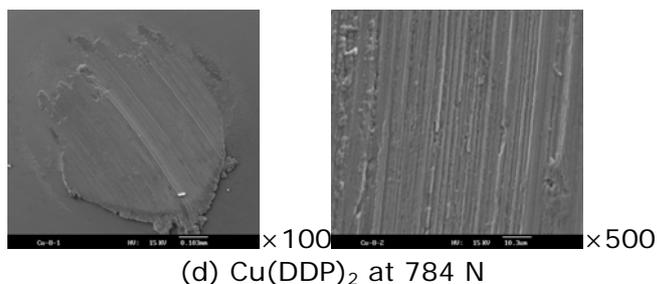


Fig. 3 SEM morphologies of wear scar lubricated with the 500SN, $\text{Cu}(\text{DDP})_2$ under different load

In addition, from Fig. 3 (b), (c), (d), we can see clearly the existence of some deposits surrounding wear scar. The elemental distribution on the wear scar at 588, 686 and 784N were estimated with EDX, the atomic concentrations of the elements evaluated on the wear scar by SEM-EDX are shown in Fig.4, in which the data are provided by a computer program with EDX and normalized to all given compositions 100. The results of EDX show that more copper atoms were formed on the wear scar at 588, 686 and 784N, and larger than sulfur, phosphorus atoms. Moreover, the contents of Copper atoms decrease with increase of loads, these changes are consistent with the enlargement of wear area and deterioration of wear surface qualities. Meanwhile, we discovered a large amount of Copper atoms exist in the deposits surrounding wear scar, these phenomenon are resulted from accumulating of copper atoms on the surface, only were gradually moved toward the border of worn scar because of lower absorption after reciprocating sliding. On the other hand, we can see clearly that atomic concentration ratios of element Cu to S on the wear scar at different loads are all far exceed the ratio of CuS 1:1 or Cu_2S 2:1, especially that on the deposit is 8.42: 2.82 under the load of 784N. So we can presume that copper (0) atoms, CuS or Cu_2S can be formed on wear surface. The phenomenon indicates that the soft Copper films formed play an important role in improving antiwear and load carrying properties of base oils, the authors believe that the copper deposited in the scratch and served as a mending material.

From the results shown, it was observed that the compounds interacted with the surface to form stable protective layers that are effective in reducing wear and increasing the load-carrying capacities. On the wear surfaces, the protective layers are comprised of sulfide, oxide, sulfate, and phosphate. Especially Copper soft metal layer may be promoted by mechanical energy, heat, and exoelectron effects under severe friction conditions [14]. Due to low melting point 220°C with CuS , and lower shear capacity of soft copper, CuS and Cu_2S , which provide positive effects on lubrication largely by improving the antiwear and load-carrying properties.

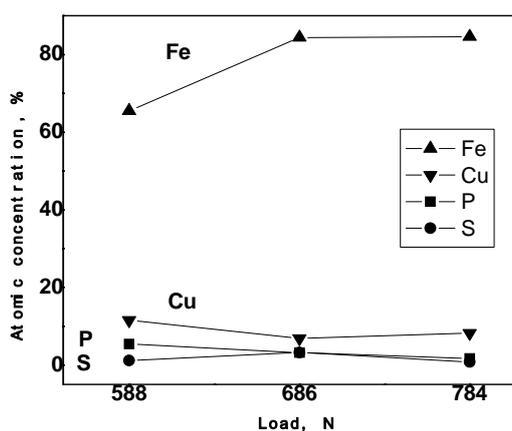


Fig. 4 Atomic concentration (%) of elements on the worn surface with different loads

5. Conclusion

(1) Copper diisopropyldithiophosphate synthesized possess good antiwear and load carrying capacities when used in lubricant formulation, and better than traditional additives T 307 and ZnDTP.

(2) The surface examination of the rubbing zone indicate that the protective layers are composed of some compounds formed from copper, oxygen, sulfur, phosphorus and iron elements in the sliding process.

(3) Existence of metal Copper (0) CuS and Cu₂S produced by tribo-reduction could be deposited on the rubbing surfaces, which help to improve the tribological performances of oil.

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