Antiwear Properties and Lubrication Mechanism of Bis(N,N-dipentylcarbamoithioylthio)cadmium in Mineral Oils

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A bis(N,N-dipentylcarbamoithioylthio)cadmium additive was synthesized. A four-ball tester was used to evaluate the tribological performance of the additive in mineral oil, and compared with same types of metal additives. The results show that it exhibits better anti-wear and load-carrying capacities. The surface analytical tools such as X-ray photoelectron spectrometer (XPS), Auger electron spectrometer (AES), Scanning electron microscopy (SEM) with Energy dispersive X-ray (EDX) were used to investigate the topography, the compositions contents and the depth profile of some typical elements on the rubbing surface of worn scar. Smooth topography of worn scar further confirms that the additive showed good anti-wear capacities, the results of XPS, AES and energy dispersive X-ray analyses indicated that tribochemical mixed protective films consists of cadmium atoms, sulfides and sulphates were formed on the rubbing surface, which contribute to improve the tribological properties of lubricants. Particularly, large amounts of sulfur and cadmium atoms play an important role in improving anti-wear properties of oils.

Keywords: bis(N,N-dipentylcarbamoithioylthio)cadmium, additive, anti-wear, load-carrying, mechanism

1. Introduction

Many organic metal compounds containing phosphorus and sulphur groups were used as extreme pressure (EP) and anti-wear (AW) additives to improve the friction and wear behavior of mineral oil based lubricants. Under boundary lubrication conditions, these chemically active compounds undergo decomposition under extreme conditions (high load and high temperature) forming a protective film through the adsorption process, so the thin layer prevents 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 the decomposition products and the chemical activity of the metal surfaces³⁻⁵⁾.

Metal dialkyl-dithiocarbamates are mainly used as antioxidants, anti-wear, extreme pressure and anticorrosive additives for lubricating oils. They can provide particularly protection against wear similar to that achieved with additives of the prior art, but at

substantially lower concentrations, or give better protection at equal concentration, metal may be selected from zinc, molybdenum, antimony, copper etc^{6,7)}.

Thin films of soft metals are generally used to reduce wear and friction between rubbing materials when the surfaces are working under severe conditions. Cadmium coating as a solid lubricant exhibits better friction and wear properties than nickel and copper coatings tested under the same conditions thought it is banned as a harmful chemical substances by European Community regulation⁸⁾. Oil-soluble Cd (II) compounds, such as dimethyl cadmium, possess good friction reducing properties as lubricant additives^{9,10)}. It is discovered that soft metal compounds, such as copper, tin can produce elemental metal atoms under tribochemical conditions, which deposit on the rubbing surfaces, and play a key role on lubrication and anti-wear protection^{11,12)}.

In view of these observations, the authors have synthesized bis(N,N-dipentylcarbamoithioylthio)cadmium additive. Its anti-wear and load-carrying properties have been studied in mineral oil. The quality of the wear scar, chemical states of elements and depth profile in the reactive films have been identified by surface analysis such as XPS, AES, SEM and EDX.

2. Experimental

2.1. Oil samples and additives

Mineral oil 500SN was used as the base oil. Bis(N,N-dipentylcarbamothioylthio)cadmium (CdDDC), was prepared by a two-step synthesis. Firstly, diamylamine was reacted with carbon disulphide in the presence of sodium hydroxide to yield corresponding sodium diamyldithiocarbamates. Further sodium salt of reactions was neutralized with cadmium chloride to produce CdDDC in distilled water. The additive antimony diamyl-dithiocarbamate (SbDDC) and molybdenum dialyl-dithiocarbamate (MoDDC) was commercially purchased from R.T. Vanderbilt company, and the dibutyl tin dibutyl-dithiocarbamate (SnDDC) and bismuth diamyl-dithiocarbamate (BiDDC) were synthesized in the lab.

2.2. Tribological tests

Tribological performances of mineral oil containing additives were evaluated with a four-ball machine 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 bearing steel (AISI52100) at a diameter of 12.7 mm with HRC of 59 to 61. The average of the three wear scar diameters was calculated and cited as the wear scar diameter reported in this paper.

2.3. Surface analysis

Profiles and elemental distributions of the worn surfaces were obtained using scanning electron microscopy (SEM). The chemical states of surface films were investigated using PHI 5300 X-ray photoelectron spectrometer (XPS). XPS analysis was investigated the chemical states of the elements present, the radiation source was Mg K α line with pass energy of 29.35 eV and Ar⁺ ions of 3000 eV energy were used for sputtering. All binding energies were compared with a reference standard of 284.6 eV for carbon. The depth profile of elements present was investigated using PHI 610 Auger electron spectrometer (AES). This was done with an electron beam energy of 3 KV. The depth profile was accomplished by sputtering through the surface layer using a 25 mA and 1×1 mm². Argon ion beam at an estimated rate of 30 nm/min. Before analysis, all

samples were ultrasonically rinsed with hexane and petroleum ether for 10 min.

3. Results and discussion

3.1. Evaluation on tribological performance in mineral oil

Bis(N,N-dipentylcarbamothioylthio)cadmium (CdDDC) was added to the 500SN oil and the resultant anti-wear properties were evaluated by the four-ball friction tester under loads of 392 and 588 N load for 30 min according to ASTM D4172-82. The load-carrying capacities of additive were 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 SbDDC, BiDDC, SnDDC and MoDDC were also evaluated.

The wear scar diameter (WSD) of tested balls and the P_B and P_D values of oil containing different additives are organized in Table 1, from which we can see clearly that the WSD adding CdDDC was smaller than base oil, and obviously smaller than SbDDC, BiDDC, SnDDC and MoDDC respectively under same conditions. Moreover, the anti-wear capacity increases are not obvious when the concentration of CdDDC is greater than 1.0%. In addition, the results summarized indicate that CdDDC could improve load-carrying properties of the base oil obviously, the P_B and P_D values of the base oil are enhanced by 75% and 56% respectively at 1.5%. The P_B and of P_D values oil containing CdDDC are better than SbDDC, SnDDC and MoDDC, only P_D value is lower than BiDDC which is an excellent extreme pressure additive. As a whole, CdDDC additive possesses better anti-wear and load carrying properties among the same types of metal additives.

3.2. Surface analysis

3.2.1 X-ray photoelectron spectroscopy (XPS)

The four-ball worn surfaces, produced by being rubbed in the oil containing 2.0% CdDDC for 30 min at a load of 588 N, were analyzed by XPS. The Cd_{3d} and S_{2p} XPS spectra are shown in Fig. 1 (a) (b). It can be seen

Table 1 Wear scar diameter and load-carrying capacities with oils containing CdDDC

Additive	Concentration wt. %	Wear scar diameter, mm		Maximum non seizure load P_B , N	Weld load P_D , N
		392 N	588 N		
500SN	0	0.632	0.873	549	1568
CdDDC	0.5	0.590	0.802	882	1960
	1.0	0.531	0.770	882	1960
	1.5	0.492	0.795	980	2450
	2.0	0.528	0.753	980	2450
SbDDC	2.0	0.633	0.835	804	1960
BiDDC	2.0	0.638	0.955	882	3920
SnDDC	2.0	0.582	0.913	745	1960
MoDDC	2.0	0.612	0.887	598	1960

Fig. 1 XPS spectra of elements Cd and S on the worn scar before and after sputtering for 5 min

from Fig. 1(a) that, before and after sputtering, cadmium atoms could be detected on the worn surface, the binding energy of Cd 3d at 405.4 eV and the difference between Cd 3d_{3/2} and Cd 3d_{5/2} is 6.7, are consistent with the standard electron binding energy of a simple cadmium atom¹³⁾. Thus, we can also confirm existence of cadmium (0) atom formed on the surface.

In Fig. 1(b), the binding energy of S 2p are 161.2 eV and 168.8 eV which correspond to FeS, FeSO₄ before sputtering, indicates that tribochemical reactions occur between the additives and metal surfaces during the sliding process. The anti-wear additive containing sulphur can be adsorbed on metal surfaces, and react with the metal to form protective films that help to reduce metal contact. However, after 10 min of sputtering, the peak (FeSO₄) at binding energy of 168.8 eV is disappear, only FeS exists on inner surface. It is concluded that FeS layer is effective on reducing the wear and increasing the load-carrying capacity.

3.2.2 Auger electron spectroscopy (AES)

Fig. 2 gives the AES spectra profiles of a wear scar lubricated with CdDDC under load of 588 N. 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 cadmium atoms on the top layer of two rubbed surfaces, and with the increase of sputter time, the contents of cadmium atoms decreased. After sputtering for 0.5 min, cadmium atoms disappeared, at the same time, the atomic concentrations of sulfur attain the maximum, then it decreased gradually with the increase of sputter time.

3.2.3 Scanning electron microscopy (SEM) with Energy dispersive X-ray (EDX)

Fig. 3 (a), (b), (c), (d) show the worn scar micrographs of the steel balls lubricated by 500SN oil and the with 0.5% CdDDC additive under 392 and 588 N. From which we can see clearly that the wear area with base oil was slightly larger than oil containing CdDDC under same loads. Especially, under load of 588N, the enlarged micrographs ($\times 500$) display the one lubricated by basic oil had already been broken, but the scratched surface lubricated by CdDDC is better than base oil, therefore, above evidences further prove that CdDDC exhibits better anti-wear properties as a lubricant additive.

In addition, the EDX spectra of worn scar are shown in Fig. 4 and 5, the atomic concentrations of the elements evaluated on the worn scars by SEM-EDX are listed in Table 2. The results of EDX show that more cadmium and sulfur atoms were formed on the worn scar at 588 N than at 392 N. It is suggested that decomposition of the additive was accelerated by increasing loads so that more sulfur and cadmium atoms were produced. On the rubbing surfaces, the sulfides formed from active sulfur could reduce wear and increase the load-carrying capacities, also cause corrosive wear deteriorating rubbing surface qualities. However, the soft cadmium layer promoted by tribo-reduction not only reduces friction and wear due to its low melting point 321°C, but also inhibits corrosion, they provides positive effects on lubrication largely by improving the anti-wear and load-carrying capacity.

Fig. 2 AES depth profile of CdDDC at 588 N

Fig. 3 SEM morphologies of worn scar lubricated with the 500SN, CdDDC under different load

4. Conclusion

- (1) Bis(N,N-dipentylcarbamothioylthio)cadmium synthesized possesses better anti-wear and load carrying capacities than other metal additives containing same structure in lubricants, such as SbDDC, SnDDC and MoDDC.
- (2) The surface examination of the rubbing zone indicated that there is a protective layer consisting of cadmium compounds, sulfides, sulphates in the sliding process. Especially the existence of FeS and cadmium atoms produced by tribo-reduction helps to improve the tribological performances of oils.

5. References

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