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# Tribological properties of oil soluble samarium isooctoxyborate<sup>①</sup>

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**[Abstract]** An oil soluble rare earth compound, samarium isooctoxyborate, was synthesized and used as an antiwear and extreme pressure additive for lubricating oils. Its tribological performances were evaluated with a four-ball machine and a ring-on-block rig. In addition, surface analyses with Auger electron spectroscopy and X-ray photoelectron spectroscopy were also conducted to study the surface film formed by the additive under boundary lubrication conditions. The test results show that the additive exhibits good friction-reducing ability, good antiwear property and excellent extreme pressure performance. Surface analyses further disclose the coexistence of organic film, oxidation film and permeating film on the rubbing surface, which contributed to improve the tribological properties of the base oil.

**[Key words]** tribology; samarium isooctoxyborate; antiwear; friction-reducing; extreme pressure

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## 1 INTRODUCTION

In tribology field, non-active wear resistance additives of lubricating oil exhibit excellent application prospect due to non-corrosiveness and no environment pollution of the active additives, such as sulfur and phosphorus containing compounds. It is well known that oil-soluble boron containing compounds are good non-active reducing-friction additives and possess anti-rust and anticorrosive properties. Unfortunately, organic boron compounds, especially boric ester, are liable to hydrolyze. Hinder phenyl boric ester is thought to be anti-hydrolytic<sup>[1]</sup>, these compounds, however, often possess large molecular mass and their efficiency as wear resistance additives decrease with their molecular mass increasing. Extreme-pressure properties of some inorganic additives have been found to be superior to some organic ones, potassium borate is an excellent example, its load-carrying capacity is much higher than that of boric ester. Unfortunately, insolubility and the difficulty of stabilizing dispersions of inorganic powder restrain their applications in lubrication oil. It is reported that there are four hydroxyl radicals and eight crystal water molecules in each structure unit of borax<sup>[2]</sup>. HU and LI, et al<sup>[1,3,4]</sup> have attempted to replace the hydroxyl radical with alkoxy radical to improve the solubility of borate, and have prepared some transition metal alkoxyborate, the results indicate that the tribological properties of these transition metal alkoxyborates are

excellent.

Research on the tribological properties of some rare earth metallic compounds has been reported in recent year. As Jost has denoted<sup>[5]</sup>: the tribological properties of some rare metallic compound, e. g. LaF<sub>3</sub>, increase the wear life of bonded coatings by 2 ~ 4 times and the load carrying capacity of grease pastes by 10% ~ 100%. Sliney<sup>[6]</sup> has reported that CeF<sub>3</sub> and CeO<sub>2</sub> as solid lubricants had good antiwear and friction-reducing properties at high temperatures. Dum Dum, et al<sup>[7]</sup> and Aldorf<sup>[8]</sup> have tested CeF<sub>3</sub> particles as a grease additive. When CeF<sub>3</sub> was dispersed in barium complex soap grease, the initial seizure load was higher than that when only MoS<sub>2</sub> or graphite was added. LIAN, et al<sup>[9]</sup> have reported that the synergism existed between CeF<sub>3</sub> and zinc dialkyl dithiophosphate (ZDDP) in lithium grease, and have believed that ZDDP could inhibit the decomposition of CeF<sub>3</sub>. In addition, marked improvement in lubrication performance has been achieved by dispersing rare earth halides in oil and water, as Segaud reported<sup>[10,11]</sup>. In order to overcome the soluble difficulty of inorganic rare earth chemicals in oil, progress has been made by preparing oil-soluble organic rare earth compounds. CHEN, et al<sup>[12,13]</sup> developed a series of oil-soluble rare metallic coordination compounds, including lanthanum, neodymium, praseodymium, samarium and gadolinium dialkyl dithiophosphates, and disclosed their good antiwear abilities.

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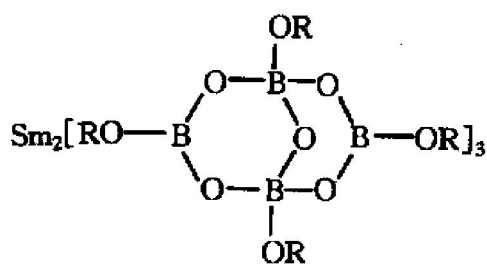
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In order to make use of the advantages of rare earth and alkoxyborate, an oil-soluble rare earth complex, samarium isooctoxyborate, has been successfully prepared in this study, its tribological performance has been evaluated when it is used as an antiwear and extreme pressure additive in lubricant, and its tribochemical behavior under boundary lubrication conditions is explored as well.

## 2 EXPERIMENTAL

### 2.1 Additive

The compound, samarium isooctoxyborate, was synthesized according to the reaction pathway similar to literature [3, 4]. The compound probably possesses the structure as<sup>[2]</sup>



(R = i-C<sub>8</sub>H<sub>17</sub>)

### 2.2 Measurement of tribological properties

A commercially available HVI500 mineral oil with a kinematic viscosity of 94.55 mm<sup>2</sup>/s at 313 K was used as the base oil. The prepared samarium isooctoxyborate was added to HVI500 base oil with heating and stirring.

The antiwear properties of samarium isooctoxyborate as additive in HVI500 mineral oil were evaluated with a four-ball machine at a rotating speed 1450 r/min, test duration 30 min, load 98, 196, 294, 392, 490 and 588 N, and room temperature about 20 °C. The balls with diameter 12.7 mm in the tests were made of GCr15 bearing steel (AISI52100) with an HRC59-61. The load-carrying capacity of the additive was obtained according to GB3142-82, similar to ASTM D-2783. An optical microscope was used to determine the wear scar diameters of the three lower balls with an accurate reading to 0.01 mm. Then, the average of the three wear scar diameters was calculated and cited as the wear scar diameter reported in this paper.

The friction coefficient of the additive was measured under a constant load of 300 N using HO-1 ring-on-block machine, in which the ring was quenched CrWMn steel ring (Cr 0.9% ~ 1.2%, C 0.9% ~ 1.05%, W 1.2% ~ 1.6%, Mn 0.8% ~ 1.1%, Si 0.15% ~ 0.35% all of mass fraction) of 49.24 mm diameter, 12.7 mm height, 62HRC hardness and a surface roughness of  $Ra = 0.27 \mu\text{m}$ , which was rotating against 45 steel block (12 mm × 6 mm ×

4 mm) with a hardness of 44.8HRC and a surface roughness of  $Ra = 0.35 \mu\text{m}$ . The rotating speed of ring was 1500 r/min.

### 2.3 Surface analysis

In order to understand the action mechanism of the additive under boundary lubrication conditions, a KYKY1000B scanning electron microscopy (SEM), a MICROLAB MKII scanning Auger microprobes (AES) and a PHI-1600 X-ray photoelectron spectroscope (XPS) were used to analyze the specimens, i. e., the steel balls after the four-ball test in the oil with 2.0% samarium isooctoxyborate under 490 N for 30 min. Prior to SEM, AES and XPS analyses, the tested balls were respectively cleaned with petroleum ether in the bath of a supersonic rinser. The wear scar morphology was visualized by SEM. AES was utilized to detect the elemental components in the rubbing surface layer of the steel ball, and a depth profile of the surface layer was further made by argon ion sputtering to disclose the approximate atomic concentration percentage of the elements. The depth profile was accomplished by sputtering through the ball surface layer at an estimated sputtering rate of 30 nm/min, referenced by SiO<sub>2</sub>. The binding energies of primary element on worn surface of the upper ball were examined using the MgK<sub>α</sub> line as the excitation source with pass energy of 50 eV. The binding energy of contaminated C (C 1s: 284.6 eV) was as a reference.

## 3 RESULTS AND DISCUSSION

### 3.1 Effect of samarium isooctoxyborate on maximum non-seized load

The maximum non-seized load ( $F_B$ ) represents the load-carrying capacity of lubricating oil.  $F_B$  values of the oil containing different content of samarium isooctoxyborate were measured. The results are given in Fig. 1. Although the maximum non-seized load of the base oil was only 549 N, it was increased with the concentration of samarium isooctoxyborate. When 2.0% samarium isooctoxyborate was added, the

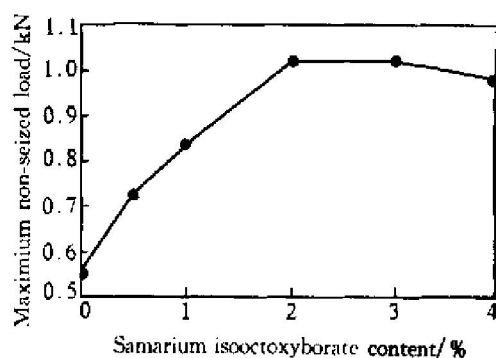


Fig. 1 Effect of samarium isooctoxyborate content on maximum non-seizure load of oil

maximum non-seized load reached its highest point at 1020 N, which is 86% higher than that of the base oil and represents the good load-carrying ability of the additive.

### 3.2 Effect of samarium isooctoxyborate on anti-wear properties

Fig. 2 gives the wear diameter of worn steel ball as a function of additive concentration in base oil. It is seen that under a load of 392 N, the addition of samarium isooctoxyborate into base oil significantly reduces the wear scar diameter of the steel ball. The wear scar diameter reached the lowest at a concentration of 2.0%, which keeps unchanged with further increasing of the additive concentration.

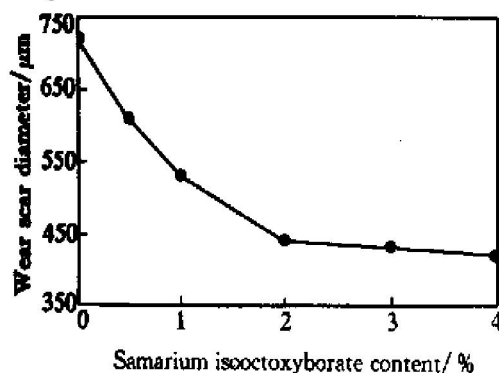


Fig. 2 Effect of additive content on wear scar diameter under 392 N, 30 min

The relationship among the applied load and antiwear properties of the additive in base oil is shown in Fig. 3. The results indicate that the wear scar diameter of base oil increases significantly with improving load, but the wear diameter of the oil containing 2.0% samarium isooctoxyborate increases tardily under different application. This implies that the samarium isooctoxyborate as additive in base oil will form an excellent protective layer on the lubricated steel ball surface, and realizes better boundary lubrication.

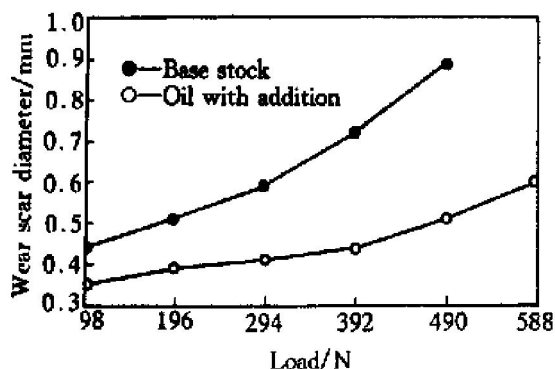


Fig. 3 Effect of load on wear scar diameter at additive content of 2.0%, 30 min

### 3.3 Effect of samarium isooctoxyborate on friction coefficient

The friction coefficients of samarium isooctoxyborate in five different concentrations are shown schematically in Fig. 4. As can be seen from Fig. 4 that the friction coefficient of the base stock was 0.0467, but it was reduced 31.3% to 0.0321 by the addition of 0.5% samarium isooctoxyborate to the oil. A higher content of samarium isooctoxyborate resulted in a lower friction coefficient. As the adding amount reached 2.0%, a 45% reduction of friction coefficient was observed. However the reduction tendency was decreased with further addition.

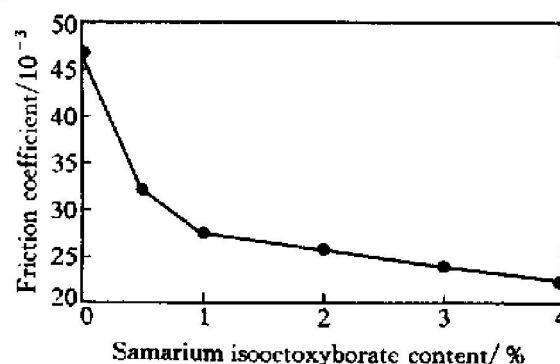


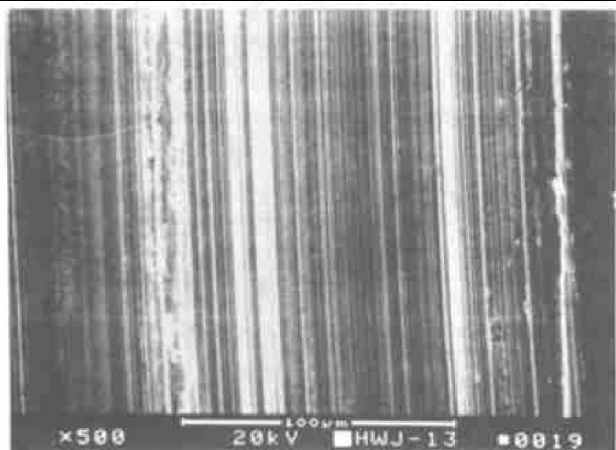
Fig. 4 Effect of additive content on friction coefficient of oil under 300 N, 30 min

The decrease of friction coefficient was attributed to the formation of adsorption film and (or) reaction film by the additive on the rubbing surface. As samarium isooctoxyborate was blended into the base stock, the additive molecules interacted with the freshly exposed worn surface to form a protective adsorption film and (or) reaction film whose shear strength was considerably less than that of the metal matrix, and the friction coefficient was decreased. The more samarium isooctoxyborate was added, the more molecular layers within the adsorption film and more reaction products were generated to prevent the asperities on the rubbing surfaces from direct contact, and the lower the friction coefficients became. On the other hand, with further increase of the additive, the adsorption process tended to be saturated, and the reaction film tended to completely separate the asperities, therefore, the reduction tendency of friction coefficients decreased.

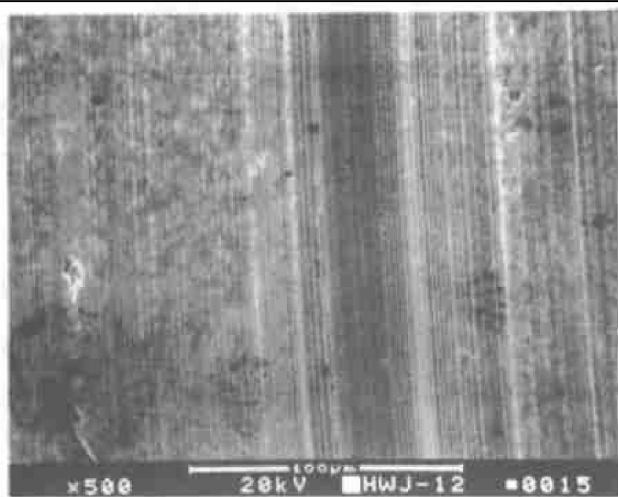
### 3.4 Surface film characterization

The enlarged SEM photographs, as shown in Figs. 5 and 6, display clearly that the scarred surface lubricated by samarium isooctoxyborate was uniform and smooth; however, the one lubricated by base oil had already been broken under the same experimental condition. These SEM results further verify that samarium isooctoxyborate possesses better antiwear behavior than base oil.

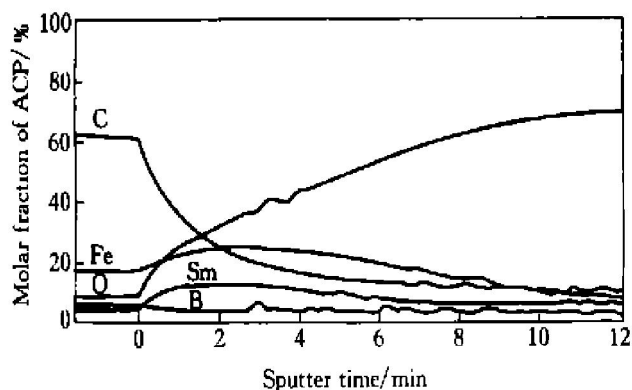
Fig. 7 is the AES spectra profile at different sputtering times (by argon ion sputtering). It is clear



**Fig. 5** Wear scar morphology of ball running in base oil



**Fig. 6** Wear scar morphology of ball running in oil with 2.0% novel additive



**Fig. 7** Depth distribution conditions of elements in rubbing surface layer

that the rubbed surface lubricated by samarium isooctoxyborate consisted of samarium, carbon, oxygen, iron and boron elements. As we can see from Fig. 7 that the carbon content on the outer surface of rubber surface is very high, which suggests that the friction polymer forms on the rubbed surface. The atomic concentration distribution of oxygen is also interesting. It gradually increases to near 25% and maintains in a certain range of depth, and then gradually de-

creases again. An explanation for the trend is that the wear scar is covered with adsorption film and friction polymer film, and the latter contains more oxygen than the former. As a result, the content of oxygen increases gradually with sputtering. It is particularly noticeable that samarium maintains a relatively high concentration in the surface layer and little decrease within the sputter time is observed. The maximum samarium content on surface layer amounts to 14%. So the conclusion that samarium atoms decomposed from samarium isooctoxyborate are easier to diffuse (or permeate) into surface layers could be drawn.

XPS not only confirms the presence of the above elemental components, but also identifies the chemical composition of the surface films. Analytical results for the key elements are shown in Table 1. It shows that the binding energy of Sm 3d on the rubbing surface is evident at about 1083.4 eV, which is corresponded to the chemical state  $\text{Sm}_2\text{O}_3$ , respectively<sup>[14]</sup>. The binding energy of B 1s on rubbing surface is only 192 eV, suggesting the presence of diboron trioxide. These imply that some samarium isooctoxyborate may be decomposed to disamarium trioxide and diboron trioxide under the action of high pressure and the high temperature brought about by frictional heat accumulation during the test time. The binding energy of O 1s further verifies the presence of diboron trioxide.

**Table 1** Binding energy of elements on rubbing surface (eV)

Sm	B	O
1083.4	192	533, 529.6

### 3.5 Discussion

Combining the results of XPS with those of AES, the action mechanism of samarium isooctoxyborate could be concisely described as follows. Under boundary lubrication conditions, the additive molecules are decomposed into a sizable quantity of debris by mechanical shear, friction heat and many other promoted effects of friction. Some debris could also combine with each other to form organic film, whose shear strength is considerably less than that of the metal matrix, and leads to the lower friction coefficient. The diboron trioxide and disamarium trioxide decomposed by samarium isooctoxyborate might deposit on worn surface to form oxidation film, the two oxides have been proved to possess excellent tribological behaviors. In addition, under mechanical activation condition, the surface imperfection content may be increased significantly. The crystal imperfections are the high-energy zones, therefore, some chemically active samarium ions may adsorb on these areas predominantly. When samarium content reaches a certain value, samarium diffuses into the sub-surface

by a very large chemical driving force. At the same time, high temperature due to friction intensifies the thermovibration of samarium atoms, promoting samarium atoms to escape from imperfection areas to permeate in steel substrate. It had been disclosed that the diffusion (or permeation) of rare earth brought about smaller crystal size, higher hardness and better wear resistance ability of the metal<sup>[15, 16]</sup>. As a result, the diffusion of decomposed samarium as an alloying element made the metallic microstructure change, and gave rise to the decrease of surface energy and the hardness increase of the metal by substitutional or interstitial hardening mechanisms, so the friction and wear were thus reduced<sup>[17]</sup>.

In summary, there are several protective films formed by the additive on the rubbing surface under boundary lubrication conditions. The first is organic film, which is formed by physically or chemically absorbed samarium isooctoxyborate molecules and by the condensation products of various decomposed debris of the additive and the base oil. The second is the oxide film, which is caused by decomposition of the additive. The last is the diffusion film of samarium element. These films are the films that have prevented the rubbing surfaces from failure.

#### 4 CONCLUSIONS

1) An oil-soluble candidate additive, samarium isooctoxyborate has been successfully prepared. The additive seems to possess good friction-reducing and antiwear abilities. The load-carrying capacity of the base oil has been also noticeably improved by the additive.

2) Samarium isooctoxyborate may form the surface lubrication layer on the rubbing surface, which consists of organic film, oxide film and diffusion film, and may effectively reduce friction and wear.

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