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SYNERGISTIC ANTIWEAR PROPERTIES BETWEEN BORATES AND ORGANIC TIN COMPOUNDS IN LUBRICANT

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Abstract

Dibutyl tin and stannous dialkyldithiocarbamates were synthesized. A four-ball tester was used to evaluate the tribological performances of these additives plus organic borate in a mineral oil. The results indicate that the combination of an oil-soluble tin compounds such as dibutyl tin and stannous dialkyldithiocarbamates with organic borates gave better antiwear protection to base oil than either component separately. The surface examination of the rubbing zone indicated that the atomic concentration of tin produced on the boundary layers by such combinations was greater than those without borates. On the basis of the results of tribological and chemical investigation, an antiwear synergistic mechanism can be postulated in which borates with electron-deficient p orbits in boron catalyse the triboreduction of tin compounds on rubbing surfaces.

Key words*:* Borate, tin, dithiocarbamate, additive, antiwear, synergistic

1. Introduction

The addition of extreme pressure (EP) and antewear (AW) additives was used to improve the friction and wear behaviors of lubricant, thus, avoiding surface damage. In the boundary lubrication regime, the formation of a surface chemical reaction film is the determining factor in minimizing the friction and wear. This depends on the nature and chemistry of additives or tribological effects of their active elements (sulphur, phosphorus, nitrogen, chlorine, etc) [1,2].

Metallic dialkyldithiocarbamates of zinc, lead, molybdenum, antimony,etc have been widely utilized as a multifunctional lubricant additive to provide antiwear protection as well as to inhibit the oxidation of petroleum lubricants [3-5].

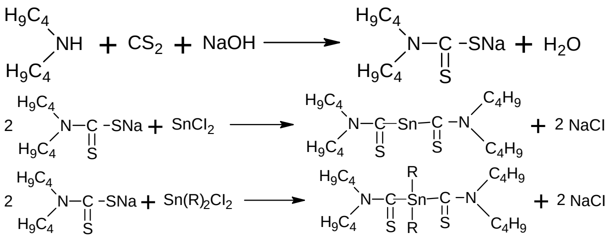
Organic borate ester compounds have good antiwear, antifriction properties and oxidation stability as lubricant additive [6-10]. It was reported that oil soluble tin compounds such as stannic sebacate, tin staterate and stannous naphenate, possessed good antiwear properties and exhibited good antiwear synergism with other additives containing boron lubricant additives [11-13].

The required functional action is achieved by appropriate balance. Investigations that can optimize the composition and expand the areas of application of additive packages, are of considerable scientific and practical interest. The present work aims to investigate the antiwear and extreme pressure properties of borate ester containing nitrogen additive combined with tin or stannous dialkyldithiocarbamates (SnDDC) respectively, and subsequent exploitation of the results for the development of a synergistic antiwear engine oil composition.

2. Experimental

2.1 Oil samples and additives

Dibutyl tin dibutyldithiocarbamates, abbreviated as SnDDC-1 and stannous diabutyldithiocarbamate, abbreviated as SnDDC-2, which was prepared according to reaction pathway outlined in Scheme 1. Firstly, dibutylamine were reacted with carbon disulphide in the presence of sodium hydroxide to yield corresponding sodium dibutyldithiocarbamates. Further sodium salt of reactions was neutralized with dibutyl tin chloride or stannous chloride to produce SnDDC-1 or SnDDC-2 in distilled water. The compound was characterized by element analysis and IR.



Scheme 1. R=C_4H_9

Mineral oil 150 SN was used as the base oil. The additive organic borate containing nitrogen (BNO) was commercial.

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 GCr15bearing steel (AISI52100) 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 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.

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

3. Results and discussion

Dibutyl tin dibutyldithiocarbamates (SnDDC-1) or Stannous diabutyldithiocarbamate (SnDDC-2) and organic borate (BNO) were added to the 150SN oil according to different proportions and the resultant antiwear properties were evaluated by the four-ball friction tester under loads of 392, 490 and 588N load 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.

3.1 Antiwear and load-carrying capacities of SnDDC-1 with BNO in mineral oil

Organic borate ester (BNO) and SnDDC-1 were added to the mineral base oil 150 SN, the wear scar diameters (WSD) of tested balls under different load are reported in Table 1. It shows that BNO and SnDDC-1 all possess better antiwear properties than base oil at each experimental load. When BNO is combined with SnDDC-1, at constant total concentration of the package, they possess synergistic and antagonistic antiwear properties, if concentration of BNO lower than or equal to SnDDC-1, the good antiwear synergism was obtained. For instance, the mixtures of 0.25% BNO with 0.75% SnDDC-1 exhibit the best antiwear synergism, and the mixtures 0.5% BNO with 1.0% is better. However, the WSD of the mixtures of 0.75% BNO with 0.25% SnDDC-1 is larger than that of 1.0% SnDDC-1 or BNO alone at 490 and 588 N, they exhibit antagonistic antiwear properties. Figure 1 presents the influence of additions of BNO and SnDDC-1 on the antiwear properties of mineral base oil 150 SN. It also clearly illustrates a similar tendency.

Table 1 Wear scar diameter with oils containing SnDDC-1 and BNO

Samples	Wear scar diameter，mm		
	392N	490N	588N
150SN	0. 63	1.09	2.35
+1.0% SnDDC-1	0.50	0.89	1.96
+1.0%BNO	0.52	0.62	1.09
+1.0% BNO +1.0% SnDDC-1	0.39	0. 46	0.49
+0.5% BNO +0.5% SnDDC-1	0.40	0.46	0.50
+0.25% BNO +0.75% SnDDC-1	0.39	0.44	0.51
+0.75% BNO +0.25% SnDDC-1	0.42	0.48	1.20
+0. 5% BNO +1.0% SnDDC-1	0.38	0.46	0.50

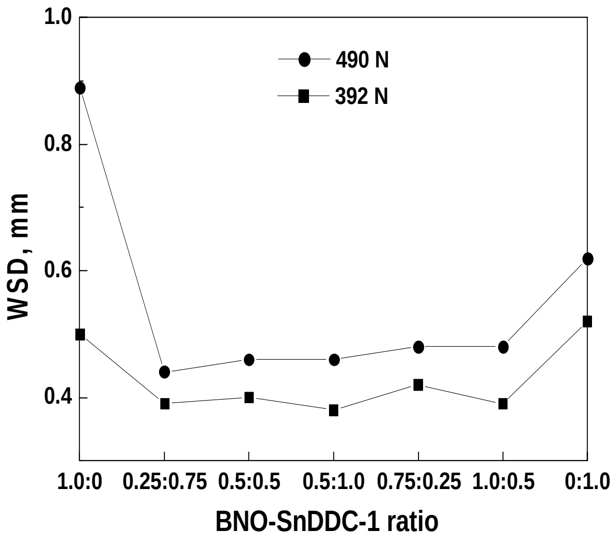


Figure 1 Influence of additions of BNO and SnDDC additives on the antiwear properties

The P_B and P_D values of oil containing different additives are summarized in Table 2, the results show that BNO and SnDDC could improve the load-carrying properties (enhance P_B and P_D values) of mineral base oils 150 SN, and SnDDC is better than BNO. After the combination BNO with SnDDC, at constant total concentration of the package, the P_B and P_D values of base oils were not improved compare with the same dosage of SnDDC without impairing the load carrying abilities.

Table 2 Evaluation on load-carrying capacities of SnDDC-1 mixed with BNO

150SN	Maximum non seizure load P_B, kgf	Weld load P_D, kgf
150SN	40	126
+1.0% SnDDC-1	76	200
+1.0%BNO	61	160
+1.0% BNO +1.0% SnDDC-1	88	200
+0.5% BNO +0.5% SnDDC-1	76	160
+0.25% BNO +0.75% SnDDC-1	76	160
+0.75% BNO +0.25% SnDDC-1	71	160
+0. 5% BNO +1.0% SnDDC-1	82	200

Table 3 Wear scar diameter with oils containing SnDDC-2 and BNO

Samples	Wear scar diameter，mm		
	392N	490N	588N
150SN	0. 63	1.12	failure
+1.0% SnDDC-2	0.72	0.81	1.03
+1.0%BNO	0.45	1.84	failure
+1.0% BNO +1.0% SnDDC-2	0.47	0. 52	0.66
+0.5% BNO +0.5% SnDDC-1	0.52	0.59	0.76
+0.25% BNO +0.75% SnDDC-2	0.56	0.62	0.71
+0.75% BNO +0.25% SnDDC-2	0.49	0.58	0.83

3.2 Antiwear and load-carrying capacities of SnDDC-2 with BNO in mineral oil

Organic borate ester (BNO) and SnDDC-2 were added to the mineral base oil 150 SN, the wear scar diameters (WSD) of tested balls under different load are reported in Table 3. It shows that BNO and SnDDC-2 all possess better antiwear properties than base oil at each experimental load. When BNO is combined with SnDDC-2, at constant total concentration of the package, they possess synergistic and antagonistic antiwear properties, if concentration of BNO lower than or equal to SnDDC-2, the good antiwear synergism was obtained. For instance, the mixtures of 0.25% BNO with 0.75% SnDDC-2 exhibit the best antiwear synergism, and the mixtures 0.5% BNO with 1.0% is better. However, the WSD of the mixtures of 0.75% BNO with 0.25% SnDDC-2 is larger than that of 1.0% SnDDC-2 or BNO alone at 490 and 588 N, they exhibit antagonistic antiwear properties.

The P_B and P_D values of oil containing different additives are summarized in Table 4, the results show that BNO and SnDDC-2 could improve the load-carrying properties (enhance P_B and P_D values) of mineral base oils 150 SN, and SnDDC-2 is better than BNO. After the combination BNO with SnDDC-2, at constant total concentration of the package, the P_B and P_D values of base oils were not improved compare with the same dosage of SnDDC-2 without impairing the load carrying abilities.

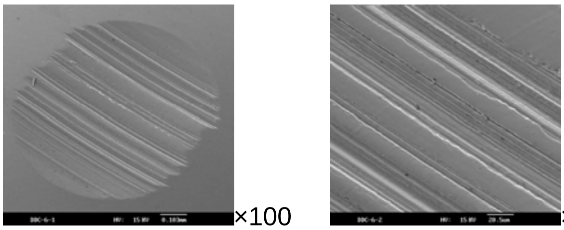
Table 4 Evaluation on load-carrying capacities of SnDDC-2 mixed with BNO

150SN	Maximum non seizure load P_B, kgf	Weld load P_D, kgf
150SN	40	126
+1.0% SnDDC-2	66	200
+1.0%BNO	61	160
+1.0% BNO +1.0% SnDDC-2	82	200
+0.5% BNO +0.5% SnDDC-1	76	200
+0.25% BNO +0.75% SnDDC-2	76	200
+0.75% BNO +0.25% SnDDC-2	71	200

3.3 Surface analysis

Figures 2 and 3 show the worn scar micrographs of the steel balls lubricated by 1.0% Dibutyl tin dibutyldithiocarbamates (SnDDC-1) and the same with 0.5% borate ester (BNO)and 0.5% SnDDC-1 at 490 N. It can be seen clearly from Figures 2, 3 that the worn scar area was significantly reduced by the combination of BNO and SnDDC-1, and scratched surface of worn scar was more uniform and smooth than it of worn scar lubricated by SnDDC-1 only. Therefore, they exhibit good antiwear synergism.

The elemental distribution on the worn scars was estimated with EDX, the atomic concentrations of the elements evaluated on the worn scars by SEM-EDX are listed in Table 5. The data in Table 5 were gained from Figures 2 and 3 by a computer program provided with EDX and normalized to all given compositions 100. The data of EDX show that the atomic concentration of tin on the worn scar with the complex of BNO and SnDDC-1 higher than that of with SnDDC-1. It was presumably that the increase in concentration of tin was catalyzed by electron-deficient p orbit of borate ester, which plays important roles in such boundary lubrication.



×100 ×500

Figure 2 SEM morphologies of worn scar lubricated with SnDDC-1 at 490 N

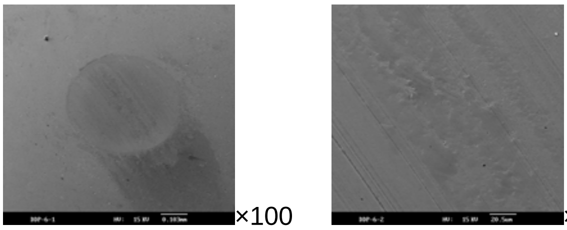


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Figure 3 SEM morphologies of worn scar lubricated with SnDDC-1and BNO at 490 N

Table 4 Atomic concentration (%) of elements on the worn scar by SEM-EDX

Location	O	S	Sn	Fe	C/B
Worn scar with SnDDC-1	6.14	2.89	0.83	69.68	20.44
Worn scar with SnDDC-1and BNO	6.65	3.46	1.82	68.82	19.25

4. Discusion

It has been suggested that Sn(I) or Sn(IV) compounds.can react with steel under tribochemical conditions, and in the reaction the tin diffuses into the steel substrate in the sliding zone to form intermetallic compounds [11]. The hypothesis of Sn-Fe bimetallic system formation in the friction zone was confirmed by the results of X-ray microanalysis and micro hardness tests of the surface layer. It was reported that the microhardness of the surface layer modified by oils containing Sn(II) or Sn(IV) was enhanced. This may be the main reason for the tin compounds' antiwear properties.

The surface effects of friction have gained extensive attention as to the efficiencies of the reaction in boundary layer [14], in which exoelectrons play a key role in the triboreduction of the tin compounds on the rubbing surfaces, as demonstrated in eqs. (1) and (2).

$$Sn^{4+} \text{ or } Sn^{2+} + 4e \text{ or } 2e \xrightarrow{\text{Tribo}} Sn \qquad (1)$$

$$Sn^{4+} \text{ or } Sn^{2+} + 4e \text{ or } 2e \xrightarrow{\text{Tribo/borate}} Sn \qquad (2)$$

The catalytic reactivity resulting from borates, as shown in eq. (2) may be due to the existence of electrondeficent q orbitals in boron. We speculate that the borate with vacant p orbitals can be absorbed on the rubbing surfaces and act as an electron carrier to lower the escape of the exoelectrons. This increases the opportunity for the reaction of Sn^{4+} or Sn^{2+} with exoelectrons so that the borate can catalyze the trioreduction of the Sn(II) or Sn(IV) compounds in boundary lubrication .This may be the major cause of the antiwear synergism between borate and Sn(II) or Sn(IV) compounds. Under friction condition the triboreduced tin atoms deposit on friction surfaces and alloy to improve the antiwer and load-carrying properties.

How the tin compound act synergistically with BNO to improve lubricants' antiwear performance, which need further and more widespread investigation.

5. CONCLUSION

Dibutyl tin and stannous dialkyldithiocarbamates synthesized possessed better antiwear and load-carrying properties compared with base oil. Moreover, Sn(IV) compounds gave better tribological performances than Sn(II) compounds.

Dibutyl tin and stannous dialkyldithiocarbamates have better synergistic antiwear properties with borate ester. Such a phenomenon may be attribute to the catalytic effect of the borates with electron-deficient porbits in boron.

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