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Investigation of anti-wear additives for synthetic esters; Amine salts of phosphonic acid

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Antiwear (AW) properties of phoshphonic acid derivatives for trimethylolpropane (TMP) esters were investigated under boundary conditions. AW effect of dialkyl phosphonates depends on polarity of base fluid. They provide good AW performance in less polar TMP esters, whereas their AW effect is not sufficient in polar TMP esters. Amine salts of phosphonic acid were developed as new AW additive system for TMP esters. They provide excellent AW performance even in polar TMP esters.

Keywords : boundary condition, antiwear additive, amine phosphonate, synthetic ester, nonpolarity index

1. INTRODUCTION

Synthetic esters have many advantages as lubricating fluid. However they still need optimization, especially in AW properties. Performance of additive is sometimes unpredictable probably due to polarity of the base fluid. In our previous work, we have found that phosphonates (or phosphites) exhibit good AW properties in TMP esters. Performance of additive depends on organic moiety of the molecule [1]. Transition points were observed in additive concentration versus delta wear chart. As shown in Figure 1, dibutyl phosphonate (DBPo) exhibits good AW properties at concentration of 10 mmol/kg or higher. Transition points with phosphonic acid triesters (TBPo, TPPo) are higher than that with DBPo. The results were considered by the effect of adsorption activity of additives [2].

Taking these backgrounds into account, we investigated effect of polarity of base fluid on AW properties of phosphonates. Development of new additive system for polar synthetic esters was also interested in.

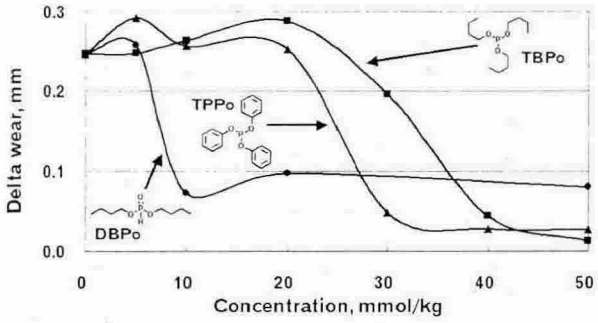

Fig.1 Concentration effect of phosphonates on anti-wear properties in Oil F

Table 1 Properties of TMP esters

Base oil		Oil A	Oil B	Oil C	Oil D	Oil E	Oil F
Number of C atoms in acyl group		6	8	9	10	12	18
Total number of C atoms		24	30	33	36	42	60
Total acid number, mgKOH/g		0.03	0.01	0.01	0.10	0.30	0.41
Viscosity, mm^2/s	40 ℃	11.2	16.9	20.1	24.7	33.6	47.8
	100 ℃	2.9	3.9	4.6	5.1	6.7	9.4
Viscosity index		108	127	151	143	161	186
Nonpolarity index		34.3	51.3	61.0	71.6	95.4	185.5

2. EXPERIMENTAL

Reagent grade phosphonic acid (H_3PO_3), tributylamine (TBA) and triphenylamine (TPA) were used as received. TMP esters were prepared by the literature method [3]. Their physical properties are listed in Table 1. Nonpolarity index (NPI) was calculated by the literature method [4].

A solution of amine phosphonate (phosphonic acid amine salt) in TMP esters was prepared by the following procedure. A 1 mol/kg solution of phosphonic acid in absolute ethanol was prepared. The ethanol solution (0.25 g) was added dropwise to a mixture of amine (0.25 mmol) and TMP esters (50 g) at room temperature. The resultant mixture was stirredor 1 h to be a clear solution for the four-ball test.

The AW properties of the samples were evaluated by means of the four-ball test, according to ASTM D 4172. After the test, the wear scar diameter (WSD) of the fixed three balls was measured with an optical microscope. The average of two test runs was obtained. The delta wear, which is the difference between the WSD and the hertz diameter (0.299 mm), is reported [5]. The morphology of the worn surface was also studied to understand the antiwear mechanism.

3. RESULTS AND DISCUSSION

AW effect of DBPo was examined in various TMP esters. The results are shown in Figure 2. Wear with additive free base oil decreases with increase in NPI. The results are easily understood by the effect of viscosity. Additive effect of DBPo varies on NPI of the base oil. Excellent AW performance was observed with Oil F, whereas fair results

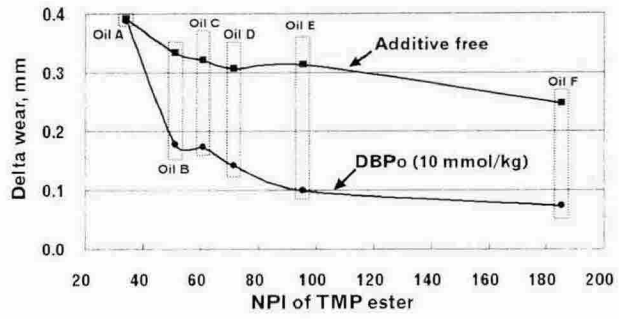

Fig.2 Relationship between anti-wear properties of DBPo and NPI of TMP ester

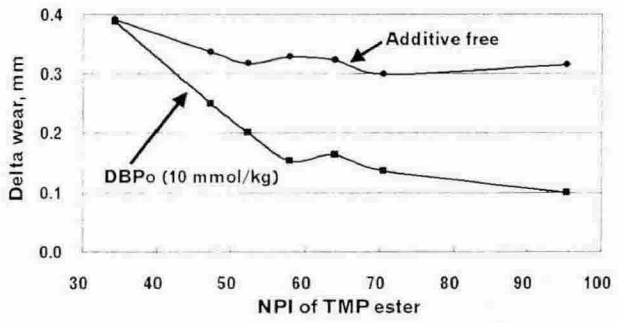

Fig.3 Anti-wear properties of DBPo in TMP ester mixture

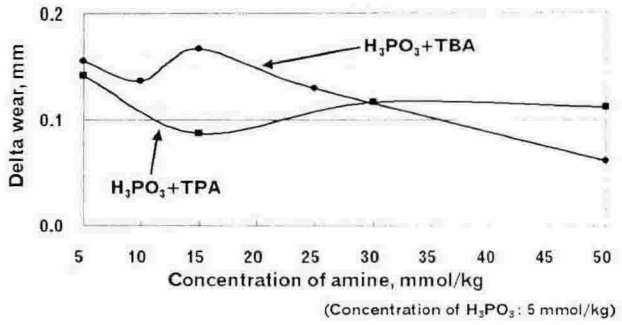

Fig.4 Effect of amine concentration on anti-wear properties of amine phosphonate in oil F

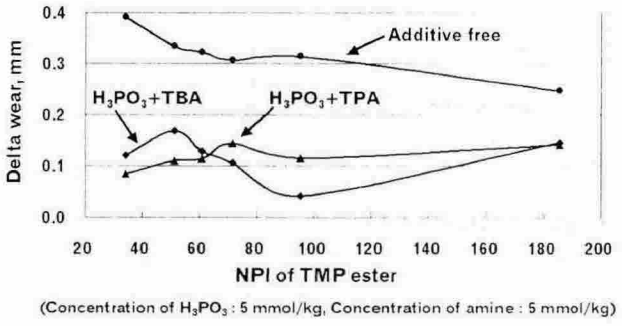

Fig.5 Anti-wear properties of aminephosphonates in TMP ester

were obtained with Oils B-D. It should be noted that almost no effect was observed in Oil A. Effect of NPI on AW performance of DBPo was also observed in a mixture of TMP esters. Oil A and Oil E were mixed to prepare base fluid having NPI in the range of 35-95. As shown in Figure 3, wear reduction by DBPo decreases with decrease of NPI. In other words, phosphonic acid esters seem to have insufficient AW effect in polar TMP esters.

Amine salt of phosphate ester had been introduced as effective AW additives for poly ether type lubricants [6]. In this study, amine phosphonates was investigated as analogous with the phosphate ester derivatives. The feature of the new additive system is simple preparative method. Phosphonic acid hardly dissolves in organic fluids. Reaction of the inorganic acid with organic amines gives amine salts in a quantitative yield. The salts dissolve easily in polar organic fluids. Another feature of the new additive system is flexibility in certain properties by modification of amine structure.

AW performance of the new additive system was examined. As shown in Figure 4, TBA and TPA salts reduce wear in Oil F. AW properties of the salts for various TMP esters were also confirmed. As shown in Figure 5, the salts reduce wear even in polar TMP esters.

4. CONCLUSIONS

1. AW properties of dialkyl phosphonates in TMP esters depend on polarity of the base fluid. They provide good AW properties in less polar TMP esters, whereas almost no effect was found in polar TMP esters.
2. Amine salts of phosphonic acid were developed as new additive system for TMP esters. They were prepared by simple reaction of phosphonic acid with organic amines. Their AW effect was excellent even in polar TMP esters.

5. REFERENCES

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