Investigation of Antiwear Additives for Synthetic Esters

Organosulfur and organophosphorus compounds were examined to investigate their antiwear properties and mechanism in naphtenyl-type synthetic esters under boundary lubrication conditions. Triaryl phosphates and dialkyl hydrogen phosphonates, which are widely used in mineral oils, reduce wear to some extent. Trialkyl and triaryl phosphonates exhibit excellent antiwear properties at an optimized concentration. Almost no antiwear effects were observed at lower concentrations of phosphonates, whereas wear reduction was achieved at higher concentrations. The results are discussed based on the adsorption activity of the additive on the frictional surface. Surface morphology analysis of the worn surface suggests the formation of an antiwear film derived from the phosphorus-containing additives. Unexpected wear promotion was observed with organosulfur compounds, which are commonly used as antiwear/extreme pressure additives in mineral oils.

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INTRODUCTION

Demand for synthetic ester fluids as lubricant base stocks has been increasing due to their various features in practical applications. For example, more than 1500 tons of synthetic esters are consumed annually in the recent Japanese market. Merits of synthetic esters compared with mineral oils have been recognized as faster biodegradability, lower flammability, better lubricity, better fluidity, lower volatility, and higher thermal and oxidation stability (Waal, et al., 1985, 1993). These properties can be enhanced to meet practical applications by means of the molecular design method. Therefore, synthetic esters are so-called tailor-made lubricants. The precursors of synthetic esters are carboxylic acids, usually isolated from natural fats. Since these natural carboxylic acids are derived from renewable resources, they are constantly available. On the contrary, from the stand point of long-term view, natural resources of mineral oils are limited. Therefore, synthetic esters are one of the promising candidates as environmentally friendly lubricants under circumstances in which environmental protection is of great importance. Taking the above advantages into account, synthetic esters can be found in such applications, like long drain oils and energy-saving lubricants.

Mineral based oils, the most widely used lubricants these days, are well formulated to meet practical applications. Generally, the lubricity of synthetic esters is better than that of mineral oils when they are compared additive-free. However the tribological properties of synthetic esters still need optimization by additive technology. Conventional additives that had been developed for mineral oils are not always effective for synthetic esters. They sometimes exhibit less effect on improvement of the tribological properties of synthetic fluids. In some cases an antagonistic effect of antiwear additives was observed, probably due to the polarity of synthetic fluids. Therefore, adequate information on the relationship between base fluid and additives would be highly desirable in this field (Waal, et al., 1988). To the best
of our knowledge, wear reduction with dialkyl phosphates (Hall, 1969), certain amine phosphates or thiophosphate (Weller, et al., 2000) for saturated neopentyl type esters had been reported.

In this work, the effect of model antiwear additives for synthetic esters was investigated. Trimethylolpropane trioleate was selected as an environmentally friendly fluid, since unsaturation in the molecule improves biodegradability (Waal, et al., 1993). This ester has been used in rolling lubrication and exhibits good lubricity. As for the model additive, organic esters of phosphate and phosphonate were selected. Sulfide was also examined to compare its tribological properties in synthetic esters. A mechanistic discussion based on the chemical properties of the additive is also given herein.

EXPERIMENTAL PROCEDURE

Chemicals

Trimethylolpropane trioleate (represented TMP-O hereafter) was used as the basestock. The physical properties of TMP-O are listed in Table 1. Four phosphorus-containing additives and one sulfur-containing additive were examined. Their structure and abbreviations are listed in Fig. 1. Dibutyl phosphonate (DBPO, or dibutyl hydrogen phosphite) is a conventional additive for mineral oils. Tributyl and triphenyl phosphonates (TBPO and TPPO, respectively) were selected as compounds analogous to DBPO. Triphenyl phosphate (TPPA) was selected as a model compound for tricresyl phosphates, which are widely used as antiwear additives. Dibenzyl disulfide (DBDS) is also a well-known antiwear additive. Zinc bis(O,O-diisopropylidithiophosphate) (ZDTP) was used as the reference for antiwear properties. Reagent grade DBDS, DBPO, TBPO, TPPA, and TPPO were used for the four-ball test without purification. TMP-O (Barnes, et al., 1957) and ZDTP (Wystrach, et al., 1956) were prepared in our laboratory according to literature methods.

Wear Test

The antiwear properties of the samples were evaluated by means of the four-ball test, according to ASTM D 4172.

![Fig. 1—Structure and abbreviation of the additives.]

![Fig. 2—Morphology of worn surface in the Four-Ball test.](image)

![Fig. 3—Effect of additives on antiwear properties.](image)

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showed almost no effect under these conditions. The sulfur-containing additive (DBDS) promoted wear obviously.

The antwear properties of phosphorus-containing compounds were examined with solutions ranging in concentration from 5 to 50 mmol/kg, as shown in Fig. 4. At higher concentrations, all phosphorus-containing additives exhibit better or similar antwear properties compared to the reference, ZDTP. The authors found a difference in effectiveness, which depends on the chemical structure of additives. Here the authors define the "Effective concentration" as the concentration at which a similar antwear effect to that of the reference sample (ZDTP at 5 mmol/kg) is achieved. The effective concentration of the individual additives was marked on Fig. 4.

It has been reported that the protecting film composed of iron phosphate on the frictional surface is derived from phosphorus-containing antwear additives (Perez, et al., 1990, Goldblatt, et al., 1970, Sakurai, et al., 1970, Faut, et al., 1983). The process of film formation includes two major steps, namely, adsorption of the additive on the metal surface, followed by triboc-chemical reaction of the adsorbed molecule. Careful study of the morphology of the worn surface leads to a discussion on the antwear mechanism. A rough surface was observed after the four-ball test with TBPo at 20 mmol/kg, whereas a smooth worn surface was found with a 40 mmol/kg solution, as shown in Fig. 5. The smooth worn surface can be understood as being the result of effective antwear film formation on the surface. Therefore, it has been concluded that the formation of an antwear film is derived from the additive at the effective concentration. The rough surface observed at lower concentrations is the result of discontinuous antwear film formation. TBPo at 30 mmol/kg showed a medium effect. The effect of the concentration on wear reduction can be explained by the total amount of molecules adsorbed on the tribological surface. In other words, the amount of adsorbed molecules at 20 mmol/kg of TBPo may be insufficient to provide the antwear film. A sufficient amount of molecules adsorbed at 30 mmol/kg of TBPo may be somewhat sufficient for effective film formation. Then sufficient amount of molecules are adsorbed at 40 mmol/kg of TBPo to provide the film. Based on these assumptions, the authors wish to propose that the effective concentration may be related to the adsorption activity of the additive molecules on the metal surface. Similar correlations between effective concentration and worn surface morphology were also observed for TPPO and DBPo, as shown in Figs. 6 and 7. A large amount of TPPO was necessary to achieve the effective concentration. However wear reduction and surface morphology were not at a satisfactory level even at the highest concentration of TPPO, as shown in Figs. 4 and 8.

In summary, the effective concentration of individual additives increases in the following order:

$$\text{DBPo} \leq \text{TPPO} \leq \text{TBPO} \leq \text{TPPa}$$

TPPa is a pentavalent phosphorus compound whereas TPPO and TBPO are trivalent ones. Trivalent phosphines have a lone electron pair which is ready to bond to the iron atom through coordination. Therefore it is considered that the adsorption activity of a phosphonate is higher than that of a phosphate. The aromatic p-electrons in TPPO may have another effect, enhancing the adsorption activity of the molecule. In fact, it has been reported that the adsorption activity of trimethyl phosphonate is higher than that of trimethyl phosphate on a nascent iron surface (Mori, et al., 1988). Additional understanding of the chemical aspect is required to explain the adsorption activity of DBPo. DBPo exists in the pentavalent form and trivalent form. In other words, two
Fig. 8—Morphology of worn surface in the Four-Ball test with TPPa.

Fig. 9—Tautomeration of D3PO.

isomers, P-form and T-form coexist at equilibrium as explained in Fig. 9. Ionic interaction of the molecule with the metal surface is possible, since the hydroxyl group in the T-form molecule is acidic. The ionic interaction, which is in a different category from the coordination type interaction, is strong. Therefore, the adsorption activity of DBPo can be estimated to be much higher than that of triesters such as TPPa and TBPo, even if a small amount of the T-form exists in the solution. In a related matter, the importance of the adsorption process in the antifriction mechanism has been reported for higher fatty acids (Jahanmir, et al., 1986).

It was found that the wear-reducing effect of phosphorus-containing additives at their optimum concentration is in the following order. Lower WSD means better antitrust effect in this equation.

(ε—higher WSD ) TPPa < DBPo < TPPo = TBPo (lower WSD →)

As the authors have explained above, DBPo contains an acidic functional group. This functionality is beneficial for better interaction with the metal surface. The authors considered another effect of adsorption activity to understand the differences in the effectiveness of phosphonates. The adsorption activity of a molecule can be understood as chemical reactivity of adsorbate (substance adsorbed) with adsorbent, if chemisorption is important in the antifriction film formation process. Too much reaction of adsorbate with adsorbent sometimes takes place under certain conditions. In a tribological process, the phenomenon is closely related to chemical or corrosive wear. Smooth worn surface, observed at higher concentration of DBPo, supports the chemical wear mechanism under these conditions. Therefore antitrust properties of DBPo are inferior to those of TPPo and TBPo. The phosphonate triesters gave almost zero value of delta wear. In addition, the small and smooth worn surface shown in

Fig. 10—Effect of additive concentration on antitrust properties with DBDS.

Figs. 5 and 6 indicate that they provide optimum lubrication under these conditions.

DBDS is a well-known antitrust and extreme pressure additive for mineral oils. However, this additive has no effect on reducing wear in TMP-O as shown in Fig. 10. Similar results have been reported with a solution of alkanethiols in vegetable oils (Minami, et al., 1999). Note that the acyl moiety of TMP-O is same as that of the major component of the vegetable oil. Therefore, the wear promotion mechanism is considered to be the same.

CONCLUSIONS

The authors wish to summarize the results of the present study as follows.

1. Tri- and di-esters of phosphoric acid reduce wear to a great extent in synthetic esters. However, triesters of phosphoric acid exhibit little antitrust effect.
2. Differences in the effective concentration of the additives were explained by the adsorption activity of the molecule on the metal surface. A lower effective concentration was observed with molecules having higher adsorption activity.
3. However, higher adsorption activity may cause corrosive wear under certain conditions.
4. The conventional sulfur-containing additive, DBDS, showed an antagonistic effect on antitrust.

REFERENCES


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