[Regular Paper]

Additive Effect for Environmental Lubricants—Decreased Phosphorus Contents in Low Viscosity Base Oils for Antiwear Performance—

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Low viscosity base oils are one of the candidates for fuel saving lubricants for internal combustion engines. These lubricants reduce viscous friction under hydrodynamic conditions, so reduce total energy loss at tribological contact. However, these oils provide thinner oil films resulting in magnified wear. Therefore, wear protection of rubbing surfaces is very important to apply low viscosity oils in practice. Effects of phosphorus-containing additives on antiwear properties of low viscosity base oils were evaluated under boundary lubrication conditions using a four-ball type wear tester according to ASTM D 4172. For mineral based oils, dialkyl phosphonates considerably reduced wear whereas trialkyl and triaryl phosphonates did not. Compatibility of additive with mineral based oil depends on the refining process of the oil. Wear prevention by phosphorus-containing additive in solvent-extracted mineral oils was sometimes unpredictable. Additive response for hydrogen-refined mineral oils was better than that for solvent-extracted oils. The results showed good accordance with phosphorus contents on the worn surfaces obtained by surface analysis. At least 0.062 mass% (620 ppm) of phosphorus is required to achieve sufficient antiwear properties in hydrogen-refined mineral oils. Synthetic esters have good lubricity in comparison with mineral oils. However, conventional antiwear additives for mineral oils are not always effective for synthetic esters, especially low viscosity esters. Hydroxyalkyl phosphates, with a polar functional group in the molecule, reduced wear effectively even at 0.016 mass% (160 ppm) of phosphorus in low viscosity synthetic esters. The new additives provided boundary films with high phosphorus contents. Kinetics of the boundary film formation were examined by the electric contact resistance method. Formation of the boundary film from the new additives was higher than that from conventional additives. The replenishment process of the boundary film under dynamic conditions is very important for low viscosity lubricants.

Keywords
Antiwear additive, Phosphorus compound, Synthetic ester, Lubrication mechanism, Tribo-chemistry, Environmental lubricant

1. Introduction

Improvement in the fuel economy of motor vehicles is of significant importance to minimize the impact on the global environment. One approach is to improve engine oils in order to reduce viscous friction at the piston-cylinder contact and other mechanical parts, by using low viscosity base oils[1)~3)]. However, the antiwear properties of such oils under boundary conditions such as the valve train system are usually unsatisfactory. Therefore, effective lubricants which prevent wear of the friction materials are required[4)]. Antiwear additives, containing hetero atoms such as phosphorus, sulfur and zinc, are commonly used to minimize wear. However, these elements are potentially hazardous to the global environment[5)]. Reduction or ideally elimination of these elements from lubricants[6),7)] by the development of alternatives is highly desirable.

The present study investigated the effects of viscosity of the base oil on the additive response under the boundary conditions. Additives and mineral oils containing phosphorus were employed for the first stage of the project. It was found that polar additives provided better results in low viscosity mineral oil. The effects of the additive also depended on the purity of the base oil. The additives reduced wear in hydro-refined oils, but not always in solvent-extracted oils. Some antagonism between the additives and sulfur contaminant was suggested. Reduced phosphorus contents may have a negative impact on antiwear performance even with highly-refined mineral oils.

Synthetic esters are inherently good lubricants, but compatibility with conventional phosphorus-containing additives is sometimes unsatisfactory. Chemical modification of the additives was investigated. Introduction

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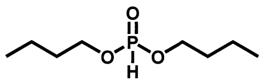
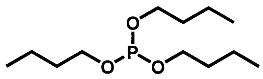
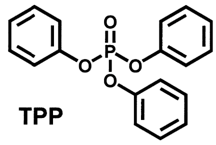
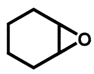
Table 1 Properties of the Base Oil

CODE	Type	Viscosity [mm²/s]		Viscosity index	Sulfur cotent [mass%]
		40°C	100°C		
M1-H	hydro-refined mineral oil	18.2	4.04	122	< 0.11
M2-HS	mixture of hydro-refined and solvent-extracted mineral oils	20.2	4.27	118	0.07
M3-HS	mixture of hydro-refined and solvent-extracted mineral oils	32.4	5.66	115	0.16
M4-H	hydro-refined mineral oil	20.5	4.39	126	< 0.11
M5-S	solvent-extracted mineral oil	21.9	4.30	102	0.11
DES	synthetic di-ester	18.3	4.50	173	—


DBP


TBP


TPP


CHO

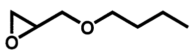

BGO

Fig. 1 Structure and Abbreviation of the Additives

of the polar hydroxyl group into the additive molecule resulted in excellent wear reduction. The effects of the hydroxyl group on the antiwear properties were investigated by surface analysis and electronic contact resistance. The polar functional groups promoted formation of the boundary film during the tribological process, resulting in higher phosphorus deposition on the rubbing surface. The modified additives exhibited good antiwear properties even at low concentrations in synthetic esters. The antiwear mechanism was studied in detail.

2. Experimental

2. 1. Chemicals

The codes and properties of base fluids are listed in **Table 1**. "M", "H" and "S" indicate "mineral-based paraffin," "hydro-reformed" and "solvent-extracted," respectively. A synthetic ester was employed as the low-viscosity base oil. Dibutyl phosphonate (DBP), tributyl phosphonate (TBP) and triphenyl phosphate (TPP) were selected as model antiwear additives. Hydroxyalkyl phosphates (HAPs) were prepared by the reaction of cyclohexeneoxide (CHO) or butoxy glysidiloxide (BGO) with phosphonic acid, according to the published procedure[8]. The additives are commercially available reagents and were used as received.

2. 2. Tribo-tests

Antiwear properties of sample lubricants were evaluated by the four-ball test, according to ASTM D 4172. Details of the test conditions are described in **Table 2**. 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, was reported. A ball-on-plate type tribo-test was also employed to study the kinetics of the boundary lubrication film formed by the additive by measuring the electrical contact resistance (ECR) during the test[9]. Details of the test conditions are described in **Table 3**.

Table 2 Conditions for the Four-ball Wear Test

[Operation parameters]		
Applied load	[N]	3.90×10^2
Hertz contact stress	[GPa]	3.0
Hertz deformation indentation	[mm]	0.30
Rotation	[rpm]	1.2×10^3
Sliding velocity	[m/s]	0.46
Oil temperature	[°C]	75
Test duration	[min]	60
[Test ball]		
Material		SUJ2 (JIS)
Contents: C (0.95-1.10%), Si (0.15-0.35%), Mn (< 0.5%), P (< 0.025%), S (0.025%), Cr (1.30-1.60%) and Fe (balance)		
Diameter	[mm]	12.7
Hardness, HR_c		62
Surface roughness, R_a	[μm]	0.040

Table 3 Conditions for the Ball-on-plate Type Tribo-test

[Operation parameters]		
Applied load	[N]	10
Hertz contact stress	[GPa]	1.3
Hertz deformation indentation	[mm]	0.06
Frequency	[Hz]	1
Amplitude	[mm]	10
Oil temperature	[°C]	20
Test duration	[min]	15
[Test ball]		
Material		SUJ2 (JIS)
Diameter	[mm]	6.35
Hardness, HR_c		62
Surface roughness, R_a	[μm]	0.040
[Test disk]		
Material		SUJ2 (JIS)
Hardness, HR_c		60-63
Surface roughness, R_a	[μm]	0.2

Table 4 Conditions for the X-Ray Photoelectron Spectroscopy Analysis

Instrument	PHI instruments 5600-CIM
X-ray source	Monochromated-Al-Kα ray (1486.6 eV) 300 W
Test area [mm]	ϕ0.12 ellipse

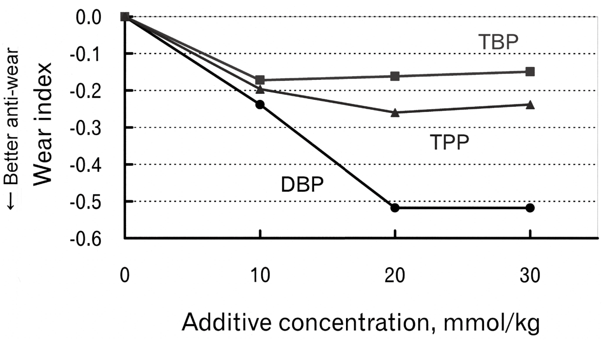


Fig. 2 Effect of Additive Concentration on Wear in M1-H

2. 3. Surface Analysis

X-Ray photoelectron spectroscopy (XPS) was applied to investigate the chemical composition on the worn surface. Prior to surface analysis, the test specimen was ultrasonically cleaned in hexane for 5 min and then in acetone for 5 min. Conditions for the analysis are listed in **Table 4**.

3. Results and Discussion

3. 1. Effects of Additives in Mineral Oils

The results of the four-ball wear test using a solution of phosphorus-containing additives in mineral oils are plotted against concentration of the additives in **Figs. 2-4**. Obviously, DBP prevented wear to a considerable extent, whereas TBP and TPP did not. The dipole moment of DBP is higher than that of TBP or

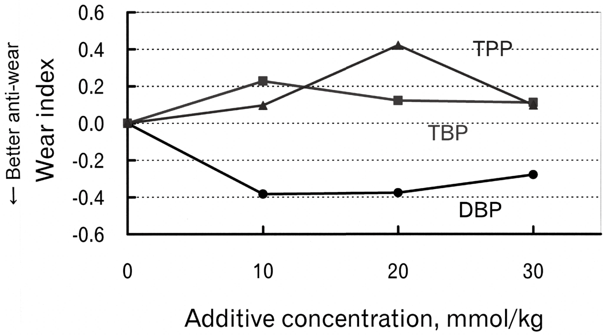


Fig. 3 Effect of Additive Concentration on Wear in M2-HS

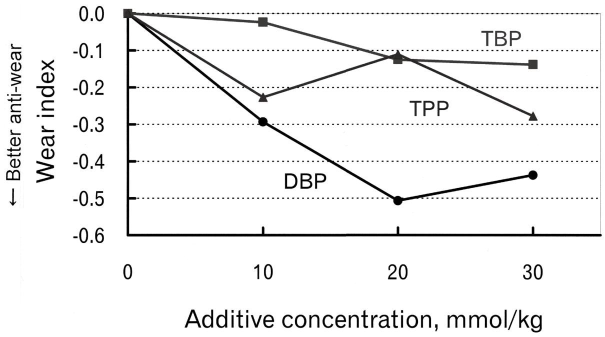


Fig. 4 Effect of Additive Concentration on Wear in M3-HS

TPP[10]. Therefore, the adsorption activity of DBP on surfaces is higher than that of the other additives. Our implicit assumption is that adsorption is the initial step of boundary film formation through tribo-chemical reactions. Higher adsorption of the additive would lead to sufficient replenishment of the boundary film even after removal of the film by rubbing. The reduction in the viscosity of oils reduces the thickness of oil films (fluid film) and results in frequent asperity-asperity contacts which cause wear magnification. Therefore, the importance of the replenishment process of the boundary film should be taken into account under these conditions. The relationship between the replenishment process and total antiwear properties will be discussed in section **3. 3.**

DBP reduced wear in M2-HS at a concentration of 10 mmol/kg, but the wear slightly increased at higher concentrations. Similarly, DBP in M3-HS increased wear, but M1-H did not. Smooth worn surface was observed on the wear scar with DBP in M2-HS and DBP in M3-HS, suggesting that the wear mechanism was corrosive. TPP in M1-H had poor antiwear properties, probably due to the low adsorption activity of TPP as described above. On the other hand, the properties of TPP in M2-HS or M3-HS were unpredictable. These three oils have different viscosity and production processes, which probably caused the variation in additive effects.

$$\text{Wear index} = \frac{(\text{WSD of additive solution}) - (\text{WSD of additive-free oil})}{(\text{WSD of additive-free oil})}$$

where WSD = average of wear scar diameter obtained by the four-ball test.

Eq. (1) Wear Reduction Index

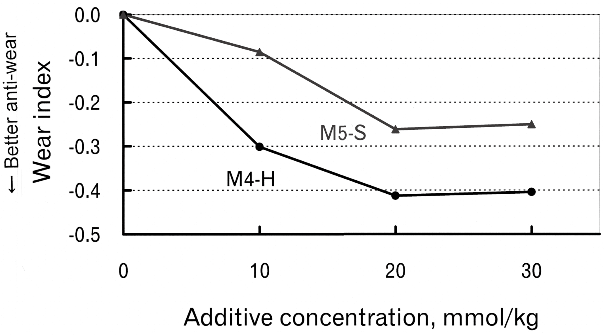


Fig. 5 Effect of DBP on Wear in M4-H or M5-S

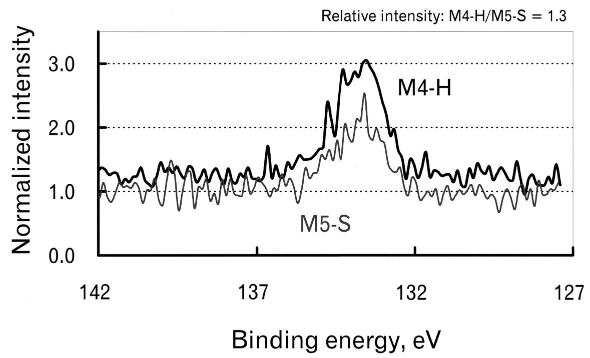


Fig. 6 XPS Spectra of P2p on Wear Track Lubricated by DBP in Mineral Oil at 20 mmol/kg

The effects of the production process of mineral oil on additive response were examined in M4-H and M5-S, which have the same viscosity grade but are prepared by the different processes. Additive-free M5-S provided lower wear scar diameter than additive-free M4-H in the four-ball wear test. To simplify the additive response for these base oils, a "wear index," calculated by Eq. (1), was introduced, with lower index value indicating better antiwear properties. M4-H exhibited better antiwear properties than M5-S for DBP at 10-30 mmol/kg, as shown in **Fig. 5**. The antiwear properties accorded well with the contents of metal phosphate at 133.7 eV on the wear track analyzed by XPS (**Fig. 6**). Higher content of phosphate seemed to be beneficial for good antiwear properties. These results indicate that DBP in M4-H provides a sufficient

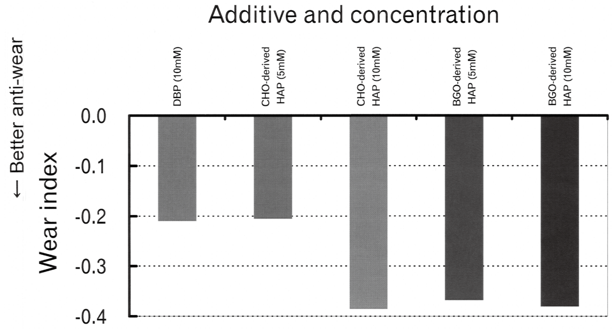


Fig. 7 Effect of Additive on Wear in DES (four-ball test)

boundary film through tribo-chemical reactions. One possible mechanism is that certain heteroatom-containing compounds in the solvent-extracted oil suppress the tribo-chemical reaction of DBP. We were interested in the relationship between the structures of these contaminants and the antagonism, but the investigation could not be pursued in this project. However, we did find that the production process may influence the effects of additives for low-viscous mineral oils. Highly refined base oil may provide better antiwear properties when combined with phosphorus-containing additives.

3. 2. Effects of Additives in Synthetic Esters

Crude oils contain many types of organic compounds. Reduction of these contaminants from mineral-based oils sometimes requires multi-step processes. On the other hand, synthetic fluids are inherently free of any undesirable elements if the production process is well designed. Generally, synthetic esters posses better tribological properties compared to mineral oils of the same viscosity grade. Besides the good tribological properties, we were interested in the availability of contamination-free base oils. Although synthetic esters may be contaminated with the catalysts for esterification and by-products, these impurities can be reduced by careful selection of the synthetic procedure.

The effects of phosphorus-containing additives in DES are summarized in **Fig. 7**. The conventional additive DBP reduced wear to some extent at a concentration of 10 mmol/kg in DES. HAP was originally introduced as an antiwear additive for polar synthetic esters[8], and exhibited similar antiwear properties at lower contents of phosphorus. Wear reduction by CHO-derived HAP at 5 mmol/kg was similar to that by DBP at 10 mmol/kg. These results suggest that phosphorus contents in lubricants can be reduced by modifying the chemical structure of the additives. In fact, BGO-derived HAP exhibited significant antiwear properties even at a concentration of 5 mmol/kg. This additive-concentration corresponds to a phosphorus content of 160 ppm.

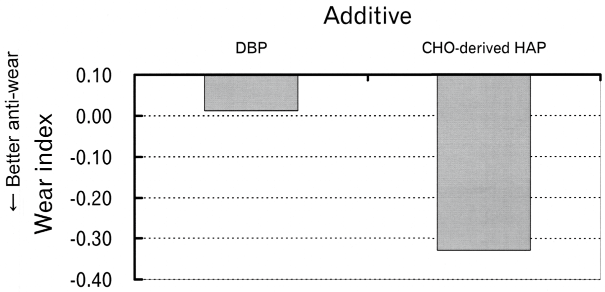


Fig. 8 Effect of Additive on Wear in DES (ball-on-plate test) at 5 mmol/kg

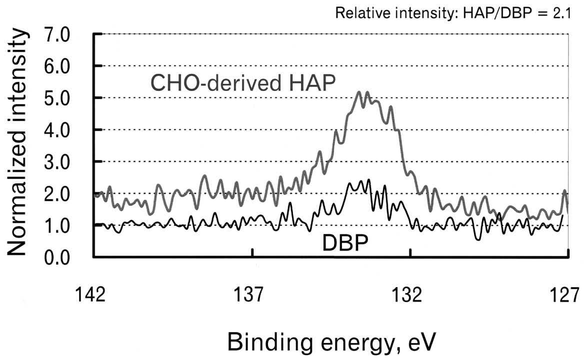


Fig. 9 XPS Spectra of P2p on Wear Track by Ball-on-plate Test Lubricated by Additive in DES at 10 mmol/kg

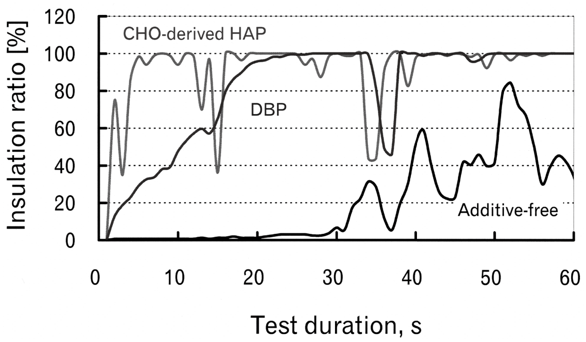


Fig. 10 ECR Trace during the Tribo-test (ball-on-plate test)

3.3. Antiwear Mechanism of Hydroxyalkyl Phosphates

A ball-on-plate reciprocating tribo-tester was employed to study the kinetics of the boundary film formation. Antiwear properties of the additives were estimated by comparing the wear scar diameter on the ball. As summarized in **Fig. 8**, CHO-derived HAP reduced wear to some extent but DBP did not. The tribological properties showed good accordance with the contents of phosphates on the wear track obtained by the XPS analysis (**Fig. 9**). Almost no phosphates were found on the surfaces lubricated with DBP in DES.

Table 5 Dipole Moment of Additives

Compound	Dipole moment [Debye]
DBP	2.6
GHO derived HAP	5.2
BGO derived HAP	5.2

The ECR method showed obvious differences in the kinetics of the boundary film formation between the additives, as shown in **Fig. 10**. The novel additive system, CHO-derived HAP, developed rapid insulation detected by the ECR method as soon as the tribo-test started. On the other hand, DBP formed the boundary film slowly. Although boundary film from additive-free DES was also formed to some extent after an induction period, the resultant film was unstable.

The tribological processes are caused by dynamic conditions at the rubbing surfaces, where formation and removal of the boundary film take place simultaneously. The removal processes are affected by the tribological conditions. Lower viscosity of lubricant leads to decreased thickness of oil film between the contacts which might cause asperity-asperity contacts. Therefore, the rate of the removal of the boundary film presumably increases if low viscosity oils are employed.

One possible method to prevent wear under these conditions is to promote the formation of the boundary film, resulting in a steady state between the formation and removal of the boundary film. The formation processes are initiated by the adsorption of the additive molecule onto the rubbing surfaces, followed by conversion into the phosphate-containing boundary film by tribochemical reactions. The novel additive, HAP, has a hydroxyl group in the organic moiety. The presence of polar functional group in the molecule increases the dipole moment of the additive (**Table 5**), so promotes adsorption of the molecule onto the surfaces[11].

4. Conclusions

(1) Dialkyl phosphonates possess better antiwear than trialkyl phosphonates/phosphates in low viscosity mineral oils. Good additive antiwear response in hydrogen-refined base oils was observed. However, reduced phosphorus contents may reduce antiwear properties even with highly refined base oils.
(2) Combination of hydroxyalkyl phosphonate and low viscosity synthetic esters provides excellent antiwear properties even at low concentrations of additives.
(3) Hydroxyalkyl phosphonates form a phosphate-containing boundary film on the rubbing surfaces to prevent wear. Contents of phosphates on the wear track show good accordance with the antiwear properties.
(4) Hydroxyl groups in the additive are important in promoting formation of the boundary film. The replenishment process of the boundary film, especially

using low viscosity oils, is also important.

Acknowledgments

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要　　旨

環境対応潤滑油に対する潤滑油添加剤の効果—低粘度基油に対する含リン耐摩耗剤低減の試み—

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低粘度基油による省エネルギーを実現するために添加剤による摩耗防止を考慮する必要がある。本研究では低粘度基油に適する含リン添加剤の耐摩耗性を境界潤滑条件下で評価した。鉱油ではジアルキルホスホン酸エステルがよい耐摩耗性を示すが，トリアルキルおよびトリアリールエステルの耐摩耗性は劣っている。添加剤の適合性は鉱油の精製プロセスにも依存する。溶剤精製油に対する添加剤効果は予測できないことがある。同じ摩擦条件では水素化精製油に対してよい添加剤効果が観察される。摩擦試験結果と，表面分析で得た摩擦面上のリン含有量にはよい相関が見られ，鉱油に対してリン濃度0.062重量％（620 ppm）以上の添加剤が必要である。合成エステル油は鉱油よりもよい潤滑性を示すが，既存の添加剤が必ずしも適応できない。これは低粘度エステル油に対して顕著であり，新たな添加剤であるヒドロキシアルキルリン酸エステルを評価した。これはリン濃度0.016重量％（160 ppm）でよい耐摩耗性を示す。この添加剤は速やかに境界膜を生成し，その結果としてよい耐摩耗性を示す。動的条件では境界膜の修復能が耐摩耗性に重要であることを示した。