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ELUCIDATION OF THE ACTION OF FUNCTIONAL GROUPS IN THE COEXISTING ASHLESS COMPOUNDS ON THE TRIBOFILM FORMATION AND FRICTION CHARACTERISTIC OF ZNDTP-FORMULATED LUBRICATING OILS

TRACK OR CATEGORY

Lubrication Fundamentals

AUTHORS AND INSTITUTIONS

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INTRODUCTION

ZnDTP performs good antiwear or antiscuffing action by forming polyphosphate tribofilm [1-4]. Generally, various additives are formulated together with ZnDTP to fulfill the requirements for lubricants. Since recent energy-saving lubricants require good temperature-viscosity characteristics, formulation of good viscosity index improvers (VII) is important. Polyalkylmethacrylates (PMAs) possess superior temperature-viscosity characteristics, and its functionalized molecules perform reduction of the boundary friction by forming adsorbed molecular layers on the friction surface [5, 6]. In this study, influence of the coexisting additives, particularly ashless FMs (polar compounds) that improve friction reducing performance, on the performance of the ZnDTP-formulated oils was investigated. The effect of polar groups such as amino, hydroxyl, and carboxyl groups on the friction reducing performance and tribofilm formation of ZnDTP was studied to elucidate the action of different polar groups.

EXPERIMENTAL DETAILS

Sample oil

- Base oil: Poly-α-olefin (PAO) (16.89 mm^2/s@40°C and 3.88 mm^2/s@100°C)
- Additives: Zinc dioctyldithio-phosphate (prim-C8 ZnDTP; 0.1 mass%P); Four types of PMA; an ordinary random homopolymer of tetradecylmethacrylate (PMA 0), random copolymers of tetradecyl-methacrylate plus one of three types of functionalized methacrylate: 2-hydroxyethyl-methacrylate (PMA-OH), dimethylamino-methacrylate (PMA-N), and methacrylic acid (PMA-COOH); N-tetraethylene-pentamin polyisobutylene succinimide (Dispersant); Dimethyloctadecylamine (DMODA); Glycerinmono-oleate (GMO); Stearic acid (StA); Oleic acid (OlA).

Tribometer

- A ball-on-disk-type rolling-sliding tribometer (ball: that for a commercially available rolling bearing, made of heat-treated high-carbon chromium bearing steel with a dia. of 25.4 mm; disk: a commercially available thrust washer for a thrust needle roller bearing, made of carbon tool steel with outer dia. 27 mm, inner dia. 16 mm, thickness 3 mm). Applied load: 63.4 N, entrainment speed: 80 mm/s, SRR: 100%, oil temp: 100°C.

- The surface roughness of the disk as received was approx. Ra=0.2 μm, and < Ra=0.02 μm after polishing.

Analysis
- A 3D laser scanning confocal microscope for observing the optical image and roughness.
- Auger electron spectroscopy (AES) for the chemical analysis of the tribofilms with depth profiles
- Electron probe micro-analysis (EPMA) for obtaining the chemical imaging data to determine the distribution of elements over the whole width of the wear track.
- Phosphorus nuclear magnetic resonance (^{31}P-NMR) for analyzing the composition of phosphorous compounds in the sample oils.

RESULTS AND DISCUSSION

The average friction coefficient at 24 h friction time of ZnDTP+Dispersant (+Dispersant) and ZnDTP+PMA-N (+PMA-N) were higher than that of ZnDTP alone, but in contrast, ZnDTP+PMA-COOH (+PMA-COOH) and ZnDTP+FMs (+GMO, +DMODA, +StA, +OlA) effectively reduced friction coefficient. ZnDTP+PMA-OH(+PMA-OH) did not show significant effect on friction coefficient (Fig. 1).

From the EPMA imaging analyses, phosphorous concentration on the friction surface (presence of tribofilm) differed significantly among lubricated sample oils (Fig. 2).

As already reported [7,8], AES analysis showed that the ZnDTP-derived tribofilm was composed of two different layers of outer ‘deposited film’ and inner ‘gradient layer’. Figure 3 shows the chemical composition of the deposited film relative to ZnDTP-alone. From these results, followings are found. Amino-group-containing-compounds (PMA-N, Dispersant, and DMODA) significantly reduced the tribofilm formation and produced sulfur-rich deposited film. Among hydroxyl-group-containing-compounds, PMA-OH did not show significant influence on tribofilm formation (P conc) whereas GMO controlled the tribofilm formation, and both compounds produced the sulfur-poor tribofilm. Among carboxyl-group-containing-compounds, stearic acid significantly reduced tribofilm formation but PMA-COOH did not, and both produced sulfur-poor tribofilm.

ZnDTP additive is known to be composed of two types; neutral-ZnDTP [$Zn(DTP)_2$] and basic-ZnDTP [$Zn_4(DTP)_6$], and both are in chemical equilibrium.

$$Zn_4(DTP)_6O \rightleftharpoons 3Zn(DTP)_2 +$$

Figure 4 shows their compositions in the sample oils analyzed by ^{31}P-NMR. It is apparent that the amino-group-containing-compounds increased basic-ZnDTP (b-ZnDTP), whereas both hydroxyl-group- and carboxyl-group-containing-compound increased neutral-ZnDTP (n-ZnDTP), particularly influence of the carboxyl-compounds

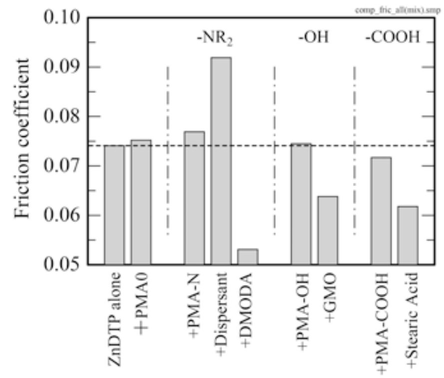

Fig. 1 Comparison of friction coefficient

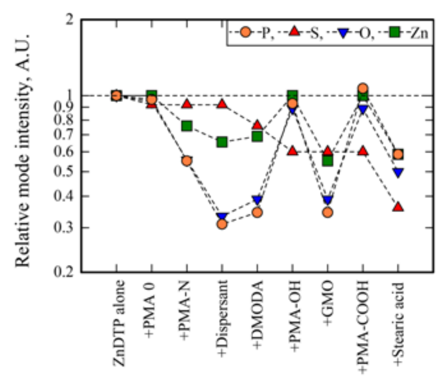

Fig. 2 Comparison of relative elemental concentration of tribofilm analyzed by EPMA

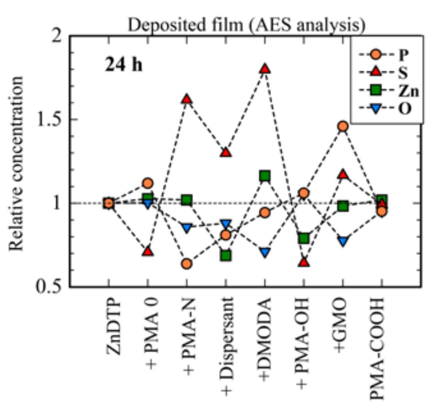

Fig. 3 Comparison of relative elemental concentration of deposited film analyzed by AES

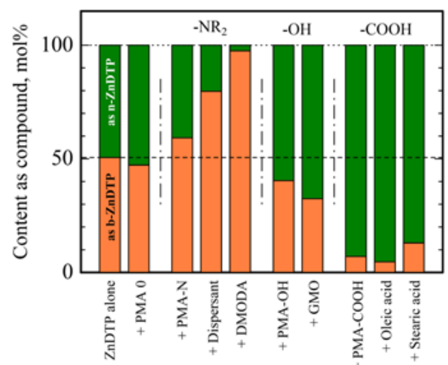

Fig. 4 ZnDTP composition of sample oils analyzed by ^{31}P-NMR

was significant. From the detailed analysis of ^{31}P-NMR spectra, both dispersant and DMODA showed the presence of coordination compounds but PMA-N did not. Although these three compounds had different level of coordination, amino-groups coordinated with zinc atom of n-ZnDTP resulted in reduction of n-ZnDTP. Carboxyl group might react with ZnO resulted in changing equilibrium state producing more n-ZnDTP. Hydroxyl group might also have some interaction with ZnO then tended to produce n-ZnDTP.

Figure 5 shows the relationship between ZnDTP composition (b-ZnDTP ratio in the oil) and tribofilm formation.

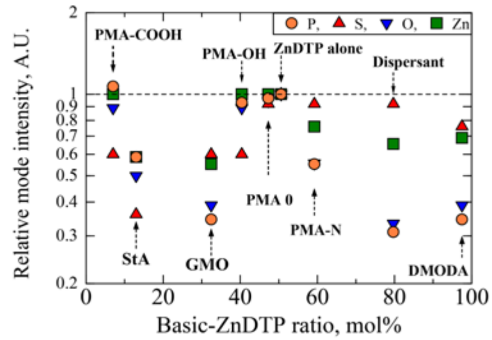

Fig. 5 Effect of ZnDTP composition in the sample oil on the tribofilm formation

GMO, DMODA and StA reduced the formation of P-containing tribofilm that might be due to the formation of rather dense aligned molecular layer on the surface. Among them, effect of StA was smaller. For other bulky polymer compounds (PMAs and dispersant) that do not form dense aligned molecular layer, formation of P-containing tribofilm was significantly reduced with b-ZnDTP ratio in the region greater than 50%. Combination of high content of b-ZnDTP and the formation of dense adsorbed molecular film significantly reduces the ZnDTP- derived tribofilm formation.

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KEYWORDS

Additives: Antiwear Additives, Boundary Lubrication: Boundary Lubrication Chemistry, Additives: VI Improvers.