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Title(English)	Effect of Coexistent Additives on the Friction Characteristics and Tribofilm formation of Zinc Dialkyldithiophosphate
Authors(English)	Saiko Aoki, Masabumi Masuko, Akihito Suzuki
Citation(English)	Proceedings of JSAE/SAE International Fuels and Lubricants Meeting, , , pp. 907-917
Pub. date	2007, 7

JSAE 20077283
SAE 2007-01-1989

Effect of Coexistent Additives on the Friction Characteristics and Tribofilm formation of Zinc Dialkyldithiophosphate

Saiko Aoki*, Masabumi Masuko and Akihito Suzuki
Tokyo Institute of Technology
*Presently, Tokyo Metropolitan Industrial Technology Research Institute

ABSTRACT

The major aim of this study is to investigate the tribofilm formation and friction-speed characteristics of ZnDTP in the presence of other lubricant additives. Simultaneous measurement of friction and electrical conductivity were employed using ZnDTP and several kinds of functionally different additives. Several analyses of friction surfaces were also carried out in order to measure the reaction film thickness and investigate the chemical composition of this film. It was demonstrated that the presence of each additive with ZnDTP prevented the formation of a ZnDTP tribofilm and thereby could provide lower friction than ZnDTP alone.

INTRODUCTION

Zinc dialkyldithiophosphate (ZnDTP) has been used as an antiwear and antioxidant additive ever since it was introduced more than sixty years ago. ZnDTP forms a protective film on the rubbing surfaces of mechanical components; this film limits direct contact of metal surfaces and thereby reduces undesirable wear and seizure. Recently, it has been recognized that this film causes some problems in automotive engines, such as increasing friction between engine components, which leads to decreased fuel efficiency [1]. For this reason, it has become important to fully understand the friction characteristics of ZnDTP when used between metal surfaces. Although many studies of the antiwear performance of ZnDTP have been conducted, there has been relatively little attention paid to the friction characteristics of ZnDTP tribofilm and namely to the mechanism by which the film influences friction.

It is believed that ZnDTP forms a protective film only on the friction surfaces. The film consists mainly of a pad-like, glassy Zn/Fe phosphate above Zn/Fe sulphide on the metal surfaces [2]. Early studies have reported that this film resulted in high friction due to the roughening of the friction surfaces; high speed was needed to generate thicker lubricant oil films; thus, it promotes a shift of the boundary lubrication regime into a mixed lubrication regime [3-5]. In recent studies, however, it has been demonstrated that the addition of other additives such as a dispersant or a detergent to a ZnDTP-formulated oil produced a smooth ZnDTP tribofilm on friction surfaces. This film also caused a significant increase in friction; therefore, ZnDTP tribofilm tended to inhibit oil entrainment at the contact, resulting in a reduction of EHD film thickness [6, 7]. These studies showed that the ZnDTP tribofilm was responsible for the friction behavior. Still, the formation of the film was changed by the coexistence of additives; for example, the presence of dispersant helped promote the removal of ZnDTP tribofilm; as a result, a thin, steady tribofilm was formed on the surfaces [8, 9]. This indicated that the mechanism by which ZnDTP formed a film on the surfaces in the presence of additives was different from [that of] ZnDTP alone.

ZnDTP can also have a different role in the presence of additives due to the synergistic effect from the interaction between ZnDTP and the additives. Molybdenum dithiocarbamate (MoDTC) forms a film on friction surfaces that consists mainly of molybdenum disulfide and partially a mixed molybdenum oxide. Molybdenum disulfide can produce low friction because it has a layer-lattice structure in which weak Van der Waals forces provide low shear resistance [10]. Recent studies have reported that a combination of ZnDTP and molybdenum dithiocarbamate (MoDTC) enhanced wear resistance as well as producing lower friction compared to MoDTC alone [11]. It has also been found that ZnDTP aided in the decomposition of MoDTC molecules and promoted the formation of molybdenum disulfide; that is, sulfur derived from the decomposition of ZnDTP promoted the formation, not of zinc sulfide but molybdenum disulfide [12]. These findings showed that the formation of ZnDTP tribofilm was changed by the presence of MoDTC, as by a dispersant. Therefore, there is a possibility that the friction characteristics of ZnDTP in the presence of additives are different from those of ZnDTP alone. However, the effect of additives on the formation of ZnDTP tribofilm or its friction characteristics has not been established because no systematic research regarding the friction characteristics of ZnDTP in the presence of additives has been conducted.

The current paper describes our investigations of the friction characteristics and tribofilm formation of ZnDTP in the presence of other lubricant additives. Simultaneous measurement of friction and electrical contact resistance (ECR) were employed using a developed tribometer. This tribometer can measure boundary friction between sliding surfaces because it undergoes significant changes in sliding speed ranging from ultraslow (5 μm/s) to moderate (8.5 cm/s). ECR measurement can monitor the formation of tribofilm on the friction surfaces if the film has high electrical resistance. Several kinds of lubricant additives were added to ZnDTP-formulated oil. After friction measurements, both the thickness and chemical composition of the films formed on friction surfaces were measured using several kinds of analytical techniques. The effects of coexistent additives on friction characteristics and film formation of ZnDTP are discussed.

EXPERIMENTAL PROCEDURE

TRIBOMETER

Simultaneous measurement of friction and ECR between sliding surfaces was made using a cylinder-on-disk tribometer in this study [13, 14]. The peripheral surface of the cylinder specimen was loaded against the rotating disk specimen. The cylinder specimen was fixed in an oil cup supported by a gimbal mechanism to ensure contact. A heating element with a temperature controller was installed on the sample oil cup to keep the sample oil temperature constant. As the disk specimen was rotated by a pulse-controlled servomotor, precise speed control across a wide range of sliding speeds from ultra-slow (5.0 μm/s) to moderate (8.5 cm/s) was achieved. As the drive motor was allowed to shift its position toward the vertical direction, an axial load was applied by dead weight via a rack-and-pinion jack. Both the friction torque and axial load were measured individually using two piezo transducers installed just under the cupholder.

ECR measurement has been used to measure real contacts in a portion of apparent contacts between electrical conductive materials because some tribofilms have such high electrical resistance that voltage is detected according to Ohm's law when applying voltage between materials [15]. Figure 1 shows a simple divider circuit diagram of ECR measurement. The voltage was applied between the rotating disk and the stationary cylinder specimens. The detected voltage was recorded through a DC amplifier by a sequential controller.

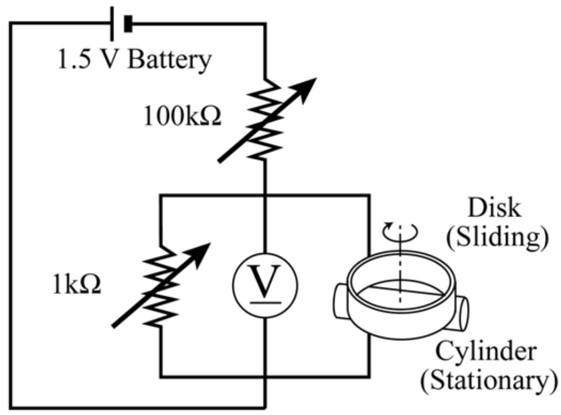

Figure 1 Schematic diagram of ECR circuit

THE OPERATION OF FRICTION TESTS

Data acquisition and the operation of the tribometer were controlled by a sequential controller connected to a computer. Any required test procedure could be programmed into it. These programs were produced with computer application software, and then transferred to the controller. The procedure for the friction test consisted of two parts: a running-in and a friction-speed measurement. The disk and cylinder specimens were attached to the pulse-controlled servomotor and in the oil cup, respectively. Both specimens were heated in sample oil without applying a load until the oil temperature rose to an experimental value. When the sample lubricant oil in the cup reached the test temperature, a dead weight was added to the disk against the cylinder. The voltage of ECR measurement was applied between the two specimens, and then the running-in was turned on. New test specimens of both the cylinder and disk were used for each test. The same sample oil and test specimens were employed for each test from the beginning of the running-in to the end of the friction experiment. Table 1 summarizes the experimental conditions and test materials.

Table 1 Experimental conditions

Axial load	84 N / mm (per 1 point)	
Hertzian mean contact pressure	615 MPa	
Temperature	100 ± 2.5 °C	
Applied voltage	16.75 mV	
Running-in	Sliding speed	20 cm/s
	Sliding distance	370 m
Friction-speed measurement	Range of sliding speed	5.0 μm/s ~ 8.5 cm/s

For the running-in before the friction test, the upper specimen was continuously rotated at 20.0 cm/s for 3500 revolutions under an experimental load and temperature using the same specimens and sample oil. Four angles, at 90° intervals on the disk specimen (0°, 90°, 180°, and 270°) were chosen for the measuring positions, as illustrated in Figure 2. Two pairs of opposite positions, (0° and 180°) or (90° and 270°), were identical, as these positions made simultaneous contact with the cylinder specimen. At each of the four positions, friction and ECR data were measured within a 5° range; 0±2.5°, 90±2.5°, 180±2.5°, and 270±2.5°, and the data obtained within the latter 3° range were used for the results in this study.

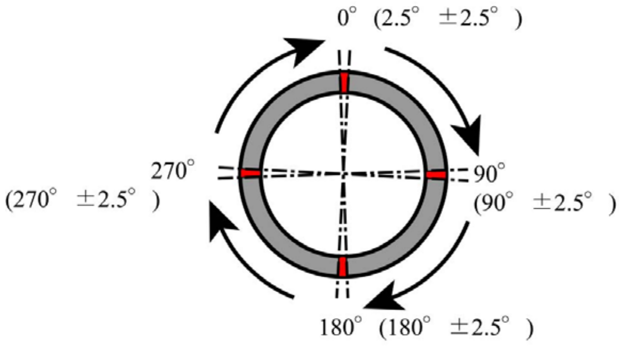

Figure 2 Data acquisition area

Two sets of friction-speed measurements were carried out after the running-in. For the friction-speed measurement, the upper disk specimen was rotated at a speed ranging from 5.0 μm to 8.5 cm /s. The rotation of the upper specimen started at a speed of 8.5 cm/s, and the measuring speed decreased down to a low speed of 5.0 μm/s. The speed increased up to 8.5 cm/s again after it reached 5.0 μm/s. The upper disk rotated once at each measuring speed. The same procedures for data acquisition were repeated at each measuring speed. Friction and ECR data were measured within a range of 5° at each of the four positions: 0±2.5°, 90±2.5°, 180±2.5°, and 270±2.5°, as with the running-in. At each position, upper specimen slides at a measuring speed for the measured 5° range and the data within the latter 3° range were collected. To shorten the total experiment time, the upper specimen moved from position to position at a speed of 5.30 mm/s if the value of measuring speed was below 5.30 mm/s.

The friction coefficient was calculated using simultaneously obtained values for the friction torque and the normal load. The separation ratio was determined by dividing the measured voltage by the applied voltage.

SAMPLE SPECIMENS

Both disk and cylinder specimens were portions of commercially available bearings made of heat-treated high-carbon chromium-bearing steel. The lower cylinder specimen (10 mm in diameter and 40 mm long) was a roller for commercially available roller bearings. The centerline circle diameter of the friction surface of the disk was 33.5 mm, and the width of the contact portion was 0.90 mm. Just before the experiment, both specimens were ultrasonically cleaned in a toluene bath, followed by drying and UV-ozone cleaning.

All disk specimens were finished using a surface polisher with abrasive paper under a stream of water. The grain size of the abrasive paper was successively decreased, finally producing a specimen with an isotropically smooth surface. The disk specimen had a roughness of approximately Ra ≈ 0.056 μm, whereas that of the cylinder was approximately Ra ≈ 0.11 μm before the experiments.

SAMPLE LUBRICANT OILS

Two kinds of base oils were used in this experiment. Their viscosity data are shown in Table 2. Five kinds of lubricant additives were used. The main one was primary C8 ZnDTP (ZnDTP), and one of four kinds of functionally different additives was added to each ZnDTP-formulated oil, respectively. In addition, all additives were also used as mono-blend oils. These additives together with the concentrations in each sample oil are listed in Table 3.

Table 2 Viscosity data for additive-free base oils

CODE	Oil	Sulfur content (mass%)	Kinematic viscosity @100°C, mm^2/s
MO5	Hydrorefined paraffinic mineral oil	< 0.01	5.00
PAO4	Poly-alphaolefin	< 0.01	4.08

Table 3 Concentration levels of additives in sample oils

CODE	Additive	Concentration level
ZnDTP	C8 primary zinc dialkyldithio-phosphate	1.5 mass % (0.1mass%P)
DISP	Polyisobutenyl-succinimide	15 mass%
DET	Ca-salicylate	9.0 mass%
MoDTC	C8 molybdenum carbamate	0.23 mass% (2.5 mmol/kg)
StA	Stearic acid	0.14 mass% (5.0 mmol/kg)

FILM THICKNESS MEASUREMENT

In this study, a Variable Angle Spectroscopic Ellipsometer (VASE®) (J.A. Woollam Co., Inc. M-2000UI™ spectroscopic ellipsometer (SE)) was employed to measure the thickness of tribofilm formed on the disk specimen after the friction test with each ZnDTP-formulated oil. The test specimen of the upper disk was cleaned in a toluene bath in order to remove any residual oil before the SE measurement was performed. SE measurement was carried out at each of four angles at 90° intervals on the disk specimen as shown in Figure 2. Experimental conditions are listed in Table 4.

After measuring ellipsometric data, a regression analysis with an optical model for the sample was required to obtain the film thickness for the measured sample [16, 17]. In this study, an optical model consisting of a single layer on a steel substrate was constructed. The analysis software program WVASE32® was used for the entire regression analysis in order to construct the model and to fit the experimental data to the data calculated from the model. The technique is further described in [18].

Table 4 Analytical parameters for spectroscopic ellipsometry

Instrument	M-2000UI™ spectroscopic ellipsometer
Angle of incidence	65, 70, 75°
No. of scans	100
Scan area	200 μm x 600 μm

AUGER ELECTRON SPECTROSCOPY (AES)

After friction measurement, AES analyses were performed to investigate the chemical composition of ZnDTP tribofilms with depth. AES analysis was also carried out at each of four angles at 90° intervals on the disk specimen as shown in Figure 2. The AES analytical conditions are shown in Table 5. The test disk specimens were ultrasonically cleaned in an n-hexane bath to remove any residual oil; then the specimens were introduced into the apparatus.

Depth profiles were obtained by alternating an acquisition cycle with a sputter cycle during which material was removed from the sample using a 10 kV Ar^+ source. The exact sputter rates in the different layers are not known. The equivalent sputter rate in SiO_2 with this source under the described beam conditions is 14.4 nm/min.

Table 5 Analytical parameters for AES

Instrument	PHI 680	
Electron beam	Beam energy	10 kV
Ion beam	Beam energy	3 kV
	Sputtering rate	14.4 nm/ min in SiO_2
Analysis area	Composition	50 μm x 50 μm

RESULTS

ZNDTP TRIBOFILM FORMATION

Figure 3 compares the experimental results obtained from ZnDTP mono-blend oil with that from additive-free base oil for the running-in period. At the running-in period, four sets of experimental data were obtained because the friction and ECR data were measured at each of the four positions at 90° intervals on the disk specimen (0°, 90°, 180°, and 270°). It should be noted that these four sets of data were almost identical to each other when the disk surface was isotropic. These similarities were due to the use of commercially available bearing parts made of well-defined materials, as well as to the carefully controlled surface finish. Therefore, in this study, the data were averaged from the original data obtained at the four positions when there was a rotation of the cylinder.

Figure 3 shows that the separation ratio of ZnDTP mono-blend increased drastically and progressed from a value of zero up to a value of 1 by less than the distance of 50 m. The separation ratio, which was determined by dividing the measured voltage by the voltage applied between the two specimens, was used to evaluate the film formation, representing a complete separation by a ratio of 1 and a complete contact by a ratio of zero [20]. This demonstrated that ZnDTP formed a nonconductive film on friction surfaces soon after the friction test began, and that the film was present at the contact without film separation throughout the friction test. On the other hand, no increase in the separation ratio for the additive-free base oil was observed. Thus, the increase in the ratio of ZnDTP was attributed to the film formed by ZnDTP. In addition, the base oil gave higher friction than ZnDTP because direct contact occurred on the sliding surfaces. These findings indicated that there was a subtle hydrodynamic effect of the base oil under the test condition employed in this study.

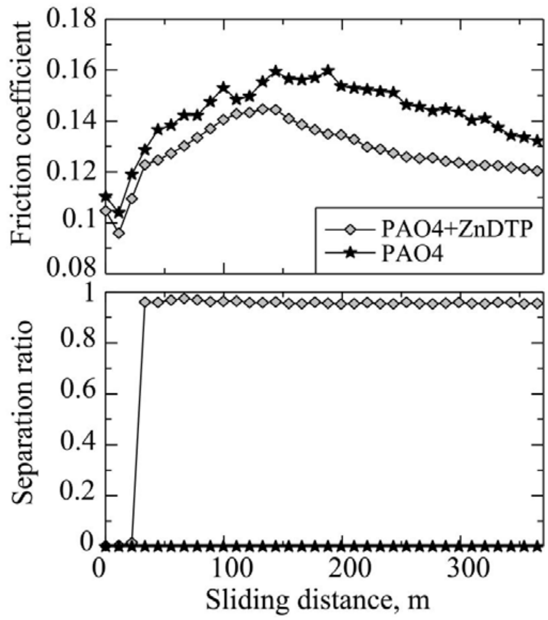

Figure 3 Friction coefficient (upper) and separation ratio (lower) vs. sliding distance plots for a ZnDTP mono-blend and an additive-free base oil

Figure 4 shows a plot of measured friction coefficients and separation ratios against sliding speed for ZnDTP mono-blend and additive-free base oils. As in the case of running-in, the data were averaged from the original data obtained from the four positions at the same speed. It can be seen from Figure 4 that the coefficient of friction for the additive-free base oil increased in the low-speed region due to the reduction of the hydrodynamic lubrication effect, although the separation ratio for the base oil did not increase with speed [13]. On the contrary, the friction coefficient for the ZnDTP mono-blend kept an almost constant value above 10^{-4} m/s and increased with decreasing sliding speed. The separation ratio for ZnDTP also kept a constant value of about one above 10^{-4} m/s while it decreased. It thus appeared that the friction of ZnDTP was related to the separation ratio, that is, how far the ZnDTP tribofilm separated the surfaces to limit direct metal-metal contact.

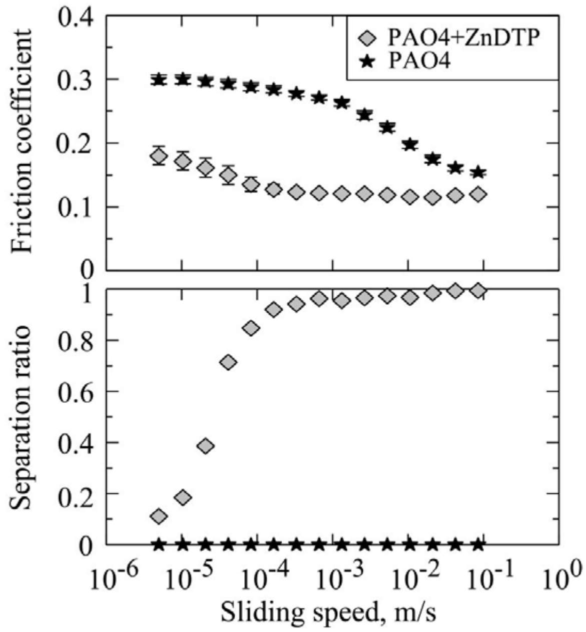

Figure 4 Friction coefficient (upper) and separation ratio (lower) vs. sliding velocity plots for a ZnDTP mono-blend and an additive-free base oil

FRICTION CHARACTERISTICS OF ZNDTP IN THE PRESENCE OF FUNCTIONALLY DIFFERENT ADDITIVES

Figure 5 shows the experimental results obtained from five kinds of mono-blend oils at the running-in period. This figure shows that ZnDTP had a higher friction coefficient than the other four additives did. On the other hand, the separation ratios obtained from the four kinds of mono-blends—DISP, DET, MoDTC, and StA—were low, ranging in value from 0 to 0.2, while the separation ratio from ZnDTP increased sharply and reached one as mentioned above. This is because the four kinds of mono-blends did not form as thick a film as ZnDTP did, or because the reaction film had high electrical conductivity even if it did form such a film; for example, MoDTC formed molybdenum sulfide (MoS_2), which has a high conducting property [20].

Figure 6 compares the experimental results for four kinds of binary-blend oils with that for ZnDTP mono-blend oil at the running-in period. In the presence of other additives, binary blends gave lower friction than ZnDTP alone. Compared with Figure 5, the friction behaviors for each binary blend were relatively similar to those for the respective mono-blend while the separation ratios differed. A significant increase in the ratio for the DET binary blend was observed (Figure 6). In addition, the ratios for DISP and MoDTC binary blends showed high values of about 0.8 while the increase in the ratio for the StA binary blend was small through the end of the running-in. These findings indicated that each binary blend also formed a film on the surfaces. However, the films formed by the various binary blends were not exactly the same as that by ZnDTP alone.

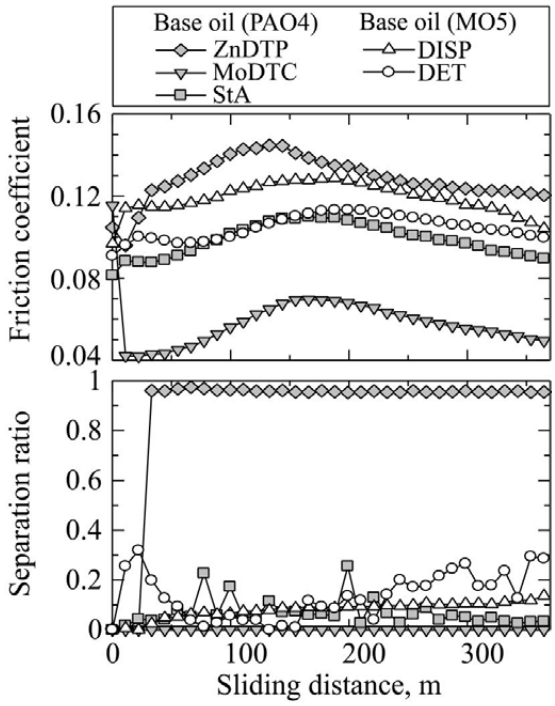

Figure 5 Comparison of plots of friction coefficient (upper) and separation ratio (lower) vs. sliding distance among five kinds of mono-blend oils

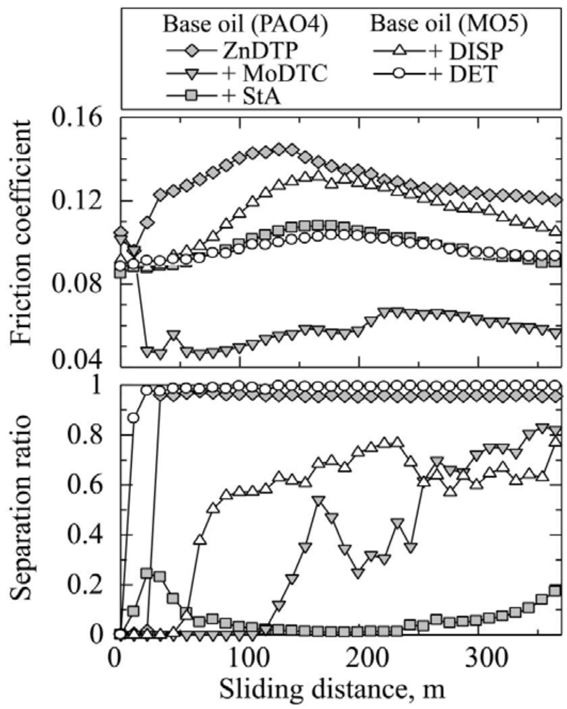

Figure 6 Comparison of plots of friction coefficient (upper) and separation ratio (lower) vs. sliding distance for four kinds of binary-blend oils with that for ZnDTP mono-blend oil

Figure 7 shows the experimental results obtained from the five kinds of mono-blend oils for the friction-speed measurement. The coefficient of friction obtained from DISP or StA increased with a decrease in sliding speed, as did that from ZnDTP. On the other hand, DET and MoDTC provided low friction with an increase in sliding speed. In addition, it can be seen from the separation ratio results of all four additives that there were no significant increases in the ratios. StA- or DISP-absorbed films lost their load-carrying capabilities under high temperature and ultra-slow speed conditions and thereby they produced high friction.

Figure 8 compares the experimental results of the four binary blends (DISP, DET, MoDTC, and StA) with that of ZnDTP mono-blend for the friction-speed measurement. The addition of additives to ZnDTP changed its friction behaviors. The separation ratios for the binary blends were also different from that of ZnDTP alone. Under the low-speed region below 10^{-4} m/s, the friction coefficients for all the binary blends maintained a low value, while the separation, ratios for all binary blends except MoDTC had high values. It should be noted that there was a relationship between high values for the separation ratio and friction reduction behaviors. In addition, compared with the respective mono-blends, both DET and StA binary blends showed low friction while the MoDTC binary blend showed high friction (Figure 7). The DISP binary blend gave slightly lower friction than the DISP mono-blend below 10^{-4} m/s. These findings suggested that the friction behaviors of additives in the presence of ZnDTP were divided into two groups: DET and StA showed friction-reducing behaviors while MoDTC or DISP showed friction-increasing behaviors.

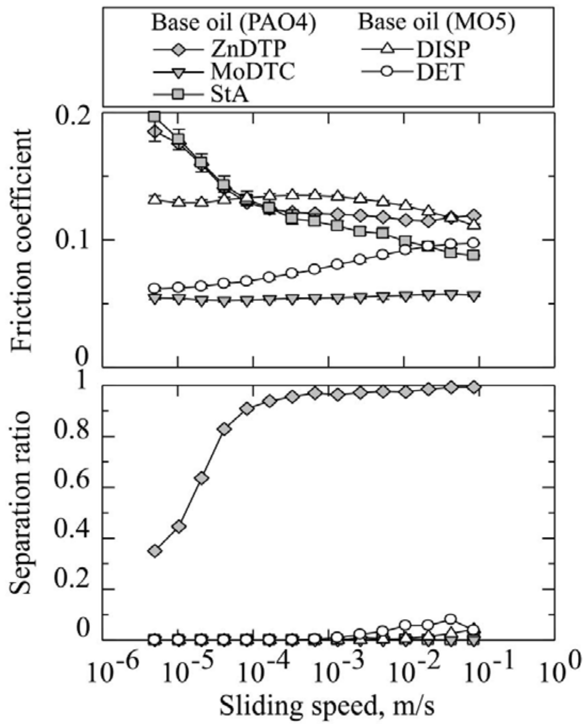

Figure 7 Comparison of plots of friction coefficient (upper) and separation ratio (lower) vs. sliding speed among five kinds of mono-blend oils

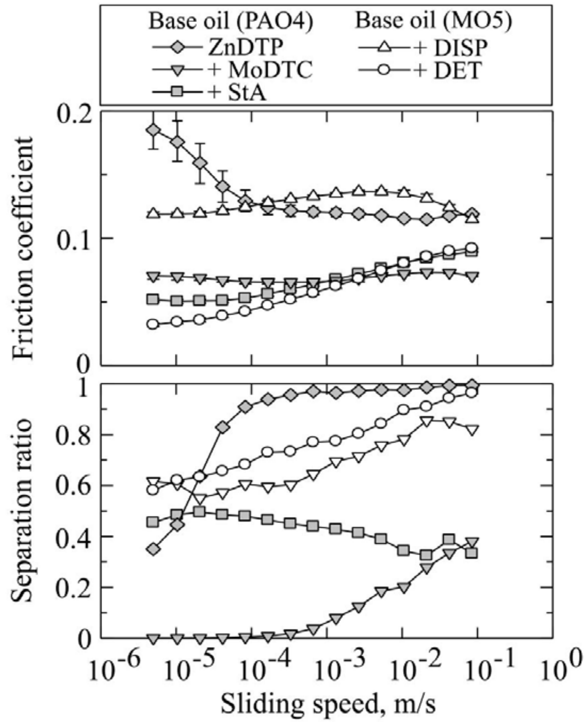

Figure 8 Comparison of plots of friction coefficient (upper) and separation ratio (lower) vs. sliding speed for four kinds of binary-blend oils with that for ZnDTP mono-blend oil

WEAR CHARACTERISTICS OF ZNDTP IN THE PRESENCE OF OTHER ADDITIVES

Figure 9 compares the wear scar area generated on the cylinder specimens after the friction tests conducted at 100°C. Calculation of the wear scar area was performed based on a three-dimensional profile measurement using a laser scanning confocal microscope. The presence of ZnDTP with additives reduced the wear scar area in the case of DET, MoDTC, and StA binary blends. ZnDTP produced the antiwear effect on these binary blends. On the other hand, the area for the DISP binary blend showed a higher value than the DISP mono-blend. Although wear reduction was observed in the MoDTC binary blend, the wear scar area of this blend showed a higher value than that of ZnDTP alone. It is possible that these increases in the area were due to corrosion by sulfur [21].

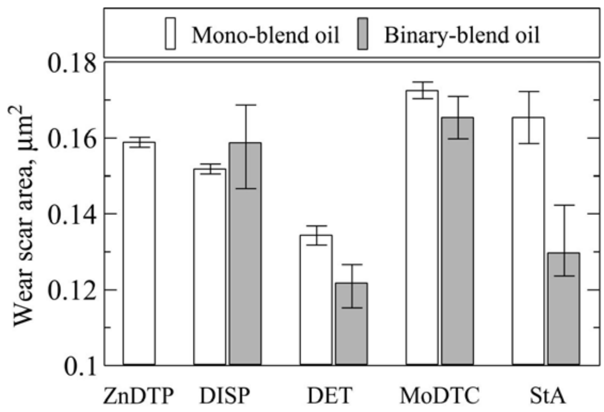

Figure 9 Comparison of wear scar area on the surface of disk specimen among all sample oils

ZNDTP TRIBOFILMS

After friction measurement, spectroscopic ellipsometry was employed in order to measure the thickness of the reaction film on the disk surface. Figure 10 shows the film thickness results for all sample oils. The comparison of film thickness obtained from the disk surface after running-in with that after the entire friction test is shown in Figure 10. There was no significant difference in thickness between these two. In friction-speed measurement after running-in, the sliding speed decreased from the maximum speed of 8.5 cm/s down to the minimum speed of 5.0 μm/s; then the speed increased up to 8.5 cm/s again. After running-in resulted in a steady thickness of ZnDTP tribofilm, the film was reformed at the end of the entire friction test because the friction measurement finished at a relatively high speed that was similar to the running-in speed of 20 cm/s.

Although the addition of ZnDTP increased film thickness, film thickness for all binary blends showed lower values than that for ZnDTP alone. ZnDTP in the presence of MoDTC provided a relatively thick film. This indicated the promotion of the formation of MoDTC tribofilm [10-12]. ZnDTP together with the other three additives (DISP, DET, and StA) produced thin films less than 40 nm.

AES surface analysis was also performed on the friction surface of disk specimens after friction tests conducted using ZnDTP and each binary blend. Figure 11 provides the atomic concentration as a function of sputtering time. In the case of ZnDTP, phosphorus (P), sulfur (S), and zinc (Zn) were detected on the surface. This indicated the formation of a ZnDTP reaction film. In the case of the DISP binary blend, nitrogen (N) was slightly detected. In the case of the DET binary blend, calcium (Ca) along with P, S, and Zn were detected. In the case of the MoDTC binary blend, both molybdenum (Mo) and N were detected. Lower levels of P, S, and Zn were detected on the surface obtained from the StA binary blend. These findings suggested that each binary blend formed different films from ZnDTP alone.

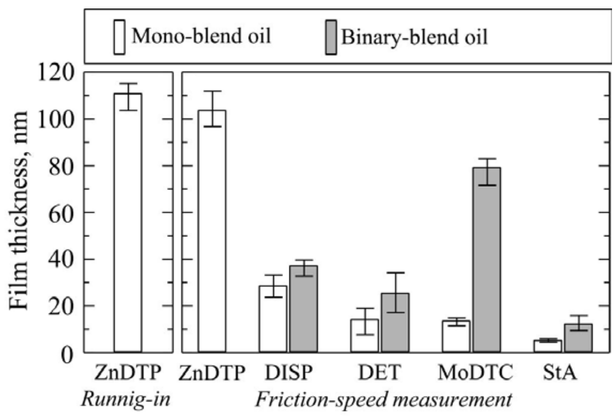

Figure 10 Comparison of thickness of the tribofilms formed on the surface of disk specimen among all sample oils

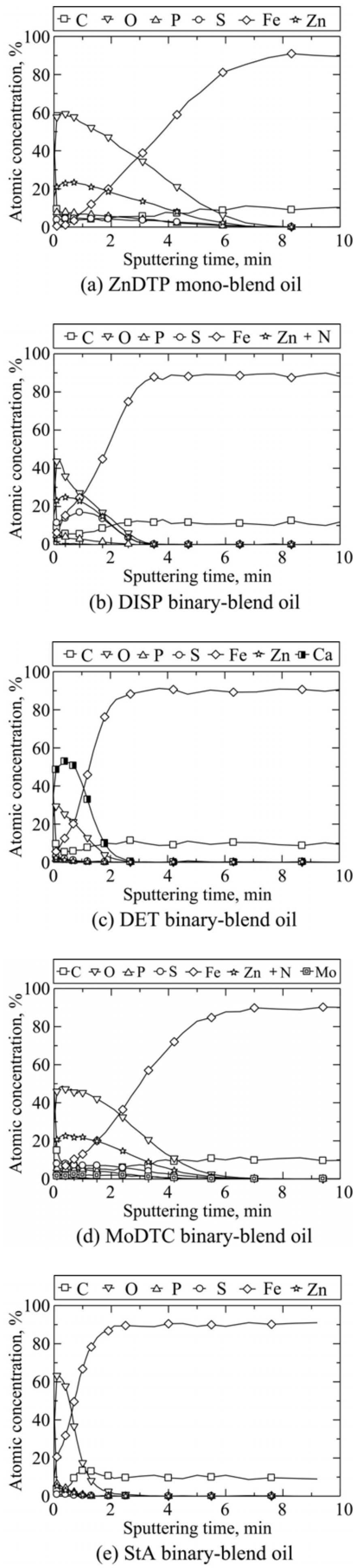

Figure 11 AES depth profile for (a) ZnDTP mono-blend and (b)~(e) four kinds of binary-blend oils

Figure 12 provides the atomic concentration of the elements for each binary blend and the ZnDTP mono-blend at a sputtering depth of about 3 nm. Compared with the atomic content for ZnDTP alone, the film obtained from the DISP binary blend was richer in S and Fe and poorer in P than that from ZnDTP alone. This is why the DISP binary blend showed such a high value for the wear scar area. The film from the DET binary blend was rich in Ca. The MoDTC binary blend formed a MoS_2 film on the surface, as it was rich in S and Mo. The film of the StA binary blend was poorer in P, S, and Zn than that of ZnDTP alone.

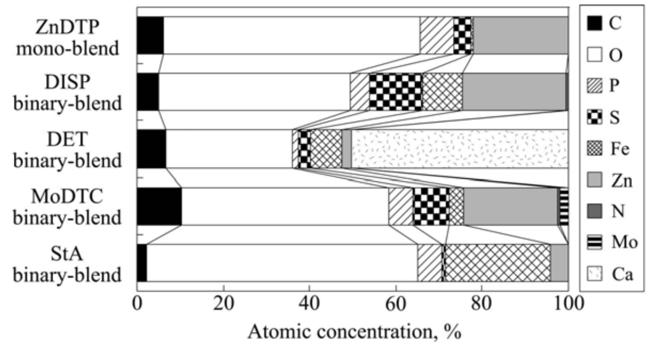

Figure 12 Comparison of atomic concentration of the tribofilm for ZnDTP mono-blend oil with that for four kinds of binary-blend oils

Figure 13 shows the relationship between film thickness obtained from ellipsometric measurement and the stabilization of iron (Fe) concentration obtained from AES depth profile [20]. The stabilization of Fe in the sputtering, i.e., achieving a rate equivalent to that of SiO_2 at 14.4 nm/min, meant the absence of any films on the surface. Ellipsometric thickness showed a proportional relationship with the AES results. Therefore, ellipsometry provided an appropriate value for the tribofilm thickness in this study.

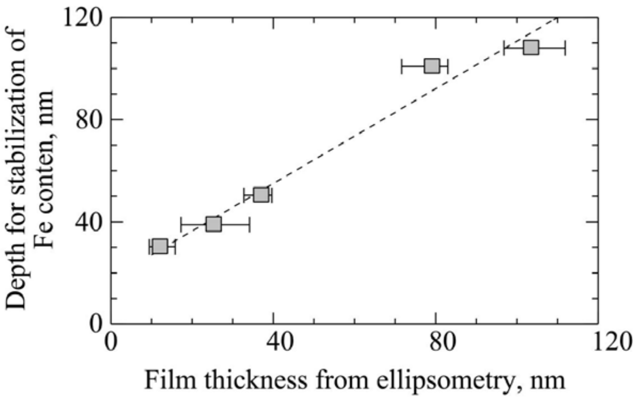

Figure 13 Correlation between film thickness and the depth of the stabilization of Fe concentration

DISCUSSION

FILM FORMATION OF ZNDTP IN THE PRESENCE OF OTHER ADDITIVES

The above results show that the coexistence of functionally different additives with ZnDTP influenced ZnDTP tribofilm formation. It is possible that the differences in separation ratio between ZnDTP and binary blends shown in Figures 6, 8, and 10 are due to differences in film thickness. Figure 10 also demonstrates that each binary blend formed a thinner film than ZnDTP alone did. These results indicated that the coexistence of additives prevented ZnDTP tribofilm formation.

In previous research [22], the authors have demonstrated the difference in adsorption rate between phosphorus and sulfur in ZnDTP molecules. At the beginning of the friction test conducted using ZnDTP, phosphorus and oxygen concentrations on the surfaces were low and increased with sliding distance. On the other hand, the sulfur concentration was high and decreased with distance. With ZnDTP alone in the oil, phosphorus film formation proceeded with sliding distance. However, in the presence of other additives, there is a possibility that the adsorption of these additive molecules occurs at the same time as the diffusion of sulfur and adsorption of phosphorus. Judging from the results in this study, the adsorption of elements from additive molecules other than phosphorus-containing ZnDTP occurred easily on the friction surface.

DISP, DET, MoDTC, and StA were used as coexistent additives in this study. Among these additives, molecules of DISP, DET, and StA contain both hydrophilic and hydrophobic groups. In the case of DISP and DET, their polar hydrophilic group adsorbs onto chemical sludge formed in engine components, and then suspends them in the oil due to the formation of micelles [23]. At the same time, they form adsorption films on the metal surfaces. When ZnDTP was present together with DISP or DET, the hydrophilic groups of DISP or DET may have been adsorbed onto decomposition products from ZnDTP, and thereby the formation of a phosphorus film on the surfaces was less likely to be promoted than in the case of ZnDTP alone. In addition, DISP or DET adsorbed on the metal surfaces and formed adsorption films. AES analysis in Figure 11 explains the formation of these adsorption films and the reduction of the products from ZnDTP. In the case of StA, although it is not clear whether its molecule forms micelles in the oil, it is considered that its adsorption film was formed more immediately than the ZnDTP tribofilm. AES analysis in Figure 11 also indicated that the content of elements such as P, S, and Zn decreased compared with ZnDTP alone.

It is widely believed that MoDTC forms a film on friction surfaces that consists mainly of molybdenum disulfide (MoS_2) and partially a mixed molybdenum oxide (MoO_3). When the electrical conductivity of the film for the MoDTC binary blend was compared with that for the MoDTC mono-blend in Figure 5 and 6, no separation ratio was detected from the film of the MoDTC mono-blend. This indicates that the film formed by MoDTC, which consisted of MoS_2 or a mixture of MoS_2 and MoO_3, has high electrical conductivity as other researchers have reported [20]. The addition of ZnDTP resulted in a high separation ratio for the film. It appeared that ZnDTP tribofilm, especially phosphorus film, was formed on the surfaces together with the formation of MoS_2 film.

AES analysis in Figure 11 shows the formation of phosphorus film from ZnDTP. A recent study using atomic force microscopy (AFM) demonstrated that a blended oil of ZnDTP and MoDTC provided a thicker film, approximately 100 nm, than the MoDTC mono-blend did [24]. The increase in film thickness of MoDTC tribofilm was also observed in this study. This is because a ZnDTP tribofilm, not a MoS_2 film alone, formed on the surface.

EFFECT OF COEXISTENT ADDITIVES ON FRICTION AND WEAR CHARACTERISTICS

The friction results described in Figure 7 shows that the coexistence of ZnDTP with functionally different additives also changed the friction characteristics of ZnDTP. However, when the friction behavior for each mono-blend was compared with that for its respective binary blend in Figure 7 and 8, there were no significant differences among them. This suggested that friction behaviors were influenced not by ZnDTP but by the additives in this study.

It should be pointed out that ZnDTP in the presence of additives provided a lower friction coefficient than ZnDTP alone did in the higher-speed region above 10^{-4} m/s (Figures 6, 8). The results of film thickness in Figure 11 indicate that the film thickness of all binary blends decreased. As mentioned above, the coexistence of ZnDTP and additives tends to prevent the formation of the ZnDTP tribofilm. It is thus possible that the effects of friction reduction observed for each binary blend was attributed to a decrease in film thickness.

In a previous study [18], the correlation between film thickness and friction behavior was described using the classical theory of boundary lubrication. In boundary lubrication, where metal-metal contact may occur directly, the friction coefficient is simply determined by dividing the critical shear stress of the interface by the plastic yield pressure of the underlying metal [25]. This indicates that to reduce friction, it is necessary to prevent a rise in the contact area and to reduce shear stress at the asperity contacts. Based on this theory, when the surfaces are separated at asperity contacts by a thin film of a softer material, the friction coefficient shows a lower value. It has been revealed from recent studies that this film is softer than the steel substrate, since it exhibits more plastic deformation than steel [26]. Therefore, when the film is thin, the friction coefficient maintains a low value. On the contrary, when the film becomes thick, the plastic yield pressure of the underlying bulk substrate might be reduced because the film can be thought of not as a thin film but as a bulk substrate. In other words, the contact area is determined not by the plastic yield pressure of the underlying metal but by that of the thicker film. In this case, the friction coefficient is higher than with a thin film, because the plastic yield pressure of the film is lower than that of the steel substrate.

In the low-speed region below 10^{-4} m/s, the friction coefficient for ZnDTP increased with decreasing sliding speed while that for all binary blends kept low values with sliding speed. In the case of ZnDTP, friction increased with the decrease in sliding speed and the separation ratio decreased. This indicated that the film thickness for ZnDTP decreased with decreasing sliding speed and thereby direct metal-metal contact likely occurred on the surface. On the contrary, the separation ratio for the DISP, DET, and StA binary blends kept higher values than ZnDTP, resulting in less direct contact than ZnDTP. In the case of MoDTC binary-blend oil, a MoS2 film was formed as well as a ZnDTP tribofilm. ZnDTP tribofilm became thin while MoS2 film maintained the separation of the surfaces with decreasing sliding speed. Therefore, friction also stayed low.

It is shown from Figure 8 that a positive slope of friction-speed characteristics, with the friction coefficient gradually decreasing with decreasing sliding speed, was obtained from the DISP, DET, and StA binary blends. As mentioned above, the molecules of DISP, DET, and StA consist of both hydrophilic and hydrophobic groups. They are adsorbed to the metal surface or to an oxide film, and then form adsorption films. However, the adsorption film gradually loses its load-carrying capability with an increase in sliding speed. The positive slope is the result. The mechanism to show a positive slope of friction-speed characteristics was proposed by the authors in previous studies [27, 28]. No positive slope was observed in Figure 7. It thus should be noted that the friction reduction effects of adsorption film were due to the coexistence of ZnDTP.

In addition, it is apparent from Figure 9 that the antiwear performance of ZnDTP was changed in the presence of other additives. DET and StA binary blends had lower wear-scar-area values while DISP and MoDTC binary blends had higher values than ZnDTP. AES results showed that the content of S was poorer in DISP than in ZnDTP while S and Fe were richer and P was poorer in MoDTC than in ZnDTP. This could be ascribed to the typical corrosive behavior of sulfur derived from the high content of sulfur and iron, as well as to the insufficient formation of an antiwear film.

CONCLUSION

In the current paper, simultaneous measurements of friction and ECR were employed in order to study the film formation and friction characteristics of ZnDTP in the presence of functionally different additives. In addition, several kinds of surface analyses such as AES and ellipsometry were carried out in order to obtain information about the chemical composition and thickness of the tribofilm on the friction surfaces. The following conclusions can be made based on the obtained results and the above discussion.

1. The film thickness obtained from ellipsometric measurement showed a proportional relationship with the depth of the stabilization of Fe concentration from AES analysis. Hence, ellipsometry can provide approximate value of tribofilm thickness.

2. ZnDTP formed a thick film of about 100 nm on the friction surface. The friction coefficient for ZnDTP increased with decreasing sliding speed because of the reduction of the separation between the surfaces by the film.

3. The coexistence of ZnDTP and functionally different additives provided significant changes in the tribofilm formation of ZnDTP. In the presence of each additive, ZnDTP formed a thinner film than ZnDTP alone did. AES analysis showed both the formation of a film by each additive and the reduction of the product or products from ZnDTP. These results indicated that each additive prevented ZnDTP tribofilm formation due to the adsorption of the other additive.

4. The coexistence of ZnDTP and functionally different additives also changed the friction characteristics of ZnDTP. In the low-speed region below 10^{-4} m/s, the friction coefficient for ZnDTP increased with decreasing sliding speed while that for each binary blend kept a low value regardless of sliding speed. In addition, a positive slope of friction-speed characteristics was obtained from DISP, DET, and StA binary-blend oils because of the friction reduction effects of adsorption film due to the coexistence of ZnDTP.

5. Antiwear performance of ZnDTP was affected by the presence of functionally different additives. ZnDTP produced an antiwear effect in DET, MoDTC, and StA binary blends. On the other hand, the DISP binary blend showed poor antiwear performance. AES analysis showed that this could be ascribed to both the thinner formation of a phosphorus-containing tribofilm and the typical corrosive behavior of sulfur derived from the high content of sulfur and iron.

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