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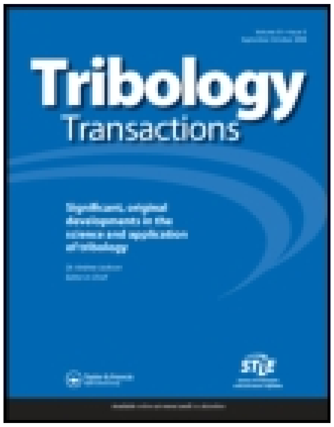

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Antiwear Tribofilm Formation on Steel Surfaces Lubricated With Gear Oil Containing Borate, Phosphorus, and Sulfur Additives

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Antiwear Tribofilm Formation on Steel Surfaces Lubricated With Gear Oil Containing Borate, Phosphorus, and Sulfur Additives©

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The formation of antiwear tribofilms plays a critical role in the longevity of automotive gears. The focus of this experimental study was on the lubrication efficacy of gear oils with different contents of borate-, phosphorus-, and sulfur-containing additives leading to the formation of protective tribofilms. Experiments were performed with AISI 52100 steel balls sliding against AISI 52100 steel disks in baths of different oils at ambient (~32°C) and elevated (~100°C) temperatures under load and speed conditions favoring sliding in the boundary lubrication regime. Friction coefficient responses accompanied by electrical contact voltage measurements provided real-time information about the formation and durability of the antiwear tribofilms. The wear resistance of the tribochemical films was quantified by wear rate data obtained from surface profilometry measurements of wear tracks on the disk specimens and sliding tests performed at ambient temperatures after the formation of the tribofilms during elevated-temperature sliding. Results indicate a strong dependence of tribofilm formation on temperature and type of additives. The slightly lower friction and higher wear resistance obtained at elevated temperatures with blended oils is attributed to the increased chemical reactivity of additives containing borate, phosphorus, and sulfur, leading to the formation of durable tribofilms. Relatively higher wear resistance and faster tribofilm formation were obtained with the borate-enriched gear oil formulations.

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KEY WORDS

Antiwear Tribofilms; Borate-containing Additives; Boundary Lubrication; Friction; Sliding; Wear Resistance

INTRODUCTION

Significant advances in boundary lubrication have been largely due to basic understanding of physicochemical phenomena involving lubricant adsorption and tribochemical effects due to asperity and wear debris interactions. However, the complex nature and simultaneous occurrence of competing tribochemical processes, especially in the case of boundary lubricants with various additives, present significant obstacles to the analysis of the tribological behaviors of lubricated machine elements. The longevity of highly loaded machine elements, such as gears and bearings, greatly depends on lubricants enabling the formation of tenacious tribochemical layers (tribofilms) at sliding interfaces to prevent metal-to-metal contact.

Reactions between chemically active components incorporated in lubricants and sliding metal surfaces have been found to lead to the formation of chemical films that decelerate wear (Begelinger and DeGee, 1972). Products of chemical reactions between zinc dithiophosphate (ZDDP) additive incorporated in paraffin oil and metal surfaces can be transformed to an adherent antiwear film by tribochemical reactions induced by surface rubbing (Georges et al., 1979). The efficiency of such tribofilms to reduce plowing friction and abrasive wear by hard asperities and wear debris in boundary lubrication (Komvopoulos et al., 1985, 1986) is affected by the regenerative capacity and stability of the tribofilms under high contact loads and elevated temperatures. These tribofilm properties strongly depend on chemisorption, decomposition, and chemical interactions between the most reactive decomposition products and the sliding metal surfaces.

TABLE 1—ANALYTICAL DATA FOR BASE OIL AND VARIOUS BLENDS*

ELEMENT	BASE OIL	BLEND 1	BLEND 2	BLEND 3
B	—	0.16 wt.%	0.20 wt.%	195 ppm
Ca	—	29 ppm	14 ppm	2 ppm
K	—	0.18 wt.%	0.23 wt.%	13 ppm
P	—	433 ppm	428 ppm	0.11 wt.%
S	618 ppm	1.05 wt.%	0.99 wt.%	1.59 wt.%
Zn	—	0.9 ppm	2 ppm	2 ppm

* Quoted from Chevron Oronite Co., Richmond, California.

Gear oils containing phosphorus-sulfur (P-S) additives have been used extensively for protection against severe wear (e.g., scuffing). Demands for increased gearbox efficiency have led to the development of new additives, such as borate (B). Alkali borate microspheres suspended by dispersants and blended in mineral oil have been reported to produce much higher load-carrying capacity and wear resistance than P-S gear lubricants (Adams, 1977). Significantly lower axle break-in wear and greater thermal stability have been observed for gear oil with dispersed solid borate additive compared to P-S synthetic lubricant (Salentine, 1990). Incorporation of molybdenum dithiocarbamate into P-S gear oil has been found to reduce friction between steel surfaces sliding in the mixed and boundary lubrication regimes, presumably due to the formation of a boundary film containing molybdenum-sulfur compounds (Jeng et al., 2002). Alkali borates result in the formation of tribofilms containing borate glass, which is believed to increase the load-carrying capacity. Electrical charging of sliding surfaces may cause migration of charged borate particles at the surface, leading to the formation of a protective borate-rich tribofilm by electrophoresis (Adams and Godfrey, 1981). A study on the possible partial replacement of ZDDP by a multifunctional additive consisting of a borate-sulphonate compound has demonstrated that sulphonate moiety influences interaction between borate additive and ZDDP (Varlot et al., 2001). However, sliding tests performed at an oil temperature of 100°C revealed a negative effect of borate on the wear resistance of steel surfaces.

A literature search indicated that despite progress in the understanding of the role of S-P type additives in gear oils, basic knowledge of the effect of borate additive in boundary lubrication with gear oils is limited and rather empirical. As an outgrowth of previous studies on the friction and wear properties of bearing steel lubricated with borate-containing additives (Kim et al., 2000), boundary lubrication experiments were performed with a ball-on-disk tribometer at lubricant temperatures of ~100°C to evaluate the efficacy of gear oil formulations with different contents of borate, phosphorus, and sulfur additives to form antiwear tribofilms. To accomplish this objective, *in situ* measurements of the coefficient of friction and electrical contact resistance (ECR) were obtained in order to investigate tribofilm formation, rupture, and replenishment during sliding. Previous studies on zinc dithiophosphates, dispersants, detergents, and fully formulated engine oils displayed significant differences in film formation rate detected after testing for ~20 min. A rise in the contact voltage (i.e., ECR) was observed upon film formation (Tonck et al., 1979; Yamaguchi et al., 1997, 1998, 2002). The ECR data were supplemented by wear rate calculations based on profilometry measurements of the worn surfaces. Results revealing the formation of durable antiwear tribofilms are presented for different lubricant formulations. It will be shown that tribofilms maintain their integrity even under relatively low-temperature sliding conditions, where the lower rates of tribochemical reactions may retard tribofilm replenishment.

EXPERIMENTAL PROCEDURES

Lubricants

Gear oils (Chevron Oronite Co., Richmond, California) with and without borate-, phosphorus-, and sulfur-containing additives were used to lubricate the steel specimens. Hereafter, the additive-free gear oil will be referred to as base oil and the three different additive-enriched base oils will be referred to as blends 1, 2, and 3. Table 1 gives information about the composition of the four lubricant formulations. Blends 1 and 2 contain two different variations of a borate additive that has been previously shown to improve both the friction and, especially, the wear properties of steel surfaces sliding at elevated temperatures (Kim et al., 2000). For comparison, commercial oil containing a sulfur-phosphorus additive (blend 3), believed to yield similar antiwear characteristics, was also tested under the same conditions as the boron-enriched oils. Additional details about the chemical composition of the oils used in this study can be found elsewhere (Kim et al., 2000).

Specimens

Balls of 0.8 cm diameter and flat round disks 0.51 cm thick and 3.16 cm in diameter, both consisting of AISI 52100 steel (96.9% Fe, 1.04% C, 1.45% Cr, 0.35% Mn, 0.275% Si (all weight percentages), quoted by Falex Co.), were used to perform sliding tests. The disks were mirror polished to an arithmetic average roughness of approximately 26.2 nm using a suspension containing alumina abrasive particles of 0.3 µm in average size. All specimens were stored in a dessicator with Ca_2SO_4 and before testing they were thoroughly cleaned with hexane and acetone.

Testing Apparatus

Friction and wear experiments were performed with a modified ball-on-disk tribometer (Falex-6, thrust washer), shown schematically in Fig. 1. The disk was secured to the pedestal and the ball was inserted in a specially designed holder that prevented rotation of the ball while the entire assembly was free to rotate, thus causing pure sliding of the ball against the stationary disk. The assembled specimens were enclosed in an oil cup heated by a band heater. Two O-rings were used to prevent oil leakage, one to seal the top of the oil cup and another to seal the disk specimen holder. Both O-rings were replaced before each test to avoid oil contamination from previous experiments. For testing at elevated temperatures, the oil in the cup was heated to the desired temperature for approximately 15 min before initiating sliding in order to ensure uniform temperature in the oil bath. A normal load of 147.12 N (15 kg_f) and rotational speed of 316 rpm (corresponding to a sliding speed of 0.34 m/s) were used in all tests. Lubricant film thickness calculations, optical microscopy studies of the test-

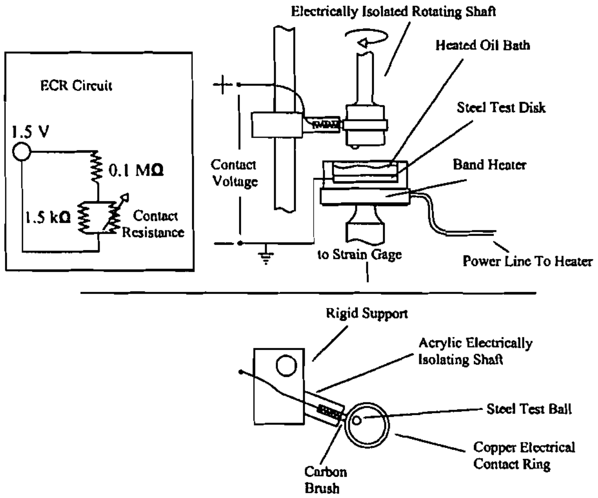

Fig. 1—Schematic of ball-on-disk tribometer (top) and specimen assembly (bottom). The inset on the left-hand side shows the circuit for electrical contact resistance (voltage) measurement.

ed surfaces, and friction coefficient measurements confirmed that sliding occurred in the boundary lubrication regime. The friction force was determined from the torque resisting the rotation of the lower-specimen pedestal measured by strain gages. The corresponding voltage signal was recorded continuously by a computer. Mean and standard deviation values of the steady-state coefficient of friction were calculated from at least five different tests with each blend.

The lubricating efficacy of the different oils was evaluated by performing sliding tests at ambient (32 ± 10°C) and elevated (100 ± 5°C) oil bath temperatures. However, the actual temperature rise at the contact interface was higher due to frictional heating (Kim et al., 2000). The test time was 1 h, and the corresponding total sliding distance was approximately equal to 1232 m. After testing, the samples were cleaned with hexane and stored in a dessicator with Ca_2SO_4 at room temperature.

To evaluate indirectly the tribofilm wear resistance and durability, special experiments (hereafter referred to as "durability" tests) were performed at an ambient atmosphere after tribofilm formation during elevated-temperature sliding. Specifically, after reaching steady-state coefficient of friction and contact voltage responses in some elevated-temperature experiments with blended lubricants, the system was allowed to cool down to room temperature over night without removing the specimens. Sliding was initiated several hours later under the same load and speed but without heating the lubricant. The objective was to examine the wear behavior of the tribofilms in the absence of temperature-induced tribofilm replenishment.

Electrical Contact Resistance Measurement

For real-time detection of tribofilm formation and removal, ECR measurements were obtained during testing. The ECR setup, shown schematically in the inset of Fig. 1, uses a carbon-to-copper sliding contact with the rotating part of the tribometer. The carbon tip was spring-loaded to maintain continuous contact with the rotating copper ring. A sufficiently stiff spring was used to prevent floating at the experimental speed. The spring, carbon tip, and rotating ball holder were electrically insulated by acrylic material to ensure that contact occurred only between the ball and the disk specimens. Tribofilm formation and removal was studied by observing the variation of the contact voltage with time (or sliding distance).

A simple voltage divider circuit design enabled variation of the voltage across the ball/disk interface in the range of 0-23 mV. According to Ohm's law, an increase in voltage is directly related to an increase of the ECR. This is the general principle that the ECR measurement relies on. In the presence of an antiwear tribofilm, direct metal-to-metal contact is inhibited and the ECR assumes a nonzero value depending on the tribofilm properties and interface topography. The contact voltage was recorded in real time using a sampling frequency of ~2 kHz.

Surface Roughness and Wear Rate Measurements

The surface roughness of the polished specimens and wear rate obtained with each blend were analyzed with a mechanical stylus profilometer (Dektak IID, Veeco Instruments). For statistical analysis, five different circumferential wear track locations were traced with the profilometer stylus under a light contact load to determine the average cross-sectional area of each wear track. The wear rate was obtained by dividing the disk wear volume (calculated by multiplying the average cross-sectional area, measured by profilometry, with the circumference of the wear track) by the total distance of sliding. Friction coefficient, wear rate, and contact voltage data were assumed to follow normal distributions. Error bars in the following figures denote one standard deviation above and below mean values.

RESULTS AND DISCUSSION

Representative results for the coefficient of friction and contact voltage demonstrating the development of antiwear tribofilms for each blend are presented in this section, followed by statistical data for the steady-state coefficient of friction, wear rate, and distance (time) of sliding corresponding to the onset of tribofilm formation (run-in period). Although the emphasis in this study is on gear oil boundary lubrication at elevated temperature, a few results from tests conducted at ambient temperature are also included to provide an assessment of the chemical reactivity of the different additives in terms of average lubricant temperature. In addition, selected results from durability experiments performed at room temperature after the detection of tribofilm formation are given to reveal indirectly the wear resistance (endurance) of the produced tribofilms.

Figure 2 shows characteristic responses of the coefficient of friction and contact voltage for base oil at ~100°C. The friction coefficient increases rapidly from an initial value of ~0.09 to values in the range of 0.10-0.12 exhibiting noticeable fluctuations, especially in the early stage of sliding (Fig. 2(a)). Such friction behavior is indicative of wear debris formation and entrapment at the contact interface, affecting the real contact area and magnitude of the friction force. Contrary to the significant changes of the friction response, the contact voltage assumed very low values (of the order of ~0.1 mV) throughout the test duration (Fig. 2(b)), indicating a negligible change in electrical contact resistance,

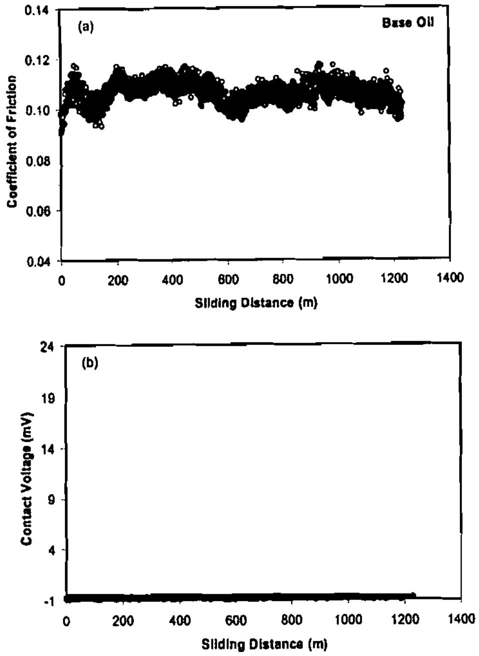

Fig. 2—Variation of (a) coefficient of friction and (b) contact voltage with sliding distance for base oil at ~100°C.

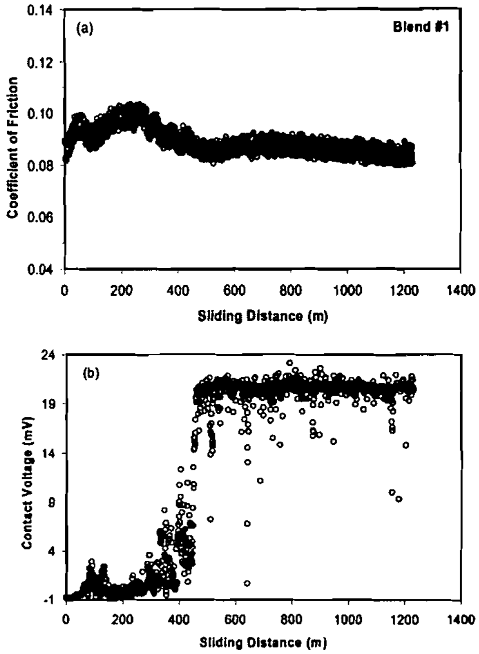

Fig. 3—Variation of (a) coefficient of friction and (b) contact voltage with sliding distance for borate-, phosphorus-, and sulfur-containing blend 1 at ~100°C.

despite surface roughening and formation of wear debris, both tending to decrease the real contact area. Thus, the weakly adsorbing molecules of the base oil did not inhibit intimate metal-to-metal contact.

Different trends for the coefficient of friction and contact voltage were observed with blended lubricants. As shown in Fig. 3(a), the coefficient of friction for blend 1 increases rapidly from a value of ~0.08 at the onset of sliding to values higher than 0.10 before decreasing eventually to an average steady-state value of ~0.085. Similar to the coefficient of friction, noticeable contact voltage changes occurred during the early stage of sliding. The sudden increase of the contact voltage at a sliding distance of ~400 m and the higher values thereafter indicate the formation of an insulating antiwear tribofilm (Fig. 3(b)). The results shown in Figs. 3(a) and 3(b) demonstrate a direct correspondence between friction coefficient and contact voltage fluctuations. For example, the temporary decrease of the coefficient of friction at a sliding distance of ~100 m correlates well with the simultaneous slight increase of the contact voltage. Moreover, the steady-state coefficient of friction is associated with a nearly constant high contact voltage of ~20 mV. (The few spontaneous spikes of the contact voltage at steady state may be attributed to localized rupture and rapid replenishment of the tribofilm.). The contact voltage was used to determine the time for the development of antiwear tribofilms because it is much more sensitive to the chemical reactivity of the additives at the sliding interface.

Figure 4 shows representative results for the coefficient of friction and contact voltage obtained with blend 2 at ~100°C. As observed for blend 1, the coefficient of friction increases from an initial value of 0.08-0.09 to a peak value of ~0.11 and then decreases gradually to a steady state in the range of 0.08-0.10 (Fig. 4(a)). However, compared to blend 1, the contact voltage response for blend 2 (Fig. 4(b)) reveals a relatively more intense chemical reactivity of the additives with the slightly higher borate content, illustrated by the high voltage values in the distance range of 50-200 m. The large fluctuations of the contact voltage at the beginning of sliding suggest the formation and removal of an insulating tribofilm affecting the magnitude of the friction coefficient. However, the increase of the contact voltage at sliding distance of ~400 m indicates the end of this transient period. The lower steady-state contact voltage compared to that shown in Fig. 3(b) may be attributed to the thinness and/or relatively less insulating capacity of the produced tribofilm.

Blend 3 (with only P-S-containing additives) demonstrated different friction and contact voltage patterns. Contrary to blends 1 and 2, the coefficient of friction obtained with blend 3 decreased with the onset of sliding from ~0.095 to ~0.075, reaching a slightly higher steady state in the range of 0.08-0.09 at sliding distance of ~900 m (Fig. 5(a)). The corresponding contact voltage response (Fig. 5(b)) is also different from those of blends 1 and 2. After a gradual rise during the early stage of sliding, the contact voltage increased rapidly in the distance range of 400-800 m, reaching a steady-state value of ~20 mV, which is close to that of blend 1 (Fig. 3(b)). Thus, blend 3 exhibits a period of tribofilm formation longer than those of blends 1 and 2 but more stable steady-state response than blend 2. Such behavior may be related to differences in the rate of formation and removal due to surface rubbing of the compositionally different tribofilms.

Since the compositions of antiwear tribofilms are not well established and electrical resistivity measurements for such films

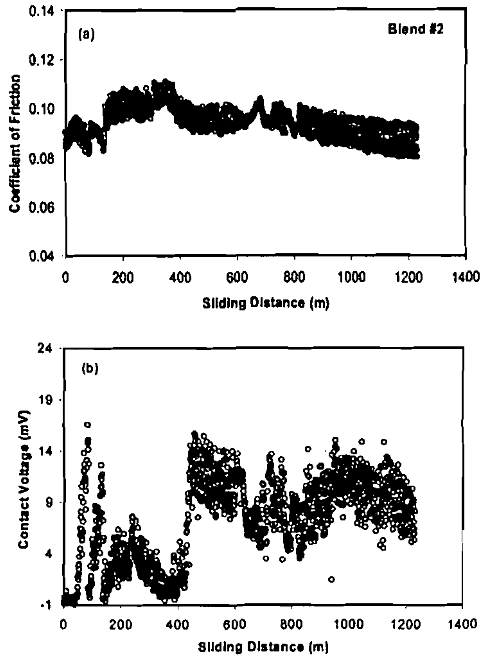

Fig. 4—Variation of (a) coefficient of friction and (b) contact voltage with sliding distance for borate-, phosphorus-, and sulfur-containing blend 2 at ~100°C.

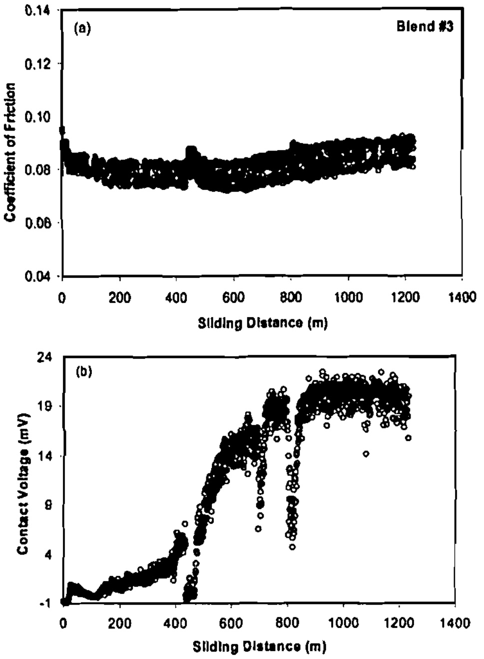

Fig. 5—Variation of (a) coefficient of friction and (b) contact voltage with sliding distance for phosphorus-sulfur-containing blend 3 at ~100°C.

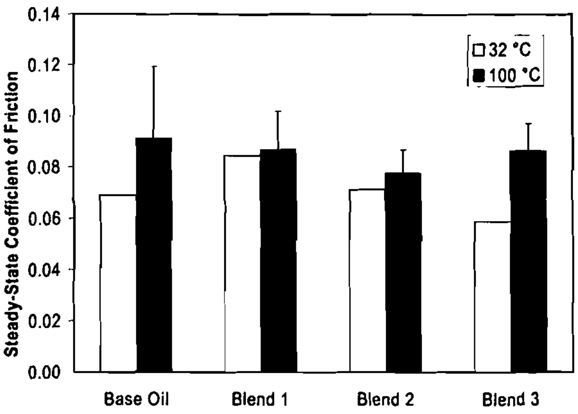

Fig. 6—Steady-state coefficient of friction for different gear oil formulations at ~32°C and ~100°C.

have not been reported, quantitative information for antiwear tribofilm resistivity is not available. Typically, inorganic antiwear tribofilms are thought to consist of metal oxides, sulfides, phosphates, and borates, with compositions depending on the additives used to generate them. Therefore, such films are ionic, insulating solids. The conduction mechanism for insulators is different from that of typical metals. Commercial copper and iron alloys exhibit resistivities of 1.7-11.4 and 10-170 μΩ•cm, respectively, whereas metal oxide resistivities are composition and temperature dependent, and are in the range of 10^9-10^{19} μΩ•cm (at 300°C) (Weast, 1975). Antiwear tribofilms formed from P- and B-containing additives are thought to be phosphate and borate glasses, respectively, and presumably have resistivities similar to those of oxides. Sulfides may be semiconductors, therefore possessing much lower resistivities, depending on the tribofilm composition and temperature of formation.

Figure 6 shows steady-state coefficient of friction results for different blends at ~32°C and ~100°C. The mean values of the coefficient of friction are in the range of 0.06-0.09, which are slightly higher than those reported previously for rougher steel surfaces (Kim et al., 2000). Generally, the coefficient of friction increases with temperature for base oil and blend 3, while for blends 1 and 2 it changes marginally with temperature. The lowest mean value and less varying steady-state friction coefficient at elevated temperature were obtained with blend 2, i.e., the lubricant with the higher borate content. The slightly lower coefficient of friction obtained with blended lubricants reflects a lower interfacial shear stress in the presence of B-, P-, and S-containing antiwear tribofilms forming at elevated temperatures that reduces the contribution of plowing to the total friction force by minimizing metal-to-metal contact. Statistical data for the coefficient of friction are given in Table 2.

The variation of the contact voltage with sliding distance provides useful information about tribofilm formation. Figure 7 shows schematics of the two contact voltage responses (curves 1 and 2) most often encountered in this study during elevated-temperature sliding. In the early stage of sliding, the contact voltage was generally low, indicating the absence of any insulating film at the contact interface. However, after sliding for relatively small distances, the contact voltage increased fairly rapidly, illustrating the formation of an electrically nonconductive tribofilm. The

Table 2—Steady-State Coefficient of Friction and Disk Wear Rate for Base Oil and Various Blends at an Oil Temperature Equal to ~100°C

Lubricant	Coefficient of Friction	Disk Wear Rate (m^3/m)
Base Oil	0.091 ± 0.028	$2.13 \times 10^{-14} \pm 4.6 \times 10^{-15}$
Blend 1	0.087 ± 0.015	$2.60 \times 10^{-15} \pm 7.1 \times 10^{-16}$
Blend 2	0.078 ± 0.009	$2.91 \times 10^{-15} \pm 3.9 \times 10^{-16}$
Blend 3	0.087 ± 0.010	$3.23 \times 10^{-15} \pm 6.3 \times 10^{-16}$

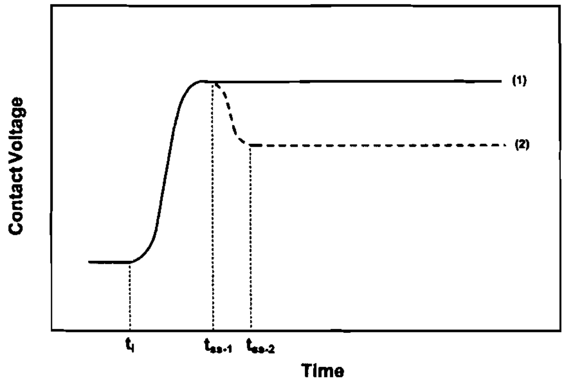

Fig. 7—Typical contact voltage variations in elevated-temperature sliding showing the initiation of tribofilm formation (t_i) and two different steady-state responses ($t_{ss\text{-}1}$ and $t_{ss\text{-}2}$).

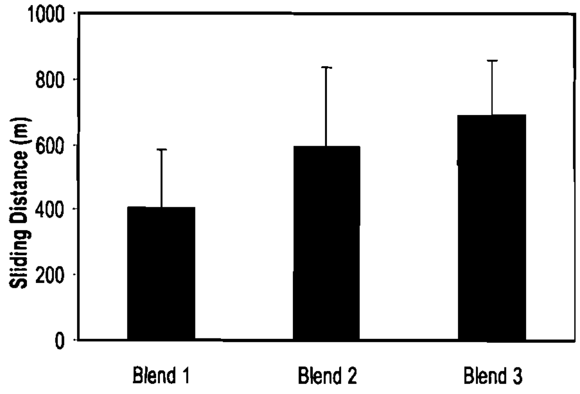

Fig. 8—Sliding distance corresponding to the initiation of tribofilm formation for different gear oil formulations at ~100°C.

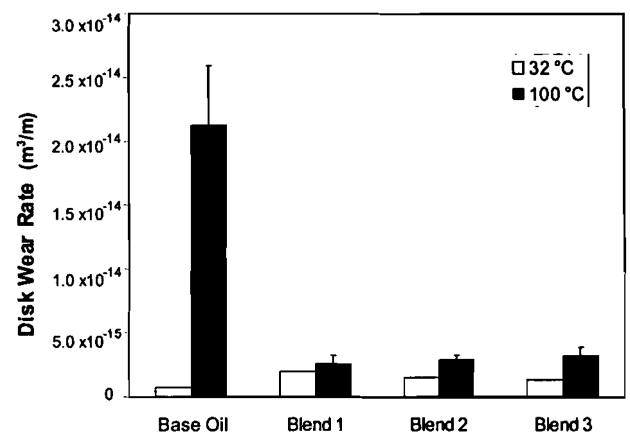

Fig. 9—Disk wear rate *vs.* temperature for different gear oil formulations.

effect of surface roughening due to sliding wear on the increase of the contact voltage is ruled out in view of the constant and very low contact voltage obtained with base oil (Fig. 2(b)). The instant at which the contact voltage begins to rise steadily defines the time that tribofilm formation commences, t_i, which is characteristic of the chemical reactivity of the additives in each blend. Moreover, the rate at which the contact voltage increases is related to the rate of tribofilm formation. After reaching a peak value, the average contact voltage either remained practically constant (Figs. 3(b) and 5(b)) or decreased to a lower steady-state value (Fig. 4(b)), depending on the blend composition (time periods $t_{ss\text{-}1}$ and $t_{ss\text{-}2}$ in Fig. 7, respectively).

Figure 8 shows statistical data for the sliding distance corresponding to the instant that tribofilm formation commences (denoted by time t_i in Fig. 7) for different blends. The relatively shortest and longest mean values of sliding distance obtained with blends 1 and 3, respectively, are indicative of the chemical reactivity of the additives in each oil under the present testing conditions. The results show a trend for the initiation time of tribofilm formation to decrease with the incorporation of borate in gear oil containing P-S additives, in agreement with the results of earlier studies (Salentine, 1990; Adams, 1977; Adams and Godfrey, 1981; Varlot et al., 2001).

Although rapid tribofilm formation is desirable for reducing plowing friction and preventing the occurrence of severe wear, the shear resistance of the produced tribofilms is equally important to the steady-state tribological behavior. Figure 9 shows a comparison of the wear rates of disk specimens obtained with different lubricants at low and elevated temperatures. Since the wear rates of the ball specimens were an order of magnitude less than those of corresponding disks, the relative differences and trends in the data shown in Fig. 9 are essentially similar to those of the total wear rate. Table 2 gives mean and standard deviation values of the disk wear rate for each lubricant at ~100°C. The wear rate data are in good agreement with those obtained with rougher steel specimens (Kim et al., 2000). Interestingly, the base oil yielded a low disk wear rate at 32°C. This may be due to the formation of an iron oxide surface film due to the presence of oxygen in the system that protected the surfaces at such low temperature. However, at higher temperature the oxide film was not sufficiently robust to prevent direct metal-to-metal contact, thus resulting in much higher wear rate. While for low-temperature sliding the additive effect on the wear behavior is not statistically discernible, a significant

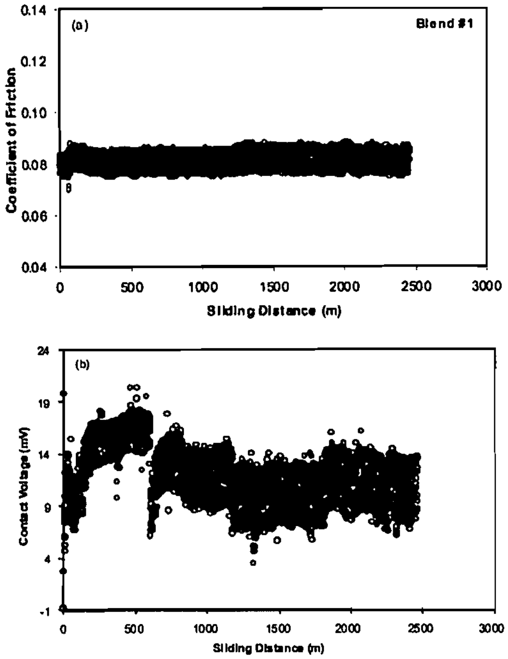

Fig. 10—Variation of (a) coefficient of friction and (b) contact voltage with sliding distance at ~32°C for borate-, phosphorus-, and sulfur-containing blend 1 after tribofilm formation.

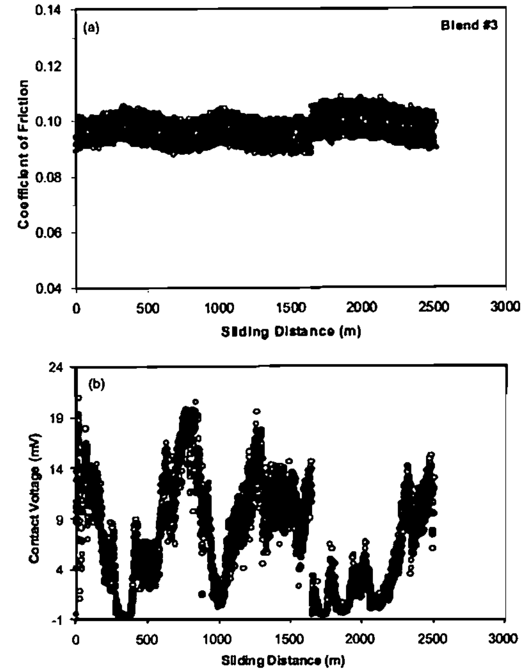

Fig. 11—Variation of (a) coefficient of friction and (b) contact voltage with sliding distance at ~32°C for phosphorus-sulfur-containing blend 3 after tribofilm formation.

improvement in wear resistance (by more than an order of magnitude) was achieved with blended lubricants at elevated temperature. A comparison of the wear rate data shown in Fig. 9 and Table 2 indicates that tribofilm formation during sliding at elevated temperature was enhanced in the presence of lubricants with B-, P-, and S-containing additives. The wear rates are of the order of 10^{-15} m^3/m, i.e., about an order of magnitude lower than those obtained with base oil (~10^{-14} m^3/m) and only slightly higher than those obtained for low-temperature sliding. Thus, the increased chemical reactivity of B-, P-, and S-containing additives at elevated temperatures resulted in the rapid formation of protective tribofilms that inhibited asperity interaction and, in turn, excessive wear by adhesion and abrasion processes encountered during sliding in the presence of base oil at ~100°C.

To evaluate the tribofilm wear resistance, representative results from the durability tests are shown in Figs. 10 and 11 for blends 1 and 3, respectively. A low and constant coefficient of friction of ~0.08 was obtained with the borate-enriched blend 1 (Fig. 10(a)), i.e., very close to the steady-state value obtained at ~100°C (Table 2), even for a sliding distance two times greater than that found in the experiments conducted at ~100°C (e.g., Fig. 3). In addition, Fig. 10(b) shows that, while the contact voltage exhibited some fluctuations and assumed values lower than those observed at elevated temperature, the average values are significantly higher than those obtained for sliding at ~32°C, i.e., in the absence of an antiwear tribofilm.

Different behavior was found in similar tests performed with the borate-free blend 3, as shown in Fig. 11. The coefficient of friction increased well above the average value of ~0.087 obtained during steady-state sliding at ~100°C (Table 2), exhibiting large fluctuations (Fig. 11(a)). Figure 11(b) shows significant variations of the contact voltage between high values (~19 mV), associated with the presence of a tribofilm, and very low values (< 0.1 mV) indicating the absence of a protective tribofilm. The direct relationship between low (high) contact voltage and high (low) coefficient of friction values suggests the occurrence of a continuous process of tribofilm removal and replenishment, despite the fact that sliding occurred at room temperature. The almost periodic variation of the contact voltage indicates that the mechanisms of tribofilm rupture and re-growth demonstrate repeatability. A comparison of Figs. 10 and 11 shows that the addition of borate into traditional P-S-containing lubricants leads to the formation of more durable and lower friction antiwear tribofilms. Borate-containing lubricants are known to produce protective tribofilms several times thicker than conventional P-S lubricants, presumably strongly bonded to the surfaces by hydrogen bonds between borate hydroxyl groups and the hydrated iron oxide layer on the steel surfaces (Adams and Godfrey, 1981). The better performance of blend 1 may be hypothesized to be due to the formation of a hard borate glass phase that enhanced tribofilm durability. Further studies on the composition of the tribochemical films must be carried out to confirm the latter possibility.

In view of the results shown in Figs. 10 and 11, it may be argued that chemical reactions between the steel surfaces and the additives during sliding at higher temperature changed the chemical behavior of the surfaces. These chemically modified steel surfaces react with the additives and replenish the tribofilm even at relatively low temperatures. The actual temperature at the contact interface during sliding was higher than the bulk oil temperature. Frictional heating causes local transient (flash) temperature rises in the range of 30-50°C, depending on the magnitude of the coefficient of friction and wear scar diameter (Kim et al., 2000). Thus, the actual temperature at the contact region in the tests performed at ambient and elevated temperatures were in the ranges of 65-90°C and 135-150°C, respectively. The combination of steel surfaces with increased chemical reactivity and flash temperatures at asperity microcontacts of 65-90°C are believed to be the main reasons for the friction and contact voltage responses observed in the experiments performed at an ambient atmosphere after tribofilm formation at elevated-temperature sliding. These experiments elucidate the durability of tribofilms produced at an elevated temperature due to tribochemical reactions between the steel surfaces and S-P additives with and without borate additions.

CONCLUSIONS

Steel specimens immersed in gear oil with and without borate-, phosphorus-, and sulfur-containing additives were tested in a ball-on-disk tribometer at an average oil temperature of 100 ± 5°C. The experiments were performed under load and speed conditions favoring sliding in the boundary lubrication regime. Real-time information about the development of antiwear tribofilms on the wear tracks of the steel surfaces was obtained from electrical contact resistance (voltage) measurements. Since the sensitivity of the contact voltage to tribochemical reactions occurring at the sliding interface is much higher than that of the coefficient of friction, *in situ* monitoring of tribofilm formation and shearing off at asperity microcontacts was accomplished by observing the evolution of the contact voltage during testing. Although the addition of borate, phosphorus, and sulfur additives in gear oil reduces the coefficient of friction slightly in elevated-temperature sliding (from ~0.09 to ~0.08), it reduces the wear rate by almost an order of magnitude (i.e., from $\sim 10^{-14}$ m^3/m to $\sim 10^{-15}$ m^3/m). This is attributed to chemical reactions between the steel surfaces and the additives incorporated in the gear base oil at elevated temperatures, leading to the formation of antiwear tribofilms.

The addition of borate into the phosphorus-sulfur additive package promotes faster formation of tribofilms exhibiting higher shear strength. The relatively higher wear resistance and endurance of borate-enriched lubricants is attributed to a hard borate glass phase and the strong attachment of the tribofilms to the steel surfaces through hydrogen bonding. Sliding at elevated temperatures in baths of gear oil containing additives increases the chemical reactivity of the steel surfaces, presumably due to the formation of reaction products that subsequently initiate tribofilm formation even at much lower temperatures. The results of this study suggest that the incorporation of borate into standard phosphorus-sulfur additives leads to the development of tribochemical films exhibiting higher wear resistance and faster rate of formation and replenishment upon shearing off at asperity microcontacts. More investigations on the chemical composition of the produced tribofilms must be conducted to elucidate the actual role of borate additives in gear oils during elevated-temperature sliding in the boundary lubrication regime.

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