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Friction Reduction and Antiwear Capacity of Engine Oil Blends Containing Zinc Dialkyl Dithiophosphate and Molybdenum-Complex Additives

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The efficacy of oil blends containing zinc dialkyl dithiophosphate (ZnDTP) and molybdenum (Mo)-complex additives to improve the tribological properties of boundary-lubricated steel surfaces was investigated experimentally. The performance of oil blends containing three different types of Mo-complex additives of varying Mo and S contents with or without primary/secondary ZnDTP additions were investigated at 100 °C. The formation of antiwear tribofilms was detected in situ by observing the friction force and contact voltage responses. Wear volume and surface topography measurements obtained from surface profilometry and scanning electron microscopy studies were used to quantify the antiwear capacity of the formed tribofilms. The tribological properties are interpreted in terms of the tribofilm chemical composition studied by X-ray photoelectron spectroscopy. The results demonstrate that blending the base oil only with the Mo-compound additives did not improve the friction characteristics. However, an optimum mixture of Mo complexes and ZnDTP additive provided sufficient amounts of S and Mo for the formation of antiwear tribofilms containing low-shear strength MoS2 that reduces sliding friction. In addition, the formation of a glassy phosphate phase due to the synergistic effect of the ZnDTP additive enhances the wear resistance of the tribofilm. This study shows that ZnDTP- and Mo-containing additives incorporated in oil blends at optimum proportions improve significantly the tribological properties of boundary-lubricated steel surfaces sliding at elevated temperatures.

KEY WORDS
Boundary Lubrication; Friction; Antiwear Tribofilms; Wear Mechanisms; Mo Complexes and ZnDTP Additives

INTRODUCTION
The efficiency of automotive engines greatly depends upon several metallic components, such as tappets (followers) and camshafts used to transmit power by sliding and/or rolling under high contact loads and elevated temperatures. In the absence of effective lubrication, these moving parts are prone to high friction and excessive wear, potentially leading to reduced fuel efficiency and short life. Mechanical energy losses in internal combustion engines typically account for 10-15% of the overall power losses due to friction in the pistons, piston rings, main bearings, connecting rod bearings, and valve trains (Kiovsky, et al. (1)). To overcome these drawbacks, interacting metal surfaces must be lubricated with properly selected oils fortified with special additives that reduce wear, corrosion, and oxidation, while providing high load-carrying capacity and low friction.

An important property of engine oils used to enhance the friction and wear characteristics is the ability to form tenacious antiwear tribofilms strongly attached to the metal surfaces. A thin oil film of thickness less than 10% of the peak-to-valley surface roughness can separate the surfaces by a continuous film provided the local shear stress does not exceed the shear strength of the lubricant (Jacobson (2)). However, in the boundary lubrication regime, an oil film generally cannot provide full coverage of the sliding surfaces (Martin, et al. (3)). This suggests that the shear strength of the oil film is exceeded by the shear stress produced at asperity contacts. Hence, it is difficult to maintain a continuous and uniform oil film thickness at boundary-lubricated sliding interfaces. For effective lubrication, it is essential that asperity contacts behave like small slider-bearings lubricated with a high-pressure
glassy lubricant and also as plastically deforming solid films so that they can be uniformly smeared across the contact interface (Jacobson (2)). It has been theorized that the minimum pressure for plastic flow to occur increases with lubricant-surface reactivity and adsorption heat (Zhang, et al. (4)).

The in situ formation and adherence of tribofilms on rubbing metal surfaces have been found to strongly depend on temperature, additive(s) type, and additive concentration in the base oil (Kim, et al. (5)). Tribofilms strongly attached to the sliding surfaces increase the wear resistance by playing a sacrificial role, thereby protecting the metal surfaces from high shear rates. The metal surfaces can be protected provided the degrading tribofilms can be replenished in situ through rapid reaction with the freshly exposed metal surfaces. Tenacious glassy tribofilms, such as phosphorus- and/or boron-containing tribofilms, are potential antiwear agents (Komvopoulos, et al. (6), (7)). However, this beneficial effect is usually accomplished at the expense of higher friction. It has been reported that the lower shear strength of sulfur-containing tribofilms compared to phosphorus-containing tribofilms is the reason for the lower coefficient of friction and higher wear rates obtained with these tribofilms (Komvopoulos, et al. (7)).

Molybdenum-containing compounds have been proven effective friction modifier additives for engine oils. The in situ formation of molybdenum disulfide (MoS2) through complex tribochemical reactions has been known to reduce friction (Grossiord, et al. (8)). The excellent lubricating efficacy of MoS2 is attributed to its lamellar crystal structure (Clauss (9)). The strong covalent bonding between Mo and S atoms in the hexagonal crystal provides penetration resistance when the load is applied normal to the crystalline lamellae, whereas the weak van der Waals forces between adjacent planes of S atoms enable sliding under a low shear stress (i.e., low friction). To perform well as friction modifiers, Mo-containing compounds must be used at relatively high concentrations and elevated temperatures (Graham, et al. (10)). The formation of MoS2 is promoted under pure sliding conditions rather than sliding/rolling conditions (Graham, et al. (10)). The capacity of Mo-containing additives to produce low-friction conditions depends on the formation of MoS2 at asperity contacts (Grossiord, et al. (8); Graham, et al. (10)).

The use of Mo-derived organic compounds alone in engine oils cannot improve the efficiency and performance because the maximum efficacy of Mo compounds depends on other additives (Vettor, et al. (11)). A well-known synergistic additive, which is generally used as an antiwear agent in Mo-containing compounds, is an organometallic, zinc dialkyl dithiophosphate (ZnDTP). The beneficial effect of ZnDTP is associated with the formation of a glassy polyphosphate film between the metal surfaces that prevents direct metal-to-metal contact and wear (Martin, et al. (3)). It has been reported that ZnDTP exhibits a two-layer structure consisting of a polymer-like zinc long-chain polyphosphate on top of a thicker layer composed of metal sulfides in transition metal short-chain polyphosphate (Martin, et al. (3); Fuller, et al. (12)). The absence of Fe from a ZnDTP tribofilm was attributed to the digestion of the abrasive iron oxides, particularly hematite (Fe2O3), by the zinc polyphosphate (Martin, et al. (3), (13)). Hematite is known to be abrasive because of its crystallized oxide hardness and relatively high melting point (>1200 °C) (Martin, et al. (3)). Despite the excellent wear protection provided by ZnDTP, its poisoning effect on exhaust system catalysts has provided motivation to reduce its content in formulated oils in order to comply with recent emission standards (Gangopadhyay, et al. (14)). Although reducing the ZnDTP content may jeopardize the lubrication efficacy, engine oils with less phosphorus can be formulated to provide similar or even better wear protection than ZnDTP (Gangopadhyay, et al. (14)).

The formation of tribofilms consisting of glassy zinc phosphate and carbon matrix containing ZnS and single MoS2 sheets has been reported for oils blended with both molybdenum dithiocarbamate (MoDTC) and ZnDTP additives (Grossiord, et al. (8), (15); De Barros, et al. (16)). It was observed that ZnDTP promotes the formation of MoS2, which is embedded in the short-chain zinc polyphosphate (De Barros, et al. (16)). It has also been suggested that the function of the ZnDTP additive is to supply excess S such that complete sulfuration of the molybdenum oxysulfide produced from the degradation of the Mo-containing compound is achieved (Vettor, et al. (11)). The presence of a lower shear strength MoS2 layer just below the surface of the MoDTC/ZnDTP tribofilm is believed to be the reason for the decrease of the coefficient of friction of sliding metal surfaces (Ye, et al. (17)). However, if ZnDTP adsors on the metal surfaces faster than the Mo compound, the ZnDTP products will dominate the near-surface region, leading faster to a stable state at the expense of a higher coefficient of friction (Muraki and Wada, (18)). Hence, there is competition between the Mo compound and ZnDTP to adsorb on the sliding surfaces, which affects the chemical composition of the tribofilm and its effect on the friction and wear behavior.

The tribochemical reaction of molybdenum dithiophosphate (MoDTP) and MoDTC/ZnDTP resulting in the formation and adhesion of MoS2 to the metal surfaces can be explained by the hard and soft acid and base principle (chemical hardness concept) (Grossiord, et al. (8); Vettor, et al. (11); Martin, et al. (13)). According to this principle, hard-base anions (PO3−4) react strongly with hard-acid cations (Fe3+ and Mo6+) before soft-base anions (R2S or S2−) react with soft-acid cations (Fe5+). The hard acid-base reaction promotes the reaction of phosphate with the iron oxide during the initial stage of the friction evolution while removing all the other products consisting of oxygen, phosphorus, and zinc outside the wear track in the form of wear debris (Grossiord, et al. (8); Martin, et al. (13)). After the removal of the iron oxide, reaction of soft-acid and soft-base species (Fe and MoS2 and/or ZnS) leads to the transfer of the MoS2 single sheets onto Fe atoms. Consequently, the resistance-free movement of the soft MoS2 sheets at the basal planes results in low-friction sliding (Grossiord, et al. (8), (15); Martin, et al. (13)).

The past experience with oil formulations containing ZnDTP and Mo compounds has been mainly with MoDTC and MoDTP. In view of the tribological improvement obtained with these two additives, it is imperative to understand the underlying mechanisms of tribofilm formation and analyze the resulting wear behavior. In this study, engine oils fortified with a different kind of Mo compound and/or ZnDTP additive were evaluated in light of
Friction and wear results. The Mo-containing additive was obtained in three similar Mo-complexes that produced different oil colors while retaining their superior wear and friction behaviors when combined with ZnDTP. In addition to the tribological properties, the formation and composition of antiwear tribofilms due to different combinations of ZnDTP with each Mo-complex additive were investigated in the context of in situ electrical contact resistance measurements and X-ray photoelectron spectroscopy results.

EXPERIMENTAL PROCEDURES

Lubricants

The tribological behaviors of various oil blends consisting of base oil blended with seven different additives of varying amounts of Mo compounds and/or ZnDTP (Chevron Oronite Co.) were evaluated by performing sliding experiments in the boundary lubrication regime. Table 1 gives the properties of the neutral base oil (Chevron 100N) used in the additive-fortified blends. A mixture of neutral and basic primary/secondary alkyl ZnDTP was used in the engine oil formulations. The relatively higher thermal instability of di-isopropyl ZnDTP (a secondary alkyl ZnDTP) provides faster film formation at elevated temperatures (Fuller, et al. (12)). This characteristic is especially desirable during the run-in stage when the sliding metal surfaces are most vulnerable to wear. The synthesis of ZnDTP (Freuler (19)) involves the reaction of 4 mol of alcohol and 1 mol of phosphorus pentasulfide, which yields 2 mol of the intermediate dialkylidithiophosphoric acid and 1 mol of hydrogen sulfide.

\[
\text{S} + 4\text{ROH} + \text{P}_2\text{S}_5 \rightarrow 2(\text{RO})_2\text{P} - \text{S} - \text{H} + \text{H}_2\text{S}
\]

The next step is the neutralization of the acid with a slight excess of 4 mol of zinc oxide to give a mixture of the neutral and basic ZnDTP salts.

\[
\text{S} + 4(\text{RO})_2 - \text{P} - \text{S} - \text{H} + 2\text{ZnO} \rightarrow \text{Zn}_2[(\text{RO})_2\text{PS}_2]_4 + 2\text{H}_2\text{O}
\]

(Dialkylidithiophosphoric Acid) (Neutral Salt)

\[
3\text{Zn}_2[(\text{RO})_2\text{PS}_2]_4 + 2\text{ZnO} \rightarrow 2\text{Zn}_2[\text{S}_2\text{P(OR)}_2]_6
\]

(Basic Salt)

Comparison studies have shown a superior antitrust performance of neutral over basic ZnDTP (Yamaguchi (20)). This is attributed to the fact that neutral ZnDTP salts adsorb more strongly to the metal surfaces through bonding of the P = S moiety (Yamaguchi, et al. (22)). In addition, a longer polyphosphate chain on the surface and the oligomeric nature of neutral ZnDTP salts provide superior surface adsorption and, in turn, a more tenacious monolayer (Fuller, et al. (12); Yamaguchi (21); Yamaguchi, et al. (22)-(24)). Hereafter, the blend containing only one additive (ZnDTP) will be referred to as Blend 1.

The three blends containing different Mo-compound additives (type I, II, and III) will be designated as Blends 2, 3, and 4, respectively. The content of Blend 2 is described in detail elsewhere (King and De Vries (25); De Vries and King (26)). A means of incorporating MoS2 in the base oil is to mix an acidic Mo compound with a basic N compound and a S source to form Mo- and S-containing complexes (King and De Vries (25)). The molecular formula of this compound is not known exactly. However, a possible Lewis acid-Lewis base complex is thought to be involved. Acidic implies that the Mo compound can react with a basic N compound, such as succinimides (King and De Vries (25)). A polar promoter (used to facilitate the interaction between the acidic Mo compound and the basic N compound) and an aromatic amine compound (improves the oxidation inhibitor behavior) were also included in the Mo complex (De Vries and King (26)). However, the Mo complex investigated in this research did not contain any aromatic amine compound. Despite its role as a dispersant, N from the amine organic chain of succinimide in the ZnDTP-containing lubricant can affect the tribofilm composition by reducing the P and Zn contents. This could be detrimental to the chemisorption of ZnDTP on the metal surfaces and may also produce abrasive iron oxide in the ZnDTP/succinimide tribofilm (Martin, et al. (13)).

Blend 3 contains a low-temperature version of the materials in Blend 2 and is characterized by a low Mo/N content, whereas Blend 4 consists of another low-temperature version of the materials in Blend 2 and possesses a high Mo/N content. The purpose of processing the Mo-compound at low temperatures is to reduce the S content significantly and, thus, achieve a lighter oil color than that of Blend 2 (dark brown). The other three blends consisted of base oil blended with ZnDTP and one of the Mo compounds (type I, II, and III). Hereafter, the lubricant formulations containing Mo types I, II, and III will be referred to as Blends 5, 6, and 7, respectively. The Mo, N, S, P, and Zn contents in the additive batches used to formulate the ZnDTP and types I, II, and III Mo-compound additives are given in Table 2, and the concentrations of these batches in the additive-fortified Blends 1-7 are given in Table 3. Analytical results of the base oil and Blends 1-7 determined after the additive batches were mixed with the base oil are given in Table 4. These results only show the dominant elements in the formulated lubricants.

Specimens

Flat circular disks and ball bearings of 52100 steel (Falex Co.) consisting of 96.9 wt% Fe, 1.04 wt% C, 1.45 wt% Cr, 0.35 wt% Mn, and 0.275 wt% Si were used as specimens. The indentation hardness of the 52100 steel specimens was 60-62 (±3) in the
Table 2—Elemental Compositions of Additive Batches Used to Produce the ZnDTP and Mo-Compound Additives*

<table>
<thead>
<tr>
<th>Element Content (wt.%)</th>
<th>Mo</th>
<th>N</th>
<th>S</th>
<th>P</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary ZnDTP</td>
<td>—</td>
<td>—</td>
<td>16.40</td>
<td>8.07</td>
<td>8.80</td>
</tr>
<tr>
<td>Primary ZnDTP</td>
<td>—</td>
<td>—</td>
<td>14.00</td>
<td>7.24</td>
<td>8.31</td>
</tr>
<tr>
<td>Mo complex I</td>
<td>6.40</td>
<td>1.99</td>
<td>4.30</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mo complex II</td>
<td>4.51</td>
<td>2.22</td>
<td>0.30</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mo complex III</td>
<td>5.67</td>
<td>1.57</td>
<td>0.30</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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

Rockwell C scale. The disks were 3.16 cm in diameter and 0.51 cm in thickness, and the balls were 0.8 cm in diameter. The disks were mirror-polished to an average roughness of ~36 nm using a liquid suspension containing ~0.3 μm Al₂O₃ abrasive particles. Before testing, the specimens were cleaned with hexane to remove any contaminants from the surfaces. The specimens were stored in an anhydrous CaSO₄-containing dessicator to avoid possible surface changes due to environmental effects.

**Tribometer**

A modified ball-on-disk tribometer (Falex-6, thrust washer), described in detail elsewhere (Komvopoulos, et al. (6), (7)), was used to perform the experiments. The ball specimen was press-fit into a holder attached to the rotating upper part of the tribometer and the flat disk was placed on the pedestal. A circular cup sealed into a holder attached to the rotating upper part of the tribometer was wrapped around the cup to maintain the oil temperature at 100 °C for ~15 min to obtain a uniform temperature in the oil bath. A normal load of 12 N (1.22 kg) and a rotational speed of 178 rpm (200 mm/s) were used in all the experiments. The data points in the coefficient of friction and ECR plots were averaged assuming that the data followed normal distributions.

**Profilometry and Wear Volume Measurements**

The roughness of the disk surfaces and cross-sectional areas of the wear tracks were measured with a mechanical stylus profilometer (Dektak IID, Veeco Instruments). The average cross-sectional area was determined from measurements obtained from five different locations around the circumferential wear tracks. Wear volume data were obtained by multiplying the average area measured from the surface profiles with the circumference of the wear tracks. The corresponding mean and standard deviation values of five wear volume measurements for each blend were calculated assuming that the data followed normal distributions.

**Scanning Electron Microscopy**

The surface topographies of the worn disks and the dominant wear mechanisms for each blend were examined with a scanning electron microscope (SEM). The evolution of the friction behavior and the formation of antistick tribofilms were studied in situ by continuously recording the coefficient of friction and the electrical contact resistance (ECR) at a sampling frequency of 0.5 Hz. The voltage output of the friction torque was measured with a strain gauge bridge and converted to a coefficient of friction response. The ECR is proportional to the contact voltage drop across the contact interface, which was measured with a voltage divider circuit. Metal-to-metal contact in the absence of an electrically insulating tribofilm at the ball/disk contact interface or formation of a conductive or semi-conductive tribofilm, such as sulfide-dominated tribofilm (Komvopoulos, et al. (7)), yielded very low contact voltages in the range of 0-3 mV. Alternatively, a relatively high contact voltage of ~20 mV was obtained in the presence of an insulating tribofilm at the contact interface due to the increased resistance to the current flow across the ball/disk interface.

The data points in the coefficient of friction and ECR plots presented in the following sections were determined as averages of corresponding data obtained from intervals of 600 s (~205 m). The calculated mean values of each test were averaged with similar values of other tests performed with the same blend. Hence, the error bars shown in the coefficient of friction and ECR plots include variations within individual tests and among similar tests at a given sliding distance.

**Coefficient of Friction and Electrical Contact Resistance Measurements**

The evolution of the friction behavior and the formation of antistick tribofilms were studied in situ by continuously recording the coefficient of friction and the electrical contact resistance (ECR) at a sampling frequency of 0.5 Hz. The voltage output of the friction torque was measured with a strain gauge bridge and converted to a coefficient of friction response. The ECR is proportional to the contact voltage drop across the contact interface, which was measured with a voltage divider circuit. Metal-to-metal contact in the absence of an electrically insulating tribofilm at the ball/disk contact interface or formation of a conductive or semi-conductive tribofilm, such as sulfide-dominated tribofilms (Komvopoulos, et al. (7)), yielded very low contact voltages in the range of 0-3 mV. Alternatively, a relatively high contact voltage of ~20 mV was obtained in the presence of an insulating tribofilm at the contact interface due to the increased resistance to the current flow across the ball/disk interface.

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Table 3—Compositions of Formulated Engine Oils*

<table>
<thead>
<tr>
<th>Blend</th>
<th>Base oil + 7.5 mmol/kg secondary ZnDTP + 5 mmol/kg primary ZnDTP in a 7.0 kg blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blend 1</td>
<td>base oil + 37.5 g Mo complex I in a 4.0 kg blend</td>
</tr>
<tr>
<td>Blend 2</td>
<td>base oil + 46.57 g Mo complex II in a 3.5 kg blend</td>
</tr>
<tr>
<td>Blend 3</td>
<td>base oil + 37.0 g Mo complex III in a 3.5 kg blend</td>
</tr>
<tr>
<td>Blend 4</td>
<td>base oil + 200.0 g secondary ZnDTP + 14.95 g primary ZnDTP + 32.80 g Mo complex I in a 3.5 kg blend</td>
</tr>
<tr>
<td>Blend 5</td>
<td>base oil + 200.0 g secondary ZnDTP + 14.95 g primary ZnDTP + 46.57 g Mo complex II in a 3.5 kg blend</td>
</tr>
<tr>
<td>Blend 6</td>
<td>base oil + 200.0 g secondary ZnDTP + 14.95 g primary ZnDTP + 37.0 g Mo complex III in a 3.5 kg blend</td>
</tr>
</tbody>
</table>

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

Table 4—Analytical Data of the Dominant Elements in the Base Oil and Blends 1-7*

<table>
<thead>
<tr>
<th>Element</th>
<th>Base Oil</th>
<th>Blend 1</th>
<th>Blend 2</th>
<th>Blend 3</th>
<th>Blend 4</th>
<th>Blend 5</th>
<th>Blend 6</th>
<th>Blend 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>587.8</td>
<td>680.7</td>
<td>592.6</td>
<td>585.2</td>
<td>621.0</td>
<td>606.2</td>
<td>592.6</td>
<td>585.2</td>
</tr>
<tr>
<td>Zn</td>
<td>899.9</td>
<td>871.7</td>
<td>881.6</td>
<td>871.7</td>
<td>881.6</td>
<td>871.7</td>
<td>881.6</td>
<td>871.7</td>
</tr>
<tr>
<td>P</td>
<td>795.1</td>
<td>771.9</td>
<td>779.5</td>
<td>771.9</td>
<td>779.5</td>
<td>771.9</td>
<td>779.5</td>
<td>771.9</td>
</tr>
<tr>
<td>S</td>
<td>7.00</td>
<td>409.5</td>
<td>39.9</td>
<td>31.7</td>
<td>2051.0</td>
<td>1673.0</td>
<td>1668.0</td>
<td>1668.0</td>
</tr>
</tbody>
</table>

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

φ = Too small amount to be detected.
electron microscope (SEM, JEOL JSM-6300). Before placing the disks in the SEM, they were ultrasonically rinsed with ethyl alcohol to remove any surface contaminants. To increase the conductivity of the specimen surfaces and improve the image resolution, the disks were coated with a thin Au-Pd film. SEM images of the wear tracks were obtained at accelerating voltages in the range of 10-15 kV using a magnification of 8000×.

**X-Ray Photoelectron Spectroscopy**

Chemical analysis of the original and tested disk surfaces was based on X-ray photoelectron spectroscopy (XPS) results obtained with a Kratos AXIS-HS spectrometer. Prior to the XPS experiments, the tested disks were immersed in the same oil used in the sliding test and stored in a dessicator to reduce oxidation due to the exposure to the ambient. The disks were cleaned with heptane and then placed in the XPS chamber where they were bombarded by an Al Kα X-ray source at 1486.6 eV. For statistical analysis, five measurements were obtained from different surface regions on and off each wear track. Element concentrations were determined from the deconvolution of the XPS C1s core–level spectra as atomic percentages. Element concentrations above 0.3 at.% were considered in the study of the tribofilm compositions.

**RESULTS AND DISCUSSION**

**Coefficient of Friction and Electric Contact Voltage**

**Base Oil and Blend 1**

The variations of the coefficient of friction and the contact voltage of the base oil with the sliding distance are shown in Figs. 1(a) and 1(b), respectively. The initial decrease of the coefficient of friction reveals a run-in stage, usually involving the removal of the highest asperities and changes in the surface topography. An increase in the coefficient of friction occurred after sliding for ~50 m, possibly due to wear of the metal surfaces in the absence of a protective liquid or solid film. A steady-state friction response was obtained after sliding for ~200 m, characterized by an average coefficient of friction of ~0.14 and a low contact voltage of ~2 mV. These data indicate that sliding was dominated by direct metal-to-metal contact due to the absence of a protective tribofilm.

A significantly different behavior was observed in the experiments performed with Blend 1. As shown in Fig. 1(c), the run-in stage was suppressed and the coefficient of friction increased slightly during the first ~150 m of sliding from an initial value of ~0.15 to a steady-state value of ~0.16. This transient period of the friction response was accompanied by a rapid increase in the contact voltage, as shown in Fig. 1(d), which can be attributed to the removal of surface contaminants and the formation of a protective tribofilm at the contact interface that prevented direct asperity contact (Grossiord, et al. (8); Martin, et al. (27)). The steady-state contact voltage of ~20 mV indicates the formation of a non-conductive tribofilm. Since the dominant additive in the oil was ZnDTP, it is presumed that the sliding conditions promoted the formation of an insulating phosphate tribofilm.

**Blends 2 and 5**

Figures 2(a) and 2(b) show the coefficient of friction and contact voltage of Blend 2 as functions of sliding distance. A gradual decrease in the coefficient of friction from ~0.13 to ~0.07 occurred during the initial stage of sliding. However, at a sliding distance of ~300 m the friction coefficient increased to the initial value...
and subsequently decreased again to a steady-state of ∼0.1. During the increase of the coefficient of friction, a gradual increase in the contact voltage was observed, as shown in Fig. 2(b). The initial decrease of the coefficient of friction can be attributed to the formation of a low shear strength tribofilm, possibly containing MoS2. With the progression of sliding, the tribofilm was depleted and replaced by an abrasive compound, possibly MoO3, which increased the coefficient of friction.

Figures 2(c) and 2(d) show that the addition of ZnDTP in type I Mo-containing oil (Blend 5) resulted in significantly different friction coefficient and contact voltage responses. During the initial ∼300 m of sliding (transient period), the coefficient of friction decreased abruptly from ∼0.14 to ∼0.05, possibly due to the formation of a tribofilm containing MoS2. Simultaneously with the decrease in the coefficient of friction, a rapid increase in the contact voltage occurred, suggesting the formation of a tribofilm. The fluctuations in the contact voltage throughout testing are indicative of the competing effects of a glassy zinc phosphate phase (non-conductive) and a carbon matrix containing MoS2 sheets (semi-conductive) in the tribofilm produced from the ZnDTP and Mo-containing additives, respectively.

Blends 3 and 6

As shown in Figs. 3(a) and 3(b), the type II Mo-containing complex in Blend 3 produced less variations in the coefficient of friction and contact voltage responses than those observed with Blend 2. In the first ∼200 m of sliding, the coefficient of friction increased to a peak value of ∼0.18, revealing the occurrence of significant asperity interactions between the sliding steel surfaces. However, with the progression of sliding, the coefficient of friction decreased gradually to a steady-state of ∼0.15. After sliding for ∼300 m, the contact voltage began to increase slowly reaching an average steady-state value of ∼5 mV at a sliding distance of ∼900 m.

An abrupt decrease in the coefficient of friction from ∼0.14 to ∼0.06 and a simultaneous sharp increase in the contact voltage from ∼0 mV to 12-15 mV occurred during the initial stage of sliding in the presence of Blend 6 (Figs. 3(c) and 3(d), respectively). The faster decrease of the coefficient of friction than that observed with Blend 5 (Fig. 2(c)) to a low steady-state of ∼0.06 indicates a higher rate of formation for this tribofilm. The relatively stable friction coefficient after sliding for ∼100 m suggests a constant and higher rate of film replenishment than film removal rate. As mentioned earlier for Blend 5, the fluctuations in the steady-state contact voltage response of Blend 6 may be associated with the competing effects of a glassy zinc phosphate phase and a carbon matrix containing MoS2 sheets produced from the ZnDTP and Mo-containing additives, respectively.

Blends 4 and 7

The friction coefficient and contact voltage behaviors obtained with Blend 4 exhibited similarities with those of Blend 3. As shown in Fig. 4(a), the coefficient of friction increased slightly during the initial ∼100 m of sliding and then decreased gradually throughout the remaining testing. The contact voltage also increased moderately after sliding for ∼300 m from an initial value close to zero to values in the range of 4-6 mV (Fig. 4(b)). The slow decrease in the coefficient of friction and the simultaneous gradual increase in the contact voltage may be associated with the formation of a low shear strength tribofilm that prevented intimate metal-to-metal contact.
The coefficient of friction and contact voltage responses of Blend 7 were also similar with those of Blends 5 and 6. The common main feature in these blends was the rapid decrease of the coefficient of friction from the onset of sliding and the simultaneous abrupt increase of the contact voltage. As shown in Fig. 4(c), the coefficient of friction decreased from an initial value of $\sim 0.14$ to a steady-state value of $\sim 0.07$ within $\sim 100$ m of sliding distance, illustrating a synergistic effect of the ZnDTP and Mo-containing additives and the potential of this additive mixture as a friction modifier. This was accompanied by a fast increase of the contact
Fig. 5—(a) Steady-state coefficient of friction and (b) disk wear volume for base oil and Blends 1-7.

Steady-State Coefficient of Friction and Wear Volume

The steady-state coefficients of friction of the base oil and the various formulated engine oils are compared in Fig. 5(a). The base oil and Blends 1-4 yielded similar coefficients of friction with average values in the range of 0.12-0.15. Among these blends, the most effective friction modifier appears to be Blend 2. However, Blends 5-7 produced significantly lower steady-state coefficients of friction with average values in the range of 0.045-0.07. The slightly higher friction coefficients of Blends 6 and 7 than that of Blend 5 can be attributed to the lower S content of the type II and III Mo-complexes. The improvement of the friction behavior illustrates a higher reactivity for the Mo compound/ZnDTP additive, implying that combinations of Mo-containing compounds and ZnDTP are more effective friction modifiers. This finding is in accordance with previous results showing that the addition of ZnDTP in an Mo-containing additive reduces the coefficient of friction through the formation of soft MoS2 sheets. In contrast, the steady-state friction coefficients of the Mo-containing only oils (Blends 2-4) were similar with that of the base oil. A plausible explanation is that transfer of MoS2 sheets to the sliding surfaces to produce a low shear strength layer did not occur because the oxide layer was not depleted due to the lack of phosphate in the Mo-fortified oils (Martin, et al. (27)). Hence, the use of Mo additives alone did not produce low friction. This implies that some amount of ZnDTP additive must be added to the Mo-containing oil to improve the friction characteristics of the sliding surfaces.

Figure 5(b) shows a comparison of wear volume data for the base oil and Blends 1-7. The results indicate a dominant effect of the ZnDTP additive on the wear behavior. While the addition of the type I Mo complex in the base oil (Blend 2) produced about the same wear as the base oil, the addition of the types II and III Mo complexes (Blends 3 and 4) improved the wear resistance. The addition of ZnDTP to the various Mo complexes generally enhanced further the wear resistance. Despite the inferior wear performance of the type I Mo complex (Blend 2) relative to those of the types II and III Mo complexes (Blends 3 and 4), it is noted that the addition of ZnDTP to the type I Mo-containing additive (Blend 5) produced superior wear resistance. The fact that the wear volume data of the ZnDTP/Mo-containing oils (Blends 5-7) are comparable with that of the oil containing only ZnDTP (Blend 1) suggests that the combination of Mo-containing and ZnDTP additives provides not only effective friction modifiers but also effective antwear agents.

Wear Mechanisms

In this section, representative SEM micrographs of worn steel surfaces lubricated with base oil and formulated blends are compared qualitatively to provide insight into the prevailing wear mechanisms and the role of the produced tribofilms in the evolution of sliding wear.
Friction Reduction and Antiwear Capacity of Engine Oil Blends

Fig. 6—SEM micrographs of wear tracks on steel disks lubricated with (a) base oil and (b) Blend 1. (The arrows indicate the sliding direction.)

Base Oil and Blend 1

Figure 6(a) shows typical wear features on disk surfaces lubricated with base oil. The formation of deep plowing grooves and smooth regions partially detached from the surfaces are the most dominant features. The deeper plowing grooves near the center of the wear track are believed to be due to the higher contact pressure at the center of contact. The topography shown in Fig. 6(a) does not provide evidence for the formation of a tribofilm on the metal surfaces. The almost zero contact voltage obtained in the presence of base oil (Fig. 1(b)) supports the former observation. Thus, the absence of a protective tribofilm resulted in severe abrasion characterized by deep plowing grooves and surface roughening.

The addition of ZnDTP in the base oil (Blend 1) resulted in mild wear, as shown in Fig. 6(b). A comparison of Figs. 6(a) and 6(b) shows that ZnDTP significantly enhanced the wear resistance. The dominant presence of smooth (glassy) regions on the wear tracks indicates the formation of an antiwear tribofilm. The inference of tribofilm formation is supported by the high (~20 mV) and steady contact voltage response (Fig. 1(d)). Multiple cracks in the smoother regions reveal a brittle tribofilm. The boundaries of the glassy regions show evidence of delamination wear, which are most likely a consequence of the large plastic strains accumulating at the interface of the tribofilm and the steel substrate due to the significant material property mismatch. The discontinuous smooth regions indicate that the tribofilm did not cover the steel surfaces uniformly, in agreement with earlier observations (Martin, et al. (4)). This can be attributed to the effect of the surface roughness and the local variations in the rate of tribofilm degradation and replenishment.

Blends 2 and 5

Figures 7(a) and 7(d) show SEM micrographs of wear tracks on disk surfaces lubricated with oils containing type I Mo-complex additive (Blend 2) and ZnDTP/type I Mo-complex additive (Blend 5), respectively. Figure 7(a) shows the formation of numerous bundle-like small patches on the wear track. The initial decrease and subsequent increase of the coefficient of friction of Blend 2 (Fig. 2(a)) and corresponding contact voltage fluctuations (Fig. 2(b)) can be attributed to the formation of wear debris leading to third-body abrasion that resulted in surface roughening. The addition of ZnDTP in the oil containing the type I Mo complex (Blend 5) produced a glassy tribofilm that reduced the surface damage (Fig. 7(d)). It appears that the sliding conditions enhanced the tribochemical reactivity of the additives, leading to the formation of a glassy (hard) antwear tribofilm. Although delamination features were observed around the glassy regions, these features did not appear to have an effect on the effectiveness of the tribofilm. Thus, the formation of a glassy tribofilm in the presence of Blend 5 yielded minimal surface damage, as evidenced by the lower wear volumes obtained with the oil containing type I Mo-complex/ZnDTP additive than the base oil and the oil containing only the type I Mo-complex additive (Blend 2) (Fig. 5(b)).

Blends 3 and 6

The SEM micrographs shown in Figs. 7(b) and 7(e) reveal representative wear features on the wear tracks of the disk specimens lubricated with Blends 3 and 6. Figure 7(b) shows the existence of small and flat patches in addition to shallow plowing grooves on the wear tracks. These features suggest that an abrasive wear mechanism dominated the wear process in the presence of Blend 3. The addition of the mixture with type II Mo-complex and ZnDTP additives in the engine oil (Blend 6) resulted in wear features significantly different from those observed with Blend 3. The dominance of smooth plateaus on the wear tracks can be attributed to the formation of a hard and glassy protective tribofilm. Delamination of these smooth glassy plateaus was also observed and can be attributed to cyclic contact fatigue caused by microcrack growth at the tribofilm/substrate interface. According to the results shown in Fig. 5(b), less wear was obtained with Blend 6 than Blend 3. This can be attributed to the higher antiwear capacity of the tribofilm produced from Blend 6.

Blends 4 and 7

Typical wear tracks on the disk surfaces lubricated with oils containing type III Mo-complex additive (Blend 4) and type III Mo-complex/ZnDTP additives (Blend 7) are shown in Figs. 7(c) and 7(f), respectively. The micrograph shown in Fig. 7(c) reveals the formation of numerous microscopic irregular patches with smooth surfaces, which exhibit some similarities with those observed with Blend 3 (Fig. 7(b)). The accumulation of these patches resulted in surface roughening, which underlines the inability of
the type III Mo-complex additive to maintain the smoothness of the original surfaces and enhance the wear resistance. However, as shown in Fig. 7(f), incorporating both the type III Mo-complex and ZnDTP additive in the base oil (Blend 7) resulted in the formation of a glassy antiwear tribofilm. Delamination features were observed but their presence did not appear to play an important role on the effectiveness of the tribofilm during sliding.

**Surface Chemistry**

XPS results provided information about element concentration on the wear tracks and the unworn surfaces of the disk specimens. Elements with concentrations greater than 5 at.% both on and off the wear tracks included: O (O1 and O2), C (C1: hydrocarbon, C2: alcohol/carbonyl, and C3: carboxylate), and Fe oxide (Table 5). The high oxygen content can be attributed to the formation of native iron oxides on the steel surfaces. Most of the carbon content is attributed to adventitious carbon, which is typical for most surfaces exposed to the ambient, especially metal oxide surfaces previously immersed in oil. The carbon content can also be attributed to surface contamination from airborne compounds and oxidized carbon present in the additives. The iron oxide might be in one of the following forms: FeO, Fe₂O₃, or Fe₃O₄. Elements with concentrations less than 5 at.% are discussed next (Figs. 8-15). Two types of sulfur peaks were detected in the XPS analysis, which will be referred to as S1 (sulfide) and S2 (sulfate).
TABLE 5—XPS RESULTS OF THE MAJOR CONSTITUENTS OF THE ELEMENTS ON THE WEAR TRACKS AND UNWORN SURFACES OF STEEL DISKS LUBRICATED WITH BASE OIL AND BLENDS 1-7

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>O1</th>
<th>O2</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>Fe Oxide</th>
<th>O Total</th>
<th>C Total</th>
<th>Fe Oxide</th>
<th>O Total</th>
<th>C Total</th>
<th>Fe Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil</td>
<td>529.3</td>
<td>531.2</td>
<td>284.8</td>
<td>287.0</td>
<td>288.6</td>
<td>709.7</td>
<td>39.41 ± 0.49</td>
<td>47.40 ± 0.77</td>
<td>10.19 ± 0.39</td>
<td>40.55 ± 0.25</td>
<td>45.33 ± 0.34</td>
<td>10.95 ± 0.37</td>
</tr>
<tr>
<td>Blend 1</td>
<td>529.1</td>
<td>531.1</td>
<td>284.8</td>
<td>287.0</td>
<td>288.6</td>
<td>709.3</td>
<td>41.86 ± 0.46</td>
<td>38.30 ± 1.25</td>
<td>8.22 ± 0.29</td>
<td>43.30 ± 0.69</td>
<td>38.02 ± 0.75</td>
<td>9.69 ± 0.39</td>
</tr>
<tr>
<td>Blend 2</td>
<td>529.4</td>
<td>531.2</td>
<td>284.8</td>
<td>286.9</td>
<td>288.6</td>
<td>709.8</td>
<td>37.07 ± 1.35</td>
<td>46.37 ± 1.82</td>
<td>9.19 ± 0.84</td>
<td>39.47 ± 0.85</td>
<td>43.20 ± 1.41</td>
<td>10.45 ± 0.33</td>
</tr>
<tr>
<td>Blend 3</td>
<td>529.1</td>
<td>530.9</td>
<td>284.8</td>
<td>286.9</td>
<td>288.0</td>
<td>709.3</td>
<td>33.31 ± 1.78</td>
<td>49.41 ± 2.57</td>
<td>10.22 ± 0.64</td>
<td>35.35 ± 1.20</td>
<td>46.14 ± 1.91</td>
<td>11.61 ± 0.64</td>
</tr>
<tr>
<td>Blend 4</td>
<td>529.4</td>
<td>531.1</td>
<td>284.8</td>
<td>287.0</td>
<td>288.4</td>
<td>709.7</td>
<td>36.97 ± 1.07</td>
<td>48.09 ± 1.71</td>
<td>10.00 ± 0.56</td>
<td>39.58 ± 0.71</td>
<td>44.69 ± 1.31</td>
<td>11.56 ± 0.46</td>
</tr>
<tr>
<td>Blend 5</td>
<td>529.3</td>
<td>531.2</td>
<td>284.8</td>
<td>286.9</td>
<td>288.6</td>
<td>710.0</td>
<td>37.21 ± 1.34</td>
<td>41.26 ± 2.07</td>
<td>5.80 ± 0.47</td>
<td>39.17 ± 0.80</td>
<td>40.09 ± 1.82</td>
<td>6.95 ± 0.90</td>
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<tr>
<td>Blend 6</td>
<td>529.3</td>
<td>531.1</td>
<td>284.8</td>
<td>287.0</td>
<td>288.3</td>
<td>709.7</td>
<td>38.25 ± 1.47</td>
<td>43.65 ± 2.31</td>
<td>7.30 ± 0.65</td>
<td>39.39 ± 0.76</td>
<td>43.53 ± 1.34</td>
<td>9.48 ± 0.49</td>
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<tr>
<td>Blend 7</td>
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<td>531.1</td>
<td>284.8</td>
<td>287.0</td>
<td>288.5</td>
<td>709.6</td>
<td>40.74 ± 1.32</td>
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<td>7.94 ± 0.61</td>
<td>41.57 ± 1.13</td>
<td>39.83 ± 1.80</td>
<td>9.78 ± 0.39</td>
</tr>
</tbody>
</table>

**Base Oil**

Figure 8 shows XPS results of the elements detected on the wear tracks and unworn surface of the disks lubricated with base oil. The Fe and Si elements, with respective binding energies of 709.7 and 152.8 eV, exhibit similar concentrations on and off the wear track. Since the steel disk and ball specimens contained both Fe and Si, the negligible differences in the concentrations on and off the wear tracks provide indirect evidence that a tribofilm did not form between the metal surfaces. This is also supported by the high coefficient of friction and nearly zero contact voltage obtained with the base oil (Figs. 1(a) and 1(b), respectively). The XPS also detected the presence of sulfur (S2 2p) and nitrogen (N 1s) both on and off the wear tracks. The nitrogen is centered at 399.5 eV and is associated with an amino functional group (NH2). The S2 2p peak is centered at 168.8 eV and reveals the oxidation of sulfur into a sulfate group (SO4).

**Blend 1**

The XPS results of the ZnDTP only containing oil (Blend 1) are shown in Fig. 9. The elements supplied by the ZnDTP additive, such as sulfur (S1 2p), zinc (Zn 2p), and phosphorus (P 2p), possess higher concentrations on the wear track than the unworn surface. This suggests an enhancement of the chemical reactivity of the additive constituents by the sliding process. In addition to the S2 2p peak centered at 169.1 eV, which was also found in the XPS spectrum of the base oil, an S1 2p peak at 162.6 eV was also observed and is attributed to the ZnDTP additive in Blend 1. The S1 2p peak can be associated with the formation of a sulfide (e.g., FeS) in the tribofilm. The Zn 2p peak centered at 1021.0 eV can be attributed to zinc sulfide and/or zinc oxide. The line position of P 2p at 133.8 eV indicates the presence of a phosphate (PO4) group. From these analyses, it can be inferred that the glassy tribofilm (Fig. 6(b)) produced on the worn disk surfaces that were lubricated with Blend 1 consisted mainly of phosphorus, zinc, and sulfur.

**Blend 2**

Figure 10 shows XPS results for the disks lubricated with Blend 2. The presence of the S2 2p peak at 169.0 eV in the XPS spectrum of the wear track and the unworn surface indicates the existence of a sulfate group. The Mo 3d peak at 231.8 eV can be assigned to MoO3. The concentration of this abrasive material is higher on the wear track. The dominance of the N 1s peak (399.7 eV) on and off the wear track can be associated with the basic amine compound contained in the Mo-complex type I in Blend 2.

**Blend 3**

Figure 11 shows the elements detected by the XPS on and off the wear tracks of the disks lubricated with Blend 3. The
Fig. 9—XPS results showing element concentrations on the wear tracks and the unworn surfaces of steel disks lubricated with Blend 1.

Fig. 10—XPS results showing element concentrations on the wear tracks and the unworn surfaces of steel disks lubricated with Blend 2.

Fig. 11—XPS results showing element concentrations on the wear tracks and the unworn surfaces of steel disks lubricated with Blend 3.

Fig. 12—XPS results showing element concentrations on the wear tracks and the unworn surfaces of steel disks lubricated with Blend 4.
concentrations of sulfate on and off the wear track, indicated by the S2 2p peak centered at 168.9 eV, are much lower than those of Blend 2 (Fig. 10). Again, the Mo 3d peak centered at 231.5 eV is associated with the MoO3 compound. Similar to Blend 2, the concentration of Mo was higher on the wear tracks than the unworn surface. As shown in Fig. 3(a), a relatively high coefficient of friction (∼0.15) was produced with Blend 3. Hence, the presence of both Mo and S in the type II Mo-complex additive was not effective in reducing the coefficient of friction. The high concentration of the N 1s peak centered at 399.5 eV can be assigned to the nitrogen-containing compound used to complex the acidic Mo compound of this blend.

Blend 4

The element concentrations on the wear tracks and unworn surface of the disks lubricated with Blend 4 are shown in Fig. 12. The binding energies of the iron, sulfur (S2 2p), molybdenum (Mo 3d), and nitrogen (N 1s) peaks are equal to 709.4, 168.8, 231.5, and 399.5 eV, respectively. The S2 2p peak reveals the oxidized form of sulfur in a sulfate group (−SO4). Since Blend 4 was not effective in reducing the coefficient of friction (Fig. 4(a)), the combination of S (in the form of −SO4) and Mo in Blend 4 was not conducive to the formation of a tribofilm exhibiting low friction characteristics. The N 1s peak corresponds to an amino functional group (−NH2). The type III Mo complex used in Blend 4 also contained some nitrogen.

Blend 5

Figure 13 shows the element concentrations on and off the wear track of the disks lubricated with Blend 5. The Fe and Si 2p peaks with binding energies equal to 709.3 and 152.6 eV, respectively, are attributed to the steel substrate. Two types of sulfur peaks were detected in the XPS spectra: S1 2p centered at 162.7 eV and S2 2p centered at 169.1 eV. While the S2 2p peak can be attributed to a sulfate group (−SO4), the S1 2p corresponds to a sulfide group, which could be in the form of FeS and/or MoS2. The Mo 3d peak at 228.6 eV also indicates the formation of MoS2. Both FeS and MoS2 are well known friction modifiers. The low coefficient of friction (Fig. 2(c)) and high steady-state contact voltage (Fig. 2(d)) obtained with Blend 5 are also indicative of the in situ formation of a low shear strength tribofilm, which could be associated with a MoS2-containing film. The Zn 2p peak centered at 1021.1 eV corresponds to ZnO and/or ZnS. The P 2p peak centered at a binding energy of 133.9 eV reveals the presence of phosphate (−PO4). According to the results of previous studies (Grossiord, et al. (8), (15); De Barros, et al. (16)), the synergistic effects of MoDTC and
ZnDTP additives lead to the formation of a tribofilm consisting of a glassy zinc phosphate phase and a carbon matrix containing ZnS and single MoS$_2$ sheets, which could serve as antiwear and friction modifier agents, respectively. Hence, the P and Zn concentrations can be associated with the formation of a glassy tribofilm (Fig. 7(d)). The higher concentrations of sulfide, molybdenum, zinc, and phosphorus on the wear track than the unworn surface reveal an enhancement of the chemical reactivity of these additives under the present sliding conditions.

**Blend 6**

Figure 14 shows XPS results for the element concentrations on and off the wear tracks of the disks lubricated with Blend 6. Similar to Blend 5, two sulfur peaks centered at 162.6 eV (S1 2p) and 168.7 eV (S2 2p) were detected in the XPS spectra, which can be associated with the presence of sulfide and sulfate groups, respectively. The Mo 3d peak at 229.6 eV and the S1 2p indicate the formation of a tribofilm containing MoS$_2$, which is believed to be responsible for the low coefficient of friction obtained with Blend 6 (Fig. 3(c)). The presence of another Mo peak at 232.1 eV indicates the formation of phosphate (PO$_4$).

CONCLUSIONS

The tribological properties of steel surfaces lubricated with base oil and blends consisting of base oil and ZnDTP additive with or without different Mo complexes were investigated in light of results for the coefficient of friction, contact voltage, and wear volume, SEM observations of the dominant wear mechanisms, and XPS analysis of the compositions of the formed antiwear tribofilms. The test conditions were selected to produce sliding in the boundary lubrication regime at 100°C. Based on the presented results and discussion, the following main conclusions can be drawn from this investigation.

1. Lubricant formulations consisting of base oil with single ZnDTP additive (Blend 1) or different Mo complexes (Blends 2-4) are not effective friction and wear reducers. However, base oil fortified with ZnDTP and Mo-complex mixtures (Blends 5-7) yield significantly improved tribological performance. The combination of ZnDTP and type I Mo compound (Blend 5) produced the lowest steady-state coefficient of friction (∼0.05), while combinations of ZnDTP with type II (Blend 6) and type III (Blend 7) Mo complexes produced steady-state coefficients of friction of ∼0.06 and ∼0.07, respectively.

2. The decrease of the coefficient of friction in the experiments performed with lubricant formulations containing ZnDTP and Mo compounds (Blends 5-7) yield significantly improved tribological performance. The combination of ZnDTP and type I Mo compound (Blend 5) produced the lowest steady-state coefficient of friction (∼0.05), while combinations of ZnDTP with type II (Blend 6) and type III (Blend 7) Mo complexes produced steady-state coefficients of friction of ∼0.06 and ∼0.07, respectively.

3. The decrease of the coefficient of friction in the experiments performed with lubricant formulations containing ZnDTP and Mo compounds (Blends 5-7) accompanied by an increase in the contact voltage from ∼0 mV to values in the range of 10-18 mV. Contact voltage fluctuations were attributed to the competing effects of semi-conducting sulfur-containing and non-conducting phosphorus-containing phases in the tribofilms.

4. The only blend to produce a steady-state contact voltage of ∼20 mV with minimal fluctuations was the ZnDTP-containing oil (Blend 1), indicating a faster rate of formation of a non-conducting tribofilm during sliding.
3. The addition of ZnDTP in the base oil (Blend 1) greatly enhanced the wear performance due to the formation of a glassy tribofilm. The addition of the type I Mo complex in the base oil (Blend 2) affected negatively the wear resistance, presumably due to the formation of abrasive compounds during sliding. Although the addition of the types II and III Mo complexes in the base oil (Blends 3 and 4, respectively) improved the wear behavior over that of the base oil, the addition of ZnDTP to the Mo-containing oils (Blends 5-7) improved more significantly the wear resistance.

4. The absence of a protective tribofilm on the steel surfaces lubricated with base oil resulted in the formation of deep plowing grooves. The addition of Mo-complex additives in the base oil (Blends 2-4) caused significant roughening of the sliding surfaces. Numerous small pads were observed on the wear tracks of the steel surfaces lubricated with Blends 3 and 4. The blends containing ZnDTP additive (Blends 1, 5, 6, and 7) produced hard glassy regions on the wear tracks that reduced wear. Although these regions exhibited delamination features along their boundaries, this was not detrimental to their effectiveness to protect the steel surfaces.

5. The similar iron concentrations on the wear tracks and the unworn surfaces lubricated with base oil provided evidence for the absence of a protective tribofilm. Sulfide was only observed on the wear tracks of the steel surfaces lubricated with ZnDTP-containing oils (Blends 1, 5, 6, and 7). The presence of both sulfide and molybdenum on the steel surfaces lubricated with Blends 5, 6, and 7 in conjunction with the low coefficient of friction indicated the formation of a low shear strength tribofilm, probably due to the dominant contribution of MoS2. The absence of sulfide from the steel surfaces lubricated with Mo-containing oils (Blends 2, 3, and 4) suggests that these Mo-containing additives cannot be used alone as friction modifiers. The presence of zinc and phosphorus on the steel surfaces lubricated with ZnDTP-containing oils (Blends 1, 5, 6, and 7) is attributed to the formation of glassy regions on the wear tracks that protected the surfaces. The higher concentrations of S, P, Zn, and Mo on the wear tracks than the unworn surfaces illustrated the profound role of surface rubbing in the formation of antiwear tribofilms.

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