

Synthesis, Physicochemical, and Tribological Characterization of *S*-Di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate

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ABSTRACT Dialkyldithiophosphates (DTPs) of zinc(II), copper(II), and other metals have been extensively used as multifunctional additives in lubricants to control friction and reduce wear in mechanical systems. Among these DTP compounds, zinc dialkyldithiophosphates (ZnDTPs) are the most common additives extensively used for more than 60 years. These additives form a protective film on steel surfaces and, thus, control friction and reduce wear. However, ZnDTPs contain zinc and large amounts of phosphorus and sulfur, which impair the environment, both directly and indirectly, by adversely affecting the performance of catalytic converters of various automobiles. For this reason, environmental legislation imposes limitations on concentrations of phosphorus, sulfur, and zinc in the lubricants. In this work, we report on zinc-free *S*-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP) lubricant additive with amount of phosphorus and sulfur reduced by half in a molecule as compared with ZnDTPs. DOB-DTP was synthesized by a reaction in two steps under inert nitrogen atmosphere. The final product, a viscous liquid, was characterized by the elemental analysis, FT-IR, multinuclear ¹H, ¹³C, ³¹P, and ¹¹B NMR spectroscopy and thermal analyses. Tribological performance of a mineral oil with this new additive was evaluated in comparison with *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) (ZnDTP) using a four-ball tribometer. The surface morphology and the elemental composition of the tribofilms were characterized using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS). The results show that DOB-DTP has a considerably better antiwear performance and higher stability of the coefficient of friction with time as compared with ZnDTP. Both phosphorus and sulfur were detected by the EDS on the worn steel surfaces at all concentrations of additives in the base oil.

KEYWORDS: *S*-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate • ZnDTP • lubricant additives • tribological characterization • thermal analysis • SEM/EDS

1. INTRODUCTION

Boron, sulfur, and phosphorus-containing additives are being used in lubricating oil formulations because of their excellent antiwear, extreme pressure, friction reducing, antioxidant, and corrosion resistance properties (1). These additives react with metal surfaces forming tribolayers, which provide low friction, low wear, and resist corrosion. The reactivity of these additives depends on their structure and concentration, applied load, sliding speed, contact temperature, time of the interaction, and surface materials.

Zinc dialkyldithiophosphates (ZnDTPs) are arguably the most successful lubricant additives ever invented. Since their introduction in the 1940s, ZnDTPs have been in continuous use over several decades and still being employed as excellent lubricant additives in practical applications (2–6). Over the past decade, demanding efforts were made by both companies developing new additives and researchers to replace ZnDTPs, which cause environmental pollution by poisoning exhaust catalysts (7). In addition to environmental

pollution, its health hazards include eye irritation, allergic contact dermatitis, and mutagenicity (8, 9). In a recent review on the history and action mechanism of ZnDTPs with metal surfaces (10), it is concluded that it has been so far proven impossible to identify any reasonably cost-effective compound having comparable antiwear properties to ZnDTPs lubricant additives. A survey of literature reveals that dialkyldithiophosphate esters (11), dialkyldithiophosphates of different metals such as molybdenum (12), cadmium (13), copper (14), titanium (15), gadolinium (16), iron, antimony, and other metals (17–19) have been introduced and used as multifunctional additives in lubricants. To the best of our knowledge, there are no open publications on boron dialkyldithiophosphates as additives in lubricants. One of the possible reasons could be lack of suitable methods of synthesis for B-DTPs. Compounds with boron–sulfur bonds are reactive and they are usually used as intermediates for the synthesis of organometallic and organometalloid sulfur compounds (20, 21). However, the reactivity of such compounds toward metals and metalloids would help in reducing wear by the reaction of boron and sulfur with metal and metalloid surfaces via formation of superhard protective layers.

On the other hand, boron-containing compounds have been already widely studied as corrosion inhibitors, antioxidants, friction modifiers, and effective antiwear additives

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either dissolved in oil or as an insoluble and inorganic borate salts dispersed in oil in the nanoparticulate form (22–27). Tribofilms from oils containing boron based additives were recognized already in 1960s. However, it is only within the past decade that these compounds have received a proper attention. Boron-containing compounds may be an attractive alternative to commercial additives, with a similar antiwear performance in the absence (or a considerable reduction) of both phosphorus and sulfur in a lubricant. It is already well-understood that boron compounds are capable of forming glassy structures in a manner similar to ZnDTP but with different glass transition temperatures (28). It is also known that crystalline or amorphous boron, boron nitride and metal boride are very hard materials. Microindentation measurements on rhenium diboride (ReB_2) indicated an average hardness of 48 GPa under the applied load of 0.49 N and scratch marks were left on a diamond surface by particles of this material confirming its superhard nature (29). Iron boride (Fe_2B) can be formed on steel surfaces thus improving the hardness of machine elements made of steel (30, 31). The hardness of crystalline boron is 30 GPa and amorphous boron thin film can also have hardness approaching that of crystalline boron (32). A high hardness of surfaces could then be provided by boron or metal boride coatings. It would provide an additional benefit for antiwear tribofilm performances by protecting metal surfaces from damage during sliding in tribological contacts. In addition, in a moisture-containing environment, the surface oxide of boron (B_2O_3) is known to react with water forming boric acid (H_3BO_3), which acts as a solid lubricant. The lubricity of boric acid has been attributed to its tendency to form a triclinic crystal structure made up of atomic layers parallel to the basal plane. In each layer, the B, O, and H atoms are closely packed and bonded to each other with covalent bonds, whereas the layers are held together with weak van der Waals forces. The latter facilitates the layers to easily slide with respect to each other that provides lubricity in the system (33).

The combined effect of different borate and ZnDTP additives on tribological performance has been studied extensively during the past few years. Combinations of potassium triborate with ZnDTP (34), calcium borate with ZnDTP (35, 36), and a boric additive with tricresyl phosphate (TCP) and ZnDTP additives (37) have exhibited improved antiwear properties compared with commercial ZnDTPs alone. These results suggest that borate additives can be a possible partial replacement of ZnDTPs additives in lubricants.

In this work, we synthesized a novel compound *S*-di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP), with both boron and a dialkyldithiophosphate group bound in a single molecule. It can be expected that such a molecule, i.e., without zinc and with reduced amounts of sulfur and phosphorus, would provide a better tribological and environmental performance when used as the additive in mineral oils. We also report on physicochemical and tribological characterizations of DOB-DTP. Its tribological performance was evaluated in comparison with *O,O'*-di-*n*-butyl-dithio-

phosphato-zinc(II), (ZnDTP) at concentrations 0–1.0 wt % in a mineral oil.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Phosphorus pentasulphide, P_2S_5 (Aldrich, 99% purity), 1-octanol (Prolabo, 97% purity), boric acid (Merck, analytical grade), and toluene (Fluka, >99.7% purity) were used as received. The commercially available ZnDTP contains a mixture of 85% *O,O'*-di-*iso*-butyl-dithiophosphato-zinc(II) and 15% *O,O'*-di-*n*-octyl-dithiophosphato-zinc(II) (38). In this study, we used ZnDTP (as a reference compound) with the same number of carbon atoms in alkyl chains as in the commercial ZnDTP additive but we selected *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) instead of Zn(II)-*i*BuDTP. *O,O'*-Di-*n*-butyl-dithiophosphato-zinc(II) is a viscous liquid at room temperature and it is easily miscible with the base oil used in this study. On the contrary, Zn(II)-*i*BuDTP is a solid at room temperature that makes it difficult to fully dissolve it in the base oil, if the ZnDTP ligand complex with a longer alkyl chain is not used in the same package of additives. *O,O'*-Di-*n*-butyl-dithiophosphato-zinc(II) was synthesized using a reported method (39). The purity of the latter ZnDTP and its corresponding potassium salt was checked by ^{31}P NMR for ZnDTP (145.70 MHz, δ): 100.29 ppm (40) and ^{31}P NMR for potassium salt (145.70 MHz, ethanol, δ) 112.72 ppm (see the Supporting Information).

2.2. Synthesis of *S*-Di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP). Step 1. Boric acid (10 mmol) and 1-octanol (30 mmol) were added to a flask with toluene (50 mL), equipped with a magnetic stirrer, a condenser, and a water separator. The reaction mixture was refluxed for 3 h. Water formed during the reaction was removed continuously using a separator. Toluene was rotary evaporated and a product was distilled under reduced pressure (0.2 mmHg) to remove toluene and residual octanol. A colorless liquid product of trioctyl borate (**I**) was obtained in 88% yield. FT-IR (KBr, cm^{-1}): 2927, 2856 ν (C–H, stretching); 1417 ν (CH_2 bending); 1337 ν (B–O strong). ^{11}B NMR (115 MHz, toluene, δ) 16.56 ppm (see SI).

Step 2. Phosphorus pentasulphide (11.28 g, 10 mmol) and trioctyl borate (45.15 g, 40 mmol) were added together with toluene to a flask equipped with a magnetic stirrer and a condenser (prebaked on vacuum to exclude any moisture). The reaction mixture was refluxed for 3 h under nitrogen atmosphere. After cooling the precipitate was filtered, the filtrate was rotary evaporated to remove toluene and distilled at 0.2 mmHg, 120 °C for 30 min. A transparent liquid product (**II**) was obtained in 52% yield (7.30 g). Anal. Calcd. for $\text{C}_{32}\text{H}_{68}\text{O}_4\text{PS}_2\text{B}$ (MW 622.76 g/mol): C, 61.71; H, 11.0; B, 1.73. Found: C, 64.7; 11.7; B, 2.2. FT-IR (KBr, cm^{-1}): 2927, 2856 ν (C–H, stretching); 1417 ν (CH_2 bending); 1336 ν (B–O, strong); 992 ν (P–OC, broad); 666 ν (P=S, medium); 531 ν (P–S, strong). ^1H NMR (359.93 MHz, CDCl_3 , δ): 0.88 (12H, t, $^3J_{\text{HH}} = 6.7$ Hz, CH_3); 1.26–1.34 (40H, m, $-\text{CH}_2$ -chain); 1.48–1.60 (4H, m, $\text{CH}_2\text{CH}_2\text{OB}$); 1.69–1.76 (4H, m, $\text{CH}_2\text{CH}_2\text{OP}$); 3.76 (4H, t, $^3J_{\text{HH}} = 6.6$ Hz, CH_2OB); 4.15 (4H, dt, $^3J_{\text{HP}} = 9.47$, $^3J_{\text{HH}} = 6.56$, CH_2OP). ^{13}C NMR (90.51 MHz, CDCl_3 , δ): 14.26 (4 \times CH_3), 22.84 (4 \times CH_2CH_3), 26.02, 29.34, 29.51, 30.14, 32.02 (20 \times $-\text{CH}_2$ -chain), 63.41 (2 \times CH_2OB), 68.62 (2 \times CH_2OP) ppm. ^{31}P NMR (145.70 MHz, toluene, δ): 84.58 ppm. ^{11}B NMR (115.48 MHz, toluene, δ): 16.36 ppm (see the Supporting Information).

2.3. Spectroscopic Characterization. FT-IR spectra were recorded on a Perkin-Elmer 2000 spectrometer in the range 4000–370 cm^{-1} . Sampling was performed by placing a droplet of a compound onto a KBr pellet. Multinuclear NMR spectra were recorded on a Varian/Chemagnetics InfinityPlus CMX-360 ($B = 8.46$ T) spectrometer in CDCl_3 (^1H , ^{13}C) or in toluene (^{31}P , ^{11}B) using TMS as an internal reference for ^1H (0 ppm), the 77.2 ppm resonance peak of CDCl_3 for ^{13}C , $\text{Et}_2\text{O} \cdot \text{BF}_3$ as an external

Table 1. Physicochemical Properties of the Mineral Base Oil Used in This Study

density (g mL ⁻¹)	0.8135
viscosity (m Pa s) at 40 °C	17.5
viscosity (m Pa s) at 100 °C	4.9
carbon (%)	86.0 ± 0.7
hydrogen (%)	14.5 ± 0.5

reference (0 ppm) for ¹¹B and H₃PO₄ (85%) as an external reference (0 ppm) for ³¹P.

2.4. Thermal Analysis. Thermal analysis of the synthesized compound was performed by Netzsch STA 409 instrument equipped with simultaneous thermogravimetric (TG), differential thermal analysis (DTA) coupled with a quadrupole mass spectrometer (QMS) at a rate of 20 °C/min and with argon flow rate of 100 mL/min. The sensitivity of this STA Instruments is ±1 μg.

2.5. Tribological Characterization. The additives were mixed with mineral oil at fixed weight (%) concentrations of 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0% using an analytical balance. The physicochemical properties and the elemental analysis of the base oil used in this study are given in Table 1. The balls used in the tests were 12.7 mm diameter and made of AISI 52100 steel with a composition of C, 0.95–1.10%; Si, 0.15–0.30%; Mn, <0.25%; P, <0.03%; S, <0.025%; Cr, 1.30–1.60%, and with a hardness HRC 60–67.

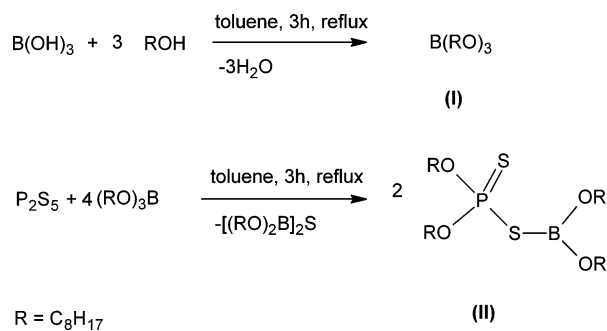
The friction and antiwear properties of these compounds as additives in the base oil were evaluated with a four ball Tribometer at a rotating speed of 1450 rpm, test duration time of 30 min, load 392 N, and at room temperature (294 K). Wear scar diameters and friction coefficients were measured at additive concentrations in the range of 0–1.0 wt %. An optical profiler (WYCO NT 1100) was used to determine the wear scar diameters of the three stationary balls. Then a mean value was calculated and reported here as the wear scar diameter (WSD). Before each test, the holder for the balls was washed with petroleum ether and the balls were cleaned ultrasonically in petroleum ether and thoroughly air-dried.

2.6. Surface Analysis. Philips XL 30 scanning electron microscope (SEM) equipped with LaB₆ emission source was used for surface studies. A link ISIS Ge energy dispersive X-ray detector (EDS) attached to the SEM was used to additionally probe the composition of the entire tribofilms on the ball surfaces. Prior to the analysis, the balls were cleaned ultrasonically for 5 min with petroleum ether, in order to eliminate the residual lubricant.

3. RESULTS AND DISCUSSION

3.1. Syntheses and Chemical Analyses. *S*-Di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP) was synthesized by a reaction in two steps (Scheme 1). In the first step, trioctyl borate (I) was synthesized by treating boric acid and octanol. This step was followed by the synthesis of DOB-DTP (II) using a reported method (41) by reacting phosphorus pentasulphide (P₂S₅) with trioctyl borate in a 1:4 molar ratio. During this reaction, B–O bonds of borate were cleaved and new B–S bonds were formed simultaneously giving rise to the final product (II). A semisolid byproduct, [(RO)₂B]₂S, formed in the same reaction was removed by filtration.

FTIR, ¹H, ¹³C, ³¹P, and ¹¹B NMR spectroscopy were used to characterize the synthesized compounds. FTIR spectra of compounds I and II show the characteristic peaks with absorption frequencies of the aliphatic C–H vibrations in the

Scheme 1. Synthesis of DOB-DTP

alkyl groups of compounds (I) and (II) in the range of 2856–2956 cm⁻¹. Strong bands were observed at 1337 and 1336 cm⁻¹ for I and II, respectively, which are attributed to the ν(B–O) band in both these compounds. Strong band at 992 cm⁻¹ and medium bands at 666 and 531 cm⁻¹ were observed in the FTIR spectrum of compound II only and are assigned to ν(P–OC), ν(P=S), and ν(P–S) bands, respectively. The latter was an additional proof that compound II was formed from the intermediate compound I.

³¹P NMR of DOB-DTP (II) in toluene reveals a singlet at 84.58 ppm that is expected for pure boron *O,O'*-dialkyldithiophosphate compounds (41, 42).

¹¹B NMR spectra of I and II were recorded in toluene and the observed chemical shifts are 16.56 and 16.36 ppm respectively, that also is consistent with the presence of the three-coordinated boron in boron *O,O'*-dialkyldithiophosphates (42). The boron nucleus in II is more shielded (by 0.20 ppm) than in I, which is in accord with a formation of a SBO₂ group instead of BO₃.

3.2. Thermal Analysis. Because most tribological contacts operate at elevated temperatures, it is important to study the effect of temperature on the physicochemical properties of the lubricant additives such as thermal stability, weight loss, and the nature of compounds in the course of thermal decomposition. Differential thermal analysis is usually represented as “exothermic” or “endothermic” peaks at elevated temperatures. Generally, exothermic peaks are the result of chemical decomposition or oxidation, which is accompanied by exothermic processes, while endothermic peaks are due to physical processes such as melting, boiling, or other phase transitions of a compound (43). The thermal decomposition temperature of dialkyldithiophosphates of different metal ions is strongly dependent on the type of alkyl groups and molecular structures of these compounds: (i) aryl dialkyldithiophosphates of zinc(II) are more stable than alkyl derivatives of ZnDTPs; (ii) primary alkyls are more stable than secondary alkyls in ZnDTPs. The differential thermal analysis of these compounds have shown that within the primary alkyl groups of ZnDTP, the hydrogen atom bound to a β-carbon atom of the *n*-alkyl group is more stable than those in the secondary alkyl groups of ZnDTP (44, 45). Therefore, the formation of olefins may occur only at relatively high temperatures.

As a result of thermal decomposition of DOB-DTP, two categories of decomposition products were obtained, both

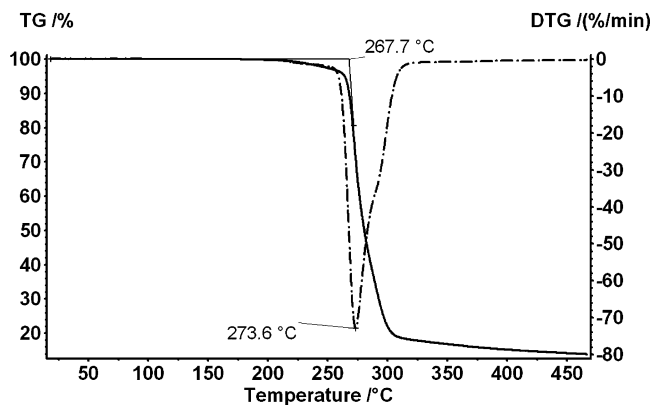


FIGURE 1. TG/DTG curves of DOB-DTP at a heating rate of 20 °C/min and argon flow rate of 100 mL/min.

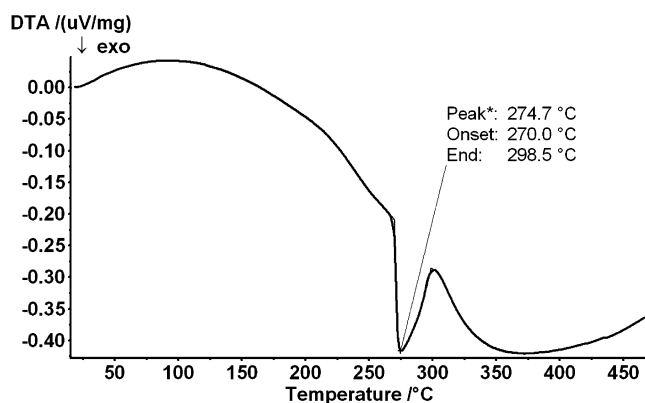


FIGURE 2. DTA curve of DOB-DTP at a heating rate of 20 °C/min and argon flow rate of 100 mL/min.

solid and volatile species. The residual product with a melting point above 500 °C was solid material. Because 200 mg of the liquid sample was used for thermal analysis, the amount of solid residue was not enough to further analyze it. The volatile products were additionally investigated by quadrupole mass spectrometer attached to the thermal analysis instrument.

Thermogravimetric/derivative thermogravimetric (TG/DTG) curves obtained for DOB-DTP are shown in Figure 1. The thermal decomposition of DOB-DTP involves only one major step, the onset of which is at 267.7 °C. This temperature indicates the complete decomposition of the molecule, which is initiated, most probably, with the breakage of the B–S bond and followed by the decomposition of *n*-octyl chains. The total weight loss during this test is 86 wt %, so much of the compound is decomposed into volatile products, whereas 14 wt % remains as a solid residue. The DTG curve represents the highest rate of the weight loss (75 %/min) at 273.6 °C. The TG and DTG analyses revealed that both the decomposition and the weight loss of this compound occur in one single step.

Differential thermal analysis (DTA) curve of DOB-DTP is shown in Figure 2. There is only one exothermic peak, representing the thermal decomposition of the compound. The exothermic peak appears in the temperature range 274–298 °C with a midpoint at 270 °C. This peak is in accord with the TG/DTG curves as discussed above. DOB-

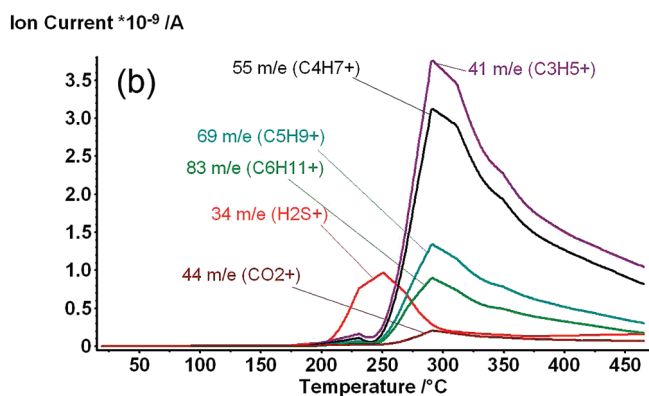
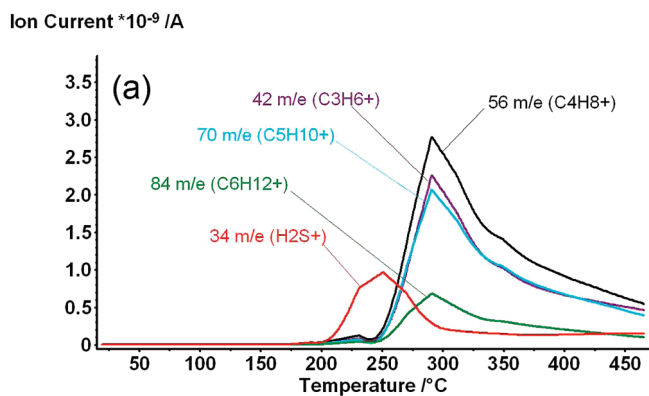


FIGURE 3. QMS profiles of DOB-DTP at a heating rate of 20 °C/min and argon flow rate of 100 mL/min. (a) Even number molecular weight fragments; (b) odd number molecular weight fragments.

DTP is almost completely decomposed into volatile products in this temperature range.

The formation of volatile products as a function of temperature under constant flow of argon gas was analyzed by QMS. Different compounds were evolved in the 20–500 °C temperature range. Evolution of some selected products by decomposition of DOB-DTP is shown in figure 3. The main volatile decomposition products of dialkyldithiophosphates are dihydrogen sulphide and olefins (46). The type of olefins formed depends on the nature of an alkyl group attached to the dithiophosphate group. For DOB-DTP the formation of dihydrogen sulphide (H_2S^+) with $m/e = 34$ was observed when the temperature exceeded 200 °C. Olefin cations with different number of carbons are formed when the parent octyl chains break down at different positions. Their relative intensities are given in comparison with H_2S^+ (see Figure 3). Relative intensities of fragments with odd number of carbons in olefin chains (Figure 3b) are higher than their corresponding species with even number of carbon atoms (Figure 3a). A propenyl cation (C_3H_5^+) with $m/e = 41$ and a butenyl cation (C_4H_7^+) with $m/e = 55$ have similar evolution patterns and they are the principle components in the mixture of volatile products of decomposition of DOB-DTP. The decomposition products with higher molecular weights have smaller relative intensities compared to these of both propenyl and butenyl cations.

3.3. Tribological Characterization. It is known that the antiwear ability of a specific additive depends on its concentration in the base oil. Figure 4 shows variations

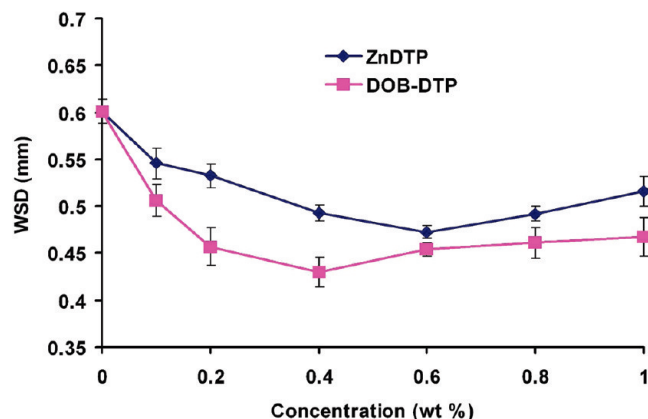


FIGURE 4. Variations of the wear scar diameter (mm) on the lower steel balls with concentration (wt %) of additives under 392 N load for 30 min at room temperature. Top (blue), ZnDTP; bottom (pink), DOB-DTP.

of the wear scar diameter (WSD) measured on steel balls lubricated with the mineral base oil containing either DOB-DTP or ZnDTP additives at different concentrations.

It was found that both DOB-DTP and ZnDTP are prone to reduce wear as measured here via mean wear scar diameters on the steel balls, when these additives were admixed into the mineral oil even at very small concentrations. In case of DOB-DTP, wear scar diameter decreases up to an additive concentration of 0.4 wt %. Then, WSD increases slightly with an increase of concentration of DOB-DTP. A similar trend was also found for ZnDTP. WSD decreases up to a 0.6 wt % concentration of this additive and then increases with the following increase of concentration of ZnDTP in the base oil. Thus, the optimum concentrations for the wear reducing ability of these additives in the base oil in the steel–steel contact under 392 N load during 30 min at room temperature were 0.4 and 0.6 wt % for DOB-DTP and ZnDTP additives, respectively.

We suggest that the concentration dependence of the wear reducing ability of the additives can be explained by their affinities to and interactions with steel surfaces. More reactive additives are prone to reduce wear even at low concentrations by forming protective tribofilms on the contacting interfaces. An excess of sulfur in the lubricant causes a chemical corrosion of steel surfaces (47, 48), which limits the antiwear performance of S-based additives at higher concentrations in the base oil. A comparative analysis of the antiwear ability of an additive as a function of its concentration in the mineral base oil reveals that DOB-DTP forms a stable tribofilm even at a very low concentration (0.1 wt %). Moreover, for this additive at concentrations 0.4–1.0 wt %, WSD increases by only 0.037 mm, i.e., 8.5% (see Figure 4 and Table 2). On the contrary, the wear scar diameter is considerably larger for ZnDTP at concentrations higher than 0.6 wt % in the base oil. Also, WSD increases sharply when concentration of ZnDTP is increased from 0.6 to 1.0 wt %.

There might be two reasons for the outstanding antiwear performance of the novel DOB-DTP additive. First, DOB-DTP contains only two sulfur atoms, whereas ZnDTP contains

Table 2. Variations of the Wear Scar Diameter (mm) and the Friction Coefficient (an average over last 10 min of the test) with Concentration (wt %) of Additives under 392 N load for 30 min at Room Temperature

additive concentration (wt %)	DOB-DTP		ZnDTP	
	WSD \pm (SD) (mm)	friction coefficient	WSD \pm (SD) (mm)	friction coefficient
0	0.602 (0.012)	0.042 (0.006)	0.602 (0.012)	0.042 (0.006)
0.1	0.506 (0.017)	0.062 (0.005)	0.546 (0.017)	0.082 (0.007)
0.2	0.457 (0.020)	0.060 (0.004)	0.533 (0.013)	0.074 (0.006)
0.4	0.430 (0.016)	0.060 (0.006)	0.493 (0.008)	0.065 (0.005)
0.6	0.454 (0.007)	0.063 (0.007)	0.473 (0.007)	0.072 (0.005)
0.8	0.461 (0.016)	0.060 (0.004)	0.492 (0.008)	0.066 (0.005)
1.0	0.467 (0.020)	0.062 (0.007)	0.516 (0.016)	0.066 (0.005)

four sulfur atoms in the molecule. As mentioned above, an excess of sulfur in an additive or a base oil may cause chemical corrosion of steel surfaces. Second, DOB-DTP contains the alkyl borate group in the molecule that enhances the antiwear ability and inhibits corrosive actions of sulfur even at higher concentrations of this additive in the base oil. In this case, the corrosive action of sulfur and antiwear performance of boron occur simultaneously. This results in a smooth increase in WSDs when concentration is increased (49).

Figure 5 shows variations in the friction coefficient with concentration (wt %) of the two additives in the base oil. It is evident from these measurements that incorporation of either DOB-DTP or ZnDTP additives in the base oil increases the friction coefficient. Even at a very low concentration (0.1 wt %) of each additive in the base oil, the coefficient of friction increases considerably from $\mu = 0.04$ to ca. 0.06 (for DOB-DTP) or ca. 0.075 (for ZnDTP). The coefficient of friction remains quite stable ($\mu = 0.060$ – 0.063) for the oil with DOB-DTP in the whole concentration range tested, 0.1–1.0 wt %. Variations in friction coefficient with concentration of ZnDTP from 0.1 to 1.0 wt % are substantially larger, $\mu = 0.065$ – 0.083 (see Figure 5 and Table 2). An increase in the coefficient of friction upon admixture of

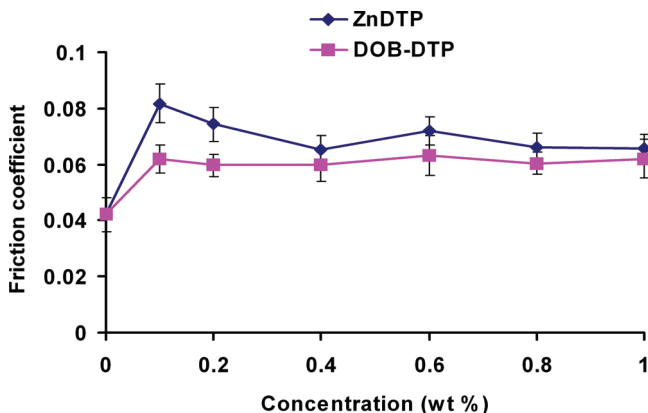


FIGURE 5. Variations of the friction coefficient with concentration (wt %) of additives under a 392 N load for 30 min at room temperature (an average over last 10 min of the test). Top (blue), ZnDTP; bottom (red), DOB-DTP.

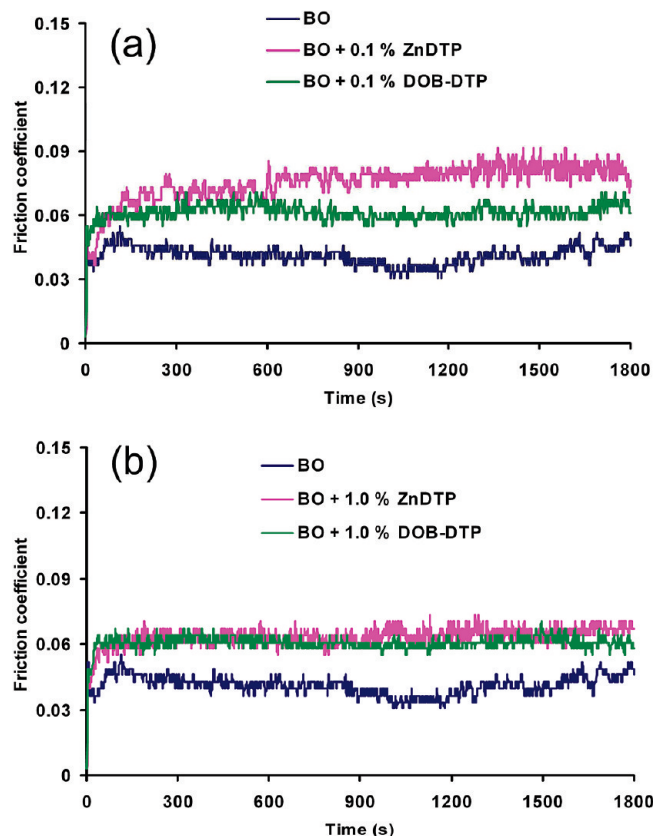


FIGURE 6. Variations of the friction coefficient with time (s) for the base oil (BO), BO with ZnDTP and BO with DOB-DTP. (a) 0.1 wt % and (b) 1.0 wt % of the additives. Top (pink), ZnDTP; middle (green), DOB-DTP; bottom (blue), BO.

additives in the base oil is caused by the formation of stable tribofilms as a result of tribochemical reactions of the additives with steel surfaces during the wear process. It is already known that the tribofilms formed by ZnDTP increase friction coefficient, which is probably due to the higher shear strength of the films formed by ZnDTP (50–52). DOB-DTP also increases friction coefficient but it is stable with time compared to ZnDTP. Here, it is suggested that both DOB-DTP and ZnDTP additives in the base oil at as low concentration as 0.1 wt % do form tribofilms on the steel surfaces.

However, a comparison of the friction properties of these two additives reveals that DOB-DTP provides lower and more stable friction in a wider range of additive concentrations in the base oil compared with ZnDTP.

Thus, both antiwear and friction properties of DOB-DTP are considerably better than those of the commercial additive, ZnDTP (compare data in Figures 4 and 5 and Table 2). We suggest that these properties depend strongly on a difference in compositions of the tribofilms formed on the steel surfaces, when either DOB-DTP or ZnDTP were tested. We will discuss these issues later in this article.

A variation of the friction coefficient with time is shown in plots a and b in Figure 6 for the base oil only and oil containing either DOB-DTP or ZnDTP additives (mean values of the friction coefficients over last 10 min of the test, when the friction coefficients have stabilized, are given in Figure 5 and Table 2). It can be seen that when the base oil is

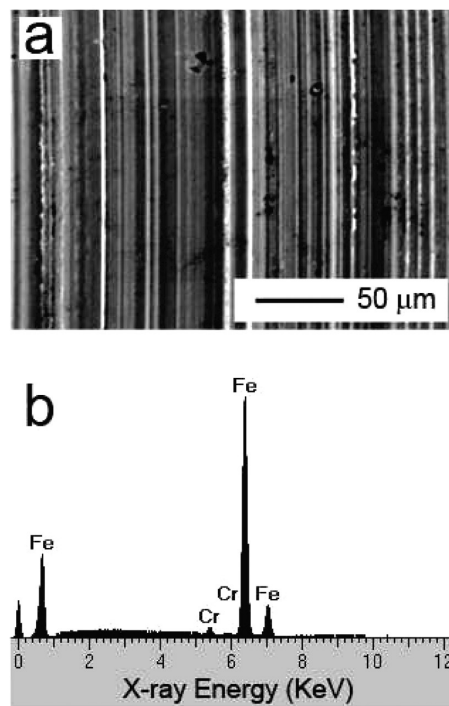


FIGURE 7. (a) SEM micrograph and (b) EDS spectrum of worn ball surface lubricated with the mineral base oil only.

formulated with either DOB-DTP or ZnDTP additives, the friction coefficient of the lubricant increases compared with the oil without additives. Though the friction coefficient of the base oil is lower than for the oil with additives, it is not stable and varies considerably with time of the test. The friction coefficient of the base oil containing ZnDTP at a low concentration (0.1 wt %) increases slowly with time (Figure 6a). The friction coefficient is stable at higher concentrations (0.8 wt %) of ZnDTP. On the other hand, the friction coefficient of the oil containing DOB-DTP does not vary much with time at both low (0.1 wt %) and high (1.0 wt %) concentrations of the additive (plots a and b in Figure 6). This test confirms the stability of the tribofilm formed by DOB-DTP at both low and high concentrations. Note that the stability of the friction coefficient with time is a very important property in mechanical systems needed for their functionality during the service life.

3.4. Surface Analysis. Figures 7–10 show results of the surface analysis obtained using Scanning Electron Microscopic/Energy Dispersive X-ray Spectroscopy (SEM/EDS) techniques. The worn surfaces of balls lubricated with the base oil containing 0.1, 0.4, and 1.0 wt % additives were studied by these methods in order to compare both the morphology and a composition of the tribofilms formed from these two additives at different concentrations. These data suggest a formation of tribofilms containing both sulfur and phosphorus at various compositions depending on the type of additive and their concentrations used in the tribological tests.

Figure 7 shows the SEM micrograph of the worn ball surface lubricated with the base oil under the load of 392 N. This micrograph shows wide grooves, which indicate a severe wear. When the additives are mixed with the base

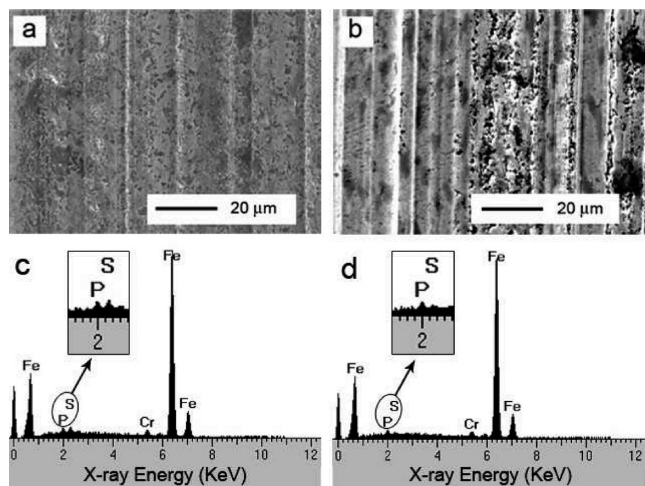


FIGURE 8. SEM micrographs of worn ball surfaces lubricated with the mineral base oil containing (a) 0.1% DOB-DTP and (b) 0.1% ZnDTP. (c, d) EDS spectra of tribofilms in a and b, respectively (the EDS spectra are the average of the whole area shown in the corresponding micrographs).

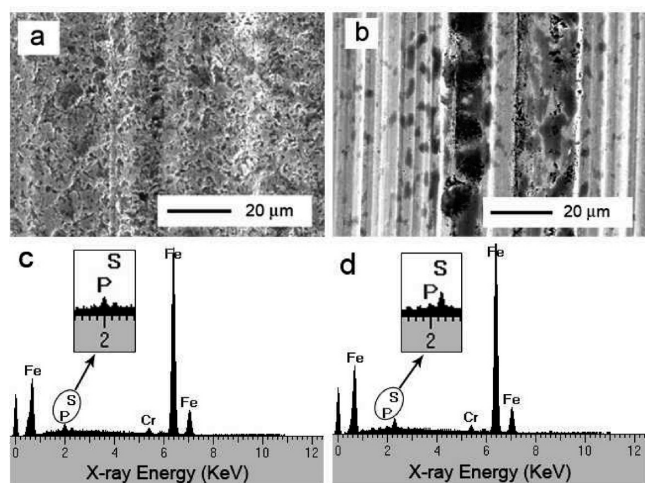


FIGURE 9. SEM micrographs of worn ball surfaces lubricated with the mineral base oil containing (a) 0.4% DOB-DTP and (b) 0.4% ZnDTP. (c, d) EDS spectra of tribofilms in a and b, respectively (the EDS spectra are the average of the whole area shown in the corresponding micrographs).

oil at very low concentration (0.1 wt %), the wear process slows down (see images a and b in Figure 8). The surfaces are smoother (see Figure 8a) as compared to the surfaces lubricated with the mineral oil. When the additive concentrations are increased to 0.4 wt %, WSDs remain close to their minimum values (images a and b in Figure 9) and the wear process further decreases, as discussed earlier (see Figure 4 and Table 2). Beyond this optimum concentration, the surfaces seem to become rougher again (see images a and b in Figure 10). Most probably, this roughness is increased by a corrosive action of sulfur. The worn ball surfaces lubricated with the mineral oil containing DOB-DTP are smoother for all the concentrations studied by SEM, as compared to those lubricated by oil with ZnDTP.

For additive concentrations of 0.1 wt % (see panels c and d in Figure 8), 0.4 wt % (panels c and d in Figure 9) and 1.0 wt % (panels c and d in Figure 10), active elements from the additives are transferred/adsorbed to the steel surfaces.

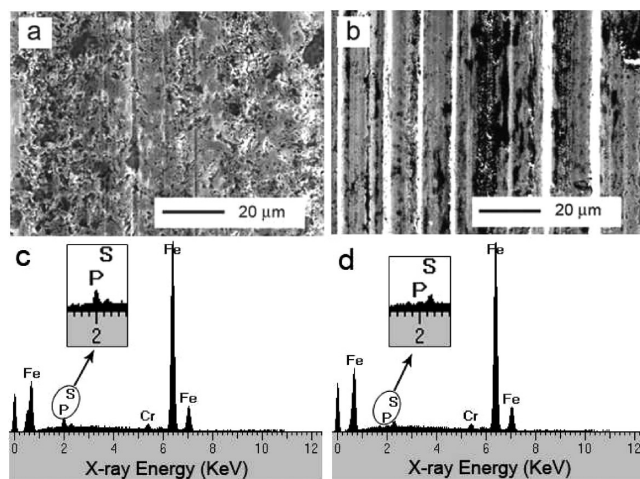


FIGURE 10. SEM micrographs of worn ball surfaces lubricated with the mineral base oil containing (a) 1.0% DOB-DTP and (b) 1.0% ZnDTP. (c, d) EDS spectra of tribofilms in a and b, respectively (the EDS spectra are the average of the whole area shown in the corresponding micrographs).

EDS analysis (Figures 8–10) shows deposition of phosphorus and sulfur on the worn surfaces for both DOB-DTP and ZnDTP additives. In the case of DOB-DTP additive, boron is not detected on the surfaces, probably because of the low sensitivity of the method.

The DOB-DTP additive is a polydentate ligand with a strong coordination capacity in terms of its molecular structure. It is expected to easily interact with the iron surfaces, forming stable protective layers that can reduce wear and inhibit corrosion of iron. We suggest the following mechanism of action of DOB-DTP with steel surfaces: Sulfur atoms present in the dialkyldithiophosphate group of this compound will interact with iron, forming iron sulfide layers on the steel surfaces. The B–S bond has a high reactivity toward metal ions including iron. Therefore, the whole molecule will then decompose and inorganic layers containing phosphorus, sulfur, oxygen, and boron will deposit on the steel surfaces, enhancing performance of the tribological contacts.

4. CONCLUSIONS

S-Di-*n*-octoxyboron-*O,O'*-di-*n*-octyldithiophosphate (DOB-DTP) was successfully synthesized and characterized by the elemental analysis, FT-IR, and ^1H , ^{13}C , ^{31}P , and ^{11}B NMR spectroscopy. The thermal behavior was characterized by TG/DTG, DTA, and QMS analyses. The tribological properties of this novel additive admixed in the mineral base oil were evaluated in comparison with *O,O'*-di-*n*-butyl-dithiophosphato-zinc(II) in a four ball tribometer. DOB-DTP has a good thermal stability up to ca. 268 °C under the conditions used in this study. Dihydrogen sulfide and olefins, which are typical products of decomposition of metals dialkyldithiophosphates, were formed upon heating of the compound above this temperature. The extent of wear was significantly reduced when both DOB-DTP and ZnDTP were admixed into the base oil, whereas the friction coefficient increased in both cases. DOB-DTP showed better antiwear and friction properties compared with ZnDTP in the concentration range (0.1–1.0 wt %) studied. The friction coefficient was stable

over time for all these concentrations of DOB-DTP in the base oil, whereas it was unstable at low concentrations of ZnDTP in the base oil. Phosphorus and sulfur were detected by SEM/EDS analysis on the worn steel surfaces at concentrations studied, 0.1, 0.4, and 1.0 wt %, for both DOB-DTP and ZnDTP additives. However, phosphorus was the predominant element in depositions from DOB-DTP, whereas it was sulfur and not phosphorus in the surface layers formed by products of decomposition of ZnDTP on steel surfaces.

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Supporting Information Available: ^1H , ^{13}C , ^{31}P , and ^{11}B liquid-state NMR spectra of DOB-DTP, ZnDTP, and triethylborate (compound I) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- Zhang, Z.; Najman, M.; Kasrai, M.; Bancroft, G. M.; Yamaguchi, E. S. *Tribol. Lett.* **2005**, *18*, 43–51.
- Gao, F.; Furlong, O.; Kotvis, P. V.; Tysoe, W. T. *Langmuir* **2004**, *20*, 7557–7568.
- Martin, J. M. *Tribol. Lett.* **1999**, *6*, 1–8.
- Taylor, L.; Dratva, A.; Spikes, H. *Tribol. Trans.* **2000**, *45*, 469–79.
- So, H.; Lin, Y. C.; Huang, G. G. S.; Chang, T. S. T. *Wear* **1993**, *166*, 17–26.
- Ito, K.; Martin, J. M.; Minfray, C.; Kato, K. *Tribol. Int.* **2006**, *39*, 1538–1544.
- Heuberger, R.; Rossi, A.; Spencer, N. D. *Tribol. Lett.* **2007**, *28*, 209–222.
- Isaksson, M.; Frick, M.; Gruberger, B.; Ponten, A.; Bruze, M. *Contact Dermatitis* **2002**, *46*, 248–249.
- Cisson, C. M.; Rausina, G. A. *Lubr. Sci.* **1996**, *8*, 145–177.
- Spikes, H. *Tribol. Lett.* **2004**, *17*, 465–485.
- Zinke, H.; Schumacher, R. *Wear* **1994**, *179*, 45–48.
- Sarin, R.; Tuli, D. K.; Sureshbabu, A. V.; Misra, A. K.; Rai, M. M.; Bhatnagar, A. K. *Tribol. Int.* **1994**, *27*, 379–386.
- Jianqiang, H.; Huanqin, Z.; Li, W.; Xianyong, W.; Feng, J.; Zhiming, Z. *Wear* **2005**, *259*, 519–523.
- Zhang, J.; Liu, W.; Xue, Q.; Wang, Q. *Wear* **1998**, *216*, 35–40.
- Sarin, R.; Tuli, D. K.; Rai, M. M.; Mehta, A. K.; Bhatnagar, A. K. *Lubr. Eng.* **1995**, *51*, 313–320.
- Boshui, C.; Junxiu, D.; Guoxu, C. *Wear* **1996**, *196*, 16–20.
- Margielewski, L.; Stanecka, R. *Lubr. Sci.* **2002**, *14*, 333–348.
- Rowe, C. N.; Dickert, J. J. *ASLE Trans.* **1967**, *10*, 85–90.
- Born, M.; Hipeaux, J. C.; Marchand, P.; Parc, G. *Lubr. Sci.* **1992**, *4*, 93–116.
- Cragg, R. H.; Husband, J. P. N.; Weston, A. F. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3685–3689.
- Ito, M.; Tokitoh, N.; Okazaki, R. *Organometallics* **1997**, *16*, 4314–4319.
- Kreuz, K. L.; Fein, R. S.; Dundy, M. *ASLE Trans.* **1967**, *10*, 67–76.
- Baldwin, B. A. *Wear* **1977**, *45*, 345–353.
- Spikes, H. *Lubr. Sci.* **2008**, *20*, 103–136.
- Liu, W.; Xue, Q.; Zhang, X.; Wang, H.; Huang, C. *Tribol. Trans.* **1992**, *48*, 475–479.
- Liu, W.; Jin, Z.; Xue, Q. *Lubr. Sci.* **1994**, *7*, 49–60.
- Herdan, J. M. *Lubr. Sci.* **2000**, *12*, 265–276.
- Feng, I. M.; Perilstein, W. L.; Adams, M. R. *ASLE Trans.* **1963**, *6*, 60–6.
- Chung, H. Y.; Weinberger, M. B.; Levine, J. B.; Kavner, A.; Yang, J. M.; Tolbert, S. H.; Kaner, R. B. *Science* **2007**, *316*, 436–439.
- Ozdemir, O.; Usta, M.; Bindal, C.; Ucisik, A. H. *Vacuum* **2006**, *80*, 1391–1395.
- Martini, C.; Palombarini, G. *J. Mater. Sci.* **2004**, *39*, 933–937.
- Klepper, C. C.; Williams, J. M.; Truhan, J. J.; Qu, J.; Riestler, L.; Hazelton, R. C.; Moschella, J. J.; Blau, P. J.; Anderson, J. P.; Popoola, O. O.; Keitz, M. D. *Thin Solid Films* **2008**, *516*, 3070–3080.
- Lovell, M.; Higgs, C. F.; Deshmukh, P.; Mobley, A. *J. Mater. Process. Technol.* **2006**, *177*, 87–90.
- Masenelli-Varlota, K.; Kasrai, M.; Bancroft, G. M.; Stasio, G. D.; Gilbert, B.; Yamaguchi, E. S.; Ryason, P. R. *Tribol. Lett.* **2003**, *14*, 157–166.
- Martin, J. M.; Grossiord, C.; Varlot, K.; Vacher, B.; Igarashi, J. *Tribol. Lett.* **2000**, *8*, 193–201.
- Grossiord, C.; Martin, J. M.; Varlota, K.; Vacher, B.; Mogne, T. L.; Yamada, Y. *Tribol. Lett.* **2000**, *8*, 203–212.
- Stanulov, K. G.; Harhara, H. N.; Cholakov, G. S. *Tribol. Int.* **1998**, *31*, 257–263.
- Li, Y. R.; Pereira, G.; Lachenwitzer, A.; Kasrai, M.; Norton, P. R. *Tribol. Lett.* **2008**, *29*, 11–20.
- Ivanov, A. V.; Antzutkin, O. N.; Larsson, A. C.; Kritikos, M.; Forsling, W. *Inorg. Chim. Acta* **2001**, *315*, 26–35.
- Larsson, A. C.; Ivanov, A. V.; Forsling, W.; Antzutkin, O. N.; Abraham, A. E.; deDios, A. *J. Am. Chem. Soc.* **2005**, *127* (7), 2218–2230.
- Nizamov, I. S.; Sergeenko, G. G.; Batyeva, E. S.; Azancheev, N. M.; Al'fonsov, V. A. *Heteroat. Chem.* **2000**, *11*, 102–106.
- Singh, O. P.; Mehrotra, R. K.; Srivastava, G. *Phosphorus, Sulfur Silicon* **1991**, *60*, 147–158.
- Choi, U. S.; Ahn, B. G.; Kwon, O. K.; Chun, Y. J. *Tribol. Int.* **1997**, *30*, 677–683.
- Kawamura, M. *Wear* **1982**, *77*, 287–294.
- Huq, M. Z.; Chen, X.; Aswath, P. B.; Elsenbaumer, R. L. *Tribol. Lett.* **2005**, *19*, 127–134.
- Joseph, J.; Jr, D.; Rowe, C. N. *J. Org. Chem.* **1967**, *32*, 647–653.
- Zhang, J.; Yang, S.; Liu, W.; Xue, Q. *Wear* **2000**, *237*, 49–53.
- Hua, W.; Jing, L.; Hongling, Y.; Xiangqiong, Z.; Lingbo, L.; Tianhui, R. *Tribol. Int.* **2007**, *40*, 1246–1252.
- Suna, Y.; Hu, L.; Xue, Q. *Wear* **2009**, *266*, 917–924.
- Fan, K.; Li, J.; Ma, H.; Wu, H.; Ren, T.; Kasrai, M.; Bancroft, G. H. *Tribol. Int.* **2008**, *41*, 1226–1231.
- McQueena, J. S.; Gao, H.; Blacka, E. D.; Gangopadhyay, A. K. *Tribol. Int.* **2005**, *38*, 289–297.
- Kano, M.; Yasuda, Y. *Lubr. Sci.* **2004**, *17*, 95–103.

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