Original Article

Institution of MECHANICAL ENGINEERS
Journal of ENGINEERING TRIBOLOGY

Proc IMechE Part J:
J Engineering Tribology
2016, Vol. 230(4) 367–375

DOI: 10.1177/1350650115601879
pij.sagepub.com
SAGE

The tribological performance of a long chain alkyl phenylboric ammonium derivative and its interaction with ZDDP

Zhipeng Li[1,2], Yawen Zhang[1], Tianhui Ren[1], Xiangqiong Zeng[3], Emile van der Heide[3] and Yidong Zhao[4]

Abstract

A long chain alkyl phenylboric ammonium derivative (DBBM) was synthesized as a lubricating additive. The tribological performances of DBBM and combinations of DBBM and ZDDP as additives were evaluated, which suggests that DBBM has better tribological properties than ZDDP. X-ray absorption near edge structure spectroscopy was used for the analysis of thermal films and tribofilms. The results indicate that the boron in additive mainly forms trigonal and tetrahedral coordination boron both in thermal films and tribofilms, while sulfur mainly generates iron sulfate in thermal films and iron sulfide, iron disulfide, and iron sulfate in tribofilms. It also can be found that it is more likely to form low valence sulfur when the concentration of ZDDP increases in the combinations.

Keywords

Phenylboric ammonium derivative, ZDDP, tribological performance, X-ray absorption near edge structure, surface analysis

Date received: 28 November 2014; accepted: 28 July 2015

Introduction

Zinc dialkyl-dithiophosphate (ZDDP) has been used as additive in lubricating oil for several decades for their excellent anti-oxidation, anti-wear (AW) and easy preparation, as well as low cost and the tribological mechanisms also have been studied.[1–5] However, with the increasing demands for the environmental protection and energy saving, some problems of ZDDP emerged simultaneously. Zinc contained in ZDDP can generate ashes that block the filters in car exhaust systems, while phosphorus will poison the emission-control catalysts.[6] Therefore, it is imperative to develop novel environmental-friendly lubricant additives to replace ZDDP totally or partially.

Boron-containing compounds have been reported as good lubricant additives for their AW property, high temperature resistance, and good film strength.[7,8] Borate esters as a kind of oil-soluble boron-containing additives with advantages of tribological performances could be potential environmental-friendly lubricating additives.[9–11] However, their susceptibility to hydrolysis is the major drawback that restricts the use in lubricants (resulting in the liberation of oil-insoluble and abrasive boric acid).[12] Inorganic borates are another type of boron-containing additives. A variety of inorganic borates have been reported as lubricating additives, such as boric acid, hexagonal boron nitride, sodium metaborate, titanium borate, zinc borate, aluminum borate, ultrafine powder strontium borate, magnesium borate, lanthanum borate, and cerium borate.[13] Nevertheless, the solubility of inorganic borates in base oil is the main limitation for wider application.[14]

In consideration of the advantages and disadvantages of borate esters and inorganic borates, we attempt to develop a new organic borate ammonium, including the advantages of borate esters and inorganic borates and avoiding the disadvantages of borate esters and inorganic borates. It has been reported that long chain alkyl phenylboric group

[1]School of Chemistry and Chemical Engineering, Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Shanghai Jiao Tong University, PR China
[2]Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, PR China
[3]Laboratory for Surface Technology and Tribology, University of Twente, The Netherlands
[4]Chinese Academy of Sciences, Institute of High Energy Physics, PR China

Corresponding author:
Tianhui Ren, School of Chemistry and Chemical Engineering, Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Shanghai Jiao Tong University, 200240, PR China.
Email: thren@sjtu.edu.cn

can significantly improve the hydrolytic stability of borate esters.[15] Therefore, long chain alkyl phenylboric acid and long chain alkyl amine were introduced to prepare the designed additive. In this paper, a long chain alkyl phenylboric ammonium derivative (DBBM) was synthesized as lubricating additive. For comparison, the tribological properties of DBBM and zinc dialkyl dithiophosphates (ZDDP) as additives in base oil were evaluated by a four-ball tribometer to determine whether DBBM is a potential candidate for the substitution of ZDDP. Furthermore, X-ray absorption near edge structure (XANES) spectroscopy was adopted to further understand the tribological reactions on the metal surfaces of frictional pairs.

Experimental details

Base oil and additives

A commercial mineral oil (HVI WH150) was used as base oil, supplied by PetroChina Lanzhou Lubricating Oil R&D Institute in Lanzhou, China. The physical properties of the HVI WH150 mineral oil are given in Table 1. The zinc propyl octyl primary-secondary dialkyl dithiophosphate (ZDDP, also coded as T205 in Chinese market) was supplied by Liaoning Tianhe Fine Chemical Co., Ltd. Both of the oil and additive were used without any further treatment. The key precursor, 4-dodecylphenylboric acid, was synthesized adapted from the reported procedures.[16–18]

The octadecylammonium dodecylphenyl borate (DBBM) (Figure 1) was prepared as follows: 4-dodecylphenylboric acid (14.51 g, 0.05 mol) and n-octadecylamine (13.48 g, 0.05 mol) were added to a 50 mL round-bottom flask, the reaction mixture was stirred for 6 h at 80 °C, resulting in (27.70 g, 0.05 mol) DBBM in 99% yield. The synthesized additive was characterized by infrared spectroscopy (IR), NMR, and elemental analysis. From the IR spectrum, the absorption for –OH and $–NH_2$ ($\sim$3400 cm^{-1}) significantly decreases (Figure 2), which indicates that the 4-dodecylphenylboric acid and n-octadecylamine have reacted to form the octadecylammonium dodecylphenyl borate. The elemental analysis result is in agreement with the calculated data (Table 2).

Octadecylammonium dodecylphenyl borate (DBBM): $C_{36}H_{70}BNO_2$. IR (KBr) (cm^{-1}): 2955.8 m ($–CH_3$); 2922.2 s, 2852.6 m ($–CH_2–$); 607.5w (C=C); 1465.8 m, 1391.0 m ($–CH_3$); 1417.8 m ($-NH_3^+$); 1334.2 s ($–CH_2–$); 1319.5 s (B–O); 1287.4 m (C–N); 759.8 m (phenyl ring). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97–7.96 (2H, phenyl ring), 7.31 (3H, $-NH_3^+$), 7.20–7.19 (2H, phenyl ring), 3.34 (2H, $–CH_2–N$), 2.70 (2H, $Ph–CH_2–$), 1.63–1.26 (52H, $–CH_2–$), 0.88 (6H, $–CH_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 133.66, 128.13, 127.65, 126.94, 41.28, 37.02, 31.99, 29.74, 29.40, 26.83, 22.74, 14.15.

Thermal stability

The thermal stability of DBBM was investigated by thermo-gravimetric analysis (TGA), performed on a TA Q5000 thermal analysis system, in nitrogen atmosphere with a heating rate of 20 °C/min from ambient temperature to 700 °C.

Friction and wear test

The tribological properties were evaluated using a MMW-1 four-ball tester made in Ji'nan instrument manufacturer, PR China. All the tests were conducted at room temperature with the rotating velocity of

Table 1. Physical properties of the HVI WH150 mineral oil.

Parameter	Value
Density (20 °C, g/cm^3)	0.844
Kinematic viscosity (mm^2/s)	
40 °C	29.95
100 °C	5.512
Viscosity index	125
Pour point (°C)	−30
Open flash point (°C)	226
Acid value (mg KOH/g)	0.01
Extrinsic feature	Transparency

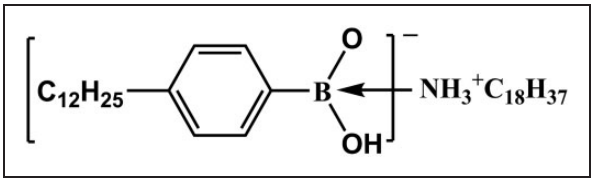

Figure 1. The molecular structure of DBBM.

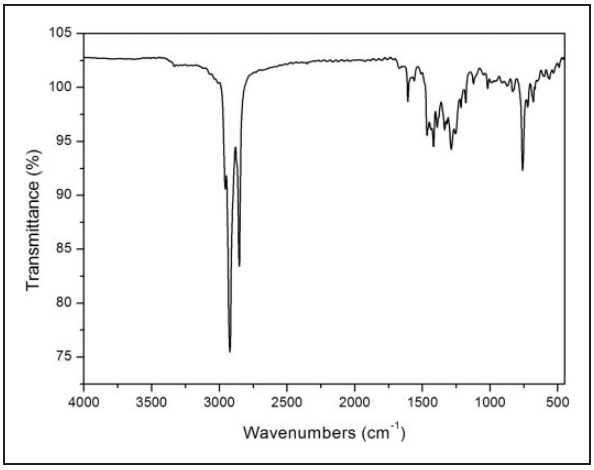

Figure 2. The IR spectrum of the synthesized additive DBBM.

Table 2. Elemental analysis result of the synthesized additive DBBM.

Item	C (wt%)	H (wt%)	N (wt%)	B (wt%)
DBBM	77.35 (77.25)[a]	12.53 (12.60)[a]	2.52 (2.50)[a]	1.85 (1.93)[a]

[a]Calculated value (balanced by oxygen).

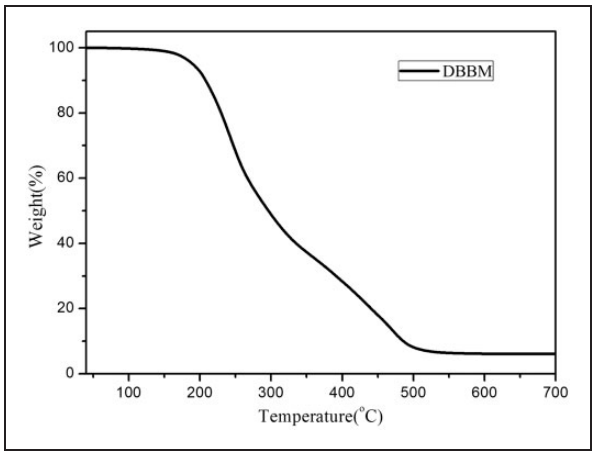

Figure 3. The TGA curve of DBBM.

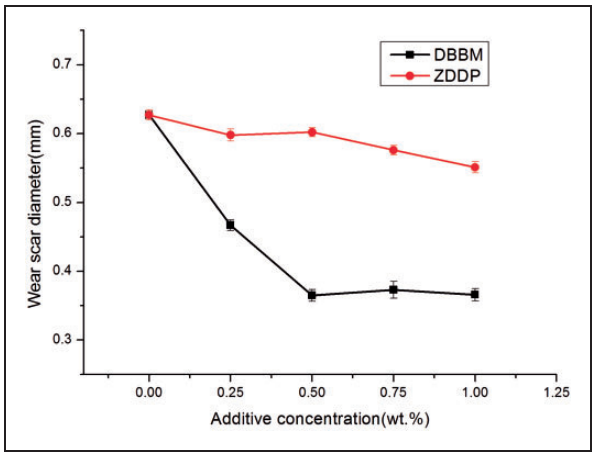

Figure 4. The effect of additive concentration on the WSD under 392 N (rotary velocity, 1450 r/min; duration, 30 min).

1450 r/min, and test duration of 30 min.[19] All the balls used in the test are of 12.7 mm diameter, made of GCr15 bearing steel, with an HRC of 59–61 (C, 0.95–1.05%; Si, 0.15–0.35%; P, <0.027%; S, <0.020%; Ni, <0.30%; Mn, 0.20–0.40%; Cr, 1.30–1.65%; Cu, <0.25%). The wear scar diameters (WSD) of the three lower balls were measured by an optical microscope with an accuracy of ±0.01 mm. The friction coefficient was automatically recorded by a computer connected to the four-ball test machine. Duplicate tests were conducted with each oil sample in case of accidental error. If the WSDs showed a relative error above 10%, additional tests would be run until at least two of the results agreed within 10%.

Worn surface analysis

A JSM-5600LV scanning electron microscope (SEM) was used to study the worn surface morphologies. The lower ball used for SEM analysis was washed ultrasonically with petroleum ether and dried in atmosphere after friction and wear test.

XANES data were collected at the Beijing Synchrotron Radiation Facility (BSRF), situated at the 2.2 GeV storage ring, BEPC.[20] Sulfur K-edge spectra were obtained on the double-crystal monochromator (DCM) covering the photon region of 2450–2500 eV at the sulfur K-edge. The photon absorption spectra were recorded in total electron yield (TEY) mode.[15] Boron K-edge spectra were recorded using the soft X-ray optics beamline. This beamline is monochromatized by a Monk-Gillieson monochromator, using an 800 mm^{-1} grating to cover the photon region of 50–1700 eV. The photon absorption spectra were recorded in total electron yield (TEY) mode with the resolution of 1000 ($E/\Delta E$) to provide the chemical information of reaction film on the metal surfaces.[21] The thermal films were prepared under the following parameters: the ball was immersed in a lubricating oil containing additive at the temperature of 150 °C for 6 h,[22] while the tribofilms for XANES evaluation were generated from the tribological tests. All the coupons were gently rinsed in petroleum ether prior to XANES analyses. And several model compounds were also scanned and recorded for identification and comparison.

Results and discussion

Thermal stability

Figure 3 shows the TGA curve of the synthesized additive DBBM. It can be seen that DBBM begins to decompose around 150 °C, which is similar to ZDDP.[23] It has been reported that the lower the decomposition temperature, the higher the reactivity of the additive to react with a metal surface to form a protective film. From this point of view, it can be considered that the synthesized additive is suitable for using as AW additive.[24]

Anti-wear performance

Figure 4 shows the relationship between the wear scar diameter (WSD) and the additive concentration of DBBM and ZDDP under 392 N. It is obvious that

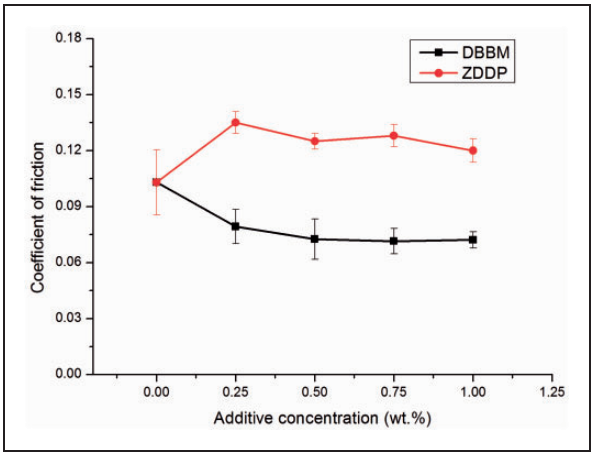

Figure 5. The effect of additive concentration on the COF under 392 N (rotary velocity, 1450 r/min; duration, 30 min).

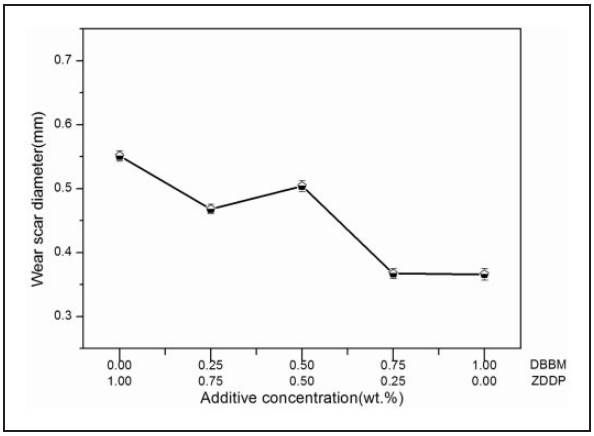

Figure 6. The variation of WSD with different combinations under 392 N (rotary velocity, 1450 r/min; duration, 30 min).

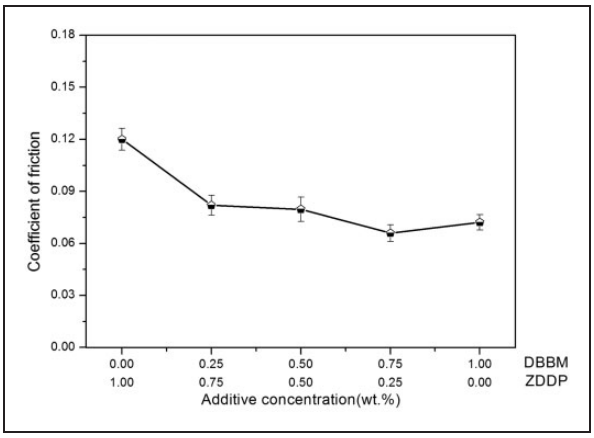

Figure 7. The variation of COF with different combination under 392 N (rotary velocity, 1450 r/min; duration, 30 min).

both the synthesized additive DBBM and ZDDP can reduce the WSD compared with the base oil, and DBBM is more effective in reducing WSD than that of ZDDP, which indicates that the synthesized additive possesses excellent AW property. Moreover, The WSDs for ZDDP decrease with the increase in additive concentration while the WSDs for DBBM firstly decrease sharply with the increase in additive concentration when the additive concentration is below 0.50 wt%, then stay relatively stable when the additive concentration is above 0.50 wt%. This may be due to the different adsorption abilities of DBBM and ZDDP on the metal surfaces of frictional pairs.[25] DBBM contains hydroxyl and amino group with high polarity, which makes it to have high affinity towards iron.[26] More DBBM adsorbs on the metal surfaces and reacts to form a protective layer reducing wear. When the additive concentration is above 0.50 wt%, due to the adsorption equilibrium, the wear scar stays relatively stable.

Friction-reducing performance

Figure 5 exhibits the friction-reducing performances of DBBM and ZDDP with different additive concentrations in base oil under 392 N. As is shown in Figure 5, the two additives, DBBM and ZDDP, exhibit completely opposite friction-reducing properties. For the performance of ZDDP, the coefficient of friction (COF) is higher than that of base oil and decreases slowly with the increase in the additive concentration. This is ascribed to the high shear strength of the polyphosphates generated from ZDDP on the metal surfaces during the sliding process.[27] However, the COF of DBBM firstly decreases significantly when the synthesized additive is added to the base oil, then the decreasing trend of the curve becomes decline, which suggests that DBBM has good friction-reducing property. This could be attributed to the formation of tribological film composed of adsorption and/or reaction film on the metal surfaces, which has lower shear strength or decreases the roughness of frictional pairs, therefore the COF of DBBM decreases.[11]

Combination of DBBM and ZDDP

The tribological performances of the combinations of DBBM and ZDDP were also evaluated (concentration of DBBM + concentration of ZDDP = 1.0 wt%). Figures 6 and 7 exhibit AW and friction-reducing properties, respectively. As for the AW property, the WSD decreases with the increase in additive concentration of DBBM, except for 0.50 wt%. This could be ascribed to the compete adsorption between DBBM and ZDDP.[28] When DBBM is added to the combination, due to the big polarity of DBBM, it preferably adsorbs on the metal surfaces to form a tribological layer composed of adsorption and/or reaction film. However, because of the influence of ZDDP (especially for 0.50 wt%), the compactness of the tribological film is not as good as that of DBBM alone, resulting in the relatively worse AW performance than that of DBBM at the same additive concentration (1.0 wt%). When the

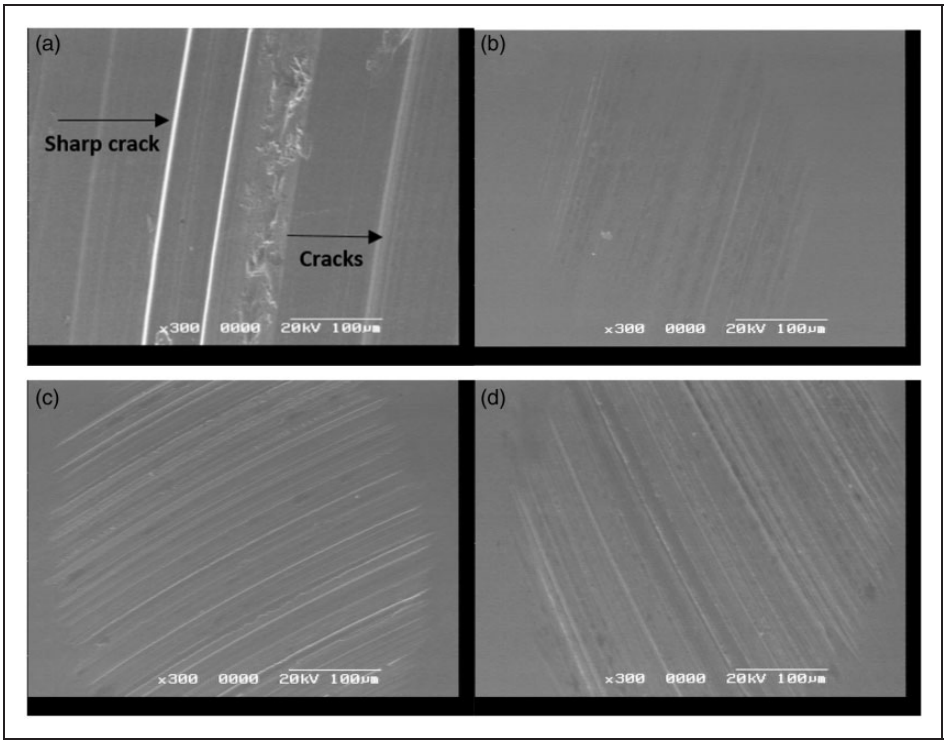

Figure 8. SEM morphologies of wear scar: (a) base oil; (b) 1.0 wt% DBBM; (c) 0.50 wt% DBBM + 0.50 wt% ZDDP; (d) 1.0 wt% ZDDP (applied load, 392 N; rotary velocity, 1450 r/min; duration, 30 min).

additive concentration of DBBM is above 0.50 wt%, the influence of ZDDP decreases, therefore the AW performance increases. For the performance of friction-reducing property, the COF also decreases with the increase in additive concentration of DBBM, suggesting that the addition of DBBM to ZDDP can improve the friction-reducing property of ZDDP, especially when the additive concentration of DBBM is 0.75 wt%. This indicates that the two additives, DBBM and ZDDP, have synergistic effect on the friction-reducing performance.

Though DBBM and ZDDP do not have a synergistic effect on the AW performance, and the AW performance is improved when the addition of synthesized additive to ZDDP; moreover, the friction-reducing property is also increased. This suggests that the synthesized additive shows a potential to replace ZDDP as lubricant additive totally or partially.

Surface analysis

It has been confirmed that the synthesized additive is effective in reducing wear and improving the friction-reducing performance of base oil. Therefore, it is worth investigating the tribological reactions of the synthesized additive on the metal surfaces.

SEM analysis of the worn surface

The SEM morphologies of wear scar lubricated by base oil, 1.0 wt% DBBM, 0.5 wt% DBBM+0.5 wt% ZDDP, and 1.0 wt% ZDDP under 392 N are displayed in Figure 8. It can be seen clearly that severe cracks and furrows occur lubricated by base oil alone (Figure 8(a)), while only slight wear tracks appear lubricated by DBBM (Figure 8(b)). Furthermore, the wear tracks lubricated by DBBM are much shallower and more uniform than that of combination of DBBM and ZDDP (Figure 8(c)) and ZDDP (Figure 8(d)), which suggests that the boundary lubricating films generated from DBBM could effectively prevent the rubbing surface from direct contact,[25] resulting in excellent AW and friction-reducing properties of the synthesized additive, corresponding to tribological data shown in Figures 4 to 7.

XANES analysis of thermal films and tribofilms

In order to obtain the chemical nature of protective film on the metal surfaces of frictional pairs, XANES spectroscopy was used to investigate the thermal films and tribofilms generated from DBBM and combinations of DBBM and ZDDP as additives in base oil. Some model compounds were also tested for comparison to determine the chemical nature of evaluated films.

Figure 9 shows the B K-edge XANES spectra of thermal films generated from DBBM and combinations of DBBM and ZDDP in base oil along with some model compounds recoded in the total electron yield (TEY) mode. The peak positions are assigned and summarized in Table 3. Using model compound spectra, peak b and peak d correspond to trigonal coordination form of boron, and peak c is the characteristic position of tetrahedral coordination form of

boron.[5,29] It can be seen that the boron in the additives generates mainly trigonal coordination form of boron while few tetrahedral coordination form of boron, which suggests that the friction heat generated from rubbing process is an important factor in the formation of protection film on the metal surfaces of friction pairs. This is in agreement with the hypothesis of antecedent report that the additive can partially undergo transformation to produce tetrahedral boron species in the thermal films.[5]

Figure 10 exhibits the B K-edge XANES spectra of tribofilms generated from DBBM and combinations of DBBM and ZDDP in base oil recoded in the total electron yield (TEY) mode, and their peak positions along with some relevant model compounds are listed in Table 4. The three spectra of DBBM with different concentrations, spectra (A), (B), and (C), all show the peaks corresponding to trigonal and tetrahedral coordination form of boron and have no significant change except for 1.0 wt%. The spectrum (C) shows a

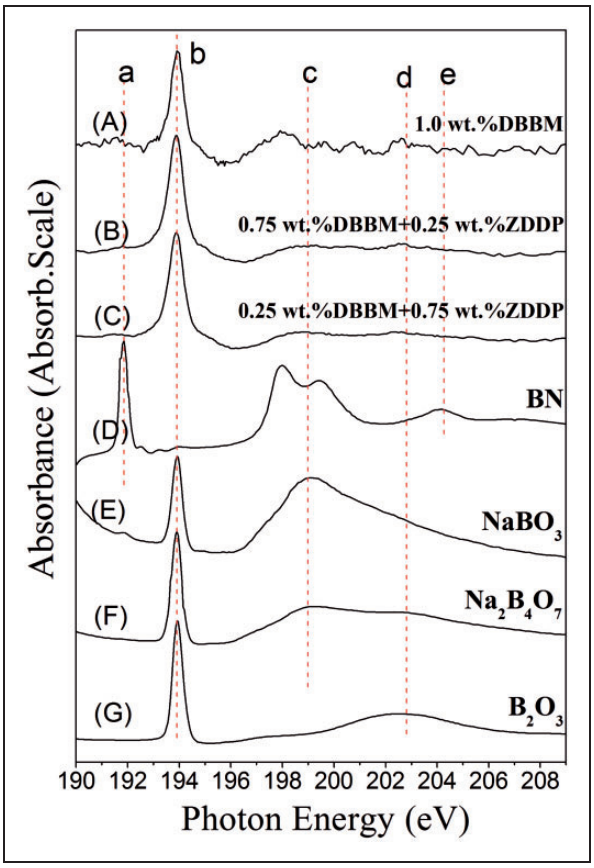

Figure 9. The B K-edge XANES (TEY) spectra of thermal films generated from DBBM and combinations of DBBM and ZDDP with several model compounds.

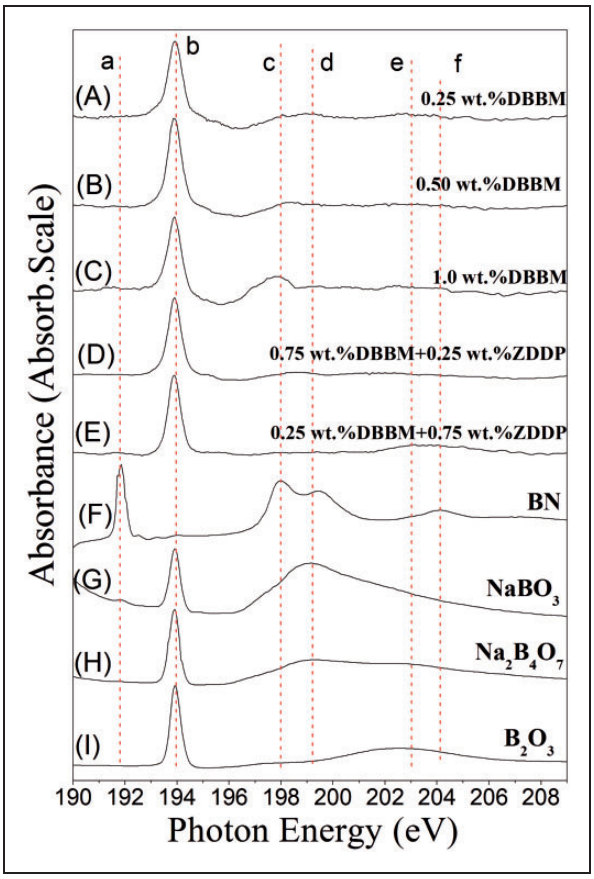

Figure 10. The B K-edge XANES (TEY) spectra of tribofilms generated from DBBM and combinations of DBBM and ZDDP with model compounds.

Table 3. Peak positions of B K-edge (TEY) spectra of thermal films along with several model compounds.

	K-edge (eV)				
Samples	a	b	c	d	e
1.0 wt% DBBM		193.9	199.0	202.7	
0.75 wt% DBBM + 0.25 wt% ZDDP		193.9	198.9	202.7	
0.25 wt% DBBM + 0.75 wt% ZDDP		193.9	198.8	202.7	
BN	191.8				204.2
$NaBO_3$		193.9	199.1		
$Na_2B_4O_7$		193.9	199.1	202.8	
B_2O_3		193.9		202.8	

Table 4. Peak positions of B K-edge (TEY) spectra of tribofilms along with model compounds.

	K-edge (eV)					
Samples	a	b	c	d	e	f
0.25 wt% DBBM		193.9		199.0	202.7	
0.50 wt% DBBM		193.9		199.0	202.7	
1.0 wt% DBBM		193.9		199.0	202.7	
0.75 wt% DBBM + 0.25 wt% ZDDP		193.9		198.9	202.7	
0.25 wt% DBBM + 0.75 wt% ZDDP		193.9			202.9	
BN	191.8		198.0			204.2
$NaBO_3$		193.9		199.1		
$Na_2B_4O_7$		193.9		199.1	202.8	
B_2O_3		193.9			202.8	

peak at about 198 eV, which belongs to BN. However, it does not show the apparent peak at 191.8 eV, peak at 199.4 eV and peak at 204.2 eV for the characteristic peak of BN, therefore it cannot determine the existence of BN in the tribofilm. Moreover, the spectrum for 0.75 wt% DBBM+0.25 wt% ZDDP (spectrum (D)) shows three characteristic peaks of boron, identified as trigonal and tetrahedral coordination form of boron, while the spectrum for 0.25 wt% DBBM + 0.75 wt% ZDDP (spectrum (E)) only shows the two peaks corresponding to the trigonal coordination boron and there is no signal for tetrahedral coordination form of boron, which should be attributed to the anti-oxidation property of ZDDP with the increase in the ratio of ZDDP.

Figure 11 shows the S K-edge XANES spectra of thermal films and tribofilms generated from combinations of DBBM and ZDDP in base oil along with some model compounds recoded in the fluorescence yield (FY) mode. The peak positions are assigned and summarized in Table 5. It can be seen that the XANES spectra of thermal films for the two different combinations of DBBM and ZDDP, spectra (A) and (C), are similar to each other, while the spectra for their trobofilms, spectra (B) and (D), are quite different. Compared with the model compounds, the peak at 2481.7 eV of thermal films and tribofilms corresponds to iron sulfate and the peak at 2477.4 eV of tribofilms is ascribed to iron sulfide. The peak e of thermal films is much stronger than any other peaks, which means that the thermal films mainly consist of iron sulfate. The weak peak at about 2473.1 eV both in thermal films and tribofilms is identified as alkyl sulfide, which suggests that ZDDP decomposes and deposits on the metal surfaces to form an adsorption film under the friction heat generated from rubbing process.[30]

Except for the peaks of sulfate and sulfide, the spectra (B) and (D) also show peaks at 2470.0 eV and 2471.3 eV, which corresponds to iron sulfide and iron disulfide, respectively. It is clear that peak a and peak b become stronger with the increase in the concentration of ZDDP in the combinations, while peak e becomes weaker. This suggests that it is more likely to form low valence sulfur when the concentration of ZDDP increases in the combinations, which may be also ascribed to the anti-oxidation property of ZDDP.

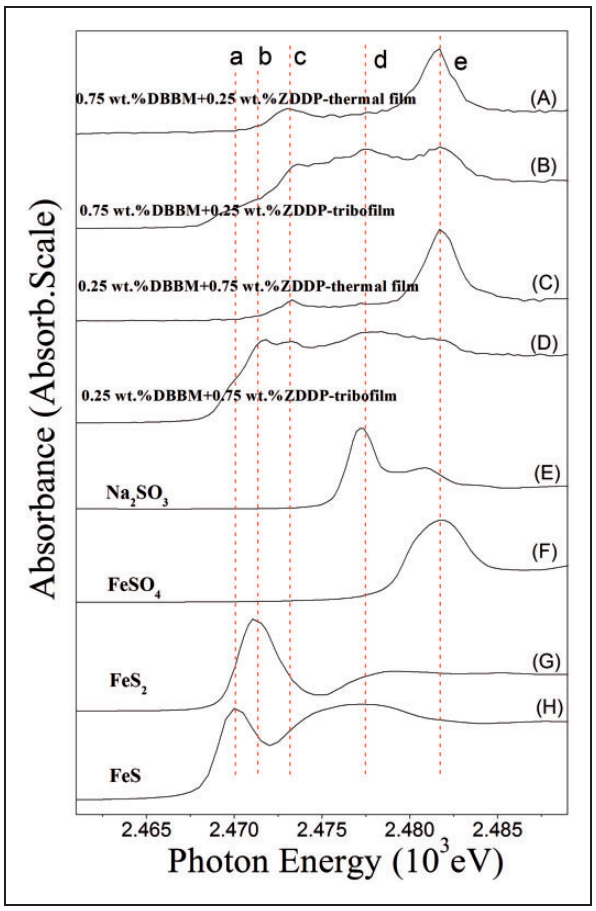

Figure 11. The S K-edge XANES (FY) spectra of thermal films and tribofilms generated from combinations of DBBM and ZDDP in base oil with model compounds.

Based on the surface analysis by SEM and XANES above, it can be concluded that under the boundary

Table 5. Peak positions of S K-edge (FY) spectra of thermal films and tribofilms with model compounds.

	K-edge (eV)				
Samples	a	b	c	d	e
0.75 wt% DBBM + 0.25 wt% ZDDP-thermal film			2473.0		2481.7
0.75 wt% DBBM + 0.25 wt% ZDDP-tribofilm	2470.0	2471.3	2473.2	2477.4	2481.7
0.25 wt% DBBM + 0.75 wt% ZDDP-thermal film			2473.1		2481.7
0.25 wt% DBBM + 0.75 wt% ZDDP-tribofilm	2470.0	2471.4	2473.1	2477.4	2481.7
Na_2SO_3				2477.3	
$FeSO_4$					2481.7
FeS_2		2471.2			
FeS	2470.0			2477.0	

lubrication condition, the tribochemical reactions of the boron in DBBM produce trigonal and tetrahedral boron species on the metal surfaces of frictional pairs, which prevents the metal surfaces from directly contact and the friction heat generated from rubbing process is an important factor in the formation of protection film. As for the combination of DBBM and ZDDP, the thermal films are mainly composed of alkyl sulfide and iron sulfate while the tribofilms mainly consist of alkyl sulfide, iron sulfide and iron disulfide as well as iron sulfate. Furthermore, the signals for iron sulfide and iron disulfide become stronger with the increase in the concentration of ZDDP in the combinations, which suggests that it is more likely to form low valence sulfur when the concentration of ZDDP increases in the combinations. This may be ascribed to the anti-oxidation property of ZDDP. In addition, according to the tribological performance of DBBM and combinations of DBBM and ZDDP, it demonstrates that the synthesized DBBM includes the advantages of borate esters and inorganic borates with good tribological properties, and avoids the disadvantages of borate esters and inorganic borates without the problems of hydrolytic stability and oil-insolubility.

Conclusions

The tribological properties of DBBM and its interaction with ZDDP have been investigated using a four-ball tester. The B and S K-edge XANES spectroscopy have been used to determine the chemical nature of thermal films and tribofilms generated from DBBM and combinations of DBBM and ZDDP. The conclusions can be summarized as follows:

1. The synthesized additive DBBM possesses better friction-reducing and AW properties than that of ZDDP. Though DBBM and ZDDP do not have a synergistic effect on the AW performance, the AW performance is improved when the addition of synthesized additive to ZDDP; moreover, the friction-reducing property is also increased, which suggests that the synthesized additive shows a potential to replace ZDDP as lubricant additive totally or partially.
2. According to the B XANES analysis of the thermal films and tribofilms of DBBM and its combinations with ZDDP, the thermal films and tribofilms are mainly composed of trigonal and tetrahedral form of boron, which suggests that the friction heat generated from rubbing process is an important factor in the formation of protection film on the metal surfaces of friction pairs.
3. As for the S XANES analysis of the combinations of DBBM and ZDDP, the thermal films mainly consist of sulfate and a little alkyl sulfide while the tribofilms are mainly composed of iron sulfide, iron disulfide and iron sulfate as well as alkyl sulfide. Furthermore, it is more likely to form low valence boron and sulfur with the increase in the concentration of ZDDP, which should be ascribed to the anti-oxidation property of ZDDP.

Acknowledgements

We gratefully thank Beijing Synchrotron Radiation Facility for the XANES analysis.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: The authors are grateful to the National Natural Science Foundation of China (grant No. 21272157), the Beijing Synchrotron Radiation Facility (Grant No. SR06033) and the open projects of The Key State Lab of Solid Lubrication in Lanzhou of China (Grant No. 1205) for the financial support to the work reported here.

References

1. Rounds F. Contribution of phosphorus to the antiwear performance of zinc dialkyldithiophosphates. *ASLE Trans* 1985; 28: 475–485.

2. So H, Lin Y, Huang GGS, et al. Antiwear mechanism of zinc dialkyl dithiophosphates added to a paraffinic oil in the boundary lubrication condition. *Wear* 1993; 166: 17–26.
3. Wan Y, Kasrai M, Bancroft GM, et al. Characterization of tribofilms derived from zinc dialkyldithiophosphate and salicylate detergents by X-ray absorbance near edge structure spectroscopy. *Tribol Int* 2010; 43: 283–288.
4. Zhang Z, Yamaguchi ES, Kasrai M, et al. Tribofilms generated from ZDDP and DDP on steel surfaces: Part 1, growth, wear and morphology. *Tribol Lett* 2005; 19: 211–220.
5. Zhang Z, Yamaguchi ES, Kasrai M, et al. Interaction of ZDDP with borated dispersant using XANES and XPS. *Tribol Trans* 2004; 47: 527–536.
6. Huang W, Dong J, Wu G, et al. A study of S-[2-(acetamido) benzothiazol-1-yl]N,N-dibutyl dithiocarbamate as an oil additive in liquid paraffin. *Tribol Int* 2004; 37: 71–76.
7. Choudhary RB and Pande PP. Lubrication potential of boron compounds: An overview. *Lubr Sci* 2002; 14: 211–222.
8. Miller BP, Kotvis PV, Furlong OJ, et al. Relating molecular structure to tribological chemistry: Borate esters on copper. *Tribol Lett* 2012; 49: 21–29.
9. He Z, Xiong L, Qian L, et al. Tribological properties and hydrolysis stability study of benzothiazole borate derivative. *Lubr Sci* 2014; 26: 81–94.
10. Yao J, Wang Q and Dong J. Borate esters used as lubricant additives. *Lubr Sci* 2002; 14: 415–423.
11. Wang Y, Li J and Ren T. Tribological study of a novel borate ester containing s, P with high hydrolytic stability as a multifunctional lubricating additive. *Tribol Trans* 2008; 51: 160–165.
12. Yao J and Dong J. Improvement of hydrolytic stability of borate esters used as lubricant additives. *Lubr Eng* 1995; 51.
13. Shah FU, Glavatskih S and Antzutkin ON. Boron in tribology: From borates to ionic liquids. *Tribol Lett* 2013; 51: 281–301.
14. Hao L, Li L, Xu X, et al. Preparation and tribological properties of a kind of lubricant containing calcium borate nanoparticles as additives. *Ind Lubr Tribol* 2012; 64: 16–22.
15. Li Z, Li X, Zhang Y, et al. Tribological study of a highly hydrolytically stable phenylboronic acid ester containing benzothiazolyl in mineral oil. *Appl Surf Sci* 2014; 308: 91–99.
16. Yan X, Zhou S, Wang Y, et al. Propylene oxide assisted one-pot, tandem synthesis of substituted-1,3,4-oxadiazole-2(3H)-ones in water. *Tetrahedron* 2012; 68: 7978–7983.
17. Hall MA, Xi J, Lor C, et al. m-Azipropofol (AziPm) a photoactive analogue of the intravenous general anesthetic propofol. *J Med Chem* 2010; 53: 5667–5675.
18. Cai J, Farhat A, Tsitovitch PB, et al. Synthesis and photochromism of 1,2-bis(5-aryl-2-phenylethynylthien-3-yl)hexafluorocyclopentene derivatives. *J Photoch Photobio A* 2010; 212: 176–182.
19. Yan J, Zeng X, van der Heide E, et al. The tribological performance and tribochemical analysis of novel borate esters as lubricant additives in rapeseed oil. *Tribol Int* 2014; 71: 149–157.
20. Li J, Ma H, Ren T, et al. The tribological chemistry of polysulfides in mineral oil and synthetic diester. *Appl Surf Sci* 2008; 254: 7232–7236.
21. Li Z, Zhang Y, Ren T, et al. Tribological studies of highly hydrolytically stable N-containing long chain alkyl phenylborate esters in mineral oil. *Proc IMechE, Part J: J Engineering Tribology* 2014; 228: 770–779.
22. McFadden C, Soto C and Spencer ND. Adsorption and surface chemistry in tribology. *Tribol Int* 1997; 30: 881–888.
23. Huq MZ, Chen X, Aswath PB, et al. Thermal degradation behavior of zinc dialkyldithiophosphate in presence of catalyst and detergents in neutral oil. *Tribol Lett* 2005; 19: 127–134.
24. Zeng X, Wu H, Yi H, et al. Tribological behavior of three novel triazine derivatives as additives in rapeseed oil. *Wear* 2007; 262: 718–726.
25. Zeng X, Li J, Wu X, et al. The tribological behaviors of hydroxyl-containing dithiocarbamate-triazine derivatives as additives in rapeseed oil. *Tribol Int* 2007; 40: 560–566.
26. Shah FU, Glavatskih S and Antzutkin ON. Novel alkylborate–dithiocarbamate lubricant additives: Synthesis and tribophysical characterization. *Tribol Lett* 2011; 45: 67–78.
27. Yin ZF, Kasrai M, Fuller M, et al. Application of soft X-ray absorption spectroscopy in chemical characterization of antiwear films generated by ZDDP. 1. The effects of physical parameters. *Wear* 1997; 202: 172–191.
28. Fan K, Li J, Ma H, et al. Tribological characteristics of ashless dithiocarbamate derivatives and their combinations with ZDDP as additives in mineral oil. *Tribol Int* 2008; 41: 1226–1231.
29. Kasrai M, Fleet ME, Muthupari S, et al. Surface modification study of borate materials from B K-edge X-ray absorption spectroscopy. *Phys Chem Miner* 1998; 25: 268–272.
30. Zhang Z, Kasrai M, Bancroft GM, et al. Study of the interaction of ZDDP and dispersants using X-ray absorption near edge structure spectroscopy - Part 1: Thermal chemical reactions. *Tribol Lett* 2003; 15: 377–384.