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Tribological study of a highly hydrolytically stable phenylboronic acid ester containing benzothiazolyl in mineral oil

Zhipeng Li [a,b], Xiufeng Li [a], Yawen Zhang [a], Tianhui Ren [a,*], Yidong Zhao [c], Xiangqiong Zeng [d], E. van der Heide [d]

[a] School of Chemistry and Chemical Engineering, Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Shanghai Jiao Tong University, 200240, China
[b] Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
[c] Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China
[d] Laboratory for Surface Technology and Tribology, University of Twente, Drienerlolaan 5, 7522 NB Enschede, The Netherlands

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ABSTRACT

A novel long chain alkyl phenylboronic acid ester containing heterocyclic compound, bis (1-(benzothiazol-2-ylthio) propan-2-yl)-4-dodecylphenylboronic acid ester (DBBMT), was synthesized and characterized. The hydrolytic stability of the DBBMT was evaluated and the results show that DBBMT is of outstanding hydrolytic stability compared with normal borate esters, which indicates that the designed molecular structure, by introducing benzene ring to conjugate with the electron-deficient boron and the benzothiazole as a hinder group, is effective on obtaining a hydrolytically stable long chain alkyl phenylboronic acid ester. The tribological properties of DBBMT and ZDDP in mineral base oil were evaluated using a four-ball tribometer, which suggests that the DBBMT possesses comprehensive tribological properties and could be a potential candidate for the replacement of ZDDP. Furthermore, in order to understand the tribological behaviors, the worn surface was analyzed by X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) spectroscopy. The results indicate that the elements S, B, O and Fe perform complicated tribochemical reactions to form the compact tribological film composed of B_2O_3, FeS, Fe_3O_4 and $FeSO_4$.

1. Introduction

Zinc Dialkyl Dithiophosphates (ZDDPs) have been widely used in engine oil due to their good capacity of anti-wear (AW) and anti-oxidation, which prevents engine wear by forming a protective film on the rubbing surface [1]. The protective film is composed of adsorption film and tribological reaction film and the mostly effective components are sulfides and phosphates [2]. However, the existence of zinc, sulfur and phosphorus will impair the environment indirectly by poisoning emission-control catalysts and by blocking filters in car exhaust systems [3]. As the worldwide consensus of maintaining integrity of environment, the development of environment friendly lubricants becomes an urgent research topic nowadays [4].

In recent years, organic borate esters attract significant attention due to their excellent combination properties [3,5–7], such as low-toxicity, anti-wear and friction-reducing abilities, biodegradability and oxidation inhibition. On the other hand, it has been proven that the derivatives of heterocyclic compounds with compact structure possess remarkable anti-wear, anti-oxidant, anti-corrosion properties and outstanding thermal stabilities as well [8–13].

However, because of the electron-deficient boron, the borate esters are inclined to hydrolyze resulting in the liberation of an oil-insoluble and abrasive boric acid. This is regarded as the main limitation of the wide application of organic borate esters [14–16]. The hydrolytic stability of the borate esters could be improved by introducing nitrogen to coordinate with boron [16]. Even so, the N-containing borate esters do not meet the expectation of tribologists, because of the weakness of the boron and nitrogen coordination bond. Therefore, new hydrolytically stable approaches for borate esters are required. It is well-known that the benzene ring is a conjugated system which leads to its stable structure [17]. Inspired by this, the long chain alkylphenyl group was introduced to link with the boron directly in the borate ester. The boron can conjugate with the benzene ring which improves the stability of the

* Corresponding author. Tel.: +86 21 54747118; fax: +86 21 54747118.
E-mail address: thren@sjtu.edu.cn (T. Ren).

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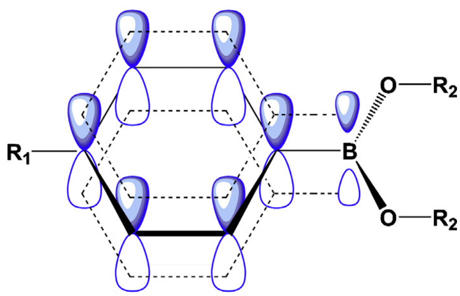

Fig. 1. Long chain alkyl phenylboronic acid esters stabilized by conjugation.

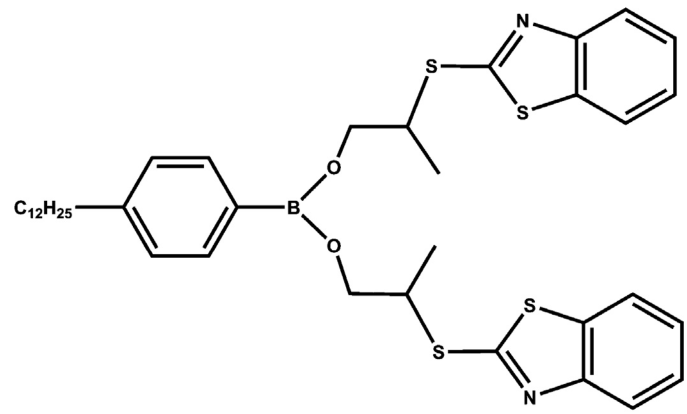

Fig. 2. The structure of the synthesized compound (DBBMT).

structure, and the long chain can act as a hydrophobic group (Fig. 1). Also, the heterocyclic group of benzothiazole was combined with the boron through esterification reaction, which acts as not only an active lubricating component, but also a hinder group to prevent the attack of water [18], and the containing nitrogen could coordinate with boron, resulting in improving the hydrolytic stability [7].

In this work, a bis (1-(benzothiazol-2-ylthio) propan-2-yl) -4-dodecylphenylboronic acid ester (DBBMT) was synthesized and characterized. The hydrolytic stability in mineral oil was analyzed with a method of accelerated hydrolysis by a wet heating treatment. For comparison, the tribological properties of DBBMT and Zinc Dialkyl Dithiophosphates (ZDDP) as additives in a base oil were evaluated by a four-ball tribometer to determine whether the DBBMT is a potential candidate for the replacement of ZDDP. Furthermore, X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) spectroscopy were adopted to further understand their tribological behaviors on the metal surfaces.

2. Experimental

2.1. Base stock and additives

A common mineral oil, hydro-isomerized and dewaxed base oil (HVI WH150), was used as base stock in the test, which is supplied by PetroChina Lanzhou Lubricating Oil R&D Institute in Lanzhou, China. The physical characteristics of the HVIW H150 mineral oil are given in Table 1. The zinc propyl octyl primary-secondary dialkyl dithiophosphate (ZDDP, also coded as T205 in Chinese market) is supplied by Liaoning Tianhe Fine Chemical Co., Ltd., China and the purity of ZDDP conforms to commercial standard. Both of the oil and additive are used without any further treatment.

The related synthetic procedures of the additive, bis (1-(benzothiazol-2-ylthio) propan-2-yl)-4-dodecylphenylboronic acid ester (DBBMT), were described briefly as follow: the 4-dodecylphenylboric acid was prepared according to the reported procedures [19–21] while the 1-(benzothiazol-2-ylthio) propan-2-ol was prepared from the reaction of 2-methyloxirane, triethylamine and 2-mercapto-benzothiazole [22]. 4-dodecylphenylboric acid (14.51 g, 0.05 mol), 1-(benzothiazol-2-ylthio) propan-2-ol (22.53 g, 0.10 mol) and catalytic amount of strong acid resin were dissolved in 150 mL of toluene in a 250 mL round-bottom flask attached with a Dean-Stark trap for water separation. The reaction mixture was refluxed for 6 h under nitrogen atmosphere. The resulting reaction mixture was filtered and rotary evaporated to remove toluene under vacuum resulting in (33.48 g, 0.05 mol) DBBMT in 95% yield. The structure of the synthesized compound is given in Fig. 2, which was characterized by means of thin-layer chromatography (TLC), infrared spectroscopy (IR) and elemental analysis as follow:

The results of IR spectrum (KBr) are (cm^{-1}): 2955.73 ($-CH_3$, medium); 2925.72 ($-CH_2$, strong), 2854.24 ($-CH_2$, medium); 1608.39 (C=C, C=N, weak); 1457.48 ($-CH_3$, medium), 1371.17 ($-CH_3$, medium); 1428.24 (benzothiazole ring, strong); 1316.72 (B—O, strong); 1241.00 (C—N, weak); 1101.56 (C—N—C, weak); 1005.72 (C—O, weak); 754.46 (benzene ring, weak); 725.46 (C—B, weak); 653.59 (C—S, weak).

The elemental analysis result of DBBMT is listed in Table 2, which is in agreement with the calculated data and within the limits and experimental error. It is necessary to note that the analytic value of boron element is a little lower than that of theoretical value (1.11 vs. 1.53), which is attributed to the low boron content in the additive molecule, resulting in relatively big analytic error.

2.2. Tribological evaluation of DBBMT

The tribological properties of DBBMT and ZDDP as additives in mineral oil were investigated using a MMW-1 four-ball tester, manufactured by the Jinan instrument manufacturer, China. Details of evaluated conditions were as follows: ambient temperature; rotating speed, 1450 rpm; duration, 30 min. The steel balls used for tribological test are 12.7 mm in diameter and made of GCr 15 bearing steel with 59–61 hardness of HRC. The friction coefficients were recorded automatically by a computer linked to the tribometer machine and the wear scar diameters (WSD) on the three lower balls were measured using an optical microscope. The standard for

Table 1
Physical characteristics of the HVIW H150 mineral oil.

Items	Index
Density (20 °C g/cm^3)	0.844
Kinematic viscosity (mm^2/s)	
40 °C	29.95
100 °C	5.512
Viscosity index	125
Chrominance, number	0
Pour point (°C)	−30
Open flash point (°C)	226
Neutralizing value (mg KOH/g)	0.01
Extrinsic feature	Transparence
Evaporation loss, Noack 250 °C, 1 h (%)	10.15

Table 2
Elemental analysis result of DBBMT.

Element	C	H	N	S	B
Analytic value (wt.%)	63.64	7.02	3.68	17.36	1.11
Theoretical value (wt.%)	64.75	7.01	3.97	18.20	1.53