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Synthesis of a novel borate ester containing a phenylboronic group and its tribological properties as an additive in PAO 6 base oil

Liping Wang [a,b], Hongxing Wu [a], Dongya Zhang [c,*], Guangneng Dong [a,**], Xiaohong Xu [b], Youbai Xie [a]

[a] Key Laboratory of Education Ministry for Modern Design & Rotor-Bearing System, Xi'an Jiaotong University, Xi'an, PR China
[b] Petro China Lanzhou Lubricating Oil R & D Institute, Lanzhou, PR China
[c] School of Mechanical and Precision Instrument Engineering, Xi'an University of Technology, Xi'an, PR China

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ABSTRACT

To reduce the dosage of zinc dialkyldithiophosphates (ZDDP) in engine oil, the synthesis and characterization of a novel borate ester containing a phenylboronic group (BDDP) was reported. The thermogravimetric analysis results showed that BDDP had a better thermo-stability compared with that of commercial additives ZDDP and F10A. The tribological properties of the PAO 6 base oils containing BDDP, ZDDP and F10A were studied using a four-ball tester and SRV tribo-meter. The oil with a BDDP concentration of 0.8% showed tribological properties superior to those of the ZDDP and F10-containing oil under varying applied loads and elevated temperature conditions. The elemental composition of the tribological film generated on the worn surfaces of the steel balls was detected by X-ray photoelectron spectroscopy (XPS), and the results indicated that the tribological film was composed of Fe_2B and B_2O_3. Thus, BDDP could be a candidate to replace ZDDP or reduce the dosage of ZDDP in engine oil.

1. Introduction

With the greater technological developments of vehicle engines and transmissions, the performance demands of engine oils have also increased, and the lubricant additives to address these needs have been rapidly developed. ZDDP is a superior additive with many advantageous behaviors, such as its anti-wear performance, effective antioxidant and corrosion resistant properties [1–3]. Hence, ZDDP is commonly used as an additive in engine oil [4,5], especially for oil used under high-load and high-temperature conditions. However, the usage of ZDDP in engine oil also has many inevitable drawbacks. Such as: (i) the element of phosphorus in ZDDP can occur chemical reaction with the active material in three-way catalytic converters, which reduces the catalytic converter efficiency [6]. (ii) Journal bearings in the engine contain copper and/or lead, and the elements of Cu and Pb are liable to cause electrochemical corrosion with Zn, which accelerates the wear of the journal bearings [7]. (iii) The maximum allowable operation temperature of ZDDP is 160 °C, because ZDDP rapidly dissociates when the temperature exceeds 160 °C, causing the degradation of the engine oils. Therefore, the development of novel, low-phosphorus additives with excellent antioxidant, corrosion resistance and anti-wear performance is definitely meaningful and urgent.

Research [8,9] had showed that the borate esters could enhance the anti-wear and anti-oxidative performances of base oils. Zhi [10] synthesized borate ester structure with a six-membered ring containing B and N, and the friction coefficient of the borate ester was reduced by 20–30% compared with that of the base oil. The study also indicated that the element B permeated into the frictional surface and formed a B_2O_3 film on the surface. Sun [8] synthesized four borate esters with different carbon chains and then added the borate esters into rapeseed oil. The tribological test results showed that the anti-wear property of the rapeseed oil was significantly improved by the addition of the compounds. Li [11] synthesized a borate ester derivative containing benzothiazol-2-yl and disulfide groups (BTSB) and showed that the tribological properties of BTSB were better than those of ZDDP. The reason for the improvement was attributed to the S in BTSB reacting with steel to generate a $FeSO_4$ film. The literature had shown that the tribological performances of borate esters were influenced by the type of alkyl chain [12–14], the type of heterocyclic compound [15,16], and the type of base oil [17,18], etc. However, the tribological behavior and lubrication mechanism of borate esters added in the PAO base oils are not well understood and need further investigation.

In this study, a novel borate ester containing a phenylboronic group

* Corresponding author.
** Corresponding author.
E-mail addresses: dyzhang@xaut.edu.cn (D. Zhang), donggn@mail.xjtu.edu.cn (G. Dong).

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(BDDP) was synthesized and used as additive in a PAO 6 base oil. The tribological performances of the BDDP and the commercial additives ZDDP and F10A were evaluated using a four-ball tester and an SRV tribometer. Meanwhile, the effects of the applied loads and elevated temperatures on the tribological performances of the additives were also investigated. XPS and scanning electron microscope (SEM) were used to analyze the composition of tribological film on the worn surface, which was beneficial for understanding the lubrication mechanism of BDDP.

2. Experiments

2.1. Synthesis of borate esters containing phenylboronic group (BDDP)

All reagents were of analytical grade and used without further purification in this experiment. 1-Butanol, phosphorus pentasulfide, sodium hydroxide, 2-bromoethanol, phenylboronic acid, petroleum ether, ether, and toluene were procured commercially and used to synthesize BDDP. BDDP was prepared according to the synthetic routine shown in Fig. 1. Phosphorus pentasulfide was added into a three-necked round flask and then uniformly dispersed in petroleum ether at room temperature. Thereafter, 1-butanol was dropwise added with stirring at a temperature below 100 °C, and then the produced transparent solution was continuously stirred for 2 h at 100 °C. The petroleum ether and excess 1-butanol were removed using a rotatory evaporator, and the resulting product was O, O-dibutylphosphorodithioic acid. The O, O-dibutylphosphorodithioic acid was dissolved in an aqueous sodium hydroxide solution and mixed with 2-bromoethanol for several hours. After the completion of the reaction, the oil phase was separated from the water phase by repeatedly extracting the water phase with ether. Then, the oil phase and ether phase were mixed, and the ether was removed under vacuum condition. The product was further reacted with phenylboronic acid under a certain amount of toluene. Nitrogen was also introduced during the process to remove the produced water. The reaction was allowed to proceed until no further water was collected. Finally, the final product was distilled under vacuum condition.

Table 1
Typical characteristics of the PAO 6 base oil.

Items	Value
Kinematic viscosity, mm^2/s	30.56
@40 °C	5.818
@100 °C	
Viscosity Index	136
Total acid number, mg KOH/g	0.00
Density @ 20 °C, kg/m^3	823.3
Flash point (cleveland open cup), °C	224
CCS viscosity @ −25 °C, mPa·s	1330
Volatility loss (Noack), wt%	6.2
Pour point, °C	−66

2.2. Additives and base oil

The base oil used in all the experiments was PAO 6 (purchased from Exxon Mobil Co, USA), and its typical characteristics are shown in Table 1. The commercial ZDDP (T202, purchased from Lanzhou Lubrizol Additive Co., Ltd., China), which is widely used as an anti-wear agent to improve the tribological performance of lubricating oils, was used as a comparison to evaluate the anti-wear properties of BDDP. Irgalube F10A (supplied by BASF) is widely used as a friction modifier for engine oils, and was selected for the comparative evaluation of the friction reduction capability of BDDP. The structure of Irgalube F10A is shown in Fig. 2.

2.3. Characterization of the additives

The thermal stabilities of the additives were investigated using a thermal analyzer (type of TA-9900). For this analysis, a 5–8 mg specimen was accurately weighed and heated from 25 °C to 800 °C under a N_2 atmosphere. The heating rate and the velocity of the N_2 flow were set as 20 °C/min and 30 ml/min, respectively.

The main functional groups of BDDP were characterized by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra was obtained using a spectrophotometer (TENSOR27, Bruker), and the spectra was

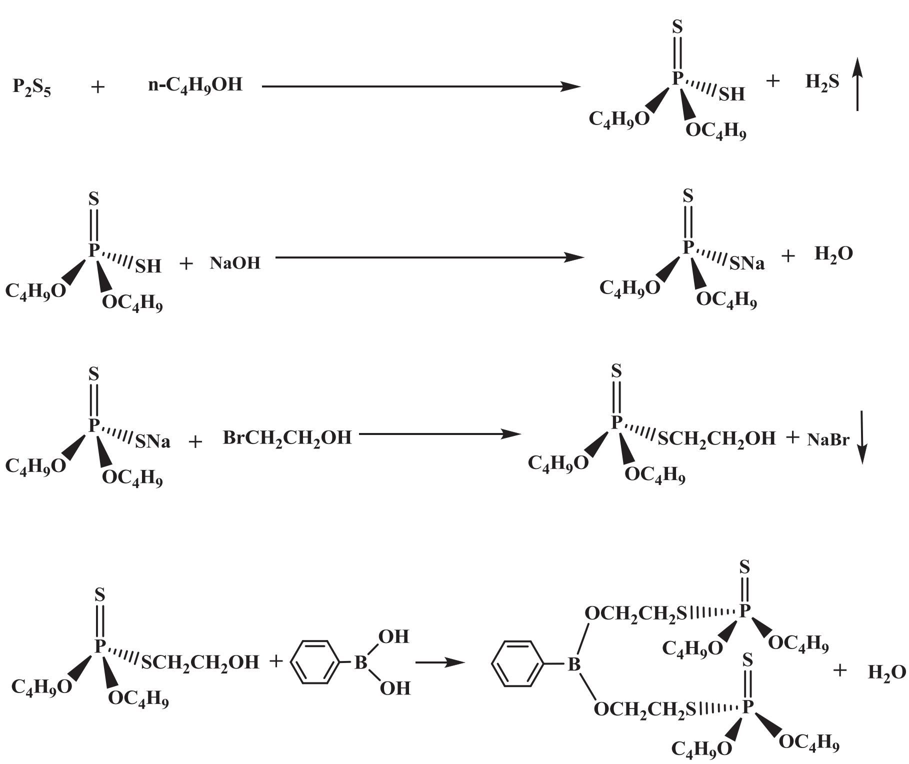

Fig. 1. Outline of the processes involved in synthesizing the borate esters containing a phenylboronic group (BDDP).