Tribological study of N-containing borate derivatives and their synergistic antioxidation effects with T531

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Abstract: Two N-containing borates, BTES and BMES, were synthesized with dodecyl phenol, 2-(N-containing heterocyclic) ethan-1-ol, boric acid, and dibutylamine, and their tribological properties in rapeseed oil (RSO) were investigated using a four-ball tester. The results showed that the load-carrying ability \((P_B)\) value of RSO can be improved by 40.9% and 67.9%, respectively, when using 0.5 wt% BTES and BMES. Moreover, the antiwear and friction-reducing performances of the additive-containing oils increased with the additive concentration. The X-ray photoelectron spectroscopy results of the worn steel ball surfaces showed that BTES and BMES formed protective films, which contained boron oxide, iron oxide, ferrous sulfate, ferrous sulfide (for BMES), and other organic nitrogen compounds, on the metal surfaces. The better load-carrying and antiwear performances of BMES than those of BTES might be due to their different sulfur contents, which result in different tribochemical reaction films on the contact surfaces. The oxidation stability tests showed that BTES and BMES possessed synergistic antioxidation activity with N-phenyl-α-naphthylamine (T531), and consequently, the oxidation activation energy of the oil sample increased by 77.85% and 82.19%, respectively, compared with that of RSO when the oil sample contained 0.05 wt% BTES/BMES and 0.25% T531.

Keywords: N-containing borate; synergistic antioxidation effect; T531; tribological property

1 Introduction

During the working process of machines, lubricating oil is oxidized, polymerized, and decomposed, and consequently, resin, coke, and oil sludge are produced on the surface of the frictional parts, leading to bearing corrosion, piston ring sticking, oil thickening, and thermal efficiency reduction. Certain antioxidants enhance the oxidation stability of the oil and prevent its rancidity and deterioration [1]. Among lubricating oil additives [2], borate has been used in gear oil and two-stroke oil [3] owing to its good tolerance to extreme pressure [4], oxidation stability [5], and anticorrosion performance [6]. Potassium borate (coded T361) and colloidal potassium borate (coded OLOA-9750) are commercialized inorganic borate additives produced by Chevron Company. These are dispersed in lubricants by surfactants, often accompanied by poor dispersion uniformity and unsatisfactory long-term storage stability. In addition, borate is sensitive to water and can be easily hydrolyzed because of the electron deficiency of boron [7], which reduces the tribological effect of borate [8].

Previous studies [9] showed that, in addition to surface modification, introducing elements with an unpaired electron into a borate molecule [7], such as nitrogen element, to form intramolecular B-N coordination bond is an effective way to improve the...
hydrolytic stability of borate. Research showed that N-containing heterocyclic compounds, such as benzotriazole and mercaptobenzothiazole, possessed good tribological properties [5, 9] when introduced into organic borate. Moreover, it is observed that these electron-rich groups can effectively improve the hydrolytic stability of borate ester [5]. A benzotriazole-type derivative [10] has been shown to have synergistic antioxidation property with 2,6-di-tert-butyl-4-methylphenol, which is a phenolic antioxidant.

Oil-soluble alkalis salts have been demonstrated to improve the thermal oxidation stability of lubricating oil [11]. So far, the alkali metal salts mainly concentrated on alkali metal alkoxides (phenoxydes) and fatty acid salts, ethylenediaminetetraacetate acid-alkyl amine-potassium salt, KOH-crown ether, and alkali metal organic phosphorus compounds. Research [12] showed that potassium perfluorobutyrate had a synergistic antioxidant effect with N-phenyl-α-naphthylamine (PAN) and P-dioctyl diphenyl amine (DODPA) in pentaerythritol fatty mixed ester, showing that the viscosity and acidity of the ester oil can be suppressed with the coexistence of potassium perfluorobutyrate and PAN/DODPA. Some alkali metal sulfonates can improve the initial oxidation temperature (IOT) of PAN [13]. Alkali metal salts showed good synergistic antioxidant activity with arylamine antioxidant in ester lubricants, polyphenylene ether, and hydrocarbon oil and perfluorinated esters. However, there have been some studies about the antioxidant activity of rapeseed oil (RSO), which is a readily oxidized oil.

In the present work, two N-containing heterocyclic borates were designed and synthesized, in an attempt to combine the functionalities of oil-solubility, antioxidation, and tribological performance of the additives. A four-ball tribometer was employed to evaluate their tribological performances in RSO. Their tribological mechanisms were explored using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) analyses. Their synergistic antioxidant effects with N-phenyl-α-naphthylamine (T531) were investigated using pressure differential scanning calorimetry (PDSC) analysis.

2 Experimental details

2.1 Materials

2-(benzotriazol-1-yl) ethanol-1-ol (coded BTE), 2-(mercaptobenzimidazol-2-ylthio) ethanol-1-ol (coded BME), and N-phenyl-α-naphthylamine (coded T531) were prepared in the laboratory. T531 is a light yellow crystal whose melting point is 59.5–62.0 °C. 4-dodecylphenol was of industrial grade, whereas other agents were chemically pure and were purchased from Shanghai Chemical Company. All the reagents were used directly without further treatment. RSO, used as the base lubricating fluid, was obtained from Fuzhou Co. Ltd of China. Its physical and chemical properties are as follows: total base number (TBN) is 0.78 mg KOH/g, viscosity index is 211, dynamic viscosity (40 °C) is 37.93 N·s/m², and basic nitrogen concentration is 0.186 mg/g.

2.2 Additive synthesis

The synthetic route of the additives is shown in Fig. 1. The specific steps are as follows. First, 200 mL benzene, 78.6 g dodecylphenol, and 24.3 g formaldehyde (at a 37 wt% content) were added to a 500 mL flask under stirring at room temperature. Subsequently, 50 mL benzene solution with 38.7 g di-n-butylamine was added. The reactant was heated up to 60 °C and maintained for 3 h, followed by cooling to room temperature. After filtration, washing, drying, and vacuum distillation, 103.3 g light yellow-brown viscous liquid 2-(N,N′-di-butyl)-methylamino-4-dodecyl phenol was obtained and denoted as DMDP. The yield was 86%.

In addition, 100 mL benzene, 80.6 g DMDP, and 8.0 g zinc acetate were mixed in a 500 mL flask under stirring...
at room temperature. When the mixture became transparent, 24.3 g formaldehyde was added in a dropwise manner. After allowing the reaction to proceed for 3 h at 60 °C, the mixture was cooled to room temperature. After filtration, washing, drying, and vacuum distillation, 68.0 g light green liquid, 2-((dibuthylamino)methyl)-4dodecyl-5-(hydroxymethyl) phenol was obtained, and denoted as DDP. The yield was 78.5%.

At room temperature, 200 mL toluene, 0.1 mol BTE or BME, 0.1 mol DDP, and 0.1 mol boric acid were added to a 500 mL flask equipped with a water-separator and subsequently stirred. The reactant was quickly heated up to 110 °C and refluxed for 3 h in a nitrogen atmosphere with an acid resin as catalyst. Using similar purification procedures as above, 59.4 g yellow transparent liquid, 2-(benzotriazol-1-yl) ethyl (3-((dibutylamino)methyl)-5-dodecyl-2-hydroxybenzyl) hydrogen borate (denoted as BTEB) was obtained with a yield of 88.6%, and 45.4 g yellow transparent liquid, 2-(benzoimidazol-2-ylthio) ethyl (3-((dibutylamino)methyl)-5-dodecyl-2-hydroxybenzyl) hydrogen borate (denoted as BMEB) was obtained with a yield of 73.6%.

In a 250 mL flask, 30.0 g BTEB/BMEB was dissolved in 100 mL toluene, and a small amount of potassium carbonate was added to the solution. After allowing the reaction and reflux to proceed for 2 h, the mixture was cooled to room temperature. After filtration and vacuum distillation, 25.6 g light yellow transparent liquid, potassium 2-(((2-(benzotriazol-1-yl) ethoxy)(hydroxy) boranyl oxy)methyl)-6-((dibutylamino)methyl)-4-dodecyl phenolate (denoted as BTES) was obtained with a yield of 72.7%.

### 2.3 Structure characterization

A Spectrum One type Fourier-transform infrared (FT-IR) spectrometer (Perkin Elmer Instruments Co. Ltd, USA) was used to analyze the chemical structures of BTES and BMES. The C, H, N, and S element contents were evaluated using a vario EL III type element analysis instrument. The element contents of B and K were determined by using a Varian 720-ES ICP. The thermochemical stabilities of BTES and BMES were investigated using a thermogravimetric analyzer (TGA, Pyris 1 TGA 4000 instrument, PE Company) in a nitrogen environment with a flow of 40 mL/min over the temperature range 50−750 °C at a heating rate of 10 °C/min. The 13C nuclear magnetic resonance (NMR) was investigated using an AVANCE 400 type NMR tester.

### 2.4 Hydrolytic stability

The hydrolytic stabilities of BTES and BMES were studied using an open method [5]. The specific process was as follows: 10 mL liquid paraffin with a concentration of 1.0 wt% BTES/BMES was stored at room temperature, and the change in the turbidity of the solution was observed. The turbidity of the solution indicated that an insoluble boric acid solid was produced. The time required for the color change was considered as the hydrolytic stability time.
Moreover, the hydrolytic stabilities of BTES and BMES were investigated at 70 °C [5]. BTES/BMES in various amounts was added to a base solution containing 24.80 g liquid paraffin and 0.2 g water. The time required for the solution to become cloudy was recorded and considered as the hydrolytic stability time at 70 °C.

2.5 Tribological test conditions

The Chinese national standard GB3142-82, similar to ASTM D-2783, was used as the standard for measuring the load-carrying ability (\(P_B\) value), antiwear, and friction-reducing properties of the additives. Accordingly, an MRS-10 type four-ball tribometer (Jinan Testing Machine Factory, China) was employed at room temperature. For evaluating the \(P_B\) value, each test was conducted for 10 s at 1450 rpm. For evaluating the antiwear and friction-reducing properties of the additives, each test was conducted for 30 min at 1450 rpm. The GCr15 bearing steel balls used for the tribological tests all contained the following compositions: C, 0.95%–1.05%; Si, 0.15%–0.35%; Mn, 0.20%–0.40%; P, < 0.027%; S, < 0.020%; Cr, 1.30%–1.65%; Ni, < 0.30%; Cu, < 0.25%, with a diameter of 12.7 mm and a hardness of HRC 59–61. Before each test, the balls were cleaned with petroleum ether. A microscope was used to determine the wear scar diameter (WSD) with an accuracy of 0.01 mm. The friction coefficient (COF) was recorded automatically by the machine during the frictional test.

2.6 Worn surface analysis

Before surface analysis, the tested balls were ultrasonically cleaned for 15 min in petroleum ether (60–90 °C). A Vega3 type SEM (Tescan Company) and a Zeiss Sigma energy-dispersive X-ray spectroscopy (EDS) analyzer were used to investigate the surface morphology and elemental distributions on the worn surface, respectively. The chemical states of typical elements on the worn surfaces were analyzed by using a PHI-5702 type XPS. The binding energy was calibrated using C1s = 284.6 eV.

2.7 Antioxidation property

The antioxidation properties of the additives can be evaluated using the IOT and oxidation induction time (OIT) of the additive-containing oil samples measured via the PDSC method. Accordingly, a DSC8000 type PDSC tester (Perkin Elmer Instruments Co. Ltd Company) was employed. The measuring conditions were the temperature range 50–350 °C at a heating rate of 40 °C/min in oxygen atmosphere.

3 Results and discussion

3.1 Structure analysis of the additives

The results of infrared analysis are shown in Fig. 2. The absorption peak at 3,000–2,800 cm\(^{-1}\) corresponds to the C-H bond stretching vibration, the peak at 1,378 cm\(^{-1}\) corresponds to the B-O stretching vibration, and the peak observed at 1,263 cm\(^{-1}\) is ascribed to the -C-N- bond. The main peaks of BTES and BMES are similar because of their similar structures.

The elemental analysis results of BTES and BMES are listed in Table 1, and the data in parentheses are

![Fig. 2](https://mc03.manuscriptcentral.com/friction)
Table 1  Elemental analysis of the synthesized compounds (wt%).

| Compound | C  | H  | N   | S   | B  | K   |
|----------|----|----|-----|-----|----|-----|
| BTES     | 65.86 (65.45) | 8.62 (8.79) | 8.39 (8.48) | 0 | 1.58 (1.67) | 5.72 (5.91) |
| BMES     | 64.59 (64.25) | 8.44 (8.54) | 6.32 (6.08) | 4.21 (4.63) | 1.49 (1.59) | 5.41 (5.64) |

The theoretical values. The measured and theoretical values are within the experimental error range. Based on the infrared spectra and element analysis, it can be concluded that the synthesized compounds were the target potassium borates.

The thermal stability of the additives is illustrated in Fig. 3. The weight change at approximately 100 °C is attributed to the evaporation of a small amount of water present in the synthetic compound. It can be observed that the initial decomposition temperatures of BTES and BMES are both approximately 210 °C, satisfying the thermal stability requirement of a lubricating oil additive. As the C-S bond in BMES is easily decomposed to produce H2S, there is no flat peak in the TGA curve of BMES.

The structures of BTES and BMES were further characterized using 13C NMR spectroscopy. The 13C NMR analysis results of BTES and BMES in CDCl3 (100 MHz, tetramethylsilane (TMS), δ/ppm) are shown in Fig. 4. The possible carbon atoms corresponding to each peak are noted by the numbers in the molecular structures of BTES and BMES.

The 13C-NMR data of BTES are as follows: δ = 163.83 ppm, 145.69 ppm, 143.27 ppm, 135.98 ppm, 134.94 ppm, 132.72 ppm, 128.68 ppm, 126.59 ppm, 126.15 ppm, 119.65 ppm, 110.10 ppm, 63.67 ppm, 62.19 ppm, 57.53 ppm, 56.47 ppm, 53.40 ppm, 36.34 ppm, 31.92 ppm, 31.20 ppm, 30.41 ppm, 29.51 ppm, 29.33 ppm, 29.12 ppm, 22.73 ppm, 20.39 ppm, 14.12 ppm, 13.78 ppm.

![TGA curves of BTES and BMES.](image1)

![13C-NMR spectra of BTES and BMES in CDCl3.](image2)
The $^{13}$C-NMR data of BMES are as follows: $\delta = 163.83$ ppm, 147.10 ppm, 143.09 ppm, 138.92 ppm, 136.11 ppm, 134.95 ppm, 128.72 ppm, 126.56 ppm, 123.16 ppm, 115.19 ppm, 63.62 ppm, 62.11 ppm, 58.53 ppm, 56.40 ppm, 42.76 ppm, 36.32 ppm, 31.88 ppm, 31.17 ppm, 30.47 ppm, 29.53 ppm, 29.28 ppm, 29.13 ppm, 22.72 ppm, 20.39 ppm, 14.13 ppm, 13.85 ppm.

3.2 Hydrolytic stability

The results of hydrolytic stability showed that the liquid paraffin solution containing 1.0 wt% BTES/BMES did not become turbid after storage for 6 months at room temperature, indicating the good storage and hydrolytic stability of BTES and BMES at room temperature.

The hydrolytic stability time of each test sample at 70 °C is listed in Table 2. For comparison, the hydrolytic stability of tributyl borate (TBB) was also investigated. It can be observed that the hydrolytic stability times of 0.25 g BTES and BMES in 25 g base solution were 8.4 times and 4.9 times that of TBB of the same amount, respectively. Moreover, the hydrolysis time of BTES/BMES increased with the increase in additive concentration. Sample D shows that the hydrolytic stability times of BTES and BMES were 65,248 s and 54,692 s, respectively, when 1 g additive was dissolved in 25 g base solution.

The results of hydrolytic stability indicate that both the synthesized additives, BTES and BMES, both possess good hydrolytic stability, which is probably due to the inner coordination of B-N bond [5].

3.3 $P_b$ properties

Before the tribological tests, the solubilities of BTES and BMES additives in RSO were investigated. It was observed that the additives showed good solubility in RSO and could be dissolved well in RSO within the concentration of 5.0 wt%.

The $P_b$ values of RSO with different amounts of BTES and BMES are listed in Table 3. The $P_b$ values of oil samples illustrate upward trends with the increase in additive concentration. When the concentrations of BTES and BMES were 0.5 wt%, the $P_b$ value of RSO was enhanced by 40.9% and 67.9% respectively. When the additive concentration exceeded 0.5 wt%, the $P_b$ value of the oil sample increased slowly with the increase in additive concentration. This indicates that there is an optimum additive concentration for real applications. Moreover, BMES shows higher ability to improve the $P_b$ value of RSO than BTES. This might be ascribed to its higher sulfur content, which has been reported to be responsible for the extreme pressure performance [15].

3.4 Antiwear properties

The antiwear properties of BTES and BMES at different loads are shown in Fig. 5. It can be observed that both BTES and BMES could improve the antiwear property of RSO. In addition, the WSD decreased with the increase in the additive concentration from 0.1 wt% to 1.0 wt% at all applied loads.

The antiwear properties of BTES and BMES differed slightly at the applied load of 196 N. At the applied load of 294 N, 0.1 wt% BTES sample showed better antiwear property than 0.1 wt% BMES sample. However, when the additive concentration exceeded 0.1 wt%, the BMES sample exhibited better antiwear property. At the applied load of 392 N, BMES showed better antiwear effect than BTES, which indicates that the sulfur element may have contributed to the antiwear property.

From Fig. 5, it can be observed that the WSD increases increased with the increase in the applied load. This may be because the formed tribofilm was easily destroyed under the high applied load [16]. In addition, BTES and BMES increased the antiwear performance of RSO at any test load when the
additive concentration was 1.0 wt%, indicating the good antiwear performances of the two additives.

3.5 Friction-reducing properties

Figure 6 presents the relationship between the COF and additive concentration under different applied loads. It can be observed that BTES and BMES could both increase the friction-reducing properties of RSO. Moreover, the friction-reduction effect of BTES was better than that of BMES at 196 N and 294 N. At 392 N, the friction-reducing property of BMES, as compared with that of BTES, was better at low concentration, but worse at high concentration (>0.7 wt%), because of the increase in sulfur content. The different friction-reducing performances of the two additives are attributed to the different boundary lubricating films formed on the frictional surfaces, caused by the different additive molecules.

3.6 SEM and EDS analysis

Figure 7 shows the SEM images of the worn surfaces lubricated with RSO, 0.3 wt% BTES, and 0.3 wt% BMES separately after a friction test for 30 min under the conditions of 392 N and 1,450 rpm.

The worn surface lubricated with RSO showed a large wear scar with wide furrows on it. However, worn surfaces lubricated with 0.3 wt% BTES and BMES showed relatively smaller wear scars and narrower furrows, indicating that BTES and BMES reduced the abrasive wear of the tribosystem. This may be due to the formation of tribofilms with low shearing strength on the metal surfaces.

Compared with the worn surface lubricated with 0.3 wt% BTES, the worn surface resulting from lubrication with 0.3 wt% BMES showed a small wear scar with a relatively smooth furrow on it. This indicates that the BMES additive might have formed a more effective boundary lubricating film on the metal surface as compared with BTES, which may be ascribed to the sulfur element in the BMES additive.

EDS analysis was employed to investigate the elemental composition of the lubricating films after friction for 30 min with RSO, 0.3 wt% BTES, and
0.3 wt% BMES samples under the conditions of 392 N and 1,450 rpm. The analysis results are shown in Fig. 8, and the corresponding elemental contents are listed in Table 4. The ferrum and chromium elements are the basic elements of GCr15-type steel ball, whereas sulfur, nitrogen, boron, and potassium elements originate from the additives. From Table 4, it can be observed that the element contents of ferrum and chromium on the lubricating film decreased after BTES and BMES additives were added to RSO. However, boron, potassium, nitrogen, and/or sulfur elements were detected on the worn surface. This indicates that the additives were adsorbed onto or reacted with the metal surface. Compared with RSO lubrication, lubricating films containing nitrogen, sulfur, and boron elements contributed to better tribological properties [7].

3.7 XPS analysis

Figure 9 shows the XPS spectra of the characteristic elements after lubricating with 0.3 wt% BTES, and Fig. 10 shows the XPS results corresponding to
lubrication with 0.3 wt% BMES.

In Fig. 9, the C_1s peak at 284.8 eV corresponds to the C-C or C-H bonds [17] in BTES and RSO, indicating that the BTES or RSO molecules were adsorbed onto the metal surface during the friction test. The O_1s peaks at 531.6 eV and 532.8 eV correspond to iron oxide [18] and C-O bond, respectively, indicating that the BTES or RSO molecules were oxidized on the metal surface.

The B_1s peak at 193.2 eV is attributed to B-O bond [18], which indicates that BTES was decomposed, and the borate part was transformed into B-O containing groups.

The N_1s peak at 399.3 eV corresponds to the

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**Table 4**  Elemental contents (wt%) of the worn surfaces analyzed using EDS.

| Lubricant     | C   | O   | Fe  | Cr  | B   | N   | S   | K   |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|
| RSO           | 71.34 | 1.63 | 25.64 | 1.39 | 0   | 0   | 0   | 0   |
| 0.3 wt% BTES  | 73.69 | 1.68 | 22.38 | 0.59 | 0.53 | 0.88 | 0   | 0.21 |
| 0.3 wt% BMES  | 75.63 | 1.24 | 20.54 | 0.66 | 0.48 | 0.94 | 0.23 | 0.28 |

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Fig. 9  XPS spectra of the characteristic elements on the worn surface lubricated with 0.3 wt% BTES (392 N, 30 min).
benzotriazole ring [19], and the peak at 400.5 eV corresponds to –NO₂ or C–N bond [20]. This indicates that BTES was adsorbed and oxidized on the metal surface.

The Fe₂p peaks at 710.8 eV and 724.8 eV should are ascribed to Fe₂O₃ (Fe₂p₃/₂) and FeOOH (Fe₂p₃/₂), respectively. In combination with the O₁s peak at approximately 530 eV, the existence of FeOₓ can be
confirmed. The $K_{2p}$ peak at 291.9 eV is attributed to potassium ferricyanide. It can be deduced that, under the action of friction, the K element participated in the tribochemical reactions and formed K-containing metal compounds.

In the C$_{1s}$ spectrum of the worn surface after lubricating with 0.3 wt% BMES sample, peaks at 284.8 eV and 288.4 eV correspond to C-C/C-H and -COOH bonds [18] in BTES or RSO, respectively. This indicates that the BMES or RSO molecules were adsorbed onto the metal surface. The O$_{1s}$ peak at 531.3 eV and 530.1 eV in Fig. 10 correspond to the C-O bond and iron oxide [21], respectively, indicating that BMES was oxidized during the friction process.

The N$_{1s}$ peaks at 399.5 eV and 400.2 eV correspond to C-N/C=N [20] and N-O bonds, respectively, further indicating that BMES was adsorbed and oxidized on the steel ball surface. The B$_{1s}$ peak at 193.2 eV is attributed to the B-O bond, indicating that BTES was decomposed, and the borate part was transformed into B-O containing groups.

The Fe$_{2p}$ peak at 710.3 eV corresponds to ferrous sulfide, which is consistent with the S$_{2p}$ peak at 161.4 eV. The Fe$_{2p}$ peak at 724.3 eV corresponds to ferrous oxides, which is consistent with the O$_{1s}$ peak at 531.4 eV. It can be concluded that ferrous sulfide and ferrous oxides can be produced during the friction test with BMES lubrication. The S$_{2p}$ peak at 161.4 eV corresponds to ferrous sulfide [22], indicating that thioether was separated from the mercaptobenzimidazole group in BMES and reacted with the steel ball surface.

The K$_{2p}$ peaks at 291.9 eV and 294.7 eV correspond to potassium ferricyanide and potassium sulfide [23], respectively. It can be deduced that the K element participated in the tribochemical reactions under the action of friction and formed K-containing metal complexes.

Based on the above XPS analysis, it can be concluded that, during the friction process, additive molecules can be adsorbed onto and react with the metal surfaces to form boundary lubrication films, containing organic matters, nitrogen organic compounds, nitrogen oxides, boron oxides, FeO, FeSO$_4$, FeS (for BMES), and K-containing metal complexes, on the steel ball surface. The formed boundary lubricating films prevented the direct contact between friction pairs and contributed to the improved tribological properties of RSO. These two functional groups yielded different tribochemical reaction films, among which the tribofilm obtained with BMES contained FeS, which might be the reason for the better tribological performance of BMES than that of BTES.

### 3.8 Antioxidation property

The synergistic mechanism between alkali metal salts and amine antioxidants is still unclear. Luo et al. [24] suggested that the synergistic antioxidation effect of alkali metal salts with aromatic amine is ascribed to the alkali metal cations. The antioxidant activity of aromatic amine depends on the rate at which free radicals are formed via dehydrogenation. The alkali metal ions can accept the free electrons from the hydrogen atom to form alkali metals. PDSC was used to detect the synergistic antioxidation effect of BTES/ BMES with T531. The IOTs of different oil samples were tested using the temperature-programmed method, and OITs were obtained using the constant-temperature method. The test results are shown in Table 5 and Table 6.

From Table 5, it can be observed that the increase in additive concentration results in increased IOT, which indicates that the oxidation resistance of the oil samples was increased. For example, the IOT of 0.025% BTES sample was 195 °C, which was only 2 °C higher than that of RSO. However, when the BTES concentration was increased to 0.25%, the IOT of the oil sample was increased to 208 °C, which was 15 °C higher than that of RSO. Compared with BTES, BMES may have a slightly stronger antioxidation capacity, because the BMES sample showed a slightly higher IOT at the same additive concentration.

From the items of 2, 4, and 6 in Table 5, it can be observed that the antioxidation activities of BTES and BMES were much lower than that of T531, which can increase the IOT of RSO by 49 °C at a concentration of 0.25 wt%. However, 0.25 wt% T531 + 0.05 wt% BTES increased the IOT of RSO by 78 °C, and 0.25 wt% T531 + 0.05 wt% BMES increased the IOT of RSO by 89 °C, and they are all much higher than the increase in IOT of RSO obtained with 0.3 wt% T531. This indicates that T531 and BTES/ BMES have a synergistic antioxidation effect.
Table 5  PDSC results of different oil samples.

| Item | Samples                | IOT (PDSC) (°C) | ∆T |
|------|------------------------|-----------------|----|
| 1    | RSO                    | 193             |    |
| 2    | 0.25 wt% T531 /RSO     | 242             | 49 |
| 3    | 0.025 wt% BTES /RSO    | 208             | 20 |
| 4    | 0.25 wt% BMES /RSO     | 197             | 5  |
| 5    | 0.025 wt% T531 /RSO    | 211             | 18 |
| 6    | 0.3 wt% T531 /RSO      | 254             | 61 |
| 7    | 0.25 wt% BTES/RSO      | 210             | 17 |
| 8    | 0.025 wt% BMES/RSO     | 215             | 22 |
| 9    | 0.25 wt% T531 + 0.05 wt% BTES/RSO | 271 | 78 |
| 10   | 0.25 wt% T531 + 0.067 wt% BTES/RSO | 281 | 88 |
| 11   | 0.25 wt% T531 + 0.1 wt% BTES/RSO | 283 | 90 |
| 12   | 0.25 wt% T531 + 0.2 wt% BTES/RSO | 289 | 96 |
| 13   | 0.25 wt% T531 + 0.05 wt% BMES/RSO | 282 | 89 |
| 14   | 0.25 wt% T531 + 0.067 wt% BMES/RSO | 290 | 97 |

From Table 5, it can be observed that the IOT of 0.05% BTES mixed with 0.25% T531 was 271 °C, which was higher than those achieved with T531 and BTES alone. The IOT increased from 271 °C to 289 °C when 0.25% T531 was mixed with BTES of concentration ranging from 0.05% to 0.2%. The IOT increased from 282 °C to 290 °C when 0.25% T531 was mixed with BMES of concentration ranging from 0.05% to 0.067%.

When BTES was mixed with T531 with the mass ratio of 1:10, they had synergistic antioxidation effects, indicating that potassium borate can improve the oxidation stability of an amine-type antioxidant in RSO. The oxidation stability of the complex oil sample was better than that of the blank oil sample because the potassium ions in the synthesis borate were replaced by hydrogen ions [25] in the oil sample to form a phenolic hydroxyl group during the oxidation process, and phenolic hydroxyl itself shows good antioxidant activity.

The OIT value of PDSC was used to study the oxidation kinetics of BTES/BMES with the ashless antioxidant T531. The oxidation process of RSO is an exothermic reaction; when the base oil begins to be oxidized, it will exhibit an exothermic peak in the PDSC curves under heating conditions with oxygen. The low OIT ($t_{on}$) of the oil sample indicates poor oxidation stability. The OITs at different temperatures are shown in Table 6.

From Table 6, it can be observed that the $t_{on}$ of oil samples reduced significantly with the increase in temperature, indicating that the higher the temperature, the easier is the oxidative reaction.

The OIT of BTES (BMES) was lower than that of T531, indicating that the antioxidant capacity of an amine-type antioxidant is stronger than that of a phenol-amine-type antioxidant at high temperatures. It can be observed from Table 6 that, with the gradual increase in the temperature, the OIT of the oil sample decreased regularly, indicating that the higher the temperature, the easier is the oxidation reaction.

The oxidation reaction of base oil and aromatic amine antioxidant is a free radical reaction [26], and the activation energy required for the oxidation reaction can be calculated by using the Arrhenius formula according to PDSC test results, which can be used to investigate the oxidation mechanism. As the chemical activation energy is a measure of the difficulty of the chemical reaction, in general, the smaller the activation energy, the more easily the reaction proceeds.

Based on the Arrhenius equation

$$\ln k = \frac{-E_a}{RT} + C$$ (1)

where $k$ is the oxidation rate constant, which is
inversely proportional to the reaction time in the initial stages of oxidation, we obtain

$$\ln \frac{1}{t} = \frac{-E_a}{RT} + C \quad (2)$$

On substituting the oxidation induction time $t_{on}$ in Eq. (2), we obtain

$$\ln t_{on} = \frac{E_a}{R} \times \frac{1}{T} - C \quad (3)$$

Therefore, with $\ln t_{on}$ on the y-axis and $1/T$ on the x-axis, a straight line can be obtained in theory, with the slope equal to $E_a / R$, to calculate the activation energy $E_a$ of the oxidation reaction. The results are shown in Fig. 11.

In Fig. 11, the resulting curves are straight lines, indicating that the oxidation curves of the base oil and additive-containing oils are in accordance with the Arrhenius formula, and that the activation energy calculated according to this method is feasible. The calculated oxidation activation energies of the oil samples are listed in Table 7.

![Fig. 11  ln $t_{on}$ vs. 1 / T curves at different temperatures.](image)

**Table 7** Oxidation reaction activation energies of the oil samples ($E_a$, kJ/mol).

| Samples                  | $E_a$ (kJ/mol) |
|-------------------------|----------------|
| RSO                     | 76.95          |
| 0.3 wt% BTES            | 92.711         |
| 0.3 wt% BMES            | 99.007         |
| 0.3 wt% T531            | 110.373        |
| 0.25 wt% T531 + 0.05 wt% BTES | 136.854 |
| 0.25 wt% T531 + 0.05 wt% BMES | 140.198 |

Table 7 shows that both BTES and BMES can increase the activation energy of the oxidation process of RSO, although their effects are lower than that of T531. Moreover, both BTES and BMES show a synergistic effect with T531 to increase the activation energy of RSO. The higher the activation energy of the oil sample, the better is the antioxidation property of the additive. Therefore, the synthesized BTES and BMES possess antioxidation properties and synergistic antioxidation effects with T531.

**4 Conclusions**

(1) The $P_b$ values of the oil samples showed an upward trend with increasing additive concentration. When the concentration of the additives was 0.5 wt%, BTES and BMES enhanced the $P_b$ value of RSO by more than 40.9% and 67.9%, respectively.

(2) The WSD decreased with increasing additive concentration in BTES and BMES from 0.10 wt% to 1.0 wt% at all applied loads; the WSD also increased when applied load was increased. When the additive concentration was 0.5 wt%, BTES and BMES reduced the WSD of RSO by approximately 15% and 38%, respectively. When the additive concentration exceeded 0.1 wt%, the BMES sample exhibited better antiwear property. At the applied load of 392 N, BMES exhibited better antiwear effect than BTES.

(3) Both BTES and BMES could increase the friction-reducing properties of RSO. Moreover, the friction-reduction effect of BTES was better than that of BMES at 196 N and 294 N.

(4) BTES and BMES could form protective films, containing boron oxide, iron oxide, or ferrous sulfate, FeS (BMES additive), and other organic nitrogen compounds on the metal surfaces. BMES exhibited better tribological capacities (load-carrying and antiwear) than BTES in RSO, owing to the differences in the tribochemical reaction films, among which the tribofilm obtained with BMES contained FeS, which might be the reason for the better tribological performance of BMES than that of BTES.

(5) BTES and BMES exhibited some antioxidant properties, and when mixed with ashless amine-type antioxidant T531, they could significantly improve the IOT of the base oil. The oxidation activation energy
of the base oil was increased by 77.85% and 82.19%, respectively, and they showed a certain antioxidant synergistic effect with T531.

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