A study of S-[2-(acetamido) benzothiazol-1-yl]N,N-dibutyl dithiocarbamate as an oil additive in liquid paraffin

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Abstract

A heterocyclic derivative of S-[2-(acetamido) benzothiazol-1-yl]N,N-dibutyl dithiocarbamate was synthesized and its tribological behavior as an additive in liquid paraffin was evaluated using a four-ball tester. The nature of the film formed on the rubbed surface was investigated by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). On the basis of the experimental results, the novel additive shows excellent antiwear property and friction reduction property similar to ZDDP, and exhibits better load-carrying capacity than ZDDP. Besides those, the novel compound has good anticorrosive property and high thermal stability. The results of XPS analyses illustrate that the prepared compound as an additive in paraffinic base oil forms a protective film containing ferric sulfide, ferric sulfate, organicsulfur compound and organicanitrogen compound on the rubbed surface.

Keywords: Additive; Thermal analysis; Antiwear; XPS analyses; Tribological mechanism

1. Introduction

Friction and wear are unavoidable in industrial applications but can be reduced by the use of appropriate additives added to lubricants. With the excellent properties of anti-oxidation and anti-wear, zinc dialkyldithiophosphate (ZDDP) is widely used as an additive of engine lubricant. Recently, because of environmental requirement, more and more automobiles are equipped with the exhaust gas catalyst converter to reduce the pollution. However, the phosphorus contained in ZDDP would poison the catalyst and so reduce efficiency. Furthermore, the zinc salts produced by ZDDP in tribological condition might also cause the potential electrolytic corrosion. Therefore, synthesizing and studying new kinds of anti-wear additives to decrease the amount of ZDDP in lubricant, even to replace it, is highly desirable.

It has been reported that some heterocyclic compounds, especially those containing N or S element in their compact and stable structures, possess excellent tribological performances [1–13]. Because some of these compounds do not contain P and Zn elements, they can meet the environmental requirement [8]. In this paper, we synthesized a derivative of dialkyldithiocarbamate containing the benzothiazole group. Its tribological performance, as an antiwear additive of lubricating oil, was evaluated by a four-ball friction and wear tester. Solid film structure of rubbed surface was analyzed using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). For comparison, a commercial zinc butyloctyldithiophospate (ZDDP) had been evaluated simultaneously.

2. Experimental details

2.1. Synthesis and characterization of the novel additive

AR grade chemicals (tetrahydrofuran, benzene, chloroform and carbon disulfide) and CR grade chemicals (di-n-butylamine, 2-amine benzothiazol, chloroacetetyl chloride) were used.
The novel heterocyclic compound of \textit{S-\{2-(acetamido)benzothiazol-1-yl\}N,N-dibutyl dithiocarbamate was synthesized according to the pathway outlined in Scheme 1.}

\begin{center}
\textbf{Scheme 1. Reaction pathway of novel compound.}
\end{center}

First step, a solution of 0.1 mol chloroacetyl chloride in 20 ml chloroform was added dropwise into a stirred solution of 0.1 mol 2-amino benzothiazol in 40 ml chloroform, then the mixture was refluxed for 2 h. The chloroform was removed by distillation and the intermediate 2-(α-chloro acetamido-yl) benzothiazol was obtained [14]. Second step, a solution of 0.1 mol CS\textsubscript{2} in 50 ml tetrahydroturan (THF) was added dropwise into a stirring solution of 0.1 mol dialkylamine in 100 ml THF at ice-bath temperature. After the mixture was stirred at room temperature for 2 h, 0.1 mol 2-(α-chloro acetamido-yl) benzothiazol was added into it, and it was then refluxed for 4 h. The THF solvent was removed by distillation; the remainder was dissolved with benzene, washed with water and dried by anhydrous MgSO\textsubscript{4}. The benzene was removed by distillation and the residue was purified by column chromatography using tetrachloromethane/n-hexane/ethanol (3/2/1) as eluent. After removing the eluent, a liquid product with dark brownish color was obtained. The product was characterized by IR, \textsuperscript{1}HNMR and elemental analysis. The results of elemental analysis listed in Table 1 are in good agreement with the required values within the limits and experimental error.

2.2. Tribological performance of novel additive

The wear properties of the novel compound in liquid paraffin were evaluated with a four-ball machine at a rotating speed 1450 rpm, test duration of 30 min, loads of 196, 294, 392, 490, 588 N, and room temperature about 20 °C. The balls used in the tests were made of GCr15 bearing steel (AISI52100) with an HRC of 59–61. The load-carrying capacity of the additive was obtained according to GB3142-82, similar to ASTM D-2783. An optical microscope was used to determine the wear scar diameters of the three lower balls with an accurate reading to 0.01 mm. Then, the average of the three wear scar diameters was calculated and cited as the wear scar diameter reported in this paper. The friction coefficients were recorded automatically with a strain gauge equipped with the four-ball tester.

For comparison, the lubricating performance of a commercial zinc butyloctyldithiophosphate (ZDDP), which was produced by Lanzhou refinery, was evaluated at the same time. Liquid paraffin with the chemical characteristics shown in Table 2 was used as the base stock.

2.3. Worn surface analysis

X-ray photoelectron spectroscopy (XPS) was conducted with a PHI-5702 X-ray photoelectron spectrometer. The upper ball used for XPS analysis was washed ultrasonically with petroleum ether and dried after testing at additive concentration of 1.0 wt.% under load of 588 N for test duration of 30 min. The MgKα radiation was used as the excitation source at pass energy of 29.35 eV. The additive sample for XPS analysis was prepared by KBr press slice method [11], and the binding energy of C1s (284.6 eV) was used as the reference. The wear scar morphology was visualized with KYKY1000B Scanning electron microscopy at voltage 20 kV.

2.4. Copper corrosion test

Copper corrosive testing was conducted at 100 °C for 3 h according to GB5095-85, similar to ASTM D-130. The polished electrolytic copper strip and a suitable vessel containing the sample oil were used.

\begin{center}
\begin{tabular}{|c|c|c|c|c|}
\hline
Elements & C & H & N & S \\
\hline
Experimental (%) & 55.02 & 6.42 & 10.31 & 24.19 \\
Theoretical (%) & 54.65 & 6.37 & 10.62 & 24.32 \\
\hline
\end{tabular}
\end{center}

Table 1
The elemental analysis result of the novel compound

<table>
<thead>
<tr>
<th>Density (g cm\textsuperscript{-1})</th>
<th>0.8465</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (mm\textsuperscript{2} s\textsuperscript{-1})</td>
<td>40 °C</td>
</tr>
<tr>
<td>100 °C</td>
<td>4.42</td>
</tr>
<tr>
<td>Viscosity index</td>
<td>117</td>
</tr>
<tr>
<td>S Content (ppm)</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

Table 2
The physical characteristics of liquid paraffin
2.5. Thermal stability

The thermal stability of the novel additive under nitrogen atmosphere was investigated by thermogravimetric analyses (TGA) over a temperature range from ambient to about 500 °C at a rate of temperature rise of 20 °C/min in Delta TGA 7 thermal analyzer.

3. Results and discussion

3.1. Copper corrosion test

The results of copper corrosive test indicate that both of the grades are 1a while tested with the oil samples containing 0.5% or/and 1% novel additive. The term “grade” represents the property of additive copper corrosion, it is judged according to the color of copper strip. The lower the copper corrosive property of additive, the lower the “grade” data. If the color of copper strip is not changed, the “grade” is determined as 1a. So it can be deduced that the additive added in base stock has low corrosive effect.

3.2. Thermal stability

According to the analytical results of TGA of the novel compound under nitrogen atmosphere, we find that the compound possesses good thermal stability (see Fig. 1). The first degradation point appears at 213 °C, this may be due to the chain part breaking down; The second degradation point appears at 250 °C, this may be also due to the chain part breaking down; The third degradation point appears at 360 °C, this is due to the ring part breaking down [12].

3.3. The maximum non-seizure load (\(P_B\) value)

The maximum non-seizure loads of the novel compound and ZDDP are listed in Table 3. The results show that the \(P_B\) value of the novel compound is higher than that of the base stock and ZDDP. This indicated that the novel compound has excellent load-carrying capacity.

3.4. AW performance

Wear scar diameter is an indication of wear amount, and therefore the relationship of wear scar diameters versus friction time will display a dependence of wear on friction time. The results of base oil as well as the oil with 1.0% novel additive are given in Fig. 2. It is shown that although both diameters increase with friction time, the rate of increase for the oil with novel additive was evidently lower than that of base oil. As a result, the former gave smaller wear scar diameter than the latter. This result indicates further that the novel additive can raise wear resistance of lubricating oil. For comparison, the performance of ZDDP was also evaluated; the result indicates that the antiwear property of ZDDP is slightly better than that of the novel additive.

Fig. 3 gives the wear scar diameter of steel ball lubricated by base stock and by base stock containing 1.0 wt% novel additive (or ZDDP). Results indicate that the novel additive exhibits excellent AW property in a wide range of applied loads as compared to the base stock.

![Fig. 1. The typical TG spectra of the novel additive.](image1)

![Fig. 2. Dependence of wear scar diameter on friction time.](image2)

Table 3

<table>
<thead>
<tr>
<th>Oil sample</th>
<th>Additive concentration/ wt.%</th>
<th>Maximum non-seizure load/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid paraffin (LP)</td>
<td>0</td>
<td>392</td>
</tr>
<tr>
<td>LP + ZDDP</td>
<td>1</td>
<td>755</td>
</tr>
<tr>
<td>LP + novel additive</td>
<td>1</td>
<td>784</td>
</tr>
</tbody>
</table>


At lower load, the AW property of novel additive is similar to that of ZDDP, however the AW property of ZDDP is slightly better than those of the novel additive at higher load.

3.5. Friction performance

The friction coefficients of novel additive in five different concentrations are shown schematically in Fig. 4. As can be seen in the figure, the friction coefficient of the base stock was 0.068, but it was reduced 25.7 percent to 0.0505 by the addition of 0.5 percent novel additive to the oil. A higher concentration of novel additive resulted in a lower friction coefficient. As the adding amount reached 2.0%, a 33.8% reduction of friction coefficient was observed. However the reduction tendency was decreased with further addition. Furthermore, it can be found that the friction reduction property of ZDDP is the same as that of the novel compound.

The decrease of friction coefficient can be attributed to the formation of adsorption film and/or reaction film by the additive on the rubbing surface. As novel additive is blended into the base stock, the additive molecules interact with the freshly exposed worn surface to form a protective adsorption film and/or reaction film whose shear strength is considerably less than that of the metal matrix, and the friction coefficient is decreased. The more novel additive is added, the more molecular layers within the adsorption film and more reaction products are generated to prevent the asperities on the rubbing surfaces from direct contact, and the lower the friction coefficients become. On the other hand, with a further increase of the additive, the adsorption process tends to be saturated, and the reaction film tends to completely separate the asperities, therefore, the reduction tendency of friction coefficients decrease.

3.6. A discussion of antiwear mechanism of novel additive

The enlarged SEM photographs (×500), as shown in Figs. 5 and 6 clearly display that the scarred surface...
lubricated by novel additive was uniform and smooth; however, the one lubricated by base oil had already been broken at the same experimental condition. These SEM results further verify that novel additive possesses better antiwear behavior than base oil.

In order to explore the lubricating mechanism of the novel compound as an additive in liquid paraffin, XPS analysis of the worn steel surface and the KBr press slice containing pure additive was carried out. Table 4 shows the binding energies of the oxygen, nitrogen, sulfur, and iron on the worn scar surface. For comparison, the binding energies of additive without any sliding are also listed.

It can be seen that the binding energy of N 1s in pure additive is 400.3 eV. For the wear tested with 1.0% additive at 588 N for 30 min, the binding energy of N 1s is 400.1 eV as shown in Fig. 7a. The results indicate that there is a strong adsorption of compounds containing N element, which may be additive or the break down compounds of additive during sliding on the worn surface. In case of sulfur, the binding energy of S 2p for pure additive is 164.2 eV. The spectrum of S 2p shown in Fig. 7b illustrates the existence of three peaks at 168.8, 164.5 and 162.3 eV, respectively, showing the tribochemical reaction that occurred between the additive with the metal surface during the sliding processes. By comparison with the standard values summarized in Table 5 [15], the binding energy at 168.8 eV corresponds to sulfate on the worn scar; the binding energy at 164.5 eV corresponds to the S in pure additive; the binding energy at 162.3 eV may be due to the existence of organosulfur compound or FeS$_2$. The Fe2p peak appearing at binding energy 710.6 eV corresponds to iron oxide and/or sulfide, indicating that the lubricated steel surface is liable to oxidize or sulfurize in the friction process. The O1s peak corresponding to iron oxide appears at 530.2 eV as shown in Fig. 7c, respectively.

Surface analysis results demonstrate that a stable lubricating film can be formed on the rubbed surface. When the specimen was lubricated with novel additive. This lubricating film is complex and consists of reaction layer and adsorption layer. The reaction layer originates from the tribochemical reaction of S element contained in the dibutyl dithiocarbamate group and benzothiazole group, and results in the formation of sulfate and organosulfur compound (or FeS$_2$). Furthermore, with the compact and

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**Table 4**

<table>
<thead>
<tr>
<th>Elements</th>
<th>O1s</th>
<th>N1s</th>
<th>S2p</th>
<th>Fe2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure additive</td>
<td>531.8</td>
<td>400.3</td>
<td>164.2</td>
<td></td>
</tr>
<tr>
<td>Wear scar</td>
<td>530.2</td>
<td>400.1</td>
<td>168.8</td>
<td>164.5</td>
</tr>
</tbody>
</table>

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**Table 5**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous sulfide (FeS)</td>
<td>161.6</td>
</tr>
<tr>
<td>Iron disulfide (FeS$_2$)</td>
<td>162.9</td>
</tr>
<tr>
<td>Elemental sulfur (S$_8$)</td>
<td>164.1</td>
</tr>
<tr>
<td>Dibenzyl disulfide</td>
<td>164.4</td>
</tr>
<tr>
<td>Sodium sulfate (Na$_2$SO$_4$)</td>
<td>168.5</td>
</tr>
<tr>
<td>Ferrous sulfate (FeSO$_4$)</td>
<td>168.8</td>
</tr>
</tbody>
</table>

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Fig. 7. XPS spectra of typical elements on worn steel surfaces.
stable structure of benzothiazole, and the lone pair electrons of N atom contained in this group, a stable adsorption layer can be formed. With such stable reaction and adsorption layers, the novel additive can effectively decrease the friction and wear, and possesses excellent tribological performances.

4. Conclusions

Based on the above results, we can draw the following conclusions:

1. The S-[2-(acetamido) benzothiazol-1-yl]N,N-dibutyl dithiocarbamate shows excellent antiwear property and friction reduction property similar to ZDDP, and exhibits better load-carrying capacity than ZDDP.
2. The novel compound has good thermal stability and low copper corrosive property.
3. Surface analyses of the rubbed surface revealed the formation of a protective film containing ferric sulfide, ferric sulfate, organicsulfur compound and organicnitrogen compound. The protective film formed during sliding processes contributed to the increase in the wear resistance and friction reduction.

Acknowledgements

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References


