ANTIWEAR AND REDUCING FRICTION PERFORMANCE OF 3-(N, N-DIALKYL DITHIOCARBAMATE-YL) ACID DERIVATIVES

Weijiu HUANG
Department of Mechanical Engineering, Chongqing Institute of Technology, ChongQing, 400050, P. R. CHINA; e-mail: huangweijiu@263.net
Junxiu DONG, Boshui CHEN
Department of Petroleum Applied Engineering Logistic Engineering College, Chongqing, 400016, P. R. CHINA
Yuanqiang TAN
Department of Mechanical Engineering, Xiangtan University, Xiangtan, 411105, P. R. CHINA

SUMMARY
The tribological performance and action mechanism of two acid derivatives, 3-(N, N-dibutyl dithiocarbamate-yl) propionic acid and 3-(N, N-dibutyl dithiocarbamate-yl) malonic acid, were investigated by tribological experiments and surface analysis. The results show that the two compounds have excellent load-carrying capacity and antiwear property; and may obviously improve the weld load of water. The tribological performances of 3-(N, N-dibutyl dithiocarbamate-yl) malonic acid are superior to those of 3-(N, N-dibutyl dithiocarbamate-yl) propionic acid. The antiwear action mechanisms of the acid compounds can be ascribed to the formation of adsorption film and chemical reaction film. The cooperation action of these films plays an important role in the prevention of tribological failure.

Keywords: water-soluble, acid derivative, antiwear, action mechanism, tribology

1 INTRODUCTION
With the advantages of high thermal capacity and thermal conduction coefficient, low compressibility, fire-resistance, reduced environmental pollution and energy conservation, water-based fluids are widely used as fire resistant hydraulic fluids and metalworking fluids [1-2].

Most water-based antiwear agents used hitherto are oil-soluble agents, which are dispersed in water by using surfactants. However, the result is not always satisfactory because of their worse solubility in water. In the lubricant research, more attention has recently been paid to modify the solubility of oil-soluble additives in water and to develop new water-soluble additives in order to improve the lubricating property of their water fluids. A lot of aqueous antiwear additives, which showed a good load-carrying capacity and antiwear property, have been reported [3-8].

In this paper, an attempt has been made to estimate the tribological functions of both 3-(N, N-dibutyl dithiocarbamate-yl) propionic acid and 3-(N, N-dibutyl dithiocarbamate-yl) malonic acid, and their antiwear action mechanisms were also discussed.

2 EXPERIMENTAL

Extreme pressure and antiwear tests were performed on four-ball machine under the rotary speed of 1450 rpm at ambient temperature. GCr15 steel balls (HRC = 59 – 61) with a diameter 12.7 mm were adopted.

The block-on-ring testing machine was used to perform the friction tests. The ring was quenched CrWMn steel ring of 49.24 mm diameter, 12.7 mm height, 62HRC hardness and a surface roughness of $R_a = 0.27 \mu m$, which was rotating against 45 steel block (19×12.35×12.35 mm$^3$) with a hardness of 44.8 HRC and a surface roughness of $R_a = 0.35 \mu m$. The test conditions were 100 N load, 600 rpm speed and room temperature. The test duration was 300 s.

The water solution with 1.0 % triethanolamine was used as base fluid. The tribological performance of 3-(N, N-dibutyl dithiocarbamate-yl) propionic acid (DTCPA) and 3-(N, N-dibutyl dithiocarbamate-yl) malonic acid (DTCMA) were evaluated. The two novel compounds were synthesized in the laboratory [9].

X-ray photoelectron spectroscopy (XPS) was conducted with a PHI-5702 X-ray photoelectron spectrometer. The Mgkα radiation was used as the excitation source at pass energy of 23 eV. The upper ball used for XPS analysis was washed ultrasonically with petroleum ether. The Mgkα radiation was used as the excitation source at pass energy of 23 eV. The binding energy of C1s (284.6 eV) was used as the reference.

3 RESULTS AND DISCUSSION

3.1 Load-carrying capacity and weld load

The influence of additive concentration on the maximum non-seizure load and the weld load are shown in Figure 1 and 2 respectively. The results indicate that the addition of novel additives significantly enhance the maximum non-seizure load and the weld load of water-based fluid. When the additive concentration is at 2 % for DTCPA and DTCMA, no augmentation of their maximum non-seizure load is observed. The maximum non-seizure load is closely related to the influence of additive concentration on the adsorption process. More
coverage and more layers of additive molecules on the frictional surfaces are conductive to raising the maximum non-seizure load. There are two carboxyl groups in DTCMA molecular and a carboxyl group in DTCPA molecular, which indicates that the adsorption amount of DTCMA molecular on metal surface is maybe larger than that of DTCPA at the same concentration, therefore the load-carrying capacity of DTCMA is superior to that of DTCPA.

3.2 Antiwear characteristics

The wear tests were performed on the four-ball tester under load of 294 N and duration of 30 min. Figure 3 shows the effect of additive concentrations on their antiwear properties. There is an optimum concentration at reducing wear scar diameter, the optimum additive concentration is at 1.5 % for DTCPA, and at 2.0 % for DTCMA. As the additive concentration falls below this point, the wear scar diameter of steel ball decreases as the additive concentration increases. As the additive concentration increases beyond this point, the wear scar diameter of steel ball increases as the additive concentration increases. The reason for the slight increase of the wear scar diameter is maybe due to the corrosion of S element in additives. This phenomenon is also observed in our previous work [10].

3.3 Frictional characteristic

The friction coefficients obtained in block-on-ring tests are showed in figure 4. It indicates that during the test duration, the friction coefficient of the water-based fluids containing the two additives is smaller than that of water, but there is a great wave of friction coefficient, and there is no obvious difference between the two additives.

3.4 XPS analysis

The DTCPA additive was tested on the four-ball tester (392 N, 1450 rpm, 30 min, 1.0 %), and the upper ball was analyzed by XPS. The experimental results are shown in table 1.
<table>
<thead>
<tr>
<th>Element</th>
<th>N</th>
<th>S</th>
<th>Fe</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy (eV)</td>
<td>401.4</td>
<td>168.6, 162.5</td>
<td>710.6</td>
<td>284.6, 286.2, 288.1</td>
</tr>
</tbody>
</table>

Table 1: The binding energy of elements on worn surface (eV)

The N 1s binding energy is 401.4 eV, it shows that the nitrogen is adsorbed on the metal surface. The binding energy of S 2p occurs at 168.6 eV and 162.5 eV, which responds to the compound of sulfate and Fe₂S respectively [11]. The binding energy of the Fe 2p is 710.6 eV, which corresponds to Fe₂O₃ or FeS [12]. The C1s binding energy indicates that there are several chemical states of carbon atom existence. Besides the referenced value of C1s at 284.6 eV, the peak at 286.2 eV is due to C=O bond, and the peak at 288.1 eV is assigned to carboxyl group, which indicates that there is still acid compound existed on the worn surface.

An antiwear mechanism of the additive, therefore, can be ascribed to the formation of adsorption film consisting of organic nitrogen compound and acid compound, and of chemical reaction film containing sulfate, FeS and FeS₂. The cooperation action of these films plays an important role in the prevention of tribological failure.

4 CONCLUSION

(1) The additions of novel compounds into water-based fluid significantly reduce the wear scar diameter of steel ball, and noticeably improves the load-carrying capacities and the weld load, but may not obviously improve the friction-reducing property of water.

(2) A stable lubricating film consisting of adsorption layer containing nitrogen atom and acid compound and reaction layer containing FeS₂, FeSO₄ and FeS is formed on the steel ball surface. It makes these novel compounds possess good antiwear properties, excellent load-carrying and extreme pressure performances.

5 ACKNOWLEDGEMENTS

The work reported here was supported financially by Chongqing Applied Science Foundation.

6 REFERENCES

[10] Huang weijiu; Li fenfang; Chen boshui; Dong junxiu: The performance and antiwear mechanism of (2-sulphurone-benzothiazole)-3-methyl esters as additives In synthetic lubricants. Tribology International. 33(2000), 8: 553-558