**[Article ID]** 1003- 6326(2001)01- 0157- 04

# Antiwear and reducing friction performance of (2-sulphurone-benzothiazole)-3-methyl dodecanoate ①

HUANG Wei-jiu(黄伟九)[1], LI Fen-fang(李芬芳)[2], CHEN Bo-shui(陈波水)[2], CHEN Guo-xu(陈国需)[2], DONG Jun-xiu(董浚修)[2]

(1. Department of Mechanical Engineering, Chongqing Institute of Technology, Chongqing 400050, P. R. China;
2. Department of Petrol Engineering, Logistic Engineering College, Chongqing 400016, P. R. China)

**[Abstract]** A heterocyclic derivative of (2-sulphurone-benzothiazole)-3-methyl dodecanoate was synthesized. Its tribological performance when added to liquid paraffin was evaluated on a four-ball tester and a ring-on-block machine. Results indicate that compared with the base oil the wear resistance and load-carrying capacities of the oil with novel additive are improved, and the friction coefficient is decreased. There is an optimal content of the novel compound, at which the corresponding oil gives the highest maximum non-seizure load. Above the content, the load carrying capacity of the oil is not increased but decreased. The nature of the film formed on the rubbed surface was investigated by X-ray photoelectron spectroscopy (XPS) analysis, and the action mechanism of the novel compound was discussed.

**[Key words]** synthesis; additive; mechanism; antiwear; friction reducing

**[CLC number]** TH 117.2 **[Document code]** A

## 1 INTRODUCTION

It is well known that friction and wear are unavoidable in mechanical equipment but can be reduced by the use of appropriate additives added to lubricants. Some compounds containing sulfur, chlorine and phosphorus may react with the metal surface at high temperature and high pressure, and form easily sheared reaction layers to prevent severe wear and seizure. So these compounds are usually used in lubricants as antiwear and extreme pressure additives. However, due to environmental and operational reasons, the use of the compounds containing chlorine and phosphorus are restricted. Therefore developing new types of friction-reducing and antiwear additives is highly desirable.

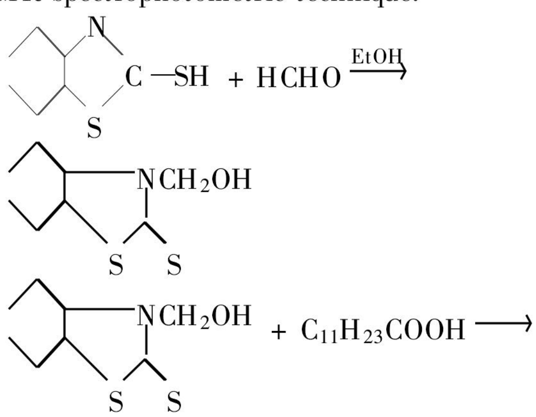
Recently, much attention has been paid to the research on the friction and wear properties of heterocyclic compounds, since heterocyclic compounds have compact and stable structures. A number of ashless compounds based on derivatives of heterocyclic compounds have been reported in recent literature as antiwear and extreme pressure additives[1~13]. And 1, 2, 4-triazole, 1, 2, 3-thiadiazole, benzothiazole and benzotriazole have been proven to possess excellent anticorrosive, antirust, copper deactivating and antiwear properties.

In this paper, the preparation of (2-sulphurone-benzothiazole)-3-methyl dodecanoate is described. The tribological performance of the novel compound used as an additive in liquid paraffin is evaluated. The rubbed surface is investigated using XPS analysis, and the antiwear mechanism is discussed.

## 2 EXPERIMENTAL

### 2.1 Preparation of additive

The additive was prepared according to the reaction pathway outlined in Eqns. (1) and (2). The intermediate, 2-sulphurone-3-hydroxymethyl benzothiazole, was synthesized according to Ref. [14], then the (2-sulphurone-benzothiazole)-3-methyl dodecanoate was prepared by esterification of the intermediate with the dodecanoic acid using classic procedures. All the chemicals are of AR grade. The product is a yellow solid, whose composition and structure have been verified by element analysis, IR and 1HNMR spectrophotometric technique.

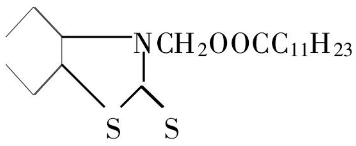



(1)

---

① **[Foundation item]** Project (59875083) supported by the National Natural Science Foundation of China

**[Received date]** 2000- 03- 08; **[Accepted date]** 2000- 06- 19




(2)

### 2.2 Tribological properties of novel compound

The load carrying capacities and antiwear properties were evaluated on MQ-800A four-ball tribotester at 1450 r/min at room temperature. The maximum non-seizure load was determined according to the national standard method GB3142-82. The wear scar diameter of the steel ball after test duration of 30 min was also measured. The balls with diameter of 12.7 mm in the tests were made of GCr15 bearing steel with an HRC of 59 to 61. Friction coefficient of oils were measured under a constant load of 300 N using HQ-1 ring-on-block tribotester, where the ring was quenched CrWMn steel ring (Cr: 0.9% ~ 1.2%, C: 0.9% ~ 1.05%, W: 1.2% ~ 1.6%, Mn: 0.8% ~ 1.1%, Si: 0.15% ~ 0.35%) of 49.24 mm diameter, 12.7 mm height, 62HRC hardness and a surface roughness of Ra as 0.27 μm, which was rotating against 45 steel block (12 mm × 6 mm × 4 mm) with a hardness of 44.8HRC and a surface roughness of Ra as 0.35 μm.

The rotating speed of ring was 600 r/min. The base oil is chemically pure grade liquid paraffin.

### 2.3 Surface film analysis

X-ray photoelectron spectroscope (XPS) was conducted with a PHI-1600 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 2.0% under load of 392 N for test duration of 30 min. The Mg $K_\alpha$ radiation was used as the excitation source at pass energy of 50 eV. The binding energy of C 1s (284.6 eV) was used as the reference. The wear scar morphology was visualized by X-650 Scanning Electron Microscopy.

## 3 Results and discussion

### 3.1 Effect of additive on friction coefficient of oil

Friction coefficients of base oil and the oil with 1% novel additive are given in Fig. 1. It can be seen that the friction coefficient of base oil increases as friction time increases at the initial stage of friction, and then decreases with rubbing time. That the friction coefficient increases probably results from an increase of real contacting area of the rubbing surface owing to wear. Due to a gradual deposition of friction product and the shearing stress decreasing, the friction coefficient decreases with rubbing time. The friction coefficient of the oil with additive has no significant change with rubbing time, and is smaller than that of base stock alone. It is indicated that the novel additive possesses reducing friction property in lubricating oil, and may be effective to decrease the energy loss owing to friction.

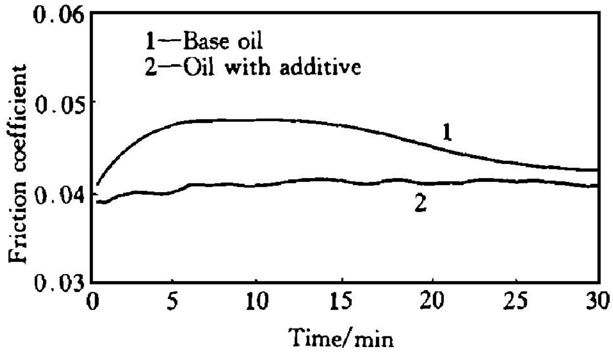



**Fig. 1** Effect of additive on friction coefficient at load of 300 N for 30 min

### 3.2 Effect of additive concentration on load carrying capacity

Maximum non-seizure load ($F_B$) is a measurement of load carrying capacity of oil. The $F_B$ values of base stock and oil with additive at different amounts are given in Fig. 2. It is shown that the oils with additive show greater maximum non-seizure load than base oil. In other words, the novel compound can strengthen the load carrying capacity of the base oil. Furthermore a maximum of $F_B$ is shown in Fig. 2. Corresponding content of additive is 1%, above the optimal content, the maximum non-seizure load of oil decreases. A possible explanation is that excessive additive may increase the ratio of organic composition in antiwear film, and lower the strength of the film.

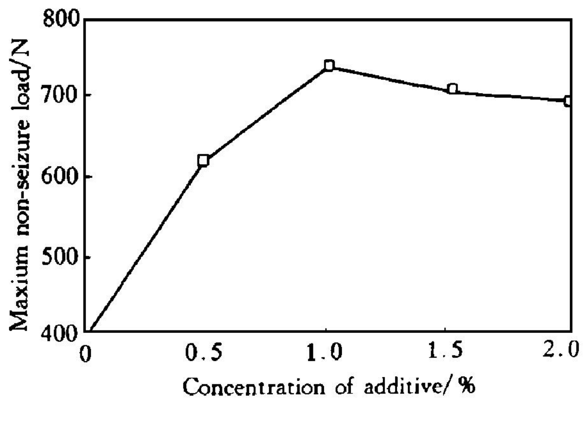



**Fig. 2** Effect of additive concentration on maximum non-seizure load

### 3.3 Effect of load and additive concentration on antiwear property of oil

Fig. 3 gives the wear scar diameter of steel ball lubricated by base stock and by base stock containing 2.0% novel additive under various loads. It can be seen that the novel additive exhibits good antiwear property in a wide range of applied loads as compared to the base stock.

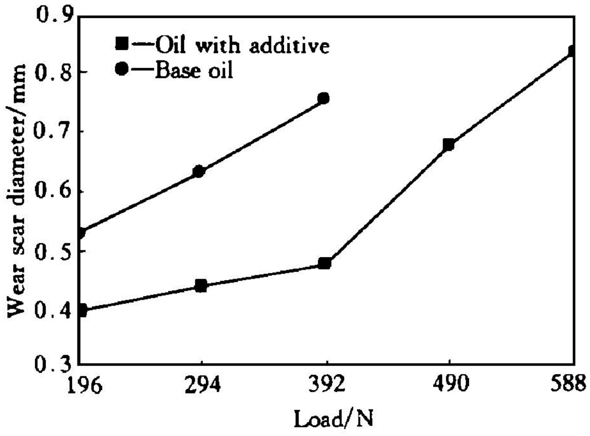



**Fig. 3** Effect of load on wear scar diameter at additive concentration of 2.0% for 30 min

Fig. 4 shows the wear scar diameter of steel ball as a function of the additive concentration in the base oil. Results indicate that the addition of the novel compound into the base oil significantly reduces the wear scar diameter under a load of 392 N, particularly at relatively low concentration.

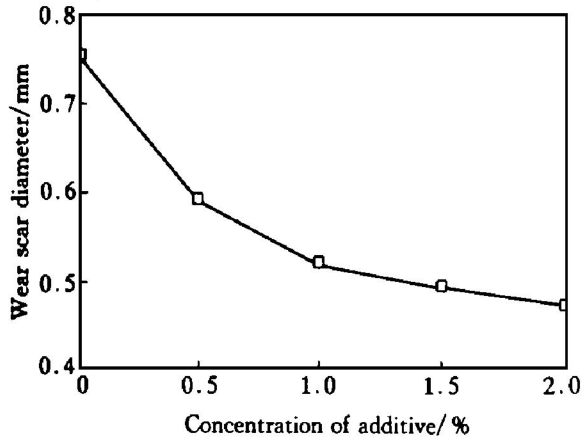



**Fig. 4** Effect of additive concentration on wear scar diameter at load of 392 N for 30 min

The wear scar morphologies of the steel ball after running in base oil and in the oil with 2% additive under 392 N for 30 min are given in Figs. 5 and 6, respectively. The grooves indicate that the wear scar does not result from elastic deformation but from evident wear. The larger the wear scar is, the more severe the wear is. Therefore, the oil with additive possesses higher wear resistance than base oil.

## 3.3 Worn surface analysis and discussion on anti-wear mechanism

It is inferred that the novel compound is effective on reducing the wear and friction of the base stock. Hence, the next step is to determine the action mechanism of the novel compound using X-ray photoelectron spectroscopy (XPS). Analysis of the chemical state of elements such as sulfur, nitrogen and iron in the lubricating film is essential for a better under-


**Fig. 5** Wear scar morphology of ball running in base oil

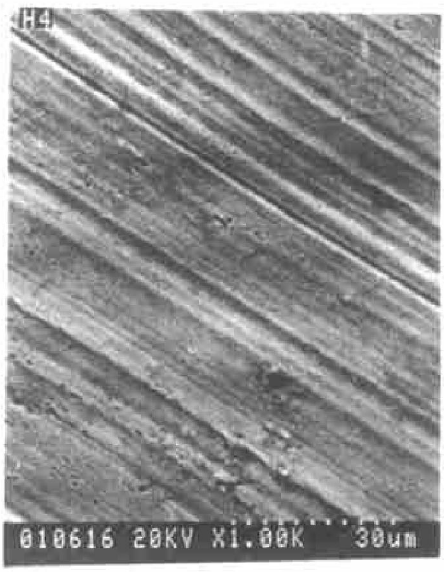



**Fig. 6** Wear scar morphology of ball running in oil with 2.0% novel additive

standing of the action mechanism of the novel compound. The XPS analytical results of the atomic concentrations of Fe, C, O, N and S elements on the surface are listed in Table 1. Table 2 shows the chemical state of the sulfur, nitrogen and iron on the worn surface. For comparison, the binding energies

**Table 1** XPS analysis results of atomic concentrations on rubbed surface %

| Element | C | O | N | S | Fe |
|---|---|---|---|---|---|
| Concentration | 73.46 | 17.94 | 1.17 | 2.49 | 4.94 |

**Table 2** Binding energy of elements in pure additive and on rubbing surface eV

| Surface | N | S | | Fe |
|---|---|---|---|---|
| Pure additive | 400.0 | 164.5 | | – |
| Worn scar | 399.8 | 168.8 | 161.9 | 710.6 |

of the elements in pure additive are also analyzed.

Table 1 shows that carbon and oxygen elements were detected with high concentrations. Nitrogen and sulphur were also present at the wear scar, although their concentrations were very low. It seems that the antiwear film is an organic layer, which is mainly composed of carbon and oxygen elements.

Table 2 indicates that the binding energy of N 1s in pure additive is 400.0 eV, after testing with 2.0% additive at 392 N for 30 min, the binding energy of N1s is 399.8 eV. The result indicates that there is a strong adsorption of additive on the metal surface.

Only one chemical state of iron on the surface is detected. The binding energy at 710.6 eV is corresponding to $Fe_2O_3$ or FeS.

In case of sulfur, the binding energy of S 2p for pure additive is 164.5 eV. The spectrum of S2p illustrates the existence of two peaks at 168.8 and 161.9 eV. In comparison with the standard value[15], the binding energy at 168.8 eV corresponds to sulfate on the worn scar, the binding energy at 161.9 eV corresponds to $FeS_2$. The results indicate that the tribochemical reaction has occurred between the additive with the metal surface during the sliding processes. It also indicates that the nitrogen and sulfur elements play important roles in enhancing load-carrying capacity and improving antiwear property.

According to the above analyses, the novel compound mechanism of action appears to be as follows. Under boundary lubrication conditions, it is decomposed by mechanical shear and other frictionally induced effects, such as heat, exoelectrons, deformation energy and fresh surfaces. The sulfur element in the novel compound may react with the metal surface to produce a thin chemical film on the surface, and nitrogen and carbon elements adsorb on the metal surface to form adsorption layer. The cooperative action between the chemical reaction layer and adsorption layer may play an important role in the prevention of tribological failure.

## 4 CONCLUSIONS

1) The (2-sulphurone-benzothiazole)-3-methyl dodecanoate seems to possess good antiwear and friction-reducing abilities, and may notably improve the load-carrying capacity of base stock.

2) There is an optimal content of the novel compound, at which the corresponding oil gives the highest maximum non-seized load; above the content, the load carrying capacity of the oil is not increased but decreased.

3) The action mechanism of the novel additive is forming adsorption and chemical reaction lubricating film on the metal surface. Although the antiwear film is an organic film, mainly consisting of carbon and oxygen elements, the nitrogen and sulfur elements play important roles in enhancing load carrying capacity, antiwear and friction-reducing properties.

## [REFERENCES]


[1] Singh T, Singh R, Verma V K, et al. A study of N, O and S heterocyclic compounds as extreme pressure lubricant additives [J]. Tribol Int, 1990, 23(1): 41- 46.

[2] Singh T and Chandrasekharan C V. The effect of nitrogen and sulphur compounds as extreme pressure lubricant [J]. Tribol Int, 1993, 26(4): 245- 250.

[3] Singh T, Hattacharga B A and Verma V K. EP activity assessment of certain nitrogen and sulphur heterocyclic compounds as potential additives in four balls test [J]. Lubr Eng, 1990, 46(10): 681- 685.

[4] REN Tian-hui, LIU Wei-ming and XUE Qun-ji. The effect of molecular structure of N-containing heterocyclic compounds on their wear properties [J]. Lubr Sci, 1993, 5(3): 205- 212.

[5] REN Tian-hui, XUE Qun-ji and WANG Han-qing. The tribological properties of S-(1H-benzotrizole-yl) methyl alkyl xanthates as additives in synthetic lubricants [J]. Lubr Eng, 1995, 51(10): 847- 850.

[6] REN Tian-hui, XUE Qun-ji and WANG Han-qing. A study of S-(1H-benzotriazol-1-yl)-methyl N, N-dialkyldithiocatbamates as novel multifunctional oil additives [J]. Wear, 1994, 172: 59- 64.

[7] REN Tian-hui, XUE Qun-ji and WANG Han-qing. A study of the tribological properties of S-(1H-benzotriazol-1-yl)-methyl, O, O'-dialkyldithiophosphates as additives in liquid paraffin [J]. Wear, 1994, 173: 167- 170.

[8] WAN Yong, PU Qing, XUE Qun-ji, et al. Antiwear and extreme pressure characteristics of 2-mercaptobenzothiazole derivative as the potential lubricating additive [J]. Wear, 1996, 192: 74- 77.

[9] ZHANG Jun-yang, LIU Wei-ming and XUE Qun-ji. The tribological behaviors of 2-mercaptobenzoxazole derives as additives in liquid paraffin [J]. Wear, 1998, 219: 184- 187.

[10] ZHANG Jun-yang, LIU Wei-ming, XUE Qun-ji, et al. A study of N and S heterocyclic compound as potential lubricating oil additive [J]. Wear 1999, 224: 160- 164.

[11] ZHANG Jun-yang, LIU Wei-ming and XUE Qun-ji. The tribological properties of the heterocyclic compound containing S, N, O and B as additive in liquid paraffin [J]. Wear, 1999, 224: 68- 72.

[12] ZHANG Jun-yang, LIU Wei-ming and XUE Qun-ji. A study of 2-(dibutylaminomethyl)-thiobenzimidazole as an oil additive [J]. Wear, 1999, 231: 279- 284.

[13] Hattacharya B A, Singh T, Verma V K, et al. The role of certain substituted 2-aminobenzothiazolylbenzoylthiocarbamides as additives in extreme pressure lubrication of steel bearing balls [J]. Wear, 1990, 236: 345- 357.

[14] HUANG Run-qiu, WANG Hui-ling and ZHOU Jia. Preparation of Organic Intermediate, (in Chinese), [M]. Chemistry Industry Press, 1997. 115.

[15] Moulder J F, William F S, Peter E S, et al. Handbook of X-ray photoelectron spectroscopy [M]. New York: Perkin- Elmer corporation, Physical Electronic Division, 1979. 215- 237.


(Edited by LONG Huai-zhong)