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Synthesis and tribological properties of antimony N, N-diethanoldithiocarbamate①

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[Abstract] Antimony N, N-diethanoldithiocarbamate was synthesized with diethanolamine, antimony trioxide and carbon disulfide. The influences of temperature, reaction time, solvents and their dosages were investigated, and the optimum synthesis conditions were: reaction temperature 15~ 20 ℃, reaction time 2.5 h, 250 mL CH_3OH as solvent and the hot CH_3OH as recrystallization solvent. Element analysis, IR, ^{1}HNMR and ^{13}CNMR spectra were used to study its chemical composition and molecular structure. Antimony N, N-diethanol-dithiocarbamate was added in the base oil, and its properties of wear resistance and extreme pressure were studied by F_B, F_D and WSD. The synthesis product behaves perfectly as wear resistance and extreme pressure additive and its extreme pressure property is superior to its wear resistance property. The mechanism of tribological action was discussed by using XPS and AES spectra, and the reason of good wear resistance and extreme pressure properties is that the synthesis product decompose element C, S and N.

[Key words] N, N-diethanoldithiocarbamate; synthesis; mechanism of extreme pressure and wear resistance
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1 INTRODUCTION

Antimony organic compound have been widely used as heat stabilizer, fire retardant, catalyzer, and medicine abroad[1~ 5]. In our country the study of antimony organic compound was seldom carried out although there are plentiful antimony resources. Here the heat stability property influences of some antimony mercaptan compound on PVC are studied, and some satisfied results are obtained[6, 7]. In this paper, a new kind of antimony organic compound—N, N-diethanol- dithiocarbamate was first synthesized[8~ 10], and its tribologlical were discussed.

2 EXPERIMENTAL

2.1 Principle of synthesis

In the presence of solvent, carbon disulfide reacts with diethanolamine to form $(C_2H_4OH)_2NCS_2H$, and then reacts with antimony trioxide to give antimony N, N-diethanoldithiocarbamate. The main reaction pathway is as

$$CS_2 + (C_2H_4OH)_2NH \longrightarrow (C_2H_4OH)_2NCS_2H$$

$$6(C_2H_4OH)_2NCS_2H + Sb_2O_3 \longrightarrow 2Sb(S_2CN(C_2H_4OH)_2)_3 + 3H_2O$$

2.2 Synthesis method

75 g diethanolamine, 40 mL CS_2 and 200 mL CH_3OH were put into a three-necked bottle with a stirrer, reflux condenser and a thermometer. Then added 29.2 g antimony trioxide at room temperature (about 25 ℃) while stirring. After 2.5 h, a yellow precipitate was obtained, filtered and washed several times with CH_3OH, then the precipitate was solved with heated CH_3OH and was filtered to remove slight unreacted Sb_2O_3, and then the filtrate was put into iced water bath to recrystallize for 3~ 4 h, the product was obtained as yellow needle solids.

2.3 Measurement of physicochemical properties

The content of Sb and S were measured by chemical analysis, and their melting points by a micro-melting point apparatus. After the product mixed with KBr, IR spectrophotometer, ^{1}HMMR and ^{13}CMMR spectra by Bruker Ac-80 spectrometer recorded. Its pulse interval is 0.5 s, pulse data 500~ 4000, exculpate ratio 0.12 Hz. The concentration of $CDCl_2$ was 5%~ 15%.

2.4 Application research and mechanism analysis

The synthesized product was added into the base lubrication oil, whose extreme pressure and wear resistance properties were tested by four-ball test machine according to GB3142-82 and then the results of WSD, F_B and F_D were obtained. The antifriction property was test by MMK-500 friction and abrasion tester. The tester was made up of iron annulus and

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lump and the diameter of annulus was 49.24 mm, 12.7 mm, the size of the lump 19 mm × 12.35 mm × 17.35 mm, the condition were: oil temperature 30 ℃, revolving speed 400 r/min, time 30 min. The base oil was 20# machine oil producted by Shanghai petrochemical factory.

The MICKOLAB MK ⅡAES spectrometer and XPS spectrometer were used to study the mechanism of extreme pressure and wear resistance.

3 RESULTS AND DISCUSSION

3.1 Effect of different condition on synthesis of antimony N, N-diethanoldithiocarbamate

The influences of reaction time, temperature, amount and type of solvents on yield of synthesized product were studied. The results are shown in Tables 1~ 4.

Table 1 Yields of antimony N, N-diethanoldithiocarbamate with different reaction times

Reaction time/min	30	60	90	120	150	180
Yield/%	48.5	65.3	73.4	75.5	77.9	77.9

Table 2 Yields of antimony N, N-diethanoldithiocarbamate at different temperatures

Temperature/℃	5	15	20	25	35	45
Yield/%	53.1	77.7	77.6	75.0	65.5	49.5

Table 3 Yields of antimony N, N-diethanoldithiocarbamate in different types of solvent

Type of solvents	CH_3OH	C_2H_5OH	CCl_3	CH_3CN
Yield/%	76.2	75.5	52.8	71.7
Type of solvents	CH_3COCH_3		C_6H_6	H_2O
Yield/%	62.6		55.1	67.9

Table 4 Yields of antimony N, N-diethanoldithiocarbamate in different amounts of solvent

Amount of CH_3OH/mL	50	100	150	200	250	300
Yield/%	62.4	65.3	73.7	76.1	76.3	76.3

The result show that the optimum synthesis condition is: 15~ 20 ℃, 250 mL CH_3OH as solvent and 2.5 h reflux time.

3.2 IR spectrum and NMR spectra

The IR spectrum and NMR spectra of antimony N, N-diethanoldithiocarbamate are shown in Figs. 1~ 3. It can be known from Fig. 1 that, peaks at 3235 cm^{-1} may be assigned to υ_{OH}, 2975, 2930 cm^{-1} to υ_{C-H}, 1200 cm^{-1} to υ_{C-N}, 1140~ 1260 and 1140 ~ 940 cm^{-1} to $\upsilon_{C=S}$, 700 ~ 600 cm^{-1} to υ_{C-S}. The deformation vibrations of C-H in $-CH_3$ and -CH appear at 1460, 1410 and 1360 cm^{-1}. The disappearance of absorption vibration at 2560 cm^{-1} manifests that antimony atom was substituted for hydrogen atom in the thiols, i.e. Sb-S bond was formed.

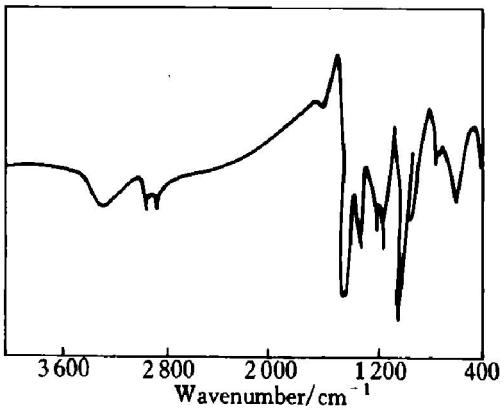

Fig. 1 IR spectrum of antimony N, N-diethanoldithiocarbamate

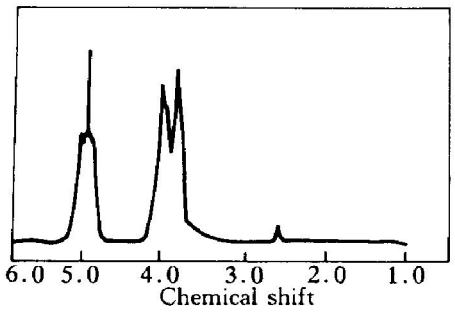

Fig. 2 ^{1}HNMR spectrum of antimony N, N-diethanoldithiocarbamate

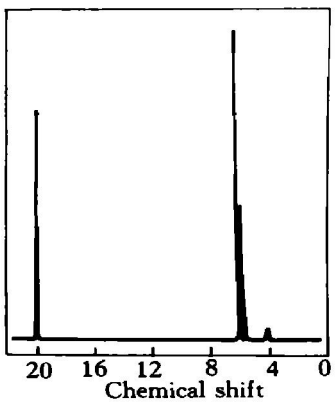

Fig. 3 ^{13}CNMR spectrum of antimony N, N-diethanoldithiocarbamate

From ^{1}HNMR spectrum we know that, the chemical shift δ(β) was 3.92, δ(α) 3.7 and

δ(γ) 4.98. From ^{13}CNMR spectrum we know that the chemical shift α-C was 57.3 and influenced by ^{14}N, the end of its peak changes wide and low. Because of the absence of -OH, the chemical shift of β-C was 58 and S-C-N 198.9.

From above it can be confirmed that the structure of antimony N, N-diethanoldithiocarbamate was $Sb(S_2CN(C_2H_4OH)_2)_3$.

3.3 Properties of extreme pressure and wear resistance

The values of F_B and F_D are 178 N and 392 N using base oil. From Fig. 4 we know that after adding antimony N, N-diethanoldithiocarbamate, value of F_B and F_D improve obviously. It shows that the product has good properties of extreme pressure and wear resistance. After adding 2%, the value F_B and F_D improve slowly and comparing the extent F_D is greater than F_B. It shows that compared with EP and AW additive, N, N-diethanoldithiocarbamate has excellent property of extreme pressure.

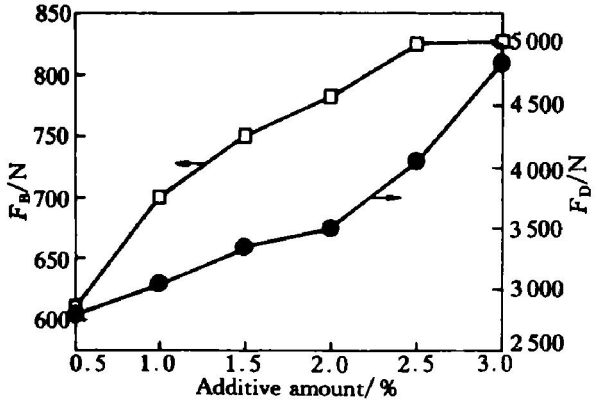

Fig. 4 Effect of amount of N, N-diethanoldithiocarbamate on pressure

From Table 5, we know that when the load is lower than 490 N, value of WSD was small, untill it is higher than 588 N, the value of WSD did not improve. So we also draw the conclusion that the lubrication oil has good properties of EP after adding the products.

Table 5 Effect of pressure on WSD

Load/N	98	196	294	392	490	588	686
WSD/mm	0.2	0.27	0.31	0.34	0.38	0.8	1.2

Note: concentration of additive is 1%.

3.4 Mechanism analysis

The result of the element composition on the friction surface of used ball in four-ball test was obtained through XPS and AES analysis, the results are shown in Figs. 5~ 6. There were sulphur, nitrogen, carbon and oxygen element on the used ball surface beside iron, chromium and manganese. And at first carbon and oxygen elements were detected with high concentrations. These declare that the lubrication film is an organic layer which is mainly composed of carbon and oxygen elements. From Fig. 5 the binding energy change's of element S (comparison with the standard value) indicates that the tribochemical reaction has occurred.

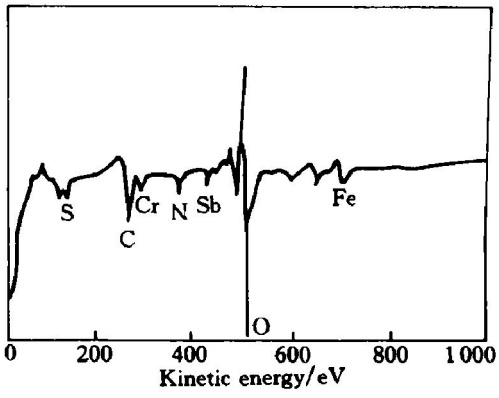

Fig. 5 AES spectra of ball surface element

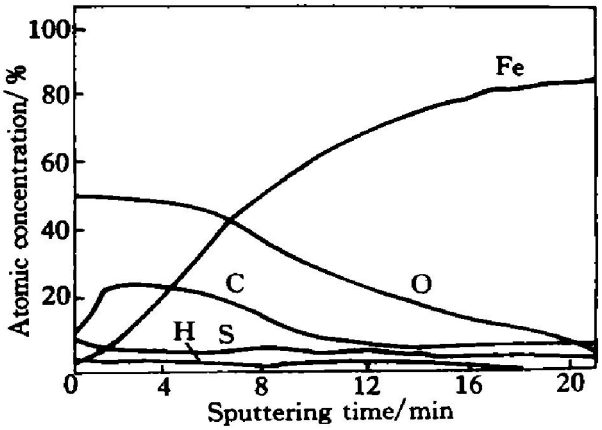

Fig. 6 AES spectra of ball depth anatomy

4 CONCLUSIONS

1) Antimony N, N-diethanoldithiocarbamate can be synthesized with triethanolamine, carbon disulfide and antimony trioxide. The optimum synthetic conditions are: temperature 15 ~ 20 ℃, reaction time 2.5 h, 250 mL CH_3OH as reaction solvent and hot CH_3OH as recrystallization solvent.

2) The data F_B, F_D and WSD of the lubrication oil added the product shows that after addition the F_B and F_D improve obviously while its WSD reduce. This manifests that the product had good properties of EP and AW.

3) The AES and XPS analyses techniques prove that the product has good properties because it decompose element C, S and N and a excellent lubrication film was formed.

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