SYNTHESIS AND APPLICATION OF ANTIMONY N, N-DIETHYLDITHIOCARBAMATE①

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ABSTRACT Antimony N, N-diethyldithiocarbamate was synthesized with diethylamine, carbon disulfide and antimony trioxide (or antimony sulfide). Its chemical composition was determined by elementary analysis, IR, ^{1}HNMR and ^{13}CNMR spectra. The influences of reaction time, temperature, molar ratio of raw materials, selection of solvents and purification method on synthesis technology were discussed. Its applications in polyvinyl chloride (PVC) resin as a heat stabilizer and in lithium complex grease as an exterme pressure anti-wear agent were studied.

Key words N, N-diethyldithiocarbamate preparation stability extreme pressure and wear resistance

1 INTRODUCTION

Antimony organic compounds containing Sb-S bonds have been widely used in industrial production because of their good applied properties, e.g. antimony mercaptide was used to stabilize polyvinyl chloride (PVC) resin against the degradative effect of heat and light[1-3]. Another type of antimony organic compound, N, N-dialkyldithiocarbamate has been reported by some patents to be used as oxidant in rap oil, ageing-resistant and vulcanization accelerator in rubber, and anti-breakage agent in fabric[4-10], but its detail synthesis conditions and its behaviors as extreme pressure (EP), antiwear (AW) additive in grease and as heat stabilizer in PVC resin were seldom reported. In this work, the synthesis of antimony N, N-diethyldithiocarbamate was studied. Its composition and structure were determined. The heat stability of PVC resin containing this compound has been discussed. The extreme pressure and antiwear properties of grease containing it has also been studied.

2 EXPERIMENTAL

2.1 The principle of synthesis

In the presence of solvent, carbon disulfide reacts with diethylamine to form $(C_2H_5)_2NCS_2H$, and then reacts with antimony trioxide or antimony trisulfide to give antimony N, N-diethyldithiocarbamate. The main reactions are as follows:

$$CS_2 + (C_2H_5)_2NH \longrightarrow (C_2H_5)_2NCS_2H$$

$$6(C_2H_5)_2NCS_2H + Sb_2O_3 \longrightarrow 2Sb(S_2CN(C_2H_5)_2)_3 + 3H_2O$$

$$6(C_2H_5)_2NCS_2H + Sb_2S_3 \longrightarrow 2Sb(S_2CN(C_2H_5)_2)_3 + 3H_2S$$

2.2 Synthesis method

Put 30 mL chloroform and 5.8 g Sb_2O_3 (or 6.9 g Sb_2S_3) into a three-necked bottle with a stirrer, reflux condenser and a thermometer, and then added dropwise 7.2 mL CS_2 and 12.4 g diethylamine at room temperature while stirring. After stirred about 1.5 h, the precipitate of Sb_2O_3 disappeared and a yellow transparent oil-phase was obtained. Heated and filtered to remove slight unreacted Sb_2O_3, and then poured the filtrate into a 200 mL conical flask. Recrystallization was performed by adding 50~60 mL mixed solvent into the flask. The product was obtained as yellow needle solids in 85% yield,

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with m. p. 132~ 134 ℃. The content of Sb was 21. 45%, and that of S 33. 36% (their theoretical contents are 21. 52% and 33. 88% respectively).

2. 3 Measurement of physicochemical properties

The contents of Sb and S were measured by chemical analysis, and their melting points by a micro-melting point apparatus. IR spectrum was recorded by a Nicolet FT-IR 740 spectrophotometer, and ^{1}HNMR and ^{13}CNMR spectra by a Bruker Ac-80 spectrometer.

2. 4 Measurement of applied functions

The synthesized product was added into the grease with lithium complex grease as base grease, whose extreme pressure, wear-resistance and high-temperature resistance were then tested. The drop point was determined according to GB3498, and the oil-film-breaking pressure, agglomerative pressure and integrated wear data were tested according to GB3141-82.

3 RESULTS AND DISCUSSION

3. 1 Effect of different conditions on synthesis of antimony N, N-diethyldithiocarbamate

The influences of reaction time, temperature, molar ratio of raw materials, amount and type of solvents and purification conditions on yield of synthesized product were studied. The results are shown in Figs 1~ 4 and Tables 1~ 2.

It can be seen that the optimum synthesis condition is: 25 ℃, 30 mL chloroform as solvent, molar ratio of Sb_2O_3 (Sb_2S_3) ∶ $HS_2CN(C_2H_5)_2$ = 1∶ 6. 05, reflux time 1. 5 h and chloroform-methanol mixture as recrystallization solvent.

Fig. 1 Effect of reaction time on yield
1 —Sb_2O_3; 2 —Sb_2S_3

Fig. 3 Effect of molar ratio of Sb_2O_3(Sb_2S_3) to $HS_2CN(C_2H_5)_2$ on yield
1 —Sb_2O_3; 2 —Sb_2S_3

Fig. 4 Effect of the amount of solvent on yield
1 —Sb_2O_3; 2 —Sb_2S_3

Table 1 Yields of antimony N, N-diethyldithiocarbamate in different solvents(%)

Solvents	methanol	ethanol	chloroform
Sb_2O_3 method	56.1	54.3	85.0
Sb_2S_3 method	51.2	50.5	72.2

Solvents	acetonitrile	acetone	benzene	water
Sb_2O_3 method	84.1	69.7	74.1	50.6
Sb_2S_3 method	70.1	61.4	67.3	42.7

Table 2 Effect of different recrystallization solvents on yield

Solvents	chloroform -methanol	benzene -methanol	chloroform -ethanol	benzene -ethanol	acetone
Yield/ %	85	78	74	77	79

Solvents	chloroform -ether	benzene -ether	chloroform -petroleum ether	benzene -petroleum ether
Yield/ %	74	75	80	76

3.2 IR spectrum

The IR spectrum of antimony N, N-diethyldithiocarbamate is shown in Fig. 5.

It can be known from Fig. 5 that, peaks at 2 870, 2 935 and 2 930 cm^{-1} may be assigned to $\nu_{C\text{-}H}$, and 1 490 cm^{-1} to $\nu_{C\text{-}N}$. The deformation vibrations of C—H in —CH_3 and —CH_2 appear at 1 360 and 1 410 cm^{-1}. The stretching vibration of >C—S appears at 990 ~ 1 050 cm^{-1}. The disappearance of absorption vibration at 2 560 cm^{-1} manifests that antimony atom was substituted for hydrogen atom in the thiols, i. e. Sb—S bond was formed.

Fig. 5 The IR spectrum of antimony N, N-diethyldithiocarbamate

3.3 NMR spectra

From ^{1}HNMR spectrum(omitted) we know that, α-H splits up into quartet peak owing to the influence of β-CH_3, with chemical shift δ(α) 3. 8~ 3. 9; β-H splits up into triad peak owing to the influence of α-CH_2, with chemial shift δ(β) 1. 29. These data coincide with $n + 1$ rule through calculation, and ratio of their peak areas is 2∶ 3.

From ^{13}CNMR spectrum (omitted) we know that, there are three kinds of carbon atoms, their chemical shifts are: β-C 11. 9, α-C 47. 9 and (S)>C—S 198. 5 respectively, and the ratio of their peak areas is 3∶ 2∶ 1 approximately.

3.4 Heat stability

Antimony organic compounds which contain sulfur can be used as stabilizer of polymer. The authors had studied antimony mercaptides as stabilizer for PVC resin[11- 12] before. In order to probe the heat stability of N, N-diethyldithiocarbamate for polymer, we added our syhthesized product into PVC resin, and compared its heat stability with other PVC resin whose stabilizer was commonly used metal soap. The result is shown in Fig. 6. It indicates that N, N-diethyldithiocarbamate is a better heat stabilizer than metal soap.

3.5 Properties of extreme pressure and wear resistance

Products containing sulfur element can be used as extreme pressure (EP) and antiwear (AW) additive. Although it has good high-temperature resistance, the usually used complex grease leads to serious wear of apparatus easily without better EP and AW properties.

This work used lithium complex grease as base grease, added synthesized antimony N, N-diethyldithiocarbamate as EP and AW additive, and then tested its applied properties.

The constituents of the sample are as follows:

mineral oil (500SN) 72%

octadecanoic acid 13%
methyl lactate 1%
lithium hydroxide hydrate 2%
Sb N, N-diethyldithiocarbamate 3%
ethene-propene copolymer
(solid content 30%) 10%

The results (See Table 3) showed that, after adding antimony N, N-diethyldithiocarbamate as EP and AW additive, drop point was higher than 250 ℃, i. e. the additive does not destroy the construction of the grease, it still has high-temperature resistance.

The four-ball test data showed that, oil-film-breaking pressure was 610 N, agglomerative pressure was 4 520 N and integrated wear value was 701 N, indicating that this grease can meet the needs of mechanical lubrication under the condition of heavy load within relatively wide temperature range.

Fig. 6 Heat stability of PVC resin with different stabilizers
(PVC 100 parts, DOP 10 parts, chlorowax-40 30 parts, additive 1 part)
1 —metal soap 5 parts; 2– antimony N, N-diethyldithiocarbamate 1 part

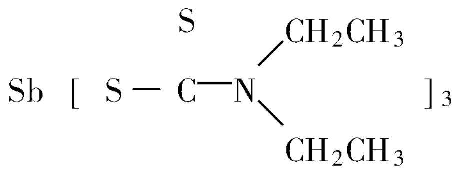
Table 3 Performance test of lithium complex grease containing synthesized product

Test results		Test methods
Drop point	> 250 ℃	GB3498
Oil-film-breaking pressure, p_B / N	610	
Agglomerative pressure, p_D / N	4 520	GB3141-82
Integrated wear data (ZMZ) / N	701	

4 CONCLUSIONS

(1) Antimony N, N-diethyldithiocarbamate can be synthesized with diethylamine, carbon disulfide and antimony trioxide (or antimony sulfide). The optimum process conditions are: molar ratio of $Sb_2O_3(Sb_2S_3)$: $HS_2CN(C_2H_5)_2$ = 1∶6. 05, temperature 25 ℃, reaction time 1. 5 h, chloroform as reaction solvent and methanol-chloroform mixture as recrystallization solvent.

(2) Data obtained from elementary analysis, IR, ^{1}HNMR and ^{13}CNMR spectra show that the formula of synthesized product is as following:



(3) Heat stability test of PVC resin manifests that synthesized product as a stabilizer is superior to metal soap with its amount only one-fifth of the latter.

(4) EP and AW tests of lithium complex grease containing synthesized product prove that it can meet the needs of mechanical lubrication under the condition of heavy load.

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