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Synthesis of antimony tris(mercaptoethyl carboxylates) as thermal stabilizer for polyvinyl chloride①

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[Abstract] A novel type of thermal stabilizers —antimony tris(mercaptoethyl carboxylates) ($Sb(SCH_2CH_2OOCR)_3$), was synthesized from carboxylic acid, antimony trioxide and 2-mercaptoethanol in two steps. The experimental results show that the molar ratio of carboxylic acid to antimony tris(2-hydroxyethyl mercaptide) is 1.2, when adding 0.6% tetra-*n*-butyl titanate as catalyst and xylene as isotropic solvent, heating and refluxing for about 2~ 4 h. The thermal stability was measured by heat-aging oven test. The thermal stability time is about 8~ 40 min(at 200 ℃) when adding 2% tetra-*n*-butyl titanate in polyvinyl chloride(PVC). Among these stabilizers, antimony tris(mercaptoethyl stearate) has best thermal stability. Its thermal stability is better than that of Ca-Zn complex and basic lead stabilizers, and equal to that of organotin. In addition, the stabilization mechanism of this kind of stabilizers for PVC was discussed briefly.

[Key words] PVC thermal stabilizer; antimony mercaptan; synthesis; thermal stability

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1 INTRODUCTION

PVC (polyvinyl chloride) is unstable because molecular defects occur in some of the polymer chains. When being subjected to heat these defects initiate a self-accelerating dehydrochlorination reaction. Stabilizers neutralize the HCl produced and introduce nucleophilic substitution reactions that prevent further degradation. Antimony mercaptides possess many advantages, such as good heat stability, low toxic effects, good property for processing and unexcelled cost/performance ratio used as stabilizers for pigmented, rigid, extruded PVC products and etc. It can partially replace the expensive organotin stabilizer[1~ 4]. The authors have done some researches in the field of synthesis and application of antimony mercaptides including antimony mercaptides salt, antimony mercaptan carboxylic ester and antimony tallate[5~ 9]. This paper reports the synthesis of a novel type of antimony mercaptides compounds —antimony tris(mercaptoethyl carboxylates) and their applications in PVC.

Generally, antimony mercaptide compounds are refer to antimony mercaptan carboxylic esters, and their molecular formulae are: $Sb(SR^1COOR^2)_3$ (R^1, R^2: alkyl). The molecular formulae in this paper are $Sb(SR^3OOCR^4)$ (R^3, R^4: alkyl). Here, similarly to “tin reverse-esters” (a kind of organotin widely used as PVC thermal stabilizers), these compounds is named as “antimony reverse-esters”. The synthesis and properties of antimony reverse-esters have not reported yet and the raw materials of synthesis of antimony reverse-esters are much cheaper than that of antimony mercaptan carboxylic esters.

2 EXPERIMENTAL

2.1 Main reagents and apparatus

All reagents, antimony trioxide, 2-mercaptoethanol, carboxylic acid, xylene, tetra-*n*-butyl titanate are chemical pure and without further treatment.

FT-IR740 spectrograph, elementary analysis instrument (Yanaco MT-3, Japan), micro melting point apparatus (XRC-1, Sichuan University Apparatus Factory), elementary analysis (Yanaco MT-3); roll mill (SK-160B, Shanghai Rubber Machine Co.), aging oven (410B, Shanghai Experiment Apparatus Factory), etc, were used in experiment.

2.2 Synthesis and characterization of antimony tris (mercaptoethyl carboxylates)

At first, antimony tris(2-hydroxy lmercaptide) was synthesized by reaction of antimony trioxide and 2-mercaptoethanol[10].

Taken antimony tris (mercaptoethyl stearate) (ATS) as an example, ATS was synthesized from antimony tris(2-hydroxyl mercaptide) and stearic acid. Certain molar fraction of antimony tris (2-hydroxyl mercaptide), stearic acid and xylene solvent were added into a dry 250 mL three necked flask equipped with heater and temperature controller, magnetic stirrer and water knockout trap. Then, tetra-*n*-butyl titanate was added as catalyst into this reactor. The reactants were heated and refluxed for a period of time until no water can be isolated from the reaction system. After being distilled at 100 ℃, 2 kPa to remove solvent from crude product, cooled, washed with ethyl ether and dried at vacuum condition, ATS was obtained with the yield of 82.5%.

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2.3 Analysis methods

Infrared spectra ware recorded in KBr on spectrograph in the range of 4 000~ 400 cm^{-1}. The antimony contents were determined by the method of oxidimetry with potassium bromate[11]. Sulfur contents were determined by the method of oxidimetry with hydrogen peroxide[11]. The melting points of products were tested using micro melting point apparatus.

2.4 Stabilities of antimony tris(mercaptoethyl carboxylates) for PVC

Various combinations of the additives were mixed into the standard resin formula. All of such stabilizer components were on parts of per hundred-resin basis. The blank resin formula with stabilizer and other additives were tested by first milling the mixtures with roll mill to form a uniform polyvinyl chloride composition for 5 min at 180 ℃, then long term heat stabilities of test samples were determined by aging oven at 200 ℃. The heat stability contribution of the stabilizer compositions were determined by ascertaining the time at the test temperature required for the samples to degrade by severe darkening to a dark red or black. Thus, the term "heat stability time" is used to indicate the amount of heat stability in minutes contributed by a composition or component to the resin formula.

3 RESULTS AND DISCUSSION

3.1 Synthesis conditions of antimony tris(mercaptoethyl carboxylates)

The reaction of antimony tris(2-hydroxylmercaptide) and carboxylic acid is an esterification process. Catalysts have great influence on the reaction. Tertrabutyl titanate, heteropolyacid and other catalysts were selected as catalysts of the reaction. The results were listed in Table 1. It shows that the esterification yield is 82.5% when tertrabutyl titanate is used as catalyst.

In addition, the influence factors on esterification yield, such as the amount of solvent, the molar ratio of acid, the reaction time and etc., were investigated. The conditions of synthesis were optimized by orthogonal test method. The orthogonal experimental results show that the amount of solvent affects the yield of the product remarkably, and reaction time was the second important affecting factor; whereas, the other factors were not obvious. The experimental conditions and results are listed in Table 2.

3.2 Properties of antimony tris(mercaptoethyl carboxylates) compounds

The physiochemical properties of antimony tris (mercaptoethyl carboxylates) compounds are listed in Table 3. These compounds can be soluble in following organic solvents: benzene, toluene, xylene, dioctyl phthalate (DOP) and butyl octyl phthalate (BOP), etc.

3.3 Infrared spectra

Compared the IR pattern of products with that of antimony tris (2-hydroxyethyl mercaptide), the absorption peak of O—H in 3 465~ 3 550 cm^{-1} of antimony tris (2-hydroxyethyl mercaptide) disappeared. The strong absorption peak in 440~ 450 cm^{-1} indicates the formation of Sb—S and 1 735 cm^{-1} peak is stretching vibration of C═O. The symmetrical and asymmetrical stretching vibrations of C—O were near 1 300 cm^{-1} and 1 150 cm^{-1}. Besides, with decreasing C═O and C—O content, the corresponding absorption strength of the derivative become

Table 1 Influence of catalyst type on reaction

Catalyst	Reaction time/h	Temperature/℃	Color	Esterification yield/%
Tetrabutyl titanate	4	210	Yellow	82.5
ZrO_2/SO_4^{2-}	1	210	–	–
Sulfuric acid	5	180	Brown	76.9
p-methyl-phenol	5.5	180	Brown	75.0
$TiSiW_{12}O_{40}/TiO_2$	4	210	Brown	73.8

Table 2 Synthetic conditions of antimony tris(mercaptoethyl carboxylates)

Compound	*n*(Acid)/mol	*n*(Alcohol)/mol	*V*(Solvent)/mL	*m*(Catalyst)/g	Time/h	Esterification yield/%
ATO	0.336	0.1	50	0.4	8.0	65.5
ATL	0.348	0.1	50	0.4	5.5	76.4
ATS	0.360	0.1	50	0.4	4.0	82.5

ATO—antimony tris(thioethyl octoate); ATL—antimony tris(thioethyl laurate); ATS—antimony tris(thioethyl stearate).

Table 3 Physiochemical properties of antimony tris(thioethyl carboxylates)

Compound	Appearance	Melting point/℃	*D*(20 ℃)	Elemental analysis (calculated)			
				w(C)/%	*w*(H)/%	*w*(S)/%	*w*(Sb)/%
ATO	Yellowish liquid	–	1.458 9	49.32(49.26)	7.86(7.80)	12.85(13.13)	16.34(16.66)
ATL	Yellowish solid	36~ 38	–	56.34(56.08)	9.14(9.01)	10.72(10.68)	13.62(13.54)
ATS	Yellowish solid	46~ 48	–	62.37(62.57)	10.05(10.17)	8.27(8.34)	10.27(10.58)

weak. On the basis of results of chemical analysis and IR analysis, we can verify that the products are antimony tris(mercaptoethyl carboxylates) .

3. 4 Heat stability

Add different amounts of stabilizers to PVC resin, mix, mill and press into PVC slice, and then carry out heat aging test. The results are shown in Fig. 1.

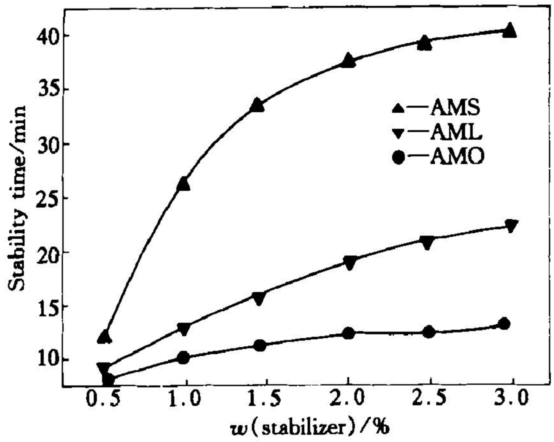


Fig. 1 Effects of mass fraction of antimony tris(mercaptoethyl carboxylates) on thermal stability for PVC

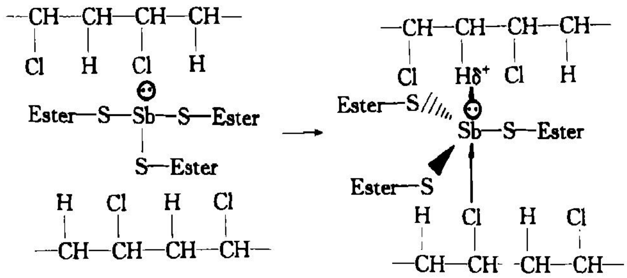
Comparing the thermal stability of ATS with other conventional heat stabilizers, the formulation of PVC and the results of aging test are listed in Table 4.

Table 4 shows that the stability of ATS is better than that of Ca-Zn complex stabilizer and basic lead complex stabilizer, and equal to that of organotin.

3. 5 Mechanism of thermal stabilization of PVC by antimony reserve-ester

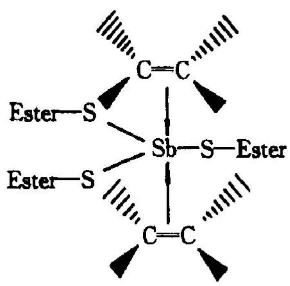
There are different explanations of the degradation and stabilization mechanism of PVC. But it is generally believed that the thermal stabilizers can react with allylic chloride in PVC and this reaction is faster than the growing of the chain and needs very strong active nucleophine ability. Once the degradation starts, the thermal stabilizers will combine allylic chloride ions, and prevent the degradation reaction from occurring. The thermal stabilizers can scavenge the HCl generated by the degradation and prevent HCl from self-catalysis to PVC degradation.

So far, the thermal stabilization mechanism of antimony stabilizer has seldom reported. Here, analogizing with the stabilization mechanism of organotin, we suggest the mechanism of stabilizer of antimony tris(mercaptoethyl carboxylates) . Antimony belongs to VA group elements. The electronic configuration of antimony atom is $5s^2 5p^3$. The antimony atom in stabilizer is sp^3 hybridization. The space configuration of the electron is denatured tetrahedron in which three s-ester groups are located on their acmes and lone-pair electrons occupy the other acmes, and the molecular structure is pyrometric cone. With rising temperature of PVC, the pyramid structure of these stabilizers will turn over. Thus, it may have a state of plane triangle, which reduces obstruction, and contributes to forming coordination compound with Cl in PVC during the rotating. The coordination compound is pyrometric cone and this active intermediate can scavenge HCl. The reaction process is:



(1)

In addition, the effect of mercaptan group in antimony stabilizer is the same as that in tin mercaptan. It can form coordination compound with multi-alkaline chain which prevent PVC from oxidizing in the initial stage effectively,



(2)

Table 4 Composition of PVC and thermal stability of PVC blended with stabilizer

Sample No.	Composition											Stability time/min
	PVC	DOP	Carboxylic acid	Calcium stearate	Zinc stearate	Calcium laurate	Zinc laurate	Dibutyltin dilaurate	Basic lead stabilizers	ATS	TM-181 (organotin)	
A	100	10	3	2.85	0.15	0	0	0	0	0	0	13
B	100	10	3	0	0	2.85	0.15	0	0	0	0	18
C	100	10	3	0	0	0	0	3.0	0	0	0	44
D	100	10	3	0	0	0	0	0	3.0	0	0	43
E	100	10	3	0	0	0	0	0	0	2.0	0	45
F	100	10	3	0	0	0	0	0	0	0	1.5	47

4 CONCLUSIONS

1) Antimony tris(mercaptoethyl carboxylates) can be synthesized from antimony tris(2-hydroyethyl mercaptide) and carboxylic acid with $Ti(OC_4H_9)_4$ as catalyst in the solvent of xylene.

2) The test of thermal stability indicates that the products have good stabilities with low dosages in PVC. Among these products, ATS has best stability and its stability time is about 45 min (at 200 ℃). Its thermal stability is better than that of Ca-Zn complex stabilizer and lead complex stabilizer. It can match organotin compounds.

3) The thermal stabilization mechanism of antimony tris(mercaptoethyl carboxylates) may be that the lone-pair electrons of antimony atom scavenge HCl generated by degradation of PVC and prevents HCl from self-catalysis decomposition. Besides, mercaptan group can form coordination compound with multi-alkaline chain and prevent PVC from oxidation.

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