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Thermal analysis of Sb_2O_3–chlorinated paraffin mixtures used for the fireproofing of polystyrene [1]

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Abstract

A mixture of antimony trioxide (Sb_2O_3) with chlorinated paraffins (CP) is used in polystyrene fireproofing. Hydrochloric acid is progressively released from the chlorinated paraffins during heating and reacts with the antimony trioxide. The antimony trichloride formed is responsible for fireproofing the polystyrene. Our study by thermal analysis under air sweeping indicates the presence of exothermic peaks (DTA) and weight losses (TGA) corresponding to the formation and volatilization of antimony trichloride between 240 and 300°C.

INTRODUCTION

An antimony trioxide–chlorinated paraffin (CP) mixture is used for the fireproofing of plastics materials, and more especially of polystyrene (Costa et al. [1]). According to these authors, antimony trichloride reaches its maximal formation speed between 300 and 350°C when thermal degradation takes place with nitrogen sweeping at 3.6 l/h^{-1}. We studied the antimony trioxide–chlorinated paraffin mixture by differential thermal analysis (DTA) and thermogravimetry (TGA).

SAMPLES AND EQUIPMENT

The antimony trioxide (Sb_2O_3) was produced by Aldrich (purity higher than 99%, melting at 655°C). The chlorinated paraffin (CP-Electrophine S 70*) was produced by CECA, a subsidiary of ATOCHEM, and constituted a mixture of long-chain C_{22}–C_{24} hydrocarbons.

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[1] This paper was presented during the 22nd annual meeting of the French Association of Calorimetry and Thermal Analysis (AFCAT) at Paris-XI–Châtenay-Malabry (27–29 May 1991).

We had at our disposal a Netzsch DTA apparatus. The thermocouples are made of Pt–Pt/Rh (10%), the sample capacity is around 150 mg, and we used kaolin as reference. Heating was executed at 2°C min^{-1} up to 650°C under an air sweep.

The thermogravimetry was performed on a TGA-Adamel TH 59 appliance equipped with Pt–Pt/Rh (10%) thermocouples and having a sample capacity of about 300 mg. Heating was executed at 2.5°C min^{-1} up to 750°C under an air sweep.

For determination of the chlorine content of the chlorinated paraffin, we mineralized the sample in a Parr–Wurzschmitt bomb, then carried out a coulometric titration. The content of chlorine in the chlorinated paraffin amounted to 1.99 equiv of Cl per 100 g, that is to say, 705 g kg^{-1} of Cl.

The antimony trioxide–chlorinated paraffin (Sb_2O_3–CP) mixtures were prepared in a mortar.

Differential thermal analysis

Figure 1 represents the DTA curves obtained with increasing contents of antimony trioxide in the antimony trioxide–chlorinated paraffin mixtures: 0, 10, 20, 33, 50, 80 and 100%.

The chlorinated paraffin alone gives two exothermic peaks, respectively at 325 and 525°C (Fig. 1, curve A), and the antimony trioxide is characterized by an exothermic peak at 544°C (Fig. 1, curve G). Heating up to 700°C under our experimental conditions (i.e. with air sweeping) does not show an endothermic melting peak for Sb_2O_3. The fact that the Sb_2O_3 gained 3% in weight leads us to explain the exothermic peak as involving the oxidation of the antimony trioxide. If one carries out the heating of antimony trioxide by an inert gas, for example argon, one can observe an endothermic melting peak at 639°C.

For the antimony trioxide–chlorinated paraffin mixtures, we observe four sorts of exothermic peak.

Ranked by increasing temperatures, there appear in Fig. 1

a first exothermic peak at 236°C for 10%, at 250°C for 20%, at 263°C for 33% and at 281°C for 50% of Sb_2O_3;

a second one due to the chlorinated paraffin at 325°C, the position of which changes to 293°C for 80%;

a third one, also due to the chlorinated paraffin, at 525°C, the position of which decreases to 435°C for 50%;

a fourth peak at 519°c for 80% and at 544°C for 100% of Sb_2O_3.

The outcome of all the DTA tests is summarized in Table 1.

Thermogravimetric analysis

The TGA curves show individual features that we can identify (ranked by increasing temperature): start point of decomposition (T_a); singular

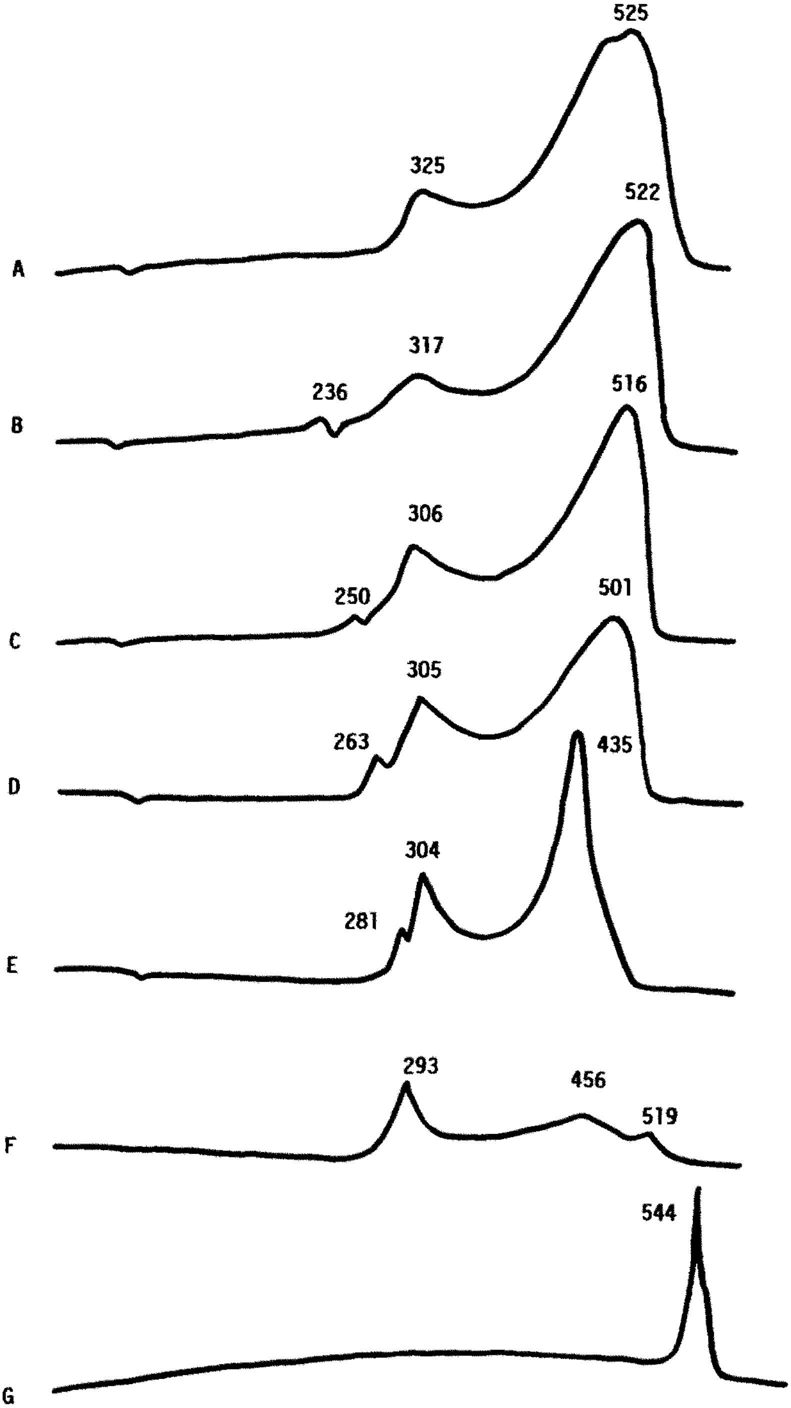

Fig. 1. DTA curves. Sb_2O_3/Sb_2O_3+CP; amount of sample (g); residue of thermolysis (%). Curve A, 0/100, 0.1526, 0.52; curve B, 10/100, 0.1370, 0; curve C, 20/100, 0.1505, 0.33; curve D, 33/100, 0.1622, 0; curve E, 50/100, 0.1253, 3.75; curve F, 80/100, 0.1249, 64.37; curve G, 100/100, 0.1623, 103.3.

TABLE 1

DTA results

$\frac{Sb_2O_3}{Sb_2O_3+CP}$	Test	Residue of thermolysis (%)	Exothermic peaks (°C)			
0/100	1	0.52		325	525	
	2	0		323	510	
	3	0.14		320	510	
	4	0.30		326	501	
10/100	5	0.63	239	313	508	
	6	0	236	317	522	
20/100	7	0.33	233	306	488	
	8	0.33	250	306	516	
33/100	9	0	263	305	501	
	10	0	271	305	489	
50/100	11	4.41	271	296	449	
	12	3.75	281	304	435	
	13	5.33	280	299	441	
	14	4.16	278	296	440	
80/100	15	64.37		293	456	519
	16	63.92		289	445	517
100/100	17	102.2				552
	18	103.3				544

point (T_b); end of growth part (T_c); singular point (t_d); end of decomposition (T_e).

Figure 2 shows the TGA curves obtained for the various Sb_2O_3–CP mixtures.

The temperature of the start point of decomposition (T_a) increases from 260°C for nil to 285°C for 80% of Sb_2O_3.

The singular point around 300°C (t_b) appears only for 10%, 20% and 33%.

The temperature of the end of the growth part (T_c) decreases from 355°C for nil to 320°C for 80% of Sb_2O_3.

The temperature of the end of decomposition (T_e) decreases from 560°C for nil to 485°C for 50% of Sb_2O_3.

Antimony trioxide alone apparently gained almost 2% in weight between 560 and 575°C.

Results of tests on each mixture are presented in Table 2.

DISCUSSION

According to the work of Costa et al. [1] and because of our findings we propose the following reaction mechanism, probably taking place in four stages.

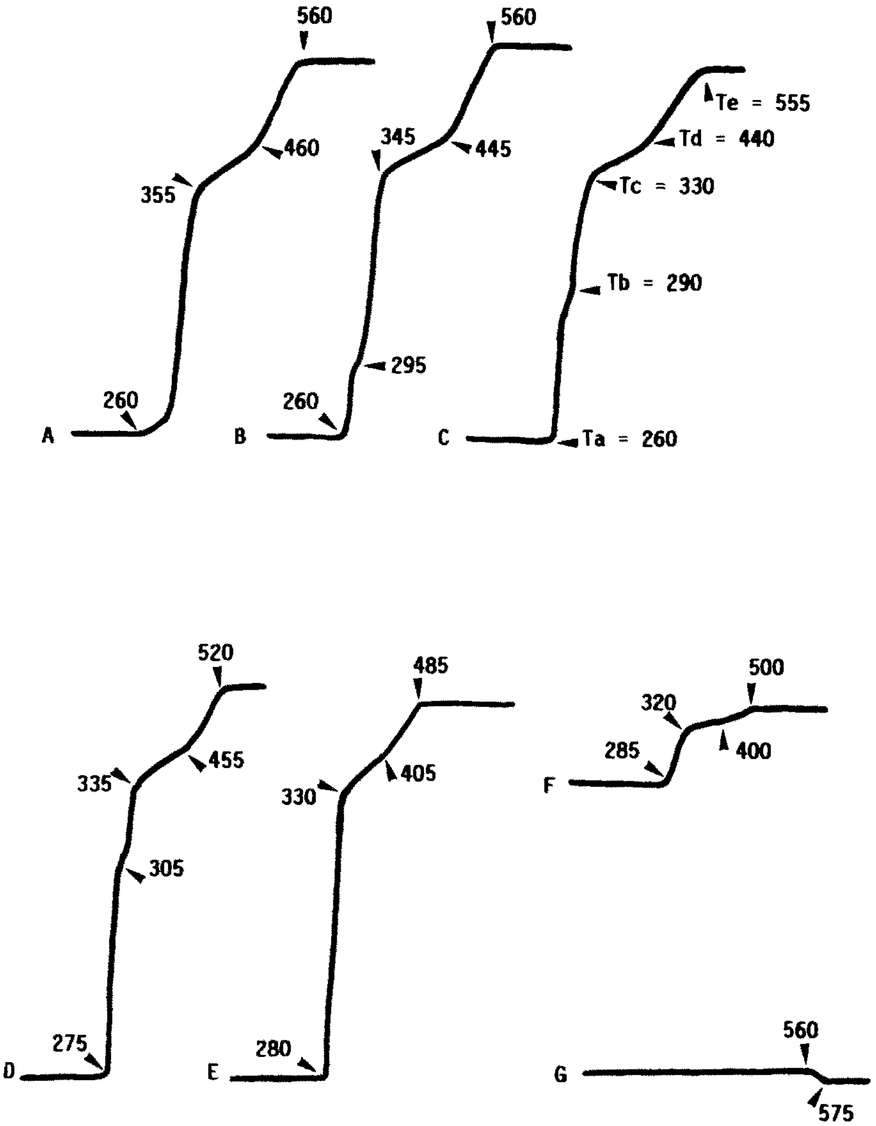

Fig. 2. TGA curves. Sb_2O_3/Sb_2O_3+CP; amount of sample (g); residue of thermolysis (%). Curve A, 0/100, 0.2745, 0; curve B, 10/100, 0.2891, 0.3; curve C, 20/100, 0.2830, 0.5; curve D, 33/100, 0.2860, 0.3; curve E, 50/100, 0.2899, 2.1; curve F, 80/100, 0.1574, 60.8; curve G, 100/100, 0.2885, 101.8.

The first stage in TGA is indicated by the points T_a and T_b (start point of decomposition and first singular point; 260–300°C) and in DTA is denoted by an exothermic peak from 240–280°C.

The chlorinated paraffin is partially dehydrohalogenated, and the hydro-

TABLE 2

TGA results (weight loss in % is presented in parentheses)

$\frac{Sb_2O_3}{Sb_2O_3+CP}$	Residue of thermolysis (%)	Start point of decomposition T_a (°C)	Singular point T_b (°C)	End of growth part T_c (°C)	Singular point T_d (°C)	End of decomposition T_e (°C)
0/100	0	260 (0)		355 (61.9)	460 (73.4)	560 (100.7)
10/100	0.30	260 (0)	295 (19.8)	345 (68.5)	445 (74.7)	560 (99.6)
20/100	0.46	260 (0)	290 (35.7)	330 (70.6)	440 (79.0)	555 (99.5)
33/100	0.30	275 (0)	305 (59.3)	335 (75.7)	455 (84.4)	520 (99.7)
50/100	2.07	280 (0)		330 (75.6)	405 (82.3)	485 (97.8)
80/100	60.8	285 (0)		320 (28.1)	400 (31.1)	500 (39.0)
100/100	102					560–575 [a]

[a] Increasing weight.

chloric acid reacts immediately with antimony trioxide to produce antimony trichloride and water.

$$Sb_2O_3 + 6HCl \rightarrow SbCl_3 + 3H_2O$$

The exothermic peak in DTA between 240 and 280°C may be due to the reaction of antimony trioxide with hydrochloric acid (exothermic reaction).

We checked the volatility of antimony trichloride by executing three tests on a sample produced by Aldrich. We detected two endothermic peaks: the first one at 72.0°C due to melting and the second at 194.3°C due to volatilization. The residue of thermolysis was lower than 1%.

The second stage is indicated in TGA by the points T_b and T_d (first and second singular points, 300–450°C) and in DTA by an exothermic peak which varies in temperature from 325 to 290°C.

The remaining chlorinated paraffin is completely dehydrohalogenated, then the residual olefin is polymerized (exothermic reaction).

The third stage is characterized in TGA by the points T_d and T_e (second singular point and end of decomposition; 460–560°C for 0% and 405–485°C for 50%) and in DTA by an exothermic peak varying from 512 to 451°C. The carbonaceous residue obtained by polymerization undergoes combustion.

The fourth in TGA involves an observed 2% gain in weight between 560 and 575°C, and in DTA an exothermic peak is observed at 518°C for 80% and at 550°C for 100% of Sb_2O_3. The antimony trioxide is oxidized in air.

The first stage featured the volatilization of antimony trichloride and water, and the second stage involved volatilization of HCl (at this stage antimony trioxide was not present in sufficient quantity to react with the evolved hydrochloric acid). From this supposition we calculated for each mixture the content of volatile products: $SbCl_3$, H_2O, HCl, and also the theoretical residue of thermolysis (it being assumed that the residue was

TABLE 3

Residue of thermolysis and volatile products

$\frac{Sb_2O_3}{Sb_2O_3+CP}$	mg-atom g^{-1} of Sb	Residue of thermolysis (mg g^{-1})		$SbCl_3+H_2O$ (mg g^{-1})		$SbCl_3+H_2O+HCl$ (mg g^{-1})		HCl (mg g^{-1})	
		Theoretical	Obtained	Theoretical	Obtained	Theoretical	Obtained	Theoretical	Obtained
0/100	0	0	0	0	0	725	734	725	734
10/100	0.686	0	3.0	175	198	753	747	578	549
20/100	1.37	0	4.6	350	357	780	790	430	433
33/100	2.29	0	3.0	583	593	816	844	234	251
50/100	3.43	17.3	20.4			845	823	0	0
80/100	5.49	607	608			338	311	0	0
100/100	6.86	1000	1018			0	0	0	0

[a] Weight loss at T_b. [b] Weight loss at T_d. [c] Weight loss between T_d and T_b.

assimilated to antimony trioxide). We compared the calculated theoretical values with those obtained experimentally (Table 3).

We calculated the theoretical proportion of antimony trioxide and chlorinated paraffin in the Sb_2O_3–CP mixture to provide chlorine and antimony in the ratio of 3 : 1 necessary for the formation of antimony trichloride. This gave 49.1% of antimony trioxide (i.e. 3.37×10^{-3} g-atom of Sb per g of mixture) and 50.9% of chlorinated paraffin. Experimentally we obtained a zone between 3.15×10^{-3} and 3.40×10^{-3} g-atom of Sb per g of mixture, and this applied also to the weight loss at $T_d(SbCl_3 + H_2O + HCl)$, and to the weight loss between T_b and $T_d(HCl)$.

CONCLUSION

The analysis by DTA and TGA of antimony trioxide–chlorinated paraffin mixtures allowed us to confirm the formation of antimony trichloride from the reaction of antimony trioxide with hydrochloric acid progressively released from chlorinated paraffin during heating. The fireproofing of the polystyrene might be derived from the antimony trichloride.

REFERENCE

1 L. Costa, G. Camino and L. Trossarelli, Polym. Degradation Stab., 5 (1983) 267.