

THERMAL ANALYSIS OF Sb_2O_3 /ORGANOHALIDE-BASED FLAME
RETARDANTS INCLUDING ATOMIC ABSORPTION DETECTION OF
THE EVOLVED SPECIES

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The mechanism of evaporation of Sb_2O_3 and the mechanism of formation and evaporation of antimony trihalides (SbX_3) from $Sb_2O_3 +$ halogen, which play important roles in the flame retardation of plastics, have been studied in the case of chlorine- and bromine-containing additives at different Sb/X mole ratios by means of complex thermal analysis, and mass-spectrometers. The temperatures of $SbCl_3$ formation and its evaporation have been determined for PVC and Cerechlor 70 as chloride donors. The formation of $SbBr_3$ could not be verified when Flammex (decabromodiphenyl ether) was used. A close correlation has been found between conventional and atomic absorption thermoanalytical curves recorded under identical experimental conditions. The atomic absorption detection of the thermally evolved products provides valuable information on flame retardation process.

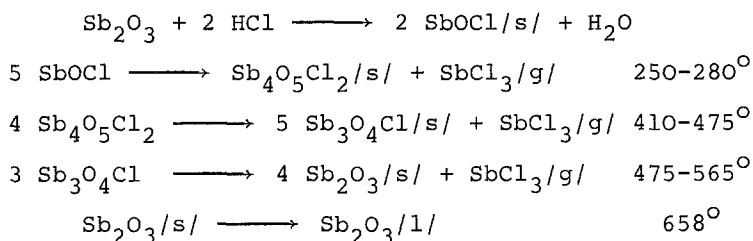
The replacement of a considerable number of traditional inorganic substances by synthetic organic ones raises the problem of an increased fire hazard and its prevention. Due to its numerous advantageous properties, antimony trioxide / Sb_2O_3 / is the most frequently used flame retardant additive [1]. The flammability of halogen-free polymers is reduced slightly in the presence of Sb_2O_3 , or not at all. In the presence of halogen, however, a fairly pronounced synergetic effect develops, this phenomenon being attributed to the formation of SbX_3 /where $X = Cl, Br$ / [2]. There are a number of mutually inconsistent

data in the literature with regard to the formation of antimony trihalide and its role in flame retardation.

The aim of this work was a systematic study on the formation of antimony halides from substances containing different halides /chloride or bromide/ and different Sb/X ratios (Sb/X = 1:3; Sb/X < 1:3; Sb/X > 1:3). Thermal analysis combined with atomic absorption detection [3] was used for the investigations.

Agrawal et al. [4] studied the thermal behaviour of Sb_2O_3 in air and an inert atmosphere. They found that Sb_2O_3 in air is oxidized to Sb_2O_4 between 510 and 600°. The TG and DTG curves show this to be a two-step process. In an inert atmosphere Sb_2O_3 undergoes no change up to 430°; then it evaporates slowly below 550°, and at a much higher rate above this temperature. The sublimed form was found to be Sb_2O_3 with a cubic structure /senarmontite/, while the residual Sb_2O_3 had an orthorhombic structure /valentinite/.

The only halogen-containing compounds of practical importance in flame retardation are chlorides and bromides of antimony. According to Pitts et al. [5] the formation of SbCl_3 from the oxide takes place through the oxychloride formation in several steps, as follows:



Using antimony- and bromine-containing additives the formation of SbBr_3 , SbOBr and $\text{Sb}_4\text{O}_5\text{Br}_2$ was detected by X-ray analysis of the residue of the heated sample [6]. In contrast, Lum [7] found that SbCl_3 is formed directly as a result of the interaction of Sb_2O_3 and HCl , and no SbOCl intermediate could be identified. Hence, the overall reaction can be written as $\text{Sb}_2\text{O}_3\text{/s/} + 6 \text{HCl} = 2 \text{SbCl}_3\text{/g/} + 3 \text{H}_2\text{O}$. In these experiments [7] the pyrolysis was carried out by means of laser beams and the products were analysed by a mass-spectrometer coupled on-line to the furnace.

A number of authors have dealt with the mechanism of flame retardant action of antimony halides. Benbow and Cullis [8-9] reported that antimony trihalide is formed in a reaction between antimony trioxide and the hydrogen halide originating from the halogen-containing compound, presumably in the melt phase. They concluded that an Sb_2O_3 -fog and halogen atoms are formed when the antimony trihalide comes into contact with regions of an oxygen rich flame. The fog acts as a catalyst in the recombination of reactive radicals, while the halogen atoms give rise to the formation of hydrogen halide, this latter being known to exert an inhibitory effect. The same authors established that the reaction between antimony and halogen under the influence of heat primarily depends on the following factors:

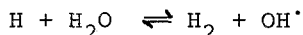
- /i/ the vaporization rate of the halogen compound used;
- /ii/ the Sb_2O_3 /halogen mole ratio;
- /iii/ the polymeric matrix.

If Sb_2O_3 is heated with halogen compounds which undergo no decomposition, it behaves as if being heated alone. If a polymer is present, a viscous melt is formed under heating; this facilitates the reaction between the oxide and the halogen. According to the above authors, the optimum Sb/X mole ratio is 1:3-5. The ratio differs somewhat for different polymeric matrices [8-10].

Handa et al. [11] studied the influence of bromine-containing flame retardant mixtures in the presence of a polypropylene /PP/ matrix at different Sb/Br mole ratios. They observed the retarded evolution of HBr, due probable to the formation of $SbBr_3$. The formation of $SbBr_3$ and of HBr was found at Sb/Br mole ratios of 1:3 and 1:4, respectively. In addition, it could be verified that the flammability parameters are the least favourable at a mole ratio of 1:4; in this case the oxygen index /OI/ has the highest value, while the DTG and DTA curves exhibit a minimum. It was presumed that a complex of composition $SbBr_3 \cdot HBr$ is formed in the melt phase. Evaporation of $SbBr_3$ is accompanied by the slow loss of HBr, which exerts a further inhibitory effect.

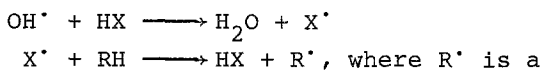
In a chemical sense, the flame is known to involve an exothermic reaction taking place in a narrow reaction zone via a

radical chain mechanism [12]. The flames of polymers consisting of carbon, hydrogen and oxygen only, resemble the widely studied hydrocarbon-oxygen flames [13]. The most frequently investigated representative of these is the acetylene-air flame, in which H, OH \cdot , O, CH \cdot , C $_2^{\cdot}$ and CHO \cdot atoms and radicals are produced [14,15]. The OH \cdot \longleftrightarrow H equilibrium is attained through the following fast process:



This equation indicates that blocking of either the OH \cdot radicals or the H atoms is equally effective to extinguish the flame. Halogen-containing compounds are decomposed at the temperature of the flame, and inhibit the combustion chain reaction. The process involves a competition between the oxygen feeding the combustion and the halogen-containing inhibitor retarding the combustion process.

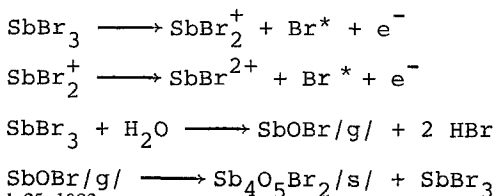
It may be assumed that hydrogen halide /HX/ reacts with the OH \cdot radical developing during the combustion of a polymer, according to the following scheme:



macromolecular radical.

Hence, HX inactivates the reactive OH \cdot radical in the first step, and the halogen radical formed reacts with a macromolecule, resulting in regeneration of HX and producing a macromolecular radical in the second step. Since the hydrogen halide molecule is regenerated, it is an effective flame retardant even in relatively small quantities. Hydrocarbon macromolecular radicals are less reactive than the OH \cdot radical and their rate of recombination is higher. As a result, the rate and mechanism of the process of combustion undergo a change.

The following chain reaction can be assumed in the presence of Sb_2O_3 with bromine-containing additives [7]:



By means of mass-spectrometry, Ballisteri et al. [16] investigated the products of thermal decomposition of the following mixtures: PVC + Sb_2O_3 ; polyvinylidene chloride /PVC₂/ + Sb_2O_3 ; and a chlorinated paraffin + Sb_2O_3 . The volatility profile of the products appearing in the gas phase was determined as a function of the temperature of decomposition. In this way the products $^{226}SbCl_3$ and $^{484}Sb_4$ were identified; moreover, the presence of metallic Sb was detected below the flash point of the polymer.

It is obvious that a knowledge of the initial temperature and the temperature range where the inhibiting component enters the atmosphere is extremely important. Sb_2O_3 has been demonstrated unambiguously to exist in the dimeric form $[Sb_4O_6]$ in the gas phase, since the volatility curve of the Sb_4O_6 molecule corresponds to the mass-spectrum of Sb_2O_3 .

EXPERIMENTAL

Materials

Sb_2O_3 /E. Merck, Darmstadt and Chemisch en Metallurgisch Bedrijf Campine n.v./, Cerechlor 70 /ICI/, Flammex /decabromodiphenyl ether/ /Billaner/, PVC and PE /Tipolen/ /Tisza Chemical Works, Hungary/.

Methods

Thermoanalytical studies were performed in air and in nitrogen atmospheres by means of a derivatograph equipped with a thermogastitrimetric unit [17] and of a model modified for determination of flash ignition temperature [18] /Fig. 1/. The flow rate of nitrogen was 30 l/h. The sample mass in the measurements was 100 mg unless otherwise noted. The crucibles were made of oxide ceramics. Heating rates of 10 and 50^o/min were used.

In the combined furnace and flame atomic absorption method [3] the dry aerosol formed from the sample vapour in the furnace is transported into the flame for the atomic absorption observations. In these measurements an acetylene-air mixture of nearly stoichiometric composition was used by supplying 1 l/min

acetylene, 6 l/min air and 3 l/min carrier air aerosol transportation. For metal specific observation, a Pye Unicam Model SP 90A atomic absorption spectrophotometer was used, with modified introduction [3]. The distance between the light path and the burner slot /observation flame height/ was 10 mm. Nitrogen at a flow rate of 20 l/h and a heating rate of 50/min were used

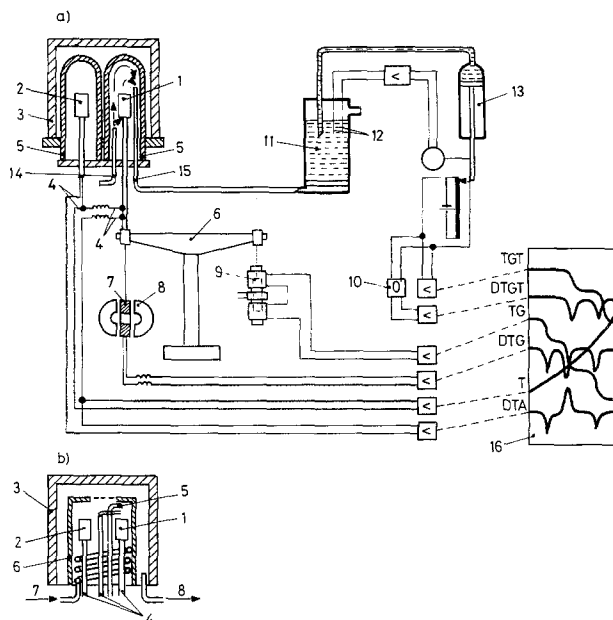


Fig. 1. a/ Derivatograph equipped with gascitrimetric unit
1 sample, 2 reference material, 3 furnace, 4 thermocouples, 5 quartz covers, 6 balance, 7 coil, 8 magnet, 9 differential transformer, 10 derivative device, 11 absorber, 12 electrodes, 13 automatic burette, 14 tube introducing the carrier gas, 15 tube for gas removal, 16 recorder.

b/ unit for ignition point determination

1 sample, 2 reference material, 3 furnace, 4 thermocouples, 5 spark source, 6 silicaglass bell, 7 air inlet, 8 air outlet.

in the furnace. The atomic absorption measurements were made using the Sb 217.6 nm resonance line, from a hollow cathode lamp. Applying solid samples of relatively high antimony concentration, the sensitivity of the atomic absorption measure-

ments was decreased by adjusting the slot burner head perpendicular to the light path.

Mass-spectrometric measurements were performed on a JEOL-OISG-2 instrument. Samples were put in glass capsules in a heated block inside the ionization chamber. The spectra recorded were analyzed with an on-line data analyzing system.

X-ray measurements were carried out on an A2G-4C X-ray diffractometer /Dresden, GDR/.

RESULTS AND DISCUSSION

Thermal Analysis

The thermal behaviour of Sb_2O_3 in air and nitrogen atmospheres is demonstrated in Fig. 2. In good agreement with literature data, the oxidation of Sb_2O_3 occurs in two steps, with DTG and DTA peak temperatures at 545 and 630°. This phenomenon

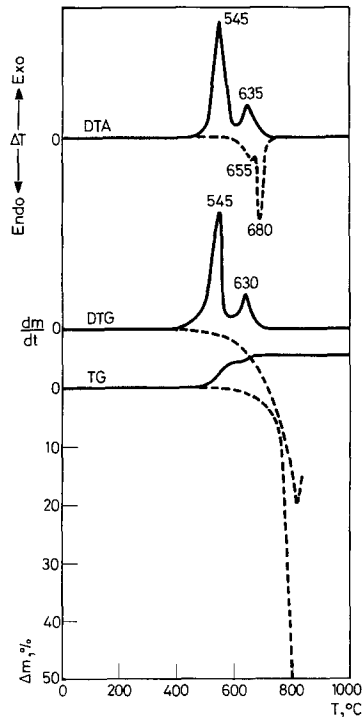


Fig. 2. TG, DTG and DTA curves of Sb_2O_3 /Merck/
 ——— in air - - - - - in nitrogen

is attributed to two crystal forms of Sb_2O_3 existing even at room temperature. Cubic Sb_2O_3 is oxidized with maximum rate at 545° , and rhombic Sb_2O_3 at 630° . The final product of oxidation is Sb_2O_4 ; the oxygen absorption is 5.3%, in complete agreement with the theoretically calculated value. In a nitrogen atmosphere, evaporation of the sample starts in the region of 560° . Two endothermic peaks are seen in the DTA curve, the first, at 655° , indicating a crystal-crystal transition and the second, at 680° , indicating melting of the sample.

Sb_2O_3 of different particle sizes /0.80, 1.35, 1.73, 2.05, 2.95 μm / is sold specifically as a flame retardant by the Belgian company mentioned above. Thermoanalytical curves of the additives with the smallest and the greatest particle size are shown in Fig. 3. The temperature of the oxidation step can be seen to shift to higher temperatures as the particle size is increased.

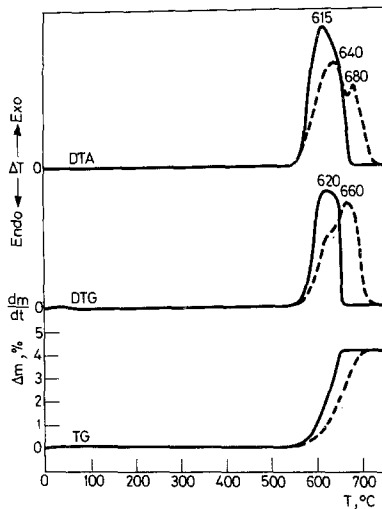


Fig. 3. Thermal behaviour of Sb_2O_3 /Chemisch en Metallurgisch Bedrijf "Campine" n.v./The effect of particle size. — 0,80 μm - - - - - 2,95 μm

This phenomenon can be explained by a change in the reaction surface. The oxidation occurs in one step, with peak temperatures in the DTA and DTG curves between 615 and 680° , depending on the particle size. The conclusion can be drawn from this

that the sample consists mainly of senarmontite. This could be verified by X-ray diffraction. The weight gain of the oxidation step was always less than the stoichiometric 4.3-4.5%, probably indicating the presence of some non-oxidizable filler.

SbCl_3 is formed as a result of a thermal reaction in a Sb_2O_3 + halogen-containing mixture. The thermoanalytical properties of pure SbCl_3 are demonstrated in Fig. 4. There is an endothermic peak at 65° in the DTA curve, corresponding to melting of the sample. The DTG curve shows that the process of evaporation starts in the region of melting, and proceeds with

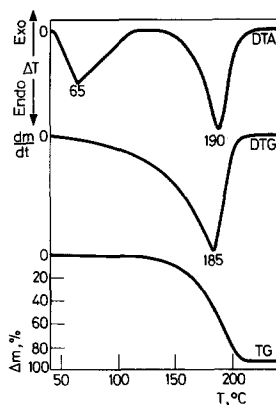


Fig. 4. TG, DTG and DTA curves of SbCl_3 .

maximum rate at 185° . SbCl_3 evaporates fully by 220° . It can be understood from the thermal curve that SbX_3 formed under the influence of heat is always in the gas phase, due to its low melting and boiling points, and it plays a prominent role in gas-phase flame retardation.

The reactions taking place between Sb_2O_3 and halogens have been studied using different model compounds. In the selection of these model compounds, industrial application was considered as being of particular importance. PVC and Cerechlor 70 were therefore used as chlorine-containing additives, and Flammex as a bromine-containing one.

The thermoanalytical study of Sb_2O_3 + PVC is described below. TG, DTG, DTA, TGT and DTGT curves of PVC produced by an emulsion technique and recorded in nitrogen and oxygen atmospheres are shown in Fig. 5 a, b. The TG curve reveals that a 58%

mass change is observed in the first step of decomposition; this corresponds to stoichiometric dehydrochlorination of PVC. Changes determined from the TG and TGT are identical, and are in good

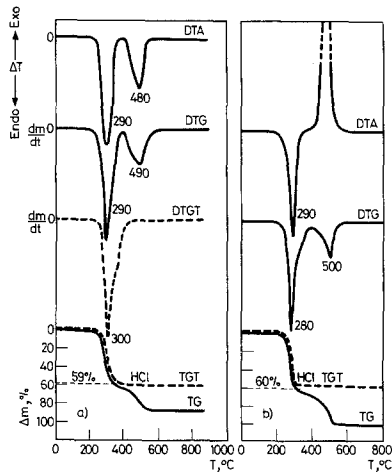


Fig. 5. TG, DTG, DTA, TGT and DTGT curves of pure PVC sample in nitrogen /a/, in oxygen /b/.

agreement with literature data [19,20]. The simultaneous titration was performed with a 0.1 M solution of NaOH. The dehydrochlorination of PVC starts above 200 $^\circ$, and proceeds with maximum rate at 290-300 $^\circ$; the process is completed at 400 $^\circ$. Thus, the reaction between Sb_2O_3 and HCl may begin from 200 $^\circ$, though Sb_2O_3 is in the solid state at 200 $^\circ$.

It can also be observed that the HCl evolution proceeds similarly both in nitrogen and oxygen atmospheres.

We attempted to follow the reaction taking place between Sb_2O_3 and HCl by thermal analysis, by adding increasing amounts of Sb_2O_3 to the above mentioned PVC sample /Fig. 6 a, b, c, d/. A peak in the region of 280-290 $^\circ$ appeared in the DTG and DTA curves, below the HCl decomposition peak of PVC. The height of this peak increased as the amount of Sb_2O_3 was increased, indicating that the HCl formed in the decomposition of PVC reacted with Sb_2O_3 , and the $SbCl_3$ formed in this reaction evaporated im-

mediately, which is expected according to the curves demonstrated in Fig. 4. This is also proved by the course of the DTGT curve, which is retarded compared to the similar curves of pure

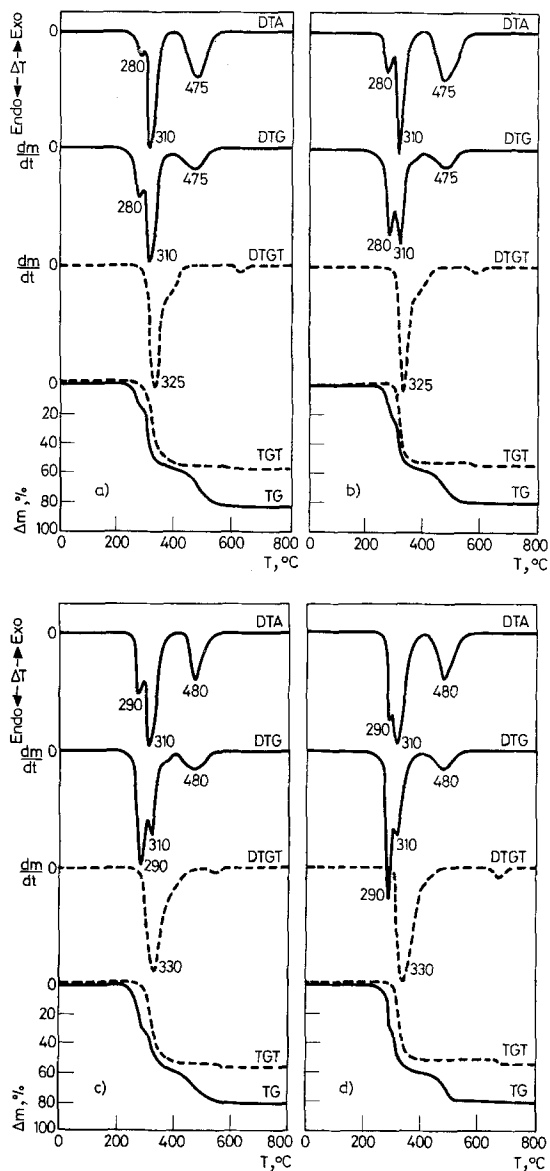


Fig. 6. TG, DTG, DTA, TGT and DTGT curves of the mixture of Sb_2O_3 + PVC. a/ 5.4% Sb_2O_3 , b/ 7.9% Sb_2O_3 , c/ 10.6% Sb_2O_3 , d/ 12.7% Sb_2O_3

PVC, indicating that the formation of SbCl_3 is the first reaction. The higher the Sb_2O_3 content, the higher the amount of SbCl_3 formed and the greater the difference between the initial temperatures in the TG and TGT curves.

Thermoanalytical curves with simultaneous recording of the flash ignition temperature curves of pure PE and a sample containing PE + Sb_2O_3 + Halogen are shown in Fig. 7. As we are concerned here with a gas-phase inhibition mechanism, the flame

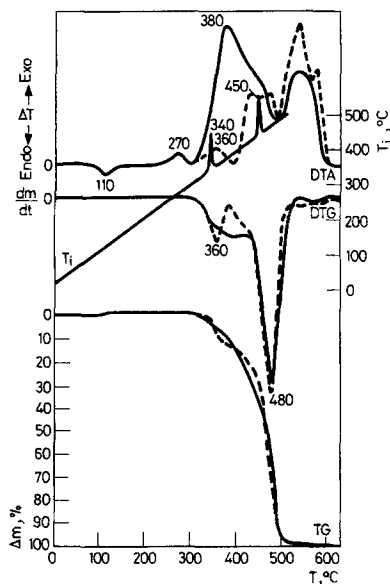


Fig. 7. TG, DTG, DTA and T_i curves of PE /Tipolen/
 pure samle ———
 treated with Sb_2O_3 + halogen donor -----

retardation effect can primarily be seen in the DTA curve and the flash ignition temperature T_i curve. The exothermic enthalpy change and the flash point of the sample are shifted toward higher temperatures under the influence of the flame retardant. The flash point of the non-treated PE sample is 340° , while that of the treated one is 450° . The DTG maximum at 360° indicates the reaction between Sb_2O_3 and the HCl taking place in the condensed phase.

Thermal analysis with atomic absorption detection

Using the combined system [3] outlined above pure Sb_2O_3 /particle size $1.73 \mu\text{m}$ / was applied into a platinum crucible and heated in nitrogen atmosphere. The absorbance vs. temperature curves /AT-curves/ of this substance with increasing sample size /0.2-2.3 mg/ are shown in Fig. 8. It can be seen that the initial observation temperature is 500° independent from the sample

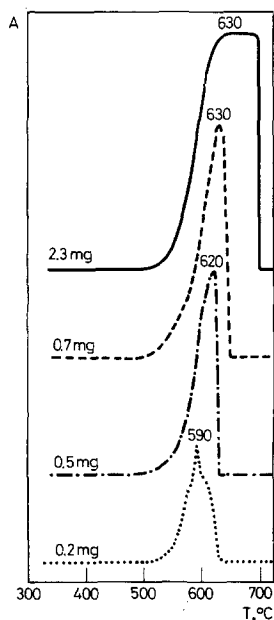


Fig. 8. AT curves of Sb_2O_3 with increasing sample size /0.2; 0.5; 0.7; 2.3 mg/.

size while the peak height and width are increased with the sample size applied. The temperature of the maximum rate of the process is shifted from 590° to 630° with increasing sample size. The vaporization process is completed by 700° with 2.3 mg Sb_2O_3 . These observations are similar to those involved in Figs. 2 and 3.

AT curves of the mixture of Sb_2O_3 + PVC are given in Fig. 9a using a ratio of $\text{Sb}/\text{Cl} = 1:3$ /i.e. the composition corresponds to that of SbCl_3 /. As it can be seen the AT curve with

maximum at 290° appears simultaneously with the main decomposition of PVC /DTG peak temperature at 295° , see also Fig. 5/. The low atomic absorption peak at 525° due probably to the vaporization of the traces of Sb_2O_3 /see Fig. 8/ which remains back after halogenation.

Figure 9b illustrates measurements when Sb/Cl ratio is smaller than stoichiometric. The first atomic absorption peak appears in the main decomposition step of PVC at 300° /Fig. 5/, and the second one is observed at 600° . This latter absorbance

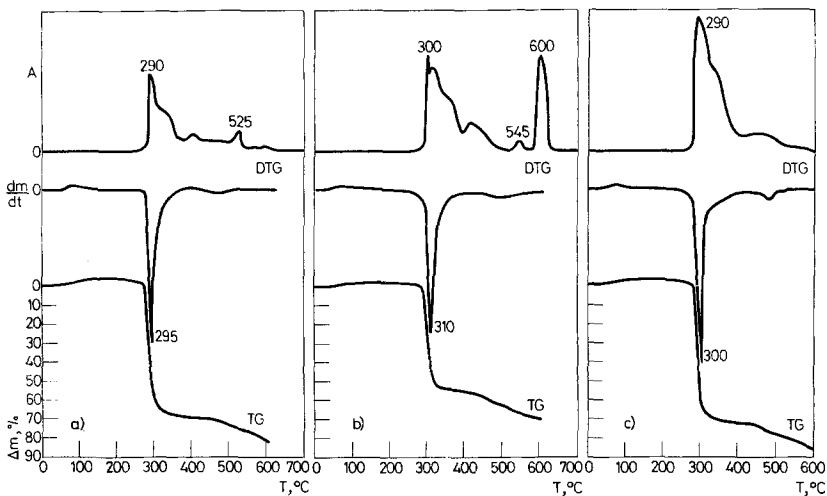


Fig. 9. AT, TG and DTG curves of the mixture of $\text{Sb}_2\text{O}_3 + \text{PVC}$. a: $\text{Sb}/\text{Cl} = 1:3$; b: $\text{Sb}/\text{Cl} < 1:3$; c: $\text{Sb}/\text{Cl} > 1:3$.

maximum proves that a considerable proportion of the Sb_2O_3 remains unchanged after halogenation which is released at the temperature characteristic for pure Sb_2O_3 .

Results of measurements when the Sb/Cl ratio is higher than stoichiometric are shown in Fig. 9c. Here a single atomic absorption peak is observed at 300° which suggests that all of the Sb_2O_3 is transformed into SbCl_3 which evaporates fully at this temperature.

Thermoanalytical curves for the other chloride donor /Cerechlor 70/ used in the model experiments are shown in Fig. 10. Cerechlor 70 has industrial applications as a plasticizer and a flame retardant additive. Its decomposition starts in the

region of 250° and proceeds with maximum rate at 335° /DTG peak/.

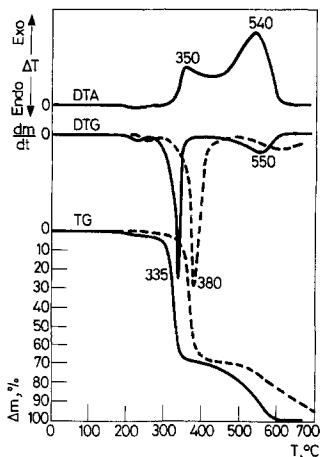


Fig. 10. Thermal behaviour of Cerechlor 70 at different heating rates. — 5 degree/min, ---- 50 degree/min.

Atomic absorption and thermoanalytical results on Sb_2O_3 + Cerechlor 70 mixtures with different ratios are demonstrated in Figs. 11 a, b, c. The results obtained are similar to those described for Sb_2O_3 + PVC mixtures.

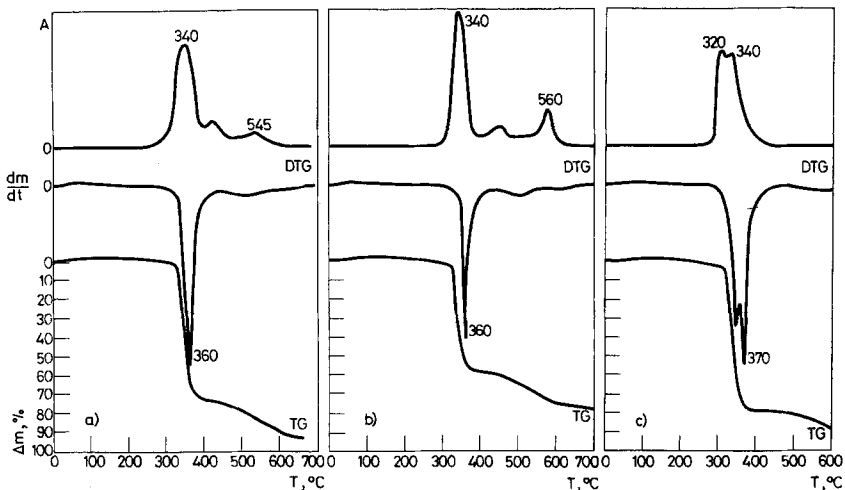


Fig 11. AT, TG and DTG curves of the mixture of Sb_2O_3 + Cerechlor 70; a: $Sb/Cl = 1:3$; b: $Sb/Cl < 1:3$; c : $Sb/Cl > 1:3$

The thermal decomposition of Flammex at different heating rates is demonstrated in Fig. 12. The substance melts at 130° , and then immediately undergoes an exothermic decomposition.

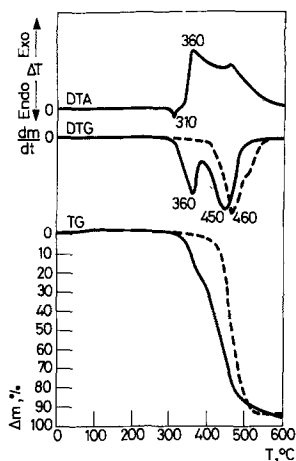


Fig. 12. Thermal behaviour of Flammex at different heating rates; — 5 degree/min, - - - - - 50 degree/min.

Atomic absorption and conventional thermoanalytical curves of mixtures of Sb_2O_3 + Flammex in different ratios are shown in Figs 13 a, b, c. In all three cases the atomic absorption signal is similar to that found with pure Sb_2O_3 /Fig. 8/. The forma-

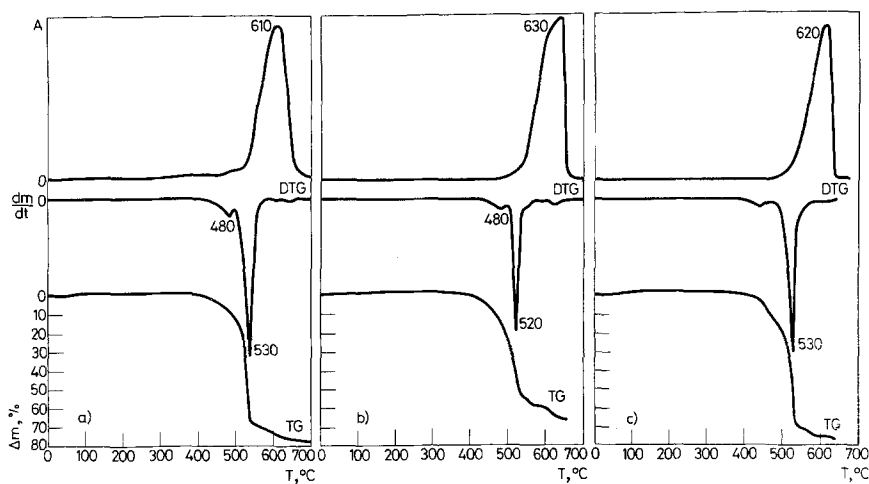


Fig. 13. TG and DTG curves of the mixture of Sb_2O_3 + Flammex; a: $Sb/Br = 1:3$; b: $Sb/Br < 1:3$; c: $Sb/Br > 1:3$.

tion of $SbBr_3$ could not be observed by the applied technique because the decomposition temperature of the additive is higher than the vaporization temperature of Sb_2O_3 .

Mass-spectrometric measurements

Mass-spectrometric measurements were performed on Sb_2O_3 + PVC, Sb_2O_3 + Cerechlor 70 and Sb_2O_3 + Flammex mixtures at $Sb/X = 1:3$.

There was no change up to 155° in the case of chlorine-containing additives. $Sb_xCl_y^+$ ions predominate in the temperature range $160-200^\circ$. Sb_n^+ ions appear in the interval $190-200^\circ$, and then $Sb_nO_m^+$ ions can be identified at higher temperatures. Identification of individual ions was carried out on the basis of mass numbers /Table 1/ and the characteristic isotopic ratios.

Table 1

Characteristic ions appearing in mass-spectra of Sb_2O_3 + PVC and Sb_2O_3 + Cerechlor 70 ($Sb/Cl = 1:3$)

$\frac{m}{e}$ values	Ions
35	Cl^+
36	HCl^+
121	Sb^+
363	Sb_3^+
484	Sb_4^+
156	$SbCl^+$
191	$SbCl_2^+$
226	$SbCl_3^+$
347	$Sb_2Cl_2^+$
417	$Sb_2Cl_5^+$
137	SbO^+
274	$Sb_2O_2^+$
290	$Sb_2O_3^+$
427	$Sb_3O_4^+$
443	$Sb_3O_5^+$
580	$Sb_4O_6^+$

In the case of the bromine-containing additive the presumed Sb_xBr_y^+ and ions of oxybromide type were not observed under our experimental conditions. Decabromodiphenyl ether is probably distilled from the mixture, since the spectrum of the sample is identical with that of the reference substance. Additionally, the ions corresponding to antimony oxide vaporization were detected.

CONCLUSION

While results obtained by simultaneous thermal analysis are adequate to study reactions taking place in the condensed phase, the atomic absorption detection of the evolved substances makes possible an approach to the problem of flame retardation from the side of the gas phase. The courses of the conventional and atomic absorption thermoanalytical curves are similar under identical experimental conditions.

The measurements showed that SbCl_3 is formed in one step at $290\text{--}310^\circ$ in the case of PVC as additive, and at $360\text{--}370^\circ$ in the case of Cerechlor 70, which evaporates immediately from the system. The formation of SbBr_3 could not be proved in the case of Flammex. On the basis of above findings, decomposition corresponding to the Pitts reaction series must be excluded.

From free enthalpy calculations /these data are summarized in Table 2/ it can be established that the formation of SbCl_3 from Sb_2O_3 and HCl is more favourable than the formation of SbOCl , but the latter cannot be excluded thermodynamically either.

Table 2

Reaction equations		ΔG		
		298 K	500 K*	600 K**
$\text{Sb}_2\text{O}_3/\text{s}/ + 6 \text{HCl}$	$2 \text{SbCl}_3/\text{s}/ + 3 \text{H}_2\text{O}/\text{l}/$	-36.48	-18.89	-
$\text{Sb}_2\text{O}_3/\text{s}/ + 2 \text{HCl}$	$2 \text{SbOCl}/\text{s}/ + \text{H}_2\text{O}/\text{l}/$	-19.43	-12.59	-
$\text{Sb}_2\text{O}_3/\text{s}/ + 6 \text{HBr}$	$2 \text{SbBr}_3/\text{s}/ + \text{H}_2\text{O}/\text{l}/$	-46.04	-	-25.34

* $\text{SbCl}_3/\text{g}/$

** $\text{SbBr}_3/\text{g}/$

It can be observed that the formation of SbBr_3 has the highest thermodynamic probability. Further investigations are necessary in order to demonstrate the formation and evaporation of SbBr_3 in the presence of different bromine containing additives.

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ZUSAMMENFASSUNG - Der Mechanismus der Bildung und Verdampfung des bei der Brennverzögerung von Kunststoffen eine wichtige Rolle spielenden Sb_2O_3 und der sich aus Sb_2O_3 und Halogenen bildenden Antimontrihalogenide (SbX_3) kann im Falle von chlor- und bromhaltigen Additiven bei unterschiedlichen Sb/X-Molverhältnissen durch komplexe thermische Analyse und damit gekoppelter Atomabsorptionsspektrophotometrie und Massenspektrometrie untersucht werden.

Die Bildungs- und Verflüchtigungstemperatur des $SbCl_3$ wurde im Falle von PVC und Cereklor 70 als Chloriddonor bestimmt. Bei Verwendung von Flammex (Dekabromdiphenyläther) wurde keine Bildung von $SbBr_3$ beobachtet.

Eine strenge Korrelation wurde zwischen unter gleichen Versuchsbedingungen erhaltenen thermoanalytischen und atomabsorptionsspektrophotometrischen Kurven gefunden.

Mit der Kombination der TA mit der Atomabsorptionsmethode eröffnet sich die Möglichkeit, den Prozess der Brennverzögerung von der Gasphase her zu untersuchen.

Резюме - В процессах замедления воспламенения полимеров важную роль играют трехокись сурьмы, а также галоидные соединения сурьмы, образующиеся в смеси трехокись сурьмы и галогена. Исследован механизм образования трехгалоидного соединения сурьмы в этой смеси, а также механизм его испарения. В случае хлор- и бромсодержащих добавок, исследованы комплексы сурьма - галоген различного молярного соотношения с помощью термического анализа, а также совмещенным методом термического анализа и атомно-абсорбционной спектроскопии, а также масс-спектроскопии. В случае ПВХ и Церехлор 70, как донора хлора, установили температуры образования и испарения треххлористой сурьмы. При ис-

пользовании фламмекса /декабромфениловый эфир/ образование трехбромистой сурьмы однозначно не было установлено. Найдена строгая корреляция между кривыми, полученными термоаналитическим и атомно-абсорбционным методами при одних и тех же экспериментальных условиях. Совмещенный метод термического анализа и атомно-абсорбционной спектроскопии открывает возможность исследовать процесс замедления воспламенения полимеров в газовой фазе.