Influence of flame-retardant additives based on Sb_2O_3 on PVC flammability*)

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DOI: https://doi.org/10.14314/polimery.2023.4.5

Abstract: Commercial flame-retardant additives based on Sb_2O_3 were evaluated. It was found that they have an acceptor, thermostabilizing and flame-retardant effect on PVC linoleum. Based on IR spectroscopy, DTA analysis, diffraction, and X-ray fluorescence analysis, it was found that one of the samples contains 100% Sb_2O_3, while the others contain microcrystalline $CaCO_3$ (50-95%) and other compounds, e.g., organochlorines and hydrocarbons. The flame-retardant mechanism of PVC linoleum consists in the synergistic action of Sb_2O_3 and $CaCO_3$ by binding gaseous hydrogen chloride formed during the combustion and thermal decomposition of PVC.

Keywords: flame retardants, stabilizers, stibium oxides, calcium carbonate.

Wpływ dodatków uniepalniających na bazie Sb_2O_3 na palność PVC

Streszczenie: Zbadano handlowe dodatki uniepalniające na bazie Sb_2O_3. Wykazują one działanie akceptorowe, termostabilizujące i uniepalniające na linoleum z PVC. Na podstawie spektroskopii IR, analizy DTA, dyfrakcji oraz analizy fluorescencji rentgenowskiej stwierdzono, że jedna z próbek zawiera 100% Sb_2O_3, natomiast pozostałe zawierają mikrokrystaliczny $CaCO_3$ (50-95%) oraz inne związki np. chloroorganiczne i węglowodory. Mechanizm uniepalniania linoleum z PVC polega na synergicznym działaniu Sb_2O_3 i $CaCO_3$ poprzez wiązanie gazowego chlorowodoru powstającego podczas spalania i rozkładu termicznego PVC.

Słowa kluczowe: uniepalniacze, termostabilizatory, tlenki antymonu, węglan wapnia, linoleum.

Year by year, the number of fires is increasing not only in Ukraine, but also in the world. Numerous human victims and significant material losses emphasize the importance of using flame retardants - special additives that reduce flammability and increase thermal stability of polymers, including poly(vinyl chloride) (PVC). The work [1] describes the interaction of stibium (III) oxide with chlorine-containing organic compounds in polyolefin-based compositions, however no data on their interaction with PVC compositions is currently available. In our previous studies, the effect of silicon dioxide modification on flammability, thermal stability, smoke formation of PVC [2] as well as the properties of PVC [3] materials in the presence of various fillers [4] were studied. The obtained data [5] was however not enough to describe the interaction mechanism of industrial flame retardants based on Sb_2O_3 [6] in polymer PVC linoleum compositions [7].

The aim of the work was to investigate the composition and mechanism of action of commercial flame-retardant additives containing Sb_2O_3 in PVC products (linoleum). The assessment was based on IR spectroscopy, DTA analysis, diffraction, and X-ray fluorescence analysis.

EXPERIMENTAL PART

Materials

Industrial samples of flame retardants (99.6% Sb_2O_3), which are used in the production of PVC linoleum were delivered from Chemproduct TD LLC, Ukraine. A medium-low molecular weight PVC homopolymer (Formolon® 622) was supplied by Burkay & Uğur Kimya, Turkey (Table 1).

PVC linoleum is one of the most popular types of floors covering in domestic premises. Its structure is presented in Fig. 1.

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*) The material contained in the article was presented at the XIX Konferencja Naukowo-Techniczna "Polimery i kompozyty konstrukcyjne" (KOMPOZYTY 2022), October 25–28, Ustroń, Poland.

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T a b l e 1. Characteristic of Formolon® 622 [3]

Parameter	Value	Testing method
Relative viscosity	2.15	ASTM D-1243
K-value (K number)	65	Fikentscher's constant
Volatility, %	0.3	ASTM D-3030
Bulk density, g/cm^3	0.52	ASTM D-1895
Residue after sieving in mesh, %: — through mesh 40 — through mesh 200	 99.9 15.0	ASTM D-1921
Quantity of contaminants	Ocs per 100 g	Ocs per 100 g

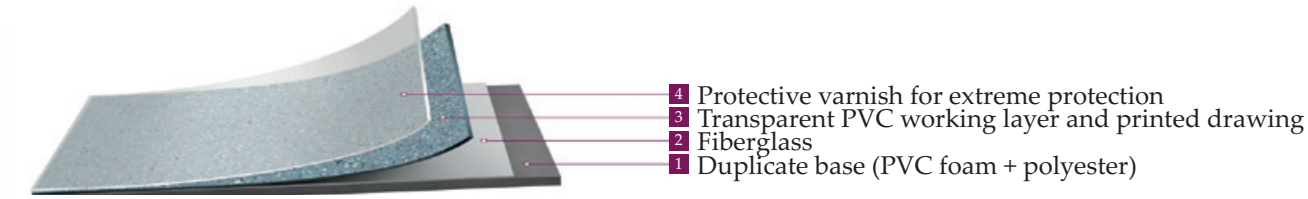

Fig. 1. PVC linoleum from Tarkett Vinisin LLC [7]

Tarkett linoleum offers several types of bases: foamed, doubled (foam + polyester), compact and calendered. According to the international classification, household floor coverings are distinguished depending on the level of their resistance to abrasion, which is indicated by two numbers - from 21 to 43. The first digit indicates the type of room (2 – domestic/residential, 3 – public, 4 – industrial), and the second is the load on the floor depending on the level of attendance (1 – low, 2 – medium, 3 – high, 4 – very high) [7, 8].

Methods

IR-spectral analysis of the studied samples was conducted on an Alpha II IR-Fourier spectrometer. Based on the data of IR spectra, the qualitative and quantitative composition of flame-retardant compositions was determined. Qualitative and quantitative differential thermal analysis (DTA) was performed on a photo-recording derivatograph of the Paulik-Erde system in the temperature range of 25 to 1000°C according to the standard method, and the calculation was carried out based on the data of curves of differential thermal analysis (DTA), differential thermal gravimetry (DTG) and thermogravimetry (TG) PRODUCER, Country. In addition, the calculation of their elemental-oxide composition was conducted using X-ray fluorescence spectroscopy and diffractometry on the "Expert 3" analyzer PRODUCER, Country [9] with the determination of the mass fraction of chemical elements and their oxides in homogeneous monolithic and powder-like bodies [10].

First, the physicochemical characteristics of four samples of flame retardants based on Sb_2O_3 were analyzed and studied. The obtained data is presented in Table2. Sample 2 does not contain organic substances. They are not identified when calcining it at 900°C for 1 hour, while the content of moisture and volatile substances does not exceed the permissible standards: 0.39% of losses when drying at 105°C for 2 hours. The presence in samples 1 and 3 of a large number of losses during calcination (11.5% and 16.8%, respectively) under the same conditions indicates the presence of organic impurities and volatile substances in their composition and a minimum amount of moisture – 0.39% and 0.49%, respectively.

RESULTS AND DISCUSSION

FTIR analysis

The qualitative composition of samples 1, 2 and 3 was determined by infrared spectroscopy. The results are shown in Fig. 2. The tested samples differed in the content of Sb_2O_3 [8], as evidenced by the change in the intensity of -Sb-O- bonds valence vibrations at the wave

T a b l e 2. Characteristics of industrial flame retardants used by Tarkett Vinisin

Parameter	Sample			
	1	2	3	4
pH of 4% water-alcohol dispersion	7.9	7.8	8.1	7.9
Bulk weight, g/l	75	72	81	76
Content of volatile substances, H_2O, 105°C, 2 h, %	0.39	0.39	0.49	0.43
Losses during calcination at 900°C, 1 h, %	11.5	0.001	16.8	13.5
Specific surface area, m^2/g [11]	0.51	1.45	1.56	0.58

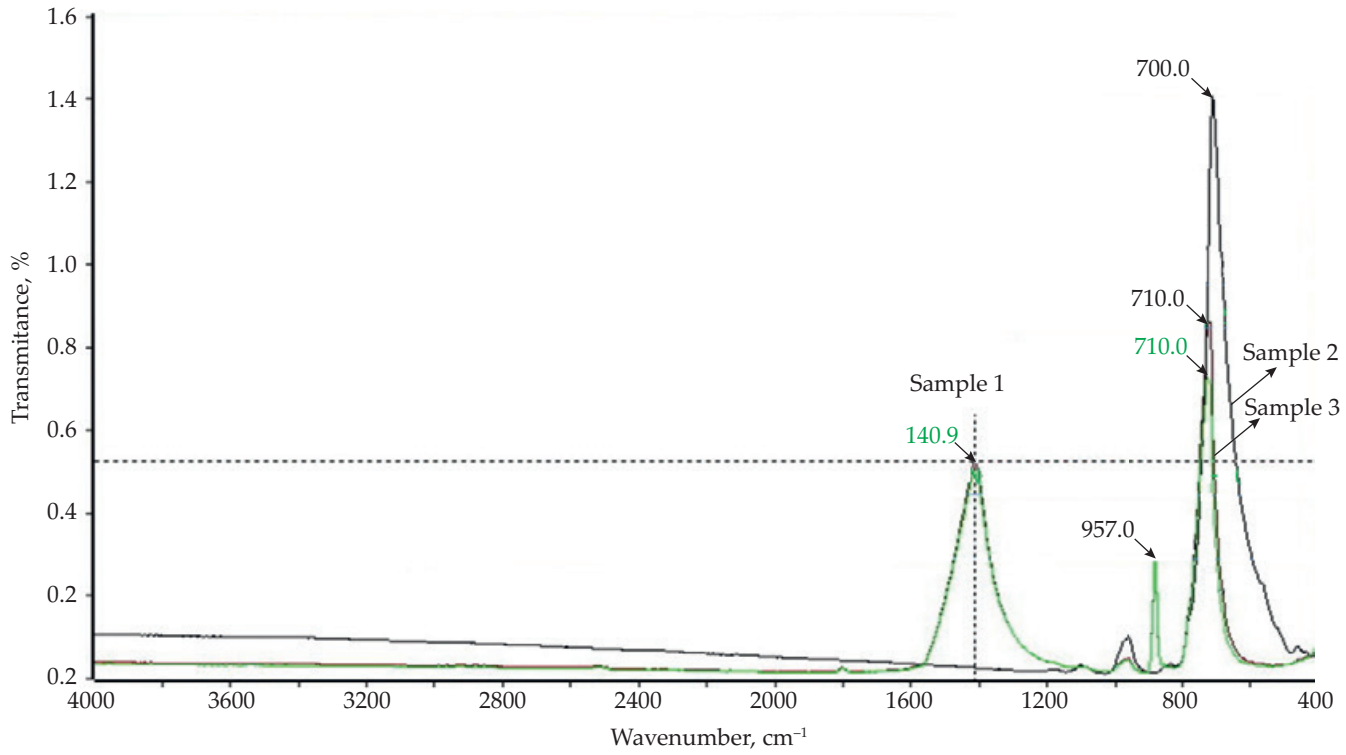

Fig. 2. IR spectra of flame retardants based on Sb_2O_3

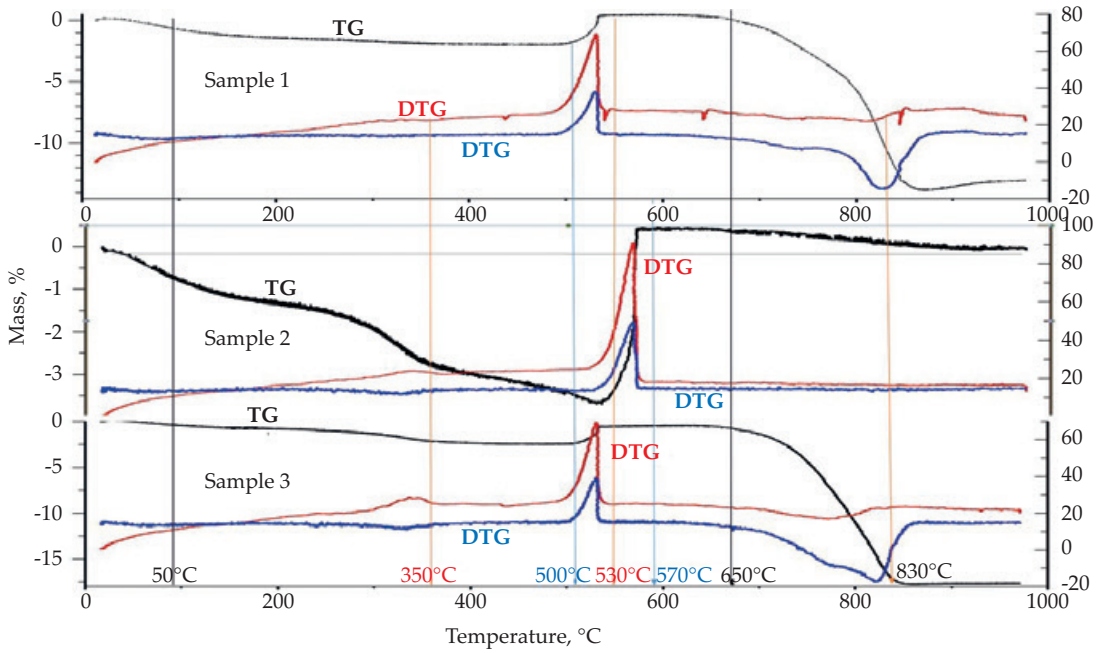

Fig. 3. DTA (red), DTG (blue), and TG (black) curves

number about 700 cm^{-1}. Based on the obtained results, the content of Sb_2O_3 in the samples was estimated, which for sample 1 was 59% (H=0.85), sample 2 – 44% (intensity H=1.4), for and for sample 3 – 25% (H=0.75). It was assumed that the content of other substances in samples 1, 2 and 3 was 41%, 56%, and 75%, respectively. In samples 1 and 3, at the wavenumber of 1409 cm^{-1}, there was a band corresponding to C–H bonds stretching vibrations of hydrocarbons. In sample 3, there was also a band at 870 cm^{-1}, which corresponded to the valence vibrations of the C–Cl bond, which may be related to the presence of organochlorine compounds acting synergistically with Sb_2O_3 [12].

Differential thermal analysis

To determine the quantitative and qualitative composition of the samples and impurities included in their composition, thermogravimetric tests were also conducted. The DTA, DTG, TG curves are shown in Fig. 3.

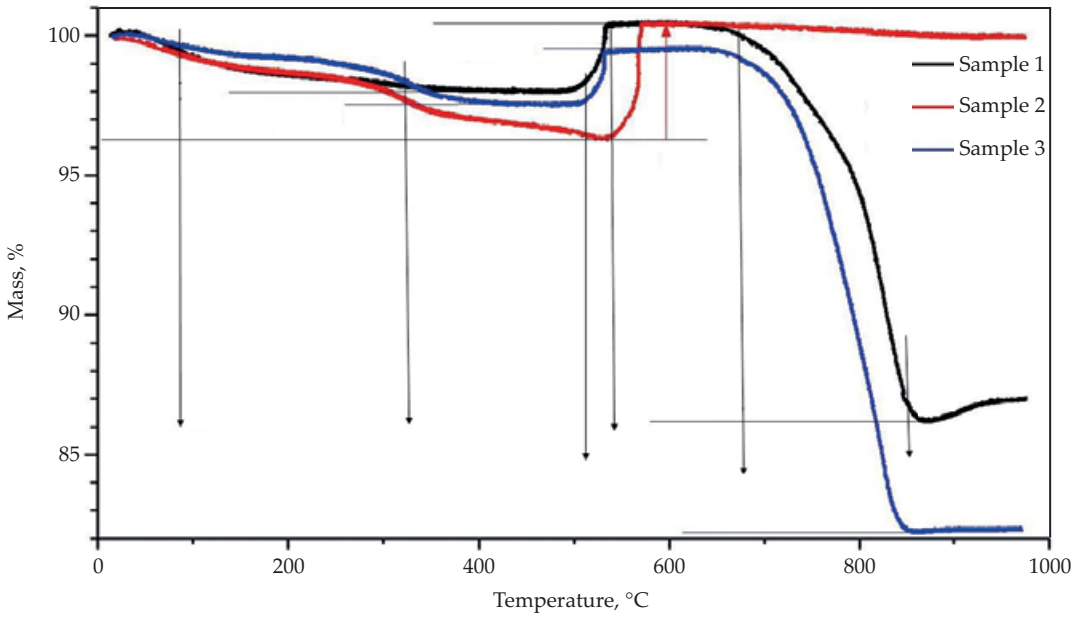

Fig. 4. TG curves of samples

Fig. 5. X-ray fluorescence diagram of flame-retardant sample 1

To analyze the mechanism of flame retardants, the TG and DTA mass loss curves of samples 1, 2 and 3 during thermal decomposition were additionally analyzed in detail, as shown in Fig. 4. The thermal decomposition of all three flame retardant samples took place with the loss of volatile substances and moisture at 50–80°C. Losses of sample 1 at 500–530°C reached about 2% (black curve, Fig. 4), for sample 3 – 2.4% (blue curve, Fig. 4), while for sample 2 – 3.7% (red curve, Fig. 4). In the temperature range of 500–530°C, there was an increase in mass for all samples, which can be explained by the oxidation of antimony(III) oxide to antimony(V) oxide.

The theoretical weight gain due to the increase in molecular weight should be 9.9%, and the experimental one showed much lower values (from 1.5 to 3.7%), which means that the oxidation reaction was not complete. When the samples were further heated to a temperature of 900–1000°C, which corresponds to the temperature of an open flame, sample 2, which contains almost pure antimony (III) oxide (98.8% Sb_2O_3), did not change its weight (Fig. 4). For comparison, the weight of sample 1 and 3 decreased by 13.8% (black curve) and 17.8% (blue curve), respectively, because their contained 15–20% of another substance decomposing at 650–850°C (Fig. 4) [13].

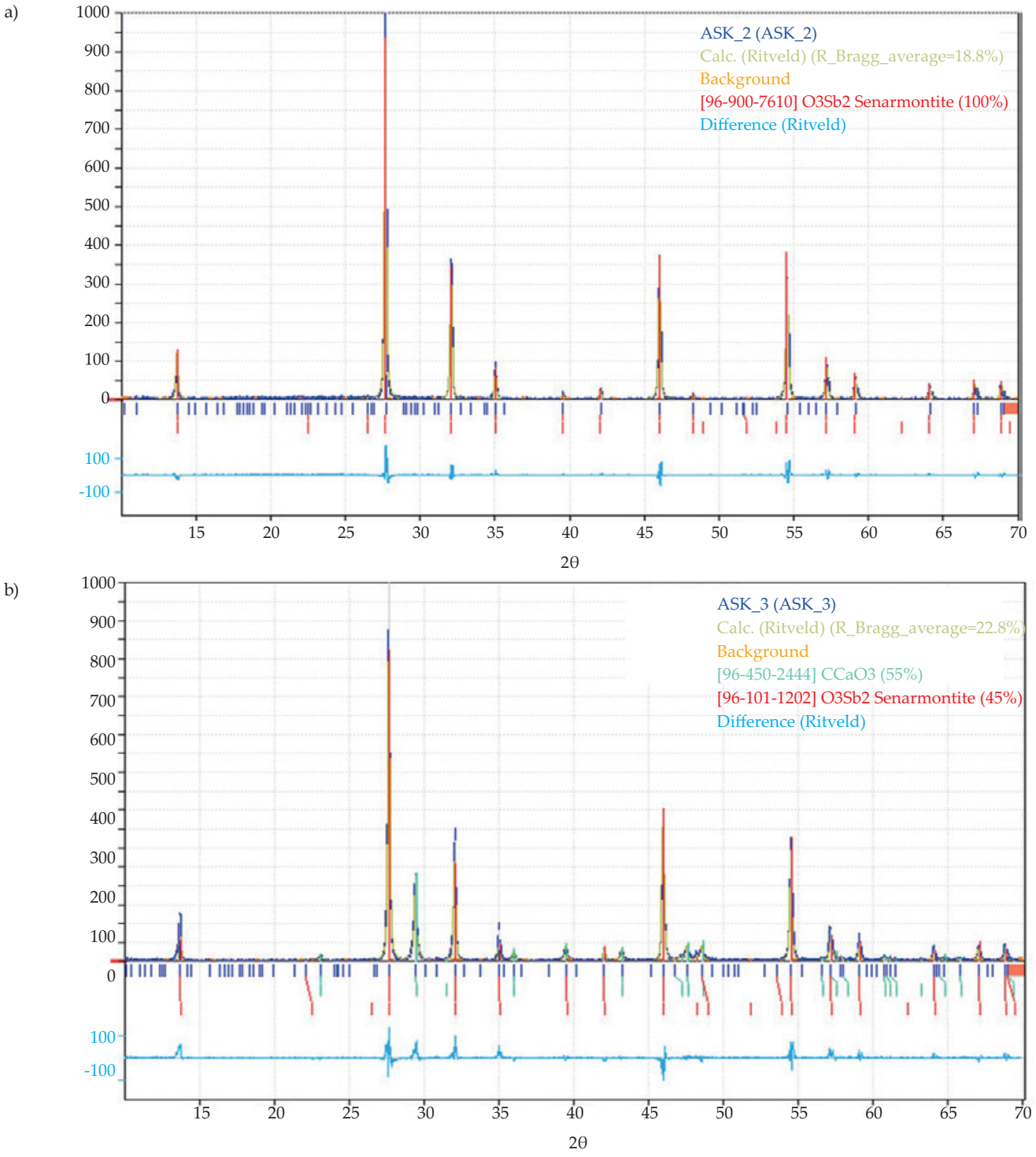

Fig. 6. Diffraction patterns of flame retardants: a) sample 2, b) sample 3

At the temperature of 500–530°C, the mass of samples 1 and 3 does not change. Partial decomposition of samples (weight loss 13–17%) takes place in the temperature range of 650–850°C, and then the mass does not change until 1000°C.

Based on the TGA, it can be concluded that samples 1 and 3 contain 85–87% and 80–83% of Sb_2O_3, respectively, as well as 13–15% and 17–18% of other substances. Sample 2 contains 98.8–99.8% of Sb_2O_3 and only 0.1–1% of other substances.

Fluorescence spectroscopy

For a more accurate qualitative and quantitative analysis of the composition of all four samples of flame retardants based on Sb_2O_3, it was necessary to conduct their X-ray fluorescence analysis. In addition, their elemental-oxide composition was calculated using X-ray fluorescence spectroscopy on the "Expert 3" analyzer. The mass fraction of chemical elements and their oxides in homogeneous monolithic and powder-like bodies was determined. The

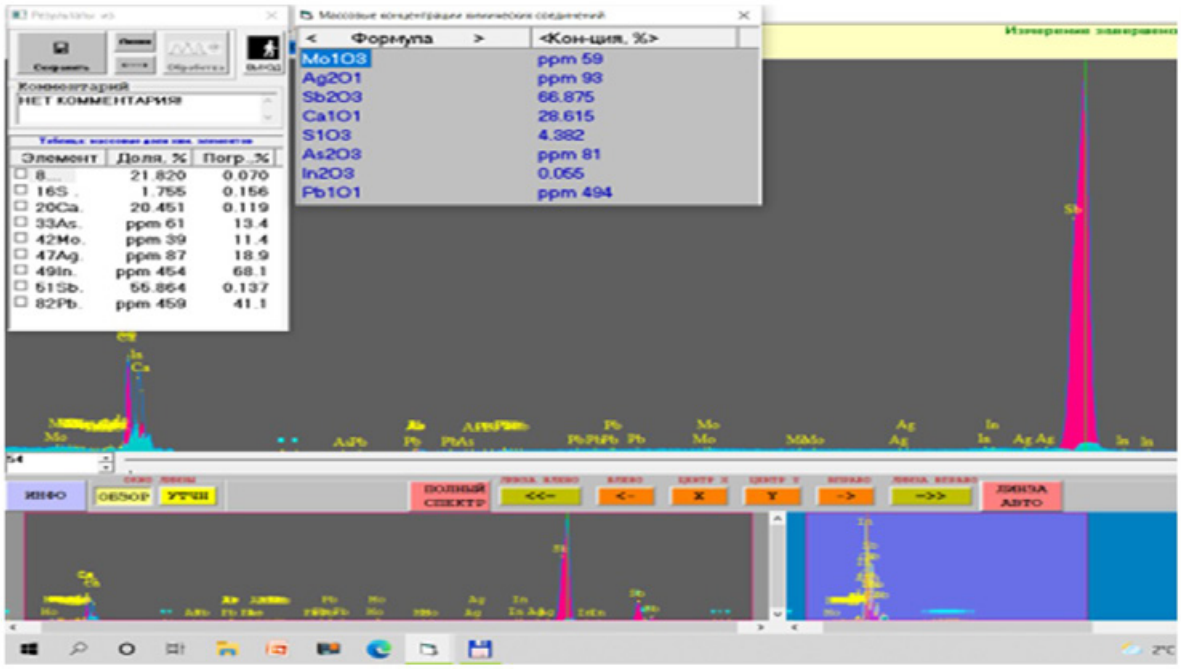

Fig. 7. X-ray fluorescence diagram of flame-retardant sample 3

results of X-ray fluorescence and diffraction qualitative and quantitative analysis are presented in Figs. 5–8.

Analyzing the data of X-ray fluorescence diagrams shown in Figs. 5-8, the following conclusions can be drawn. Samples 1, 3 and 4 consist of two phases of inorganic components, namely flame retardant Sb_2O_3 as well as an additional component – microcrystalline calcium carbonate $CaCO_3$ (according to the X-ray fluorogram in terms of CaO_x) with admixtures of organic substances, in quantities corresponding to [14], whereas sample 2 remains as pure antimony(III) oxide (about 100%).

The phase and chemical composition of flame-retardant samples 1-4 according to the results of X-ray fluorescence analysis (Figs. 5–8) and in terms of $CaCO_3$ is presented in Table 3.

Based on the obtained experimental data, one could predict a mechanism of heat-stabilizing, acceptor, and flame-retardant action of four samples based on Sb_2O_3 in PVC materials subjected to combustion.

It is described below by chemical equations reaction (1–6). PVC decomposes according to the dehydrochlorination reaction (1) with the release of gaseous hydrogen chloride (HCl). Calcium carbonate can interact with released hydrogen chloride during the thermal decomposition and burning of PVC according to reaction (2) and acts as a chemical acceptor of HCl:

$$(–CH_2–CHCl–)_n \xrightarrow{140^\circ C} (–CH=CH–)_n + nHCl\uparrow \quad (1)$$

$$CaCO_3 + 2HCl \xrightarrow{140–500^\circ C} CaCl_2 + H_2O + CO_2 \quad (2)$$

$$Sb_2O_3 + 6HCl \xrightarrow{500^\circ C} 2SbCl_3\uparrow + 3H_2O \quad (3)$$

$$Sb_2O_5 + 10HCl \xrightarrow{500^\circ C} 2SbCl_5\uparrow + 5H_2O \quad (4)$$

After further heating and burning of PVC, in reactions (3) and (4) of HCl chemisorption, antimony(III) and antimony(V) oxides form the corresponding antimony(III, V) chlorides, which are removed as volatile compounds and evaporate from the reaction zone at a temperature of 260-300°C, isolating the material from the access of oxygen from the air.

T a b l e 3. Chemical composition of inorganic substances in samples 1-4 according to X-ray fluorescence analysis

Components	Content, %			
	Sample			
	1	2	3	4
Determined by X-ray fluorescence analysis				
Sb_2O_3	59.49	100.0	66.88	25.28
CaO	39.16	0.00	28.62	74.30
Listed based on diffraction analysis data on CaO content				
Sb_2O_3	30.07	100.0	48.90	5.28
$CaCO_3$	69.62	0.00	51.09	94.72

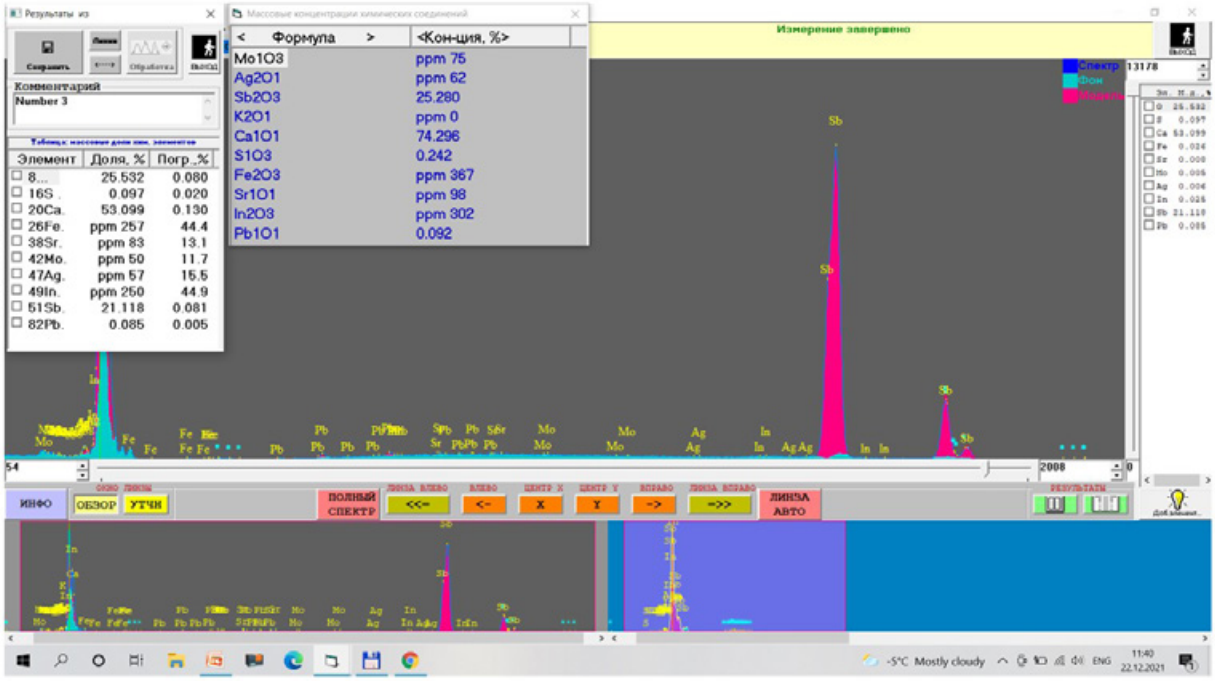

Fig. 8. X-ray fluorescence diagram of sample 4

When heated above 675°C, according to the DTA analysis, calcium carbonate begins to decompose to release calcium oxide and carbon dioxide according to reaction (5), which inhibits the combustion of the material because it insulates the material from the oxygen in the air.

$$CaCO_3 \xrightarrow{675–825^\circ C} CaO + CO_2\uparrow \quad (5)$$

In addition, calcium chloride is formed from calcium oxide and hydrogen chloride according to reaction (6), resulting in high resistance to heat and fire.

$$CaO + 2HCl \xrightarrow{825^\circ C} CaCl_2 + H_2O \quad (6)$$

CONCLUSIONS

The composition of four samples of Sb_2O_3-based flame retardants was evaluated. According to X-ray fluorescence spectroscopy, sample 1 contained 30.07% Sb_2O_3 and 69.62% $CaCO_3$, sample 2 contained 100% Sb_2O_3, sample 3 contained 48.9% Sb_2O_3 and 51.09% $CaCO_3$, and sample 4 contained 5.28 % Sb_2O_3 and 94.72% $CaCO_3$. Other substances were also found in the samples based on qualitative IR analysis. Sample 1 contains hydrocarbons and sample 3 contains hydrocarbons and organochlorines. Thermal decomposition of all flame-retardant samples begins with the loss of volatile substances and moisture at the temperature of 80–530°C (1.97–3.7%). At the temperature of 500–530°C, the mass of samples 1 and 3 does not change. Partial decomposition of samples (weight loss 13–17%) takes place in the temperature range of 650–850°C, and then the mass does not change until 1000°C. The mechanism of the flame-retardant action of Sb_2O_3 + $CaCO_3$ can be explained by the binding of HCl released during the thermal decomposition of PVC and the formation of the corresponding antimony and calcium chlorides.

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Received 21 XI 2022.