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# PVC MATERIAL FIRE RETARDANTS

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**Abstract**. *Since polyvinyl chloride (PVC materials) is easily flammable, it is added to different chemical compounds, as a fire retardant, which make it resistant to the effects of fire. Fire retardants frequently used in the production of PVC materials today include zinc stannate, zinc hydroxystannate and antimony (III) oxide. Although antimony (III) oxide shows the best properties as a fire retardant PVC material, this work points to its high toxicity, offering a reason why it should not be used.*

**Key words**: *polyvinyl chloride, fire retardant, toxicity*

## 1. INTRODUCTION

Polyvinyl chloride (PVC) is one of the most widely used type of plastic that is, due to its flexibility and low cost, used for a variety of purposes: as packaging, as insulation for electric cables, for making furniture, toys, auto parts, medical supplies and, generally, various building material. However, its prevalence has led to it becoming one of the most significant environmental problems due to its toxicity at all stages of production, use and disposal. Compared to the realized profit, PVC is one of the most valuable products in the chemical industry. Over 50% of PVC produced in the world was used in construction. In recent years, PVC has replaced traditional building materials such as wood, concrete and clay in many areas [6].

Since polyvinyl chloride is flammable, during its production process, the use of additives such as zinc stannate, hydroxystannate zinc and antimony white to enlarge its resistance to fire has increased.

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## 2. FIRE RETARDANT PVC MATERIAL

Of all the additives that are added to PVC materials zinc stannate is the safest. When using it, it is important to avoid contact with the skin and eyes. One should also not inhale its fumes. It should be kept in tightly closed containers. Zinc stannate is stable up to 400 ˚C and therefore may be involved in the process of polymer melting at this temperature. The main physical-chemical properties of zinc stannate are given in Table 1.

**Table 1.** The main physical-chemical properties of zinc stannate

| Name | Zinc Stannate |
|---|---|
| Molecular formula | $ZnSnO_3$ |
| Molecular mass | 232,06 |
| CAS registration number | 12036-37-2 |
| Chemical family | Inorganic compound |
| Combustibility | 0 |
| Reactivity | 0 |
| Toxicity | 1 |
| Flash point | Not flammable |
| Melting point | > 570 °C |
| Specific gravity | 3,9 [g/cm$^3$] |
| Look | White powder |
| LD 50 | 5 000 mg/kg |

Zinc hydroxystannate is a white powder whose physical and chemical properties are given in Table 2. Zinc hydroxystannate contains hydroxyl groups that fall apart at a temperature of about 180˚ C, and in the early stages of the fire show a cooling effect and slow down the combustion reaction. Nevertheless, it is inconvenient for the production of parts whose processing requires higher temperatures.

**Table 2.** The main physical-chemical properties of zinc hydroxystannate [1]

| Chemical formula | $ZnSn(OH_6)$ | |
|---|---|---|
| CAS registration number | 12036-37-1 | |
| Look | White powder | |
| Chemical analysis - content | Sn | 41% |
| | Zn | 23% |
| | CI | < 0.1% |
| | Free $H_2O$ | < 1% |
| Specific Density Mass [g/cm$^3$] | 3,3 | |
| Overflow Density Mass [g/cm$^3$] | 0,5 – 0,6 | |
| Medium size particles [µm] | 2,3 | |
| Solubility in water at 20 [$^0$C] | <0.01% | |
| Temperature of chemical decomposition [$^0$C] | > 180 | |

The compound which has been given priority in recent years as a fire retardant PVC material is antimony (III) oxide, whose physical and chemical properties are given in Table 3.

Although it has good properties as a fire retardant, the use of antimony (III) oxide carries with it a number of risks that are shown in Table 4.

**Table 3.** The main physical-chemical properties of antimony (III) oxide [1]

| Name | antimony (III) oxide |
|---|---|
| Other names | White antimony, |
| Molecular formula | $(Sb_2O_3)_x$ |
| Molecular mass | 291,5 |
| CAS registration number | 1309-64-4 |
| Look | White crystalline powder |
| Chemical properties | At the higher temperature breaks down in a very toxic gas (decomposes at $Sb_2O_3$ that the standard conditions of gas in contact to water and moisture from the air is building a group of very toxic compounds stibines. |
| Density | 5,67 [$g/cm^3$] |
| Boiling point | 1550 [°C] |
| Melting point | 656 [°C] |
| Solubility in water | g/100 ml at 30°C: 0,0014 |
| Vapour pressure | 133 Pa at 574°C |
| MDK | 0,5 [$mg/m^3$] – air<br>0,05 [$mg/dm^3$] – water |
| $LD_{50}$ | > 20 000 |
| **Warnings** | Toxicity: 3<br>Carcinogenic category: 2<br>Mutagens group: 3A;<br>The substance is absorbed into the body by inhalation of the powder. Short-term inhalation causes irritation of the eyes, skin and respiratory tract. Prolonged contact causes dermatitis. Tumors, a negative effect on reproductive organs and development have been detected in animals. It is a very toxic substance for aquatic organisms.<br>It is explicitly required that the substance does not enter the environment |

**Table 4.** The types of hazards in the use of antimony (III) oxide [1]

| Types of risk | Symptoms | Prevention | First Aid |
|---|---|---|---|
| Fire | Do not burn. Emits toxic gases at high temperatures! | | In case of fire, use cover for protection of respiratory organs! |
| Inhalation | Cough, headache, sore throat, vomiting. | Local ventilation. | Fresh air and medical assistance |
| Skin | Redness, pain, blisters. | Protective gloves. | Remove contaminated clothing, wash skin with soap and water. Medical assistance. |
| Eyes | Redness, pain. | Safety glasses in combination with breathing mask. | Rinse with a lot of water and seek medical advice. |
| **Food ingestion** | Abdominal pain, diarrhea, sore throat, vomiting. | Do not eat, drink and smoke during the work. | Rinse mouth, medical assistance. |

## 3. EU STANDARDS FOR DETERMINING THE FLAMMABILITY OF PVC MATERIALS

Flammability is the ability of a material to initiate combustion and to retain this state of combustion when exposed to the action of sources of ignition. It is quantified by the flammability tests. The ranking of flammable materials is used in the installation of building materials, electrical insulation materials, synthetic fabrics etc.

The Serbian standard SRPS Z.CO.005 – classified materials and goods based on their behavior in case of a fire 1979 [3]:

1. Based on the kind of danger, according to which all materials and goods are divided into three groups:
   - materials and goods that contain the risk of a chemical and physical explosion Ex,
   - materials and goods that may directly or indirectly participate in the process of combustion and are denoted by Fx and
   - materials and goods that are not readily flammable, but in case of fire damage, or destruction the material is marked by Dx.
2. Based on class of danger, and the degree of risk, materials and goods are divided into:
   - risk class I - highly flammable and quickly burnable materials,
   - risk class II – easy flammable and quickly burnable materials,
   - risk class III – flammable materials,
   - risk class IV – burnable materials,
   - risk class V – hardly burnable materials and
   - risk class VI – non-flammable materials
3. According to the aggregated state at room temperature of 200 C and the normal pressure of 1 bar, materials and goods are divided into:
   - A – gaseous substances,
   - B – liquid substances and
   - C – solids.
4. According to their physical-chemical properties, materials and goods are divided into:
   - D – explosive materials,
   - E – self-igniting materials,
   - F – substances which when heated release flammable and toxic decomposition products,
   - G – oxidants,
   - H – non-flammable substances which develop flammable gases in contact with water,
   - I – non-flammable substances which develop heat in contact with water.

This standard SRPS Z.CO.005 "Marking materials and goods based on their behavior in case of fire", marking of substances is not identical to the SRPS Z.CO.003 standard [2], "Marking the class of fire", which can lead to confusion in applying these standards. This should be changed in accordance with EU standards.

According to the European classification, materials that are installed in buildings will be divided into seven classes. The classification is given based on the results of appropriate tests. Material classes according to ignition are: A1, A2, B, C, D, E and F. Materials that belong to the class A1, A2 and B do not contribute to the development of fire, class C materials contribute to the development of fire after 10 minutes, class D materials contribute after 20-10 minutes, class E materials for less than 2 minutes. Class F materials are those that cannot be classified into the previous categories.

The flammability of materials is often determined by the oxygen index LOI based on the ASTM D2863-2000 method. Samples of materials are exposed to a source of fire in 5 the vertical position. The LOI (Limiting Oxygen Index) determines the degree of slowing burning. The LOI value according to ISO 4589 corresponds to the low concentration of oxygen in the volume percentage of the mixture of oxygen and nitrogen, yet maintains combustion, Table 5.

**Table 5.** The classification of material based on its ability to conduct fire, borderline values of the oxygen index [6]

| | | |
|---|---|---|
| LOI | $\leq 23$ | combustible materials |
| LOI | 24-28 | partially slow burning |
| LOI | 29-35 | slow flame |
| LOI | $\geq 36$ | especially slow flame |
| LOI | ca45 | a maximum value reached |
| LOI | >45 | BETAflam |

The flammability of a material is determined through the smoke it creates:

- TSV [$dm^3$] – the total amount of smoke,
- SEA [$m^2/kg$] – the total smoke area per unit of mass of the sample used in the study,
- TSR [$m^2/m^2$] – the smoke production rate as a parameter that is indicative of the amount of smoke that is created in large fires,
- SP [MW/kg] – average index of smoke and
- SF [$MW/m^2$] – smoke factor, according to ISO 5659-2.

PVC samples could be examined by using the "M test". This test is commonly used in Europe for testing materials used as fabrics for households. Fabric samples were subjected to radial heating and an ignition source for 5 s. The ignition source is held in a position below sample 5 which is then taken down. This is repeated every 20 s until 5 minutes have passed. Sets of three types of plastic materials are tested on the front side and three on the back. The samples were considered fire resistant if they do not have any damage and then have an M1 rating. Those who have a burn mark are marked M4.

The production of smoke during fire has many adverse consequences. Thick smoke can reduce visibility significantly (by cable with PVC insulation up to 90%), which is a great difficulty for a successful rescue attempt, and may be the cause suffocation (CO, carbon monoxide). Using a cable without halogens during fire exposure can reduce it to 15-29%, which does not substantially worsen the conditions for successful rescue.

Due to the increase in the number of cables in the buildings, the requirements were eventually increased and new standards were introduced in EU countries. In addition to EU standards there are also German standards, DIN, shown in table 6.

**Table 6.** Comparison EU and DIN standards

| | |
|---|---|
| It is used for: | Cables or ducts for power or signals or bands (diameter <20mm, cross-section $\leq$ 2,5mm$^2$) |
| Standard | EN 13501-3; EN 50200 |
| Classification of PH, fire resistance, [min] | 15 30 60 90 |
| It is used for: | Electrical and optical cables as accessories, fire resistant installation |
| Standard | EN 13501-3; EN 1366-12 |
| Classification of PH, fire resistance P [min] | 15 20 30 45 60 90 120 180 240 |
| It is used for: | Electric fire-proof installation with the preserved features |
| Standard | DIN 4102-12 |
| Classification E [min] | 30 60 90 |

## 4. LATEST SCIENTIFIC RESEARCH INTO FIRE PVC MATERIAL RETARDANTS

Since their development 20 years ago, zinc stannate (ZS) and zinc hydroxystannate (ZHS) they have been known as additives that are added to synthetic materials, which have a retardant feature and protect material from flames. In addition, there is also the use of antimony III oxide (ATO). These chemical compounds are used alone or added to flammable material to create a certain mixture, in which case we are referring to their synergetic (joint) actions. The latest scientific research suggests the presence of antimony (III) oxide, although it is far more dangerous because of its toxic properties than the previous two retardants.

Whether antimony (III) oxide should be added to zinc stannate and zinc hydroxystannate depends on the manufacturer, based on knowledge of their synergetic combinations of properties, suppression of smoke and non-toxicity.

We will proceed to show the research results of a team of scientists from Bolton [6].

### 4.1. Material and Methods

Three samples of PVC material without and with 5 and 10% fire retardant values were examined.

Testing the efficiency effects of the present retardant characteristics in PVC materials was carried out using a calorimetric cup that measures the oxygen index (LOI), ignition delay time (TTI), the amount of released heat (PHRR), the quantity of released heat (THR), and parameters related to smoke under flux heat in the range 35 – 150 kW/m$^2$.

The calorimetric cup shown in Figure 1 is a next generation device for ignition testing. This instrument is equipped with an electric heater in the form of a cone, and hence its name the calorimetric cup. Samples are placed in the device in standard dimensions 100 × 100 × 5 mm and exposed to heat flux up to 150 kW/m$^2$. A spark provides ignition. The lighter is 13 mm above the sample.

Products of combustion are carried out through the exhaust system. The exhaust system consists of channels that have an embedded thermometer, centrifugal fan, hood and flow meter. Standard air flow is 0,024 $m^3/s$. The concentration of oxygen is measured with an accuracy of 50 ppm. The amount of released heat is also measured.

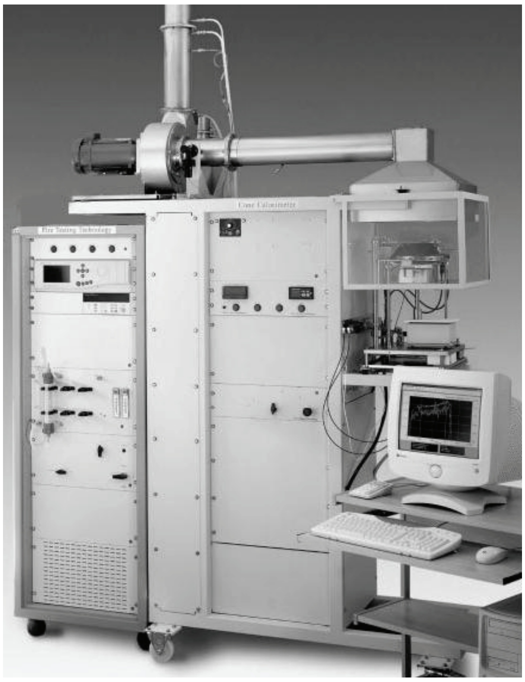

**Fig. 1.** Calorimetric cup test scores in the fire behavior of various materials

Smoke is measured in the exhaust channel laser instrument. Also, the exhaust channel can consist of instruments for the analysis of flue gases. All of the data were collected using a computer with software that records data continuously at fixed intervals of several seconds until the test has been concluded.

The calorimetric cup is used to determine the following materials: a critical index of oxygen, the amount of heat liberated per unit mass and surface, time delay ignition, mass loss rate, total weight loss, as well as smoke coefficients, which can be expressed differently. This device is used according to the ASTM E 1354 method.

The flammability of the samples was measured based on the oxygen index LOI using the ASTM D2863-2000 method. The samples were exposed to the source of ignition for 5 seconds in a vertical position.

The calorimetric method was used to buy sample sizes of 100 x 100 x 5 mm with technological instruments to test fire according to the ISO 5660 at a heat of 35 or 50kW/$m^2$. The software of the calorimetric method collected reports on the amount of smoke in every second, which then showed the data on smoke expressions in different units. The total amount of smoke (TSV) is expressed in $dm^3$ (or litres). The amount of smoke can be expressed and the total smoked area per unit mass of the sample used in the study (SEA, $m^2$/kg); it is usually expressed as the average SEA for a given time. Since SEA values depend on the masses and do not count towards the rate at which the smoke is produced, this parameter is not an accurate indicator of the production of smoke. The calorimetric method also expresses the rate of production of smoke as the TSR parameter that is indicative of the amount of smoke that is created in large fires. The smoke factor can be shown using the average index of smoke (SP), which is a product of SEA and the total smoke free TSV. The smoke factor, SF, gives the results similar to those obtained using the ISO 5659-2.

PVC samples were also examined using the "M test". This test is commonly used in Europe to test synthetic material. The samples were subjected to radial heating and an ignition source for a period of 5s. The ignition source is held in position under the sample for 5 seconds and then removed. This is repeated every 20s until 5 minutes have passed. Sets of three types of plastic materials have been tested on the front side and three on the back. The samples were considered resistant to fire there was no damage and then were given the M1 grade. Those who have a burn mark received an M4.

### 4.2. Research results

Table 7 and Figure 2 present the results of the oxygen index (critical oxygen index) of various samples of PVC: without the presence of fire retardant and with fire retardant and with 5% and 10% zinc stannate, 5% and 10% zinc hydroxystannate and 5% and 10% Antimony (III) oxide.

**Table 7.** Results of the oxygen index for plastic materials [6]

| Type of sample | Retardant | LOI |
|---|---|---|
| PVC | – | 22 |
| PVC – ZS5 | Zinc Stannate 5 % | 25,1 |
| PVC – ZS10 | Zinc Stannate 10 % | 26,4 |
| PVC – ZHS5 | Zinc Hydroxystannate 5 % | 25,5 |
| PVC – ZHS10 | Zinc Hydroxystannate 10 % | 26,7 |
| PVC – ATO5 | Antimony (III) oxide 5 % | 26,9 |
| PVC – ATO10 | Antimony (III) oxide 10 % | 28 |

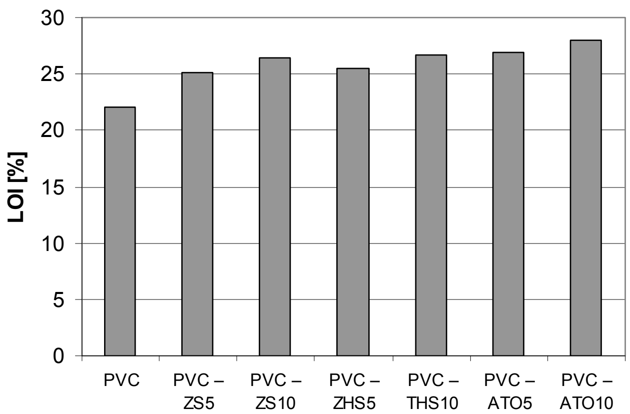


**Fig. 2.** The graphic representation of the oxygen index of plastic material with and without the presence of a fire retardant

As can be seen from Table 7 and in Figure 2 a PVC material with 10% antimony (III) oxide has the most appropriate index of oxygen, and if that is the only indication, antimony (III) oxide should be given priority as a fire retardant PVC.

Table 8 and in Figure 3 show the Smoke indexes for samples of various PVC materials: the absence of fire retardant and fire retardant, with 10% zinc stannate, 10% zinc hydroxystannate and 10% Antimony (III) oxide.

As can be seen from Table 8 and in Figure 3 the best results, as far as smoke, were obtained for zinc stannate and zinc hydroxystannate, and at the same time antimony (III) oxide gives more smoke, even more than pure PVC material.

**Table 8.** The results of the smoke index [6]

| Type of sample | Retardant | TSR [$m^2/m^2$] | TSV [l] | SF [$MW/m^2$] | SP [MW/kg] | SEA [$m^2/kg$] |
|---|---|---|---|---|---|---|
| PVC | – | 4455 | 892 | 988 | 358 | 954 |
| PVC – ZS10 | Zinc Stannate 10 % | 3642 | 740 | 577 | 188 | 800 |
| PVC – ZHS10 | Zinc Hydroxystannate 10 % | 3800 | 759 | 422 | 108 | 591 |
| PVC – ATO10 | Antimony (III) oxide 10 % | 5483 | 1097 | 505 | 146 | 875 |

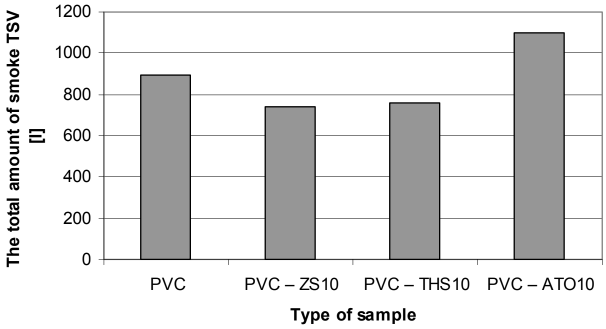


**Fig. 3.** The graphic display of the smoke index for TSV PVC material with and without fire retardant

At the end of the study, the results obtained using the "M test" are presented in Table 9. to the study included pure PVC material and plastic material with 10% retardants - zinc stannate, zinc hydroxystannate and antimony (III) oxide.

**Table 9.** Flammability rating with the "M test" [6]

| Type of sample | Retardant | M |
|---|---|---|
| PVC | – | M4 |
| PVC – ZS10 | Zinc Stannate 10 % | M2 |
| PVC – THS10 | Zinc Hydroxystannate 10 % | M2 |
| PVC – ATO10 | Antimony (III) oxide 10 % | M1 |

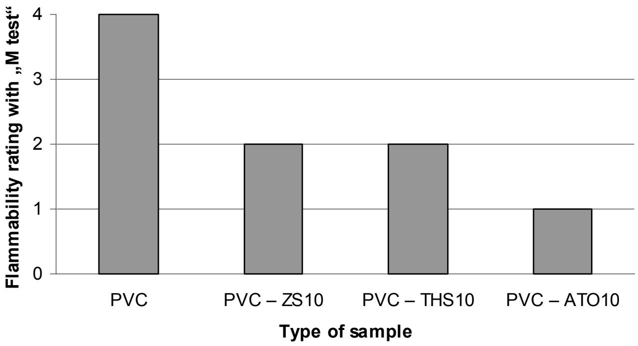


**Fig. 4.** The graphic display which marks the "M test" ignition PVC with and without the presence of fire.

## 5. Risk Assessment in the Use Antimony (III) Oxide

Since research [6] give priority to antimony (III) oxide, we carried out risk assessment in its use as a fire retardant for PVC material, because regardless of its good properties in terms of fire resistance, it should not be forgotten that its level of toxicity is 3, carcinogenic group 2 and mutation 3A.

The delineation of hazard modeling was performed by modeling [5] propagation of gaseous decomposition products of PVC material with a minimum content of 5% antimony (III) oxide. Modeling was carried out for a door weighing of 15 kg, for the content of antimony (III) oxide of 0.75 kg. The assumption was that any changes on the door would be a result of the fire at a temperature of 80 degrees C. At that temperature 6 [mg/$m^3$] antimony (III) oxide will be emitted, which is 12 times the value of MDK. However, this concentration should be kept short, for a period of 1.5 min at a wind speed of 3 [m/s], (Figure 5.) and extended to 120 m in wind direction.

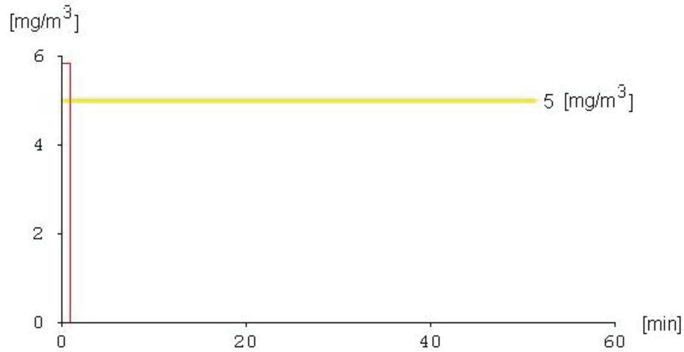


**Fig. 5.** The duration of the risk level of intoxication indoors [5]

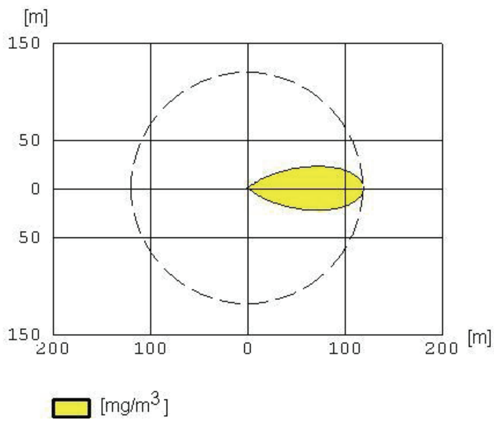


**Fig. 6.** Zone with risk toxicity level [5]

When analyzing the vulnerability zone caused by the use of antimony (III) oxide as a fire retardant plastic material we should not lose sight of the fact that the simulation was done only for one door made of from PVC material and that the concentration of harmful products of thermal destruction of the retardant will be far greater in areas in which all the windows are made of PVC material and would be retained much longer if there were no air flow.

## 7. CONCLUSION

The objectives of research, related to fire retardant PVC material, which is now being carried out around the world, is to prove the excellent properties of Antimony (III) oxide as a fire retardant, with a recommendation for its use, if not as self-retardant, then combined with zinc stannate and zinc hydroxystannate. However, in the analysis of the results, its high toxicity was never mentioned (Table 3), or its carcinogenic and mutagenic effects.

In areas affected by fire with PVC windows and doors, in which the antimony (III) oxide is present, the outcome to be expected is its decomposition into toxic, carcinogenic and mutagenic gases (Table 3) and the appearance of their concentrations above MDK values (Figures 5 and 6). As a result, high smoke occurs during antimony (III) oxide testing as a fire retardant PVC (Table 8). In addition, the decomposition of antimony (III) oxide and the emission of toxic gases during a fire have been proven by fact that the victims of fire had antimony in their blood [4].

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# PROTIVPOŽARNI PVC MATERIJALI

**Emina Mihajlović, Sveta Cvetanović, Amelija Đorđević, Ivan Krstić, Danilo Popović**

*S obzirom na to da je polivinil hlorid (PVC materijal) lako zapaljiv, dodaje se različitim hemijskim jedinjenjima koja zatim imaju dejstvo protivpožarnog materijala i čine ga otpornim na uticaj vatre. U protivpožarni materijal koji se često koristi u proizvodnji PVC materijala spadaju cink stanat, cink hidroksistanat i antimon (III) oksid. Iako antimon (III) oksid ima najbolje odlike kao protivpožarni PVC materijal, u ovom radu ukazuje se na njegov visok nivo toksičnosti, pa se iz tog razloga ne bi trebalo koristi.*

Ključne reči: *polivinil hlorid, protivpožarni materijal, toksičnost*