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## **SELECTION OF PRECURSORS OF SAFE SILICA-BASED FIREPROOF COATINGS FOR TEXTILE MATERIALS**

The selection of the inorganic precursor  $\text{SiO}_2$  as the main component of the simplified safe technology for obtaining flame-retardant coatings on textile materials was carried out. By thermographic research of organic and inorganic  $\text{SiO}_2$  precursors, performed on an OD-102 derivatograph under conditions of heating at a rate of  $10^\circ\text{C}/\text{min}$  in an air environment, the processes of decomposition of the coating that occur during the action of fire were investigated. Gels based on inorganic precursors produced by industry (silica sol, silica gel) and silicic acid, which was obtained by the exchange reaction of an aqueous solution of sodium silicate of liquid glass and acetic acid, were studied for the comparative characteristics of thermal destruction of coatings. As organic precursors of  $\text{SiO}_2$ , gels of ethyl silicate-32 and methyltriethoxysilane were studied, which were obtained by hydrolysis of organosilicon compounds in an acidic water-alcohol medium with subsequent polycondensation of the hydrolysis products. The effect of temperature on the nature of thermal destruction of silica gel, silica sol, silicic acid and organosilicon gels of ethyl silicate and methyltriethoxysilane was investigated. It is shown that inorganic precursors differ favorably from organosilicon precursors in terms of the overall thermal effect during their decomposition, mass loss during heat treatment, and the rate of change of this parameter. Considering that, in addition to total mass loss, the increase in mass loss during heating is less than 1 % in compositions based on inorganic precursors, it is possible to use all three types of inorganic precursors, but from the point of view of acidity and safety of impregnation compositions, preference is given to silicic acid obtained by the exchange reaction of silicate sodium liquid glass with acetic acid.

**Keywords:** liquid glass, siliceous coatings, fire protection of textile materials, precursors of inorganic and organic origin

### **1. Introduction**

The sol-gel method is very widely used in various fields of science and technology. Obtaining protective coatings securely attached to fabric fibers is due to the processes that occur during the sol-gel transition.

Organosilicon compounds of different chemical composition, degree of polymerization and modification are usually used as starting components. But, regardless of the chemical composition of the organosilicon component, the processes that take place in the sol and lead to its transformation into a gel can be described by sequential-parallel reactions of hydrolysis and polycondensation. With the help of sol-gel transformation, it is possible to obtain materials of a new generation with increased physical and chemical properties [1, 2].

Recently, the sol-gel method is used not in its pure form, but as an auxiliary method for creating a layer-by-layer coating [3], as well as for creating nanoparticles of metal and non-metal oxides for their deposition on the surface of textile material [3]. The so-called hybrid protective coatings are quite often used, in which, in addition to the organic component in the form of a sol of the organosilicon component, there are inorganic compounds of varying degrees of water solubility [4].

Given that the formation of a siloxane framework can only occur after the appearance of OH- hydroxo groups in the structure of the organosilicon component (after the hydrolysis reaction), which are prone to condensation with the formation of oxygen

bridges in the siloxane structure, a large number of technical literature sources are devoted to the study of these processes and their influence on the formation of dense protective coatings on textile materials [5].

Organosilicon components usually have a developed structure and contain phenolic groups to increase fire resistance [6], but such structures need to be synthesized in advance, which is quite a difficult task. In addition, organophosphorus compounds containing halogens, amino or nitro groups also need to be synthesized first. The developed structure of the components of the fire-resistant coating ensures the formation of a coke residue during the action of fire on the treated fabric, that is, the fabric is quickly destroyed. In addition, halogenated organophosphorus compounds and their thermal decomposition products are usually toxic.

Considering the above, the issue of developing a technology for obtaining gel coatings based on safe components is urgent.

## 2. Analysis of literature data and problem statement

The use of the sol-gel process allows you to create a gel silicate film on the surface of fabric fibers, which acts as an insulating barrier [7]. The principle is the type and structure of the sol-gel precursor: depending on the number and type of functional groups that can be hydrolyzed, the presence of aromatic rings, etc. it is possible to obtain a different degree of distribution of the silicon dioxide dispersion on the fibers. For example, work [8] shows that not only the type of organosilicon precursor affects the structure of the gel coating, but also the quantitative ratio of the components. It is shown that the time of modification and the content of tetraethylorthosilicate directly affect the number of  $\text{SiO}_2$  nanoparticles formed on the surface of fabric fibers. The main drawback is the need to strictly control the kinetic parameters of the sol-gel transition in order to obtain a more or less uniform coating.

Addition of aluminum titanate, zirconate, or aluminum isopropylate to the  $\text{SiO}_2$  sol allows modification of the gel film containing  $\text{Si-O-Al-}$  or  $-\text{Si-O-Zr-O-Si-}$  blocks and other types of architecture to obtain an organic-inorganic coating with increased flame retardant properties. But the authors [9] observed the formation of dense coating films in the gaps between the fibers, and the film was partially fixed on the surface of the fibers, which, of course, negatively affects the elasticity and softness of the fabric.

In the case of using a phosphorus-containing compound during the sol-gel process, for example, using orthophosphoric acid in the hydrolysis of alkoxy silane, it is possible to improve the fire-retardant effect of the siloxane coating on the fibers of cotton fabrics [10] due to thermal shielding, which ensures the presence of silicon dioxide, and carbonization by due to the presence of phosphoric acid. But the amount and concentration of orthophosphoric acid have a different effect not only on the fire-retardant properties of impregnated fabrics, but also on the spatial structure of the siloxane film on the cotton fibers. Although orthophosphoric acid mainly affects the linear polycondensation of the organosilicon precursor  $\text{SiO}_2$ , the structure of the gel film will be very heterogeneous due to the low rate of hydrolysis of alkoxy silane and the much higher rate of the polycondensation reaction, i.e. in different local areas the structure of the gel film will differ, accordingly, the development of deformation stresses is possible in the case of fire, which leads to the destruction of the coating, which is confirmed by research [11].

Complication of the structure of the fire-resistant coating leads to negative consequences in relation to the ecological situation of the environment. The synergistic effect of phosphorus-, nitrogen- and halogen-containing organosilicon substances is a logical

explanation for their wide use as components of fire-resistant coatings on textile and building materials. But, taking into account that there are no eternal materials and there is always a moment of disposal of the material protected by a fire-resistant coating [12], it is necessary to pay attention to the processes of thermal decomposition of fire-resistant compositions and treated fabrics. Usually, disposal takes place in high-temperature furnaces and is accompanied by the release into the air of a large amount of flue gases, which contain toxic components [13]. During the thermal decomposition of textile materials, in addition to the gas component, a large number of small solid particles are released into the air, which are carried with flue gases over long distances and gradually settle on soil and water [14]. The smallest particles move long distances with the air. This is confirmed by a number of studies carried out by scientists from different countries [15]. For example, Swedish scientists conducted research on the quality of air that moved from the southern regions of Europe to the north [16]. The results of the measurements proved the presence in the air of the remains of the decomposition of the brominated cycloalkane hexabromocyclododecane, which is widely used in Europe and is not used in Sweden [17]. Large-scale measurements of air, soil, water, food products (sea fish, etc.) showed high concentrations of hexabromocyclododecane, which indicates bioaccumulation [18].

Summarizing the above, known effective flame retardant compositions for textile materials contain toxic halogenated organophosphorus compounds, which are attached to organosilicon polymers with a developed spatial structure and require a preliminary complex synthesis. Under the action of fire, the coating swells, which makes further use of the textile material impossible, and the decomposition products of the coating negatively affect the environment.

Thus, it is determined to be expedient to replace organophosphorus compounds with inorganic phosphorus-containing safe substances, and instead of high-cost organosilicon compounds to use inorganic  $\text{SiO}_2$  precursors, which will simplify the technology of obtaining coatings and their application to fibers of textile material.

### **3. The purpose and tasks of the research**

The purpose of the work is to substantiate the choice of the inorganic precursor  $\text{SiO}_2$  as a silica base for safe flame retardant compositions for textile materials.

To achieve the goal, the following research tasks needed to be solved:

- to investigate the processes of thermal destruction of inorganic silica-containing precursors;
- to investigate the effect of mass loss of silica-containing precursors on the microstructure of fire-resistant coatings.

### **4. Research materials and methods**

The main hypothesis is that silicic acid, which is formed during the exchange reaction of sodium silicate with acid, is able to polymerize and form a protective film, but the type of mineral or organic acid affects the nature of this polymerization and the spatial structure of the polymer. Therefore, it is important to investigate the influence of the conditions of production of silicic acid on the processes of its thermal destruction. Sols and  $\text{SiO}_2$  gels of inorganic origin were used for research: silica sol, silica gel, and silicic acid obtained by the exchange reaction between sodium silicate (liquid glass) and acetic acid. Ethyl silicate-32 gel (ETS gel) and methyltriethoxysilane (MTEOS gel) were used as organic precursors.

Processes of thermal destruction of silica-containing precursors of flame retardant compositions were studied using differential thermal and X-ray phase analysis methods and optical microscopy. DTA curves were obtained on an OD-102 derivatograph in the temperature range of 20–1000 °C with a temperature rise rate of 10 °C/min. X-ray phase analysis was performed using a DRON-3M X-ray diffractometer in CuK $\alpha$  radiation. Microscopic analysis of the coating surface was performed in reflected light using a Digital Microscope S10 1000 $\times$  optical microscope.

### 5. Results of the study of processes of thermal destruction of silica-containing precursors

DTA curves of inorganic gel coating precursors are shown in Fig. 1. DTA curves are similar in shape. A diffuse, low-intensity endothermic effect in the temperature range of 85–125 °C, which is accompanied by a slight loss of mass, corresponds to the beginning of the thermal decomposition of silica sol, silicic acid, and silica gel.

When the inorganic precursors are further heated to a temperature of about 640 °C (Fig. 1), anhydrous amorphous SiO<sub>2</sub> is formed, which is accompanied by a slight exothermic effect without a change in mass. Minor exothermic effects at a temperature of 820 °C without a noticeable change in mass can be attributed to the crystallization of SiO<sub>2</sub>.

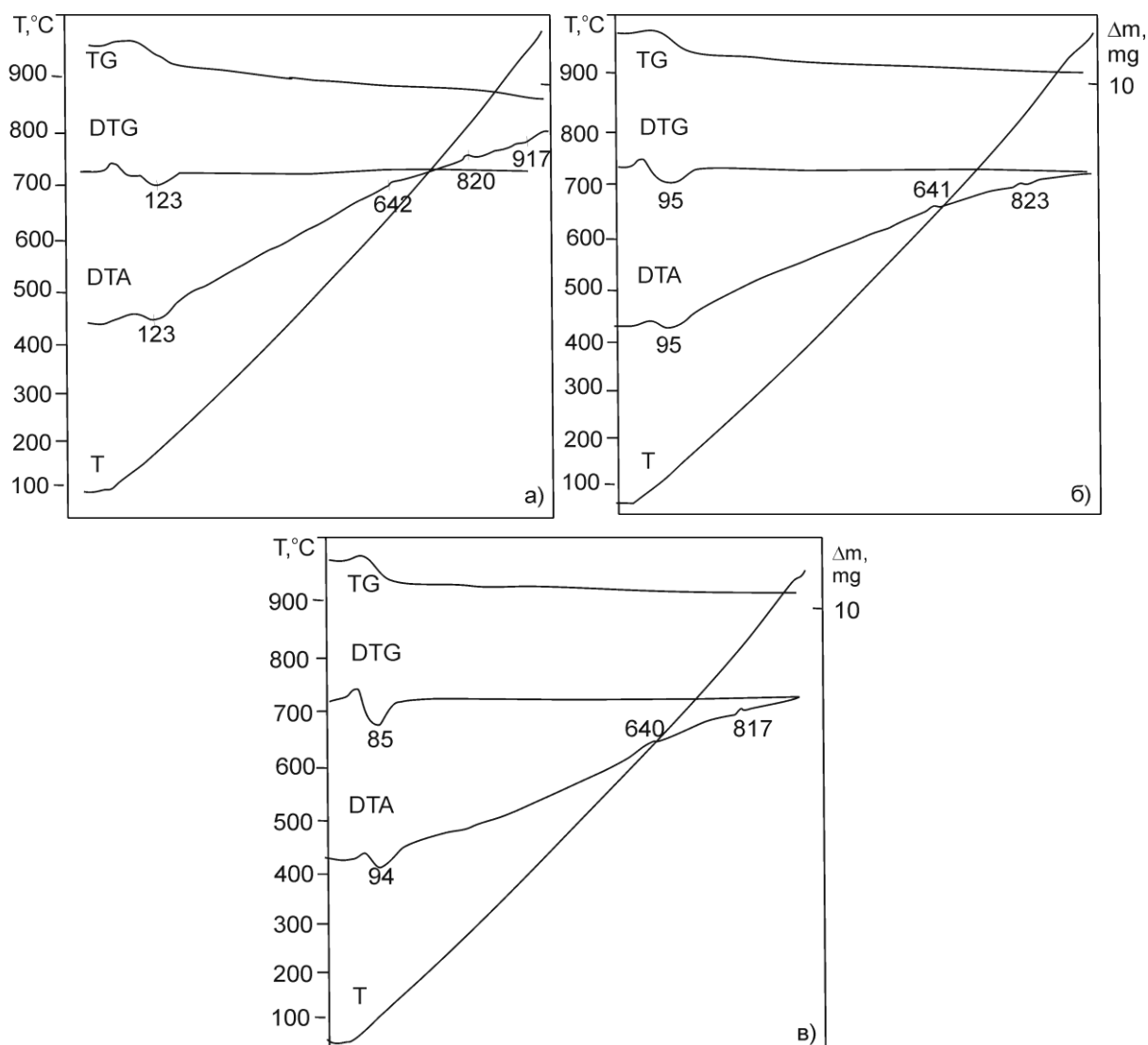


Fig. 1. Differential-thermal organosilicon gels based on: a – silica gel; b – silicic acid; c – silica sol

The low intensity of the exothermic effect indicates that the crystallization process is insignificant, which is confirmed by x-rays: on the x-ray pattern of silicic acid, heat-treated at a temperature of 840 °C (exposure for 1 hour), only an increase in the intensity of the halo is observed, and the formation of diffraction peaks of very weak intensity on it (at the level of the main background X-ray diffraction pattern) corresponding to cristobalite (Fig. 2).

Unlike silica gel and silicic acid, the thermogram of silica gel (Fig. 1a) shows a weak endothermic effect at a temperature of 917 °C, which is accompanied by a slight loss of mass and probably corresponds to the process of destruction of clathrates.

Organosilicon precursors decompose with a significant endothermic effect (Fig. 3).

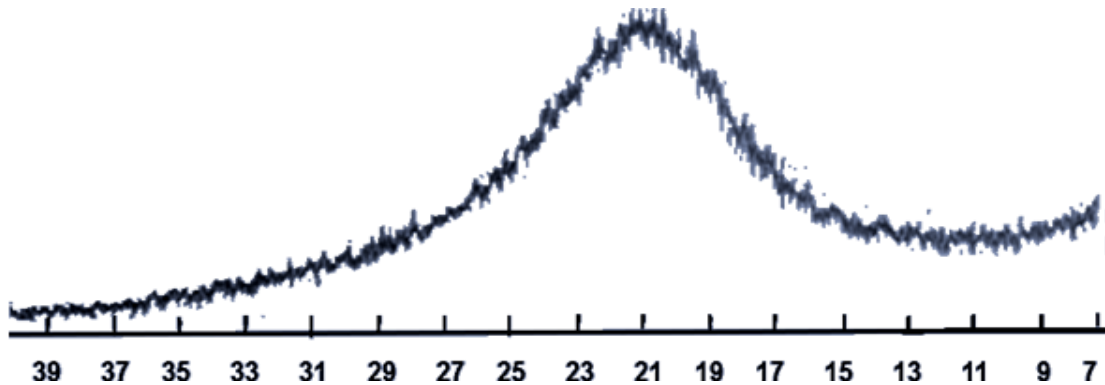


Fig. 2. X-ray pattern of silicic acid fired at 840 °C/1 hour

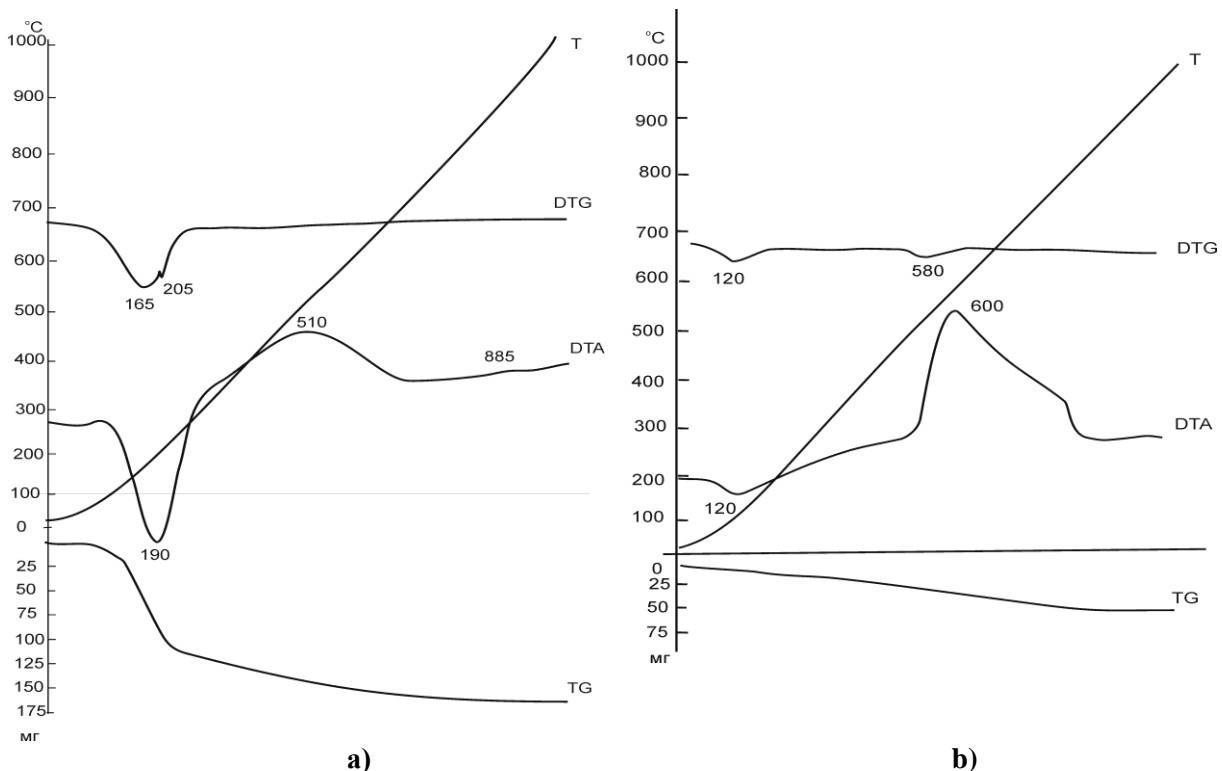


Fig. 3. Differential thermal analysis of organosilicon gels based on: a – methyltriethoxysilane; b – ethyl silicate-32

In addition, gels based on organosilicon precursors undergo thermo-oxidative destruction with a significant exothermic effect in the range of 520–600 °C, which is accompanied by additional mass loss. A slight exothermic effect at a temperature of 885 °C indicates the beginning of crystallization of SiO<sub>2</sub>.

## 6. The effect of mass loss of silica-containing precursors on the microstructure of fire-resistant coatings

The mass loss of silica gel, silicic acid, and silica sol is half as much as the mass loss of ethyl silicate gel during heating (Tab. 1). The total mass loss of silicic acid is 8,22 %, silica sol – 6,91 %, silica gel – 11,52 %. The increase in mass loss during heating of these precursors is less than 1 %, and at the points of the endothermic effect – 0,86–2,3 %.

Unlike inorganic precursors, the ethyl silicate gel decomposes more actively: at the point of endothermic effect, a mass loss of up to 13 % is observed, and the increase in mass loss is 5,97 %. But a noticeable increase in mass loss persists in the temperature range of 100–250 °C, that is, to the temperature that corresponds to the end of the processes of thermal destruction of the ethyl silicate gel and the exit of the DTA curve to the baseline. Thermo-oxidative destruction of ethyl silicate gel at temperatures of 300–650 °C is accompanied by an increase in mass loss in the range of 0,31–0,8 %.

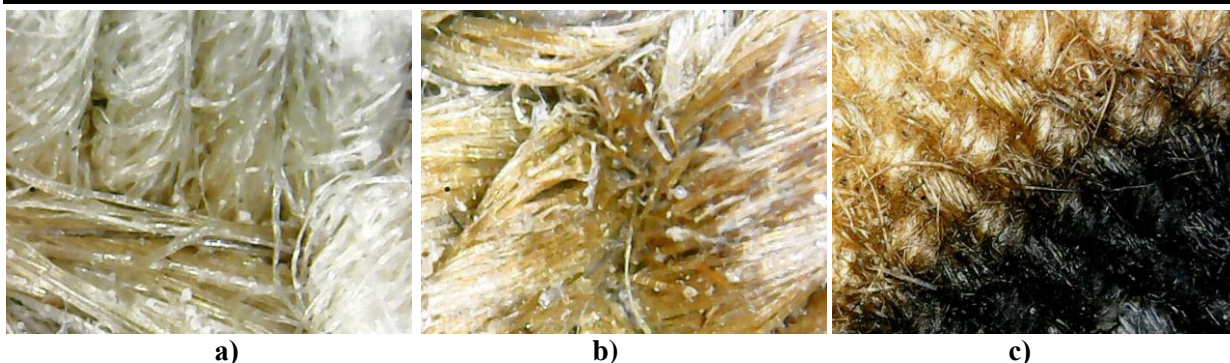
**Tab. 1. Mass loss of gel coating precursors\***

T, °C	A silica precursor									
	silica sol		silicic acid		silica gel		ETS gel		MTEOS gel	
	L <sub>m</sub>	ΔL <sub>m</sub>	L <sub>m</sub>	ΔL <sub>m</sub>	L <sub>m</sub>	ΔL <sub>m</sub>	L <sub>m</sub>	ΔL <sub>m</sub>	L <sub>m</sub>	ΔL <sub>m</sub>
100	4,32	0	2,47	0	0,77	0	2,19	0	0,36	0
150	5,18	0,86	4,11	1,64	3,07	2,3	8,16	5,97	0,72	0,36
200	5,18	0	4,52	0,41	3,84	0,77	13,13	4,97	1,08	0,36
250	5,62	0,44	4,93	0,41	4,61	0,77	16,88	3,75	1,58	0,5
300	5,62	0	5,45	0,52	4,61	0	17,5	0,62	2,02	0,44
350	5,62	0	5,45	0	5,37	0,76	18,3	0,8	2,52	0,5
400	5,62	0	5,75	0,3	5,76	0,39	19,06	0,76	2,74	0,22
450	6,05	0,43	6,17	0,42	6,53	0,77	19,69	0,63	3,24	0,5
500	6,05	0	6,57	0,40	6,91	0,38	20,00	0,31	3,24	0
550	6,91	0,86	6,99	0,42	7,68	0,77	20,63	0,63	3,96	0,72
600	6,91	0	6,99	0	8,06	0,38	20,94	0,31	4,32	0,36
650	6,91	0	6,99	0	8,45	0,39	21,25	0,31	5,04	0,72
700	6,91	0	7,40	0,41	8,83	0,38	21,56	0,31	5,76	0,72
750	6,91	0	7,40	0	9,21	0,38	21,75	0,19	6,12	0,36
800	6,91	0	7,40	0	9,21	0	21,88	0,13	6,48	0,36
850	6,91	0	7,40	0	9,60	0,39	21,96	0,08	6,48	0
900	6,91	0	7,81	0,41	9,98	0,38	22,19	0,23	6,48	0
950	6,91	0	8,22	0,41	10,75	0,77	22,19	0	6,62	0,14
1000	6,91	0	8,22	0	11,52	0,77	22,19	0	6,84	0,22

\* L<sub>m</sub> – mass loss, % ΔL<sub>m</sub> – increase in mass loss, %

Methyltriethoxysilane gel loses 6,84 % of mass when heated to 1000 °C. The increase in mass loss practically does not differ from the results obtained during the thermographic analysis of silicic acid. At the point of exothermic effect (600°C), the mass loss was 0,31 %, which practically corresponds to the mass loss of inorganic precursors.

Figure 4 shows the microstructure of fabric samples treated with flame retardant compositions based on MTEOS, ETS and silicic acid obtained from liquid glass.



**Fig. 4. Microstructure of coatings on cotton fabrics based on: a – methyltriethoxysilane; b – ethyl silicate-32; c – silicic acid**

The structure of the coatings is not destroyed after fire tests. The coating based on an inorganic precursor (Fig. 4, c) was not destroyed even in the area of fire on the fabric, but it shrank as a result of partial pyrolysis of the cellulose fibers of the fabric.

### **7. Discussion of the results of studies of thermal destruction processes of silica-containing precursors**

It is known that  $\text{SiO}_2$  sols become stable over time, that is, they do not coagulate in two pH intervals: less than 2 and more than 10 [5].

Sols obtained in the alkaline pH range are characterized by the greatest stability in the case of low concentrations. Stabilizers – sodium oxide or aqueous ammonia – are added to concentrated sols to prevent coagulation. The amount of stabilizer depends on the amount of silica sol concentration and is directly proportional to this amount.

The studied gels are most often used in various industries, in particular as starting components (precursors) of flame retardant compositions for textile and construction materials. Inorganic silica sols, which do not contain inclusions of hydrocarbon radicals on the surface of the colloidal particles of the solid phase, are produced by industry with controlled dispersion of the solid phase, concentration and pH level. Usually, the concentration of silica sols varies in the range (200–450 g/l), and the size of the micelles is 5–15 nm.

In silica sols of industrial production, the pH is kept in the range of 8,5–10,5. If modifier additives are used, pH 1,3–2 can be obtained (provided chromium oxide is added). But in both the first and second cases, the use of such silica sols is not advisable for fire protection of textile materials, because long-term exposure to a strongly alkaline or strongly acidic environment negatively affects the physical and mechanical properties of textiles, as well as human skin in case of moistening of impregnated fabric. In addition, it should be taken into account that during disposal in high-temperature furnaces in an oxidizing environment, high-temperature oxidation of trivalent chromium into the highly toxic carcinogenic form of chromium VI occurs. Therefore, in accordance with the purpose of these studies to create a safe technology of fire-resistant coatings, the use of silica sol is not advisable.

According to the results of DTA, silica gel can be used as a component of a flame retardant coating, but, taking into account the presence of an endothermic effect in the region of 900–1000 °C, which can be attributed to the process of destruction of water clathrates formed during polycondensation in acidic conditions to obtain  $\text{SiO}_2$  sol, doubts arise about the homogeneity of the gel. In previous studies, it was established that the more homogeneous the initial  $\text{SiO}_2$  sol, the denser the gel coating on the fibers of the fabric threads and the higher the fire protection of the textile material.

Silicic acid, obtained by the exchange reaction of sodium silicate and acetic acid, to

the greatest extent meets the requirements for precursors of flame retardant coatings. The acidity of the original sol is 5,5–6. Very weak crystallization of  $\text{SiO}_2$  (practically the formation of a cryptocrystalline phase) indicates the presence of an opal-like glass phase  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , the so-called technical opal, which is formed during the polycondensation of silicic acid under conditions of a slightly acidic environment and makes it difficult for crystals to form [1] and prevents the destruction of the coating during fire of research (Fig. 4).

The main disadvantage of organic precursors is the presence of significant exothermic effects on the DTA curves, which correspond to thermo-oxidative destruction and additionally increase the temperature of the coating during the action of the flame.

## 8. Discussion of the results of the study of the influence of mass loss on the microstructure of the fire-resistant coating

From the point of view of the mass loss of the studied gels, not only the total mass loss of the coating, but also the rate of its loss, that is, the increase in mass loss, is fundamental. Despite the fact that in the range of 20–1000 °C inorganic precursors lose about 7–12 % of mass, the coating does not break down during fire tests. This is explained by the small values of the increase in mass loss in the temperature intervals in which endothermic effects are present on the thermograms. The same situation is observed in the case of the use of ethyl silicate or methyltriethoxysilane as precursors: despite the significantly greater total mass loss during the heat treatment of gels based on organosilicon compounds, the low rate of increase in mass loss prevents the destruction of the coating during fire tests, due to which the treated fabrics do not catch fire, but gradually charred under the action of fire.

## 9. Conclusion

1. Through thermographic research of organic and inorganic precursors of silica coating, the processes of thermal destruction of  $\text{SiO}_2$  gels based on various precursors: organic (methyltriethoxysilane, ethyl silicate) and inorganic (silica sol, silica gel, silicic acid) were investigated. The main disadvantage of organic precursors is the presence of significant exothermic effects on the DTA curves, which correspond to thermo-oxidative destruction and additionally increase the temperature of the coating during the action of the flame.

2. The effect of gel mass loss during heating on the integrity of the fireproof coating was investigated. It was established that during thermal destruction, inorganic  $\text{SiO}_2$  precursors have significantly lower mass losses, which makes them promising for obtaining flame-retardant compositions for textile materials.

Considering that, in addition to total mass loss, the increase in mass loss during heating is less than 1 % in compositions based on inorganic precursors, it is possible to use all three types of inorganic precursors, but from the point of view of acidity and safety of impregnation compositions, preference is given to silicic acid obtained by the exchange reaction of silicate sodium liquid glass with acetic acid.

## References

1. Carosio, F., Alongi, J. (2016). Influence of layer by layer coatings containing octapropylammonium polyhedral oligomeric silsesquioxane and ammonium polyphosphate on the thermal stability and flammability of acrylic fabrics. *Journal of Analytical and Applied Pyrolysis*, 119, 114–123. doi: 10.1016/j.jaap.2016.03.010
2. Zelinski, B. J., Uhlmann, D. R. (1984). Gel technology in ceramics. *Journal Physics and Chemistry Solids*, 45(10), 1069–1090. doi: 10.1016/0022-3697(84)90049-0
3. Alongi, J., Carosio, F., Malucelli, G. (2014). Current emerging techniques to



impart flame retardancy to fabrics: An overview. *Polymer Degradation and Stability*, 106, 138–149. doi: 10.1016/j.polyimdegstab.2013.07.012

4. Panda, A., Varshney, P., Mohapatra, S., Kumar, A. (2018). Development of liquid repellent coating on cotton fabric by simple binary silanization with excellent self-cleaning and oil-water separation properties. *Carbohydrate Polymers*, 181, 1052–1060. doi: 10.1016/j.carbpol.2017.11.044

5. Skorodumova, O., Tarakhno, O., Chebotaryova, O., Bezuglov, O., Emen, F. (2021). The use of sol-gel method for obtaining fire-resistant elastic coatings on cotton fabrics. *Materials Science Forum*, 1038, 468–479. doi: 10.4028/www.scientific.net/MSF.1038.468

6. Alongi, J., Ciobanu, M., Malucelli, G. (2011). Cotton fabrics treated with hybrid organic–inorganic coatings obtained through dual–cure processes. *Cellulose*, 18, 1335–1348. doi: 10.1007/s10570-011-9564-5

7. Alongi, J., Ciobanu, M., Malucelli, G. (2012). Sol–gel treatments on cotton fabrics for improving thermal and flame stability: Effect of the structure of the alkoxy silane precursor. *Carbohydrate Polymers*, 87(1), 627–635. doi: 10.1016/j.carbpol.2011.08.036

8. Raabe, J., de Souza Fonseca, A., Bufalino, L. (2014). Evaluation of reaction factors for deposition of silica (SiO<sub>2</sub>) nanoparticles on cellulose fibers. *Carbohydrate Polymers*, 114, 424–431. doi: 10.1016/j.carbpol.2014.08.042

9. Alongi, J., Ciobanu, M., Malucelli, G. (2012). Thermal stability, flame retardancy and mechanical properties of cotton fabrics treated with inorganic coatings synthesized through sol–gel processes. *Carbohydrate Polymers*, 87(3), 2093–2099. doi: 10.1016/j.carbpol.2011.10.032

10. Alongi, J., Colleoni, C., Rosace, G., Malucelli, G. (2014). Sol–gel derived architectures for enhancing cotton flame retardancy: Effect of pure and phosphorus-doped silica phases. *Polymer Degradation and Stability*, 99, 92–98. doi: 10.1016/j.polyimdegstab.2013.11.020

11. Skorodumova, O. B., Semchenko, G. D., Goncharenko, Y. N., Tolstoi, V. S., (2001). Crystallization of SiO<sub>2</sub> from ethylsilicate-based gels. *Glass and Ceramics*, 58(1–2), 31–33. doi: 10.1023/A:1010933028152

12. Gou, J., Zhuge, J. (2013). Nanotechnology Safety in the Marine Industry. In R. Asmatulu (Ed). *Nanotechnology Safety*, 161–174. doi: 10.1016/B978-0-444-59438-9.00012-6

13. Doroudiani, S., Doroudiani, B., Doroudiani, Z. (2012). Materials that release toxic fumes during fire. *Toxicity of Building Materials. Woodhead Publishing Series in Civil and Structural Engineering*, 241–282. doi: 10.1533/9780857096357.241

14. Covaci, A. (2003). Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples – a review. *Environment International*, 29(6), 735–756. doi: 10.1016/S0160-4120(03)00114-4

15. Ilyas, M., Sudaryanto, I. A., Setiawan, E., Riyadi, A. S., Isobe, T., Tanabe, S. (2013). Characterization of polychlorinated biphenyls and brominated flame retardants in sludge, sediment and fish from municipal dumpsite at Surabaya, Indonesia. *Chemosphere*, 93(8), 1500–1510. doi: doi.org/10.1016/j.chemosphere.2013.07.048

16. Egebäck, A–L., Sellström, U., McLachlan, M. S. (2012). Decabromodiphenyl ethane and decabromodiphenyl ether in Swedish background air. *Chemosphere*, 86(3), 264–269. doi: 10.1016/j.chemosphere.2011.09.041

17. Remberger, M., Sternbeck, J., Palm, A., Kaj, L., Strömberg, K., Brorström-

Lundén, E. (2004). The environmental occurrence of hexabromocyclododecane in Sweden. *Chemosphere*, 54(1), 9–21. doi: 10.1016/S0045-6535(03)00758-6

18. Karlsson, M., Julander, A., van Bavel, B., Hardell, L. (2007). Levels of brominated flame retardants in blood in relation to levels in household air and dust. *Environment International*, 33(1), 62–69. doi: 10.1016/j.envint.2006.06.025

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### ВИБІР ПРЕКУРСОРІВ БЕЗПЕЧНИХ КРЕМНЕЗЕМИСТИХ ВОГНЕЗАХИСНИХ ПОКРИТТІВ ДЛЯ ТЕКСТИЛЬНИХ МАТЕРІАЛІВ

Виконано вибір неорганічного прекурсорів  $\text{SiO}_2$  як основного компонента спрощеної безпечної технології одержання вогнезахисних покриттів по текстильних матеріалах. Шляхом термографічного дослідження, виконаного на дериватографі ОД-102 в умовах нагрівання зі швидкістю  $10^\circ\text{C}/\text{хв}$  у повітряному середовищі, органічних та неорганічних прекурсорів  $\text{SiO}_2$  досліджено процес розкладання покриття, що відбуваються під час дії вогню. Для порівняльної характеристики термодеструкції покриттів досліджували гелі на основі неорганічних прекурсорів, які випускаються промисловістю (кремнезоль, силікагель), та кремнекислоту, яку було одержано обмінною реакцією водного розчину силікату натрію рідкого скла та оцтової кислоти. В якості органічних прекурсорів  $\text{SiO}_2$  досліджували гелі етилсилікату-32 та метилтриетоксисилану, які були одержані гідролізом кремнійорганічних сполук в кислому водно-спиртовому середовищі з подальшою поліконденсацією продуктів гідролізу. Досліджено вплив температури на характер термодеструкції силікагелю, кремнезолу, кремнекислоти та кремнійорганічних гелів етилсилікату та метилтриетоксисилану. Досліджено вплив втрат маси гелів при нагріванні на цілісність вогнезахисного покриття. Показано, що прекурсор неорганічного походження вигідно відрізняються від кремнійорганічних прекурсорів з точки зору загального теплового ефекту під час їх розкладання, втрати маси під час термообробки та швидкості зміни цього параметру. Враховуючи, що окрім загальних втрат маси приріст втрат маси під час нагрівання складає менше 1 % в композиціях на основі неорганічних прекурсорів, можливо використовувати всі три типи неорганічних прекурсорів, але з точки зору кислотності та безпечності просочувальних композицій перевагу надано кремнекислоті, що одержана обмінною реакцією силікату натрію рідкого скла з оцтовою кислотою.

**Ключові слова:** рідке скло, кремнеземисті покриття, вогнезахист, текстильні матеріали, прекурсор

#### Література

1. Carosio F., Alongi J. Influence of layer by layer coatings containing octapropyl ammonium polyhedral oligomeric silsesquioxane and ammonium polyphosphate on the thermal stability and flammability of acrylic fabrics. *Journal of Analytical and Applied Pyrolysis*. 2016. Vol. 119. P. 114–123. doi: 10.1016/j.jaap.2016.03.010

2. Zelinski B. J., Uhlmann D. R. Gel technology in ceramics. *Journal Physics and Chemistry Solids*. 1984. Vol. 45. № 10. P. 1069–1090. doi: 10.1016/0022-3697(84)90049-0

3. Alongi J., Carosio F., Malucelli G. Current emerging techniques to impart flame retardancy to fabrics: An overview. *Polymer Degradation and Stability*. 2014. Vol. 106. P. 138–149. doi: 10.1016/j.polymdegradstab. 2013.07.012

4. Panda A., Varshney P., Mohapatra S., Kumar A. Development of liquid repellent coating on cotton fabric by simple binary silanization with excellent self-cleaning and oil-water separation properties. *Carbohydrate Polymers*. 2018. Vol. 181. P. 1052–1060. doi: 10.1016/j.carbpol.2017.11.044

5. Skorodumova O., Tarakhno O., Chebotaryova O., Bezuglov O., Emen F. The use of sol-gel method for obtaining fire-resistant elastic coatings on cotton fabrics. *Materials Science Forum*. 2021. Vol. 1038. P. 468–479. doi: 10.4028/www.scientific.net/MSF.1038.468
6. Alongi J., Ciobanu M., Malucelli G. Cotton fabrics treated with hybrid organic–inorganic coatings obtained through dual–cure processes. *Cellulose*. 2011. № 18. P. 1335–1348. doi: 10.1007/s10570-011-9564-5
7. Alongi J., Ciobanu M., Malucelli G. Sol–gel treatments on cotton fabrics for improving thermal and flame stability: Effect of the structure of the alkoxy silane precursor. *Carbohydrate Polymers*. 2012. Vol. 87. № 1. P. 627–635. doi: 10.1016/j.carbpol.2011.08.036
8. Raabe J., de Souza Fonseca A., Bufalino L. Evaluation of reaction factors for deposition of silica (SiO<sub>2</sub>) nanoparticles on cellulose fibers. *Carbohydrate Polymers*. 2014. Vol. 114. P. 424–431. doi: 10.1016/j.carbpol.2014.08.042
9. Alongi J., Ciobanu M., Malucelli G. Thermal stability, flame retardancy and mechanical properties of cotton fabrics treated with inorganic coatings synthesized through sol–gel processes. *Carbohydrate Polymers*. 2012. Vol. 87. № 3. P. 2093–2099. doi: 10.1016/j.carbpol.2011.10.032
10. Alongi J., Colleoni C., Rosace G., Malucelli G. Sol–gel derived architectures for enhancing cotton flame retardancy: Effect of pure and phosphorus-doped silica phases. *Polymer Degradation and Stability*. 2014. Vol. 99. P. 92–98. doi: 10.1016/j.polymdegradstab.2013.11.020
11. Skorodumova O.B., Semchenko G. D., Goncharenko Y. N., Tolstoi V. S. Crystallization of SiO<sub>2</sub> from ethylsilicate-based gels. *Glass and Ceramics*. 2001. Vol. 58(1–2). 31–33. doi: 10.1023/A:1010933028152
12. Gou J., Zhuge J. *Nanotechnology Safety in the Marine Industry/ Nanotechnology Safety*. London: Elsevier. 2013. P. 161–174. doi: 10.1016/B978-0-444-59438-9.00012-6
13. Doroudiani S., Doroudiani B., Doroudiani Z. Materials that release toxic fumes during fire/ Toxicity of Building Materials. *Woodhead Publishing Series in Civil and Structural Engineering*. 2012. P. 241–282. doi: 10.1533 /9780857096357.241
14. Covaci A. Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples – a review. *Environment International*. 2003. Vol. 29. № 6. P. 735–756. doi: 10.1016/S0160-4120(03)00114-4
15. Ilyas M., Sudaryanto I A., Setiawan E., Riyadi A. S., Isobe T., Tanabe S. Characterization of polychlorinated biphenyls and brominated flame retardants in sludge, sediment and fish from municipal dumpsite at Surabaya, Indonesia. *Chemosphere*. 2013. Vol. 93. Issue 8. P. 1500–1510. doi: 10.1016/j.chemosphere.2013.07.048
16. Egebäck A–L., Sellström U., McLachlan M. S. Decabromodiphenyl ethane and decabromodiphenyl ether in Swedish background air. *Chemosphere*. 2012. Vol. 86. Issue 3. P. 264–269. doi: 10.1016/j.chemosphere.2011.09.041
17. Remberger M., Sternbeck J., Palm A., Kaj L., Strömberg K., Brorström-Lundén E. The environmental occurrence of hexabromocyclododecane in Sweden. *Chemosphere*. 2004. Vol. 54. № 1. P. 9–21. doi: 10.1016/S0045-6535(03)00758-6
18. Karlsson M., Julander A., van Bavel B., Hardell L. Levels of brominated flame retardants in blood in relation to levels in household air and dust. *Environment International*. 2007. Vol. 33. Issue 1. P. 62–69. doi: 10.1016/j.envint.2006.06.025

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