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Study of Phosphorus-Containing Silica Coatings Based on Liquid Glass for Fire Protection of Textile Materials

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Abstract. By introducing, in addition to phosphorus, nitrogen and halogens into the structure of the organosilicon compound, a synergistic effect of the flame retardant effect of the fabric is achieved, but the issue of protecting the environment from the effects of thermal decomposition products of the flame retardant composition arises. In view of the numerous publications on the impact of thermal destruction products of flame retardants on the ecological state of the environment, the problem of finding safe types of flame retardants that do not release toxic decomposition products during thermal destruction has arisen. The aim of the work was to develop a phosphorus- and nitrogen-containing silicate fire-retardant composition based on safe components that do not produce toxic products during thermal destruction of the treated fabric. As a result of the conducted research, it was established the possibility of using modifying additives (orthophosphoric acid and ammonium dihydrogen phosphate) in the composition of protective sol based on liquid glass. It was established that the introduction of small additions of orthophosphoric acid into the SiO_2 sol contributes to the formation of continuous thin silica films on the surface of the fibers of cotton fabric threads and significantly increases the time of the beginning of the destruction of the fabric under the action of fire. A positive result was achieved under conditions of single impregnation with sol of low concentration (8 % SiO_2). It has been established that the addition of ammonium dihydrogen phosphate also has a positive effect on increasing the flame retardant properties of the fabric. The optimal range of concentration of the solution of the phosphorus-containing additive is 10–15 %. Additional impregnation with a flame retardant solution increases the fire-resistant properties of textile materials and prevents final burning and smoldering.

1 Introduction

Textile materials are very widely used in various industries, in everyday life, as upholstery and decoration materials due to their elasticity, sufficient tear strength, abrasion resistance, easy dyeing process and aesthetics [1]. However, a big disadvantage is a high tendency to flash, which often occurs with the release of a large amount of heat, which adds problems not only during a fire [2], but also during its extinguishing [3–5]. Therefore, an important issue is the development of new ways of reducing the fire hazard from textile materials, especially in places with large crowds of people [6, 7]. In some cases, such fires also cause significant damage to the environment [8, 9].

Recently, more and more publications have been published on research in the field of finding new methods of surface treatment of fibers of textile materials with the aim of increasing flame retardant properties [10, 11]. Many publications are devoted to the methods of introducing nitrogen and phosphorus atoms into the structure of the flame retardant composition based on organosilicon substances of various classes, the degree of surface development and the number of grafted functional groups [12–14]. But mostly emphasis is placed on the use of complex organosilicon structures that undergo polycondensation with the formation of inclusion compounds or clathrates of phosphorus or

nitrogen in the layer of the protective composition on the surface of textile fibers. Red phosphorus [15], organophosphorus compounds [16], various phosphates [17], polyphosphates [18], orthophosphoric acid [19], nitrogen-phosphorus sums [20] etc. are used as a phosphorus precursor for flame retardant compositions.

The method of applying the protective composition affects the level of fire protection. The sol-gel method [21], layer-by-layer assembly [22], deposition of nanoparticles on the fiber surface [23], as well as chemical modification of synthetic fibers directly during their extraction from the melt [24] are most often used.

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 [25–27]. But 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 homogeneity of the distribution of silicon dioxide on the fibers, as well as to obtain an uneven structure of a protective silica film, the structure of which corresponds to the opal-like glass phase [28].

Recently, a combined method of layer-by-layer assembly is used, when layers of organosilicon compounds are applied using the sol-gel method, and flame retardant solutions or their mixtures are applied by the method of deposition on the surface of the silicate coating with subsequent fixing by appropriate heat treatment [29]. This approach makes it possible to control the kinetic parameters of the reactions of hydrolysis and polycondensation of organosilicon precursors, and the main stages of the sol-gel transition for the formation of layers of silicate coating, which can significantly increase the fire resistance of the fabric [30].

2 Unresolved Issues

Usually, a toxic compound or silicophosphate compound is formed in the complex of an organophosphorus compound with an organosilicon component of a complex spatial structure, which decomposes under the action of fire with the formation of toxic products of thermal destruction [31, 32]. The introduction, in addition to phosphorus, of nitrogen and halogens into the structure of the organosilicon compound achieves a synergistic effect of the flame retardant effect of the fabric, but the thermal decomposition products of such compositions significantly pollute the environment [33, 34]. In view of the numerous publications on the impact of thermal destruction products of flame retardants on the ecological state of the environment, the problem of finding safe types of flame retardants that do not release toxic decomposition products during thermal destruction has arisen.

In view of the above, the aim of the work was to develop a phosphorus- and nitrogen-containing silicate fire-retardant composition based on safe components that do not produce toxic products during thermal destruction of the treated fabric.

3 Main Part

Silicic acid sols were used for research, which were prepared by mixing an aqueous solution of liquid glass with a solution of acetic acid. Additions of orthophosphoric acid and ammonium dihydrogen phosphate (ADHP) were introduced into the composition slowly, monitoring the pH. Experimental coatings were applied to the fabric by the bath method. After a single application of the coating layer and removal of excess sol, the experimental samples were dried by heating in a drying cabinet at a temperature of (60–80) ºC. An aqueous solution of flame retardant - diammonium hydrogen phosphate (DAHP) - was also applied by the bath method.

During the fire tests, the time of the beginning of carbonization of the fabric, the time of the beginning of its destruction, and the time of final burning and smoldering were determined.

Study of the influence of the composition on the rheological properties of impregnating compositions. In the induction period of aging of SiO_2 sols, nanoparticles are formed from associates of silicic acid micelles, their sizes increase, and recondensation of small particles on the surface of larger ones occurs according to R. Eiler's theory. A change in the size and number of nanoparticles

leads to a change in the value of the optical density of the sol, therefore, measurements were made using a CPC-2 photocolorimeter.

The curves of changes in the optical density of sols containing orthophosphoric acid practically overlap each other (Fig. 1). The increase in the angle of inclination of the tangents to the curves shows that the process of growth of colloidal sol particles and their aggregation into large associates begins after approximately 45 minutes in the composition with 0.1 % and 4 % H_3PO_4 after preparation and after 60 minutes in the composition with 2 % H_3PO_4 . This term is sufficient to impregnate a large area of fabric.

After the coagulation process is completed, the composition remains transparent. Thin films of the composition, which were obtained by applying to the glass surface, have a uniform dense structure, soft and elastic.

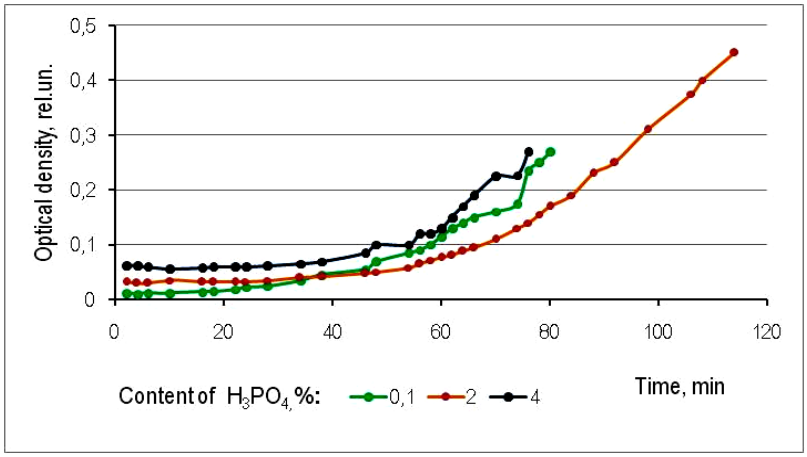

Fig. 1. Changes in the optical density of sol-gel compositions based on liquid glass over time.

Figure 2 shows the curves of changes in the optical density of sol-gel compositions containing ammonium dihydrogen phosphate (ADHP) as a phosphorus-containing compound. Despite the fact that the pH of the colloidal solution remains approximately 6, the process of growth of colloidal sol particles and their aggregation into large associates begins earlier than in compositions containing orthophosphoric acid, and is about 25 min for compositions containing 15 % and 20 % solutions of ADHP and about 30 min for compositions with a lower concentration of ADHP.

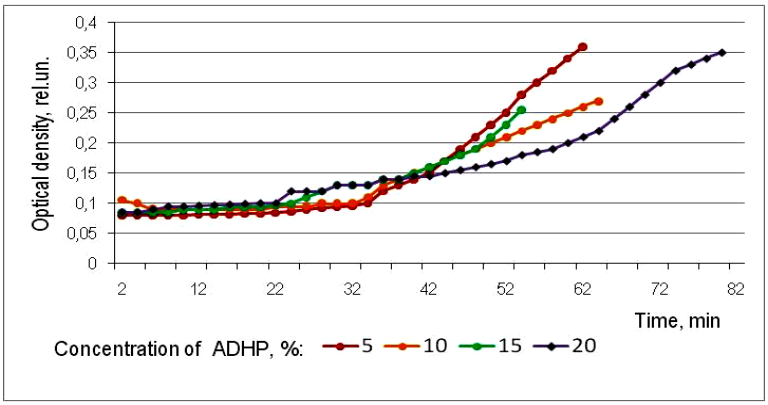

Fig. 2. Changes in the optical density of compositions with the addition of ADHP over time.

Thus, despite the fact that the life of such compositions is about 1 hour, it is desirable to impregnate the fabric in the first 30 minutes after preparing the compositions.

The structure of the gel film of the composition with ADHP is slightly different from the composition with orthophosphoric acid: it is porous and less uniform, but also elastic and transparent.

Study of the influence of the content of orthophosphoric acid on changes in the fire-retardant properties of impregnated cotton fabric samples. The composition of the experimental compositions is given in Table 1. With an increase in the content of orthophosphoric acid, the time of the beginning

of charring and the beginning of destruction practically does not change (Fig. 3). After the fire source was removed, only the 4 % orthophosphoric acid sample showed final combustion. The smoldering time of all samples not treated with flame retardant decreased with increasing H_3PO_4 content.

Table 1. Compositions of experimental compositions with orthophosphoric acid and results of fire tests.

No. compo-sition	DAHP	H_3PO_4 content [%]	The time of the beginning of charring, [sec]	The time of the beginning of destruction, [sec]	Final burning time, [sec]	Decay time, [sec]
0	not treated		3	4	27	50
1		0.1	4	6	0	90
2	+	0.1	5	154	0	0
3		2	3	4	0	75
4	+	2	4	74	0	0
5		4	4	6	16	79
6	+	4	5	121	0	0

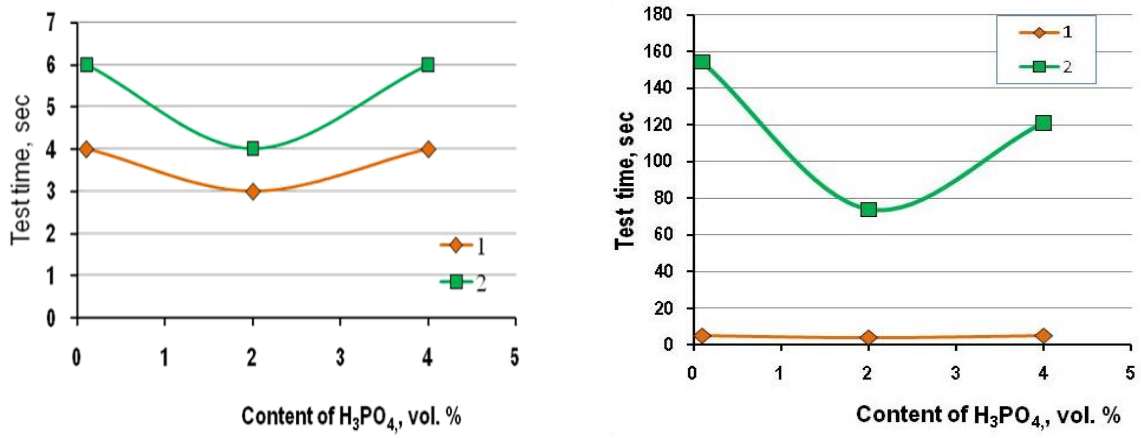

Fig. 3. Influence of the content of orthophosphoric acid on the time of the beginning of charring (1) and destruction (2) of samples without flame retardant (a) and with DAHP flame retardant (b).

In the case of additional impregnation with a flame retardant solution, final burning and smoldering were not observed, and the time of the onset of destruction increased from 4 to 154 sec. It can be seen from the graph that the best results can be obtained by introducing a micro-addition of orthophosphoric acid (0.1 %). Figure 4 shows the microstructures of the samples before and after fire tests.

The single-layer coating is transparent, colorless, not visible on the fibers of the fabric threads. The samples do not lose their elasticity. In the case of additional application of an aqueous solution of diammonium hydrogen phosphate, the tissues become a little stiffer, but they also do not lose elasticity.

No. of the composition	H_3PO_4 content	Presence of flame retardant	Microstructure of fabric samples	
			before the tests	after the tests
1	0.1	–		
2	0.1	DAHP		
4	2	DAHP		
5	4	–		
6	4	DAHP		
7	not treated			completely burned

Fig. 4. Microstructure of experimental samples.

During fire tests, impregnated samples do not support combustion, but gradually char. After removing the fire, smoldering is observed for 0.5–1.5 minutes. If flame retardant is used, smoldering and final burning are not observed.

The structure of the samples after fire remains dense. The photos show that after long-term exposure to fire, the coating is not destroyed even in the immediate area of fire.

Investigation of the effect of ammonium dihydrogen phosphate (ADHP) content on the fire-retardant properties of impregnated cotton fabric samples. Ammonium dihydrogen phosphate solutions have a pH of 6, so their addition to the composition based on liquid glass did not affect the pH change.

At the first stage of research, the influence of the content of the 5 % ADHP solution was studied. Table 2 shows the results of fire tests of experimental samples. It was established that the content in terms of dry matter of 0.5 % of ADHP significantly increases the time of onset of tissue destruction. At the same time, it is not important whether a diluted solution was added to the composition in an amount that ensures the introduction of 0.5 % ADHP, or whether such an amount of ADHP was added in the form of a more concentrated solution. As can be seen from the table, there is a synergistic effect of the action of ADHP and DAHP: the time to the beginning of tissue destruction increases sharply.

Table 2. Compositions of compositions with ammonium dihydrogen phosphate and results of fire tests.

No of the compo-sition	DAHP	ADHP concent-ration, [%]	ADHP content, [%]	The time of the beginning of charring, [sec]	The time of the beginning of destruction, [sec]	Final burning time, [sec]	Decay time, [sec]
8		5	0.25	3	5	9	50
9	+		0.25	5	57	0	0
10			0.5	4	6	30	71
11	+		0.5	4	73	0	0
12			0.75	4	6	4	20
13	+		0.75	4	9	0	0
14		10	0.5	4	22	0	100
15	+		0.5	5	177	0	0
16	+		0.5				
17		15	0.75	1	5	0	64
18	+		0.75	4	9	6	0
19	+		0.75			0	
20		20	1	2	6	0	90
21	+		1	4	9	0	0
22	+		1				
23	not treated			5	6	18	46

Considering that the SiO_2 sol has a sufficiently low concentration, the addition of a diluted solution of the additive further reduces the concentration of the impregnating composition, so the effect of the concentration of ADHP on the flame-retardant properties of the impregnated samples was further studied.

Without flame retardants, the samples smoldered, and the smoldering time depended not so much on the concentration of ADHP, but on the texture of the cotton fabric and the presence of defects on it. Therefore, we can conclude that the average smoldering time was about 60 seconds.

More important information is provided by the curve of the dependence of the time of the beginning of tissue destruction under the action of fire on the ADHP concentration: the graph shows an extremum in the area of 10 % ADHP concentration (Fig. 5a). Under the conditions of use of this particular concentration, a significant increase in the time of the onset of destruction (approximately 3–4 times) is observed. Under the conditions of additional impregnation with a solution of flame retardant - diammonium hydrogen phosphate - this composition shows an increase in the time of the beginning of tissue destruction from 22 s to 177 s, that is, almost 9 times (Fig. 5, b).

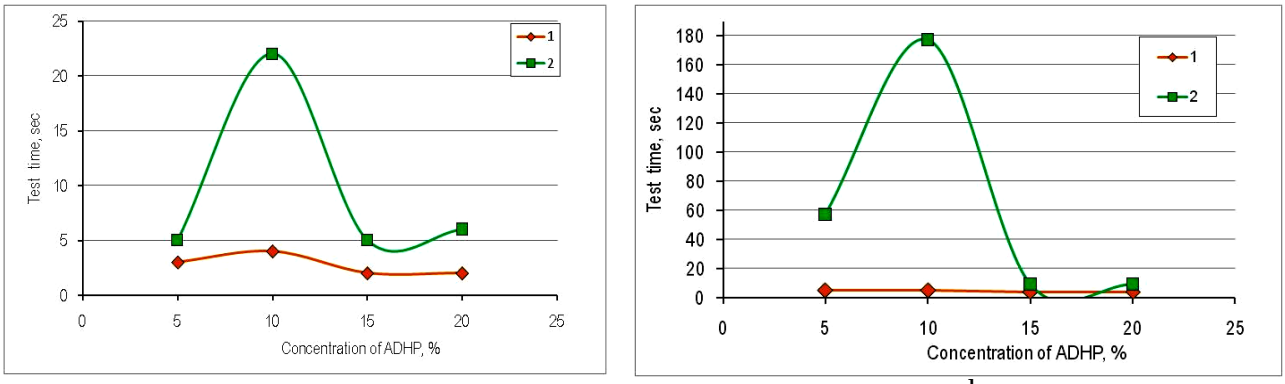

Fig. 5. Influence of the concentration of ammonium dihydrogen phosphate additive on the time of the beginning of charring (1) and destruction (2) of experimental samples without flame retardant (a) and with flame retardant (b).

Ammonium dihydrogen phosphate decomposes under the influence of temperature with the release of meta phosphoric acid, which is capable of polymerization, and ammonia. But, taking into account that in terms of dry matter, its content was in the range of 0.25–1 % of the amount of impregnation composition, the coating did not collapse, but pores formed in it, due to which thermal destruction of fabric threads was activated (Fig. 3.5). In the case of using DAHP flame retardant, complete tissue destruction in the flame zone was not observed. This can be explained by the fact that the adsorbed and thermal shock-fixed flame retardant layer on the surface of the gel protects against ADHP decomposition. Further research of compositions based on liquid glass, which contain, in addition to orthophosphoric acid, ammonium dihydrogen phosphate is promising.

4 Conclusion

As a result of the conducted research, it was established the possibility of using modifying additives in the composition of protective sol based on liquid glass. It was established that the use of small additions of orthophosphoric acid contributes to the formation of continuous thin silica films on the surface of the fibers of cotton fabric threads and significantly increases the time of the beginning of fabric destruction under the influence of fire. A positive result was achieved under conditions of single impregnation with sol of low concentration (8 % SiO_2). Additional impregnation with a flame retardant solution increases the fire-resistant properties of textile materials and prevents final burning and smoldering.

It has been established that the addition of ammonium dihydrogen phosphate also has a positive effect on increasing the flame retardant properties of the fabric. The optimal range of concentration of the solution of the phosphorus-containing additive is 10–15 %. Additional impregnation with a flame retardant solution significantly enhances the positive effect of the protective coating on the fire-retardant properties of the fabric.

References

[1] B. Pospelov, V. Andronov, E. Rybka, R. Meleshchenko, S.Gornostal, Analysis of correlation dimensionality of the state of a gas medium at early ignition of materials, Eastern-European Journal of Enterprise Technologies, 5/10 (95) (2018) 25–30.

[2] S. Ragimov, V. Sobyna, S. Vambol, V. Vambol, A. Feshchenko, A. Zakora, E. Strejekurov, V. Shalomov, Physical modelling of changes in the energy impact on a worker taking into account high-temperature radiation, Journal of Achievements in Materials and Manufacturing Engineering, 91(1) (2018) 27–33.

[3] A.N. Semko, M.V. Beskrovnaya, S.A. Vinogradov, I.N. Hritsina, N.I. Yagudina, The usage of high speed impulse liquid jets for putting out gas blowouts, Journal of Theoretical and Applied Mechanics, 52(3) (2014) 655–664.

[4] Y. Abramov, O. Basmanov, J. Salamov, A. Mikhayluk, Model of thermal effect of fire within a dike on the oil tank, Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, 2 (2018) 95–100.

[5] K. Korytchenko, O. Sakun, D. Dubinin, Y. Khilko, E. Slepuzhnikov, A. Nikorchuk, I. Tsebriuk, Experimental investigation of the fire-extinguishing system with a gas-detonation charge for fluid acceleration Eastern-European Journal of Enterprise Technologies, 3/5 (93) (2018) 47–54.

[6] P.J. Wakelyn, Environmentally friendly flame resistant textiles, Advances in Fire Retardant Materials Woodhead Publishing Series in Textiles, (2008) 188–212.

[7] C.K. Kundu, L. Song , Y. Hu, Chitosan-metal oxide nanoparticle hybrids in developing bi-functional polyamide 66 textiles with enhanced flame retardancy and wettability, Applied Surface Science Advances, 7 (2022) 100202.

[8] S. Vambol, V. Vambol, O. Kondratenko, Y. Suchikova, O. Hurenko, Assessment of improvement of ecological safety of power plants by arranging the system of pollutant neutralization, Eastern-European Journal of Enterprise Technologies, 3/10 (87) (2017) 63–73.

[9] O. Rybalova, S. Artemiev, M. Sarapina, B. Tsymbal, A. Bakhareva, O. Shestopalov, O. Filenko, Development of methods for estimating the environmental risk of degradation of the surface water state, Eastern-European Journal of Enterprise Technologies, 2/10 (92) (2018) 4–17.

[10] A. Chernukha, A. Teslenko, P. Kovaliov, O. Bezuglov, Mathematical modeling of fire-proof efficiency of coatings based on silicate composition, Materials Science Forum, 1006 (2020) 70–75.

[11] O. Skorodumova, O. Tarakhno, O. Chebotaryova, Y. Hapon, F. M. Emen, Formation of fire retardant properties in elastic silica coatings for textile materials, Materials Science Forum, 1006 (2020) 25–31.

[12] N. Didane, S. Giraud, E. Devaux, Fire performances comparison of back coating and melt spinning approaches for PET covering textiles, Polymer Degradation and Stability, 97 (2012) 1083–1089.

[13] A. Keshavarzian, M. N. Haghighi, F. A. Taromi, H. Abedini, Phosphorus-based flame retardant poly (butylene terephthalate): Synthesis, flame retardancy and thermal behavior, Polymer Degradation and Stability, 180 (2020) 109310.

[14] C. K. Kundu, C. Sekhar, R. Gangireddy, L. Song, Y. Hu, Flame retardant treatments for polyamide 66 textiles: Analysis the Role of Phosphorus compounds, Polymer Degradation and Stability, 182 (2020) 109376.

[15] E. Gibertini, F. Carosio, K. Aykanat, A. Accogli, G. Panzeri, L. Magagnin, Silica-encapsulated red phosphorus for flame retardant treatment on textile, Surfaces and Interfaces, 25 (2021) 101252.

[16] S. Wang, L. Du, P. Zhu, Z. Jiang, Influence of hydroxyl-terminated phosphoramidates on the flame retardancy of microfiber synthetic leather, Polymer Degradation and Stability, 199 (2022) 109897.

[17] M.E. Hall, A.R. Horrocks, J Zhang, The flammability of polyacrylonitrile and its copolymers, Polymer Degradation and Stability, 44 (1994) 379–386.

[18] N.K. Kim, D. Bhattacharyya, Development of fire resistant wool polymer composites: Mechanical performance and fire simulation with design perspectives, Materials & Design, 106 (2016) 391–403.

[19] J. Alongi, C. Colleoni, G. Rosace, G. Malucelli, Sol–gel derived architectures for enhancing cotton flame retardancy: Effect of pure and phosphorus-doped silica phases, Polymer Degradation and Stability, 99 (2014) 92–98.

[20] I. Borisenko, O. Burmenko, N. Deyneko, O. Zobenko, Y. Yivzhenko, G. Kamyshentsev, V. Muraviov, Yu. Mykhailovska, V. Khrystych, S. Kryvonis, Development of a method for producing effective cds/cdte/cu/au solar elements on a flexible substrate designed for backup supplying systems prevention of emergency situations, Eastern-European Journal of Enterprise Technologies, 6/5 (114) (2021) 6–11.

[21] R. Olawoyin, Nanotechnology: The future of fire safety, Safety Science, 110 (2018) 214–221.

[22] J. Wang, J. He, L. Ma, Y. Zhang, L.Shen, S. Xiong, K. Li, M. Qu, Multifunctional conductive cellulose fabric with flexibility, superamphiphobicity and flame-retardancy for all-weather wearable smart electronic textiles and high-temperature warning device, Chemical Engineering Journal, 390 (2020) 124508.

[23] J. Alongi, F. Carosio, G. Malucelli, Current emerging techniques to impart flame retardancy to fabrics: An overview, Polymer Degradation and Stability, 106 (2014) 138–149.

[24] S. Nehra, S. Hanumansetty, E.A. O'Rear, J.B. Dahiya, Enhancement in flame retardancy of cotton fabric by using surfactant–aided polymerization, Polymer Degradation and Stability, 109 (2014) 137–146.

[25] A. Sharshanov, O. Tarakhno, A. M. Babayev, O. Skorodumova, Mathematical Modeling of the Protective Effect of Ethyl Silicate Gel Coating on Textile Materials under Conditions of Constant or Dynamic Thermal Exposure, Key Engineering Materials, 927 (2022) 77–86.

[26] A. Chernukha, A. Chernukha, P. Kovalov, A. Savchenko, Thermodynamic study of fireprotective material, Materials Science Forum. 1038 (2021) 486–491.

[27] A. Chernukha, A. Chernukha, K. Ostapov, T. Kurska, Investigation of the processes of formation of a fire retardant coating, Materials Science Forum, 1038 (2021) 480–485.

[28] O.B. Skorodumova, G.D. Semchenko, Y.N. Goncharenko, V.S. Tolstoi, Crystallization of SiO_2 from ethylsilicate-based gels, Glass and Ceramics, 58(1–2) (2001) 31–33.

[29] O. Skorodumova, O. Tarakhno, O. Chebotaryova, Improving the Fire-Retardant Properties of Cotton-Containing Textile Materials through the Use of Organo-Inorganic SiO_2 Sols, Key Engineering Materials, 927 (2022) 63–68.

[30] O. Skorodumova, O. Tarakhno, O. Chebotaryova, O. Bezuglov, F .M. Emen, The use of sol-gel method for obtaining fire-resistant elastic coatings on cotton fabrics, Materials Science Forum, 1038 (2021) 468–479.

[31] V. Andronov, Y. Danchenko, Y. Makarov, T. Obizhenko, Colloid-chemical regularities of reagent wastewater treatment of dairies, Materials Science Forum, 1038 (2021) 235–241.

[32] V. Loboichenko, V. Andronov, V. Strelets, O. Oliinykov, M. Romaniak, Study of the State of Water Bodies Located within Kharkiv City (Ukraine), Asian Journal of Water, Environment and Pollution, 17(2) (2020) 15–21.

[33] Y. Hapon, M. Chyrkina, D. Tregubov, O. Romanova, Co-Mo-W galvanochemical alloy application as cathode material in the industrial wastewater treatment processes, Materials Science Forum, 1038 (2021) 251–257.

[34] B. Pospelov, E. Rybka, R. Meleshchenko, S. Gornostal, S. Shcherbak, Results of experimental research into correlations between hazardous factors of ignition of materials in premises, Eastern-European Journal of Enterprise Technologies, 6(10) (2017) 50–56.