

Study of Gelation Processes in Flame Retardant Compositions of the SiO₂ Sol System – A Phosphate-Containing Additive

LYSAK Nataliia^{1,a}, SKORODUMOVA Olga^{1,b*}, CHERNUKHA Anton^{1,c},
KOCHUBEI Viktoriia^{2,d} and SOTIRIADIS Konstantinos^{3,e}

¹National University of Civil Defence of Ukraine, 94 Chernyshevskya Str. Kharkiv 61023, Ukraine

²Lviv Polytechnic National University, 12 Bandery St., Lviv 79000, Ukraine

³Institute of Theoretical and Applied Mechanics of the Czech Academy of Sciences, Prosecká 809/76,
19000 Prague 9, Czechia

^an.m.lysak@gmail.com, ^bcxxt@nuczu.edu.ua, ^can_cher@nuczu.edu.ua,
^dviktorii.v.kochubei@lpnu.ua, ^esotiriadis@itam.cas.cz

Keywords: fire-resistant coatings, SiO₂ gels, phosphate-containing additive, building materials.

Abstract. One of the promising directions for ensuring the fire resistance of wooden building materials is the development of silicon phosphate compositions, thanks to which the formation of a protective layer is possible, which effectively prevents the spread of fire. The paper examines the possibility of using orthophosphate acid as a modifying additive for silicic acid sols. The influence of H₃PO₄ concentration on the rheological characteristics of the studied sols was determined. Sols with small amounts of orthophosphate acid (1–2%) lost their fluidity in the interval of 45–70 minutes. Increase of the additive content to 8% led to a sharp increase in optical density values and extended the survivability interval of the sol to 24 hours. Coatings based on gels with 1–2% orthophosphate acid were elastic, but increasing the content of the additive led to the formation of hard, inelastic coatings.

According to the results of infrared (IR) spectroscopy, the effect of orthophosphate acid on the nature of polycondensation was confirmed. The degree of polycondensation was estimated by the ratio of intensity (I) and band width (d) at 1050 cm⁻¹, which corresponds to the vibrations of Si-O-Si bonds. Based on the comparison of I/d indicator values, the formation of linear siloxane chains was confirmed in the case of the use of small H₃PO₄ additions. Linear polycondensation ensures greater homogeneity of the gel, which was confirmed by IR spectroscopy of gels heat-treated at 800 °C and by microscopic observations. The coating on the wood surface, based on a fire-resistant silica-containing composition with small additions of orthophosphate acid, had the most uniform and continuous structure.

1 Introduction

A well-known problem of wooden structures is their vulnerability to fire [1, 2], thus, a large number of studies are devoted to the development of fire-resistant compositions for this type of material [3, 4]. According to state standards, the use of means of preventing the occurrence of fire-hazardous situations in the construction of wooden structures [5, 6] is possible only if the required level of fire resistance of premises and objects of various types is ensured [7]. The use of fire-resistant materials is determined by the type, size and purpose of the premises [8, 9].

Phosphorus compounds are one of the most effective groups of flame retardant compositions. The main advantages of such substances compared to halogen-containing flame retardants, which are effective but dangerous for human health and the environment, are environmental friendliness, low toxicity, and low smoke-generation capacity. Environmental friendliness of fire protection materials is most relevant when used in household and construction conditions [10, 11]. Instead, industrial capital buildings usually have metal or reinforced concrete structures [12, 13], where non-combustible panels, plates [14, 15], heat-resistant plasters [16, 17], fire-retardant paints and coatings are mainly used [18, 19]. The effectiveness of the use of phosphorus-containing

compounds in the field of fire protection is based on their pyrolysis products that inhibit reactions in the gas phase due to the deactivation of active radicals in the flame [20, 21].

Since the formation of a swollen carbonized layer, which prevents the spread of flames, is important for fire protection, it is organophosphorus substances that are widely used. These compounds are substitutes for environmentally harmful brominated flame retardants (in particular, polybrominated diphenyls, which are classified as persistent organic pollutants according to the Stockholm Convention and are currently banned for use). Organophosphorus flame retardants rank second in terms of use in Europe after aluminum hydroxide [22]. Such compounds are organic esters of phosphoric acid: triethylphosphate (TEP) [23], tris(phenyl)phosphate (TPHP) [24], tris(3,5-xilylenyl)phosphate (TXP), isodecyldiphenylphosphate (IDPP) [25], tris(2-chloroethyl)phosphate (TCEP) [26], tris(2-butoxyethyl)phosphate (TBOEP), tris(1-chloro-2-propyl)phosphate (TCIPP), tris(2,3-dichlorodipropyl)phosphate (TDCIPP) [27, 28].

2 Unresolved Issues

Despite the fact that organophosphorus flame retardants are safer for the environment compared to brominated derivatives and are presented in many works as eco-friendly, the issue of the safety of these compounds remains the subject of study by many scientists [29, 30]. Toxicological studies have revealed the danger of using such substances, since these components are not chemically bound to the material being protected and can be released into the environment through evaporation, leaching or wiping, or decompose into toxic components during a fire [31, 32].

Therefore, an important stage in the development of flame retardant compounds is the incorporation of phosphorus into the polymer matrix to obtain thermally and energetically stable bonds [24, 33]. Such materials are obtained, as a rule, with the help of the sol-gel method, which allows obtaining homogeneous fire-resistant coatings thanks to the regulation of the conditions of hydrolysis and polycondensation of organosilicon compounds [34, 35]. Low-toxic inorganic phosphorus-containing substances can be used as precursors for phosphorus in Si–O–P bonds: ammonium phosphates [36], phosphoryl chloride [37], phosphorus pentoxide [24], phytic acid [38]. The incorporation of phosphorus into the structure of the siloxane frame allows to increase the resistance of such environmentally safe substances to leaching.

In this context, orthophosphate acid is interesting for studying the effect on flame retardant properties. The safety of this compound for the human body is obvious, as it is widely used in the food and pharmaceutical industry [32]. It is also known that orthophosphate acid is widely used as a binder system for the formation of fire retardants [39, 40], which indicates its predicted effectiveness as a component of a flame retardant composition [41].

In earlier studies [42], it was established that buffer systems ensure the formation of silicic acid sols with high fluidity. In particular, the buffer pair $\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$ can be formed by acetic acid, which is used during the production of silicic acid sol from liquid glass [42]. Orthophosphate acid is able to dissociate in an aqueous environment, forming a pair of $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$ and providing an additional weak buffering effect. This aspect provides an additional rationale for studying the properties of orthophosphate acid as part of a silica-containing composition.

Taking into account the above, the aim of the work was to investigate the effect of orthophosphate acid on the rheological properties of silicic acid sols, as well as the type of polycondensation in SiO_2 hybrid gels, which are the basis of fire-retardant coatings for wood.

3 Main Part

Silicic acid sols were prepared by mixing aqueous solutions of liquid glass and acetic acid, adding orthophosphate acid solutions (1, 2, 4, and 8 wt. %).

Study of the influence of phosphate-containing additives on the rheological properties of silicic acid sols. The optical density of the experimental sols was measured using a photocolormeter KFK-2 at a wavelength of 490 nm. The curves of changes in optical density depending on the composition of the SiO_2 sol are presented in Fig.1.

The small content of orthophosphate acid practically did not affect the optical density in the first 20 minutes of sol maturation. Increasing the content of orthophosphate to 4–8% led to a sharp increase in optical density values.

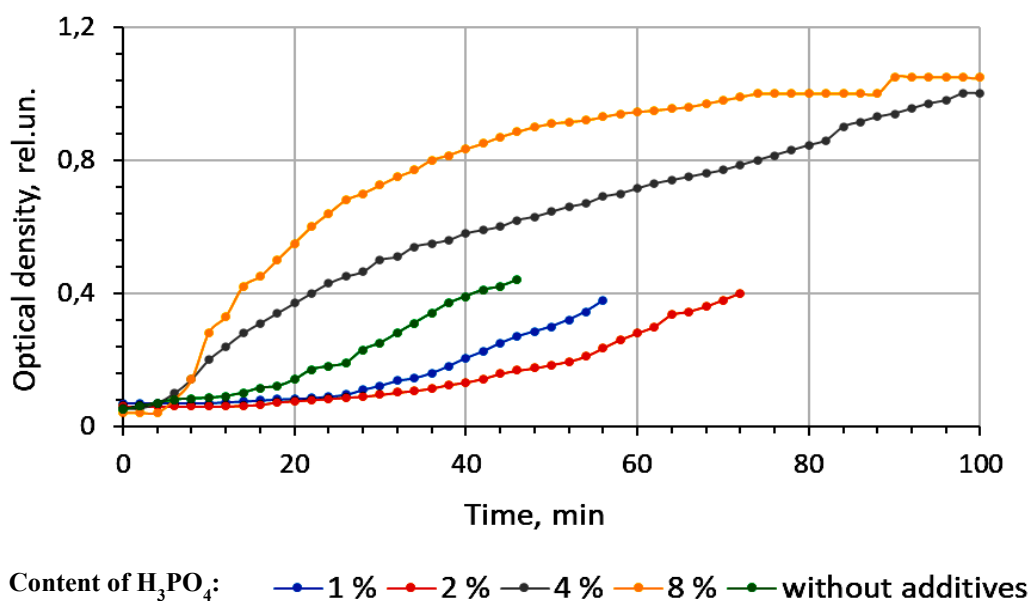


Fig. 1. Dependence of the change in optical density of experimental silicic acid sols on time

The addition of small amounts of orthophosphate acid (1–2%) did not exceed the buffer capacity of the acetate buffer solution formed during the preparation of the SiO_2 sol, so the pH of the mixture remained at 6, corresponding to the pH of the sol without the addition. Such sols lost their fluidity in the interval of 45–70 minutes. Increasing the content of orthophosphoric acid reduced the pH to 3 and extended the survival interval to 24 hours.

Study of the effect of a phosphate-containing additive on gelation processes in SiO_2 sols.

Gelation processes were studied using IR spectroscopy. For raw and heat-treated samples of gels (800 °C, holding at the maximum temperature for 2 hours, temperature rise rate 4–5 °C/min), IR absorption spectra were recorded on an infrared spectrophotometer FTIR-8400S (Shimadzu) equipped with a QATR 10 attachment (Shimadzu) in the range of 400–4000 cm^{-1} . IRsolution and ACD/Labs software were used to analyze the spectra.

Fig. 2 presents the IR absorption spectra of raw SiO_2 gels. The IR spectrum of the gel without additives (Fig. 2, a) is characterized by a wide absorption band located in the range of 2800–3600 cm^{-1} and associated with valence vibrations of O–H bonds. O–H deformation oscillations can also be observed in the interval 1300–1700 cm^{-1} ; the most intense are the absorption bands at 1410, 1540, and 1635 cm^{-1} . Clearly resolved absorption bands at 790, 1050 cm^{-1} correspond to Si–O valence vibrations. The absorption band at 970 cm^{-1} characterizes deformation vibrations of $\equiv\text{Si}-\text{OH}$ bonds. In the range of 400–460 cm^{-1} , deformational rotational vibrations of Si–O bonds are recorded [43, 44]. A set of vibration absorption bands of Si–O, $\equiv\text{Si}-\text{OH}$, O–H bonds indicates the presence of polysilicic acid in the gel.

The addition of orthophosphate acid to the SiO_2 sol is manifested in the IR spectra by an increase in the intensity of the specified bands and is due to the fact that the characteristic absorption bands of polysilicic acid and orthophosphate acid practically coincide (Fig. 2, b–e). The fluctuation of P–O bonds is recorded in the range 650–800 cm^{-1} .

In the range 500–530 cm^{-1} , bond fluctuations in the PO_4^{3-} groups are evident. Asymmetric vibration of the P=O bond on the IR spectrum was registered in the range 1115–1300 cm^{-1} [45, 46].

According to [47], the band at 1540 cm^{-1} may be characteristic of acetate, namely, it corresponds to fluctuations of the C=O bond. Moreover, the peak at 1129 cm^{-1} corresponds to the vibrations of

the Si–O–P bonds. Considering this, it can be assumed that Si–O–P bonds are present in the experimental samples.

The intensity of the characteristic absorption bands varied depending on the content of orthophosphate acid (Fig. 2). The intensity of the band at 1047–1054 cm^{-1} increased with increasing content of orthophosphate acid. At the same time, the relative intensities of the bands at 1410, 1540, 1635 cm^{-1} decreased when orthophosphate acid was introduced.

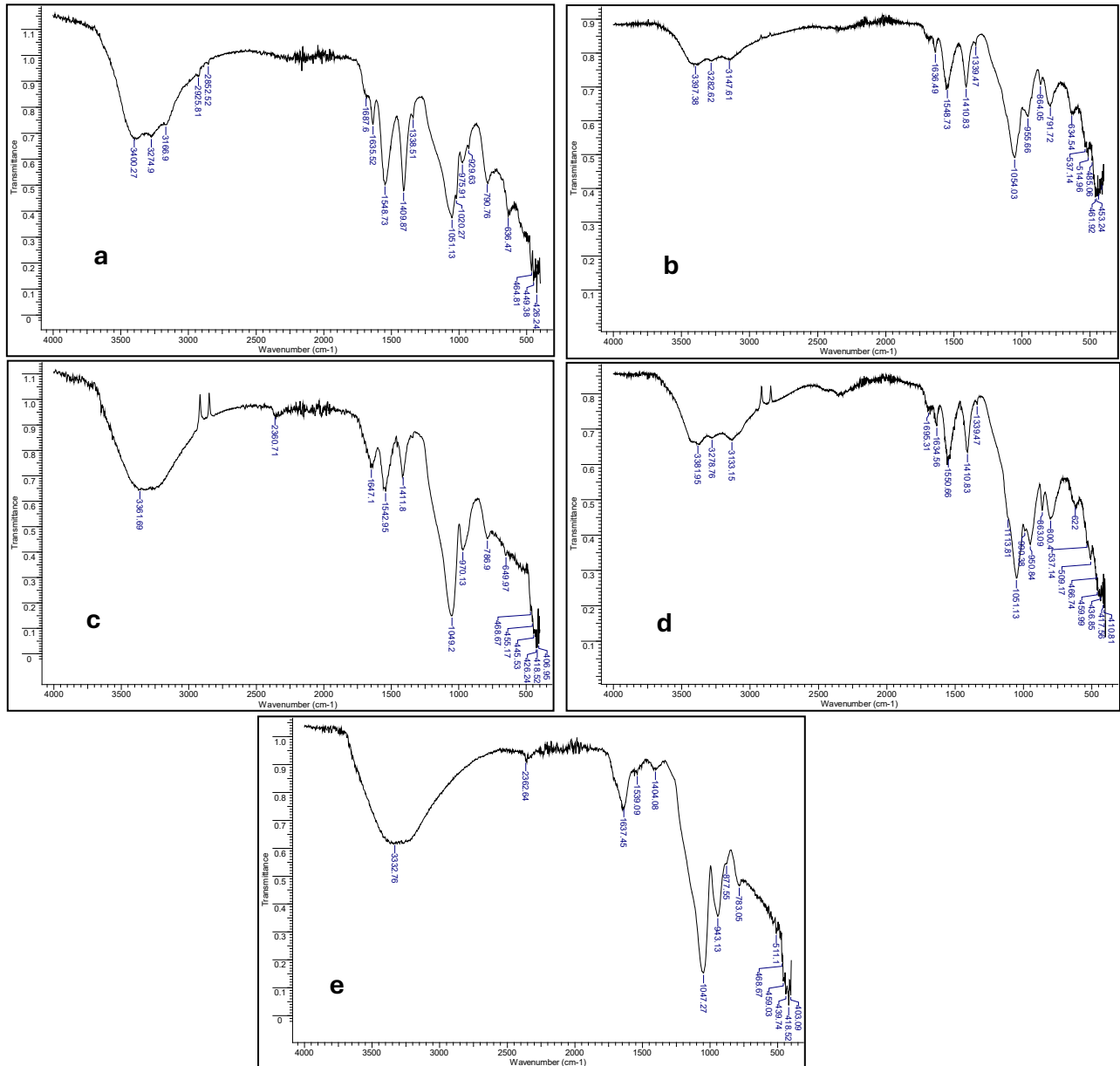


Fig. 2. IR spectra of raw SiO₂ gels: unmodified (a) and with H₃PO₄ content: 1% (b), 2% (c), 4% (d), 8% (e)

It is known that the higher the degree of polycondensation, the higher the intensity of the band corresponding to the vibrations of Si–O–Si bonds (1050 cm^{-1}) formed because of this process. It is also known that the durability of SiO₂ sol increases under acidic conditions, but polycondensation under such conditions takes place with the participation of hydroxonium ion with the formation of mesh siloxanes. Diluted orthophosphate acid affects not only the rate of polycondensation, but also its mechanism [48]. Adding small amounts of it to a sol leads to the initiation of linear polycondensation. In the spectra, this will be manifested in the form of a decrease in the intensity of the 1050 cm^{-1} (I) band and an increase in its width. Therefore, the ratio of the intensity of this band

to its half-width (d), i.e., the width of the band in the middle of its intensity, gives information about the mechanism of polycondensation. If this ratio decreases, we can conclude about a predominantly linear polycondensation. If this ratio increases, then mainly net polycondensation occurs. Fig. 3 shows the influence of the orthophosphate acid content on the value of the I/d indicator.

A branched mesh structure is formed in the event of an increase in the content of orthophosphate acid. With the use of such compositions, the resulting coating will be more "hard" and less elastic.

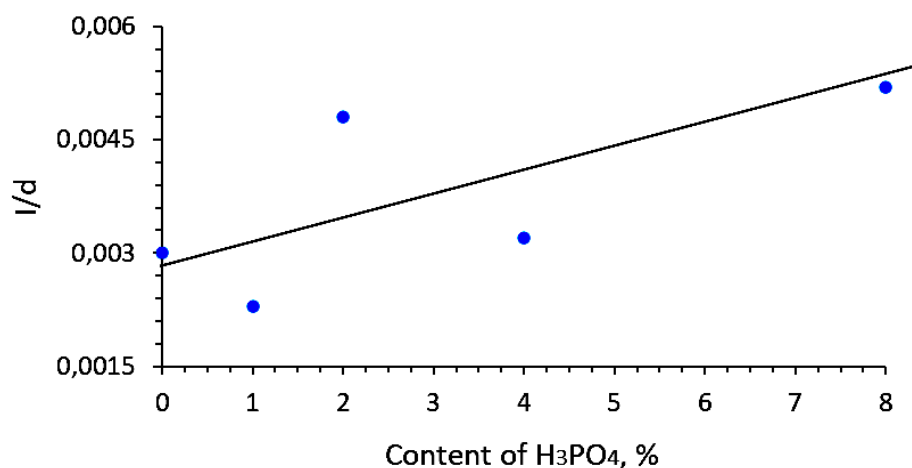


Fig. 3. Influence of the additive content on the nature of polycondensation in SiO₂ gels

Addition of a small amount of orthophosphate acid (1%) leads to the initiation of linear polycondensation and, as a result, an elastic coating is formed. This fact was experimentally confirmed in [42]. The coating was applied to the textile cellulose-containing material by the bath method. After removing the remains of the sol and heat treatment, water-resistant, transparent, very thin coatings were obtained, which had a fire-retardant effect.

The polycondensation mechanism also affects the degree of homogeneity of the resulting gel. Mesh polycondensation leads to the formation of an extremely heterogeneous gel, which in the process of heat treatment transforms into an opal-like glass phase [48]. The greater the degree of homogeneity of the gel, the more likely and easier the crystallization of SiO₂ during heat treatment.

Fig. 4 presents the results of infrared spectroscopy of heat-treated samples of the investigated SiO₂ gels. Silica gels were subjected to high-temperature treatment at a temperature of 800 °C with a temperature rise rate of 4–5 °C/min in an oxidizing medium (air), with exposure at the maximum temperature of 2 h.

After high-temperature treatment of the SiO₂ gel without additives (Fig. 4, a), the absorption band in the range of 2800–3600 cm⁻¹ disappeared completely, and the bands corresponding to deformation oscillations of H–O–H, which may be the result of water removal, also practically disappeared. It should also be noted the appearance of a broad absorption band in the range 850–1100 cm⁻¹ as a result of overlapping peaks that were clearly expressed in the IR spectrum of the crude gel. This form of the combined band is characteristic of synthetic cristobalite, which contains nuclei of the quartz phase (as a result of the heterogeneous structure of the initial gel), which are fixed in the form of a doublet in the region of 780–790 cm⁻¹. Probably, the combined absorption band in the region of 900–1050 cm⁻¹ indicates the formation of intraskeletal silanol groups during the restructuring of the gel structure under the influence of high temperatures.

The addition of orthophosphate acid (Fig. 4, b) led to the separation of the general absorption band in the region of 1050 cm⁻¹ and a decrease in its intensity. This indicates the predominant linear polycondensation of the gel with the addition of 2% H₃PO₄.

In the IR spectrum of the heat-treated gel with the addition of 8% H₃PO₄, an increase in the intensity of the absorption band at 1046 cm⁻¹ is observed, while the characteristic quartz doublet is absent. According to [49, 50], the bands of asymmetric oscillations of Si–O–Si bonds in this region can also overlap with the peaks of valence oscillations of PO₄³⁻ in the temperature range 550–950 °C.

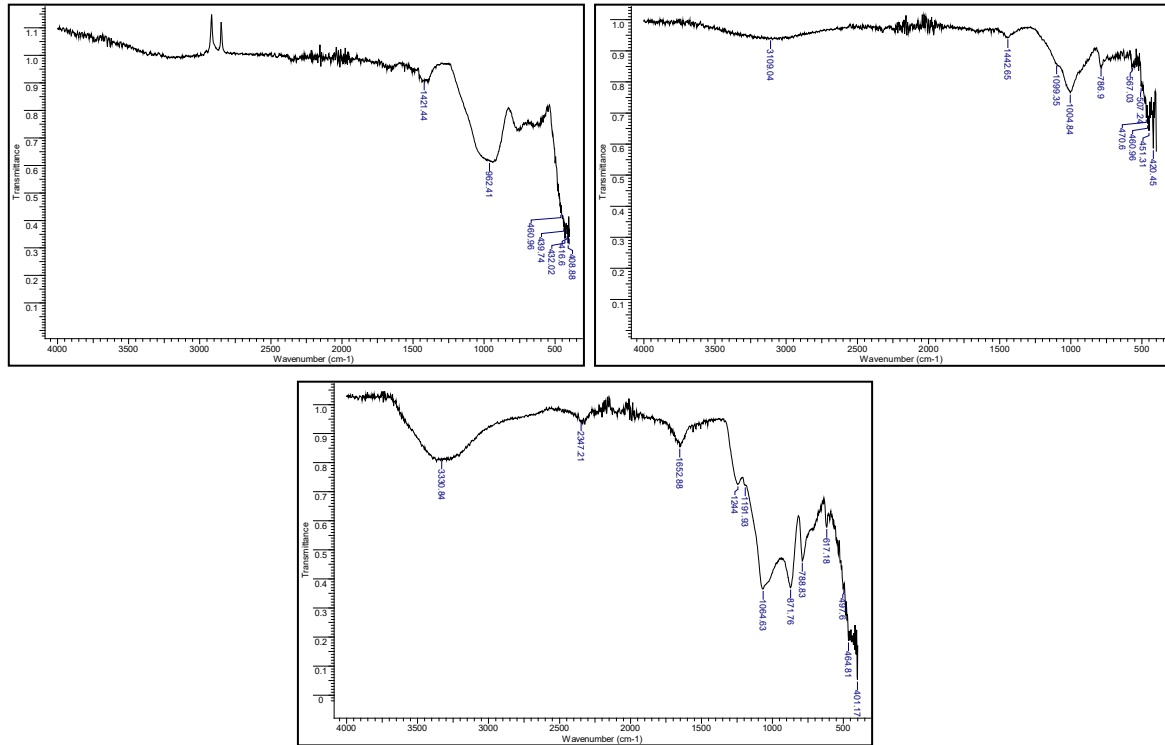


Fig. 4. IR spectra of heat-treated SiO₂ gels: unmodified (a) and with H₃PO₄ content: 2% (b), 8% (c)

An increase in the intensity of deformational rotational vibrations of Si–O–Si bonds in the range 400–460 cm⁻¹ is observed. In the region of 3200–3400 cm⁻¹, a sufficiently large absorption band of vibration of O–H bonds appeared, which indicates the presence of water clathrates in the network structure of the SiO₂ gel

Study of the effect of orthophosphate acid concentration on coating properties.

Experimental two-layer coatings were applied to wood surface by the bath method. After applying each layer of the composition, the test samples were dried by heating in a drying chamber at a temperature of 80 °C. The structure of the obtained flame retardant coatings was evaluated using an optical microscope. The structure of coatings obtained on the surface of wood, based on compositions with different content of orthophosphate acid, is presented in Fig. 5

It can be observed that the most continuous and homogeneous is the coating obtained on the basis of the composition with H₃PO₄ content of 1%. The absence of cracks and cavities on the surface of the coating protects the wood surface from the action of oxygen during a fire. Thus, it can be concluded that linear polycondensation in SiO₂ sols contributes in obtaining the most uniform coating without cracks, which is important for its fire-retardant efficiency.

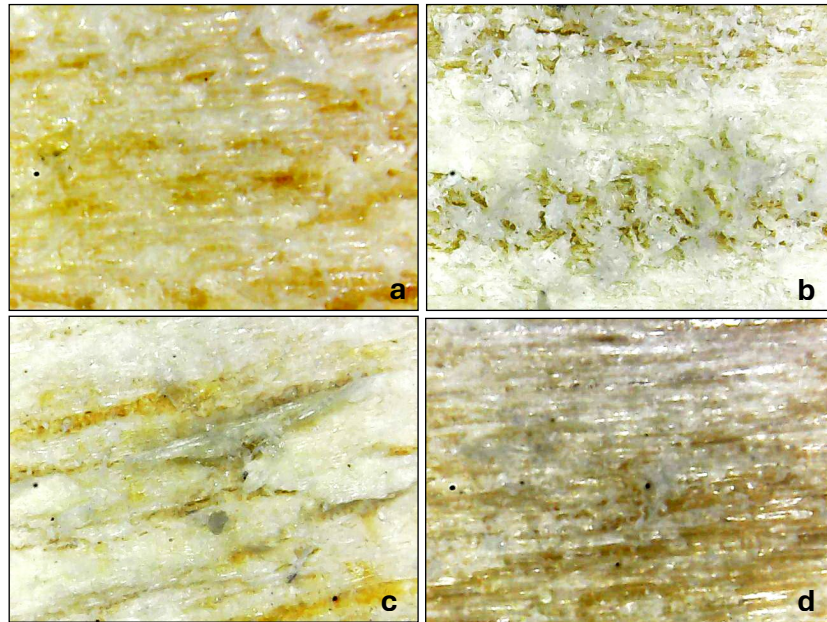


Fig. 5. The structure of coatings on the surface of wood obtained on the basis of compositions containing orthophosphate acid (wt.%): a – 1, b – 2, c – 4, d – 8.

4 Conclusion

The influence of orthophosphate acid on the rheological properties of silicic acid sols, as well as the type of polycondensation in combined SiO_2 gels, which is the basis of fire-resistant coatings for wood, was determined. The processes of gel formation in experimental compositions were studied and it was shown that small additions of H_3PO_4 contribute to the initiation of linear polycondensation, which leads to obtaining a homogeneous gel and a coating based on it. The influence of the degree of homogeneity of the gel on the phase composition of heat-treated compositions was studied, which provides additional information about how fire-resistant coatings will behave in fire conditions. It was established that linear polycondensation in the composition provides a uniform coating without cracks and surface defects, which is the key to fire protection of wood.

References

- [1] Chernukha, A., Teslenko, A., Kovaliov, P., Bezuglov, O. (2020). Mathematical modeling of fire-proof efficiency of coatings based on silicate composition (2020) Materials Science Forum, 1006 MSF, 70-75.
- [2] Pospelov, B., Rybka, E., Meleshchenko, R., Gornostal, S., Shcherbak, S. (2017). Results of experimental research into correlations between hazardous factors of ignition of materials in premises. Eastern-European Journal of Enterprise Technologies, 6/10 (90), 50–56.
- [3] S. Park, Y. Han, D.W. Son, (2020). Flame retardancy of wood products by spreading concentration and impregnation time of flame retardant, Journal of the Korean Wood Science and Technology, 48(4), 417–430.
- [4] P. Mali, N. Sonawane, V. Patil, G.P. Lokhande, R. Mawale, N.S. Pawar, (2021). Morphology of wood degradation and flame retardants wood coating technology: an overview, International Wood Products Journal, 13(1), 21–40.
- [5] Chernukha, A., Chernukha, A., Kovalov, P., Savchenko, A. (2021). Thermodynamic study of fire-protective material Materials Science Forum, 1038 MSF, 486–491.

-
- [6] Zmaha, M., Pozdieiev, S., Zmaha, Y., Nekora, O., Sidnei, S. (2021). Research of the behavioral of the wooden beams with fire protection lining under fire loading IOP Conference Series: Materials Science and Engineering, 1021/1, 012031.
- [7] Dubinin D., Korytchenko K., Lisnyak A., Hrytsyna I., Trigub V. (2018). Improving the installation for fire extinguishing with finelydispersed water. Eastern-European Journal of Enterprise Technologies, 2/10 (92), 38–43.
- [8] Medved, I., Otrosh, Y., Kovalov, A., Mykhailovska, Y. (2023). Search for solutions in the problems of calculation of building structures. AIP Conference Proceedings, 2840(1), 040003.
- [9] Pospelov, B., Rybka, E., Meleshchenko, R., Gornostal, S., Shcherbak, S. (2017). Results of experimental research into correlations between hazardous factors of ignition of materials in premises. Eastern-European Journal of Enterprise Technologies, 6/10 (90), 50–56.
- [10] Pospelov, B., Andronov, V., Rybka, E., Krainiukov, O., Karpets, K., Pirohov, O., Semenyshyna, I., Kapitan, R., Promska, A., Horbov, O. (2019). Development of the correlation method for operative detection of recurrent states Eastern-European Journal of Enterprise Technologies, 6/4 (102), 39–46.
- [11] Pospelov, B., Andronov, V., Rybka, E., Popov, V., Romin, A. (2018). Experimental study of the fluctuations of gas medium parameters as early signs of fire. Eastern-European Journal of Enterprise Technologies, 1/10 (91), 50–55.
- [12] Sadkovyi, V., Andronov, V., Semkiv, O., Kovalov, A., Rybka, E., Otrosh, Y., Udianskyi, M., Koloskov, V., Danilin, A., Kovalov, P. (2021). Fire resistance of reinforced concrete and steel structures. Fire resistance of reinforced concrete and steel structures, 1-166.
- [13] Myrgorod, O., Shabanova, G., Ruban, A., & Shvedun, V. (2021). Experiment Planning for Prospective Use of Barium-Containing Alumina Cement for Refractory Concrete Making. In Materials Science Forum, 1038, pp. 330–335.
- [14] Kovalov, A., Otrosh, Yu., Surianinov, M., Kovalevska, T. (2019). Experimental and computer researches of ferroconcrete floor slabs at high-temperature influences. Materials Science Forum, 968 MSF, 361–367.
- [15] Vasilchenko, A., Danilin, O., Lutsenko, T., & Ruban, A. (2021). Features of Evaluation of Fire Resistance of Reinforced Concrete Ribbed Slab under Combined Effect “Explosion-Fire.” In Materials Science Forum, 1038, pp. 492–499.
- [16] Kovalov, A., Otrosh, Y., Ostroverkh, O., Hrushovinchuk, O., Savchenko, O. (2018). Fire resistance evaluation of reinforced concrete floors with fire-retardant coating by calculation and experimental method. E3S Web of Conferences, 60, № 00003.
- [17] Vasilchenko, A., Danilin, O., Lutsenko, T., Ruban, A., & Nestorenko, D. (2020). Features of some Polymer Building Materials Behavior at Heating. Materials Science Forum, 1006, 47-54.
- [18] D. Tregubov, O. Tarakhno, V. Deineka, F. Trehubova. (2022). Oscillation and Stepwise of Hydrocarbon Melting Temperatures as a Marker of their Cluster Structure Solid State Phenomena, 334, p. 124–130.
- [19] Y. Hapon, D. Tregubov, O. Tarakhno, V. Deineka. (2020). Technology of safe galvanochemical process of strong platings forming using ternary alloy Materials Science Forum, 1006 MSF, p. 233–238.
- [20] A. Chernukha, A. Chernukha, K. Ostapov, T. Kurska, (2021). Investigation of the processes of formation of a fire retardant coating, Materials Science Forum, 1038, 480–485.
- [21] B. Pospelov, V. Andronov, E. Rybka, K. Karpets, E. Kochanov, (2021). Development of the Method of Operational Forecasting of Fire in the Premises of Objects Under Real Conditions Eastern-European Journal of Enterprise Technologies. 2/10, (110), 43–50.

-
- [22] Blyznyuk, O., Vasilchenko, A., Ruban, A., & Bezuhla, Y. (2020). Improvement of Fire Resistance of Polymeric Materials at their Filling with Aluminosilicates. In *Materials Science Forum*, 1006, pp. 55–61.
- [23] I. Van Der Veen, J. De Boer, (2012). Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis, *Chemosphere*. 88(10), 1119–1153.
- [24] S.K. Witchey, V. Sutherland, B. Collins, G. Roberts, K.R. Shockley, M. Vallant, J. Krause, H. Cunny, S. Waidyanatha, E. Mylchreest, B. Sparrow, R.A. Moyer, M. Behl, (2023). Reproductive and developmental toxicity following exposure to organophosphate ester flame retardants and plasticizers, triphenyl phosphate and isopropylated phenyl phosphate, in Sprague Dawley rats, *Toxicological Sciences*. 191(2), 374–386.
- [25] K. Kademoglou, F. Xu, J. A. Sánchez, L. S. Haug, A. Covaci, C. Collins, (2017). Legacy and alternative flame retardants in Norwegian and UK indoor environment: Implications of human exposure via dust ingestion, *Environment International*. 102, 48–56.
- [26] N. R. Maddela, K. Venkateswarlu, M. Megharaj, (2020). Tris(2-chloroethyl) phosphate, a pervasive flame retardant: critical perspective on its emissions into the environment and human toxicity, *Environmental Science: Processes & Impacts*. 22(9), 1809–1827.
- [27] C. He, C. Lin, J.F. Mueller, (2020). Organophosphate flame retardants in the environment: Source, occurrence, and human exposure, In *Comprehensive Analytical Chemistry*. 88, 341–365.
- [28] C. Yao, H. Yang, Y. Li, (2021). A review on organophosphate flame retardants in the environment: Occurrence, accumulation, metabolism and toxicity, *Science of the Total Environment*. 795, 148837.
- [29] A. Blum, M. Behl, L.S. Birnbaum, M.L. Diamond, A.L. Phillips, V. Singla, N.S. Sipes, H.M. Stapleton, M. Venier, (2019). Organophosphate ester flame retardants: Are they a regrettable substitution for polybrominated diphenyl ethers, *Environmental Science and Technology Letters*. 6(11), 638–649.
- [30] A.K. Rosenmai, S.B. Winge, M. Möller, J. Lundqvist, E.B. Wedebye, N.G. Nikolov, H.K.L. Johansson, A.M. Vinggaard, (2021). Organophosphate ester flame retardants have antiandrogenic potential and affect other endocrine related endpoints in vitro and in silico, *Chemosphere*, 263, 127703.
- [31] B. Pospelov, E. Rybka, R. Meleshchenko, O. Krainiukov, S. Harbuz, Yu. Bezuhla, I. Morozov, A. Kuruch, O. Saliyenko, R. Vasylchenko, (2020). Use of uncertainty function for identification of hazardous states of atmospheric pollution vector, *Eastern-European Journal of Enterprise*. 2/10, (104), 6–12.
- [32] V. Sadkovyi, B. Pospelov, V. Andronov, E. Rybka, O. Krainiukov, A. Rud, K. Karpets, Yu. Bezuhla, (2020). Construction of a method for detecting arbitrary hazard pollutants in the atmospheric air based on the structural function of the current pollutant concentrations, *Eastern-European Journal of Enterprise*. 6/10, (108), 14–22.
- [33] Pasternak, V., Ruban, A., Surianinov, M., Otrosh, Y., & Romin, A. (2022). Software Modeling Environment for Solving Problems of Structurally Inhomogeneous Materials. In *Materials Science Forum*, 1068, pp. 215–222.
- [34] O. Skorodumova, O. Tarakhno, O. Chebotaryova, O. Bezuglov, F.M. Emen, (2021). The use of sol-gel method for obtaining fire-resistant elastic coatings on cotton fabrics, *Materials Science Forum*, 1038, 468–479.
- [35] O. Skorodumova, O. Tarakhno, O. Chebotaryova, (2022). Improving the Fire-Retardant Properties of Cotton-Containing Textile Materials through the Use of Organo-Inorganic SiO₂ Sols, *Key Engineering Materials*, 927, 63–68.

-
- [36] O. Zybina, M. Gravit, *Intumescent coatings for fire protection of building structures and materials*, Springer series on polymer and composite materials (2020).
- [37] Z. Jiang, H. Li, Y. He, Y. Liu, C. Dong, Flame retardancy and thermal behavior of cotton fabrics based on a novel phosphorus-containing siloxane, *Applied Surface Science*. 479 (2019) 765–775.
- [38] X. Cheng, C. Liang, J. Guan, X. Yang, R. Tang, Flame retardant and hydrophobic properties of novel sol-gel derived phytic acid/silica hybrid organic-inorganic coatings for silk fabric, *Applied Surface Science*. 427 (2018) 69–80.
- [39] T. Leber, D. Kenn, F. Matt, M. Scheller, T. Tonnesen, J. González, Julián, Phosphate-bonded refractories in hydrogen containing atmosphere, *Open Ceramics*. 17 (2024) 100511.
- [40] Pasternak, V., Samchuk, L., Huliieva, N., Andrushchak, I., & Ruban, A. (2021). Investigation of the Properties of Powder Materials Using Computer Modeling. *Materials Science Forum*, 1038, 33–39.
- [41] Ruban, A., Pasternak, V., & Huliieva, N. (2022). Prediction of the Structural Properties of Powder Materials by 3D Modeling Methods. In *Materials Science Forum*, 1068, pp. 231–238.
- [42] O. Skorodumova, O. Tarakhno, A.M. Babayev, A. Chernukha, S. Shvydka, Study of Phosphorus-Containing silica coatings based on liquid glass for fire protection of textile materials, *Key Engineering Materials*. 954 (2023) 167–175.
- [43] M. Zhao, X. Zou, Q. Wei, S. Meng, H. B. Zhang, C. Su, Preparation and Characterization of Na₂O-Y₂O₃-P₂O₅-SiO₂ Transparent Glass Ceramics, *Solid State Phenomena*. 281 (2018) 692–698.
- [44] M. Zribi, S. Baklouti, Investigation of Phosphate based geopolymers formation mechanism. *Journal of Non-Crystalline Solids*. 562 (2021) 120777.
- [45] S. Bellayer, M. Jimenez, B. Prieur, B. Dewayilly, A. Ramgobin, J. Sarazin, B. Revel, G. Tricot, S. Bourbigot, Fire retardant sol-gel coated polyurethane foam: Mechanism of action, *Polymer Degradation and Stability*. 147 (2018) 159–167.
- [46] R. Karan, P. Pal, P. Maiti, K. Das, Structure, properties and in-vitro response of SiO₂-Na₂O-CaO-P₂O₅ system, based glass-ceramics after partial replacement of Na₂O by Li₂O, *Journal of Non-Crystalline Solids*. 556 (2021) 120554.
- [47] A. Stýskalík, D. Škoda, Z. Moravec, M. Babiak, C. E. Barnes, J. Pinkas, Control of micro/mesoporosity in non-hydrolytic hybrid silicophosphate xerogels. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*. 3(14) (2015) 7477–7487.
- [48] O.B. Skorodumova, G.D. Semchenko, Y.N. Goncharenko, V.S. Tolstoi, Crystallization of SiO₂ from ethylsilicate-based gels, *Glass and Ceramics*. 58(1–2) (2001) 31–33.
- [49] M. Abbasi, B. Hashemi, Fabrication and characterization of bioactive glass-ceramic using soda–lime–silica waste glass. *Materials Science and Engineering*: 37 (2014) 399–404.
- [50] N.F.B. Pallan, X.A. Matori, M. Hashim, R.S. Azis, N. Zainuddin, F.M. Idris, I.R. Ibrahim, L.C. Wah, S.N.A. Rusly, N. Adnin, M.Z.A. Khiri, Z.N. Alassan, N. Mohamed, Effects of different sintering temperatures on thermal, physical, and morphological of SiO₂-Na₂O-CaO-P₂O₅ based glass-ceramic system from vitreous and ceramic wastes, *Science of Sintering*. 51(4) (2019) 377–387.