

Effect of H₃PO₄ and Phenol Additives on Gel Formation in Silica Fire Retardant Coatings for Building Materials

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Abstract. Increasing the fire resistance of wooden building structures is quite effectively ensured thanks to the development of fire-fighting compositions with aromatic components that contribute to the formation of a carbonized layer on the surface of the material during combustion. It is also known about the mutual positive influence of benzene fragments and phosphate-containing compounds on the fire-resistant characteristics of wood. The paper considers the possibility of complex use of phenol and orthophosphate acid to improve the flame retardant properties of SiO₂-based coatings. The effect of modifying additives on the rheological properties of silicic acid sols was determined.

Based on the results of IR spectroscopy, the influence of components on the nature of polycondensation in experimental SiO₂ sols was evaluated. It is shown that the use of orthophosphate acid as a modifier leads to the initiation of predominantly linear polycondensation in experimental sols. It was established that small additions of phenol practically do not affect the course of polycondensation in experimental sols. Increasing the phenol content to 0.5% showed an effect on gel formation due to the possible addition of phenol to the skeletal silanol groups by the donor-acceptor mechanism, which makes it possible to have a synergistic effect of the complex additive of orthophosphate acid and phenol on the properties of the silica-containing flame retardant composition.

1 Introduction

Wood is a material widely used in construction. Building structures are very diverse in their purpose and application [1, 2]. The reliability and safety of their work depends on many factors: geometric dimensions, materials used, external loads and their combinations, etc. [3, 4]. Among the advantages of wooden structural elements, we can highlight cost and availability - wood is a relatively cheap building material, especially in regions with rich forests. Also, this material is easy to process, has natural thermal insulation properties, is characterized by high strength and durability. In addition, wood is an ecological building material and a relatively renewable resource [5]. Despite the small number of positive aspects of the use of this material, it has a significant drawback – flammability [6], which significantly limits its use [7, 8]. Therefore, the use of building structures made of wood is possible only under the conditions of ensuring fire safety [9, 10].

Among the substances that can be used in the context of fire protection of wood, it is possible to single out halogenated hydrocarbons [11, 12], such compounds are highly effective flame retardants, but their use is limited due to the toxic effect on the environment [13, 14] and the human body [15, 16]. Carbon monoxide, which is formed in a fire, is fatal for human life and health [17, 18]. There are many fire retardant compositions based on inorganic substances: aluminum [19, 20]

and magnesium [21] hydroxides, carbonates [22], Boron [23] and Phosphorus [24] compounds, which are environmentally safe, but unstable to the effects of negative climatic factors [25,26].

A common variant of fire protection of wood is its treatment with compositions based on phenol-formaldehyde resins [27]. Resistance to high temperatures is ensured mainly by the presence of aromatic rings, which have a stable chemical structure and are not prone to oxidation reactions. A rigid three-dimensional structure formed by cyclic benzene fragments also plays a role, which resists thermal loads. The carbon content in aromatic hydrocarbons is quite high, which contributes to the formation during combustion of an effective volumetric carbonized layer, which is quite important for fire protection [28, 29].

2 Unresolved Issues

When exposed to high temperatures, phenol-formaldehyde resins often release residual free methanal, which can be part of their composition. It can cause irritation of the upper respiratory tract, eyes, and skin, and when inhaled in significant quantities, cause a carcinogenic effect [30, 31]. In 2023, the EU Regulation on Chemical Substances and Their Safe Use (European REACH regulation) introduced restrictions on formaldehyde and its emitting compounds. Accordingly, the number of works [32, 3] dedicated to reducing the content of free formaldehyde in such flame retardants increased, mainly due to the improvement of the mechanical properties of the resin. On the other hand, there is also the problem of disposal of formaldehyde resins [33].

As the main flame retardant properties are provided by aromatic fragments, it would be logical to use phenol as a separate component in the flame retardant composition, however, its individual effect on the flame retardant properties of wood is insufficiently studied.

It is known that the fire resistance of phenolic resins can be increased due to the introduction of phosphorus- and nitrogen-containing flame retardants [34].

Research on improving the fire-retardant properties of phenolic resins due to colloidal silica particles obtained on the basis of the sol-gel process is also worthy of attention. It has been established that such modifications make it possible to obtain much higher temperatures of thermal decomposition of composites [35, 36], as well as to improve the mechanical properties of the fire-resistant coating [37, 38].

Considering the above, it is possible to predict a positive synergistic effect of the composition based on silica, phenol and phosphorus-containing flame retardant in the field of fire protection of wooden building structures.

The selection of the phosphorus-containing component of the fire-retardant composition was based on previously conducted studies [39], which were devoted to the study of fire-retardant properties of silica-based coatings with the addition of orthophosphate acid for cellulosic materials. A positive effect from the introduction of the additive was noted - the fire resistance of the experimental samples increased significantly.

Therefore, the aim of the work was to study the combined effect of orthophosphate acid and phenol on the rheological properties of silicic acid sols, as well as the type of polycondensation in SiO₂ hybrid gels, which is the basis of fire-resistant coatings for wood.

3 Main Part

Silicic acid sol was obtained by mixing solutions of liquid glass and acetic acid, adding orthophosphate acid and phenol as modifying additives. The phase composition, optical properties, and durability of experimental sols with orthophosphate acid (2 wt. %) and different phenol contents (0.1, 0.3, and 0.5 wt. %) were studied.

Study of the effect of phenol content on the rheological properties of silicic acid sols. Changes in the optical density of sols over time were determined using a KFC-2 photocolormeter at a wavelength of 490 nm. Distilled water was used as a comparison solution. Dependences of changes in optical density over time for pure sol and sols with the addition of orthophosphate acid and different phenol content are presented in Fig. 1.

The curves of changes in the optical density of silicic acid sols containing phenol practically overlap each other. The survivability of the sols with an increase in the content of the organic additive practically did not change: for the composition with 0.1% phenol it was 40 minutes, 0.3% - 38 minutes, 0.5% - 36 minutes. The increase in the angle of inclination of the tangents to the curves shows that the process of growth of colloidal particles and their union into associates begins approximately 20 minutes after the preparation of the composition.

The curve of change in optical density of sol with H_3PO_4 is located much lower, compared to the curve for pure sol. Since orthophosphate acid is quite strong in the first degree of dissociation, it can form dihydrophosphates $H_2PO_4^-$. These ions are bulky and can create spatial complications in the polycondensation pathway by joining silanol groups.

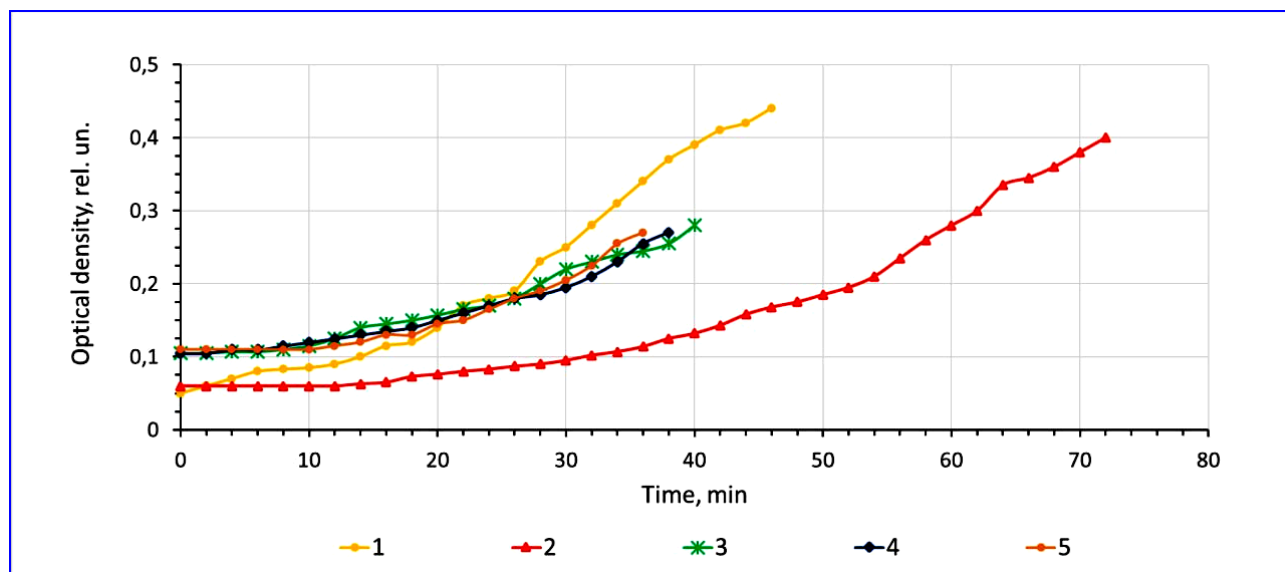


Fig. 1. Dependence of change in optical density of experimental silicic acid sols over time: 1 – without additives, 2 – with orthophosphoric acid (2 mas.%), 3–5 – with orthophosphoric acid (2 mas.%) and phenol: 3 – 0.1 %; 4 – 0.3 %, 5 – 0.5 %

Study of the effect of phosphorus-containing flame retardants on the nature of polycondensation in SiO_2 hybrid gels. The obtained silica gels were subjected to high-temperature processing in a muffle furnace at 800 °C with exposure at the maximum temperature for 2 hours in the temperature regime of temperature rise of 4–5 °C/min in an air environment. For raw and heat-treated gel samples, 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} . IR solution and ACD/Labs software were used to analyze the spectra.

Fig. 2 and 3 present the IR absorption spectra of raw SiO_2 gels without additives and with the addition of orthophosphate acid.

A wide absorption band located in the range of 2800–3600 cm^{-1} , characterizes the IR spectra of all presented samples. As a rule, in this interval there are vibration bands corresponding to valence vibrations of O–H bonds, which may correspond to silanol and phenolic hydroxyls.

In the range of 3700–4000 cm^{-1} for the spectra of samples with phenol (Fig. 3, a–c), a large number of small peaks can be noted, which characterize the vibrations of vicinal silanol groups connected to each other by a hydrogen bond through an oxygen atom. Bands at 2330 cm^{-1} and 2360 cm^{-1} also appear on the spectra, which can characterize the oscillations of P–H bonds. In the case of adding orthophosphoric acid as a separate additive, these bands are weaker.

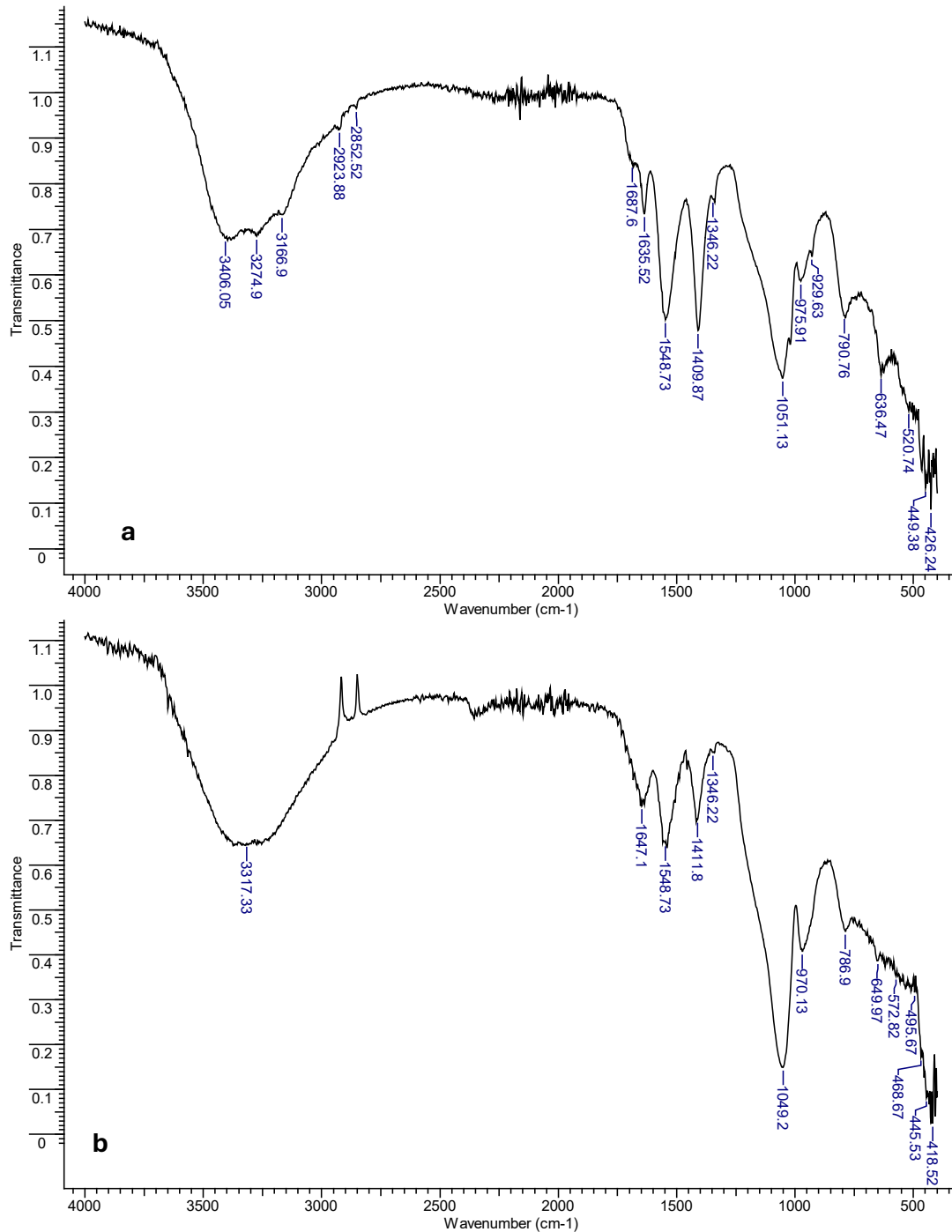


Fig. 2. IR spectra of raw SiO₂ gels: unmodified (a) and with the addition of 2% H₃PO₄ (b)

The spectrum of pure gel and modified H₃PO₄ is characterized by the presence of three clear bands in the range of 1400–1600 cm⁻¹ (Fig. 2). When modified with phenol, many small peaks appear on these bands (Fig. 3). As is known, bands at 1450, 1500, 1580, and 1600 cm⁻¹ are most characteristic for vibrations of the C–C bonds of the aromatic ring. The intensity of the band at 1540 cm⁻¹, which corresponds to the vibrations of the C=O bond, decreases when the sol is modified with orthophosphate acid, and it becomes even lower when phenol is added [40].

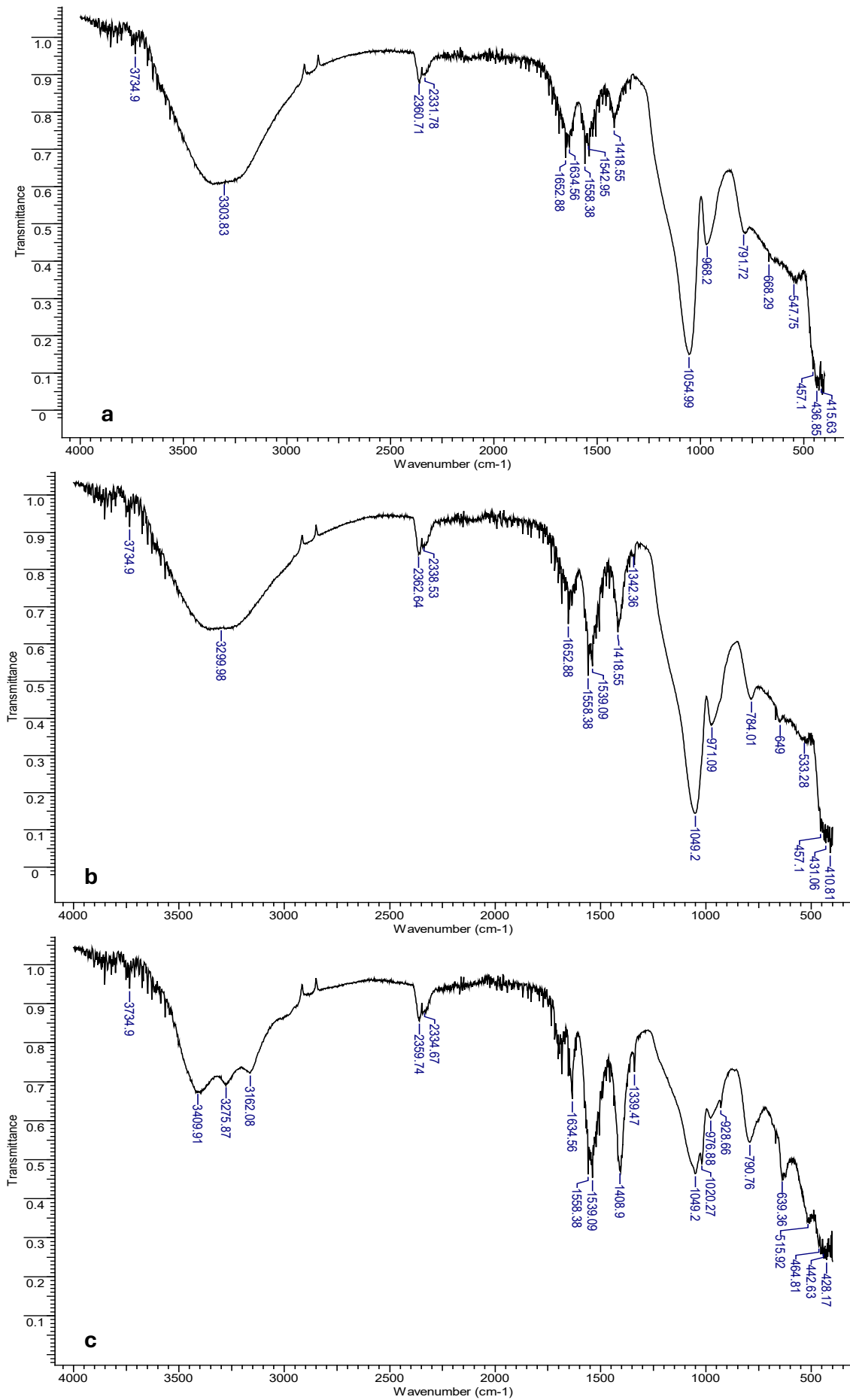


Fig. 3. IR spectra of raw SiO₂ gels with the addition of 2% H₃PO₄ and phenol: 0.1% (a), 0.3% (b), 0.5% (c)

Clearly expressed absorption bands at 790 cm^{-1} correspond to valence vibrations of $\equiv\text{Si-OH}$ bonds, at 1050 cm^{-1} - to valence vibrations of Si-O-Si bonds [41, 42]. The maximum intensity of the band at 790 cm^{-1} is observed for the gel with 0.5% PhOH. At the same time, we observe a significant increase in the intensity of the band at 1050 cm^{-1} for compositions containing orthophosphate acid and 0.1 and 0.3% phenol. For the experimental sample with a PhOH content of 0.5%, the intensity of the band at 1050 cm^{-1} decreases sharply. The absorption band at 970 cm^{-1} characterizes deformation vibrations of $\equiv\text{Si-OH}$ bonds, and has a greater intensity for samples containing orthophosphate acid, as well as 0.1 and 0.3% phenol. At a phenol content of 0.5%, this band practically disappears [43, 44].

Absorption bands are located in the range of $400\text{--}550\text{ cm}^{-1}$, which may be due to the combined presence of deformational rotational vibrations of both Si-O-Si and P-O-P bonds. There may also be bands characteristic of PO_4^{3-} bond vibrations [45, 46].

According to the research of the authors of the paper [47], the peak at 1129 cm^{-1} may correspond to the fluctuations of the Si-O-P bond. But all spectra have a strong composite band in the range between 900 and 1350 cm^{-1} , which makes it difficult to assess its presence.

After high-temperature treatment in the spectra of pure SiO_2 gel and gels modified with phenol, the absorption band in the range of $2800\text{--}3600\text{ cm}^{-1}$ completely disappears. For the sample containing only orthophosphate as an additive, the absorption band in this range is preserved, but becomes less intense compared to the non-heat-treated gel.

For all spectra, the appearance of a broad band in the range of $850\text{--}1100\text{ cm}^{-1}$ is observed, it has the lowest intensity for the gel with H_3PO_4 additive. However, for the experimental sample with a phenol content of 0.1%, the bands at 860 , 950 , and 1060 cm^{-1} are clearly defined in this range. Peaks at 620 , 670 , 790 cm^{-1} also appear for all samples with phenol.

It is also worth noting that the band at 790 cm^{-1} after high-temperature treatment becomes more intense in the IR spectra of gels with phenol additives.

In the range of $3600\text{--}3900\text{ cm}^{-1}$, absorption bands are visible only for samples modified with phenol, as in the case of SiO_2 gels that were not subjected to high-temperature treatment.

The degree of polycondensation of silanol bonds can be determined by the intensities of bands at 790 , 970 cm^{-1} [48, 49], which correspond to $\equiv\text{Si-OH}$ bonds and at 1050 cm^{-1} , which characterize Si-O-Si vibrations [50, 51].

The values of the relative intensities of the characteristic bands of raw SiO_2 gels with additives are presented in Fig. 4.

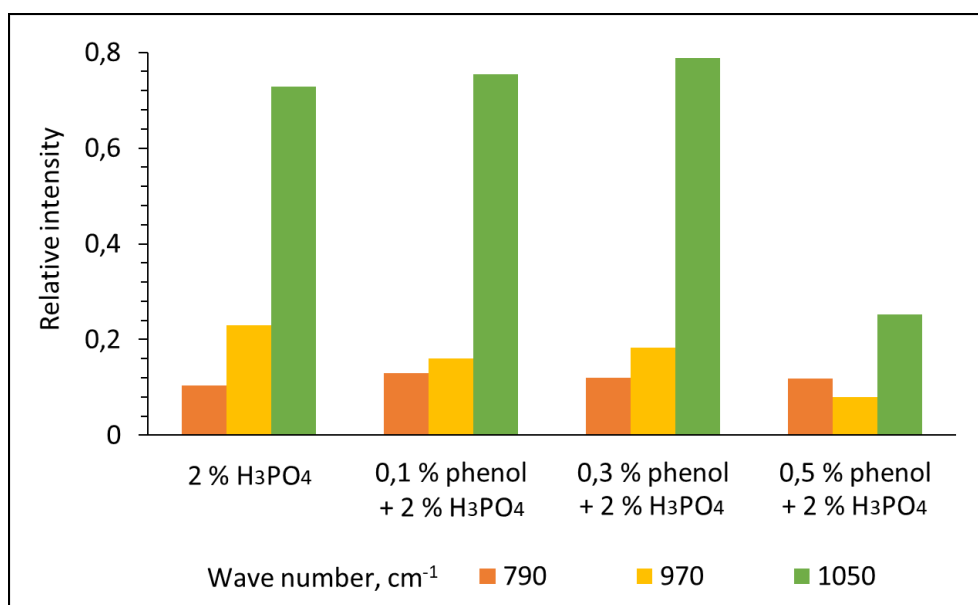


Fig. 4. Change in the relative intensity of characteristic bands of raw SiO_2 gels with additives

It can be seen from the figure that in the case of phenol content of 0.1 and 0.3%, the relative intensities of the characteristic bands are almost the same and almost do not change compared to the sample where H_3PO_4 was used as a separate additive. Probably, small additions of phenol do not have a significant effect on the polycondensation process.

Increasing the phenol content to 0.5% leads to a sharp decrease in the intensity of the band at 1050 cm^{-1} , i.e., the number of siloxane bonds becomes smaller. This can probably be explained by the fact that phenol prevents the formation of new Si–O bonds due to the steric effect. Hypothetically, phenol can bind to $\equiv\text{Si}-\text{OH}$ groups by the donor-acceptor mechanism due to the available unshared oxygen electron pairs and free silicon orbitals. It can be assumed that the hydroxyl groups of cellulose and the $\equiv\text{Si}-\text{OH}$ groups of the gel are covalently linked during the condensation process. Orthophosphate ions can be embedded in the structure of the siloxane framework or connect the OH groups of wood cellulose and the skeletal silanol groups of the SiO_2 gel. An approximate mechanism for the formation of a silica-containing coating on the surface of wood is shown in Fig. 5.

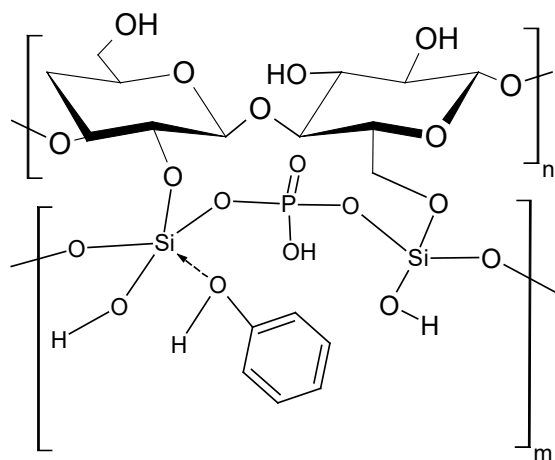


Fig. 5. Scheme of the formation of a silica-containing coating, modified with additives of orthophosphate acid and phenol, on the surface of wood

Therefore, phenol can have a positive modifying effect on the fire-retardant composition based on SiO_2 , with a content of more than 0.5%. It is possible that phenol will increase the strength and density of the silico-phosphate coating and will protect the wood from insect pests and microorganisms due to its antiseptic properties. But such a model of fire-resistant composition will require additional study and further improvement to ensure a longer solidification time of the ash, and, accordingly, a more effective application of the coating on the building material.

4 Conclusion

As a result, of the research, the effect of orthophosphate acid and phenol additives on the gelation processes in liquid glass-based gel fireproof coatings for wooden building structures was studied.

It is shown that the use of orthophosphate acid as a modifier leads to the initiation of predominantly linear polycondensation in experimental sols. It was established that small additions of phenol practically do not affect the course of polycondensation in experimental sols. Increasing the phenol content to 0.5% showed an effect on gel formation due to the possible addition of phenol to the skeletal silanol groups by the donor-acceptor mechanism, which makes it possible to have a synergistic effect of the complex additive of orthophosphate acid and phenol on the properties of the silica-containing flame retardant composition.

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