Research of a new flame retardant material with set parameters of operational properties taking into account features of glued wooden structures

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Abstract. The questions of peculiarities of using fireproof composition for glued wooden structures are considered. The results of testing the fire-protective efficiency of the composition, the influence on reducing the combustibility and flammability of wooden structures, compatibility with different glue components of glued wooden structures are given. The results of performance properties estimation are described.

1. Introduction

In modern construction, despite the emergence of many different kinds of building materials, environmentally friendly wood still remains relevant. Currently, the use of wood in the construction of buildings and structures mainly comes down to the use of high-tech glued wooden structures.

By glued wooden constructions we mean constructions, whose main cross section consists of glued layers of boards joined together in length and glued in width. Gluing elements of wooden constructions with different polymeric adhesives expands engineering and architectural possibilities of wood application. Glued wooden structures can overlap the spans inaccessible to other materials, the distance between the supports of glued structures can reach 40 m, laminated - up to 55 m, bent-glued frames up to 70 m. Even entire stadiums, swimming pools and water parks are covered with glued wooden structure systems.[2-3].

However, any wooden structures are still among the combustible materials that spread fire quickly, which causes significant damage to buildings and structures and significantly reduces their fire safety in general. The study of fire resistance of glued wooden structures began in the 1970s due to the fact that glued and bent-glued wood began to be widely used as supporting structures in construction. [4] The issue of fire safety of such structures has become a priority and remains relevant today.

Recently, the demand for flame-retardant treatment of glued wooden constructions has especially increased, as their installation is carried out without confirmation of performance characteristics by certification bodies. Subsequent verification by fire authorities finds that it is necessary to ensure the compliance of glued wooden structures with fire safety requirements. Another difficulty is the fact that it is often impossible to identify glued wood samples and assess their fire resistance limit. Therefore, it is necessary to use fire protection coatings to reduce the fire hazard of glued wooden structures.
The first solutions concerning fire protection compositions for glued wooden structures were liquid-silicate pastes-slippings with asbestos, vermiculite or clay filling. In this way it was only possible to increase the fire resistance limit to 30 and 45 minutes. Nowadays, in order to increase the fire resistance limit of glued wooden structures, constructive fire protection has become the most widespread, namely: sheathing with mineral-based slab materials and fibrous fireproof mats with subsequent cladding. Essential drawbacks of this solution are the complexity of installation, high consumption and cost of passive fire protection, additional costs for cladding and decorative properties.

The use of the latest impregnation compositions and standard fire protection paints does not essentially affect the fire resistance limit of glued wooden structures, however, their use allows to increase the time of ignition and reduce the spread of flame over the structure.

2. Progress of work

Development of a complex fireproof coating on an organic basis for glued wooden structures allows to maintain operating properties under conditions of open atmosphere, temperature changes, high humidity and increase the reliability of the coating for the period up to 25 years.

The mechanism of fire protection of existing analogues of coatings is based on bloating, so it is necessary to have a fairly thick layer of coating and high consumption, to ensure a sufficient amount of foamcok.

The action of the complex fire protection coating is based on the non-combustible properties due to liquid chlorinated organic phosphate. Coatings containing chlorinated phosphoric acid esters have high heat resistance, hydrolysis resistance, low viscosity, excellent resin compatibility.[7]

Due to the introduction of organic chlorinated phosphate, glued wood treated with a complex flame retardant coating has the properties of a non-combustible and non-flammable material. At the same time, the chemical structure of chlorinated flame retardant does not reduce the depth of penetration of the complex flame retardant coating into the treated wood and thus is securely fixed on it. Due to this unique development the complex flame retardant coating has low consumption and low required thickness of the required coating.

The efficiency of phosphorus compounds as flame retardants is linked to the following factors:
- the specific effect of phosphorus compounds on the combustion processes in the gas phase;
- the formation of a surface molten layer of polymetaphosphoric acid on the surface of glued wood, which is a barrier to heat transfer from the flame to the polymer and for the diffusion of oxygen to the surface, and pyrolysis products - into the flame.[8]

Copolymer of styrene with methacrylic acid is used as a film-forming substance in the formulation. Its polymeric matrix in interaction with liquid flame retardant leads to slowdown of the thermal destruction process, reduction of the amount of volatiles emitted, strengthening of carbonization and formation of carbonized residue resistant to oxidation, with high fire and heat protection properties. Fire retardant effect of silicon dioxide in the complex fireproof coating is due to the release of water vapor during decomposition in the flame, which leads to cooling the combustion zones and the formation of oxide film on the burning surface. Coverings filled with silicon dioxide have transparent matte texture that does not reveal the surface of glued wood.

Complex fireproof coating also has fungicidal properties due to the use in the formulation of additives based on oktilisothiazolinone and 3iodo-2-pinyl-butyl carbamate, and can be used on a variety of wooden surfaces and materials based on them, guaranteeing a long service life of coating, up to 25 years. In the course of development, the compatibility of the complex fireproof coating with the polymer adhesives available on the market for the production of glued structures has been established, the complex fireproof coating has low consumption and high technological efficiency in application.

Thus, as a result of the interaction of a mixture of flame retardants in the formulation of the flame retardant material, the processes of reducing the spread of flame and the formation of stable thermodynamic systems prevail over the reactions of thermal destruction, which reduces the rate of
release of volatile compounds and toxicity of pyrolysis products and increases the fire resistance limit of glued wooden structures. Also, due to the combination of flame retardants of different effect in the formulation, the flame retardant material has low consumption and the coating thickness required for protection, while having high decorative and aesthetic properties (figure 1).

![Figure 1. Appearance of new fireproof material.](image)

3. Methods of testing
One of the main technical tasks was the development of a flame retardant material compatible with various adhesive components of a wood compound, as the polymer glue can influence the flame retardant properties, and a flame retardant material on an organic basis - on cohesion in an adhesive layer.

Compatibility of three types of glued wooden structures - laminated, solid and combined - with various adhesive layers was assessed. There are five types of polymer adhesives according to the type of resin component: phenol-formaldehyde, phenol resorcin-formaldehyde, aminoplast, polyurethane, emulsion polymer-isocyanate (EPI-glues). [9] The latter corresponds to both domestic and some foreign standards for the production of glued woodblock. Emulsion polymer-isocyanate adhesive does not contain formaldehyde and belongs to the safest group of adhesives, it is universal and transparent.

Evaluation of the compatibility of the flame retardant material with various adhesive components was carried out visually, by fixing changes in the appearance of the glue joint and the structure of the
glued wooden structures in general. Compatibility of final adhesive films with fire protection material was also tested. According to the results of the compatibility testing and of testing the effect of flame retardant material on the glue joint of the glued wooden structure it was concluded that the coating does not affect the strength properties of the glue, and the glue in its turn does not affect the fire retardant properties.

Fire tests of treated glued structures were carried out in accordance with GOST 30402-96 with the assessment of the critical surface density of the thermal flow (SFD) of the ignition process, flame propagation over the material surface with the determination of the flame propagation index (FPI) in accordance with GOST 12.1.044-89 p. 4.19.

When determining the flammability parameters, record was taken of the time and place of ignition, the nature of destruction of the sample under the influence of thermal radiation and flame, as well as of melting, swelling, delamination, cracking, swelling or shrinkage of the exposed surface. Based on the results of determining the ignition time for the samples under the influence of external heat flux of various intensities of 20, 30 and 40 kW/m², the values of critical surface heat flux density (CSHFD) were determined. CSHFD is characterized by the minimum value of the heat flux density, at which the samples burn with a steady flame.

When assessing the flame propagation index value, it was important to determine the time of flame passage by the front of each section of the sample surface, the temperature of the off-gases, the time of achieving maximum temperature values, the flame propagation velocity over the sample surface.

Determination of the flame retardant efficiency index of the flame retardant material was carried out during the mass loss tests of the sample in accordance with GOST R 53292-2009. As samples were used glued wooden structures made of laminated veneer lumber, treated with flame retardant material, with the consumption specified in Table 1.

Further, the operational properties of the coating were investigated. Samples of flame retardant material were tested for water absorption of the final film, moisture absorption of the loose film in a humid atmosphere was determined, and parallel testing was carried out in a climatic chamber for resistance to conditions of moderately cold climate.

To confirm the compliance with the declared area of application, the resistance of the flame retardant material to damp environment was tested experimentally. Water absorption of the film was determined without destruction by 24-hour liquid exposure of the sample glued wooden structure treated with flame retardant material.

In addition, moisture absorption of a loose film of the flame retardant material in a humid atmosphere was determined. The climate of swimming pools and water parks is characterized by the value of humidity of 50-60%. For our experiment we artificially created the humidity of 95% by filling the exciter with a saturated solution of sodium sulphide. The experiment was carried out by comparing the weight of a single film before the test and after conditioning for 24 hours in a humid atmosphere.

Resistance to environmental factors is also one of the main parameters required for a flame retardant material. Accelerated climatic testing of samples was carried out using a climatic chamber by means of formation of modes of temperature and humidity differences corresponding to conditions of a moderately cold climate during several cycles. In the course of tests changes in decorative and protective properties were recorded.

4. Test results

As a result of the test for the flame retardant material the flammability group - B1 was determined. Figure 2 demonstrates the appearance of samples after the test with flame retardant treatment (b) and without it (a).

According to the results of the test for the flame propagation index, the flame retardant material was identified as not spreading the flame over the surface. Figure 2 shows the samples of glued structures treated with the flame retardant material after the flame propagation test in accordance with GOST R 51032-97.
The weight loss test showed that the flame retardant material provides Group I fire protection efficiency, weight loss of the samples does not exceed 8.5%.

**Table 1.** Test results according to GOST R 53292-2009.

| Flame retardant material | Number of layers | Consumption (gr/m²) | Sample mass loss (%) |
|--------------------------|------------------|---------------------|----------------------|
|                          | 3                | 340                 | 8.3                  |
|                          | 4                | 360                 | 7.2                  |
|                          | 3                | 335                 | 8.5                  |
|                          | 4                | 350                 | 8.1                  |
|                          | 3                | 375                 | 8.1                  |
The appearance of the coatings after the tests is shown in figure 3.
As a result, the value of water absorption coefficient equal to 0.08 kg/(m² h 0.5) characterizes the water absorption of the flame retardant film as low as compared to samples of competition flame retardant materials (figure 4).

Figure 4. Weight gain of coating samples of Analog 1, Analog 2, new flame retardant material during film water absorption test

Dehumidification of loose film of the flame retardant material amounted to 10% in accordance with GOST 21513-76.

The accelerated climatic tests of the flame retardant material according to GOST 9.104 - 91 showed that in enclosed premises the service life of the material is not less than 30 years, and under the influence of temperature, humidity and UV radiation the protective properties are preserved for not less than 25 years. Figure 5 shows the state of samples with the CFR after accelerated climatic tests.

Figure 5. The state of the treated samples after 100 cycles of exposure in a climatic chamber 1,2 - tested samples, 3 - control samples.
Conclusions
The research of fire-technical characteristics of glued wooden structures samples treated with the new flame retardant material showed that protection of glued structures with the consumption of 350 g/m² makes the wood low-flammable. The new flame retardant material also reduces the spread of flame to group 1 and provides Group I fire protection efficiency. The results showed the possibility of using the new material for fire protection of supporting structures, finishing facades of buildings of all classes of fire resistance and fire hazard. The conducted researches of operational properties of the material have proved guaranteed service life of the fireproof material in conditions of open air for 25 years and indoors for 30 years.

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