Longevity enhancement of wooden civil structures

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Abstract. A method of longevity enhancement of wooden civil structures by absorption-chemical modification of timber surfaces is described herein. The modifiers were phosphoric acid ethers. The properties of the superficial layer were studied by IR-spectroscopy and elementary analysis by Energy Dispersion X-Ray Spectroscopy (EDX) for build-up detection of covalent bonds of the modifier with the timber surface. During mycological studies, quantities of vital spores on surfaces of wooden structures were measured. As a result, the modified surface of the timber features durable a high degree of biological and fire protection enhancing the longevity of timber structures. The obtained results were practically introduced for longevity enhancement of the timber structures in Ryazan Kremlin, Anglican Church in Archangel'sk City, Nikol'skaya Church (Lyavlya Village, Archangel'sk Region), in Yaroslavl' Wooden Architecture Museum, Holy Trinity Sergius' Lavra, in construction of individual housings in Moscow Region.

1 Introduction

Timber is excellent and naturally renewable construction material. Increased service life of wooden structures and materials contribute to preservation of forest stocks and improvement of the natural habitat. Wooden structures have been traditionally used in the house-building. For the time being, they are also utilized in high-rise buildings construction. For the time being, multi-storied buildings of wooden structures are getting more popular. High-rise buildings of wooden structures were built in the Netherlands, Austria, Norway, Canada. Multi-storied buildings of wooden structures are designed in Russia as well [1]. The longevity enhancement of wooden civil structures by means of soft superficial modification is a vital objective. Long-term fire [2] and biological resistance allow for solving of the problem of the longevity enhancement of wooden civil structures and the integrity of the wooden architectural heritage.

2 Materials and methods

In Russia, as well as in many other countries, pine timber is the basic material for wooden structures. The most active pyrenes for wooden materials are phosphoric compounds [3].

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The samples for experimental testing were made of pine sapwood [4]. During the experiment, ethers of phosphoric and phosphorous acids, and 6-chloro-3-cyclophosphazene were used. The aqueous solutions of the modifiers (with 20%-40% concentration) were applied to the surface of the samples with 180 g/m2 specific consumption for thin-layer coating. Fire-hazard tests included exposure to needle-shape flame of a burner. The weight loss of the samples was measured.

The bonding of the modifier with the timber surface was studied by IR-spectroscopy and elementary analysis. The IR-spectroscopy was carried out with Magna-750 (Nicolet) [5] Fourier IR-spectrometer. The elementary analysis was carried out by Energy Dispersion X-ray Spectroscopy (EDX) [6].

The highest concentration of chemically bonded phosphorus with timber surface is characteristic for BMP and BEP ethers of phosphorous acid. The build-up of covalent bonds between the modifier and the timber provides for longevity of the protective property enhancing the longevity of wooden structures.

The biological resistance was studied by means of the mycochemical method [7]. The quantity of vital spores on the surface was measured on samples immersed in sterile nutrient media at 27°C, and 90% humidity. The samples were incubated within a week. The quantity of vital spores was measured by means of a binocular microscope with 600x magnification.

3 Results and discussion

The fire-resistance properties and the results of the elementary analysis of the modifier-treated samples, see Table 1.

Table 1. Efficiencies of different anti-pyrene modifiers for fire-proofing of timber

Indicators	Modifiers					Control
	TCEP[2]	TCPP[1]	BMP[3]	BEP[2]	HCCT[4]	
% of Ph. in the superficial layer	0.43	0.26	2.6	4.7	0.13	
Weight loss during burning, Δm_{cp}, % (GOST R 53292-2009)	11.6	16.7	6.9	8.6	16.6	89.0
Fire-protection efficiency group	II	II	I	I	II	III

Table 1 makes it evident that all samples under study (modifiers of phosphorus acid ethers) make the timber fire-proof, however, the best results are delivered by BMP and BEP phosphorous acid ethers [8]. The highest phosphorylation degree of timber surface (% of phosphorous) is characteristic also for BMP and BEP.

The MSUCE has developed a method of soft adsorption-chemical modification of wood [9], which is later used in different countries [10]. The basic provisions of the methods are reduced to the following formula: timber longevity follows surface properties. In soft modifying (18°C-25°C) at 5%-40% solution concentration, efficient modifiers build-up covalent bonds in the superficial timber layer. Furier IR-spectroscopy delivers information

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[2] Modifiers: Phosphoric acid ethers
[3] Phosphorous acid ethers
[4] 6-chloro-3-phosphazene

on the nature of the covalent bonds in the system. It allows for detection of covalent bonding of the substrate with the modifier.

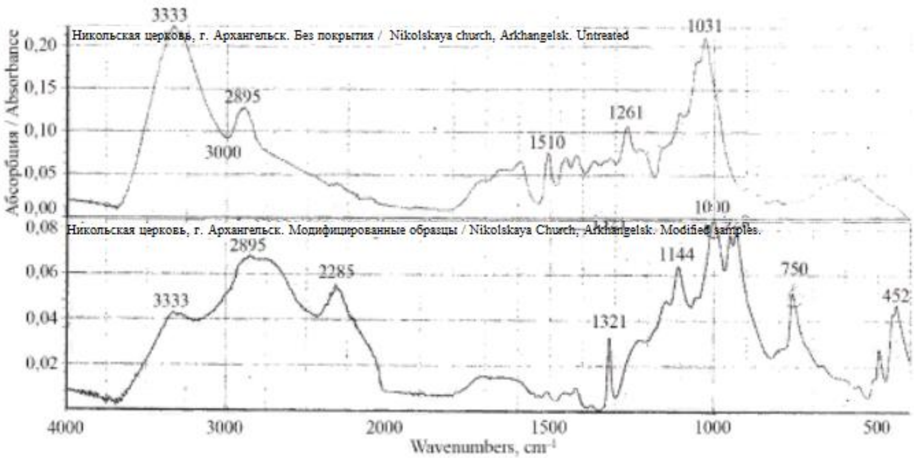

Fig. 1. IR spectra of external enclosure surface of Nikol'skaya Church, Archangel'sk Region, Lyavlya Village.

The analysis of IR spectra of raw and modified timber demonstrates in the modified timber appearance of bands in the absorption region of 926 cm^{-1}, 1144 cm^{-1}, 1321 cm^{-1} and 2285 cm^{-1} characteristic frequencies The bands in the absorption region of 926 cm^{-1}, 1144 cm^{-1} characteristic frequencies represent the build-up of P-O-C bonds. The 1321 cm^{-1} frequency represents the presence of P=O bonds. The frequency of 2285 cm^{-1} indicates the presence of bonded hydroxyl groups. It is the proof of the covalent bonds build-up between the modifier and the substrate. The modification process can be shown as follows:

$$(R-O)_2-\overset{\overset{\displaystyle O}{\|}}{P}-H \xrightarrow{\text{cell.}} \text{cell.}-O-\overset{\overset{\displaystyle O}{\|}}{P}-O-R$$

Fig. 2. Diagram of cellulose modification with phosphorous acid ethers.

The build-up of covalent bonds between the modifier and the timber provides for longevity of the protective effect enhancing the longevity of wooden structures.

The longevity of wooden structures is affected by biological deterioration. Figures 3 and 4 show the deterioration due to biological agents.

Fig. 3. Biological deterioration of a log house. Kostroma Region.

Fig. 4. Biological deterioration of the enclosure of Nikol'skaya Church. Archangel'sk Region, Lyavlya Village.

The presence of organic carbon-based polymers cellulose and lignin in timber stipulates the susceptibility of wooden structures to biological corrosion. For study of the biological deterioration of construction materials, in particular, that of the timber, a mycochemical method was developed [11]. Mycological studies were carried out in the Institute of Environmental Problems of the Russian Academy of Sciences, Moscow City (Yu.L. Koval'chuk). In samples of superficial layers of wooden structures in operation, mold fungi, wood-destroying fungi and vital spores were identified [12, 13]. See Table 2.

Table 2. Quantity of vital spores (VS) of fungi in wooden structure samples.

Sampling place	**Germs**		**Quantity of VS per 1 cm^2**	**Germs concentration in 1 g of sample (total quantity)**
	Wort agar	**Sabouraud's medium**		
Kizhi, Seryogin's House	Aspergillus niger; Ophistoma; Aspergillus flavus; Fusarium; Serpula lacrimans	Serpula Actinomyces Lypomyces yeasts	126	CFU 4.10^3
Nikol'skaya Church, Lyavlya Village, eastern altar wall, external	Trichoderma viride; Trichoderma koningii; Cladosporium herbarium; Ophistoma	Penicillium Aspergillus Lypomyces yeasts	214	CFU 9.10^5

Holy Trinity Sergius' Lavra, Assumption Cathedral, wooden foundation piles	Aspergillus niger; Mucor hiemalis; Ophistoma; Fusarium; Penicillium capculatum	Lypomyces yeasts	193	CFU 2.10[7]
Maly Vlasyevskiy Pereulok, 4. Wall section in loft rooms	Penicillium biforme; Penicillium cyaneo-fulvum; Aspergillus glaucus; Aspergillus niger; Stemphylium sp	Penicillium Aspergillus Yeast Lypomyces Candida Rhodotoruba	112	CFU 8.10[3]

The concentration of vital spores (VS) on the wooden structures' surface was 67 to 214 pcs./cm^2. As known from references, the VS concentration above 80 pcs./cm^2 is critical in terms of timber biological corrosion growth.

The influence of the VS concentration per cm^2 on the fluctuation of cellulose and lignin in wooden structures is demonstrated in Fig. 5.

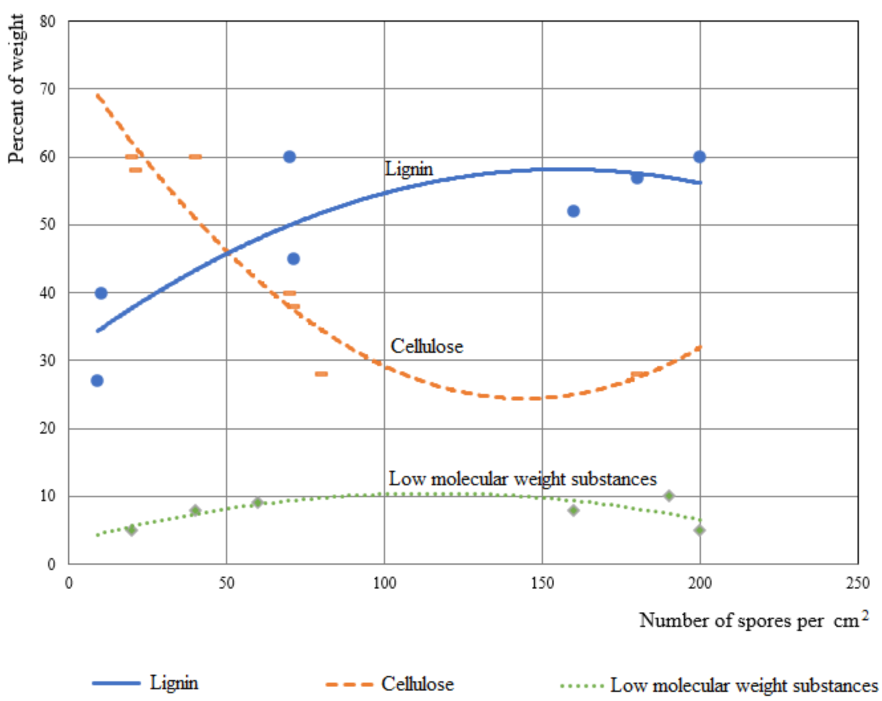

Fig. 5. Timber component contents dependent on VS/cm^2 concentration.

In the course of time, the cellulose content goes back with the biological corrosion leading to reduced timber strength. The longevity of wooden structures (except for fires) is mostly dependent on the activity of biological destroying agents which get active at increased temperature and humidity of the surfaces of the structures. When the humidity of the structure surface is increased by 35%, the VS concentration gets higher by 2.7 times.

The analysis of the dependency of VS on the temperature can be expressed by the following equation:

$$Vt_2=Vt_1\cdot\gamma^{1,3}$$

where Vt_2, Vt_1 are the VS growth rates at different temperatures;
γ is the temperature coefficient with experimental value of 1-1,5. $t_2> t_1$.

The biological deterioration of the timber follows the principle of hydrolytic decomposition, thereby, the wood-destructing fungi act as active process catalysts. In terms of the chemistry, the cellulose, lignin and pentosane contents are changed during timber deterioration. At a humidity above 18%, hydrolytic decomposition takes place with build-up of carbonyl-containing fragments.

As antiseptics, phosphorous acid ethers were studied (see Table 1) [14] providing for high fire protection ratings. The results of the mycological analysis of the surface of wooden structures of different buildings and facilities after treatment with a BMP-based composition are presented in Table 3.

Table 3. Results of the mycological analysis of wooden structures of buildings after treatment with a BMP-based composition.

Item No.	Sampling place	Identified germs		VS per 1 cm^2 of the surface	
		After treatment	After 1 year	After treatment	After 1 year
1.	Kizhi, Seryogin's House	None	None	0	0
2.	Nikol'skaya Church, Lyavlya Village, eastern altar wall, external	None	None	0	0
3.	Maly Vlasyevskiy Pereulok, 4. Wall section in loft rooms	None	None	0	0

As it is evident from Table 3, the superficial treatment of wooden structures with a phosphorus-containing composition on phosphorous acid ether basis imparts to the structures long-term biological resistance, thus making the material of wooden structures biologically resistant fire-proof materials and enhancing the longevity of wooden civil structures for construction of wooden housing and preservation of wooden architectural heritage [15].

4 Conclusion

The superficial thin-layer modification with phosphorous acid ether solutions assigns the wood in a soft manner to the class of fire-proof biologically resistant materials. The long-term sustainability of protective properties is stipulated by the build-up of covalent bonds between the modifier and the timber. Stable covalent bonds of P-O-C type are generated. The thin-layer soft superficial modifying of a structure enhances its longevity, does not increase the weight of the structure and does not change its aesthetic appearance important for wooden house building. The paper indicates that phosphorous acid ethers combine the properties of anti-pyrenes and antiseptics, being efficient modifiers building up covalent bonds to the substrate, thus enhancing the longevity of wooden structures. The conducted studies and the obtained results on the longevity enhancement of wooden civil structures are taken into consideration during the manufacturing of wooden structures and in repairs of wooden architectural heritage assets.

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