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Corrosion-resistant epoxy coating for protection of structural glued-laminated timber in high humidity conditions

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Abstract. The article presents a solution to practical problem - the development of epoxy coating of low combustibility with corrosion-resistant properties for the protection of glued-laminated timber in conditions of high humidity. Based on the test results obtained, it was found that when using the developed epoxy polymer protective coating, the resistance of wooden beams to distilled and seawater increases by more than two orders of magnitude, ensuring the integrity of wood products and structures, protecting the ends and not causing warping of the material. In conditions of medium aggressiveness of the environment i.e. 10% H₂SO₄, 10% NaOH, 10% NaCl, the application of the developed epoxy polymer coating to glued-laminated timber provides their high indicators of bio- and chemical corrosion protection (water resistance, resistance to sea water and aggressive aqueous solutions). The developed protective coating has fungicidal properties, protecting structures from the appearance of blue stains, mold and wood-destroying fungi. Revealed a good correlation between the concentration of biocide and fungicidal coating properties. A comprehensive assessment showed that the developed epoxy coatings have increased biocorrosion-resistant properties and can be used as protective coatings for glued-laminated timber structures exposed to mold fungi, high temperatures and high humidity.

1. Introduction

Innovative technologies in the woodworking industry make it possible to obtain wood-based structural composite materials that exceed solid wood in terms of physical and mechanical characteristics. In modern practice, glued timber is widely used, obtained by gluing sheets of peeled coniferous veneer with phenol-formaldehyde glue. The technology for the production of glued timber of this type allows reducing the negative impact of natural deficiencies of wood, significantly increases the levels of its strength indicators [1].

Such glued materials make it possible to create new structural systems and architectural forms, expand the scope of wood use - low-rise residential buildings, public - buildings and some industrial and agricultural structures, where wood is used in load-bearing and enclosing structures. Compared to similar reinforced concrete structures, the use of glued wood structures allows to reduce the weight of the structure by 4-5 times, labor intensity of manufacturing and installation by more than 2 times [2].

The greatest economic effect from the use of glued structures is achieved when they overlap large spans (18-36 m) - such spans have cinemas, indoor markets, swimming pools, exhibition halls, athletics arenas, equestrian facilities, and they are also used in buildings and structures exposed to chemicals aggressive environment. The complex application of load-bearing timber glued structures together with lightweight enclosing structures is also practiced. In Europe, water parks and indoor pools are very popular, the vaults of which are usually made of glued wooden structures [3]. Also, the trends of recent years have shown an increase in interest in glued wooden structures in the countries of the equatorial belt, as well as in countries on the coast of the seas in other belts, where there is high humidity.



However, significant disadvantages of such glued wooden structures in conditions of high humidity are low resistance to water and aggressive environmental action, aqueous solutions and biological damage.

Wooden products and structures that are constantly (regularly) exposed to salt (sea) water according to BS EN 335:2013 «Durability of wood and wood-based products. Use classes: definitions, application to solid wood and wood-based products» belong to the class of wood exploitation Hazard Class 5.

Under conditions simulating external environmental influences of medium aggressiveness (high humidity over 60-90% and temperatures over 20 °C, as well as aggressiveness of the environment), it is imperative to provide for constructive and chemical methods of protecting structures and elements based on glued wood.

The chemical measures to protect such wooden structures from bio- and chemical corrosion in conditions of high humidity and medium aggressiveness of the environment i.e. 10% H₂SO₄, 10% NaOH, 10% NaCl provide application of moisture-proof and chemically resistant moisture-proof coatings on wooden structures, such as acrylic, acrylic-alkyd, alkyd, urethane-alkyd, epoxy [4-6] according to SR 28.13330.2012 «Protection of building structures from corrosion».

The modern market for such protective coatings for glued timber is diverse and has a number of advantages and disadvantages when providing one or another protective function. So, as antiseptics, impregnating primers Belinka Impragnan, Belinka base, Pinotex Wood Primer, Fentak are used, intended for the main preventive protection of wood from biological pests (insects, blue fungus and rotting). Protective and decorative (moisture-proof) coatings such as Belinka exterior, yacht varnish Protex Yat Vernik, MeritYahti 30, Poli-R, Miranol paint, enamel PF-115, Enamel, Master 30 provide moisture resistance of structures, while the application of such coatings is carried out on already primed wooden surfaces.

However, the selection of such protective coatings for glued wood is complicated by the fact that the technology of its manufacture includes gluing wood elements with polymer adhesives of various chemical natures.

It is noted [7] that the presence of a polymer adhesive interlayer leads to a change in the structure of wood and its properties, which must be taken into account when selecting bio- and chemical protective agents. The phenol-formaldehyde adhesive used in Ultralam™ is not resistant to water and aqueous solutions, which eliminates the use of water-based protection. Taking into account all these factors significantly narrows the range of products that can be used for bio- and chemical protection of glued-laminated timber Ultralam™.

In modern construction, methods of applying polymer coatings to the surface of wooden structures and materials are increasingly used, which at the same time can protect wood from the effects of high air humidity, corrosive gases, fire and fungi, increasing the service life of wooden structures [8].

A promising direction for a comprehensive solution to these problems is the development of an epoxy polymer coating of low combustibility with corrosion-resistant properties for the protection of glued-laminated timber in conditions of high humidity. The advantage of epoxy polymer compositions over others is the ability to combine all the necessary properties in one material, they have high adhesion to wood and metal, and the technology of their preparation and application can take into account external climatic conditions [9-12].

According to [13] Ultralam™ belongs to the following fire hazard groups: E - highly flammable, C_{fl} - with a moderately spreading flame, s₃ - with a high smoke-generating ability, with high toxicity during combustion according to EN 13501. To improve the fire hazard properties of Ultralam™, as well as to expand the area of use, treatment with protective polymer coatings is necessary.

Earlier, in our work [14], it was found that the developed two-component composition based on epoxy oligomers, inorganic flame retardants and amine hardeners for fire protection of glued wood Ultralam™ provides a transfer according to the flammability group of group E building materials to A2, according to EN 13501.

However, it is necessary to solve the following tasks for the use of this composition as a protective coating with increased corrosion-resistant properties for glued-laminated timber in conditions of high humidity:

1. To assess the effect of a fire retardant on water and chemical resistance, as well as a biocide on fungal resistance of epoxy composites.
2. Determine the main physical and mechanical properties of the developed coating and carry out its comprehensive assessment to protect glued timber in conditions of high humidity.

2. Materials and methods

To obtain a protective coating used epoxy oligomer ED-20 with content of epoxy groups of 20.5%; modifying additive Laprolat-803 with the content of cyclocarbonate groups - 27.1% and epoxy groups - 2.17%; hardener PEPA; fire retardant - Exflam APP-201 with a particle size of 8-12 microns; modifying additives PMS-10, as well as biocide (guanidine phosphate).

The content of the fire retardant EXFLAME APP-201 in epoxy amine compositions is selected in the amount of 7-14 wt. %, which made it possible to increase the oxygen index of the coverage to 41% [15]. The content of biocide (guanidine phosphate) in epoxy amine compositions is selected in the amount of 0.2-5 wt. %.

To determine the resistance to water and aqueous solutions, samples of Ultralam™ beams (30x30x70 mm.) with and without coating were kept at a temperature of 18-25 °C in distilled water and in a solution whose salt composition imitated sea water. At the same time, attention was paid to the fact that the beams were completely immersed in solutions throughout the exposure time. Water resistance and resistance to sea water (w, %) was calculated as the relative weight gain over a certain time.

The tests of fungus resistance carried out in two ways. According to method «A», the samples were infected with an aqueous spore suspension of *Trichoderma* Sp. and exposed for 56 days with an intermediate view after 28 days. This method was used to determine the fungal resistance of materials by the degree of use of the latter as a food source for microscopic fungi.

Method «B» was used to determine the fungicidal properties of new polymeric materials and fungal resistance of the material by the degree of suppression and (or) suppression of the growth of those fungi on it, which are assimilated by other, besides the material itself, life-giving substrates. Experimental samples were placed in Petri dishes on agar nutrient medium, infected with a spore suspension of the fungus *Trichoderma* Sp in the same medium, diluted with water, and exposed for 28 to 84 days.

Some indicators of physical and mechanical characteristics of glued-laminated timber structures were determined according to standard methods.

3. Experimental

Results of water resistance and resistance to sea water (w, %) are shown in Figure 1-3. From the data obtained (Figure 1) it is seen that most intensively samples of glued-laminated timber Ultralam™ without a protective coating absorb water during 5 hours (0.167 days) exposure in distilled and sea water. The samples collect the maximum amount of water (up to 80% in distilled water and up to 70% in seawater) within 4 days. With further keeping the samples in water for the next day, the water absorption by the samples fluctuates within 1-2%.

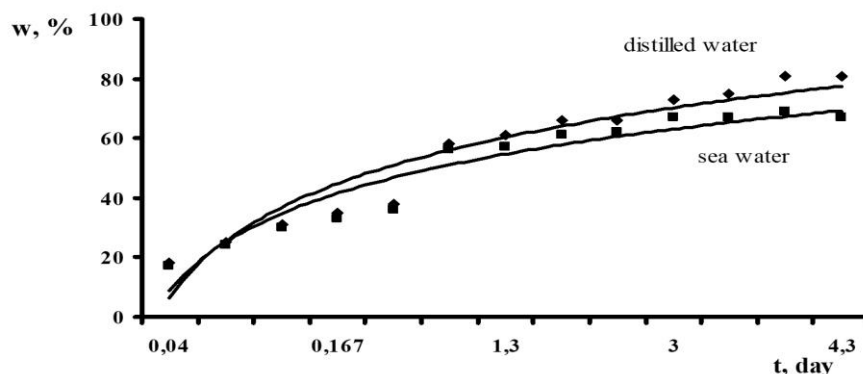


Figure 1. Water resistance and resistance in sea water of uncoated glued-laminated timber.

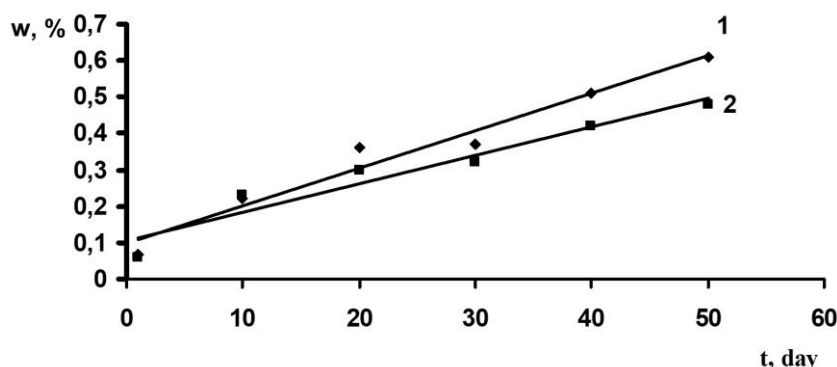


Figure 2. Water resistance of glued-laminated timber coated of epoxy composition: 1 - 7 wt. % and 2 - 14 wt. % fire retardant.

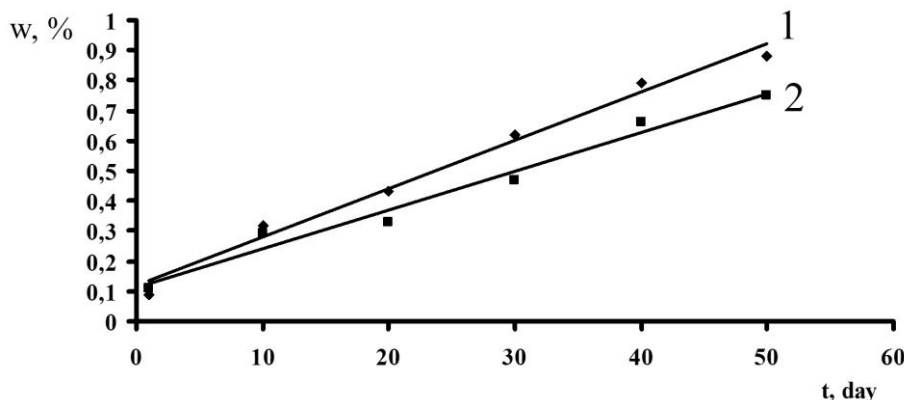


Figure 3. Sea water resistance of glued-laminated timber coated of epoxy composition: 1 - 10.5 wt. % and 2 - 14 wt. % fire retardant.

According to earlier studies [16] on strength, it was found that under exposure to moisture (soaking and boiling), the strength of adhesive joints decreases by 46% and 55% for wet and dry Ultralam™ samples, respectively.

The decrease in strength under such temperature and humidity effects is largely due to the fact that wood and glue are characterized by unequal swelling coefficients. Thus, with a change in humidity in the area of the adhesive joint, the amount of deformation of the adhesive joint occurs, which entails the occurrence of stresses that form concentrations in the areas of joint of materials with different physical and mechanical properties. The stress concentration zone can be the places of the beginning

of destruction under the action of moisture stresses, as well as when they are combined with stresses from an external load.

Humidification adversely affects the sides of the ends, as a result of which uneven stress occurs, which leads to delamination of the material. Humidification of the planes causes warping of the material, which is the reason for a decrease in the operational reliability of structures.

In Figure 1 and 2 show that when using a protective coating, the resistance of the beams to distilled and seawater increases by more than two orders of magnitude. Increasing the amount of fire retardant to 14 wt. % does not impair the protective properties of the coating. Also, the protective coating ensures the integrity of the product and structures of Ultralam™, protecting the ends and not causing warping of the material.

Research samples in aggressive environments i.e. 10% H₂SO₄, 10% NaOH, 10% NaCl were carried out for 2000 hours in accordance with GOST 12020-72. The results are shown in Table 1.

Table 1. The results of testing the resistance of samples to aggressive environments.

Indicator name	Indicator value
Resistance to 10% H ₂ SO ₄ at a temperature of 20 ± 5 °C, %	1.85-2.05
Resistance to 10% NaOH at a temperature of 20 ± 5 °C, %	0.54
Resistance to 10% NaCl at a temperature of 20 ± 5 °C, %	1.08-1.20
Resistance to H ₂ O at a temperature of 20 ± 5 °C, %	0.2

As can be seen from Table 2, under conditions of medium aggressiveness of the environment i.e. 10% H₂SO₄, 10% NaOH, 10% NaCl, the application of the developed epoxy polymer coatings to glued-laminated timber structures ensures their high indicators of chemical corrosion protection.

Under conditions of operation with high or variable humidity, the developed protective coating must have fungicidal properties in order to protect structures from the appearance of blue stains, mold and wood-destroying fungi. Therefore, fungi resistance tests of epoxy polymers were carried out. The essence of the method lies in the exposure of materials contaminated with mold spores in conditions that are optimal for the development of mold.

The growth rate of microorganisms on the material is the opposite of the fungus resistance of the material. The highest score for fungal resistance is «0» (no growth of test cultures on the material when observed under a microscope). The lowest - score «5» (visual inspection clearly shows the development of fungi, covering 25% of the tested surface). The results of testing epoxy polymers are shown in Table 2.

Established based on the presented data Table 2:

- according to method «A», the development of fungi was observed under a microscope and only in sample No. 1, into which no biocide was added. In all other variants, with different quantitative biocide ratios, the development of fungi was not detected. According to the test results according to method «A», all investigated samples are fungus-resistant;
- according to method «B», the control samples were overgrown with fungal spores on the 84th day, which was accompanied by intensive sporulation of biotests (5-point degree of development of micromycetes). On the studied samples, the development of the fungus was noted only after 28 days of exposure. It is shown that samples № 3, 4 have an expression of fungicidal properties.

Table 2. Assessment of the resistance of the developed epoxy polymer coating to the effects of mold fungi.

№ composition	Biocide content, wt. %	Degree sample contamination							
		Method «A», 24 hours				Method «B», 24 hours			
		5	28	56	5	28	56	84	
1	0	0/0	2/1	4/1	20/1	30/5	50/5	50/5	
2	0.2	0/0	0/0	0/0	0/0	10/4	20/4	20/4	
3	2	0/0	0/0	0/0	0/0	5/3	10/3	10/3	
4	5	0/0	0/0	0/0	0/0	2/1	2/1	5/1	

Note: the numerator shows the affected area of the samples, %, the denominator - the assessment of fungal resistance, points.

As a result of the research a stable correlation was found between the concentration of the biocide and the fungicidal properties of the polymer.

The main physical and mechanical properties of the developed coating have been determined and a comparative characteristic of glued-laminated timber structures with and without coating has been carried out (Table 3).

Table 3. Basic physical and mechanical characteristics of glued-laminated timber structures with and without coating.

Indicator name	Indicator value		Test Method
	without epoxy coating	with epoxy coating	
Flammability group	E	A2	EN 13501
Flame spread	C _{fl} -	B _{fl} -	EN 11925
Smoke generating ability	s ₃	s ₂	EN 9239-1
Adhesion strength, MPa	-	13.2	GOST 14760-69
Abrasion index, cm ³ /m	0.36	0.19	ISO 9352
Impact strength, kJ/m ²	6.6	9.4	ISO 8256:2004
Resistant to mold fungi	Not fungus resistant	Fungus-resistant	GOST 9.48-9.049-75
Smoke production coefficient, m ² /kg	974	480	EN 13823:2010
Water resistance,%	20	0.2	GOST 12020-72

As a result of comprehensive studies, it was shown that the developed coating has a complex of improved physical and mechanical properties: high adhesive strength, increased wear resistance, impact strength, which indicates its high operational capabilities and the possibility of using it as a protective coating for glued wood structures exposed to mold, mushrooms, high temperatures and high humidity.

4. Conclusions

As a result of the conducted studies on water and chemical resistance, it was found that when using a protective coating, the resistance of glued-laminated timber to distilled and sea water increases by more than two orders of magnitude, ensuring the integrity of wooden products and structures, protecting the ends, and not causing warping of the material.

In conditions of medium aggressiveness of the environment (in conditions of 10% H₂SO₄, 10% NaOH, 10% NaCl), the application of the developed epoxy polymer coating to wooden structures provides their high indicators of bio- and chemical corrosion protection (water resistance, resistance to sea water and aggressive aqueous solutions).

The developed protective coating has fungicidal properties, protecting structures from the appearance of blue stains, mold, and wood-destroying fungi. Revealed a good correlation between the concentration of biocide and fungicidal coating properties.

A comprehensive assessment showed that the use of two-component polymer composite materials based on epoxy oligomers, fire retardants, biocide and hardeners for glued-laminated timber provides a coating with increased corrosion-resistant properties, as well as high adhesion to the processed surface. therefore, the developed epoxy polymer composition can be used as a protective coating for glued-laminated timber exposed to mold, high temperatures and high humidity.

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