Physical and mechanical properties of the surface of pine wood modified with an organomineral composition

A O Belyaev¹, V E Danilov* and M V Morozova¹

¹Department of Composite Materials and Environmental Engineering, Northern (Arctic) Federal university named after M.V. Lomonosov, Severnaya Dvina Emb, 17, Arkhangelsk, 163002, Russia

E-mail: v.danilov@narfu.ru

Abstract. The percentage of wooden buildings damaged or even lost due to the lack or insufficient technical measures for their preservation is growing every year. This fact makes it mandatory to treat the surface of wood building materials with protective and decorative agents. Within the framework of this study, a multifunctional protective composition for wood was developed that can increase its physical and mechanical properties. Modification of the wood surface with organomineral compositions leads to an increase in its density, hardness and strength. The hardness of the treated wood is 24% higher and the compressive strength along the fiber is 20% higher than that of untreated wood. After treatment, the surface of the wood darkened and slightly yellowed, which does not prevent its use in the construction and reconstruction of buildings. The results of measuring the color coordinates of the modified samples indicate the stability and durability of the developed protective coating even after 4 months of exposure to atmospheric conditions. Judging by the slight return of the color coordinates of the treated wood back to values of the original wood, it can be concluded that the composition is partially washed out.

1. Introduction

Wood is one of the most common traditional building materials around the world. In the thousand-year history of Russia, wooden structures prevailed for seven centuries. Dwelling houses and outbuildings, churches, palaces, fortifications and mills were erected from wood [1–3]. Unfortunately, the percentage of wooden buildings damaged or even lost due to the lack or insufficient technical measures for their preservation, as a result of fires, collapses, and acts of vandalism, is growing every year [4, 5]. This problem is significantly complicated in the Far North and in the Arctic, where the surface condition of wooden structures additionally deteriorates significantly due to harsh climatic conditions, namely: strong winds, high relative humidity, atmospheric precipitation and prolonged exposure to ultraviolet light permafrost, long winters, hurricanes and blizzards; and weather contrast: changes in air temperature from minus 60 degrees in winter to plus 40 degrees in summer [6].

This fact makes it mandatory to treat the surface of wood building materials with protective and decorative agents. Natural wood is protected from external influences by the bark; however, in the production of boards, plant raw materials are debarked and cut into several parts. In this form, wood is not able to withstand external influences for a long time. Therefore, wooden building structures, which are monuments of wooden architecture and created in past centuries, can be irretrievably lost for future generations without a complex of special measures for their restoration with subsequent protection.
from adverse natural and climatic factors. This is especially true for the North of Russia, where wood has always been the oldest and most popular material for construction [7, 8].

The main problem with wooden surfaces is high moisture permeability. Wet wood is an excellent medium for the cultivation of pathogens (bacteria, fungi, mosses) [9, 10]. In addition, in this case, there is a significant deterioration in the technical and decorative parameters of the material. There are not many varieties of wood with high density, hardness and resistance to moisture and they are not used as a building material. The most common types of wood are characterized by good moisture permeability. In addition, natural ultraviolet radiation causes the destruction of wood lignin and the surface of the material becomes gray, friable [11, 12]. In this case, moisture begins to be absorbed not only more intensively, but also deeper. Therefore, actions to protect the surface of wood building materials should pursue two main goals: to reduce the moisture permeability of wood and to increase its resistance to UV radiation.

This effect can be achieved using modern sealants, antiseptics, bleaches and primers. These substances relate mainly to preparatory materials used during the recovery periods of the product. Then, protective and decorative compounds are used as topcoats. At the same time, the use of all of the above means has one significant drawback associated with the temporary period of action of the formed protective layers (oxidative destruction, mechanical damage, destruction under the influence of alternating temperatures, etc.) [13–15]. Therefore, restoration and constructive construction work using building materials made of wood should be based on a completely different principle associated with the modification transformations of the plant matrix by means of a controlled process of its mineralization and hydrophobization of the plant polymer surface.

In this regard, the purpose of these studies was the development of a multifunctional protective composition that can be applied superficially to a variety of wooden structures, thereby increasing the physical and mechanical properties. To achieve this goal, the tasks of synthesizing this protective composition, applying it to pine wood samples and their subsequent holding under conditions of alternating temperatures for 4 months were solved with periodic testing of the strength characteristics of the processed and control wood samples. For this purpose, a water-soluble organomineral complex based on a natural compound of arabinogalactan (a polysaccharide isolated from larch wood) and finely dispersed materials of silica-containing rocks of the mineral resource base of the Arkhangelsk region (polymineral sands) is ideally suited, followed by processing as a hydrophobizing composition based on TEOS.

2. Materials and methods

Scots pine (Pinus silvestris) sapwood (in the form of an edged board) was chosen to study the influence of treatment with the organomineral complex based on arabinogalactan and silica.

Dusty polymineral quartz-feldspar quarry sand from the Kholmogorske deposit (Arkhangelsk region) was chosen as a mineral component of a wood preservative. Polymineral sand was preliminarily mechanically activated in a Retsch PM100 planetary ball mill for 30 minutes at a rotor speed of 420 rpm by 2 cm large grinding balls to obtain a finely dispersed mineral powder.

Industrial food supplement "Lavitol-arabinogalactan" (TM ZAO "Ametis") was purchased for further preparation of organomineral complex.

An aqueous solution of an organomineral modifier was prepared as follows: weighed portion of arabinogalactan (AG) is mixed with water until it is completely dissolved. Then mechanically activated sand (finely dispersed mineral powder) is added to the solution and mixed until a homogeneous mixture is obtained. Then complex is aged in a Binder drying cabinet for 40 minutes at a temperature of 80 degrees Celsius. After that, the hot complex is thoroughly mixed and poured into containers with samples. Pine samples were treated with an organomineral complex containing 10% arabinogalactan and 10% polymineral sand by weight. This ratio, as well as the complexation time of 40 minutes at a temperature of 80 degrees Celsius, is optimal and was chosen based on our previous studies [16, 17].

After processing the samples with an organomineral complex, we prepared a hydrophobic composition. To prepare the silica sol, we used tetraethylorthosilicate (TEOS) of analytical grade TU 6-09-
11-2153-94 (Spectrum Chem), water ammonia "analytical grade" GOST 3760-79 (Sigma Tech), technical isopropanol. The hydrophobizing composition, TEOS-based silica sol, was synthesized by the Stober method. Silicon alkoxide — tetraethylorthosilicate (TEOS), aqueous ammonia (NH$_4$OH), and isopropyl alcohol — were used as a raw materials for the sol-gel process. Silica sol was obtained by alkaline hydrolysis of TEOS in an NH$_4$OH solution in isopropanol (20 ml of NH$_4$OH was dissolved in 300 ml of isopropyl alcohol). The solution was kept at a temperature of 25 °C for 15 minutes, after which 20 ml of TEOS was added dropwise with constant stirring. Stirring was continued for 2 hours until a dense milky sol was formed.

Next, the resulting sol was transferred to a hand sprayer and applied to wood samples from a distance of 15 cm at an angle of 45 degrees until a visible liquid film was formed on the surface of the samples. Each subsequent layer was applied after drying in the air of the previous one, then the samples were kept for 2 days at room temperature, 1 hour at 80 °C. Wood surface treatment with a hydrophobizing composition in the form of silica sol based on TEOS was carried out in 7 layers, because during preliminary studies it was found that the contact angle of wood surface wetting with water ceases to increase significantly after applying 7 layers of silica [18].

After 7-layer hydrophobic coating was applied, the samples were fixed outside the laboratory to study the effects of precipitation, wind, and UV radiation over time. The studies were carried out for 110 days, during which samples were taken for intermediate tests. The general scheme of the experiment and the equipment used are presented on Figure 1.

![Figure 1. Scheme of experiment.](image)

The determination of the ultimate compressive strength along the fibers of the treated wood samples was carried out on a TP-100 press at a speed of 0.42 kN/s. Brinell hardness was measured on a Shimadzu AG-5kNX testing machine by pressing a 10 mm steel ball with a force of 245.2 N into the surface of wood samples within 15 seconds. The hardness was calculated by the reconstructed imprint method according to Equation 6:
where HBS is the Brinell hardness (MPa); F is the applied load (N); D is the diameter of indenter (mm); \(d\) is the diameter of indentation (mm).

Color changes caused by the effect of organomineral complex treatment were measured by using the CIE L*\(a^*b^*\) system. The L* scale measures lightness, and varies from 0 (black) to 100 (perfect white). The \(a^*\) scale measures red-green, with ‘+a’ meaning redder and ‘-a’ meaning more green. The \(b^*\) scale measures yellow-blue, with ‘+b’ meaning more yellow and ‘-b’ meaning bluer. The total color difference (\(\Delta E\)) is calculated according to Equation (7):

\[
\Delta E = \left( (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right)^{0.5} (\%)
\]

Measurements were made using a spectrophotometer (X-Rite 964, USA) with a D65 light source, a 7 mm aperture size, and a 10° normal observer. Six measurements per specimen were carried out using a pattern to minimize wood structural influences on the results (e.g. earlywood and latewood).

3. Results and discussions
The silica dispersions obtained by mechanical dry grinding and used for organo-mineral composition synthesis are detailed in Table 1.

### Table 1. Details of silica dispersions used for partially soluble organo-mineral suspension synthesis.

| Grinding time, min | Particle size, \(D_{(n)50}\) (nm) | Surface Area BET method (m\(^2\)/kg) | Zeta potential (mV) |
|--------------------|-----------------|-------------------------------|------------------|
| 30                 | 230.5           | 952                           | -19.58           |

\(D_{(n)50}\) is the median average particle size by number distribution.

One of the controlled parameters were the color coordinates of the wood surface in the CIE LAB system. In samples treated with the complex, the L (lightness) value decreases (i.e., the sample darkens from the complex), but further color change over time towards darkening is negligible (Figure 2).

![Figure 2. Change of wood color coordinates L and a* after 110 days of exposure in atmospheric conditions.](image-url)
For untreated samples, a decrease in L-scale values can be noted on the graph, which indicates the beginning of an irreversible process of darkening of wood, apparently associated with exposure to UV radiation.

The values of the chromatic coordinates a* and b* of the samples treated with the complex approach the coordinates of the control wood over time, which may indicate a gradual washout of the protective composition from the wood surface (figure 3). We assume that the use of numerical values of chromatic coordinates over time in combination with strength tests will allow us to determine the durability of the developed protective composition.

The parameter of color difference or color distance ΔE, which was calculated for the samples before and after exposure to atmospheric conditions, is six times less for the treated samples (1.06) than for the control (6.41), which indicates the stability and durability of the developed protective coating.

**Figure 3.** Change of wood chromatic coordinates a* and b* after 110 days of exposure in atmospheric conditions.

The next controlled parameter was Brinell hardness. On day 110, the difference in hardness between the treated wood and the control sample is 24%, which indicates a better preservation of the surface of the pine wood samples with the applied protective composition (table 2). Highly dispersed particles of silicon dioxide attached to it give an increased hardness of the treated wood surface. The values of the strength characteristics obtained after testing in accordance with GOST show that the difference between the treated and untreated samples exceeds 20%, therefore, the samples after processing better retain their strength properties, and the resulting linear dependence suggests that the difference will persist in the further time period after 110 days (table 2).

**Table 2.** Brinell hardness and compressive strength along the fibers of the wood samples.

| Day of exposure | Control samples | Treated samples |
|-----------------|-----------------|-----------------|
|                 | HBS, MPa | Rc, MPa | HBS, MPa | Rc, MPa |
| 0               | 1.57 | 69.00 | 1.57 | 76.50 |
| 14              | 1.44 | 61.20 | 1.44 | 74.50 |
| 28              | 1.37 | 60.75 | 1.18 | 71.00 |
| 110             | 0.80 | 53.50 | 1.05 | 69.50 |

The appearances of the samples after 2 weeks and 4 month of exposure to atmospheric conditions are shown in Figure 4.
4. Summary

The results of the study confirmed that the physical and mechanical properties of pine wood can be increased due to its surface treatment with organomineral complexes based on arabinogalactan and mechanically activated polymineral sand. As a result of surface treatment of wood samples with an organomineral complex, their strength increases due to its penetration and subsequent polymerization on the walls of pores, capillaries and tracheids. In the same time highly dispersed particles of silicon dioxide, which prevail on the surface of the treated wood, give it increased hardness and resistance to UV radiation.

The results of studying the effect of the environment on the physical and mechanical properties of wood showed that the hardness and strength of the treated samples decrease less intensively than that of the control samples.

5. References

[1] Kisternaya M and Kozlov V 2012 Preservation of historic monuments in the “Kizhi” Open-Air Museum (Russian Federation) Journal of Cultural Heritage 13(3) 74–78 https://doi.org/10.1016/j.culher.2012.03.013

[2] Kisternaya M, Kozlov V, Grishina I and Leri M 2016 Tree rings as criteria for selection of timber for building of chapels in the Republic of Karelia Dendrochronologia 40 143–150 https://doi.org/10.1016/j.dendro.2016.10.002

[3] Zayats I 2015 The History of Mills in Russia in the Context of Architectural Traditions Procedia Engineering 117 696–705 https://doi.org/10.1016/j.proeng.2016.08.235.

[4] Vacca P, Caballero D, Pastor E and Planas E 2020 WUI fire risk mitigation in Europe: A performance-based design approach at home-owner level Journal of Safety Science and Resilience 1(2) 97–105. https://doi.org/10.1016/j.jnlssr.2020.08.001

[5] Yargina Z N and Yargin S V 2013 On the preservation of monuments of wooden architecture, Young scientist Molodoj uchenyj 5(52) 599–603 (In Russian)

[6] Inzhutov I, Zhadanov V, Melnikov P, Amelchugov S and Melnikova I 2019 Buildings and constructions on the base of timber for the Arctic regions E3S Web of Conference 110 01089 https://doi.org/10.1051/e3sconf

[7] Jargin S 2009 Old and New Wooden Architecture of Northern Russia Project: Architecture and urban design in Russia https://www.researchgate.net/publication/275712848_Old_and_New_Wooden_Architecture_of_Northern_Russia

[8] Voyce A 1957 National Elements in Russian Architecture Journal of the Society of Architectural Historians 16(2) 6-16 doi:10.2307/987741

[9] El-Gamal R, Nikolaivits E, Zervakis G I, Abdel-Maksoud G, Topkas E and Christakopoulos P 2016 The use of chitosan in protecting wooden artifacts from damage by mold fungi,
Electronic Journal of Biotechnology 24 70–78

[10] Hiscox J and Boddy L 2017 Armed and dangerous – Chemical warfare in wood decay communities Fungal Biology Reviews 31(4) 169–184 https://doi.org/10.1016/j.fbr.2017.07.001

[11] Teacă C-A, Roșu D, Bodirău R, and Roșu L 2013 Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements - A brief review BioRes 8(1) 1478–1507

[12] Cogulet A, Blanchet P, and Landry V 2016 Wood degradation under UV irradiation: A lignin characterization Journal of Photochemistry and Photobiology B: Biology 158 10.1016/j.jphotobiol.2016.02.030

[13] Groenier J and Lebow S 2006 Preservative-Treated Wood and Alternative Products in the Forest Service Report number 0677-2809-MTDC USDA Forest Service doi:10.13140/RG.2.1.3650.3523

[14] Hyvonen A, Piltonen P, Niinimaki J 2017 Biodegradable substances in wood protection (Ch. 5.4.) Sustainable Use of Renewable Natural Resources – From Principles to Practices University of Helsinki 200534 (e-publication)

[15] Teodorescu, Ioana & Țăpuși, Daniela & Erbasu, Ruxandra & Bastidas-Arteaga, Emilio & Aoues, Younes 2017 Influence of the Climatic Changes on Wood Structures Behaviour Energy Procedia 112 450-459 10.1016/j.egypro.2017.03.1112

[16] Kiliusheva N V, Ayzenshtadt A M, Danilov V E and Belyaev A O 2020 Modification of Wood by Organic-Mineral Complex Industrial and Civil Engineering 2 47–51 doi: 10.33622/0869-7019.2020.02.47-51

[17] Kiliusheva N V, Danilov V E, Ayzenshtadt A M and Belyaev A O 2020 Compounding and technological methods for increasing the efficiency of wood matrix mineralization Journal of Physics: Conference Series 1697 012242 doi: 10.1088/1742-6596/1697/1/012242

[18] Danilov V E, Klipa V V and Aizenshtadt A M 2020 Improvement of methods for preserving wooden structures using colorimetry as a way to control the quality of the application of a hydrophobic coating Theory and practice of increasing the efficiency of building materials: materials of the XV International scientific and technical conference Penza: PGUAS 17–23

Acknowledgments
The research was carried out on the unique scientific equipment “Physical Chemistry of Surfaces of Nano-Dispersed Systems” with the financial support of the Russian Foundation for Basic Research, Project No. 18-43-292002r_mk.