Research of Bioproof Materials at Superficial Modification of Wood

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Abstract. The mechanism and conditions of surface modification of wood by phosphorous-containing and siliceous organic compounds have been studied. Wood has the ability to absorb moisture from the air, and the moisture content of wood produces a significant effect on the physical and mechanical properties of wood. Traditional water-repellent agents of lignocellulosic materials are Organic Silicon Compounds (OSC). Our research is aimed at developing a “soft” silylation technology, in which the degree of chemical modification is negligible, and the content of chemically bound Si amounts to ~ 1%. As silylating agents, alkylhydride siloxanes, alkoxy silanes were used. From alkylhydride siloxanes, polyethylhydride siloxane (PEHS) and polymethylhydride siloxane (PMS) with different n-polymerization degrees were used. Activating hydrophilic additives were ammonium fluoride, potassium fluoride and titanates. The treatment of wood with salts, with the subsequent treatment with OSCs facilitated the penetration of OSCs into the wood while the processes of “soft” silylation proceeded. “Soft” silylation of wood with polyalkylhydride siloxanes proceeds in the presence of catalyst additives, the degree of silylation is low and depends on the nature of the additives. The dependence of distribution of OSCs in the wood on the nature of the additives is evidenced by the method of scanning electron microscopy. Phosphorous-containing organic compounds (FOC) have a high penetrating ability, while completely filling the intercellular structure of the wood. With the sequential impregnation of the wood with FOCs and OSCs, organic silicon compounds enter the intercellular space of the wood, with dense spongy OSC deposits, which in some places completely fill the internal cavities of cellular tubes of the wood. As FOC, for example, a 40% solution of trichloroethylphosphate (TCEP) was used. Decaying of wood over time starts from the surface, since there are no diffusive limitations in the sorption process. Surface modification of wood can increase its durability due to increased biological stability and hydrophobic behaviour, which will ensure a long-lasting protection. Long-lasting protection is due to the formation of covalent bonds of wood (cellulose) with a modifier. Wood samples after surface “soft” modification with FOCs and OSCs were tested for hydrophobic behaviour and biological stability. The samples were tested in the climate chamber with irrigation of the samples with water in a mode of -30°C to +40°C. To determine the hydrophobic behaviour, the limiting wetting angle was determined. The biological stability was determined by the growth of testing cultures of the fungi Aspergillus, Penicillium, Trihoderma and some others according to GOST 9.048-89. The amount of the data obtained allows to make a conclusion about the non-durable decrease in water absorption capacity during surface modification of wood with OSCs. Long-lasting biological and water resistance is achieved only in cases when surface application of OSCs is carried out on the pre-phosphorylated wood. Phosphorylation thus leads to the formation of covalent bonds. The compounds developed were successfully used for 10-15 years to preserve the monuments both of wooden architecture and the buildings and structures made of stone, bricks, and concrete.
1. Introduction
The mechanism and conditions of surface modification of wood by phosphorous-containing and siliceous organic compounds have been studied. Fundamentally new fire- and biosecurity preparations have been developed and introduced.

Wood has the ability to absorb moisture from the air, and the moisture content of wood produces a significant effect on the physical and mechanical properties of wood. When the moisture content of wood is increased by 30%, its mechanical strength is reduced by 70%. Increasing moisture content of wood leads to its decay. At the present time, due to environmental pollution, atmospheric moisture often contains acidic agents. Exterior wood structures are subject to significant hydrological destructions by virtue of the contact with acidic atmospheric moisture. Hyrophobization of wood is carried out with the help of polymers and organic silicon compounds, whereas the effect of hygroscopicity reduction is due to the blocking of hydroxyl groups, the filling of the capillary porous structure of the wood, as well as the change in the cross-link density of the ligno-carbohydrate matrix. However, with a significant content of polymer in the wood, the density of the polymer network is violated, which leads to deterioration of the material properties and sometimes to a spontaneous destruction [1-10].

2. Materials and methods
Traditional water-repellent agents of lignocellulosic materials are Organic Silicon Compounds (OSC). To create a sustainable effect of hydrophobization, it is necessary to carry out silylation of wood. Wood impregnation with OSC presents certain difficulties, since OSCs are water-repellent agents. Impregnation is carried out by vacuum-pressure method, hot and cold bath method with a temperature difference of 15°C to 20°C, with impregnation duration of at least 7 hours. These impregnation methods involve a large consumption of materials and are energy-intensive.

Our research is aimed at developing a “soft” silylation technology, in which the degree of chemical modification is negligible, and the content of chemically bound Si amounts to ~ 1%. As silylating agents, alkylhydride siloxanes, alkoxy silanes were used. To facilitate the penetration of OSCs into the wood, various hydrophilic additives were used, which at the same time had to reduce the activation energy of the silylation reaction, so as to convert silylation into a “soft” mode.

From alkylhydride siloxanes, polyethylhydride siloxane (PEHS) and polymethylhydride siloxane (PMS) with different n-polymerization degrees were used. Activating hydrophilic additives were ammonium fluoride, potassium fluoride and titanates [11-13].

3. Results and discussions
The treatment of wood with salts, with the subsequent treatment with OSCs facilitated the penetration of OSCs into the wood while the processes of “soft” silylation proceeded (Table 1).

The degree of OSC polymerization produces a little effect on the hydrophobic behaviour of wood. The nature of the alkyl radical with the silicon atom CH3 (PMS), C2H5 (PEHS) also does not affect water absorbing capacity of the silylated wood.

As can be seen from Table 1, “soft” silylation of wood with polyalkylhydride siloxanes proceeds in the presence of catalyst additives, the degree of silylation is low and depends on the nature of the additives. The dependence of distribution of OSCs in the wood on the nature of the additives is evidenced by the method of scanning electron microscopy. In the treatment of wood with OSCs (10% solution of methyl-tripropoxysilane in toluene), a slight deposition of the product in the marginal area of bordered pores is observed. Modification with the use of poly-butyl titanate (PBT) leads to the accumulation of a small amount of polymer in the intercellular space with the formation of a film polymer mass in the form of folds. In the presence of fluorides (NH4F, KF, CsF), polymeric deposit has a completely different appearance, with the capillary-porous structure of the wood being filled most completely.
Table 1. Data for physical chemistry methods of analysis of IR-spectroscopy

| OSC         |PROCESS ACTIVATES the additive-catalyst | Si, % | Data for physical chemistry methods of analysis of IR-spectroscopy | Measurement of water absorption in n times over 30 days |
|-------------|----------------------------------------|-------|---------------------------------------------------------------|-----------------------------------------------------|
| PMS -20 PBT |0.63                                    |0.61  |There are absorption bands                                      |1.84 1.50                                           |
|             |0.44                                    |       | (2150 cm⁻¹)                                                   |1.36                                               |
|             |0.31                                    |       | (1050 cm⁻¹)                                                   |0.98                                               |
| PMS -200 PBT|0.31                                    |0.98  |                                                                |                                                    |
|             |-                                       |       | (1100 cm⁻¹)                                                   |                                                    |
| PMS - 1000 PBT |0.68                                    |0.56  |                                                                |                                                    |
|             |0.16                                    |0.16  |                                                                |                                                    |
| PEHS        |0.16                                    |0.16  |                                                                |                                                    |
|             |0.20                                    |0.20  |                                                                |                                                    |
| PMS -20 - 0 PEHS |0.16                                    |0.16  |                                                                |                                                    |
| PEHS        |0.16                                    |0.16  |                                                                |                                                    |

The most interesting results were obtained using sequential phosphorylation and silylation in “soft” conditions. Phosphorous-containing organic compounds (FOC) have a high penetrating ability, while completely filling the intercellular structure of the wood. With the sequential impregnation of the wood with FOCs and OSCs, organic silicon compounds enter the intercellular space of the wood, with dense spongy OSC deposits, which in some places completely fill the internal cavities of cellular tubes of the wood. As FOC, for example, a 40% solution of trichloroethylphosphate (TCEP) was used, and alkoxy-silanes as OSC. Wood and TCEP interaction be represented by the following scheme (figure 1)

Figure 1. Wood and TCEP interaction

The evolution of p-chloroethyl alcohol during the reaction was proved. When cellulose (wood) was treated sequentially with TCEP and then with methyl-tripropoxysilane (MTPS), the propyl alcohol was determined by gas-liquid chromatography, as shown in Table 2.

Table 2. Content of liquid components in the reaction mixture Treated TCEP cellulose – MTPS

| t, h | Exhalation C₃H₇OH, % (a) | Consumption CH₃-Si(OCH₃H₇)₃, % (b) | a/b |
|------|-------------------------|------------------------------------|-----|
|      |                         | Temperature 50°C                    |     |
| 1    | 0.02                    | 0.01                               | 2.0 |
| 2    | 0.04                    | 0.02                               | 2.0 |
| 3    | 0.06                    | 0.03                               | 3.0 |
| 4    | 0.08                    | 0.03                               | 2.6 |
| 5    | 0.10                    | 0.04                               | 2.5 |
| 6    | 0.13                    | 0.05                               | 2.6 |
| 7    | 0.14                    | 0.05                               | 2.8 |
The material balance of the silylation reaction of cellulose modified with TCEP and MTPS at temperatures of 50°C, 60°C and 80°C shows (Table 2) that when one MTPS molecule is consumed, about three molecules of propyl alcohol are released. This indicates that all three MTPS propoxy groups participate in the reaction with OH groups of cellulose.

The cumulative results obtained in the study of the reaction of silylation of cellulose pretreated with TCEP suggests that during the subsequent modification of cellulose with FOCs and OSCs the coordination of OSCs takes place with the formation of an intermediate comprising coordination of the type =P:->Si= of the functional groups of OSCs with the cellulose OH groups.

Decaying of wood over time starts from the surface, since there are no diffusive limitations in the sorption process. Surface modification of wood can increase its durability due to increased biological stability and hydrophobic behaviour, which will ensure a long-lasting protection. Long-lasting protection is due to the formation of covalent bonds of wood (cellulose) with a modifier.

Wood samples after surface “soft” modification with FOCs and OSCs were tested for hydrophobic behaviour and biological stability. To determine the hydrophobic behaviour, the limiting wetting angle was determined. The biological stability was determined by the growth of testing cultures of the fungi Aspergillus, Penicillium, Trihoderma and some others according to GOST 9.048-89. The data is presented in Table 3.

### Table 3. Wood samples after surface “soft” modification

| FOC | OSC | wetting angle (°) | Water absorption d₀ for 30 days, % | Resistance to fungi according to GOST 9.048-89 |
|-----|-----|------------------|----------------------------------|-----------------------------------------------|
| Control sample | - | 38,8 | 200 | - |
| TCEP | - | 32,8 | 180 | + |
| EHS | 125,5 | 120 | + |
| TES | 129,7 | 103 | + |
| MTES | 129,7 | 111 | + |
| MTBS | 131,1 | 104 | + |
| PMS | 126,1 | 80 | + |
| TCP | - | 39,9 | 190 | - |
| EHS | 120,7 | 118 | - |
| TES | 117,4 | 125 | - |
| MTES | 119,4 | 106 | - |
| MTBS | 118,1 | 108 | - |
| PMS | 116,1 | 90 | - |
TCP – tricresyl phosphate; EHS – ethylhydride siloxane; TES – tetraethoxysilane; MTES – methyltriethoxysilane; MTBS – methyltributoxysilane; PMS – sodium methylsiliconate.

The samples were tested in the climate chamber with irrigation of the samples with water in a mode of -30°C to +40°C. Reference samples of wood, as well as the samples modified only with OSCs or TCP and TCPs+OSCs, become overgrown after exposure in the climate chamber to the colonies of Penicillium and Aspergillus fungi over a large area. On the samples treated with TCEP, and then with various OSCs, a decrease in water absorption capacity of 2-2.5 times and good biological stability were observed. Modification of wood only with OSCs does not make it biologically stable [14-17].

4. Conclusions
The amount of the data obtained allows to make a conclusion about the non-durable decrease in water absorption capacity during surface modification of wood with OSCs. Long-lasting biological and water resistance is achieved only in cases when surface application of OSCs is carried out on the pre-phosphorylated wood. Phosphorylation thus leads to the formation of covalent bonds.

The study made it possible to create a number of compositions that, when being used for surface modification of wood, ensure its biological stability for a long period of time. The biosecurity composition Mipor (TU 2435-001-47366993-01) and the fire-protective compound MGSU (TU 2435-002-02066523-2005) were certified for biological and fire resistance, as well as for environmental safety.

The compounds developed were successfully used for 10-15 years to preserve the monuments both of wooden architecture and the buildings and structures made of stone, bricks, and concrete. In the Kizhi museum preserve, wooden barns located near the Chapel of Three Hierarchs and Alexeyev's house were treated. In Holy Trinity-Saint Seraphim-Diveyevo Monastery of nuns, the compositions were used for restoration of the wooden structures of the archiepiscopal hotel. In the Trinity Lavra of St. Sergius the ground floor of the Refectory church, the dossal area of the Holy Trinity Cathedral, the rooms of the Hospital Chambers, etc. were treated with the compositions. In addition, a number of churches in Moscow and Nizhny Novgorod, as well as the wooden structures of the memorial house of P.I. Tchaikovsky in Klin were treated. Long-term observations of these objects confirm the high efficiency of the use of the compositions developed to preserve the monuments of wooden architecture.

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