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Study of antiseptic properties of the flame retardant solution provided by oxidized plant waste with regard to wood staining and mold micromycetes

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Abstract. Antiseptic properties of the obtained aqueous solution of pine wood flame retardant with regard to 25 types of micromycetes have been evaluated. It was shown that aqueous flame retardant solution suppressed actively such species as *Aspergillus terreus* Thorn., *Discula pinicola* (Naumov) Petr., *Leptographium fungi lundbergii* Lagerb. & Melin, *Penicillium purpurogenum* Stoll., *Paecilomyces variotii* Bainier. The obtained solution of flame retardant in concentration below than 3% showed that the average affected area for all tested groups of fungi was 50.4%. Therefore, this flame retardant solution was attributed to the medium effective antiseptic agent for pine wood.

Wood is widely used in industry as a structural material for the construction of residential, public, industrial, agricultural, livestock, storage and other buildings and structures, as well as in transport infrastructure. In the northern and northeastern climatically cold regions of the country rich in forests, the construction of timbered buildings and structures (mainly in small towns and rural settlements) is still popular. Current trends in the global construction industry indicate that not only one- and two-storeyed building objects can be built from wood (townhouses and individual cottages, agricultural buildings, religious and other objects), but also buildings of apartment and multi-storey houses, hotels and restaurants, shops and offices. This practice is quite dynamic in a number of European countries, Australia, USA and Canada. According to the forecast in the near future low-rise wooden construction could be one of the most promising construction areas in the world. In the near future, the national programs of the countries of the European Union are aimed at ensuring the share of wooden houses at 75–80% in low-rise housing stock. The average annual growth rate of demand for wood is expected to be in the range of 20–25% until 2020 [1].

Wooden buildings and structures have a high fire risk. The process of burning wood is complex, multistage, and takes place in a wide range of temperatures [2].

To prevent fires in buildings and structures with bearing and enclosing structures, as well as finishing and veneering materials made of wood, flame retardants are used. Flame retardants differ in



the method and quantity of application parameters and the fire protection mechanism. It should be noted that the development of fire protection products and their use are currently reduced, as a rule, to a decrease in the flammability of wood material.

The fire resistance of the wood element is increased with the use of fire-resistant structural panels or fire-retardant intumescent coatings. The effectiveness of wood protection depends on the thickness and durability of coatings. Therefore, fire protection for wood can be developed in two groups: (1) flame retardants, reducing the spread of flame on the surface and (2) refractories, reducing the rate of charring.

Currently, for fire protection of natural wood, such methods as surface and deep impregnation with special compositions containing flame retardants, as well as the application of fire retardant coatings are popular [3].

Intumescence or swelling in the process of burning on the surface occurs under the action of simultaneous foaming and carbonization of the burning material. Intumescent additives are considered to be environmentally friendly fire retardants, due to the practical absence in the environment of highly toxic combustion products [4]. Since the first intumescent coatings (materials) were patented in 1938, the mechanism of fire protection through the formation of coke-forming foam has been explained in terms of the insulating barrier action between the flame and the surface of the material exposed to temperature and combustion.

Particularly attractive is the use of thin layer of intumescent fire retardant coatings. Even when they are relatively thin, they demonstrate high efficiency of fire protection and allow the use of modern mechanized methods of application on the protected item, while maintaining the basic texture of wood and its aesthetic appearance.

Surface impregnation, with its cheapness and manufacturability, is less effective than deep impregnation, but it allows, by wetting the surface with compounds, to protect assembled wooden structures directly on construction sites. To obtain reliable fire protection of wood in a similar way is extremely difficult. This is largely due to the weak penetration of the flame retardant salts into the wood structure. In this regard, to achieve the required performance of flame retardant efficiency requires a high consumption of the composition. Deeper penetration of the fire retardant solution into the surface layers of wood is provided by hot-cold baths, as well as processing in industrial apparatuses — autoclaves in the mode of successive increase in pressure or alternation of vacuum and increased pressure (vacuum impregnation). A number of technological difficulties, the need for a large consumption of flame retardants, the need for special equipment for conducting deep wood impregnation with flame retardants limit the practical use of this method of fire protection on a scale smaller than industrial. At present, a large number of flame retardant impregnating compositions for wood have been developed, which differ from each other in different sets of quantitative combinations of low molecular weight inorganic substances and derivatives of organic compounds exhibiting the properties of flame retardants.

A relatively new direction in the creation and study of flame retardants is the creation of environmentally-friendly flame retardants created from waste that do not represent food or feed value, which can not only solve the problem of creating new materials with valuable properties, but also simultaneously solve the environmental problem of recycling ballast high-tonnage products.

Lignin [5] and lignin-containing wastes that are difficult to biodegrade and accumulate as byproducts of paper production and wood hydrolysis, as well as due to its wide distribution in nature, can be used as such production wastes.

In the case of using woodworking waste as a lignin-containing substrate, for example, sawdust, a complex action flame retardant is obtained, combining the properties of a radical chain inhibitor with the properties of an intumescent (coke-forming) flame retardant that is formed during oxidation of carbohydrate-containing products, for example, starch [6]. The mechanism of its flame retardant action is associated with the formation on the treated surface during high-temperature heating or with the direct action of a foamed coke layer flame. The foamcoat layer exhibits a heat-shielding and barrier effect during mass transfer of both combustible materials to the flame reaction zone and

oxygen of the air to the material surface. It has been experimentally confirmed that flame retardants based on lignin-containing woodworking waste substrates are effective representatives of a new class of intumescent flame retardants [7,8].

However, there is no information in modern literature on the antiseptic properties of such compounds, which determine the performance characteristics of wood-treated materials with fire retardants.

The purpose of this work was to study the antiseptic properties of the flame retardant solution.

To obtain a flame retardant solution with excellent intumescent properties, both the qualitative and quantitative composition of the initial combined substrate is important. Of the possible starch-containing components, the use of crushed rice grains is optimal, since allows you to get the final product with the best consumer properties. From the point of view of economic feasibility, it is preferable to use unsuitable products - substandard rice grain with expired or food production waste containing rice. Experiments have shown that the best result is achieved by using as a lignocellulosic component of the combined substrate wood flour of coniferous species, and not sawdust.

The viscosity of the final product and the technological conditions of oxidation depend on the total amount of substrate introduced into the reaction, which is chosen empirically depending on the specific characteristics of the feedstock. Experiments on the selection of oxidation conditions showed that the use of the initial mixtures containing 20 - 22% of the mass. oxidizable substrate allows the reaction under optimal conditions, and the final product obtained after filtration is an aqueous composition containing a mixture of products of the joint oxidation of the combined substrate, suitable for use as a flame retardant without further concentration and purification. During bulk processing of samples, it easily penetrates into the pores of the material, and upon surface treatment it exhibits good adhesion to the surface and, after drying in air, forms a durable, almost transparent coating that preserves the natural appearance of the treated wooden surface.

The flame retardant solution is synthesized by the method of liquid-phase catalytic oxidation of the mixture (crushed rice - wood flour) in an alkaline medium. Gaseous oxygen is used as an oxidizer.

The synthesis is in a steel, hermetic reactor. The temperature of the oxidation process is 75 °C. The reaction time was controlled by changing of the solution pH and was 10 hours. The resulting solution was filtered on a nylon filter. The oxidation process is single-stage and waste-free. The flame retardant solution is environmentally friendly, as the products of combustion are no more toxic than the products of combustion of wood and / or cereals.

The joint oxidation of these products leads to a non-additive effect due to the fact that during the joint oxidation of starch-containing and lignocellulosic substrates a complex mixture is formed, including salts of polyoxycarboxylic acids and polyoxyphenolic compounds, low molecular weight hydroxyphenol compounds, etc., as well as their interaction products. Compared with protective coatings containing monosubstrate oxidation products, the coating formed when wood is processed with a synthesized fire retardant solution not only has intumescent flame retardant properties, but is also more resistant to external climatic factors due to the formation of additional chemical crosslinks on the surface of the material. An additional factor contributing to the preservation or improvement of the strength characteristics of fire-protected material is the good penetration of the flame retardant into the wood. Moreover, in addition to forming a surface coating, products formed during the process of joint liquid-phase catalytic oxidation of a mixture of starch-containing and lignocellulosic products diffuse into the wood and form additional hydrogen bonds in the microfibrillar structure of cellulose fibers and the porous structure of lignin. The result of the formation of such weak bonds is the physical hardening of the wood structure.

Studies of the antiseptic properties of the obtained flame retardant solution were carried out on samples of wood with dimensions of 10 × 55 × 75 mm, where the last dimension is indicated along the length of the fibers. Samples were made of straight-layer freshly sawn wood of sapwood with a density of 0.48-0.52 g/cm³ in the air-dry condition.

To study the antiseptic properties, studies have been carried out on the effectiveness of the flame retardant solution with respect to wood-staining and mold fungi. Samples of wood (pine) were

impregnated with flame retardant by immersion in the solution. The average consumption of flame retardant was 261.9 g /m². Beyond that, for fifteen days, wood samples (10 × 55 × 75 mm) were kept in wet chambers using the “closed space - moisture reserve” principle with a large evaporation surface, under conditions most favorable for the activity of biological agents (mold fungi), with the subsequent determination of the average area of damage to the surface of the samples and the stage of development of the microorganism.

The tests were carried out on micromycetes, composed in three groups and presented by the following species (table 1). Part of the work, including reseeded, cultivation, storage of strains of microorganisms, was performed using the equipment of State collection of phytopathogenic microorganisms and identifying varieties (differentiators) of pathogenic microorganism strains based in All-Russian Research Institute of Phytopathology (<http://www.vniif.ru/vniif/page/ckp-gkmf/1373>).

When conducting the experiment used a suspension of spores obtained from pure cultures of fungi grown in bacteriological tubes on beveled agar wort. For the preparation of a spore suspension, cultures of fungi aged from 14 to 28 days were used, counting from the time of subculture, whose colonies filled the entire surface of the agar and had well-developed sporulation.

The spore suspension was prepared separately for each species of fungus by washing off the spores into chemical beakers containing 25 cm³ of distilled water. The number of fungal spores in the suspension was calculated using a Goryaev counting chamber. The concentration of spores in suspension was $(N \pm 0.001) \cdot 10^6$ spores/ml. Next, they prepared a working suspension of fungi to infect sawdust in desiccators, taking into account the concentration of spores by mixing suspensions of certain types of fungi belonging to a certain group. To prepare a working suspension, a calculated amount of individual species of fungi was taken from each suspension in order to ensure the content of 106 spores (or 1 million spores) in a calculated volume of 1 ml. Measured volumes of suspensions of each species of fungus were introduced into a beaker and made up to (100 ± 1) ml with distilled water. The shelf life of the suspension did not exceed 1 hour from the moment of preparation.

For each variant of the test (group of fungi 1,2,3 according to table 3) a separate desiccator was prepared (a total of three desiccators - 1E, 2E, 3E). In the desiccators, sterile sawdust ($80 \pm 5\%$) sawdust from healthy pine saplings was filled up to 1/4 of the vessel's height. A suspension of fungi of a certain group was introduced into each desiccator (1E-1, 2E-2, 3E-3). Sawdust was irrigated with a working suspension of fungi with a volume of 100 ml using a spray bottle. The desiccators were closed with a ground-in lid and placed in a room at room temperature, in the dark. The growth of mycelium continued for 15 days from the start of the test.

Table 1. List of mold fungi cultures used in the experiment

№	Name of micromycete species
1 group	
1	<i>Alternaria humicola</i> Oudem.
2	<i>Aspergillus niger</i> Tiegh.
3	<i>Aspergillus terreus</i> Thorn.
4	<i>Fusarium moniliforme</i> J. Sheld.
5	<i>Fusarium sporotrichiella</i> var. <i>poae</i> (Perk.) Bilai.
6	<i>Penicillium brevicompactum</i> Dierckx.
7	<i>Penicillium chrysogenum</i> Thorn.
8	<i>Penicillium ochrochloron</i> Biourge.
9	<i>Cadophora fastigiata</i> Lagerb. & Melin. [= <i>Phialophora fastigiata</i> (Lagerb. & Melin) Conant.]

№	Name of micromycete species
2 group	
1	<i>Aspergillus hennebertii</i> Blochwitz.
2	<i>Cladosporium cladosporioides</i> (Fresen.) G.A. de Vries.
3	<i>Cladosporium herbarum</i> (Pers.) Link.
4	<i>Discula pinicola</i> (Naumov) Petr.
5	<i>Exophiala jeanselmei</i> var. <i>heteromorpha</i> (Nannf.) de Hoog.
6	<i>Fusarium javanicum</i> Koord.
7	<i>Fusarium merismoides</i> Corda.
8	<i>Paecilomyces marquandii</i> (Masse) S. Hughes.
9	<i>Paecilomyces variotii</i> Bainier.
3 group	
1	<i>Alternaria tenuis</i> Nees.
2	<i>Aspergillus amstelodami</i> Thorn & Church.[= <i>Eurotium amstelodami</i> L. Mangin]
3	<i>Aureobasidium pullulans</i> var. <i>pullulans</i> (de Bary) G. Arnaud.
4	<i>Fusarium culmorum</i> (W.G.Sm) Sacc.
5	<i>Leptographium lundbergii</i> Lagerb. & Melin.
6	<i>Penicillium purpurogenum</i> Stoll.
7	<i>Trichoderma harzianum</i> Rifai.

Then the prepared wood samples were installed in special stands with external dimensions of $60 \times 94 \times 28$ mm and three grooves with dimensions of $22 \times 60 \times 15$ mm. Then, in each of the desiccators in the peripheral zone, at three equal intervals, three supports were placed, on which 6 samples were placed, protected by a protective agent of the same concentration, and two control samples (without impregnation with a protective agent). In total, 18 samples (6 for each of the three groups of fungi) were tested for each variant of the experiment.

The area of damage to the surfaces of the samples by fungi (%) or the state of the samples was assessed visually after 5, 10, 15 days using the “palette” method with a grid step of 5x5 mm.

The assessment of the current state of the samples was recalculated for the average area of fungal damage relative to the area of a rectangular parallelepiped or sample (in percent). The following results are obtained defeat the samples:

- group 1 - on the 5th day: in the experiment - 0%, in the control - 3%; for 10th day: in experience - 3-11%, in control - 27-41%; for 15th day: in the experience - 44-82%, in the control - 40-49%;
- group 2 - for 5th days: in the experiment - 0%, in the control - 0%; for 10th day: in the experience - 7-15%, in the control - 3-15%; for 15th day: in the experience - 31-49%, in the control - 33-77%;
- group 3 - for 5th days: in the experiment - 0%, in the control - 0%; for 10th day: in experience - 1-10%, in control - 1-17%; for 15th day: in the experience - 29-69%, in the control - 65-94%.

In the course of the research, the antipyrene solution actively suppressed such species of fungi as *Aspergillus terreus* Thorn., *Discula pinicola* (Naumov) Petr., *Leptographium lundbergii* Lagerb. & Melin, *Penicillium purpurogenum* Stoll., *Paecilomyces variotii* Bainier.

The effectiveness of the test flame retardant solution was equal in the case of a flame retardant solution concentration of less than 3% - the average lesion area for all test groups of fungi was 50.4%, so the product can be attributed to medium-effective antiseptics.

As a result of research, it was found that in order to prevent wood materials treated with synthesized flame retardants from being infected by wood-dyeing and mold fungi the additional treatment with antiseptic agents is not required.

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