Effectiveness of the flame retardant antiseptic properties from plant waste against fungi on alnus glutinosa

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Abstract. The purpose of the research was to study the antiseptic properties of flame retardants. Our studies have shown that Alnus glutinosa wood is highly susceptible to staining. It should be noted that it is possible to distinguish species diversity in the work of antipyrene against the development of fungi. However, this requires deeper scientific research with the change of numerous factors, to reflect the natural conditions of the passage of industrial wood. Studies have shown that the biological effectiveness of the obtained antipyrene solutions reaches up to 88.3% under laboratory conditions. The obtained data allow to judge about the prospects of the direction of innovative use of waste and wood protection.

Wood substance is a construction material for the building of residential, public, industrial, agricultural, livestock, storage and other edifices. This practice is developing quite fast-moving in a number of European countries, Australia, the USA and Canada. The average annual growth rate of demand for wood materials is expected to be in the range of 20–25% by 2020 [1].

Currently, for fire protection of natural wood, such methods as surface and deep impregnation with special compounds containing flame retardants, as well as the application of fire retardant coatings are popular [2 - 13].

In 2000-2015, the development of flame retardants based on biopolymers became widespread [14-17]. Thus, biological substances (fumaric acid [18], phytic acids [19, 20], chitosan [19, 21], sorbitol xylitol [22], cyclodextrin [22, 23], starch [22, 24-28]. Thus, biological substances (fumaric acid [18], phytic acids [19, 20], chitosan [19, 21], sorbitol xylitol [22], cyclodextrin [22, 23], starch [22, 24-28]) are used for the development of intumescent systems.

A new direction in the field of safe export and use of wood substance is the creation and study of fire retardants with antiseptic properties. Environmentally-safe property gives such fire retardants additional benefits. Created from wastes that do not represent food or feed value, fire retardants allow not only to solve the problem of creating new materials with valuable properties, but at the same time to solve the environmental problem of disposing of ballast high-tonnage products [29].
As such production wastes it is possible to use lignin [30] and paper production wastes and wood hydrolysis. A large number of flame retardant compositions and technologies in which lignin is used as an auxiliary component, for example, as a binder [31 - 33], surfactant [34], lightweight filler [35], dispersing agent and emulsifier [36] and others.

It should be noted that the use lignosulfonate and other unmodified lignin containing waste, does not allow for creation of effective flame retardants, and sometimes leads to the opposite phenomenon, contributing to the development of the flame. To obtain effective lignin-based flame retardants, it is advisable to use lignin-containing wastes subjected to chemical modification [29].

Brominated sulfogel, in the form of an aqueous or alkaline solution can be used for surface treatment or impregnation of combustible materials. Transformation at elevated temperatures forms dioxins, which prevents the use of this product due to environmental insecurity [37].

The basis of the biomass flame retardant properties of antipirene is the chemical structure of oxidized lignin-containing wastes consisting of phenol-containing structures. Phenol derivatives, being one of the most powerful inhibitors of oxidation processes, interact with free radicals of the branched chain reaction of combustion and block the development of the chain process [40]. The resulting flame retardant can be used in the superficial method of processing by spraying and with the introduction of the dry mixture as a composite additive.

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 (carbon forming) flame retardant, which, according to the invention [41], is formed during oxidation in similar conditions of carbohydrate-containing products, including cellulose. 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 carbide layer flame. The coked cellular material 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.

Oxidized starch reagents, as well as oxidized lignin, can be used as effective flame retardant impregnations, flame retardants in the manufacture of various polymeric materials based on water-soluble polymers and latexes, as well as in extinguishing fires. The oxygen index values for various types of paper, sawdust and synthetic materials showed that the oxygen index in all cases exceeds 25% and sometimes 40% [42].

We have not found a scientific description of research aimed at studying the antiseptic properties of flame retardants in the literature.

The purpose of this study was to study the antiseptic properties.

The original flame retardant solution for research was obtained by our team according to the procedure described in [38, 39]. Conducted studies on the flammability of wood samples (150×60×30 mm) showed that the samples treated with a flame retardant solution lose a mass of 5-8% when exposed to an open flame for 2 minutes. It was established that the mass loss depended on the flow rate and the type of impregnation.

To research the antiseptic properties, studies have been carried out on the effectiveness of the flame retardant solution with respect to wood-staining and mold fungi. Wood samples (European black alder (Alnus glutinosa (L.) Gaertn. [X23]) were impregnated with a fire retardant solution. The average flame retardant consumption was 261.9 g/m2.

The main research methodologies consisted of a fifteen-day exposure of wood samples (10×55×75 mm) in wet chambers (a desiccator model with a diameter of 115 - + 5 mm; a depth of 54 - + 3 mm), operating according to the «closed space - moisture reserve» principle with large evaporation surface. Such conditions were created for better growth and development of mold and wood-coloring fungi. After 15 days, an analysis was carried out (definitions: microbial development, area occupied on the sample surface, depth of penetration into the alder; stages of microbial development), compilation of measurement tables and analytics of the materials obtained.

Tests were carried out on fungi, fire retardants were used in three concentrations (groups), all study designs for points, types of fungi and control options are presented in Tables 1 and 2. Part of the work,
including reseeding, cultivation, storage of strains of microorganisms, was performed using 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).

For each variant of the study, a separate desiccator was prepared, the placement of which was carried out in the conditions of a common use center at the Artificial-climate laboratory at the All-Russian Research Institute of Phytopathology (http://vniif.ru/vniif/center-cku/). Sterile moistened (80±5%) sawdust from healthy sapwood of alder at 1/4 of the height of the vessel was filled into desiccators. A suspension of fungi was introduced into each desiccator (which was increased in the conditions of a common use center State collection of phytopathogenic microorganisms and identifying varieties (differentiators) of pathogenic microorganism strains based in All-Russian Research Institute of Phytopathology (http://vniif.ru/vniif/page/). 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 a temperature of 21-24°C in the dark. The growth of mycelium was performed for 15 days.

Assessment of the stage of development of fungi on the samples was carried out on a 6-point scale, taking into account the characteristics (consolidated requirements of all-Union State Standard, the generally accepted international system of prevalence and development of plant diseases, trees in points), are given in Table 1.

Table 1. Scale for assessing the stage of fungi development per samples

| Rating | Stage of fungi development |
|--------|----------------------------|
| 0      | absolutely clean samples by visual inspection and under a microscope |
| 1      | visually clean samples; under a microscope small foci are visible in the form of stains of wood-staining or mold fungi (with a total coverage of > 0 to 25%); the stage of sporulation is absent; superficial development of mycelium of wood-coloring or mold fungi in the form of spots (with a coverage of > 25 to 50%); the stage of sporulation is absent; plentiful growth of mycelium of wood-dyeing or mold fungi (coverage area > 50-75%); the beginning of sporulation stage; clearly visible growth of fungi by visual inspection (coverage area 75-90%); various stages of wood-coloring or mold fungi sporulation; deep damage by wood-painting or mold fungi of the entire sample area (coating > 90-100%); intensive sporulation. |

The effectiveness of the concentrations (3; 6 and 9%) of the investigated fire retardant solution was selected in agreement with physicochemical, chemical and biological characteristics according to the methods and conditions of preparation [38, 39]. In particular, to create the studied low-cost environmentally safe effective biomass-based flame retardant (lignin-containing waste from wood processing), it is necessary to use a mixture of oxidation products of the original substance. In the process of liquid-phase oxidation of a lignin-containing substrate in an alkaline medium at a temperature not exceeding 90°C, a mixture of oxidation products is formed. They contain a solid residue insoluble in water and organic solvents of mineral products of destruction of lignin-containing substrates and the liquid fraction used as a flame retardant. The liquid fraction includes: a) salts of polyhydroxyphenolic compounds, which are products of incomplete oxidative depolymerization of lignin, as well as secondary condensation products of low-molecular compounds formed during the oxidation of lignin-containing substrates; b) low molecular weight hydroxyphenolic compounds formed during the oxidation of lignin-containing substrates; c) hydrocarbons. The oxidation can be carried out in the presence of catalysts, or without them under the action of air, oxygen, ozone or hydrogen peroxide. Physicochemical properties are described in more detail [38, 39].
In the Russian forests naturally grows from various sources of 15 of the 50 known species of the genus alder (Alnus, Betulaceae). The most common – European black alder (A. glutinosa (L.) Gaertn.), grey alder (A. incana (L.) Moench), Siberian alder (A. sibirica (Fisch)). The total area of alder forests in the European part of Russia is about 1.6 million hectares, with a timber reserve of more than 170 million m3, including black alder forests - 1.0 million hectares with a reserve of 110 million m3, the rest of the forests are mostly grey alder forest [43]. The dynamic issues of afforestation and the use of industrial wood are diverse in terms of phytosanitary condition such as production, technological preparation (harvesting), «wood ripening», bringing it to the required condition by technological methods [44, 49]. Nevertheless, new pathogens appear in the decade, while the relevance internationally in the commercial quality of wood is also confirmed [50]. In our opinion there is a perspective of preservation of the received wood from defeat by wood-painting or wood-destroying fungi.

However, the choice of remedies in the «List of permitted pesticides and agrochemicals in the territory of the Russian Federation» is very poor. The topical issues are the search for suitable methods, ways to protect the industrial wood, accumulated «wealth» from the loss of quality of industrial wood Alnus glutinosa.

Results.
Studies have established that Alnus glutinosa wood is highly susceptible to staining, and not all genera have successfully manifested themselves.

Table 2. The growth and development of fungi, depending on the concentration of flame retardant (2018)

| № | Research Option                                               | Prevalence, % | Development, % |
|---|---------------------------------------------------------------|---------------|----------------|
| 1 | Control (wood samples with water, micromycetes)               | 83,3          | 70,8           |
| 2 | Control (wood samples)                                        | 0             | 0              |
| 3 | Control (wood samples with micromycetes without water)        | 83,3          | 20,8           |
| 4 | Control (wood samples with water without micromycetes)        | 33,3          | 8,3            |
| 5 | Aspergillus hennebertii Blochwitz.                            | 100           | 66,7           |
| 6 | Aspergillus niger Tiegh.                                     | 100           | 50             |
| 7 | Aspergillus amstelodami Thorn & Church.[=Eurotium amstelodami L. Mangin] | 100           | 50             |
| 8 | Aspergillus terreus Thorn.                                    | 100           | 45,8           |
| 9 | Penicillium brevicompacturn Dierckx.                          | 100           | 79,2           |
| 10| Penicillium chrysogenum Thorn.                                | 100           | 79,2           |
| 11| Penicillium ochrochloron Biourge.                             | 100           | 79,2           |
| 12| Penicillium purpurogenum Stoll.                               | 100           | 70,8           |
| 13| Control (wood samples)                                        | 0             | 0              |
| 14| Control (wood samples with micromycetes without water)        | 50            | 12,5           |
| 15| Control (wood samples with water without micromycetes)        | 33,3          | 8,3            |
| 16| Aspergillus hennebertii Blochwitz.                            | 100           | 37,5           |
| 17| Aspergillus niger Tiegh.                                     | 100           | 45,8           |
| 18| Aspergillus amstelodami Thorn & Church.[=Eurotium amstelodami L. Mangin] | 100           | 41,7           |
| 19| Aspergillus terreus Thorn.                                    | 100           | 37,5           |
| 20| Penicillium brevicompacturn Dierckx.                          | 100           | 29,2           |
| 21| Penicillium chrysogenum Thorn.                                | 100           | 54,2           |
| 22| Penicillium ochrochloron Biourge.                             | 100           | 58,3           |
| 23| Penicillium purpurogenum Stoll.                               | 100           | 45,8           |
Concentration 9 %

|   |                                    |     |     |
|---|-----------------------------------|-----|-----|
| 24 | Control (wood samples)            | 0   | 0   |
| 25 | Control (wood samples with micromycetes without water) | 33.3 | 8.3 |
| 26 | Control (wood samples with water without micromycetes) | 33.3 | 8.3 |
| 27 | Aspergillus hennebertii Blochwitz | 100 | 33.3|
| 28 | Aspergillus niger Tiegh.          | 100 | 29.2|
| 29 | Aspergillus amstelodami Thorn & Church. [=Eurotium amstelodami L. Mangin] | 100 | 33.3|
| 30 | Aspergillus terreus Thorn.         | 100 | 25  |
| 31 | Penicillium brevicompactum Dierckx.| 100 | 41.7|
| 32 | Penicillium chrysogenum Thorn.     | 100 | 37.5|
| 33 | Penicillium ochrochloron Biurge.   | 100 | 49.7|
| 34 | Penicillium purpurogenum Stoll.    | 100 | 33.3|

At an antiseptic concentration of 3%, the average affected area of Alnus glutinosa is different for all the tested variants. At the same time, Alnus glutinosa is affected differently in the control variants, creating an essential composition of materials for probit analysis. The prevalence of fungal infection in all application options for the selected fungi on Alnus glutinosa was around 100%. 15 days of growth and development of fungi gave the results. The qualitative indicator of the development of fungi differed significantly. According to studies, our observations found obtaining 4 points for fungal infection. Concentrations significantly altered scoring by fungi.

Efficiency was not considered a control option (wood samples) as the development of fungi did not occur there.

Biological effectiveness from the two controls is given sequentially through a semicolon for each concentration.

Comparison of the development of fungi with application (of all of the studied representatives in the form of a total solution) showed a greater growth of the development of fungi with a decrease in fire retardant concentration. In particular, at 3% development reached 20.8% (biological effectiveness 70.6%); at 6% 12.5% (biological efficiency 82.3%), while at 9% it was 8.3% (biological efficiency 88.3%) is actually a state of biological purity. Since this value was within the accuracy of the experiment in all repetitions, where the fungi were not specifically used. However, conditions were created for development of wood-staining and mold fungi by means of humidity. In our studies, we have achieved the desired concentration in the resulting fire-retardant solution as a working agent against mycosis of wood.

Work concentrations are also approximately characterized by the individual representatives of the two genera of fungi common on wood and reduce its quality.

It should be noted that it is possible to distinguish species diversity in the work of fire retardant against the development of fungi. However, this requires deeper scientific research with the change of numerous factors, to reflect the natural conditions of the passage of industrial wood. In general, the use of the obtained fire-retardant solutions in the laboratory has a biological efficacy of up to 88.3%. This seems to be a promising area for innovative waste management and wood protection.

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