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I. Bazhelka¹, A. Kanavalava¹, L. Radkevich²¹Belarusian State Technological University²A. V. Luikov Heat and Mass Transfer Institute of National Academy of Science of Belarus**EVALUATION OF COMPOSITIONS FOR BLEACHING WOOD AFFECTED BY WOOD-COLORING AND MOLD FUNGI**

This article presents the results of tests to evaluate compositions for bleaching wood affected by wood-coloring and mold fungi. In the course of the work, the analysis of bleaching agents used in the pulp and paper, textile, and also in the woodworking industries was carried out. The advantages and disadvantages of using various bleaching agents for various types of wood are considered. As a result of the analysis of bleaching agents, four experimental compositions based on hydrogen peroxide (H₂O₂), six formulations based on sodium hypochlorite (NaClO) (in three of which stabilizing additives were added). Experimental compositions were applied immediately after their preparation to samples of wood completely affected by wood-coloring and mold fungi. The treatment was carried out by applying a bleaching solution with a brush along the fibers to the surface of the sample on one side. The tests were carried out at room temperature and humidity 60 ± 5%. 24 hours after the application of the formulations, the effectiveness of these formulations was evaluated. As a result of the tests, compositions based on sodium hypochlorite showed a higher bleaching effect in comparison with compositions based on hydrogen peroxide.

Keywords: bleaching of wood, chlorine-containing compounds, compounds without chlorine.

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В данной статье представлены результаты испытаний по оценке составов для отбеливания древесины, пораженной деревоокрашивающими и плесневыми грибами. В ходе работы был проведен анализ отбеливающих агентов, применяемых в целлюлозно-бумажной, текстильной, а также деревообрабатывающей промышленности. Рассмотрены преимущества и недостатки использования различных отбеливающих агентов для разных пород древесины. В результате проведения анализа отбеливающих агентов были приготовлены 4 экспериментальных состава на основе перекиси водорода (H₂O₂), 6 составов на основе гипохлорита натрия (NaClO) (в 3 из которых были добавлены стабилизирующие добавки). Экспериментальные составы были нанесены сразу после их приготовления на образцы древесины, полностью пораженной деревоокрашивающими и плесневыми грибами. Обработку проводили путем нанесения отбеливающих растворов кистью вдоль волокон на поверхность образца с одной стороны. Испытания проводили при комнатной температуре и влажности 60 ± 5%. Спустя 24 ч после нанесения составов была произведена оценка их эффективности. В результате проведения испытаний составы на основе гипохлорита натрия проявили более высокий эффект отбеливания в сравнении с составами на основе перекиси водорода.

Ключевые слова: отбеливание древесины, хлоросодержащие составы, составы без хлора.

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Introduction. Currently, softwood is widely used in woodworking, especially in the manufacture of furniture and joinery. However, the features of the anatomical structure and chemical composition of

coniferous wood, the presence of a large number of knots, resinous areas, cracks, fungal stains have a significant impact on the processing process, as well as on the quality of products [1].

The resistance of wood is called its ability to resist destruction under the influence of various physical, chemical, biological and mechanical factors. Under the influence of the combined influence of changes in air humidity and temperature, direct exposure to precipitation and solar radiation, cracks appear on the surface of the wood, increasing over time, the integrity of the wood is violated and its gradual destruction occurs, thereby creating favorable conditions for the impact of various types of biological factors (bacteria, fungi, insects). The main type of reduction in the quality and cost of timber is the defeat of its wood-coloring and mold fungi, leading to a change in color, both the surface of the material and loosening and deformation of the structure in its volume, but not leading to the loss of the operational properties of wood. Cellulose and hemicellulose do not affect the color of technical cellulose [2]. The color of cellulose is given by chromophore groups of lignin, which are formed as a result of the oxidation of phenolic hydroxyl groups of lignin into quinones, as well as metals of variable valence that form colored complexes with phenolic groups.

There are many ways to restore the natural color of wood without changing its structure and natural properties. The process of bleaching the surface of wood consists in the discoloration of lignin or in the destruction and destruction of colonies of mold and wood-coloring fungi, followed by their discoloration. Bleaching agents are compounds that bleach or lighten the substrate by dissolving the substances that give color or by changing their light-absorbing properties. Bleachers are widely used in the pulp and paper industry, the textile industry, as well as in the woodworking industry. Wood bleaching agents are divided into two types: compounds without chlorine and chlorine-containing compounds.

The chemistry of bleaching agents consists mainly of oxidizing agents that destroy fungi and discolor wood fibers: chlorine (Cl_2) and some of its compounds or peroxide compounds, such as hydrogen peroxide (H_2O_2), ozone (O_3) and sodium perborate (NaBO_3). The bleaching reaction usually involves the removal of chromophore sites in which electron delocalization by conjugated double bonds has made the substrate capable of absorbing visible light [3]. The bleaching agent usually reacts by irreversibly splitting or attaching these double bonds. Sodium hypochlorite (NaClO), calcium hypochlorite ($\text{Ca}(\text{ClO})_2$), chlorine dioxide (ClO_2) or bleach ($\text{Ca}(\text{OCl})_2 \cdot \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$) are usually used as the main active ingredient in chlorine-containing bleaches. Bleachers without chlorine contain hydrogen peroxide (H_2O_2), ammonia (NH_3), oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) and others [4]. These substances bleach wood due to the reaction of its oxidation by a peroxide group and a small amount of oxygen formed during the decomposition of peroxide compounds. When bleaching

materials with hydrogen peroxide, activators of various nature are used to accelerate and facilitate the bleaching process.

In the process of bleaching cellulose-containing materials with hydrogen peroxide compositions, the TAED ($(\text{CH}_3\text{C}(\text{O}))_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}(\text{O})\text{CH}_3)_2$) bleaching activator is widely used, which significantly reduces the temperature of the process, and also gives the composition bactericidal, virucidal and fungicidal properties [5]. This method of bleaching has several advantages, it is a softer treatment of cellulose and a lower consumption of bleaching agents, while maintaining the strength of the fibers. It should be noted that despite the fact that bleaching with hydrogen peroxide is the most economical method, its use is limited by the physico-chemical properties of wood. Wood of some species when bleached with peroxide, can acquire a wide variety of shades of color. For example, oak peroxide compounds are not bleached, but painted green, walnut with its contrasting texture gives gray-blue or pink shades of color when bleached, and anatolian walnut acquires a bright golden color. At the same time, peroxide compounds are ideal for bleaching birch, beech or walnut [6].

The use of peracetic acid ($\text{C}_2\text{H}_4\text{O}_3$) as a promising highly effective bleaching agent is known when processing cellulose pulp in the technology of complete absence of chlorine [7], the possibility of enzymatic bleaching using the fungal laccase – mediator system with subsequent bleaching with hydrogen peroxide [8] is also being considered, which allows to increase the level of pulp bleaching by more than 2.5 times and low the content of lignin. However, these developments are insufficiently studied, although they have significant potential.

Some bleaching compounds act by chemical reduction. These include sulfur dioxide (SO_2), sulfurous acid (H_2SO_3), hydrosulfite (HSO_3), sulfite (Na_2SO_3) and sodium dithionate ($\text{Na}_2\text{S}_2\text{O}_6$), as well as sodium tetrahydroborate, borohydride (NaBH_4) and their use is mainly associated with the production of paper pulp and textiles, where it is believed that the bleaching effect occurs due to the reduction of the chromophore carbonyl group. To date, these technologies have not been widely used.

Thus, compositions based on a solution of sodium hypochlorite can be considered the most affordable and bleaching of almost any wood. The preparation of such compositions does not require special equipment and can be used in almost any enterprise of the woodworking industry.

Main part. The purpose of this work is to study and analyze bleaching compounds and identify the most effective among them for bleaching wood affected by wood-coloring and mold fungi.

During this experiment, the wood of the common pine (*Pinus sylvestris* L.), affected by wood-coloring and mold fungi over the entire surface was used as

the material to be processed. Wood samples were cut from one uniformly affected board measuring 50 mm (length) × 50 mm (width) × 20 mm (thickness). For processing, aqueous solutions of bleaching compounds prepared immediately before application to the samples were used. The treatment was carried out by applying a bleaching solution with a brush to the surface of the sample on one side. The bleaching effect of the solutions was assessed visually by changing the color of the affected surface of the wood sample after 1 hour and after 24 hours (sustained to increase the penetration depth of the solution). The tests were carried out at room temperature and humidity $60 \pm 5\%$.

To assess the effectiveness of bleaching agents, aqueous solutions based on hydrogen peroxide or sodium hypochlorite were studied, the component composition of which is presented in Table 1 and Table 2.

Table 1
Hydrogen peroxide-based formulations used in bleaching damaged wood

Composition number	Component composition of bleaching aqueous solutions	
	Stage 1	Stage 2
1	Hydrogen peroxide 30% Sodium hydroxide Sodium liquid glass	Hydrogen peroxide 30%
2	Water ammonia 25%	Hydrogen peroxide 30% Potash
3	Sulfuric acid Hydrogen peroxide 30% Oxalic acid	Hydrogen peroxide 30%
4	EDTA (heat the solution to 50–60 °C before use)	Hydrogen peroxide 30% Sodium hydroxide

Table 2
Sodium hypochlorite-based formulations used in bleaching damaged wood

Composition number	Component composition of bleaching aqueous solutions
5	Sodium hypochlorite 40% Sodium hydroxide 50%
6	Sodium hypochlorite 40% Activator № 1 – based on isocyanuric acid Sodium hydroxide 50%
7	Sodium hypochlorite 40% Activator № 2 – based on bromine EDTA Boric acid

The process of processing samples with solutions containing hydrogen peroxide was carried out in two stages without washing and pre-drying, by successive application of solutions to the surface of the sample.

The process of processing wood samples with solutions based on sodium hypochlorite consisted of one stage.

At the first stage of the research, bleaching compositions based on hydrogen peroxide were tested (compositions No. 1–4). In composition No. 1, hydrogen peroxide and sodium silicate were used together at the first stage of treatment, which, as is known [9], allows increasing the activity of the bleaching process of wood aged under atmospheric conditions, but it will restore the brightness and hardness of the material. At the second stage of bleaching, dilute hydrogen peroxide was used.

Since the pretreatment of the wood surface with ammonia before interacting with hydrogen peroxide makes it possible to prepare (mercerize) the surface, and the introduction of a carbonate group makes it possible to stabilize the hydrogen peroxide solution or prolong the bleaching effect of the agent somewhat, when preparing the second experimental composition (No. 2), the following were used: in the first stage of treatment – aqueous ammonia; in the second stage – peroxide hydrogen and potash.

The composition of agent No. 3 at the first stage included a mixture of dilute acids, which, when processing the surface of the samples, increase the surface activity of wood due to interaction with the OH groups of cellulose. The second stage of bleaching included treatment with dilute hydrogen peroxide.

Pretreatment with a hot EDTA solution leads to the binding of polyvalent metal cations on the wood surface, destabilizing the hydrogen peroxide solution and reducing its activity. In this regard, for the preparation of the fourth experimental composition (No. 4), EDTA was used as the main components for the first stage. For the second stage – dilute hydrogen peroxide stabilized with sodium hydroxide.

At the second stage of the research, bleaching formulations containing sodium hypochlorite were used – formulations No. 5–7.

It is known that an excess of free base (sodium hydroxide) increases the pH of the sodium hypochlorite solution to 12.5–13.5 and acts as a stabilizer, and in addition, prevents the formation of hypochlorous acid [10] and allows mercerizing the surface of wood samples.

To prepare the fifth composition (No. 5), sodium hypochlorite and sodium hydroxide were used.

Bleaching activators were additionally introduced into bleaching formulations No. 6 and 7, which increase the efficiency of the process.

Composition No. 6 consisted of: sodium hypochlorite, activator No. 1 and sodium hydroxide.

As part of the seventh experimental composition (No. 7), sodium hypochlorite, activator No. 2, EDTA and boric acid were used.

Fig. 1 shows photographs of a control sample of pine wood affected by wood-coloring and wood-destroying fungi, and wood samples treated with experimental bleaching compounds. Photos of samples treated with bleaching compounds were taken 24 hours after treatment.

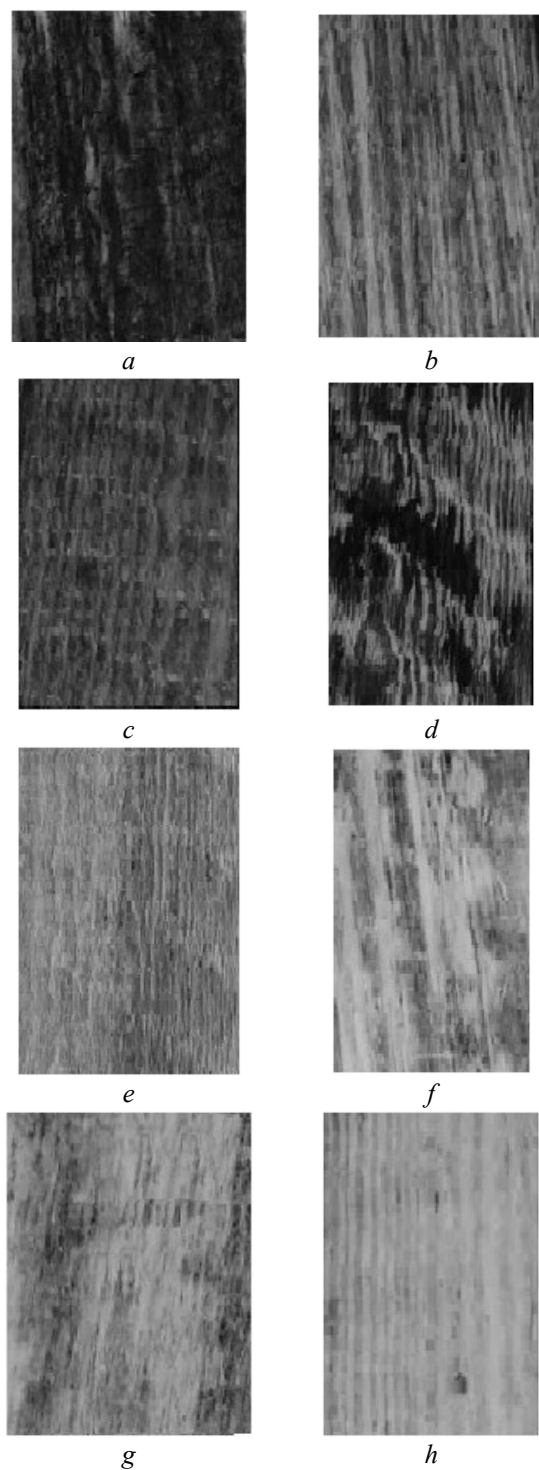


Fig. 1. Control sample of affected wood (*a*) and samples treated with experimental bleaching compounds (*b–e* – compositions based on hydrogen peroxide No. 1–5; *f–h* – compositions based on sodium hypochlorite No. 5–8)

As can be seen from Fig. 1, bleaching compositions No. 1–4 based on hydrogen peroxide are ineffective under these experimental conditions. The treatment of wood samples with composition No. 3, which has a complex composition of the solution of the first stage, not only did not lead to the restoration of the color of the wood, but also caused some of the affected areas to turn dark brown. A higher bleaching ability among compositions based on hydrogen peroxide was noted in composition No. 4. This is due to pretreatment with a hot EDTA solution, which provided deeper penetration of the hydrogen peroxide solution in the second stage. As noted above, bleaching agents based on peroxide compounds show good results when processing textiles or cellulose pulp. They work in a thin layer, for example, when processing plywood, and are little used in the processing of timber, where anisotropy of properties, heterogeneity of anatomical structure and chemical composition have a great influence on the finishing process.

Compositions based on sodium hypochlorite No. 5–7 have a higher bleaching effect. Compositions No. 6 and 7 containing bleaching activators of various nature are most effective. The action of activator № 1 in composition No. 6 can be explained by the fact that chlorine-substituted derivatives of the sodium salt of cyanuric acid in an aqueous solution undergo hydrolysis with the formation of the sodium salt of cyanuric (isocyanuric) acid and the release of active chlorine, which leads to an increase in the oxidative effect during a neutral reaction of the medium. In addition, hydrolysis is quite slow, and the effect of such a drug will have a prolonging effect. However, it is necessary to note the highly toxic properties of the activator based on isocyanuric acid [11], as well as its high cost. Thus, the most affordable and effective is bleaching compound No. 7.

Aqueous solutions based on sodium hypochlorite have a short shelf life. It is known that the addition of polyatomic alcohols (for example, galactite, mannitol, sorbitol, inositol and pentaerythritol) is used to stabilize aqueous solutions of hypochlorites, as well as products based on them, and the addition of amides or amines, bromides, arylsulfanilamides or their derivatives, isocyanuric acid, etc. increases the light resistance of hypochlorites [12]. Also, orthophosphoric acid salts, sodium silicates or boric acid are additionally introduced to stabilize sodium hypochlorite solutions [13]. Examples of possible pH correctors of aqueous solutions of sodium hypochlorite are mixtures of compounds of sodium tetraborate, sodium bicarbonate and sodium carbonate [14], sodium monohydrophosphate or sodium dihydrophosphate [15], sodium silicate [16]. In addition, boron compounds are known for their antiseptic properties.

For a comparative evaluation of the effectiveness of bleaching properties, three compositions based

on sodium hypochlorite with compounds that increase its stability in aqueous solutions were prepared. As stabilizers were used: stabilizer No. 1 and stabilizer No. 2 are based on boric compounds, stabilizer No. 3 is based on sodium salts.

For the preparation of composition No. 8, sodium hypochlorite, activator No. 2, EDTA and stabilizer No. 1 were used. For the preparation of composition No. 9, sodium hypochlorite, activator No. 2, stabilizer No. 2, sodium hydroxide and sodium liquid glass were used. In the preparation of composition No. 10, sodium hypochlorite, activator No. 2, stabilizer No. 3 and sodium hydroxide were used.

As can be seen from Fig. 2, bleaching compositions based on aqueous solutions of sodium hypochlorite with stabilizing additives show almost the same effectiveness. It should be noted that the bleaching effect in all compositions of this series (No. 8–10) is manifested already within the first two minutes of applying the composition to the affected area of wood. The rate of restoration of wood color increases with an increase in the concentration of the activator in the composition and does not depend much on the nature of the stabilizing additives. It is also worth noting that over time, when stored in a solution of agent No. 9, a small precipitate formed.

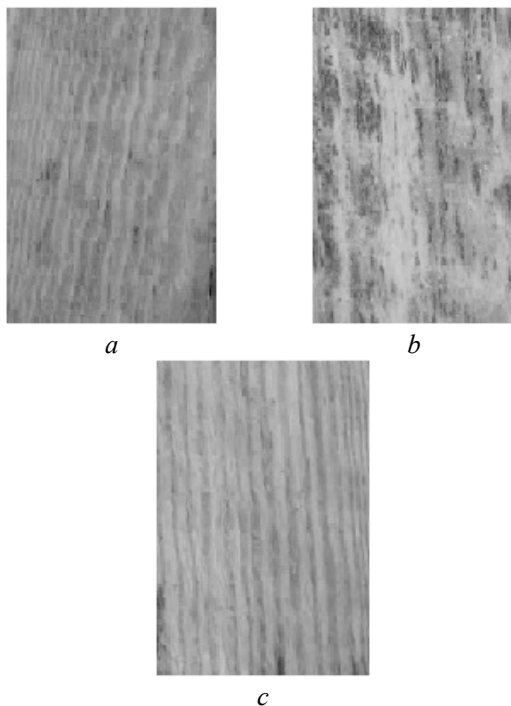


Fig. 2. Samples of affected wood treated with bleaching compounds based on sodium hypochlorite with stabilizers (*a–c* – compositions No. 8–10)

As can be seen from Fig. 2, bleaching compositions based on aqueous solutions of sodium hypochlorite with stabilizing additives show almost the same effectiveness. It should be noted that the bleaching effect in all compositions of this series (No. 8–10) is manifested already within the first two minutes of applying the composition to the affected area of wood. The rate of restoration of wood color increases with an increase in the concentration of the activator in the composition and does not depend much on the nature of the stabilizing additives. It is also worth noting that over time, when stored in a solution of agent No. 9, a small precipitate formed.

Conclusion. Thus, when evaluating compositions for bleaching of oxidative nature for coniferous wood affected by wood-coloring and mold fungi, it was found that aqueous solutions of hydrogen peroxide exhibit a negligible effect with deep lesions of wood. Compositions based on aqueous solutions of sodium hypochlorite with a bleaching activator and stabilizing additives have optimal bleaching properties in the presence of deep sapwood blues. As a result of testing the prepared experimental formulations, the best bleaching properties were shown by formulations No. 8 and 10, which are prepared on the basis of sodium hypochlorite with the addition of activators and stabilizers that enhance the oxidative effect and increase the shelf life of the formulations. When treated with these formulations, a rapid rate of restoration of wood color, deeper bleaching of the affected areas of wood and the absence of sediment formation in the formulations during storage were observed.

Chlorine, being a strong oxidizer, provides antimicrobial action by inhibiting bacterial enzymes, which leads to irreversible oxidation of sulfhydryl groups, which are the main component of these enzymes. Sodium hypochlorite is also a strong base ($\text{pH} > 11$). The high pH of sodium hypochlorite provokes a violation of the integrity of the cytoplasmic membrane through irreversible enzyme inhibition, biosynthetic modification of cellular metabolism and phospholipid degradation during lipid peroxidation. As a result of the chlorination reaction of amino acids, chloramines are formed, which also negatively affect cellular metabolism. Oxidation enhances the effect of irreversible inhibition of enzymatic bacterial activity, replacing the available hydrogen with chlorine. In this connection, the use of sodium hypochlorite in bleaching compounds allows not only to whiten the affected wood, but also gives the composition bactericidal properties.

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