Досліджено хімічний склад природного бішофіту із свердловини № 1 Затуринського родовища та виявлено достатню насиченість $MgCl_2$ для його використання як екологічно орієнтованої основи композиційних складів для вогнезахисту деревини. Експериментальними дослідженнями підтверджена ефективність застосування органічних синтетичних барвників (метиловий оранжевий, бромтимоловий синій) як фарбувальних добавок для заявлених композиційних складів. Визначено технологічні особливості застосування пігментних концентратів ТМ «Amber» та ТМ «Sniezko», які утворюють з розчином природного бішофіту двофазні системи. Доведено, що запропоновані фарбувальні добавки забезпечують стійке забарвлення деревини та насичений колір її поверхні. У лабораторних умовах підтверджена ефективність застосування фарбувальних добавок (бромтимоловий синій та метиловий оранжевий; пігментних концентратів ТМ «Amber» та ТМ «Sniezko») для розроблених композиційних складів для вогнезахисної обробки деревини. Експериментальними дослідженнями встановлено, що час займистості деревини, обробленої композиційним складом без фарбувальних добавок, збільшується у 4 рази у порівнянні із необробленою деревиною. Вогнезахисний механізм дії розроблених композиційних складів обумовлений послідовними процесами перетворення солі бішофіту під впливом температури та додаванням ортофосфорної кислоти, що є сильним антипіреном. А введення до композиційного складу фарбувальної добавки (барвника) метилового оранжевого збільшує час займистості більш ніж у 4 рази, у порівнянні із необробленою деревиною. Таким чином, є підстави стверджувати, що розроблені композиційні склади, що містять фарбувальні добавки (барвники), є екологічно орієнтованими та економічно доцільними. Разом із тим, отримані результати вирішують комплексне завдання, а саме забезпечення вогне- та біозахисту, а також візуалізації наявності обробки будівельних конструкцій житлових та нежитлових будівель із деревини

Ключові слова: бішофіт, фарбувальна добавка, пігментний концентрат, композиційний склад, вогнезахисний засіб, візуалізація обробки

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DEVELOPMENT OF COMPOSITION FORMULATIONS, BASED ON NATURAL BISCHOFITE, TO PROTECT WOOD FROM FIRE

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1. Introduction

The increased interest in the results of scientific advancements in the field of fire protection is due to the need to create highly effective products to protect building structures from the impact of fire, as well as their implementation [1]. Fire protection of building structures is an important component in the system of fire prevention activities. Such protection ensures fire prevention, reduces flammability of materials, prevents fire, slows down, or even stops the start of a fire and helps localize it quickly. All this improves the environmental situation where such buildings are located.

Different materials can be used in the building structures – both in origin and by the class of fire hazard. Structures of wood (lathing of roofs, wooden structures of roofs, slings, structural elements of podiums, scenes, etc.) remain common building materials. Along with the advantages that distinguish it from other building materials, wood has

disadvantages as well, the main of which is easy flammability and combustibility. Fire-retardant treatment of wood implies an increase of the actual limit of fire resistance of structures to the required values, and is required to limit the spread of fire over their surface, including reduction of harmful side effects [2]. The task of reducing the fire hazard of wood, used in construction, is not only an economic issue, but it has a social and environmental focus. In modern construction, there is an increasingly intensive search for new highly effective means to protect wood from fire. Wood, a widespread building material, must undergo the appropriate fireproof treatment [3, 4], required by fire regulations and rules for such facilities [5].

By combining the means and techniques of wood impregnation, one can achieve almost any parameters of fire protection. It might seem the problem does not exist. At the same time, fire protection, which is often applied in practice, while solving the task, typically a narrow one, necessitates a combination of fire-protection treatment and the visualization of its application, which in turn could ensure control over its absence or presence. Recently, there have emerged the means that relate to multifunctional, capable of solving, simultaneously with fire protection, the tasks of operational nature. The main disadvantage of these means is significant energy and transportation costs. This is due to the need to use impregnating plants, which are located at a considerable distance from the construction sites. During transportation to a construction site, in the process of installation and operation there is a need to preserve fire-retardant treatment from a washout by atmospheric precipitation. In addition, the disadvantage is the fact that processing the impregnated wood with cutting tools not only damages fire protection but also is a factor of rapid wear of tools. And at the same time, treating damaged areas does not provide the appropriate flame-retardant effect; if the damage resulting from finishing the articles is significant, the effectiveness of such protection would be compromised.

In modern construction, new highly effective means to protect wood from fire have been increasingly searched for. At the same time, fire protection should provide not only for reducing the flammability of wood, but also ensure the preservation of its operational and aesthetic properties, as well as solve issues related to environmental safety, durability, and reliability. Thus, for example, solving a task on maintaining operational properties when developing flame-retardant means requires the appropriate assessment and adjustment of dozens of different parameters, from strength indicators, corrosion activity, to bioprotective wood properties [6].

Construction industry, to increase fire resistance of structures and materials made of wood, exploits different flame retardant means and technologies. An analysis of these means and their practical application reveals that those technologies and tools are prioritized that are capable, at minimum cost, of ensuring the required parameters of fire protection. The best ones are the technologies of wood impregnation under the action of capillary forces, which simplifies the processes of impregnation, creating a possibility to carry out fire protection operations directly under conditions of a construction site. Such technologies are economically more expedient than impregnation at autoclaves under a stationary setting [3].

Thus, there is an acute issue related to protecting wood from fire by different ways, the most effective of which is the treatment with flame retardant coatings and impregnation with special compositions. Among the multitude of solutions that ensure the fire resistance of wooden structures and the reduction of their fire hazard class, one should point to formulations that contain natural bischofite. The obvious advantage of natural bischofite is that, in addition to protecting wood from fire, it improves its bioprotective ability.

Therefore, it is a relevant task to develop an environmentally-friendly composition formulation for fire protection of wood based on natural bischofite with appropriate coloring capability. The specified composition formulation would make it possible to visually control the application of a fire-retardant treatment on structures at residential buildings and non-residential facilities made of wood. At the same time, it is important to develop a protective agent using which could enable the treatment of wood directly at a construction site, which is economically reasonable. This, consequently, necessitates undertaking a research in this field.

2. Literature review and problem statement

The loss of fire resistance and bearing capacity of wood structures is predetermined by the process of charring of wood, which occurs after heating the wood above a temperature of thermal decomposition, close to the temperature of its ignition. The result of fire protection of structures made of wood is, on the one hand, the cases of fire that may occur are prevented, and, on the other hand, that in the event of a fire the period between the moment of its occurrence and a structure collapse is prolonged [4]. One of the tasks in the development of fireproof wood impregnation is to achieve a high flame-retardant effectiveness. It can be achieved both by ensuring the penetration of a composition into the surface layers, and by preserving it in them for a long time, with a possibility of using mechanical application techniques thereby providing for safety in operation [5].

Widely applied are the methods for treating timber structures directly at construction sites [4]. In this case, the environmental safety of constructed facilities and municipal infrastructure is associated with a wide spectrum of issues concerning protection of people from real or potentially negative influences exerted by utilized urban facilities [7]. All these facilities are exposed to the microbiological factors from the environment, resulting in the disruption of conditions that form safe and environmentally-friendly living conditions. The search for effective measures to counteract the environmental bio-damage to construction facilities and local infrastructure is one of the relevant scientific-practical problems. There is a need to develop and implement measures to prevent and eliminate the consequences of bio-damage to various building materials and structures. Specifically, the mineral bischofite allows for an effective environmental safety of materials and operation of building facilities [8, 9].

Bischofite ($MgCl_2 \cdot 6H_2O$) is the most soluble natural salt, extracted to the surface by underground dissolution with fresh water; in terms of the total activity of natural radionuclides, it refers to a first class and can be used without restrictions. Bischofite is a cheap, non-volatile, safe reagent, which spreads over the surface by adsorbing moisture from air. Large fields of bischofite have been explored in Belarus, Germany, the Netherlands, China, Thailand, Kazakhstan, on the African continent, as well as in Ukraine (Poltava and Chernihiv oblasts). The projected resources of bischofite within the south-east Dnieper-Donets acetabulum alone amount to about 10 billion tons. The concentrated solutions

of bischofite ($w_{MgCl_2} = 29\,\%$) are obtained by the method of underground dissolution at a deposit, followed by diluting them to the required concentration [10, 11]. Owing to its unique properties, bischofite is widely used in housing and communal services [12], medicine [11, 13], chemical industry [10, 14, 15], in agriculture [16, 17]. Bischofite is also used as a refrigerant and an antifreeze agent, for applying road coatings, as a chemical stabilizer for granulated pavement [18], an anticorrosive agent [19, 20], a means to store thermal energy [21–26], etc.

Bischofite has been applied [27] not only as a firefighting means, but also as an agent to impregnate wood in order to provide it with bio-protection and fire resistance. The developed means solve the following technical tasks:

– a decrease in the consumption of a fire-retardant composition for impregnation, per unit of treated surface, at the expense of using orthophosphoric acid, while ensuring its high flame-retardant properties [28];

– obtaining wood with flame-retardant properties resistant to washout by increasing the depth of impregnation by fixing magnesium chloride at the inner structure, which is up to 40 % [29];

– the increased penetrating and fireproof capability of the composition and its bioprotective efficiency at the reduced toxicity and aggressiveness [30];

– the enhanced penetrating and flame-retardant capacity of the composition at a simultaneous decrease in costs per unit surface and a decrease in its corrosion activity and toxicity [31];

– the increased antiseptic and flame-retardant capability of the composition due to synergy effect of the resulting product while reducing the solution consumption per unit of surface [32];

– preservation of high flame-retardant properties even at intensive washout [8].

However, these fire- and-bioprotective means fail to address a promising issue – visualization of the application of a fire-bioprotective wood treatment based on changes in its color. This is probably due to the limited range of tasks set by researchers when developing fire-bioprotective means for wood and which contain bischofite. The presence of a coloring additive in a composition formulation would enable control bodies to check the application of a fire-protective treatment, implied by fire regulations and rules for building structures made of wood.

Paper [7] proved that the proposed fire-bioprotective composition for impregnating wood surface, based on the mineral bischofite and zinc, is characterized by a set of environmentally-effective protective properties. It was proven that the use of this additive contributes to improving stability of building materials against the influence of aggressive media. The fungicidal additive forms a safe environment for human living and provides for the environmental safety of various constructed facilities and urban infrastructure. However, adding the modified additives to the proposed compositions, based on bischofite, in order to achieve the required operational indicators of treated wood, increases the cost of fire extinguishing compositions; in some cases, it can exert harmful influence on people and the environment.

A composition formulation based on bischofite (variant 3) was proposed in [28] for protecting wood from fire; it refers to group 1 of fire-protective efficiency. This composition implies the loss of mass by the treated wood not exceeding 9 % and provides for fire-retardant properties for a period of up to 7 years. It was proven in [28] that the use of orthophosphoric acid significantly reduces the consumption of a flame-retardant composition for wood impregnation and ensures its high flame-retardant properties. However, the lack of a coloring additive [28] does not make it possible to control the application of such a fireproof treatment. Insufficient attempts to solve a scientific and applied task on the development of composition formulations for fire-bio-protection and the visualization of the applied treatment predetermine the importance and relevance of research in a given field. That is why the proposed composition formulations based on bischofite imply the use, in addition to orthophosphoric acid, the coloring additives (colorants and pigment concentrates).

Therefore, solving a scientific and applied task of visualizing the fire-bioprotective treatment of building structures made from wood necessitates the development of composition formulations with the addition of coloring additives (colorants and pigment concentrates). Studying the influence of components in a composition formulation, as well as a treatment technique, on the fire protection of wooden construction structures would make it possible to develop effective means with the possibility of their visualization. The above necessitated our research into this area.

3. The aim and objectives of the study

The aim of this study is to develop composition formulations, based on natural bischofite, with the addition of coloring additives, for wood fire protection. This would make it possible to solve a task on visualizing the applied treatment and ensuring effective fire protection of building structures made of wood.

To accomplish the aim, the following tasks have been set:

– to explore a solution of natural bischofite extracted from well No. 1 at Zaturin deposit, in order to establish its suitability to use it as a raw material as the base for composition formulations to protect wood from fire;

– to experimentally prove a possibility and efficiency of using organic colorants as coloring additives for composition formulations for fire protection of wood, based on natural bischofite;

– to experimentally investigate a technological possibility of using the pigment concentrates TM «Amber» and TM «Sniezko» as coloring additives for composition formulations for fire protection of wood, based on natural bischofite;

– to control the quality of applying a wood fire-retardant treatment using the proposed composition formulation for fire protection of wood based on natural bischofite with the addition of coloring additives;

– to determine the flammability time of wood samples, treated with the proposed composition formulations for fire protection of wood, based on natural bischofite containing a coloring additive (colorant – methyl orange).

4. Materials and methods to study the components of composition formulations to protect wood from fire

4. 1. The examined materials used in the experiment

The environmentally safe base for composition formulations to protect wood from fire is a solution based on natural bischofite from Zaturin deposit (Poltava oblast, Ukraine). The bischofite extracted here is an ecomineral in terms of its

chemical composition [11]. For experimental study, we used bischofite solutions with a mass fraction of $MgCl_2$ of 18 % from well No. 1 at Zaturin field with the addition of H_3PO_4 in a concentration of 3 %. The addition of orthophosphoric acid to the bischofite solution stabilizes it from the loss of salts, and also reduces the consumption of a fire-retardant composition on impregnation in order to provide high flame-retardant properties [28].

A coloring additive to the composition formulations that was investigated included a series of organic substances-colorants, as well as pigment concentrates from different manufacturers. Working solutions of coloring additives were prepared by diluting the starting solutions of colorants.

Bromothymol blue is a triphenylmethane colorant, weakly soluble in water, acid-base indicator. The starting 0.1 % solution of bromothymol blue was prepared by dissolving a precise batch in ethyl alcohol in the measuring flask. The resulting solution was aged for 24 hours. The precise volume of 0.1 % of bromothymol blue solution was dissolved in a solution of bischofite in a measuring flask. For our study, we used a solution of bischofite with bromothymol blue at concentration of 0.001 %.

Fuchsine is an aniline colorant from a triphenylmethane series. A solution of bischofite with fuchsine at concentration 0.1 % was prepared by dissolving a precise batch of the colorant in bischofite solution in a measuring flask. The starting 0.1 % fuchsine solution was prepared by dissolving a precise batch of the colorant, ground in a mortar, in 20 ml of ethyl alcohol; after complete dissolution, we added 80 ml of distilled water. The prepared 0.1 % colorant solution was stored in a tightly closed vial in a dark place. For our study, we used a solution of bischofite with the addition of methyl orange at concentration 0.001 %.Methyl orange is an organic synthetic colorant from the group of azo dyes, acid-base indicator. The starting 0.1 % methyl orange solution was prepared by dissolving a precise batch in distilled water in a measuring flask.

The resulting solution was aged for 24 hours. The precisely measured volume of 0.1 % of methyl orange solution was dissolved in bischofite solution in a measuring flask. For our study, a solution of bischofite with the addition of methyl orange at concentration 0.001 % was used.

Solutions of the pigment concentrates, TM «Amber» (Amber, pigment concentrate. Composition: pigments, water, auxiliary substances. Country-producer, Ukraine) and TM «Sniezko» (Sniezka COLOREX Universal pigment concentrate. Ingredients: organic and inorganic pigments, water, auxiliary substances. Country-producer, Republic of Poland), at a concentration of 5, 10, 15 %, were prepared in in volumetric flasks by dissolving precise batches of the pigment concentrates in a solution of bischofite. Before treating wood, the composition formulations were carefully agitated.

To control the quality of fire-retardant treatment, we fabricated samples from a straight-ply air-dry wood of pine, humidity (9±2) %, rectangular shape, length 60 mm, width 35 mm, thickness 2.5 mm. The samples without apparent imperfections and resin inclusions were used. The side surfaces were trimmed, the ends were trimmed and sanded. The samples of wood, before applying a flame-retardant composition, were aged in a desiccator with a saturated solution of 6-aqueous zinc at a temperature of (23±5) °C.

We applied composition formulations to the conditioned samples from all sides (Table 1).

Before the study, the samples were aged for 24 hours in a laboratory at a flat open surface (tables) at 20 °C and air relative humidity (65±2) %.

To determine the time of flammability, we fabricated samples from straight-ply air-dry pine sapwood with a density of 0.45–0.55 g/cm^3, without apparent imperfections and resin inclusions. The samples dimensions were 15×15×6 mm (the last size along the fibers). Deviation from the sample sizes did not exceed ±0.5 mm. Before treatment, the samples were labeled and conditioned at a temperature of (23±5) °C and air relative humidity (65±2) % until achieving their equilibrium moisture content.

Table 1

Variants of composition formulations to protect wood from fire, based on natural bischofite, containing colorant additives (colorants)

Variant of composition formulations	Type of coloring additive	Title of coloring additive	Concentration of colorant additive, %
1 (control)	Without coloring additive (colorant)		
2	Colorant	Bromothymol blue	0.001
3	Colorant	Methyl orange	0.001
4	Pigment concentrate	TM «Amber»	5
5	Pigment concentrate	TM «Amber»	10
6	Pigment concentrate	TM «Amber»	15
7	Pigment concentrate	TM «Sniezko»	5
8	Pigment concentrate	TM «Sniezko»	10
9	Pigment concentrate	TM «Sniezko»	15

To determine the flammability time, we used:

– samples 1 – non-treated;

– experimental samples 2–4 – treated with a composition formulation;

– experimental samples 5–7 – treated with a composition formulation containing a coloring additive (methyl orange colorant) at concentration 0.001 %.

Before the study, the treated wood samples were laid on their sides in open Petri dishes and aged for three days at a temperature of (20±2) °C and air relative humidity (65±2) %. Next, they were placed for 14 days in the desiccator with a saturated solution of 6-hydrous zinc nitrate, enabling the samples to achieve a moisture content of (9±2) %.

4. 2. Methods to study bischofite solutions

Chemical analysis of the solutions of bischofite was conducted according to GOST 7759-73 «Technical magnesium chloride (bischofite). Technical specifications». The content of K^+ and Na^+ ions was determined by a flame-photometric method, that of Mg^{2+} and Ca^{2+}– by complexometric titration with a solution of trilone B using the murexide indicator. The content of Cl^- was determined by mercurimetric, that of Br^- – by hypochlorite iodometric, that of SO_4^{2-} – by gravimetric (weight deposition in the form of $BaSO_4$)

methods, respectively. The content of microelements was determined by atomic-emission (at the device «Optima 5300DV», made by Perkin-Elmer, country of manufacture is the USA) and atomic-absorption methods of spectral analysis (at the atomic-absorption complex CAS-120.1, with a computer registration of the analytical signal, software 38 «KAS» developed by AT «Selmi», country of origin is Ukraine). The sensitivity of spectral analysis methods is 10^{-5} %. Detection error of each element present in the concentration of 10^{-4} did not exceed 3–5 %.

4. 3. Procedure for applying composition formulations, based on natural bischofite, to protect wood from fire

Composition formulations were applied to the samples of pine, cleared of bark, bast, dirt, dust. Before the treatment, when studying model samples treated with the composition formulations, containing various coloring additives, the moisture content of wood was not more than (9±2) %. The wood surface treatment was carried out at 20 °C and air relative humidity (65±2) %. A roller was used to apply the solution. Composition formulations were applied evenly, without gaps and sagging. We treated the surface of wood by applying 1, 2, 4 layers at intervals of 20–40 minutes using a «wet on wet» technique. In this case, each subsequent application was carried out upon a wet, slightly dried preceding layer, avoiding the washing of the previously applied solution.

4. 4. Method for controlling the quality of wood fireproof treatment and for determining the flammability time of wood

To control the quality of a fire-retardant treatment and to determine the time of wood flammability, we used a laboratory tripod, the tripod holders, a Bunsen burner (with adjustable flame height).

Before the study, we adjusted the height of the laboratory tripod at a distance of (60±2) mm from a sample to the Bunsen burner. Next, we started the Bunsen burner. The height of the flame was adjusted so that its upper part touched, at a point, the upper edge of the bottom movable part of the holder of the sample. Then we switched off the Bunsen burner.

The testing was carried out in the following sequence:

– a sample was arranged in the holder of the laboratory tripod;

– the Bunsen burner was started;

– the sample was exposed to flame for 40 seconds (to control the quality of a fireproof treatment), 2 minutes (when determining the time of wood flammability), then the Bunsen burner was disabled;

– the sample was left in the holders of the laboratory tripod for cooling it and the holders to an ambient temperature.

During the test, we prevented air flows from affecting the flame of the burner. We visually observed and inspected the samples during testing and after removing them from the holders of the laboratory tripod (to control the fireproof treatment quality). The samples were monitored during the test. The flammability time of the fabricated samples was recorded by a mechanical stopwatch (when determining the time of wood flammability).

5. Results of studying the chemical composition of bischofite and the selected colorant additives (colorants)

5. 1. Results of studying the chemical composition of bischofite

According to the results from analyzing the micro-composition of samples of bischofite solution from well No. 1 at Zaturin deposit, the content of mineralization components was established (*C*, mg/l): Pb – 1.2; Cd – 0.315; Zn – 0.036; CU – 0.028; Cr – 0.005; U – $2.6 \cdot 10^{-6}$; J – 42.53; Br – 3,520.0; Sr – 40.0. The results of analyzing the samples of bischofite solution for the content of microelements indicate that the concentrations:

– of Si, Al, Ti, B are at the level of thousandths of a percent $0.95–1.03 \cdot 10^{-3}$;

– of Mn, Cu, Ag are at the level of ten thousandths of a percent;

– of Zr, Co, Ni, Cr, Be, As, Ga, Mo, Ge, V, Y, Yb, La, Pol, Rh, Gd, Sn, Sb, Bi, Se, Au, Pt are below the threshold of sensitivity of the atomic-emission and atomic-adsorption methods of spectral analysis.

The results obtained from studying the chemical macro-composition of bischofite solution are given in Table 2.

Table 2

Chemical macro-composition of bischofite solution from well No. 1 at Zaturin deposit

Cations	*C*, g/l	*w*, equivalent %	Anions	*C*, g/l	*w*, equivalent %
Potassium+Sodium	1.0610	0.58	Chlorine	273.0420	96.90
			Sulphate	11.6591	3.05
Calcium	2.0000	1.26	Carbonate	–	–
Magnesium	94.8480	98.16	Bicarbonate	0.2074	0.05
Total	97.9090	100.00	Total	284.9085	100.00

Our study (Table 2) indicates that the solution of bischofite from well No. 1 at Zaturin deposit is saturated enough with $MgCl_2$ to allow its use in order to provide flame retardant properties to wood.

5. 2. Experimental study of the efficiency of using organic colorants as the coloring additives for a composition formulation

To study the efficiency of coloring additives, we used a bischofite solution with a mass fraction of $MgCl_2$ of 18 % from well No. 1 at Zaturin deposit with the addition of orthophosphoric acid of concentration 3 %. The concentration of orthophosphoric acid was chosen based on its proven effectiveness [28].

Under laboratory conditions, we conducted experimental study to select coloring additives (colorants) for composition formulations.

Considering the chemical nature of the composition formulation for fire protection of wood, which contains bischofite and orthophosphoric acid, we selected colorants for our study. We have chosen colorants with acid-base indicators, such as bromothymol blue and methyl orange, as well as aniline dye fuchsine.

Characteristic of the examined coloring additives in a natural bischofite solution with a mass fraction of $MgCl_2$

of 18 % with the addition of orthophosphoric acid at concentration 3 % (the content of a coloring additive is 0.001 %) is given in Table 3.

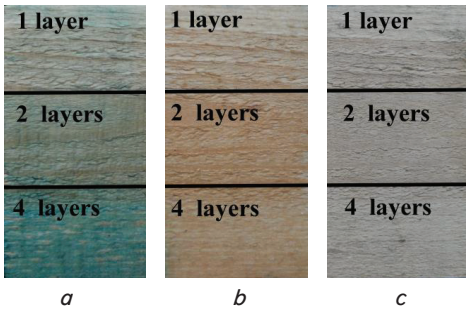
Table 3

Characteristic of the examined coloring additives for composition formulations to protect wood from fire, based on natural bischofite

Colorant title	Composition formulation color	Stability during storage	Solubility of starting solution of coloring additive
Bromothymol blue	Blue	Excellent	Full
Methyl orange	Pink	Excellent	Full
Fuchsine	Brown	Satisfactory	Full

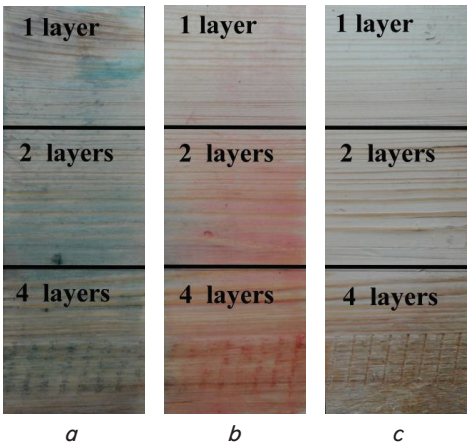
The examined colorants form coagulative resistant solutions with a solution of bischofite, which makes them the most promising group for use as an additive to the highly concentrated solutions of bischofite.

To establish the possibility and efficiency of using organic colorants (bromothymol blue, methyl orange, fuchsine) for composition formulations, we experimented on model samples of wood, shown in Fig. 1, 2.



a *b* *c*

Fig. 1. Model samples of wood (non-treated surface) that were treated with bischofite solutions with the addition of various colorants (colorant concentration 0.001 %): *a* — bromothymol blue; *b* — methyl orange; *c* — fuchsine



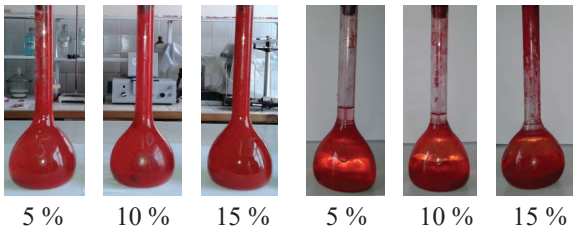
a *b* *c*

Fig. 2. Model samples of wood (treated surface) that were treated with bischofite solutions with the addition of different colorants (colorant concentration 0.001 %): *a* — bromothymol blue; *b* — methyl orange; *c* — fuchsine

The positive effect of the coloring additives (colorants) bromothymol blue and methyl orange is obvious, because in the presence of these reagents wood (with non-treated and treated surface) acquires a steady coloration (the observation lasted for a month). The coloration of wood with the addition of fuchsine proved unstable; when exposed to light, it is destroyed over several days (Fig. 1, 2).

5. 3. Results of studying a technology of using pigment concentrates as coloring additives for a composition formulation

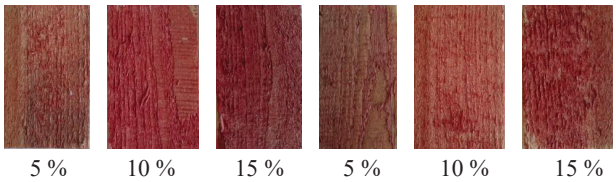
In parallel with studying organic colorants as coloring additives for composition formulations, we investigated the pigment concentrates of TM «Amber» and TM «Sniezko» (Fig. 3). For the study, we used bischofite solutions with a concentration of pigment concentrates of 5, 10, 15 % (TM «Amber»), and 5, 10, 15 % (TM «Sniezko»).



a *b*

Fig. 3. Bischofite solutions with different concentration of pigment concentrates: *a* — TM «Sniezko»; *b* — TM «Amber»

The research results indicate that the bischofite solutions containing a coloring additive of the pigment concentrates of TM «Amber» and TM «Sniezko» are unstable as storing the composition is accompanied by phase stratification in 12 hours (Fig. 3). Before treating wood, a solution of bischofite containing a coloring additive of the pigment concentrates of TM «Amber» and TM «Sniezko» requires thorough agitation. The treated model samples of wood are shown in Fig. 4.



a *b*

Fig. 4. Model samples of wood colored by bischofite solutions with the addition of pigment concentrates of different concentrations: *a* — TM «Sniezko»; *b* — TM «Amber»

Thus, using the pigment concentrates of TM «Amber» and TM «Sniezko» as the coloring additives for composition formulations is technologically feasible and effective. This makes it possible to obtain a saturated color of the surface of the treated wood (Fig. 4).

5. 4. Studying the quality of fireproof wood treatment and establishing the time of its flammability

When studying the quality of fireproof treatment, our visual observation did not reveal, on all studied wood samples:

– self-combustion after disabling a Bunsen burner;

– through burn until a hole formation;

– charring of the sample surfaces, treated with the composition formulations, with and without the addition of coloring additives (colorants), over the entire area, limited by the frame of the holder of the laboratory tripod;

– charring to the full depth in the area of the Bunsen burner flame in the presence of ignition signs (flame combustion outside the area exposed to the flame of the Bunsen burner).

To establish the flammability time of wood exposed to the Bunsen burner, we studied the prepared samples:

– 1 (control and non-treated);

– 2–4 (treated with a composition formulation to protect wood from fire, based on natural bischofite);

– 5–7 (treated with a composition formulation to protect wood from fire, based on natural bischofite, containing the colorant methyl orange). The choice of the specified colorant is due to the fact that it renders wood a steady coloration, of pink color. This visualizes more effectively the application of a fire-retardant treatment than blue color (when adding the colorant bromothymol blue to a composition formulation). However, it was experimentally proven that both colorants are promising candidates for using them as an additive to the highly concentrated solutions of bischofite.

During the experimental study, we recorded a flammability time of the prepared samples of wood, namely the time from the beginning of the study to a persistent combustion flame. Results from processing experimental data on establishing the time of flammability are given in Table 4.

Our study has shown (Table 4) that the non-treated samples 1, exposed to the burner, demonstrated a steady combustion flame in 15 seconds from the start of the study. The ignition time of the treated samples of wood (2–4) increases by 33 % when applying a single layer and substantially increases (by 4 times) when applying two layers. The introduction of the colorant supplement (colorant) methyl orange at concentration 0.001 % (experimental samples 5–7), rather than reducing the ignition time, increases it when applying two layers by more than 4 times. Further increase in the number of layers of application confirms that there is no need for further additional treatment of wood.

Thus, it is established that the flammability time of wood samples treated with 2 layers of a composition formulation increases by 4 times compared with the untreated wood. And the treatment of wood with 2 layers of a composition formulation with the colorant additive (colorant) methyl orange at concentration 0.001 % increases the time of flammability by more than 4 times, respectively.

6. Discussion of results of studying the proposed composition formulations, based on natural bischofite, to protect wood from fire

A fire-retardant mechanism of the proposed composition formulations implies the consecutive processes of converting the salt of bischofite under the influence of temperature. At a temperature rise and at the treated wood burning (depending on the natural composition of bischofite), the following is observed:

– 107–117 °C – release of unbound water and melting of bischofite salt;

– 150 °C – stage-wise process of release of bound (molecular) water;

– 410 °C – the process progresses with the formation of fire-resistant magnesium oxide [30].

The chemical composition of the examined bischofite solution from Zaturin deposit confirms the sufficient saturation with $MgCl_2$ salts and the expediency of its use as the base for composition formulations to protect wood from fire.

It was experimentally proven that an important stage in the creation of composition formulations is the choice of a colorant additive that provides for a steady coloration of the treated wood and does not degrade the fire-retardant properties of bischofite.

The colorants, which were selected as an additive for composition formulations, must have met the following requirements:

– the chemical structure of the colorant based on fundamental theoretical provisions;

– coagulative resistance in a bischofite solution;

– fire-retardant effect;

– non-toxicity and safety for personnel and the environment;

– economic efficiency when used industrially.

It was established experimentally that introducing to a composition formulation the colorant additive, bromothymol blue and methyl orange, whose mass fraction in the solution is 0.001 %, forms coagulative resistant solutions. It is proven that the most effective coloring additives for the developed composition formulations are the colorants bromothymol blue and methyl orange, because they make it possible to form a stable coloration under acidic environment. These organic synthetic colorants are acid-base indicators, so they form a stable coloration in acidic solutions. The developed composition formulations contain orthophosphoric acid, which ensures the formation of a steady blue coloration in the presence of bromothymol blue (Fig. 1, 2, *a*), and pink – in the presence of methyl orange (Fig. 1, 2, *b*).

Water-soluble fire-retardant products used to protect wood from fire are obtained by mixing individual chemicals, for example inorganic salts, which are washed out. Penetrating the timber to depth, such fire-retardant agents enter the space of macro-capillaries (vessels and tracheids); and removing moisture, they stay put in macro-capillaries in the form of crystals. When moistening wood, the crystals of flame-retardant substances dissolve

Table 4

Results of establishing flammability time of wood samples

Sample designation	Concentration of colorant additive, %	Number of layers applied	Flammability time, s
1 (control)	Non-treated		15
2	Without coloring additive (colorant)	1	20
3	Without coloring additive (colorant)	2	60
4	Without coloring additive (colorant)	4	45
5	0.001	1	35
6	0.001	2	70
7	0.001	4	50

in a moist environment and, through the macro-capillaries, along or across the fibers, and also through microcapillaries, gradually go out; over time, the flame-retardant effect decreases. The less resistant to moisture the components that are part of the flame retardant means, the shorter the term of their fireproof efficiency. Acidic flame retardants, when penetrating the air space of wood, can penetrate the cell walls, entering the interaction with wood fiber. For such means, fluctuations in the wood equilibrium moisture content is not dangerous in terms of the creation of conditions for the migration of substances onto the surface. However, the acidic fire-retardant means, when penetrating the depth, and in interaction with fiber, worsen the strength parameters. If the depth of their penetration is significant, the reduction in strength could become dangerous, and such means cannot be used for responsible load-bearing structures. When using the surface fire protection, such danger does not exist [3].

The need to ensure the stability and durability of fireproof treatment without compromising the strength of structures has predetermined the choice of an application technique for composition formulations, namely, applying a roller.

The use of coloring additives of the pigment concentrates of TM «Amber» and TM «Sniezko» with a solution of natural bischofite ensures the formation of two-phase systems, which require careful agitation prior to use (Fig. 3). However, the use of these pigment concentrates makes it possible to obtain a saturated coloration of the surface of the treated wood (Fig. 4).

Given that we did not register on any samples of wood self-burning, through combustion, surface charring, charring at full depth, when controlling the fireproof treatment quality, the test results can be considered positive. Thus, the surface fire-retardant treatment is considered to be of high quality because the positive test results were obtained for all experimental samples. Our study has proven that the use of coloring additives in the developed composition formulations do not degrade the quality of fireproof treatment on wood samples. Consequently, the advantages of the specified composition formulations that contain colorant additives (colorants), in addition to wood fire protection, include a fact of visualizing the corresponding treatment.

The high rate of flammability of the untreated samples 1 is predetermined by the lack of surface treatment of wood with a flame-retardant agent (Table 4). However, the research results (Table 4) indicate an increase in the flammability time of the experimental samples of wood 2–7. The fire-retardant mechanism of the developed composition formulation is due to the successive processes of converting bischofite salt under the influence of an elevated temperature, which confirms the results from studies [30, 33]. At the same time, the slowdown of flammability time of the experimental wood samples is affected by the addition of orthophosphoric acid to the developed composition formulations, which is a strong fire retardant, thereby ensuring high fire-retardant properties of the developed composition formulations. This is consistent with data from [28]. In this case, the introduction of methyl orange to composition formulations prolongs the time of flammability (Table 4).

The results obtained indicate that the presence in the developed composition formulations of a bischofite solution (with a mass fraction of $MgCl_2$ of 18 %) and H_3PO_4 (concentration of 3 %) reduces flammability time. At the same time, the developed composition formulation also solves the task of environmental safety, durability, and reliability. Adding methyl orange (concentration of 0.001 %) to the developed composition formulation ensures a stable wood coloration in pink (which visually confirms the application of a fire-retardant treatment) and increases the flammability time of wood. Our findings are consistent with the research reported in [34], according to which the fire-retardant effect of the wood treated with retardants is strengthened due to the pigments available in the protective coating system.

We have experimentally proven the efficiency of wood treatment by applying the developed composition formulations using a roller, thus allowing the fireproof treatment at a construction site. Treatment efficiency is increased when applying a composition formulation containing methyl orange in 2 layers (as indicated by data from Table 4). The interval of the application should be long enough to allow for the composition formulation to impregnate before the surface is dried («wet on wet»). It should be noted that the wood treatment by applying the developed composition formulations onto the surface using a roller would ensure economic efficiency, in contrast to the use of immersion under stationary conditions. Thus, choosing a technique (method) for applying a fireproof agent on construction structures should take into consideration the structural, technological, and economic conditions.

Our conclusions could be considered relevant from a practical point of view, because they make it possible to use the developed composition formulations and the application technique.

Special features of the developed composition formulations are:

– the use of a bischofite solution with a mass fraction of $MgCl_2$ of 18 % extracted from well No. 1 at Zaturin deposit, with the addition of orthophosphoric acid at concentration 3 % (proceeding from its proven effectiveness [28]);

– the introduction to the composition formulation of coloring additives – bromothymol blue and methyl orange, whose mass fraction in the solution is 0.001 %;

– the introduction to a composition formulation of coloring additives of the pigment concentrates TM «Amber» and TM «Sniezko» (concentration 5, 10, 15 %);

– protection of the interior structures, made of wood, at residential buildings and non-residential facilities from flammability, spreading the flame along a surface; mold, houses and wood-destroying fungi and tree insects;

– allowing the visualization of the applied protection based on changes in the color of wood;

– the non-toxic components, the absence of harmful effects on the human body; – ensuring the safety in line with regulatory documents;

– positive impact on the environmental condition of buildings in general.

That is, the developed composition formulation, in terms of its components, can be attributed to environmentally-friendly. Its constituents refer to non-toxic products according to GOST 12.3.034-84 «Occupational safety standards system. Operations to protect wood. General safety requirements». It does not exert any harmful effect on the human body given that bischofite is non-toxic by its chemical composition (Table 2). Orthophosphoric acid, which is included in the composition formulation, in terms of the degree of influence on the human body refers to hazardous substances of class 2 in accordance with GOST 12.1.005-88 «Occupational safety standards system. General hygiene requirements for workplace air». The maximum permissible concentration of the product (by phosphoric anhydride) in the air of

working areas at industrial premises is 1 mg/m^3. Methyl orange, according to the safety passport in accordance with Regulation (EU) No. 1272/2008, refers to toxic substances only if swallowed (Category 3). The proposed technique for applying the developed composition formulation under construction conditions makes it economically feasible. After all, it does not require the use of significant energy resources and transportation costs associated with the application of the composition formulation on structures at impregnating workshops, which could be located at a considerable distance from construction sites. At the same time, the issue of preserving the fire-protection of wood from washout by atmospheric precipitation during its transportation to the construction site and during installation is resolved, as well as during operation. Renovating building structures made of wood, treated by the technique of deep impregnation, which lost their fire-retardant properties during operation, is very problematic. The proposed technique for applying the developed composition formulation provides for the possibility, if necessary, to carry out a periodic restoration of the flame-retardant coating without any problems and additional costs (except for the composition formulation itself). At the same time, the complex task is being dealt with, namely, fire- and bio-protection, as well as the visualization of the applied treatment of materials and structures at residential buildings and non-residential facilities made of wood. Thus, the developed environmentally-friendly composition formulations are designed to protect against flammability, the spread of flame along a surface; mold, tree-destroying fungi and tree-eating insects in the structures made of wood. However, the practical application of the developed composition formulation might be recommended for wood structures not directly exposed to the effect of atmospheric precipitation.

The obtained experimental results could be reproduced under condition of using the suggested materials, complying with the described research methods and treatment procedure. Results of experimental research could be affected by the application, as the base of a composition formulation, of natural bischofite extracted from well No. 1 at Zaturin deposit (Poltava oblast, Ukraine). The use of model samples of pine wood for fireproof treatment is predetermined by its widespread utilization as a structural material in construction, as well as a standard sample for studying flame-retardant properties of protective means for wood.

Further research could be directed towards theoretical and experimental studies into the intensity of processes of biological destruction of wood, treated with the proposed composition formulations to protect wood from fire, based on natural bischofite. And establishing the interconnection between the components and properties of the fire-bioprotective means against microbiological destruction.

7. Conclusions

1. The mass fraction of $MgCl_2$ in the bischofite solutions from Zaturin deposit is 28.5 %, which characterizes them as a promising raw material to be used as the base of a composition formulation to protect wood from fire.

2. It has been established that introducing to composition formulations that protect wood from fire, based on natural bischofite, a coloring additive, bromothymol blue and methyl orange, whose mass fraction in a solution is 0.001 %, forms coagulative resistant solutions. It has been experimentally proven that the most effective coloring additives (colorants) in a solution of natural bischofite, which make it possible to ensure a stable coloration of wood, are the additives of bromothymol blue and methyl orange. In the presence of bromothymol blue, wood acquires a persistent blue coloration, methyl orange – pink.

3. Coloring additives of the pigment concentrates TM «Amber» and TM «Sniezko» form two-phase systems with a solution of natural bischofite. The proposed composition formulations to protect wood from fire based on natural bischofite, which contain coloring additives of the above pigment concentrates, should be thoroughly agitated before treating wood, which makes it possible to obtain the saturated color of the finishing surface.

4. The quality control of wood fireproof treatment has proven the efficiency of using coloring additives (bromothymol blue and methyl orange; pigment concentrates TM «Amber» and TM «Sniezko») in the developed formulations.

5. It has been established that the flammability time of wood treated with a composition formulation to protect wood from fire, based on natural bischofite, under condition of a double layer application, increases by 4 times compared to untreated wood. Introducing to the composition formulation to protect wood from fire, based on natural bischofite, the coloring additive (colorant) methyl orange, under condition of a double layer application, prolongs the flammability time by more than 4 times. The specified composition formulations to protect wood from fire, based on natural bischofite, could be widely used in woodworking and construction industry, namely for fire protection of wood and visualization of the applied treatment. Thus, they meet the criterion of «industrial application».

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