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ESTABLISHING FIRE PROTECTION PATTERNS IN WOOD USING IMPREGNATION COMPOSITIONS FROM INORGANIC SALTS

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An issue related to using inorganic salts for fire protection of wood is to ensure their flame-inhibiting ability and compatibility with wood and application technology. That is why the object of research was to establish the effectiveness of inhibitory properties of mixtures of inorganic salts during interaction with the flame and enabling interplay with wood. A synergistic increase in the inhibitory capacity of mixtures of aqueous solutions of salts of diammonium phosphate and ammonium sulfate at a ratio of 2:1, and for a mixture based on orthophosphoric acid, urea, and oxyethylidenediphosphonic acid in the concentration range of 20–25 % by mass, has been proven. During the interaction of the specified mixtures with the wood surface, it was found that after application to the wood surface, the dispersed component of the free energy of the wood surface decreased to zero; instead, the polar component increased 13 times, which indicates a change in the wood surface. During the tests of wood samples on the effect of the burner flame, it was found that the untreated sample ignited on second 53, and the flame spread throughout the sample for 102 s. On the other hand, the samples treated with a mixture of an aqueous solution of phosphate and ammonium sulfate, as well as a mixture of aqueous solutions based on orthophosphoric acid and urea and oxyethylidenediphosphonic acid, did not catch fire, the flame did not spread over the surface, and the flammability index was 0. The practical significance is that the results were taken into account when designing flame retardant compositions for wood. Thus, there are reasons to assert the possibility of targeted regulation of wood protection processes through the use of mixtures of inorganic salts capable of forming a protective layer on the surface of the material that inhibits the burning of wood

Keywords: phosphorous-ammonium salts, protective agents, growth in wood mass, wood surface treatment, free energy of wood surface

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1. Introduction

Wood, as a building material, is widely used for the manufacture of structures in construction and architecture due to its mechanical and operational properties. However, because of its high flammability, it is a fire-hazardous material, and its use requires compliance with fire safety requirements. Therefore, when it comes to existing wooden structures, the most common way to increase the level of fire safety is fire-resistant treatment, namely improving their reaction to fire by treating wood with flame retardants.

The introduction of flame retardants into the material improves the fire resistance of wood by reducing the amount of heat released in the initial stages of a fire, slowing down the spread of flames, and limiting the formation of smoke and flammable volatile substances. But all flame retardants based on inorganic salts have disadvantages, such as insufficient efficiency and a limited period of use. And they are also prone to washing out under the influence of external conditions since the durability of fire-resistant coatings under wet conditions is closely related to the water solubility of chemicals used as composites. In addition, the process of impregnating wood with flame retardants depends on their surface properties, in particular, such as surface and interfacial tension, and therefore the application of impregnating compositions, flame retardants, their spreading, and sticking to wood is due to the free energy of the surface.

Combinations of phosphorus and nitrogen are preferred because of the observed synergism that improves the fire resistance and inhibition capacity of the composition. In particular, the presence of nitrogen creates a synergistic effect for phosphorus, while the endothermic release of ammonia occurs during heating of the composition, which dilutes the fuel in the gas phase, inhibiting ignition. This leads to increased resistance to flame propagation and directs pyrolysis to more coal and less volatile combustion products. The addition of other substances to this combination may reduce the effectiveness of the flame retardant.

Therefore, establishing the parameters for the use of mixtures of inorganic compounds as fire-retardant compositions for wood and identifying changes in surface properties when treating wood is an unresolved component of fire resistance that determines the need for research.

2. Literature review and problem statement

In work [1], an innovative macromolecular phosphorus-nitrogen flame retardant (PDPSB) was successfully developed and synthesized to study its effect on fire resistance, combustion behavior, thermal stability, and properties of polycarbonate (PC) composites. In addition, an in-depth study of the potential flame retardant mechanism was conducted. Combustion results showed that the samples exhibited a high Limiting Oxygen Index (LOI) of 33.0 %. Compared with the pure sample, the peak heat release rate (PHRR), total heat release (THR), and total smoke generation (TSP) values of PC-3 decreased by 37.9 %, 11.1 %, and 4.9 %, respectively. It should be noted that the amount of coal residues for PC-3 was increased from 7.4 % for pure PC to 15.8 % with an increase to 113.5 %. Thermogravimetric analysis (TGA) results under N_2 atmosphere revealed that PDPSB has better thermal stability with an initial decomposition temperature (initial) of 342.6 °C and a higher residual char yield of 48.4 %. As the amount of PDPSB increased, the maximum rate of mass loss (Rpeak) was reduced and the yield of residual char increased for PC/PDPSB composites. Based on the study of the flame retardancy mechanism of PDPSB, the excellent fire resistance of PC/PDPSB composites was confirmed. In the gaseous state, the release of pyrolysis gases is inhibited, and the active radicals are captured by the generated phosphorus free radicals. In the condensed phase, the stable carbon residue with phosphorus and nitrogen elements acted as a barrier to prevent heat, flame, and oxygen. However, optimal decisions regarding its concentration have not been determined.

Paper [2] used the liquid reactive flame retardant strategy and synthesized six new liquid phosphorus-containing reactive compounds as flame retardants. The results show significant increases in fire resistance and strength, as well as unchanged resin viscosity and strength. When the phosphorus content does not exceed 3 wt %, the Limiting Oxygen Index (LOI) of the resin can reach over 30 %, and UL-94 corresponds to a V-0 rating. The structure of the compounds significantly affects their fire protection mechanism. In particular, compounds rich in the P-O-C structure are more resistant to condensed phase flame (promoting charring) and are more favorable for improving LOI. Compounds rich in P-Ph and P-C structures have higher thermal stability and mainly exhibit flame resistance in the gas phase, which is more useful for improving the self-extinguishing properties of materials. However, it is not indicated how these materials affect the environment.

Work [3] investigated the fire resistance of bamboo treated with fire retardants, which have water-soluble and ecological properties. The synergistic effect of flame retardant in the form of a complex of APP and P-N-B on fire resistance was evaluated, and the absorption capacity and rate of moisture absorption were also evaluated depending on the duration of impregnation and the concentration of the solution. The results showed that the absorption capacity increased with the duration of impregnation and the concentration of the solution. It was observed that solution concentration had a significant effect on moisture uptake for both the APP and P-N-B complex series. It was found that the ideal duration of impregnation and the concentration of the solution are 6 hours and 30 %, respectively. The APP and P-N-B series of complexes significantly improved the fire resistance of bamboo, but the latter showed a better effect due to the synergistic combination of P, N, and B. The FPI of the APP and P-N-B series of complexes increased by 2.4 and 4.1 times compared to untreated. Both of them contributed to the formation of stable coal layers. However, it has not been determined how they exerted their influence in the gas phase due to the release of non-combustible gas to dilute the fuel and soften the action of flame radicals.

A flame retardant (CeHPP) was synthesized in [4] to develop an antimony-free BFR synergist and improve the high heat and smoke output of BFR due to its gas shielding mechanism. CeHPP was prepared by the hydrothermal reflux method and incorporated into PC/DBDPO by melt blending. CeHPP showed better synergistic effect with DBDPO than Sb_2O_3 in PC matrix. For PC/DBDPO/CeHPP (92/7/1, wt %), the sample did not ignite, the limiting oxygen index (LOI) value increased to 39.2 % and achieved a UL 94 V0 rating in the vertical burning test. According to cone calorimetry, CeHPP and DBDPO/CeHPP could effectively suppress the heat and smoke generation from the PC composites, while DBDPO and DBDPO/Sb_2O_3 would accelerate the heat and smoke generation during combustion. The synergistic flame retardant mechanism confirmed that the carbon barrier effect of CeHPP transferred to the free radical trapping effect of BFR from the gas phase to the condensed phase. This prevents the chain reaction of oxidation of free radicals and the release and spread of gases and smoke. However, there is no mention of the impact on the ecosystem.

A new and effective flame retardant reported in [5], consisting of ammonium tris (2-hydroxyethyl) isocyanurate triphosphate (ATITP), was obtained by a solvent-free synthesis method to improve the fire resistance of dense poplar boards. The flame retardant mechanism was investigated and the combustion radical scavenging mechanism synergistically contributing to charring and heat suppression was summarized. A density board treated with 20 % ATITP had a final oxygen index (LOI) of up to 65.1 %. In a cone calorimetry experiment (CONE), the total heat release (THR) of the fireproof dense board was reduced by 73.9 % compared to the pure dense board sample. The heat release rate (HRR), the formation of CO and CO_2 were greatly reduced. In addition, analysis by thermogravimetric infrared coupler (TG-FTIR) and thermal cracking gas mass spectrometer (Py-GC–MS) revealed that the flame retardant exhibits performance in the gas and condensed phases upon thermal decomposition. However, nothing is said about the conditions for using flame retardant.

Work [6] discusses the development of metal organic frameworks (MOFs), which are used as flame retardants. The flame retardant mechanisms in the gas phase and condensed phase of original MOF materials, modified MOF composites, and MOF-derived composites as flame retardants were analyzed, respectively. The effects of carbon-based materials, phosphorus-based materials, nitrogen-based materials, and biomass on the flame retardant properties of polymers are discussed in the context of MOFs. The design of multi-structured MOF flame retardants is also presented, and the variety of MOF-based flame retardants with different morphologies is shown to expand ideas for further research. But nothing is said how this affects their strength during operation.

In study [7], a new biomass-based flame retardant (Acc) was developed using ammonium polyphosphate (APP) as raw material in combination with biomass materials carrageenan (CAR) and collagen (COL). The combustion efficiency of biomass-based fire retardants on wood was investigated using various analytical and testing methods. The results showed that the flame retardant with a CAR:COL:APP ratio of 1:1:3 showed the best flame retardant effect with an LOI of 31.8 %. The peak heat release rate was reduced to 53.8 % compared to untreated wood, and the peak smoke release rate and total smoke release were reduced by 63.2 % and 49.2 %, respectively. Mechanism analysis revealed that APP, COL, and CAR produced non-combustible gases such as ammonia and gases containing P and S during fire. These gases dilute oxygen and eliminate •H and •HO radicals in the gas phase, thus exhibiting flame retardant effects. However, does their stability under the strong influence of fire play a key role?

As part of study [8] on passive flame retardant polymeric materials, both reactive and additive ways, including compounds containing phosphorus, were used. They included inorganic and organic substances, and in the latter case, phosphorus-containing groups differed in chemical environment (phosphite, phosphate, phosphine, phosphine oxide, and phosphonate ether) and oxidation state of the P atom (i.e., III or V). The overall flammability profiles of wood substrates coated with phosphorus-containing compounds were obtained using cone calorimetric measurements. It was found that the inorganic solid additive, i.e. $(NH_4)_2HPO_4$, underwent a two-step degradation to form ammonia gas and phosphoric acid. In addition, liquid additives, due to their volatility compared to solid ones, showed a relatively greater presence in the vapor phase than the volatile fragments released from the latter (i.e., phosphine and phosphine oxides). However, nothing is said about the environmental friendliness of these products.

Paper [9] discusses traditional methods of fire prevention with flame retardants, which are used to modify wooden materials. Since wood is an extremely environmentally friendly material, there is considerable interest in its use in the construction industry from the point of view of modern construction. However, safety requirements, including fire safety requirements, are becoming increasingly demanding. Therefore, more efficient and environmentally friendly approaches to the treatment of wood materials related to this topic are the subject of research interest in laboratories around the world. The rapid development of nanotechnology offers new materials with unique properties, which in the future will be able to partially or even replace conventional chemicals, often toxic to the environment. In addition, a broad literature review discussed the potential use of nanomaterials for wood. However, nothing is said about the conditions of operation of these products.

Study [10] used tetrakis(hydroxymethyl)phosphonium sulfate (THPS) for the intercalation modification of montmorillonite (MMT). Subsequently, we achieved an environmentally friendly and efficient exfoliation of MMT by reacting urea with hydroxyl groups, leading to the simultaneous preparation of effective organic/inorganic synergistic flame retardants (THPSU-MMT). Epoxy (EP) composites containing 5 wt % THPSU-MMT, can obtain UL-94 V0 classification. In addition, the peak heat release rate (PHRR), total heat release rate (THR), and maximum CO release rate can be reduced by 78.42 %, 62.26 %, and 72.50 %, respectively. The results show that THPSU-MMT exhibits a dual flame retardant effect in both gas and condensed phases. In addition, the combination of MMT and THFSU significantly increases the presence of phosphorus-containing pyrolysis products in the condensed phase. The flame retardancy index (FPI) of EP flame retardant increased from 0.05 $m^2/s/W$ in pure EP to 0.36 $m^2/s/W$, attributed to enhanced catalytic carbonization and assisted free radical capture in the gas phase. In addition, the flame spread index (FGI) decreased from 11.55 kW/m/s in pure EP to 1.18 kW/m/s, indicating a significant increase in fire safety. In addition, THPSU-MMT synergistic flame retardants improved the tensile strength of EP composites. This study offers an environmentally friendly and efficient approach for the effective exfoliation of MMT and also presents new concepts for the development of effective organic–inorganic synergistic flame retardants. However, the values of these parameters do not cover a wide range of applications.

In [11], the pyrolysis behavior of aluminum hypophosphite (AHP), aluminum diethylphosphinate (AlPi), poly(1,4-butylene terephthalate) (PBT), and PBT composites was investigated using mass spectrometry (PY-PI-TOFMS) at different temperatures in real time. The gas-phase mechanism of flame retardancy of AHP in PBT is considered to be the flame inhibition effect of PH3, H3PO2, and P4 pyrolyzed from AHP. AlPi in PBT is believed to be phosphorus-containing compounds and a kind of phosphorus radicals pyrolyzed with AlPi as flame retardants, and the pyrolysis of AlPi by PBT matrix is synchronous with this. The eight-membered cyclic noncovalent adduct of the C2H5–(O=)P•–OH radical and the diethylphosphinic acid molecule through the intermolecular double hydrogen bond interaction can more efficiently produce PO-type radicals in the flame. The results of thermogravimetric analysis correspond to the results of pyrolysis. The much better flame retardancy effect of AlPi in the gas phase than AHP in PBT obtained from the combustion tests is interpreted by the pyrolysis results, which provides a powerful guide for the development of highly effective flame retardants. But nothing is said about the cost of production.

Thus, it was established from the literature that one of the conditions for the use of mixtures of inorganic salts is the effective inhibition of the hydrocarbon flame and the treatment of the wood surface. But the interrelationships between the parameters that ensure high efficiency in reducing the active radicals of the flame, the values of which are necessary for the design and manufacture of fire-extinguishing substances, have not been defined. The paucity of experimental studies to explain and describe the process of formation of surface properties during treatment leads to a decrease in their effective use. Therefore, establishment of parameters of flame inhibition and the influence of mixtures of inorganic salts on the process of wood processing predetermined the need for research in this area.

3. The aim and objectives of the study

The purpose of our work is to identify patterns in the fire protection of wood by compositions of aqueous solutions of inorganic salts. This makes it possible to substantiate the mechanism of action of phosphoric-ammonium salts, urea, and salts of phosphoric acids to suppress wood burning.

To achieve the goal, the following tasks were solved:

– to conduct modeling of the hydrocarbon flame inhibition process when interacting with mixtures of aqueous solutions of inorganic salts;

– to establish patterns in the formation of surface properties of mixtures of inorganic salts and changes in the surface properties of wood during processing.

4. The study materials and methods

4. 1. The object and hypothesis of the study

The object of our study is the inhibitory properties of mixtures of inorganic salts during interaction with n-heptane flame and changes in the surface properties of wood.

The scientific hypothesis assumes reducing the flammability indicators of the n-heptane flame when interacting with aqueous solutions of inorganic salts and establishing surface and interphase tension when applying impregnating compositions of flame retardants to wood.

In the course of the research, assumptions and simplifications were adopted that relate to the specificity of the n-heptane combustion process and other processes at the modeled objects. Namely, they determine the impact of changes in external conditions on the object of research and the flow of the process of supplying inorganic compounds to the flame and to the surface of the wood: the same temperature, humidity while pressure is not variable.

4. 2. Researched materials used in the experiment.

To determine the nature of the inhibitory ability of the composition, heptane vapor obtained by the carburation method was used as a combustible substance. To conduct studies on the determination of the inhibitory capacity of inorganic salts, solutions of phosphate and sulfate ammonium salts with a concentration of 2.5; 5.0; 10.0; and 20.0 wt % were used. Mixtures of phosphoric acid and urea with a concentration of 10.0; 12; and 20.0 % by weight were also studied, with the addition of 5 % by weight of oxyethylidenediphosphonic acid. The studied inorganic salt solution was sprayed using a pneumatic nozzle and fed into the flame coaxially with it. The nature of the interaction of these substances with wood was also studied. To establish the energy characteristics of the materials and determine the marginal angle of wetting, samples of fire-resistant pine wood with dimensions of 50x50 mm and a thickness of 10 mm were used. To determine the flammability and flame propagation index, samples of size 320 140 mm, thickness 6 mm, untreated and treated with a mixture of aqueous solutions of inorganic salts with a consumption of 270 g/m^2 were used.

4. 3. Methodology for determining n-heptane flame inhibition indicators and their interaction with wood

Determination of flame inhibition parameters of n-heptane with mixtures of inorganic salts was carried out according to the procedure given in [12].

The test for determining the edge wetting angle was carried out according to the methodology from [13], the essence of which was to apply a drop of coating on the substrate of the test material, and after the drop reached an equilibrium state, its height and diameter were determined using a microscope.

To estimate the surface energy of aqueous solutions of mixtures of inorganic salts and fire-resistant wood when the coating is applied, the Fowkes method was used, which allows taking into account dispersion, hydrogen, and dipole-dipole interactions at the "solid-liquid" phase boundary [14]:

$$(1+\cos\theta)\sigma_{la} = 2\left(\sigma_{sa}^{d}\cdot\sigma_{la}^{d}\right)^{0.5} + 2\left(\sigma_{sa}\cdot\sigma_{la}\right)^{0.5}, \qquad (1)$$

where θ is the edge wetting angle;

σ_{sa}, σ_{la} – surface energy of solid and liquid, respectively; the p index is the component of the total surface energy due to hydrogen and dipole-dipole interactions; index d – due to dispersion interactions.

This equation has two unknown quantities σ_{sa}^{d} and σ_{sa}^{p} and for practical use, contact angle data for two different test materials with known surface tensions σ_{la}^{d} and σ_{la}^{p} are required (Tables 1, 2).

Table 1

Surface tension and dispersed and polar components for test materials

Material	σ_{sa}^{d}	σ_{sa}^{p}	σ_{sa}
Teflon	20.0	0	20.0
Polyethylene terephthalate	13.1	20.0	33.1

Table 2

Surface tension and dispersed and polar components for test liquids

Material	σ_{la}^{d}	σ_{la}^{p}	σ_{la}
Water	21.8	50.8	72.6
Ethylene glycol	29.3	19.0	48.3

The flammability and flame spread index of wood were determined according to the methodology given in [15].

5. Results of determining the effectiveness of aqueous solutions of mixtures of inorganic salts for the fire protection of wood

5. 1. Results of research on changes in flame active radicals when aqueous solutions of inorganic salts are introduced

Fig. 1, 2 show the results of studies on determining the effect of mixtures of aqueous solutions of inorganic salts on the intensity of radiation of active flame radicals.

From Fig. 1, it was established that ammonium sulfate salt solution has the least effect on reducing the concentration of OH radicals (curve 4), and diammonium phosphate salt solution has a greater effect (curve 2). With the addition of a solution of diammonium phosphate to a solution of ammonium sulfate (mixtures with a molar ratio of 1:1), the intensity of the radiation of OH radicals in the n-heptane flame is significantly reduced. The greatest effect on the intensity of OH radical radiation in the n-heptane flame is observed when a mixture of salts is fed in a molar ratio of diammonium phosphate and ammonium sulfate of 2:1.

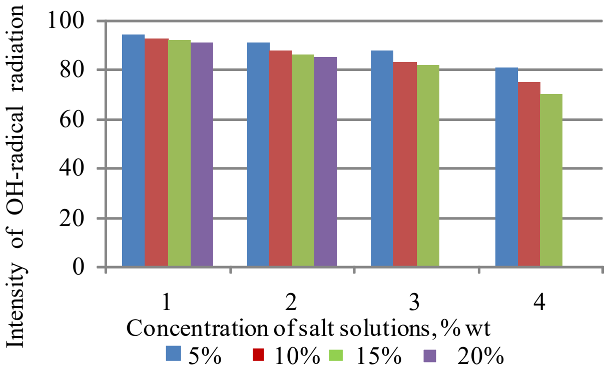

Fig. 1. Dependence of the relative intensity of OH-radical radiation on the concentration of salt solutions supplied to the burner: 1 – $(NH_4)_2SO_4$; 2 – $(NH_4)_2HPO_4$+$(NH_4)_2SO_4$ (1:1); 3 – $(NH_4)_2HPO_4$; 4 – $(NH_4)_2HPO_4$+$(NH_4)_2SO_4$ (2:1)

As can be seen from Fig. 2, a change in the concentration of aqueous solutions of orthophosphoric acid and urea in the mixture fed to the burner has different effects on the intensity of the radiation of OH radicals. It was found that at a concentration of orthophosphoric acid in an aqueous solution in the range of 18–22 wt % the relative radiation intensity of OH radicals decreases by about 18 %. These properties are also preserved for the composition based on orthophosphoric acid and urea with the addition of 5 % oxyethylidenediphosphonic acid in the concentration range of 20–25 % by mass the relative radiation intensity of OH radicals decreases by about 24 %.

Thus, experimental studies on the inhibitory capacity of aqueous solutions of salts of diammonium phosphate and ammonium sulfate showed that mixtures of these salts at a ratio of 2:1 have a non-additive increase in inhibitory capacity, that is, they show a synergistic effect.

The mixture based on orthophosphoric acid, urea, and oxyethylidenediphosphonic acid in the concentration range of 20–25 % by weight shows the same synergistic effect on the flame, which makes it possible for them to be used in fire protection.

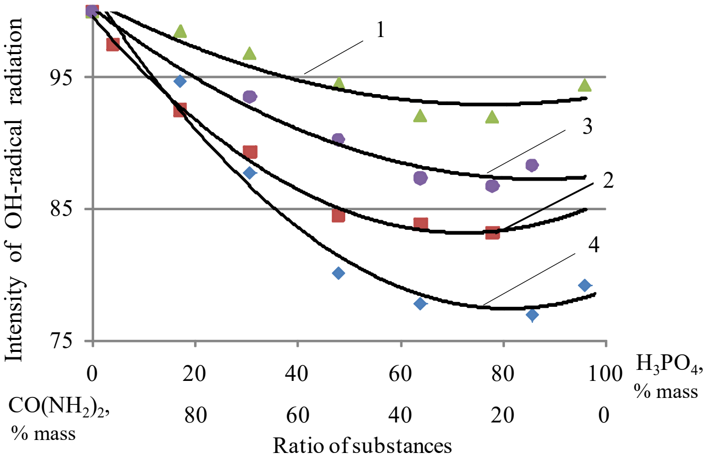

Fig. 2. Dependence of the relative intensity of the radiation of hydroxyl radicals on the mass ratio of the solution fed into the flame of *n*-heptane in a mixture of orthophosphoric acid and urea with a concentration of 1–10 %; 2–20 % and in a mixture of orthophosphoric acid and urea concentration: 3–12 %; 4–20 % with the addition of oxyethylidenediphosphonic acid at a concentration of 5 %

5. 2. Results of studying surface energy characteristics of mixtures of aqueous solutions of inorganic salts and wood

To study the surface energy characteristics of mixtures of aqueous solutions of inorganic salts, the edge wetting angle was determined on the samples of the test materials listed in Table 1.

Conducting the test: a drop of an aqueous solution of flame retardant mixtures was applied to a sample of the test material using a pipette (Fig. 3, 4). After the drop reached an equilibrium state, its height and diameter were determined using a microscope with a certain degree of magnification.

The results (Fig. 3, 4) show that a mixture of aqueous solutions of inorganic salts based on orthophosphoric acid, urea, and oxyethylidenediphosphonic acid forms an angle of about 62° when Teflon is wetted. And when wetting, a mixture of an aqueous solution of phosphate and ammonium sulfate forms an angle of about 45°.


a *b*

Fig. 3. Coating a base of the mixture of urea orthophosphoric acid and oxyethylidenediphosphonic acid, which is applied to the test material: *a* – Teflon; *b* – polyvinyl chloride

However, when polyvinyl chloride is wetted, a mixture of aqueous solutions of inorganic salts forms an angle of 30°.

The results of determining the edge angle of wetting of mixtures of aqueous solutions of inorganic salts of test materials and determining the corresponding components of the surface free energy are given in Table 3.

The results of determining the edge angle of wetting by test liquids and determining the corresponding components of the free energy of the surface of pine wood are given in Table 4.

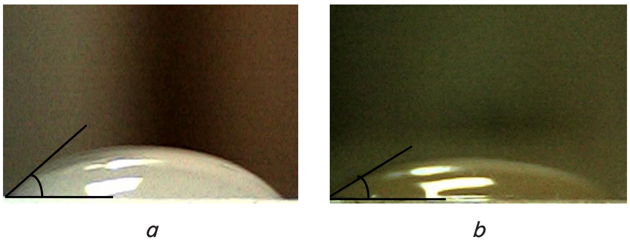

Fig. 4. Coating a base of the mixture of phosphate and ammonium sulfate applied to the test material: *a* — Teflon; *b* — polyvinyl chloride

The effectiveness of applying a mixture of inorganic salt solutions, their spreading and sticking to the wood surface is due to the free energy of the surface, in terms of the polar and dispersed parts of both components, both the mixture of inorganic salt solutions and the wood surface.

At the next stage, a change in the surface energy characteristics of pine wood after its treatment with mixtures of aqueous solutions of inorganic salts was determined. For this purpose, we determined the edge angle of wetting of wood samples with test liquids and calculated the components of the free energy of the surface of fire-resistant wood, which are given in Table 5.

As our study showed, the dispersed component of the free energy of the wood surface after treatment with mixtures of inorganic salt solutions decreased to zero, while the polar component increased 13 times, which indicates a change in the wood surface.

After studying the relationship between wood and mixtures of aqueous solutions of inorganic salts, a study was conducted to determine the flammability and flame propagation index.

Fig. 5 shows the process of testing a sample of untreated wood, Fig. 6 – samples (No. 1) of wood treated with a mixture of aqueous solutions of inorganic salts. On the basis of orthophosphoric acid, urea, and oxyethylidenediphosphonic acid, Fig. 7 shows as an example a sample (No. 2) of wood treated with a mixture of an aqueous solution of phosphate and ammonium sulfate.

The results in Fig. 5–7 show that under the influence of high temperature, ignition of the untreated sample was established. On the other hand, the absence of ignition and flame propagation was recorded for the flame retardant, which is associated with the decomposition of flame retardants under the influence of temperature with the absorption of heat and the release of non-combustible gases (nitrogen, carbon dioxin). Also, by changing the direction of decomposition in the direction of the formation of a non-flammable coke residue on the surface of the wood. Studies on the determination of flammability are given in Table 6.

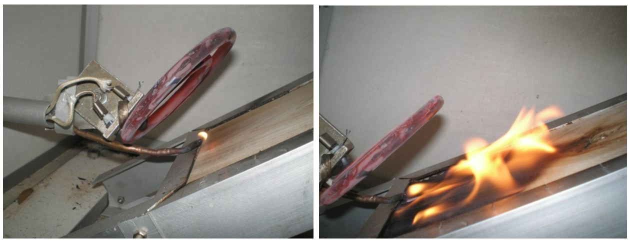

Fig. 5. The process of testing an untreated wood sample

Fig. 6. The process of testing a sample of wood treated with a mixture of an aqueous solution of phosphate and ammonium sulfate

During the tests of wood samples on the effect of the burner flame, it was found that the untreated sample ignited on second 53, the flame spread throughout the sample for 102 s. On the other hand, the samples treated with a mixture of an aqueous solution of phosphate and ammonium sulfate and a mixture based on urea, orthophosphoric and oxyethylidenediphosphonic did not catch fire, the flame did not spread over the surface, the flammability index was 0.

Table 3

The edge wetting angle and the surface free energy component of a mixture of inorganic salt solutions

A mixture of solutions of inorganic salts on the basis	Edge wetting angle, θ, °		Surface free energy, mJ/m^2			Polarity, %
	Teflon	Polyvinyl chloride	Total	Polar	Dispersed	
Orthophosphoric acid, urea and oxyethylidenediphosphonic acid	62	30	28.9	17.0	11.0	58.8
Ammonium phosphate and sulfate	45	30	12.3	6.9	5.4	56.1

Table 4

Edge wetting angle and free energy component of wood surface

Wood	Edge angle		Surface free energy, mJ/m^2			Polarity
	Water	Ethylene glycol	Total	Polar	Dispersed	
Pine	73.2	42.4	49.6	8.2	41.4	16.5

Table 5

Edge wetting angle and free energy component of treated wood surface

Pine wood is fireproofed with a mixture on the basis	Edge wetting angle, θ, °		Surface free energy, mJ/m^2			Polarity, %
	Ethylene glycol	Water	Total	Polar	Dispersed	
Orthophosphoric acid, urea, and oxyethylidenediphosphonic acid	48	22	108.4	107.5	0.9	99.2
Ammonium phosphate and sulfate	45	30	90.01	90	0.01	99.9

Table 6

The time of passage of the control points by the flame front

A sample of wood	Flue gas temperature, °C		Ignition time, s	The time of passage of the sample areas by the flame front, s									Time to reach the maximum temperature of flue gases, s	Sample burning length, mm	Flammability index
	T_1	T_{max}		1	2	3	4	5	6	7	8	9			
Raw	58	324	53	2	7	8	11	7	9	6	7	8	102	292	177.0
Sample No. 1	55	80	–	–	–	–	–	–	–	–	–	–	600	–	0
Sample No. 2	57	83	–	–	–	–	–	–	–	–	–	–	600	–	0

Fig. 7. The process of conducting tests on a wood sample treated with a mixture of aqueous solutions of inorganic salts based on orthophosphoric acid, urea, and oxyethylidenediphosphonic acid

6. Discussion of results related to flame inhibition and studies of surface energy characteristics of mixtures of aqueous solutions of inorganic salts and wood

When studying the process of applying mixtures of aqueous solutions of inorganic salts for fire protection of wood, it is natural to establish relationships with flame inhibition (Fig. 1, 2). There is also a need for effective treatment of the wood surface, which follows from our results (Tables 3, 5). This is due both to the synergistic effect of phosphorus atoms and ammonium salts during decomposition under the influence of flame, which slows down the burning process, and to changes in the components of the surface free energy of treated wood.

It should be noted that the compatibility of mixtures of aqueous solutions of inorganic salts with wood and application technology is an important factor that should be taken into account when developing fire retardant materials. Obviously, this mechanism of operation of these coating mixtures is the factor regulating the process, due to which the fire resistance of wood is ensured. In this sense, the interpretation of the results of the determination of the flammability index of wood after exposure to flame, namely the formation of a coke-resistant layer during thermal exposure, takes place. During the tests of wood samples, it was established (Table 6) that the untreated sample ignited on second 53, the flame spread throughout the sample for 102 s, on the other hand, the sample treated with a mixture of inorganic salts did not catch fire, the flame did not spread over the surface, the flammability index was 0. This indicates the formation of a barrier on the surface of the material for temperature, which can be identified by the method of thermal impact on the studied samples. This means the opening of possibilities for effective fire protection of wood and the use of mixtures of aqueous solutions of inorganic salts at objects of various purposes.

A comparison of experimental studies on flame inhibition by mixtures of aqueous solutions of inorganic salts shows the processes of inhibition of flame propagation. And the study on the determination of the components of the free energy of the surface when wood is treated with mixtures of inorganic salts indicates changes in the surface of the wood. At the same time, it was established that the dispersed component of the free energy of the wood surface after treatment with mixtures of aqueous solutions of inorganic salts decreased to zero, while the polar component increased by 13 times (Table 5). This does not differ from the practical data, well known from works [1–3, 7], the authors of which also associate changes in the free energy of the wood surface with the addition of flame retardants under the influence of fire protection. But, in contrast to the results of research reported in [16], the obtained data on the effect of aqueous solutions of inorganic salts on inhibition of the wood combustion process allow us to state the following:

– the main regulator of the process is not only the formation of a heat-shielding layer of inflammable coke but also the decomposition of flame retardants with the release of non-combustible gases. In particular, nitrogen, carbon dioxide, which interact with the flame and inhibit the oxidation process in the gas and condensed phase;

– a significant influence on the process of protection of combustible material when applying a fire-retardant coating is carried out in the direction of reactions in the pre-flame area to the side of the formation of soot-like products on the surface of wood.

Such conclusions can be considered appropriate from a practical point of view because they allow us to approach the development of fire retardants for wood, taking into account the effect of mixtures of aqueous solutions of inorganic salts on the flame. However, they also affect the change in the surface properties of wood when they are applied [17]. From a theoretical point of view, the data of the study allow us to assert the definition of the process mechanism of both the inhibition of the flame combustion process and the formation of a “wood-fire retardant” composite layer on the surface of the wood, which are certain advantages. However, it is impossible not to note that the results of the determination (Tables 3, 5) indicate an ambiguous influence of mixtures of aqueous solutions of inorganic salts on the change in the free energy components of the treated wood surface. This is manifested, first of all, in charred wood, which is formed on the surface of the sample during testing.

Such uncertainty imposes certain restrictions on the use of our results, which can be interpreted as the shortcomings of this study. The impossibility of removing the mentioned limitations within the framework of this study gives rise to potentially interesting areas for further research. It, in particular, can be focused on detecting the moment of time when the fire-retardant properties fall under the influence of high temperature. This will make it possible to investigate the structural transformations of the wood surface, which begin to occur at this time, and to determine the input variable parameters of the process that significantly affect the onset of such transformation.

7. Conclusions

1. Experimental studies of the inhibitory capacity of aqueous solutions of salts of diammonium phosphate and ammonium sulfate showed that mixtures of these salts at a ratio of 2:1 have a non-additive increase in inhibitory capacity, that is, they show a synergistic effect. The mixture based on orthophosphoric acid, urea, and oxyethylidenediphosphonic acid in the concentration range of 20–25 % by weight shows the same synergistic effect on the flame, which makes it possible for them to be used in fire protection.

2. It was established that after applying mixtures of aqueous solutions of inorganic salts to the wood surface, the dispersed component of the free energy of the wood surface decreased to zero, while the polar component increased 13 times, which indicates a change in the wood surface.

During the tests of wood samples on the effect of the burner flame, it was found that the untreated sample ignited on second 53, the flame spread throughout the sample for 102 s. On the other hand, the samples treated with a mixture of an aqueous solution of phosphate and ammonium sulfate and a mixture based on urea, orthophosphoric and oxyethylidenediphosphonic did not catch fire, the flame did not spread over the surface, the flammability index was 0.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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