

An issue related to using a weather-proof reactive coating for fire protection of wood is to ensure resistance to high-temperature flame via application technology. Therefore, the object of research was the fire-retardant properties of reactive coating based on mixtures of organic-inorganic substances during interaction with flame. It has been proven that the samples of the reactive coating represent an accumulation of fine-dispersed equally sized substances surrounded by a polymer binder, which begin to decompose under thermal action; in particular, ammonium polyphosphate decomposes and releases phosphoric acid. That leads to the dehydration of pentaerythrite with the formation of soot while the decomposition of melamine is accompanied by the release of non-combustible gases that cause the soot to foam, thereby forming foamcoke. The mechanism of fire protection of wood has been established, which is related to the decomposition of flame retardants under the influence of temperature, the release of non-combustible gases, and the formation of a non-flammable coke residue. Thus, when the content of ammonium polyphosphate and pentaerythrite in the reactive coating was increased by 5 %, the volume of combustible gases decreased by more than 11 %, and the volume of nitrogen increased by more than 10 %. When their content was increased by 14 %, the volume of combustible gases decreased by more than 2 times, and the volume of nitrogen increased by more than 1.45 times. That also affected the formation of a foamcoke layer, which was recorded at the lowest content of ammonium polyphosphate at the level of 12 mm and increased for higher values up to 15.5 mm, and the multiplicity of foam increased by 1.25 times. The practical significance is that the results are taken into account when designing the reactive coating. Thus, there are reasons to assert the possibility of targeted regulation of the wood protection process by applying coatings capable of forming a protective layer on the surface

Keywords: reactive coating, wood preservatives, wood surface treatment, volatile combustion products, swelling of the coating

DEFINING PATTERNS IN THE FIRE PROTECTION OF WOOD WITH REACTIVE COATING

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1. Introduction

Environmentally safe materials made of wood are gaining more and more popularity in construction but, in terms of flammability group, they are categorized as combustible

materials and require fire retardant treatment. The main requirements for fire resistance of natural combustible materials made of wood are the ability to resist the action of fire and not to spread the flame over the surface. The change in the thermal destruction of wood at flame-retardant treat-

ment is aimed at the formation of non-combustible gases and inflammable coke residue, as well as the inhibition of oxidation in the gas and condensed phases.

Modern methods for fire protection of building structures are based on the use of impregnation solutions, which are complex systems of organic and inorganic components capable of penetrating the structure of wood and forming a protective layer of coke in case of fire. But these compositions are washed out of the wood during temperature and humidity fluctuations, thereby reducing fire protection. The simplest fire retardants based on inorganic binding materials are characterized by little elasticity and crumble during operation under the influence of temperature and humidity fields, changing the aesthetic appearance of the structure as well as thermal resistance.

In this area of research, there are studies aimed at designing intumescent coatings, which under thermal action form a heat-insulating foamcoke layer on the surface of wood. The presence of such a layer makes it possible to slow down the heating of wood and preserve its functions during a fire over a predefined period. In addition, there is a need to operate such a coating when there are wide temperature and humidity fluctuations. The use of environmentally safe reactive coatings based on water-resistant binders requires conducting fundamental studies of their impact on the stability of products to the operating conditions of the environment.

Therefore, production of weatherproof reactive coatings and determining the effect of components that are part of them on fire protection is a basis for ensuring the fire resistance of building structures. This, accordingly, predetermines the necessity of such studies.

2. Literature review and problem statement

In work [1], different amounts of boric acid BA (1.25, 2.5, 3.75, and 5.0 wt.%) were used to increase the effectiveness of the intumescent fire protection system (IFR) consisting of ammonium polyphosphate (APP) and pentaerythrite (PER) in polypropylene (PP), including 2 wt.% montmorillonite nanoclay (MMT). The fire resistance of the composites was investigated by UL 94, limiting oxygen index (LOI), and cone calorimetry tests. Thermal properties were determined using thermogravimetric analysis, differential scanning calorimetry, and thermal conductivity measurements. Experimental results showed that although the addition of 1.25 and 2.5 wt.% BA with 2 wt.% MMT significantly increased the thermal and fire resistance of PP composites, the addition of 3.75 and 5.0 wt.% BA caused antagonistic effects and worsened the fire resistance composites. The sample with the addition of 2.5 wt.% BA achieved the best fire resistance. The LOI value has been increased from 18 to 31 % with a UL 94 V-0 rating. In addition, the peak heat release rate was reduced from 668.6 to 150.0 kW/m², and the total heat release value was reduced from 247.9 to 98.4 MJ/m². At the same time, the thermal conductivity was increased from 0.22 to 0.28 W/mK. In addition, CO, CO₂, and smoke generation were significantly reduced relative to PP. However, the conditions for establishing optimal solutions for its use have not been established.

In [2], phosphate-filled fibers (CFF) with a layered silicate outer coating were developed into an effective intumescent flame retardant (IFR) system for polypropylene (PP). A small content of silicate (0.4 wt.%) leads to a decrease in

the content of phosphate by 27 wt.% to achieve the same level of fire resistance for PP. In addition, the efficiency of the loaded phosphate, as measured by a cone calorimeter, is 14 % higher than that of the commercial IFR, ammonium polyphosphate (APP). Thermogravimetric analysis and cone calorimeter tests demonstrate suppressed decomposition of phosphorus and CFF at higher temperature due to strong char formation. Characterization of coal residues using SEM elemental analysis confirms silicate-reinforced coal. However, there are no data on their impact on ecology.

In study [3], ammonium polyphosphate (APP) and aluminum hydroxide (ALH) with different mass contents were used as flame retardants (FR) on plant-based natural flax fabrics reinforced with polymers (FFRP). For both flame retardants, the results showed that the thermal decomposition temperature and LOI values of the composites increased with increasing FR content. According to the vertical UL-94 test, FFRP composites with 20 % and 30 % APP (i.e., by mass content of the epoxy polymer matrix) self-extinguished within 30 and 10 s after flame removal without any combustible droplets, respectively. However, there is no mention of the effect of flame retardants on the ecosystem.

In [4], a fully biological fire retardant coating (PAGS) was produced using phytic acid (PA) and guanosine (GS). PAGS was used as a universal fire retardant coating for wood. The PAGS coating significantly inhibited heat generation. P-containing free radicals in the gas phase were able to interact with highly reactive H⁺, HO⁺, and alkyl radicals, blocking the chain reaction during combustion. The density of the combustible gas was also diluted with non-combustible gases. The formed continuous porous and dense swelling layer of coal prevented heat and oxygen. However, it has not been established how they affected the flame in the gas phase and the mitigation of the action of flame radicals.

In paper [5], in order to improve the fire-resistant properties of wooden plywood, intumescent fire-resistant coatings were designed using melamine, borate, pentaerythrite, and urea as the main ingredients and vein rock as a modified additive. The results show that when the mass fraction of vein rock was 8 wt.%, the exothermic reaction rate, total smoke generation, and total exothermic coating volume were significantly reduced. In addition, the addition of waste rock contributed to the formation of a continuous and dense structure of the carbon layer, which, during the combustion process, formed a molten substance that effectively isolated oxygen and heat, enhancing fire-retardant and heat-insulating properties. The results of the study provide valuable information on the development of flame retardant coating compositions, however, there are no data on the conditions of operation of the coating.

In [6], it is stated that using a combination of simultaneous thermal analysis, microscale combustion calorimetry, and conical calorimetry, plywood impregnated with vacuum pressure is covered with a thin layer of water-based fireproof coating. The coating layer was found to delay sustained burning for a longer period of time than impregnated wood and delayed burn-through, which is critical to the rate of fire development. But there are no data on how their strength changes during operation.

Paper [7] investigated the behavior of intumescent paints for the protection of wood pre-treated with phosphate or silicate-based fire retardant. In addition, the effect of swelling paint on aging under several conditions was investigated. Pretreatment showed improved fire resistance of samples with intumescent coatings. Also, the experiments showed a

difference in fire resistance depending on the aging method. UV aging preserved thermal insulation properties, while acid-immersed samples experienced a sharp decrease in fire resistance. The latter aging test increased the pore size of the coal, which led to a decrease in the coefficient of expansion and a decrease in the thermal insulation characteristics of the expanded material. However, does their stability under the strong influence of fire play a key role?

The research reported in [8] is aimed at devising an optimal approach to the synthesis of fire-resistant coatings through a comparative study of different methods related to the protection of materials such as wood and polymer when exposed to fire. The formulation of coatings is based on ammonium polyphosphate (APP) and other flame retardant additives and fillers, in which epoxy resin is used as a binder. The effect of flame retardant additives and fillers is characterized by thermogravimetric analysis (TGA), oxygen index test, smoke density test, and flammability test. TGA revealed that the addition of graphite as a filler increases the maximum degradation temperature. A combination of graphite, flame retardant additives and fillers has been found to provide the best flame retardant properties with good adhesive properties, but there is no information about the source of resulting good coal bed expansion and good thermal stability.

Paper [9] discusses the development of solvent-free intumescent flame retardant epoxy (ER) coatings with good durability. In the work, a micro/nanostructured phosphorus/nitrogen/silica-containing flame retardant (APP@Si) was synthesized by ammonium polyphosphate modified with silica nanoparticles, which was used to prepare a high-performance intumescent fire retardant epoxy resin (EP) coating by a solvent-free method. APP@Si improves fire protection, smoke suppression, toxicity reduction, mechanical properties, and durability of coatings, with an oxygen index limit of 32.4 % and a UL-94 V-0 rating. Meanwhile, APP@Si reduced the maximum heat release rate, smoke coefficient, and peak CO production level for EP/10APP@Si by 77.5 %, 92.6 %, and 56.4 %, respectively. The increase in fire protection of the EP/APP@Si coating is mainly due to the formation of a swelling and dense carbon layer with high strength. However, there are no data on the environmental friendliness of these products.

The research reported in [10] considers the application of intumescence in the field of fire protection (resistance to fire) and fire resistance (reaction to fire) of the material. It begins by describing the basics of intumescence and provides the main intumescent products available on the market related to their typical applications. It covers the fire response of intumescent polymers and textiles, including recent developments in flame retardants as well as synergists. Fire resistance is also considered when using intumescent coating on a large and small scale. Mechanisms of action are always discussed in terms of chemical, physical, and thermal aspects. However, the values of these parameters do not cover a wide range of applications.

Work [11] reported that spent coffee grounds (SCG) were modified with ammonium m-xylylenediaminephosphonate (MAP) to create a bio-based flame retardant (SCG-g-MAP) for water-based epoxy resin (WEP). The structure and composition of SCG-g-MAP were analyzed through a series of characterization tests, and the effects of SCG-g-MAP on the thermal stability, fire resistance, and fire resistance of WEP composite coatings were discussed. It was found that WEP composite coating with 10 % SCG-g-MAP and partially conventional intumescent flame retardant fillers resulted in LOI

value of 29.5 % and self-extinguishing ability. In addition, the coating showed significantly improved fire resistance and thermal insulation properties due to better thermal stability and superior barrier function of carbon layer formation. The work presents a new attempt and inspiration for the application of waste biomass such as SCG for green flame retardant fillers. But there are no data on the cost of production.

Study [12] describes a methodology for constructing a pyrolysis reaction model that captures the flammability behavior of intumescent epoxy resin (EP/IFR) fireproof coatings as a function of material composition. This approach uses thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and microscale combustion calorimetry (MCC) experiments, as well as inverse modeling of experimental results using ThermaKin2Ds and the COMSOL Multiphysics simulation framework. It was found that the model built is capable of reproducing TGA/DSC/MCC data within established criteria for EP/IFR mixtures with different material compositions. The model's ability to extrapolate was further validated by accurately predicting experimental TGA data at different temperature conditions and for mixtures with different IFR ratios that were not used for model development. Additional TG-FTIR and XPS experiments were performed to quantify the effect of the IFR additive on gas evolution and char formation. With a higher IFR, the volume of fuel-diluting gases (i.e., CO₂, NH₃) was increased and the volume of combustible organic gaseous products was decreased. However, there are no data on the conditions of operation of these products.

Thus, it has been established from the literature [2, 3, 5, 7, 12] that fire-resistant coatings are able to protect the surface of wood from the effects of fire during operation but the parameters that ensure resistance to the loss of fire-resistant properties are not defined. The paucity of research to explain and describe the process of fire protection of wood with wide fluctuations in moisture and temperature, neglecting the use of organic substances for the formation of elastic coatings leads to the burning of wooden structures. Therefore, establishing the parameters of wood protection and the effect of coatings on this process has necessitated our conducting research into this area.

3. The aim and objectives of the study

The purpose of our work is to identify the regularities of the formation of a layer of foamcoke under the influence of high temperature on wood fire-protected by a weatherproof reactive coating based on an organic binder. This would make it possible to justify the use of a fire-resistant coating for wood at facilities with high humidity.

To achieve the goal, the following tasks were solved:

- to investigate the process of forming the structure of the reactive coating when changing active substances;
- to model the mechanism of fire protection of wood with a reactive coating under the action of high temperature.

4. The study materials and methods

4.1. The object and hypothesis of the study

The object of our study is the fire-retardant properties of a reactive coating based on mixtures of organic-inorganic substances during interaction with a flame.

The scientific hypothesis assumes reducing the flammability of wood when interacting with a high-temperature flame and establishing the effectiveness of the formation of a heat-insulating layer of foamcoke on the surface of wood.

In the research process, the following assumptions and simplifications were adopted, which relate to the peculiarities of the wood fire protection mechanism at the modeling object. These include features that determine the impact of changes in external conditions on the object of research and the process of formation of a layer of foamcoke on the surface of wood: they are the same, temperature, humidity, and pressure are not variable.

4. 2. Researched materials used in the experiment

To establish the fire protection mechanism of the reactive coating, we used wood samples treated with a coating capable of creating a foam-coke protective layer on the surface under the influence of high temperature. Namely, a mixture of ammonium polyphosphate 20÷34 %, pentaerythrite 12÷26 %, melamine 8÷16 %, titanium dioxide 2.6÷4 %, chloroparaffin 2.4÷3.7 %, which were dissolved in acrylic resin and diluted with a solvent to the required consistency. The following samples of reactive coating were prepared for research (Table 1).

Table 1

Samples of reactive coating

No. of entry	Composition of reactive coating
Sample 1	ammonium polyphosphate 20 %, pentaerythrite 12 %, melamine 16 %, titanium dioxide 4 %, chloroparaffin 3.7 % and acrylic resin
Sample 2	ammonium polyphosphate 25 %, pentaerythrite 17 %, melamine 11 %, titanium dioxide 3.6 %, chloroparaffin 3.4 % and acrylic resin
Sample 3	ammonium polyphosphate 30 %, pentaerythrite 22 %, melamine 8 %, titanium dioxide 3 %, chloroparaffin 2.9 % and acrylic resin
Sample 4	ammonium polyphosphate 34 %, pentaerythrite 26 %, melamine 6 %, titanium dioxide 2.6 %, chloroparaffin 2.4 % and acrylic resin

The resulting mass was mixed and applied to a polyethylene film and a wood sample. For the study of thermal destruction, wood samples with the size of 5×5×5 mm were made, and to determine the swelling capacity, samples of 40×40×10 mm were made, which were covered with a coating with a consumption of approximately 248÷254 g/m². The thickness of the coating film was approximately 0.5 mm.

After exposure for 14 days, the resulting coating and fire-resistant wood samples with the applied protective coating were tested for fire protection effectiveness.

4. 3. Methods for researching the properties of wood and its structure

The structure of the reactive coating was determined by Fourier transform infrared spectroscopy (FTIR) and identification by thermogravimetric analysis.

Obtaining gaseous products of thermal destruction of wood covered with a reactive coating was carried out according to the methodology from [13]. Sample analysis was performed on a 6890 N Agilent gas chromatograph. Analysis conditions: detector – katharometer, detector temperature – 250 °C; carrier gas – helium, flow rate – 60 ml/min;

column – PLOT HP-MOLSIV, 15 m long, column temperature – 50 °C/min from 50 °C to 200 °C. The dose is 0.25 ml. The calculation of component concentrations was carried out by the method of peak area normalization. Gas samples were introduced directly into the dispenser of the chromatograph, squeezing out of the hermetic vessels with a saline solution.

Fourier transform infrared spectroscopy (FTIR) was performed taking into account [14]. Research method: 0.5 mg of the sample, crushed from 70 mg of potassium bromide (cleaved from a single crystal). From the resulting mixture, the tablet was compressed under a pressure of 10 MPa, achieving maximum optical transparency (to reduce scattering). The spectrum was recorded in the range of 4000–400 cm⁻¹, with an optical slit width of 4 cm⁻¹, the spectrum was averaged over 12 scans. The analysis was performed on a Spectrometer Spectrum One (Perkin Elmer) (USA).

Thermogravimetric analysis was performed according to [15]. In order to determine the range of temperatures at which the thermal destruction of wood occurs most intensively, a thermogravimetric study of destruction processes was conducted under a dynamic mode. Thermogravimetric studies were carried out on a Linseis STA 1400 derivatograph (Germany). Samples weighing 10 mg were heated in an air atmosphere from 20 to 700 °C at a rate of 10 °C/min.

The study of the process of formation of the heat-insulating layer of the reactive coating foamcoke was carried out according to the methodology given in [16]. The essence of the method for determining the coefficient of swelling of fire-resistant coatings is to expose a sample of fire-resistant coating, which is applied to a wooden floor, to a heat flux of high density and measure the formed layer of foamcoke after it cools.

5. Results of determining the mechanism of the fire-protective effect of reactive coating in the fire protection of wood

5. 1. Results of research on the structure of the reactive coating and its identification

Fig. 1 shows IR spectra of the studied reactive coating samples.

The analyzed samples have the same composition in different ratios of components, in particular: ammonium polyphosphate, pentaerythrite, melamine, chloroparaffin, titanium dioxide. Transmission spectra in Fig. 1 are characterized by intensities for the same values of infrared radiation bandwidths. The transmission band at 3,300 cm⁻¹ is characteristic of valence vibrations of OH groups of pentaerythrite. C–H valence vibrations for CH₂ groups are represented by the 2,950 cm⁻¹ band, and the 2,880 cm⁻¹ band corresponds to symmetric vibrations. Bands 735 cm⁻¹, 1,357 cm⁻¹, 1,167 cm⁻¹ represent C–H deformation vibrations for the CH₂ group. Bands <700 cm⁻¹ represent out-of-plane deformation vibrations of OH groups. Also, the transmission band of 550 cm⁻¹ can be assigned to TiO₂. The 1,617 band and the 3,225 cm⁻¹ shoulder correspond to the deformational vibrations of adsorbed water molecules held by titanium dioxide. The transmission band at 1,230 cm⁻¹ corresponds to the vibrations of the P=O group, which corresponds to ammonium polyphosphate. The spectrum

of melamine is superimposed on the spectra of pentaerythrite and TiO_2 . In the FTIR spectra of melamine, the transmission peaks at 3,469, 3,419, 3,334, and 3,129 cm^{-1} are attributed to valence vibrations of $-\text{NH}_2$; while those at 1,654, 1,550, and 813 cm^{-1} are attributed to the triazine ring, respectively. In chlorinated paraffin, transmission bands are observed at 650 and 1,230 cm^{-1} . These bands are associated with stretching of the C–Cl bond in the chloromethylene ($-\text{CHCl}-$) group and C–H deformation in the $-\text{CH}_2-$ group, respectively. The presence of these bands confirms that the paraffin is chlorinated, with a chlorine atom replacing hydrogen to form a C–Cl bond.

Thus, the samples of the reactive coating represent the accumulation of fine-dispersed, uniformly sized substances surrounded by a polymer binder.

In order to establish the individual characteristics of the reactive coating samples (Table 1), thermogravimetric analysis was performed. Graphic images of thermogravimetric analysis are shown in Fig. 2–5.

In all samples of the reactive coating at temperatures up to 100 °C, endothermic processes occur, which are accompanied by mass loss and are caused by the evaporation of adsorbed water without destruction of the material of the samples and other easily volatile substances.

Endothermic effects in the temperature range of 180–200 °C are associated with the melting of ammonium polyphosphate, rearrangement, and dehydration of pentaerythrite. In the temperature range of 200–300 °C, pentaerythrite begins to decompose with the formation of aldehydes and a cell of foamcoke is born. When melamine interacts with aldehydes, methylol, derivatives of varying degrees of substitution, and then polymer-oligomeric structures of amino resin are formed.

Intensive decomposition into ammonia and polyphosphoric acid occurs at temperatures of approximately 300–370 °C. As can be seen from the comparison of DTA curves, endothermic peaks (melting of crystalline structures) characterize polyphosphates. The onset of intense mass loss coincides with a temperature of 320–330 °C, which is superimposed on the melamine sublimation peak starting at 330 °C, and which ends at temperatures above 420 °C (at higher temperatures – after the relative mass loss has already reached 60–70 %). Such a difference in the effect of modified materials on the course of destruction at different stages is caused by different mechanisms by which the mass loss of samples occurs. In the first stage, there is mainly pyrolysis with the separation of volatile products, the rate of which does not depend on further chemical transformations of these products; in the second stage, the rate of mass loss is determined by the kinetics of the interaction of the carbonized residue with the oxidant.

Thus, on the basis of thermogravimetry, it was established that chemical reactions in the coating are initiated under thermal action.

In particular, ammonium polyphosphate decomposes and releases phosphoric acid, which in turn affects the dehydration of pentaerythrite with the formation of soot. The subsequent decomposition of melamine is accompanied by the release of non-combustible gases, which cause the soot to foam, thereby forming foamcoke.

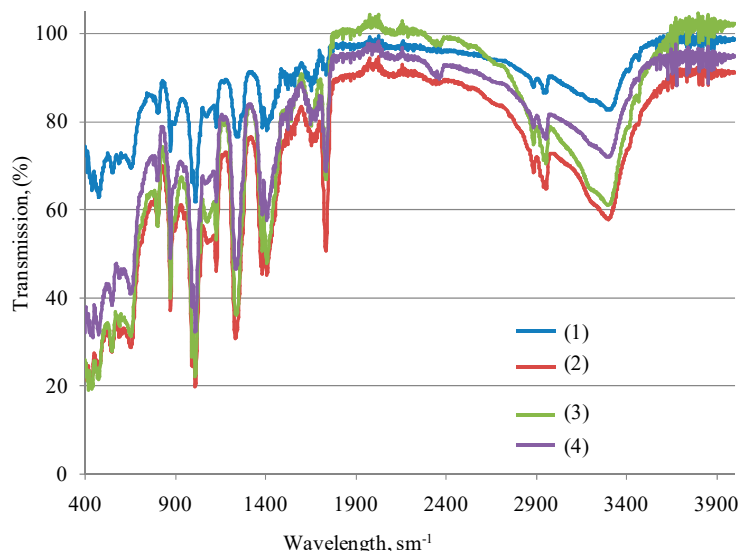


Fig. 1. Absorption spectra of reactive coating samples with different ratios of components (Table 1): 1 – sample No. 1; 2 – sample No. 2; 3 – sample No. 3; 4 – sample No. 4

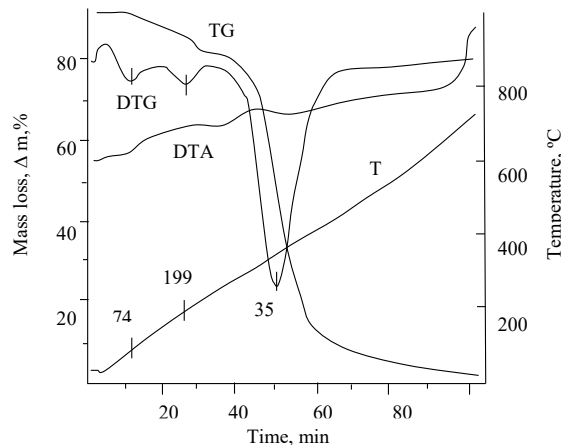


Fig. 2. Thermogravimetric analysis curves for reactive coating sample No. 1: T – temperature curve; DT – curve of mass loss depending on temperature increase; DTA – curve of thermal effects; DTG – differential curve

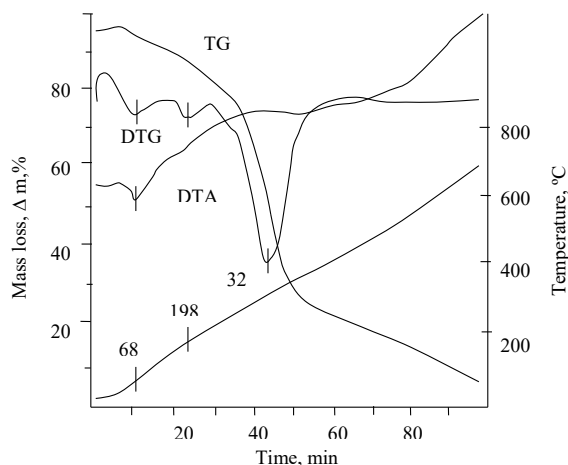


Fig. 3. Thermogravimetric analysis curves for reactive coating sample No. 2: T – temperature curve; DT – curve of mass loss depending on temperature increase; DTA – curve of thermal effects; DTG – differential curve

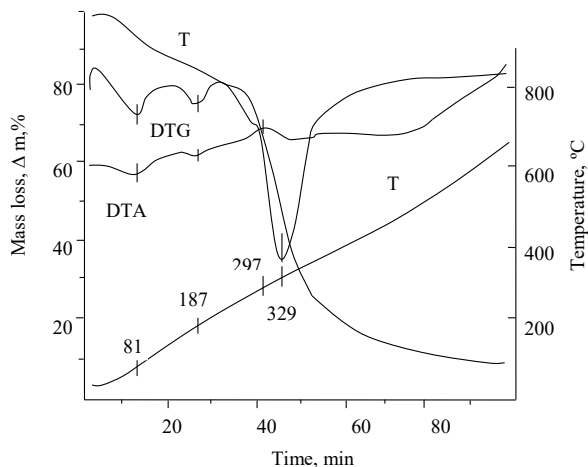


Fig. 4. Thermogravimetric analysis curves for reactive coating sample No. 3: T – temperature curve; DT – curve of mass loss depending on temperature increase; DTA – curve of thermal effects; DTG – differential curve

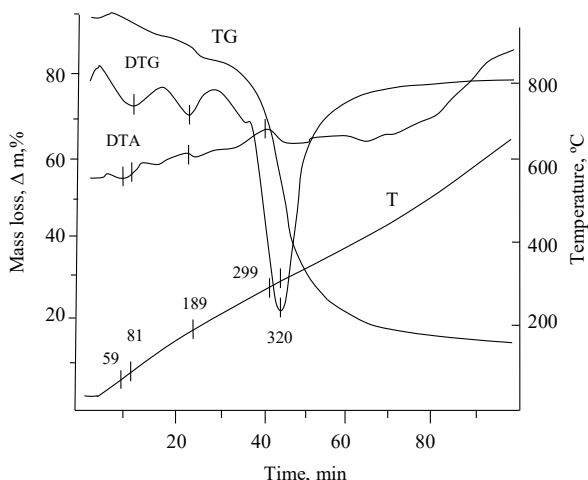


Fig. 5. Thermogravimetric analysis curves for reactive coating sample No. 4: T – temperature curve; DT – curve of mass loss depending on temperature increase; DTA – curve of thermal effects; DTG – differential curve

5. 2. Results of modeling the process of thermal destruction of fire-resistant wood with a reactive coating

From the thermograms, the temperatures at which the mass loss of the samples is achieved were determined and the stages of decomposition processes were estimated, as well as the relative mass loss when heated to 700 °C. Taking into account the results of thermogravimetric studies, the process of thermal destruction of coating samples was carried out under conditions under which the formation of gaseous products occurs at the highest speed.

The results of gas chromatographic analysis of the obtained combustible gas mixtures are given in Table 2.

As can be seen from Table 2, after the pyrolysis of wood treated with a reactive coating, the mixture of destruction products differs significantly in the content of carbon dioxide, nitrogen, and the volume of combustible gases. Thus, when the content of ammonium polyphosphate and pentaerythrite in the reactive coating was increased by 5 %, the volume of combustible gases decreased by more than 11 %, and the volume of nitrogen increased by more than 10 %.

An even greater difference was recorded when the content of ammonium polyphosphate and pentaerythrite in the reactive coating was increased by 14 %, in particular, it was found that the volume of combustible gases decreased by more than 2 times, and the volume of nitrogen increased by more than 1.45 times.

Table 2

Qualitative and quantitative composition of gaseous products of thermal destruction of wood

Component	Content of components in volatile destruction products of pine wood, % vol.				
	Raw [13]	Coated Sample 1	Coated Sample 2	Coated Sample 3	Coated Sample 4
CO	39.08	19.11	16.50	14.27	10.26
CO ₂	51.93	38.43	36.60	34.27	32.27
CH ₄	6.05	2.67	2.22	2.25	0.43
C ₂ H ₆ +C ₂ H ₄	0.45	0.58	0.74	0.57	0.33
C ₃ H ₈	0.19	0.17	0.22	0.01	0.18
C ₃ H ₆	0.32	Not detected	Not detected	Not detected	Not detected
H ₂	0.73	0.24	0.67	0.55	0.13
O ₂	0.26	Not detected	Not detected	Not detected	Not detected
N ₂	0.99	38.80	43.05	48.08	56.40

Fig. 6, Table 3 show the results of research into the swelling process of the coating.

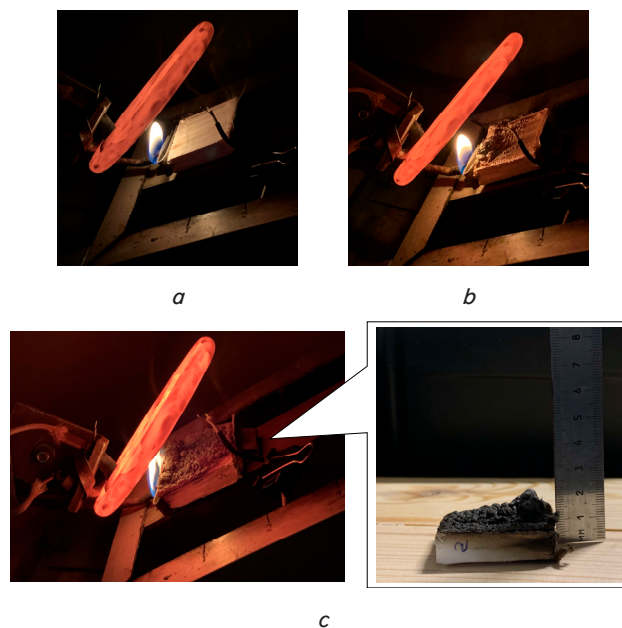


Fig. 6. Results of studies on the reactive coating swelling process: a – the effect of the flame on the sample; b – the beginning of the decomposition of the coating; c – swelling of the coating over the entire surface, determination of the swelling height

As can be seen from Fig. 6, under the action of the radiation panel, the coating swelled, which is associated with the decomposition of flame retardants under the influence of temperature with heat absorption and release of non-combustible gases (nitrogen, carbon dioxide). 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.

Table 3

Determining the efficiency of swelling of the reactive coating under the influence of heat flow for variable values of the concentration of components

No. of entry	Swelling start time, s	Flue gas temperature, °C	Foamcoke layer height, mm	Foam multiplicity, score
Sample 1	88	68	13.0	26.0
Sample 2	76	72	12.3	24.6
Sample 3	79	88	13.4	26.8
Sample 4	46	96	15.5	31.0

When the radiation panel acted on the reactive coating, swelling and the formation of a heat-insulating layer of foamcoke occurred. Thus, for sample 1, the swelling onset time of 88 s was recorded, which then gradually decreased by almost two times, which is associated with an increase in the volume of ammonium polyphosphate. This also affected the formed layer of foamcoke, which was recorded at the lowest content of ammonium polyphosphate at the level of 12 mm and increased for higher values up to 15.5 mm, and the multiplicity of foam increased by 1.25 times.

6. Discussion of results of investigating the process of fire protection of wood with a reactive coating

Samples of the reactive coating represent the accumulation of fine-dispersed, uniform substances surrounded by a polymer binder, as indicated by the results of research (Fig. 1), which begin to decompose under thermal action. Ammonium polyphosphate, as indicated by the research results in Fig. 2–5, decomposes already at a temperature of 180 °C with heat absorption and releases phosphoric acid, which causes the dehydration of pentaerythrite with the formation of soot. At the same time, the decomposition of melamine begins, which is accompanied by the release of non-combustible gases that cause the soot to foam, forming foamcoke.

Gas chromatographic studies (Table 2) showed that with an increase of ammonium polyphosphate and pentaerythrite in the coating by 5 %, the volume of combustible gases decreased by more than 11 %, and nitrogen increased by 10 %. And when their content was increased by 14 %, the volume of combustible gases decreased more than 2 times, and the volume of nitrogen increased more than 1.45 times. As can be seen from Fig. 6, under the action of the radiation panel, the coating swelled, which is associated with the decomposition of flame retardants under the influence of temperature with heat absorption and release of non-combustible gases (nitrogen, carbon dioxide). This also affected the formation of a layer of foamcoke (Table 3), which was recorded at the lowest content of ammonium polyphosphate at the level of 12 mm and increased for higher values to 15.5 mm. At the same time, the multiplicity of the foam increased by 1.25 times. This shows the inhibition of heat transfer through the foamcoke layer, which can be identified directly by high-temperature exposure to reactive coating samples [17, 18].

In contrast to previous studies [2, 3, 7, 9], in which the attention was paid to coatings containing aluminosilicate substances, this study considered the type of reactive coating widely represented in the market.

However, in contrast to the results reported in [19] regarding the fire protection mechanism, the following can be asserted:

- the main regularity of the process of fire protection with a reactive coating is not so much the release of the volume of gases that affect the flame since certain fire protection coatings, for example, aluminosilicate, release a significant volume of water vapor under thermal influence;

- the mechanism of the reactive coating is that chemical reactions in the coating begin under thermal action, in particular, ammonium polyphosphate decomposes and releases phosphoric acid. That, in turn, affects the dehydration of pentaerythrite with the formation of soot, and the decomposition of melamine is accompanied by the release of non-combustible gases that cause the soot to foam, thereby forming foamcoke.

This approach warrants a greater practical significance of our results since the studied reactive coating was demonstrated to react to the action of a high-temperature flame, which reflects the real circumstances of its operation. The results of the experiments showed that the designed reactive coating has the potential, which is manifested, first of all, in the formed layer of coke foam. Determining the swelling ratio during the tests shows the effect of the coating on the fire resistance of the building structure.

The results have certain limitations with a certain volume of volatile products due to the unpredictability of the process of inhibition of heat transfer to the plant material. Taking into account the fire resistance of the reactive coating is possible provided that the heat-insulating properties of the foamcoke layer, which is formed during thermal action on the coating, are ensured.

In addition, the response of the fireproof coating to thermal impact may give insufficiently predictable indicators due to the small volume of data on the transformation of the reactive coating into a foamcoke layer, which limits the application of our results. The disadvantage of the applied experimental approach is a certain laboriousness, which can limit the determination of the swelling effect of the coating. However, thanks to fire tests, it is possible to obtain reliable results, which make it possible to establish the mechanism of the reactive coating. Further development of research into designing a reactive coating may involve potentially interesting areas, in particular, the optimization of experimental data on devising a formulation.

7. Conclusions

1. Samples of the reactive coating represent the accumulation of fine-dispersed, uniform substances surrounded by a polymer binder, which begin to decompose under thermal action, in particular, ammonium polyphosphate decomposes already at a temperature of 180 °C and releases phosphoric acid. That, in turn, affects the dehydration of pentaerythrite with the formation of soot, and the decomposition of melamine is accompanied by the release of non-combustible gases that cause the soot to foam, thereby forming foamcoke.

2. The mechanism of fire protection of wood with reactive coatings has been established, which is associated with the decomposition of flame retardants under the influence of temperature with heat absorption and the release of non-combustible gases and a change in the direction of decomposition towards the formation of a non-flammable coke residue. Thus, when the content of ammonium polyphosphate and pentaerythrite in the reactive coating was increased by 5 %, the volume of combustible gases decreased by more than 11 %, and the volume of nitrogen increased by more than 10 %. And when their content was increased by 14 %, the volume of combustible gases decreased more than 2 times, and the volume of nitrogen increased more than 1.45 times. This also affected the formation of a foamcoke layer, which was recorded at the lowest content of ammonium polyphosphate at the level of 12 mm and increased for higher values up to 15.5 mm, and the multiplicity of foam increased by 1.25 times.

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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References

- Demirhan, Y., Yurtseven, R., Usta, N. (2021). The effect of boric acid on flame retardancy of intumescent flame retardant polypropylene composites including nanoclay. *Journal of Thermoplastic Composite Materials*, 36 (3), 1187–1214. <https://doi.org/10.1177/08927057211052327>
- Jung, D., Bhattacharyya, D. (2021). Combined effect of silicate coating and phosphate loading on the performance improvement of a keratinous fiber-based flame retardant. *Chemical Engineering Journal*, 424, 130484. <https://doi.org/10.1016/j.cej.2021.130484>
- Bachtiar, E., Kurkowiak, K., Yan, L., Kasal, B., Kolb, T. (2019). Thermal Stability, Fire Performance, and Mechanical Properties of Natural Fibre Fabric-Reinforced Polymer Composites with Different Fire Retardants. *Polymers*, 11 (4), 699. <https://doi.org/10.3390/polym11040699>
- Liu, J., Qi, P., Chen, F., Zhang, J., Li, H., Sun, J. et al. (2024). A universal eco-friendly flame retardant strategy for polylactic acid fabrics and other polymer substrates. *International Journal of Biological Macromolecules*, 260, 129411. <https://doi.org/10.1016/j.ijbiomac.2024.129411>
- Huang, H., Deng, J., Xu, B., Kang, L. (2024). Synergistic effect of coal gangue on intumescent flame retardants. *Journal of Physics: Conference Series*, 2819 (1), 012052. <https://doi.org/10.1088/1742-6596/2819/1/012052>
- Hansen-Bruhn, I., Hull, T. R. (2023). Flammability and burning behaviour of fire protected timber. *Fire Safety Journal*, 140, 103918. <https://doi.org/10.1016/j.firesaf.2023.103918>
- Markert, F., González, I., De La Parra Rogero, C., Hosta, E. S. (2023). Protection of pre-treated wood and construction materials using intumescent coatings. *Journal of Physics: Conference Series*, 2654 (1), 012084. <https://doi.org/10.1088/1742-6596/2654/1/012084>
- Sarathiraja, M., Devanathan, S., Kannan, M. (2020). Tuning parameters for flame-retardant coatings on wood and polymer. *Materials Today: Proceedings*, 24, 1138–1146. <https://doi.org/10.1016/j.matpr.2020.04.427>
- Ou, M., Cui, J., Zhao, Z., Li, R., Guan, H., Liu, L. et al. (2023). Solvent-free intumescent fire protection epoxy coatings with excellent smoke suppression, toxicity reduction, and durability enabled by a micro/nano-structured P/N/Si-containing flame retardant. *Progress in Organic Coatings*, 183, 107762. <https://doi.org/10.1016/j.porgcoat.2023.107762>
- Bourbigot, S. (2024). Intumescence-Based Flame Retardant. *Fire Retardancy of Polymeric Materials*, 116–146. <https://doi.org/10.1201/9781003380689-7>
- Wu, D., Yang, M., Wu, T., Shen, Y., Wang, T. (2024). Green one-step modification of spent coffee grounds as synergistic bio-based flame retardant for waterborne epoxy resin. *Progress in Organic Coatings*, 191, 108409. <https://doi.org/10.1016/j.porgcoat.2024.108409>
- Ding, Y., Chen, Z., Tang, C., Huang, W., Ren, X., Zhou, K., Hu, H. (2024). Development of a pyrolysis reaction model for epoxy based flame retardant composites: Relationship between pyrolysis behavior and material composition. *Chemical Engineering Journal*, 495, 153628. <https://doi.org/10.1016/j.cej.2024.153628>

13. Tsapko, Y., Tsapko, A. (2017). Establishment of the mechanism and fireproof efficiency of wood treated with an impregnating solution and coatings. *Eastern-European Journal of Enterprise Technologies*, 3 (10 (87)), 50–55. <https://doi.org/10.15587/1729-4061.2017.102393>
14. Pettersen, R. C. (1984). The Chemical Composition of Wood. *The Chemistry of Solid Wood*, 57–126. <https://doi.org/10.1021/ba-1984-0207.ch002>
15. Broido, A. (1969). A simple, sensitive graphical method of treating thermogravimetric analysis data. *Journal of polymer science part a-2: polymer physics*, 7 (10), 1761–1773. <https://doi.org/10.1002/pol.1969.160071012>
16. Kryvenko, P., Tsapko, Y., Guzii, S., Kravchenko, A. (2016). Determination of the effect of fillers on the intumescent ability of the organic-inorganic coatings of building constructions. *Eastern-European Journal of Enterprise Technologies*, 5 (10 (83)), 26–31. <https://doi.org/10.15587/1729-4061.2016.79869>
17. Tsapko, Y., Tsapko, A., Likhnyovskiy, R., Sukhanevych, M., Zapolskiy, L., Illiuchenko, P., Bedratiuk, O. (2024). Establishing patterns in reducing fire-dangerous properties of sip panels fire-protected with reactive coating. *Eastern-European Journal of Enterprise Technologies*, 1 (10 (127)), 47–54. <https://doi.org/10.15587/1729-4061.2024.298266>
18. Tsapko, Y., Likhnyovskiy, R., Tsapko, A., Bielikova, K., Poteriaiko, S., Illiuchenko, P., Bondarenko, O. (2023). Determining patterns in the formation of an insulation layer of foam coke when protecting concrete against fire by reactive coating. *Eastern-European Journal of Enterprise Technologies*, 6 (10 (126)), 65–72. <https://doi.org/10.15587/1729-4061.2023.293685>
19. Tsapko, Y., Likhnyovskiy, R., Tsapko, A., Kovalenko, V., Slutska, O., Illiuchenko, P. et al. (2023). Determining the thermal-physical characteristics of a coke foam layer in the fire protection of cable articles with foaming coating. *Eastern-European Journal of Enterprise Technologies*, 2 (10 (122)), 22–30. <https://doi.org/10.15587/1729-4061.2023.275550>