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Features of the organic-mineral intumescent paints structure formation for wooden constructions fire protection

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Abstract. The paper presents the results describing the features of the organic-mineral paints structure formation of the intumescent type for wooden structures fire protection. On the research basis a diagram of the coke formation process has been developed. It is shown that the introduction of titanium oxide and aluminum hydroxide in an amount of 5% promotes the ordering of the foam layer structure, an increase in its thermal stability and the achievement of the highest value of the swelling coefficient – up to 47, which is 1.7 times higher than the values of the swelling coefficient of the base composition. It was found that at 700 °C the formation of refractory compounds of the type TiP_2O_7, $Mg_3(PO_4)_2$, $AlPO_4$ occurs, which prevent the burnout of the formed coke foam and increase its strength and heat resistance. On the basis of the main provisions of fuzzy mathematics and data from physicochemical studies, a model of the mechanism of structure and coke formation and control of this process is proposed.
Keywords: organic-mineral paints, swelling, fire protection, wooden constructions, structure formation, foam coke, mineral components, coke-formers.

1. Introduction and literature review

During 2020 fires destroyed and damaged 28029 buildings and structures of various purposes, of which 7106 were completely destroyed, including 796 residential buildings. Of the total number of buildings and structures destroyed and damaged by fires in 2020 – 11707 (41.8%) – had III degree of fire resistance, 5373 (19.2%) – V degree of fire resistance, 2889 (10.38%) – had IIIa degree of fire resistance. Of the 7106 buildings completely destroyed in 2020, 2263 (31.9% of the total number of destroyed buildings and structures) had a V degree of fire resistance, 1531 (21.6%) had a III degree of fire resistance, 841 (11.8%) – IIIa degree of fire resistance, 431 (6.1%) – IV degree of fire resistance, 246 (3.5%) – IIIb degree of fire resistance, 108 (1.5%) - IVa degree of fire resistance, 86 (1.2%) – II degree of fire resistance and 12 (0.2%) – I degree of fire resistance. Wooden constructions are used in buildings and structures of III, IIIb, IV degrees of fire resistance with mandatory fire protection [1].

Recently in Ukraine there has been an increased interest in the results of scientific developments in the field of creating highly effective means of protecting building structures from the effects of fire and their implementation. [2].

One of the factors on which fire safety is based during the design and operation of buildings and structures for various purposes is to ensure fire resistance of building structures and their ability to spread fire. Compliance with the principles of fire safety in construction is based on an engineering approach to assess the required level of safety in the design, construction, expansion, reconstruction, technical re-equipment, overhaul, change the functional purpose of buildings and structures necessary measures and

safety tools. The basic requirement for fire safety in construction is to limit the spread of fire, smoke and maintain the load-bearing capacity of the structure for a certain period of time, and an important way to ensure these principles is to manufacture fire-resistant building structures and study their fire resistance, including fire-resistant constructions.

In this regard, the need to research in this direction is determined with the provision of special attention to the development of effective fire retardant coatings for the purpose of their use in the construction of both general construction and special purpose facilities, where the use of impregnating mixtures is ineffective [3]. In addition, a number of resonant accidents at military facilities (Artemovsk, 2003, Novobogdanovka, 2004, Tsvitokha, 2005, Lozovaya, 2008) revealed a low level of safety assurance for the operation of arsenals, bases and warehouses in connection with the use of wood in building constructions, structures and storage facilities that are highly sensitive to the effects of high temperature and fire, and therefore, to improve the safety of operation of ammunition storage facilities, to prevent and limit the hazardous factors of combustion of wood products, fire protection of materials is used [4-6]. Analyzing the results on the development of fire retardant coatings based on alkaline aluminosilicate binders [7, 8], it was established that a significant thickness of the protective layer should be applied to building structures and the coatings become rigid during operation (low elasticity), which leads to a loss of adhesion properties and shedding under the influence of temperature and humidity fluctuations [9-11].

Modern fire retardant coatings are characterized by the formation of an expanded layer of coke on the surface of a building construction [12-14], which significantly reduces the processes of heat transfer to the material, and are complex systems of organic and inorganic components [15-17], but when exposed to flame they are characterized by high smoke-forming ability and toxicity [18-20].

As an alternative solution to the problem of wooden constructions fire protection, it is possible to use coatings based on organic-mineral binders, which will reduce the above indicators by adding mineral fillers to the organic base and form a more stable expanded foam coke layer [21, 22].

As shown by the analysis of scientific research [23, 24], in the formation of the predicted level of quality, in particular, the functionality and durability of coatings, an important place is occupied by the type of film-former of the original composition, the type of filler and the structure of the coating. However, they cannot provide reliable protection of constructions at temperatures above 1273 K, since at higher operating temperatures, the organic component is destroyed, and the coating becomes porous, which significantly worsens its operational properties.

2. Literature review

Foaming and coke formation of intumescent coatings is accompanied by various physicochemical processes, which, as a rule, proceed in a certain sequence as the temperature effect on the composition increases [25-28].

The swelling mechanism of such coatings has not been sufficiently studied. This is due to the fact that the main reactions leading to the production of a protective foam-coke layer occur in the high temperature range (up to 900 °C), which complicates the modeling of these processes. In addition, they belong to multicomponent composite materials. This leads in turn to a large number of possible interactions between the components formed by the fire retardant coating, especially at high temperatures. At the same time, it is also rather difficult to foresee the direction of high-temperature reactions. According to many experts, the swelling mechanism of fire retardant coatings consists of the following stages [29]:

- an inorganic acid evolution capable of esterification of carbonization of materials (polyols) at 150-215 °C, depending on the type of acid derivative;

- the esterification of the polyol was acidified at a temperature just above the temperature of the first stage. In the presence of amines, the reaction is accelerated and completed at a lower temperature;

- melting the mixture of intumescent coating components immediately prior to or during esterification;

- chemical transformations - the formation of an ester of a polyol with an inorganic acid as a result of dehydration, resulting in the formation of carbon-inorganic (usually carbon and phosphorus) structures, which are further involved in coking processes;

- foaming the carbonaceous mass with incombustible gases that are released during the decomposition of the foaming agent, as well as water vapor that is formed as a result of dehydration of the polyol;

- gelatinization, and then solidification of the foamed mass at the end of the coking process.

This solid mass consists of finely porous foam and is a good heat insulator. An example of a different interpretation of the mechanism of swelling of coatings can be the data of [30]. In particular, based on the results of a comprehensive thermal analysis of various mixtures of components of organic-mineral coatings and IR spectroscopy of coke foam, it is assumed that pentaerythritol is not esterified with phosphoric acid, but decomposes under conditions of elevated temperature and acidic environment into formaldehyde and acetaldehyde (Figure 1):
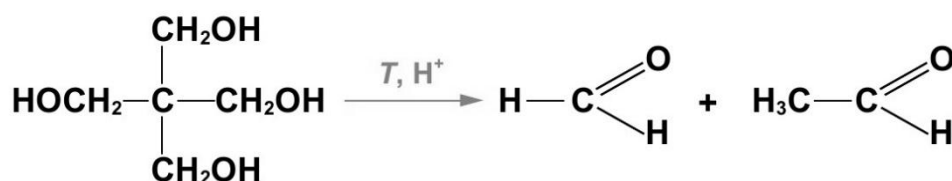

Figure 1. Reaction of pentaerythritol decomposition during coating swelling.

Aldehydes formed as a result of the decomposition of pentaerythritol are involved in the synthesis of aldehyde-melamine resin, a precursor of the foam-coke framework (Figure 2).
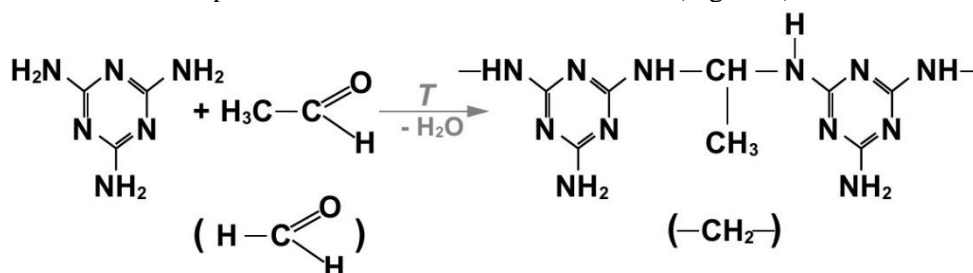

Figure 2. A foam-coke framework formation.

In turn, ammonium polyphosphate acts as a growth regulator for the aldehyde-melamine resin, being chemically bonded on one side to the substrate, and on the other to melamine.

Typically, a fire retardant coating contains the following main components: a catalyst that decomposes when the temperature rises to form an inorganic acid; a carbohydrate, which reacts with said acid to form a carbon layer; a binder that melts when the temperature rises, contributes to the formation of a charred insulating layer; swelling agent, which decomposes simultaneously with the melting of the binder, releases a significant amount of non-combustible gases and is accompanied by foaming and multiple (up to 40 times) increase in the thickness of the coating, transformed into an insulating carbon layer that protects the building structure from further exposure to high temperatures [31].

Fire retardant intumescent compositions are rather complex multicomponent systems, since they include three main components: a coke-formation catalyst, coke-forming and foaming agents. As a rule, the catalyst is phosphorus-containing compounds and, most often, ammonium polyphosphate. The content of ammonium polyphosphate in the composition in many formulations is explained by its participation in the formation of the coke structure. As a raw material for the formation of the carbon framework of the foamed layer, polyalcohols are usually used, and as a porophore, organic amines or

amides, which emit non-combustible gases at elevated temperatures – carbon dioxide, nitrogen, ammonia, which foam the system. The most popular in modern formulations of intumescent coatings from polyalcohols are glycerin and pentaerythritol, and from amines – melamine and carbamide. To perform conventional protective and decorative functions and for long-term storage of fire retardant characteristics during operation, thermoplastic polymers are most often used as film formers in the manufacture of fire retardant intumescent compositions, namely vinyl acetate homo- or copolymers or other water-dispersive binders [32, 33].

In the initial state, fire retardant compositions are solid heterogeneous, heterophase granular systems, consisting of randomly spaced particles ranging in size from 1 to 40 microns and a large number of pores. When the fire retardant coating is heated, a series of chemical reactions begins: ammonium polyphosphate decomposes and releases phosphoric acid, phosphoric acid causes pentaerythritol or dipentaerythritol to dehydrate to form a protective layer for such materials.

The use of minerals in organic-mineral compositions can reduce smoke generation and increase weather resistance and develop a new type of fire retardant coatings for building constructions, the presence of which will slow down the heating of the material and maintain their functions during a fire for a given period of time.

According to [21, 26, 27, 34] fillers as formers of a porous structure are divided into two groups:

- contribute to the formation of a porous (foamed) structure of coke (titanium dioxide, borates of barium and zinc, magnesium hydroxide)

- suppress the formation of foam in coke (aluminum hydroxide, intumescent graphite, zeolite, sodium tripolyphosphate).

Compounds of the first group act as active bubble generators and cause the formation of a more regular and stable foam in comparison with foam-coke produced from similar compositions without filler (pigment). The most effective foaming agents are titanium dioxide and magnesium hydroxide.

In turn, the second group compounds suppress the formation of foam in coking layer. For example, intumescent graphite provides coke with its structure, while suppressing foaming of the organophosphate mass, and foamed coke, which is formed in the presence of sodium tripolyphosphate, has significant fluidity.

Inorganic fillers contribute to the swelling of coatings, which decompose at elevated temperatures with the formation of non-combustible gaseous products (for example, CO_2, water vapor) and remove heat. These include aluminum hydroxide, calcium, cadmium and zinc carbonates, boric acid salts.

Materials such as zinc borate, siloxanes, talc, kaolin, fiberglass and others are added to the compositions of organic-mineral paints of the intumescent type to form glassy and ceramic structures in coke at elevated temperatures, and strengthen the foam-coke framework. For example, at temperatures up to 600 °C, ammonium polyphosphate interacts with talc to form crystalline products such as $Mg_2P_4O_{12}$, MgP_4O_{11}, SiP_2O_7, $Si_5O(PO_4)_6$, and at temperatures close to 1000 °C, to form glassy magnesium and silicon phosphates.

Titanium dioxide at a temperature of about 600 ° C reacts with ammonium polyphosphate to form titanium pyrophosphate TiP_2O_7 – a fireproof material that stabilizes the insulating foam at high temperatures, when most of the carbon is oxidized and burned out to form CO_2. In this case, a white bloom appears on the coke layer [28, 29, 35].

Intumescent fire retardant paints/coatings are widely used and this is due to their low thermal conductivity under fire conditions due to the formation of a fine-meshed carbon layer of the coating, which complicates the heating of wood, lengthening the phase of its preparation for active participation in the combustion process. During swelling, the components soften with simultaneous endothermic decomposition of fire retardants and blowing agents, which increases the fire-retardant properties of coatings during swelling [25, 32].

The aim of this work is to study the processes of structure formation of organic-mineral paints of the intumescent type for fire protection of wooden constructions. The implementation of the goal of the work is carried out by solving the following tasks, namely: to develop a scheme for the process of coke formation; to study the influence of mineral fillers on the processes of structure formation; to develop a

mathematical model of the processes of structure formation of organic-mineral paints of the intumescent type.

3. Materials of research

To obtain organic-mineral paints of the intumescent type, polyvinyl acetate (PVA) dispersions were used as a binder [36]; as a catalyst and coke-forming agent – ammonium polyphosphate (PFA) [37], melamine [38], pentaerythritol (PER) [39] (table 1); as mineral fillers – titanium dioxide, talc, aluminum and magnesium hydroxide, and their mixtures [40].

Table 1. Characteristics of organic components

Component	Chemical formula	Melting temperature, ^{o}C	Solubility in water at 25 °C, g/100 ml	Density, g/sm^3	Particle size, microns
PFA	$(NH_4PO_3)_n$	312	0.8	1.9	15
M	$C_3H_6N_6$	354	3.2	1.573	40
P	$C(CH_2OH)_4$	215	7.1	1.394	40

Note: PFA – ammonium polyphosphate; P – pentaerythritol; M – melamine

Organic-mineral paint of the intumescent type was obtained by the technology of water-dispersion paints with the introduction of the necessary technological additives in a laboratory dissolver [40].

4. Methods of research

The study of features of structure formation processes was performed using X-Ray diffraction (XRD), differential thermal analysis (DTA) and digital microscopy.

X-ray phase analysis was carried out on a DRON-3M and DRON-4-07 diffractometer with a copper tube at a voltage of 30 kV, a current of 10 ... 20 mA, and a range of angles $2\Theta=10...60°$ at a counter rotation speed of 2° per minute. New materials were identified based on the PDF-2 Data Base (Sets 1-50 plus 70-88) with the JCPDFWIN 2.1 software module (JCPDS-ICDD, 2000). Differential thermal and thermogravimetric analysis was carried out on a derivatograph of the R. Paulik, I. Paulik, L. Erdey by the MOM company (Hungary). The samples were heated at a rate of 10 °C per minute to a temperature of 1000 °C.

The obtained experimental data were interpreted according to [41, 42]. The macrostructure of the foamed paint layer was determined using a Dino-Lite Pro-AM413T5 digital microscope manufactured by ANMO Electronics Corporation (Taiwan) with a 1.3 Mpix camera at x500 digital magnification.
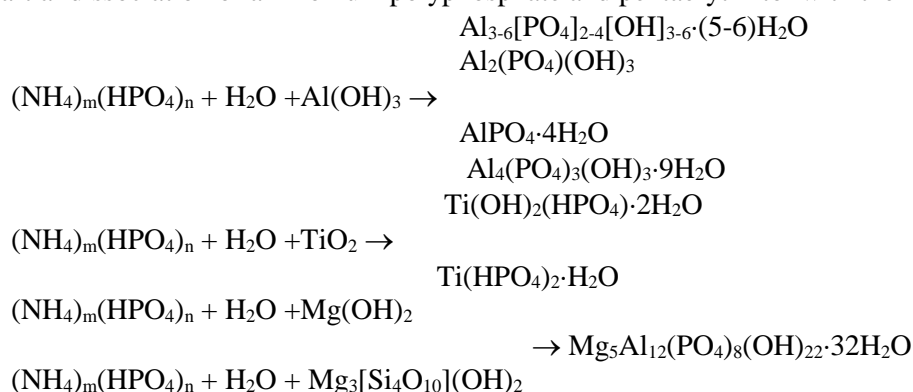
Determination of the coefficient of swelling of fire-retardant coatings was determined according to [43].

5. Study of mineral composition, size particles and surface area of quartz dispersed materials

It is possible to increase the thermal and mechanical stability of the coke foam to the effects of variable heat fluxes, besides modifying the organic component, by introducing refractory oxides and reactive water-containing reagents into the base composition, which at high temperatures pass into anhydrous phases, and contribute to an increase in its thermal stability.

Considering that an aqueous solution of modified PVA dispersion was chosen as a binder in the studies, it is hypothetically possible to imagine the mechanism of dissolution of ammonium polyphosphate in it, the interaction of the products of its dissociation with fillers: $Al(OH)_3$, TiO_2, $Mg(OH)_2$ and $Mg_3[Si_4O_{10}](OH)_2$:

I partial dissociation of ammonium polyphosphate and pentaerythritol with the formation of:

$$Al_{3-6}[PO_4]_{2-4}[OH]_{3-6} \cdot (5\text{-}6)H_2O$$
$$Al_2(PO_4)(OH)_3$$

$$(NH_4)_m(HPO_4)_n + H_2O + Al(OH)_3 \rightarrow$$

$$AlPO_4 \cdot 4H_2O$$
$$Al_4(PO_4)_3(OH)_3 \cdot 9H_2O$$
$$Ti(OH)_2(HPO_4) \cdot 2H_2O$$

$$(NH_4)_m(HPO_4)_n + H_2O + TiO_2 \rightarrow$$

$$Ti(HPO_4)_2 \cdot H_2O$$

$$(NH_4)_m(HPO_4)_n + H_2O + Mg(OH)_2$$

$$\rightarrow Mg_5Al_{12}(PO_4)_8(OH)_{22} \cdot 32H_2O$$

$$(NH_4)_m(HPO_4)_n + H_2O + Mg_3[Si_4O_{10}](OH)_2$$

II partial decomposition of ammonium polyphosphate, pentaerythritol and phosphates Al, Ti and Mg with the formation of phosphate clusters:

$$T \approx 250 - 280 \text{ °C}$$

$$(NH_4)_m(HPO_4)_n \rightarrow {}_mNH_3 + (HPO_3)_n$$
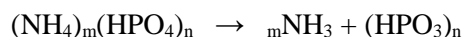
III formation of coke foam due to decomposition, foaming, dehydration and reactions in solid phases:

$$T \approx 300 - 1000 \text{ °C}$$

$(HPO_3)n$, pentaerythritol, melamine, PVA dispersion, phosphate Al, Ti and Mg, dehydration of $Mg_3[Si_4O_{10}](OH)_2$ with the formation of anhydrous mineral phases capable of reinforcing the foam-coke layer and increasing its thermal stability and mechanical strength.

Based on the scheme of the coke formation process, in the base composition, according to XRD data (Figure 3, curve 1), diffraction bursts of type II ammonium polyphosphate insoluble in water are recorded – $(NH_4)m(HPO_4)n$ d = 0.939; 0.781; 0.696; 0.605; 0.566; 0.557; 0.534; 0.482; 0.486; 0.457; 0.4221; 0.389; 0.374; 0.349; 0.312; 0.307; 0.265; 0.260; 0.251; 0.248; 0.237; 0.223; 0.211; 0.201; 0.187; 0.176; 0.172; 0.168 0.160; 0.155; 0.152 nm. There are no diffraction bursts of pentaerythritol and melamine in the diffractogram. Their presence is confirmed by DTA data on a number of endothermic effects characteristic of these components (Figure 4, curve 1). This curve shows the exothermic effect in the temperature range (+) 60–70 °C, which explains the partial oxidation (resinification) of pentaerythritol. With an increase in temperature, partial destruction of pentaerythritol occurs, as evidenced by the presence of endothermic effects on the DTA curve at temperatures: (–) 255, 300 and 350 °C, which describe the chemical transformations of this component of the binder, namely, the passage of the pyrolysis stage with the formation of methanol, formaldehyde, the release of water and subsequent destruction in the direction of the formation of acrolene, carbon dioxide, resin residue and the synthesis of alphamethylacrolene.

Simultaneously with this process, the destruction of the PVA dispersion occurs - the endothermic effect at a temperature of (–) 200 °C, which is associated with the release of acetic acid and the formation of double bonds in carbon atoms. An increase in the action temperature leads to the thermooxidation of the PVA dispersion - an exothermic effect at a temperature of (+) 400 °C and the thermal decomposition of melamine, which is characterized by significant gas release, which leads to the formation of a porous layer of coke foam of a disordered structure (Figure 3, pos. A).

The process of coke formation is similar for other compositions, but something with its own specifics. Thus, the introduction into the organic-inorganic composition of 10% $Al(OH)_3$ d = 0.309; 0.248; 0.229; 0.204; 0.169; 0.162; 0.145 nm (Figure 3, curve 2) leads to an increase in the swelling coefficient (Table 2) due to two-stage dehydration of hydrargilite: endoeffects in the temperature range (–) 250–300 and 500–550 °C (Figure 4, curve 2). A further increase in temperature contributes to the additional release of water vapor from the hydroxide structure and contributes to the polymorphic transition of γ-Al_2O_3 to α-Al_2O_3 exothermic effect at a temperature of (+) 800 °C and the

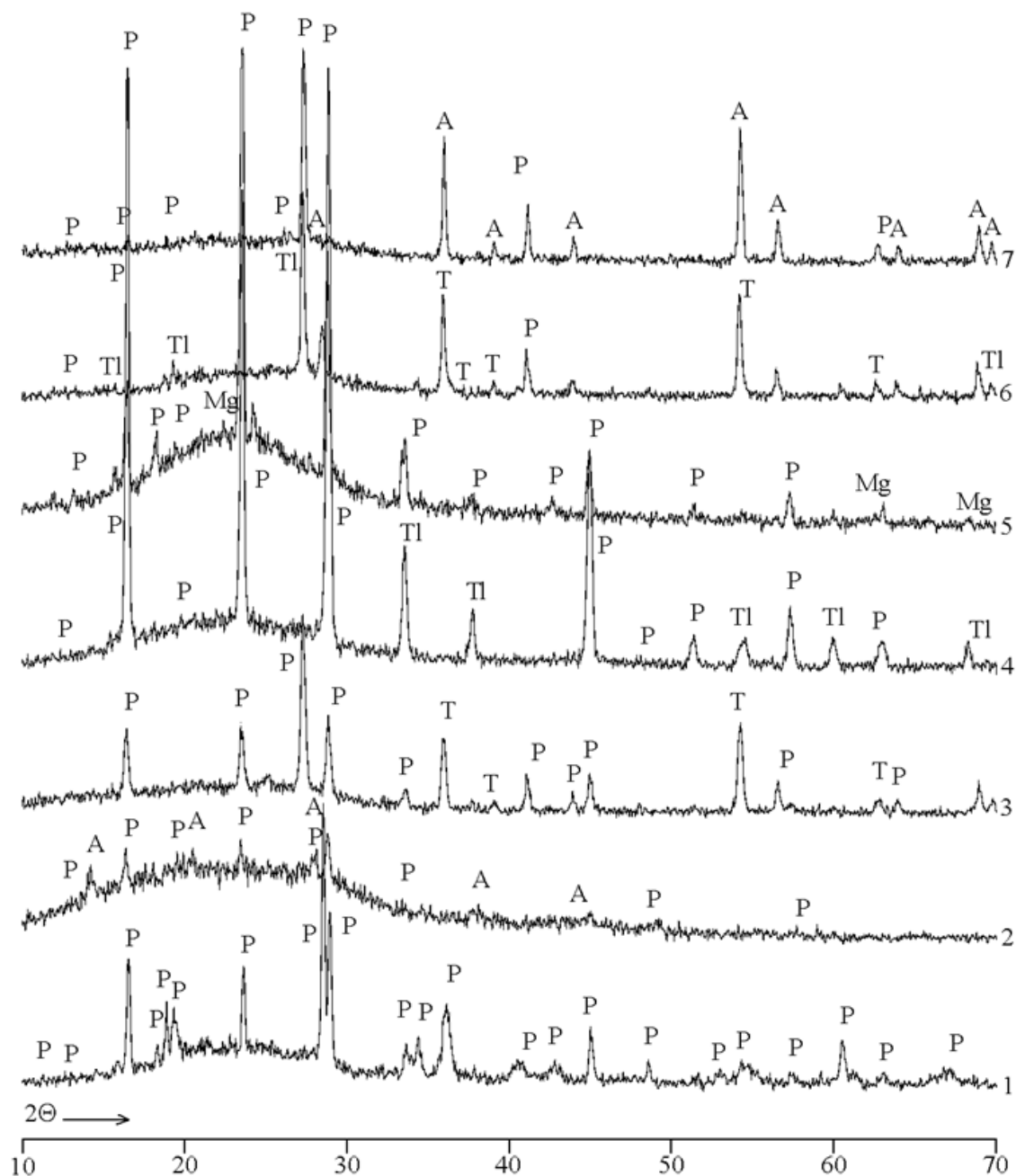**Figure 3.** Sciagrams of an organic-mineral fire retardant composition: 1 – base composition; 2 – base + 10% Al(OH)$_3$; 3 – base + 10% TiO$_2$; 4 – base + 10% Mg$_3$[Si$_4$O$_{10}$](OH)$_2$; 5 – base + 10% Mg(OH)$_2$; 6 – base + 5%TiO$_2$ + 5% Mg$_3$[Si$_4$O$_{10}$](OH)$_2$; 7 – base + 5% TiO$_2$ +5%Al(OH)$_3$. Designations: P – ammonium polyphosphate; A – aluminium hydroxide; T1 – titanium dioxide; T – talc; Mg – magnesium hydroxide

formation of aluminum orthophosphates of various structural types with the effect of reinforcing the porous foam coke layer (Figure 5, pos. b).
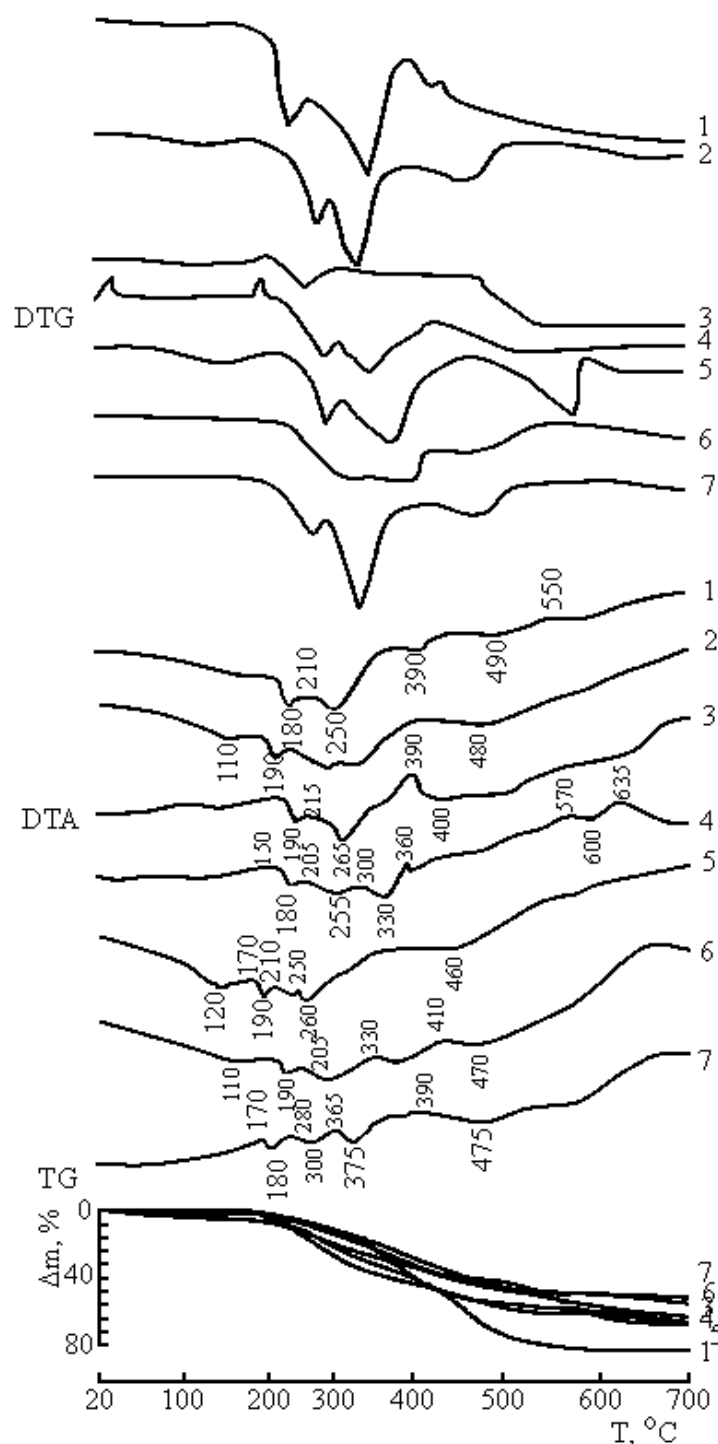
Figure 4. Thermograms of an organic-inorganic fire retardant composition: 1 – base composition; 2 – base + 10% Al(OH)$_3$; 3 – base + 10% TiO$_2$; 4 – base + 10% Mg$_3$[Si$_4$O$_{10}$](OH)$_2$; 5 – base + 10% Mg(OH)$_2$; 6 – base + 5%TiO$_2$ + 5% Mg$_3$[Si$_4$O$_{10}$](OH)$_2$; 7 – base + 5% TiO$_2$ +5%Al(OH)$_3$

As a result of these processes, the coke foam structure is compacted and strengthened due to the formation of smaller pores compared to the previous type of structure (Figure 5, pos. A). In an organic-inorganic fire retardant composition containing up to 10% TiO$_2$ (Figure 3, curve 3), besides to the phases of ammonium polyphosphate, diffraction bursts are recorded, which are characteristic of TiO$_2$ (d =

0.2929; 0.249; 0.168; 0.154 nm). The XRD curve does not show diffraction reflections, which would be characteristic of titanium phosphates.

It is likely that titanium phosphates of the type $Ti(OH)_2(HPO_4)$ $2H_2O$ and $Ti(HPO_4)$ $2H_2O$ are formed as a result of the solid-phase reaction between TiO_2 and the product of partial dephosphorization of ammonium phosphate $(HPO_3)n$. With an increase in temperature from 300 to 600 °C on the DTA curve, an endothermic effect (–) 600 °C was noted, which is characteristic of the onset of dehydration of the above phases with the formation of anhydrous high-temperature titanium phosphates (Figure 4, curve 3), which significantly increase the thermal resistance of the coke foam layer (Figure 5, item c). The macrostructure of the coke foam layer consists of large globules in comparison with the macrostructure of the composition containing 10% $Al(OH)_3$.

When up to 10% talc $(Mg_3[Si_4O_{10}](OH)_2)$ is added to the organic-mineral composition, diffraction bursts are recorded on the XRD curve (Figure 3, curve 4), which are characteristic of this mineral d = 0.266; 0.238; 0.175; 0.171; 0.159; 0.155 nm.

Dehydration of talc $(Mg_3[Si_4O_{10}](OH)_2)$ in the direction of enstatite formation takes place at temperatures of 930-950 °C. Enstatite reacts with partially dephosphised (HPO_3) n to form magnesium silicophosphate. This phase is sufficiently temperature resistant and significantly increases the temperature resistance of the coke foam layer. The macrostructure of the coke foam is somewhat similar to the macrostructure of the base composition, but differs from it in its continuity (Figure 5, pos. D).

The introduction of up to 10% magnesium hydroxide into the base composition does not fundamentally change the formation of the macrostructure of the coke foam layer (Figure 5, pos. E). Dehydration $Mg(OH)_2$ d = 0.47; 0.179; 0.149 nm (Figure 1, curve 5) occurs in the temperature range 400-550 °C (Figure 4, curve 5) with the formation of MgO and its subsequent interaction with $(HPO_3)n$ in the direction of magnesium phosphate synthesis, as a high-temperature phase, which strengthens the structure coke layer and increases its resistance to high temperatures. Macrostructure of a scaly-type coke foam layer (Figure 5, pos. E).

The combined introduction of inorganic additives of titanium dioxide and talc in the amount of 5% does not lead to a significant change in the phase composition of the coke foam. The XRD curve (Figure 3, curve 6) shows diffraction bursts of ammonium phosphate, titanium dioxide (d = 0.293; 0.249; 0.168; 0.154 nm) and talc (d = 0.688; 0.33; 0.238; 0.190; 0.176; 0.142 nm). The macrostructure of the coke foam layer becomes denser due to its reinforcement with particles of titanium-magnesium phosphates (Figure 5, pos. F).

In our opinion, the most expedient is the introduction into the base, organic-mineral composition, a mixture of titanium dioxide with aluminum hydroxide in an amount of 5% each. On the XRD curve (Figure 3, curve 7) the diffraction bursts that are characteristic of ammonium polyphosphate and aluminum hydroxide (d = 0.309; 0.248; 0.229; 0.204; 0.169; 0.162; 0.145 nm) differ quite significantly. Diffraction bursts for titanium dioxide (d = 0.292; 0.262; 0.249; 0.2017; 0.168; 0.154 nm) are characterized by a lower intensity. With an increase in temperature in the composition of the products, the formation of mixed titanium-aluminum phosphates is possible, which differ from titanium-magnesium phosphates in increased heat resistance. The macrostructure of the coke foam layer is similar to the composition, containing up to 10% aluminum hydroxide (Figure 5, pos. B), but differs from it in a greater degree of ordering (Figure 5, pos. G).

Taking into account the data of physicochemical studies, it is possible to propose a model of the mechanism of structure formation of an expanded coke foam layer and the main directions of control of this process based on fuzzy mathematics [44,45].
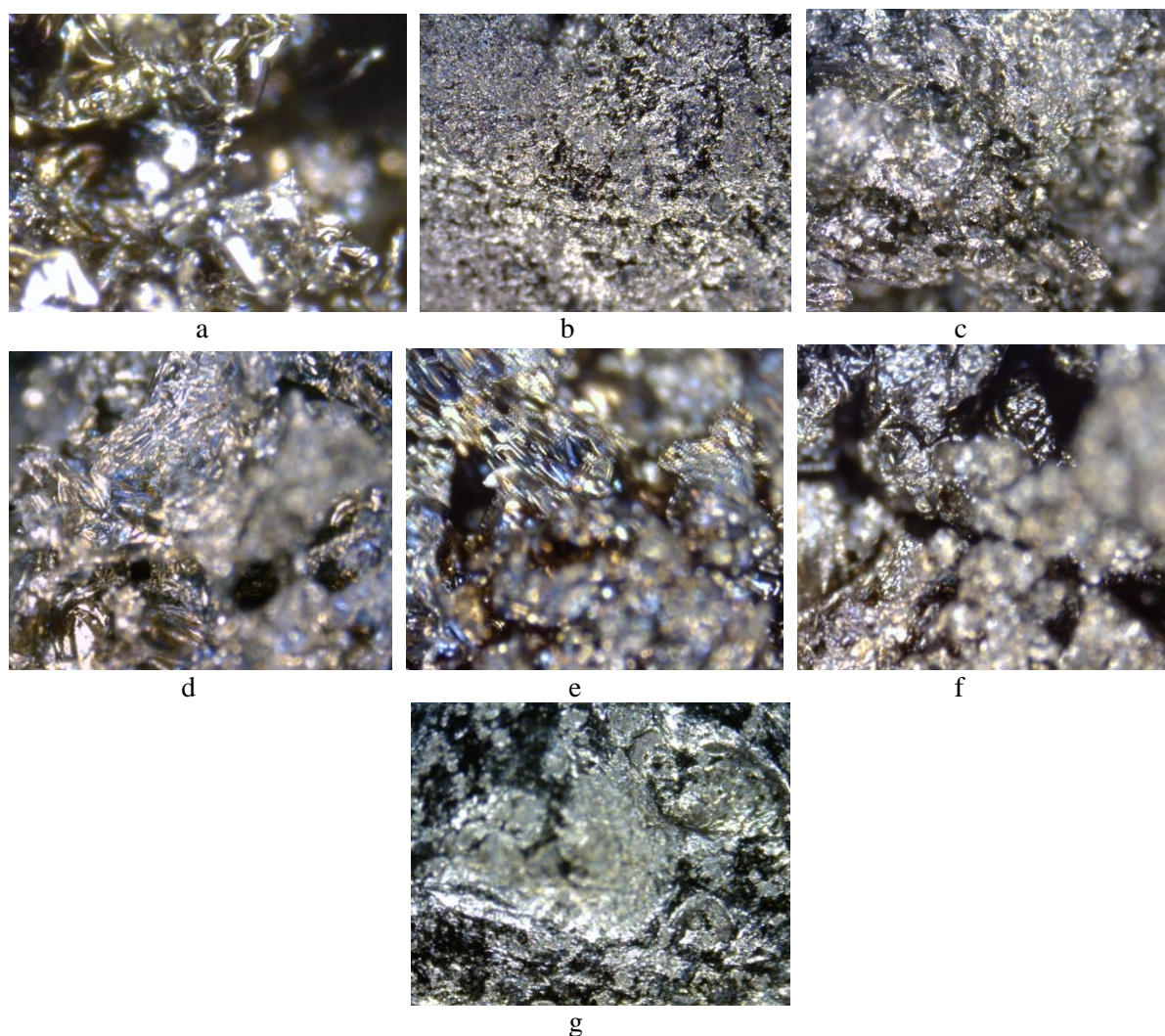
Figure 5. Digital photos (x500) of the coke foam layer after swelling at a temperature of 500 °C: a – base composition; b – base + 10% Al(OH)$_3$; c – base + 10% TiO$_2$; d – base + 10% Mg$_3$[Si$_4$O$_{10}$](OH)$_2$; e – base + 10% Mg(OH)$_2$; f – base + 5%TiO$_2$ + 5% Mg$_3$[Si$_4$O$_{10}$] (OH)$_2$; g – base + 5% TiO$_2$ +5%Al(OH)$_3$.

Table 2. Compounds of organic-mineral fire retardant compositions

№	Composition	Amount and type of additive, %	Swelling coefficient value
1	Base	–	26.8
2	Base +	10% Al(OH)$_3$	36.7
3	Base +	10% TiO$_2$	17.2
4	Base +	10% Mg(OH)$_2$	32.1
5	Base +	10% Mg$_3$[Si$_4$O$_{10}$](OH)$_2$	30.1
6	Base +	5%TiO$_2$+5% Al(OH)$_3$	47.0
7	Base +	5%TiO$_2$+5% Mg$_3$[Si$_4$O$_{10}$](OH)$_2$	42.0

A fuzzy model of the structure formation process can be presented in the following form:
$$\mu^k(lt) = \cap_{j=1}^{12} \cup_{i+1}^{11} \left(x_i \rightarrow x_y \right), \tag{1}$$

where $\mu^k(lt)$ – the measure of belonging of the linguistic variable lt, which characterizes the development of the process; lt matters: the speed of the process, the type of process, the type of materials and equipment; k – type of object of protection (wooden constructions of industrial, residential premises; x_i = 1 ... 5 – input linguistic variables (table 3); x_y = 6 ... 12 – input linguistic variables (table 4).

The basis for fuzzy inference is a knowledge base containing a set of fuzzy production rules (FPRs) that determine the strategy for solving the structure formation process and the ability to control it. A typical rule base production rule consists of a premise (antecedent): fuzzy statements in the form "if" and a conclusion (consequent) in the form "then ...".

Table 3. An example of formalization of direct parameters of the structure formation process of an organic-inorganic fire retardant composition.

Process types	Terms for linguistic evaluation
x_1 – structure organization processes	diffusion (df); coagulation (cg); solid phase (sp)
x_2 – process development	constant intensity (ci); variable decelerating intensity (vdi); variable accelerating intensity (vai)
x_3 – types of processes	material (m); technological (t)
x_4 – life cycle of processes	inception (in); acceleration (ac); deceleration (dc); age (ag); attenuation (at)
x_5 – interaction of processes	component composition set (ccs); reactionary components set (rcs); structure formation period (sfp)

An antecedent can contain several premises, which are combined depending on the strategy using logical connectives "and" or "or". Each of the rules of fuzzy rules can have some weight $Fi = [0,1]$, which determines the significance of the rule or confidence in the degree of truth of the conclusion obtained by a separate fuzzy rule. In general, the base containing m rules is as follows: R1: if $x1$ is $A11$ ... and (or) ... xn is $A1n$, then y is $R1$; Ru: if $x1$ is $Ai1$ ... and (or) ... xn is Ain, then y is Ru; Rm: if $x1$ is $Ai1$ ... and (or) ... xn is Amn, then y is Rm, where: xk – input variables, $k=1, ..., n$; y – output variable; Aik – given fuzzy sets with membership functions ($i = 1, ..., m; k = 1, ..., n$).

Table 4. An example of formalization of indirect parameters of the structure formation process.

Diagnostic parameters of incoming data	Terms for linguistic evaluation
x_6 – influence of temperature and humidity on the reaction rate	insignificant (is), significant (s)
x_7 – component view of materials	common (c), innovative (in)
x_8 – type of equipment	standard (sd), non-standard (nsd)
x_9 – cost of materials	low (l); medium (m), high (h)
x_{10} – hardening time	slow (sl), normal (nl), fast (ft)
x_{11} – influence of fire factors	short-term (st), long (lg)
x_{12} – influence of rheological factors	viscous (v), normally viscous (nv), fluid (fd)

When using fuzzy clustering algorithms (formula 1), if the weight coefficients or the degree of influence of each significant factor of external conditions are not determined, the result of the algorithm depends on the order of the diagnostic parameters that form the input data vector. That is why, in order to reduce the level of risk of making a wrong decision, it is proposed to take into account the degree of influence of various environmental factors when forming the vector of input data using their sorting.

In case of a conflict of rules, the fuzzy system will recommend making decisions according to the criterion with a lower ordinal number (in the absence of other rules). On the basis of fuzzy statements,

the truth of which is established as a result of fuzzification, the degree of truth of fuzzy statements is assessed, and is the conclusion of the corresponding FPRs.

Next, a procedure (aggregation) is performed to determine the degree of truth of the left parts (cut-off levels – ai) for each of the rules of the fuzzy inference system using the FUZZY EXPERT software [46, 47].

6. Conclusions

The peculiarities of structure formation of intumescent type organic-mineral paints for fire protection of wooden structures have been studied. On the basis of research, a scheme of the coke formation process has been developed. It has been shown that the introduction of mineral fillers in the composition of organic-mineral paints in an amount of 10% promotes an increase in the swelling coefficient from 30 to 36.7, which is 1.5 ... 1.84 times higher than the values of the swelling coefficient of the base organic-mineral paint. The introduction of up to 10% TiO_2 contributes to a decrease in the swelling coefficient by a factor of 1.16 in comparison with the base one, but significantly increases the thermal stability of the formed coke foam. The introduction of titanium oxide and aluminum hydroxide in an amount of 5% promotes the ordering of the structure of the foam layer, an increase in its thermal stability and the achievement of the maximum value of the swelling coefficient – up to 47, which is 1.11 times and 1.7 times higher than the values of the swelling coefficient with the introduction of aluminum hydroxide and basic compositions. The introduction of a mixture of titanium oxide and talc in an amount of 3.3% increases the values of the swelling coefficient by 1.12 times in comparison with the introduction of titanium oxide and talc in an amount of 5%, and 1.08 times more than the values of the swelling coefficient with the introduction of aluminum hydroxide and talc in the amount of 5%. It was found that organic-mineral paint at high temperatures is capable of significant weight loss, namely at 700 °C due to the formation of refractory compounds of the type TiP_2O_7, $Mg_3(PO_4)_2$, $AlPO_4$, which prevent the burnout of the formed coke foam. Taking into account the data of physicochemical studies, on the basis of fuzzy mathematics, a model of the mechanism of structure and coke formation and control of this process are proposed.

Determining the fire retardant ability and effectiveness for passive fire retardant coatings will increase the competitiveness and reduce the cost of such materials. In order to ensure the necessary fire resistance of the structure, determined in accordance with the current regulatory documents, wooden constructions are subjected to fire retardant treatment – an important and expensive stage of construction. For the owner of the building, effective fire protection makes it possible to ensure the safe evacuation of people from the building, preserve material values and create an opportunity for the safe work of rescue units [48].

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