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DETERMINATION OF THE EFFECT OF FILLERS ON THE INTUMESCENT ABILITY OF THE ORGANIC-INORGANIC COATINGS OF BUILDING CONSTRUCTIONS

Запропоновано методику та обладнання для визначення кінетики спучування вогнезахисних покриттів. Досліджено вплив наповнювачів на коефіцієнт спучування покриття на основі неорганічних та органічних речовин в процесі термічного впливу. Встановлено вплив наповнювачів при дії високотемпературного теплового потоку на зміну процесу спучення вогнезахисного покриття та визначено механізм кінетики дії наповнювачів, який характеризується зниженням швидкості та втрати маси

Ключові слова: спучуючі покриття, температура печі, кінетика спучування покриття, тугоплавкі наповнювачі, ефективність покриття

Предложены методика и оборудование для определения кинетики вспучивания огнезащитных покрытий. Исследовано влияние наполнителей на коэффициент вспучивания покрытия на основе неорганических и органических веществ в процессе термического воздействия. Установлено влияние наполнителей при воздействии высокотемпературного теплового потока на смену процесса вспучивания огнезащитных покрытий и определен механизм кинетики действия наполнителей, характеризующийся снижением скорости и потери массы

Ключевые слова: вспучивающиеся покрытия, температура печи, кинетика вспучивания покрытия, тугоплавкие наполнители, эффективность покрытия

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1. Introduction

In recent years, there has been increased interest in the results of scientific research in the field of high-performance protection of building structures in Ukraine from the effects of fire and its implementation.

Known methods provide the required fire resistance of building structures, such as concreting, plastering with cement-sand solutions, the use of brick, which are ineffective. The use of lightweight materials, lightweight aggregates having high heat insulating property, namely, expanded perlite, and vermiculite, inorganic fiber, results in significant material costs. Boards and panels of thermal insulating materials on the basis of gypsum and gypsum sheets would significantly increase the volume of the building structure.

Modern methods of fire protection of building constructions based on the use of intumescent coatings which are complex systems of organic and inorganic components. However, with prolonged exposure to a flame they are capable of gradual fading and thus reducing the fire resistance of the structure, which requires the addition thereto of mineral fibers capable of forming a stable layer of foam-coke.

So the need to develop works in this direction was identified. Special attention is required to develop effective flame retardants for the construction of various facilities, where the use of existing tools is inefficient, and the application of new needs in a reliable way to study the properties of the coating.

The main event to improve the resistance of coatings is the use of mineral fibers, which are characterized by high temperature resistance. But recently refractory oxides and hydroxides, which are able to generate refractory compounds when burning have gained widespread use. Therefore, there is a need to establish the kinetics of swelling of such compositions, which requires the development of reliable methods of evaluation.

2. Literature review and problem statement

A feature of fire protection of building structures from fire exposure is to create heat-insulating screens on the surface of structural elements that can withstand high temperatures. The presence of such screens can slow down the heating of the material (steel structure) and maintain its functions in case of fire for a specified period of time and converts timber to the nonflammable material [1].

Simple flame retardants based on inorganic binding materials bound water, which evaporates when heated and blocks the heat transfer to the protected surface. Sodium water glass, Portland cement, aluminous cement, phosphate and aluminosilicate binders are mainly used as a binder [2]. Such materials are characterized by low elasticity, when the temperature factor in the effect only water vapor is emitted into the environment [3]. However, such coatings are short-lived and ineffective and do not provide sufficient adhesive strength since they have a large temperature coefficient of linear expansion. But coatings based on organic and inorganic substances are capable of forming expanded coke layer on the protected surface which significantly reduces heat transfer processes [4].

Efficacy of flame retardants based on organic substances is shown in the papers [5], where through the action of the foaming agents and flame retardants significant influence on the pore layer of foam-coke, namely, its stability, density and strength due to the modified polymeric additives [6].

These studies are directed to the manufacture of polymer and inorganic flame retardants, which can not provide fire resistance and smoke-forming capability of building structures for quite a long time and are too expensive. Evaluation of the behavior of coatings swelling when exposed to smoldering fires has shown some effectiveness, but not their behavior during rapid fire [7].

The performed investigations [8] have established that the addition of fillers (oxides, hydroxides, borates) to the organic-inorganic coatings changes the structure of the coke layer and the foaming process, but they found no effect on the thermal conductivity of the foam-coke formed. The effect of inorganic fillers on the characteristics of water-containing fire-retardants is shown in the work [9].

Therefore, an important issue is the establishment of an intumescent coating capacity during prolonged exposure to temperatures and components included in their composition, and their role in providing fire resistance, and the development of reliable, up-to-date, objective methods to assess the swelling process, causing the need for research in this direction.

3. The goal and objectives of the research

The goal of the research was to study the effect of fillers on the intumescent ability of the fire-retardant coating on the basis of organic and inorganic substances.

The following objectives were solved in order to achieve the goal:

– to develop a methodology and equipment to assess the kinetics of swelling of the flame retardant coating with the addition of fillers;

– to establish the effectiveness of different types of fillers on the multiplicity of swelling of coatings and heat conduction process.

4. Materials and methods

4. 1. Test materials and equipment used in the experiment

Studies were conducted using an organic-inorganic system, consisting of an ammonium polyphosphate (APP), melamine, pentaerythritol (PER) and the PVA-dispersion based binder, fillers – titanium dioxide, talc, aluminum hydroxide and magnesium, and mixtures thereof.

Experimental samples of coatings were prepared on the basis of the organic-inorganic system containing 18÷20 % APP, 12÷14 % melamine, 10÷12 % PER, 16 % PVA-dispersion, and water. The resulting mass was stirred, adding fillers in an amount of 10 % and applied on a steel plate with a thickness of 0.5÷0.6 mm (Fig. 1).

Fig. 1. A sample of the coating on the steel plate

Fillers do not change significantly the appearance and structure of the coating.

4. 2. Development of a method and equipment for determining the kinetics of swelling of fire protective coatings, and the results of the study

Intumescent fire-retardant materials operate on the principle of a significant reduction in thermal conductivity of the coatings formed by them as a result of their conversion in foam-coke cellular layers under the intense thermal action that significantly postpone the heat transfer process and the time of the destruction of the building structure.

Determination of a swelling coefficient of fire-retardant coatings [10] is carried in a muffle furnace at appropriate temperatures. The disadvantage of this method is that it is only suitable for classification comparison of flame retardants, but gives no information about the actual intumescent ability of the coating.

The method of determining the swelling coefficient of fire-retardant coatings lies in the impact of the heat flow in a muffle furnace on the steel plate sample and measuring of the formed layer after cooling. Research evidence that when exposed to the heat flow there was minor swelling of geocement coating, which continued until the temperature of 500 °C and a swelling coefficient was 3.1 (Table 1).

Table 1

A swelling coefficient of the coating after the test

Sample of coating	Coating thickness, mm	Furnace temperature, °C	Swelling coefficient
geocement	1	500	3.1
organic-inorganic	1	500	47.0

Then, the samples with organic-inorganic fire-retardant coatings were tested. Exposure of the samples of the organo-mineral fire-retardant coating to the heat flux, found that when the temperature reaches about 500 °C, the swelling coefficient is 47.0 (Table 1).

The method for determining the heat insulating properties is known, where the prepared sample was placed in a holder and inserted into the test oven and fixed ~~a~~ so that the end of the control thermocouple is pressed against the rear surface of the sample. Heating of the test cell is started and the temperature in front of and on the back surface of the sample was controlled, the measured values are used to determine the insulating ability of the material. The criterion for evaluating the insulating properties is the behavior of the flame retardant coating sample upon exposure to heat flow and the time of heating of the sample metal substrate to the critical temperature of the metal (for steel – 500 °C, aluminum – 250 °C) at which the design loses its load-bearing capacity under thermal impact [11].

The disadvantage of this method is that it does not allow to reliably estimate the process of swelling of fire protective coatings, namely, to take into account the effect of changes in temperature and the kinetics of destruction of the samples under thermal action.

It is known that during the one-sided heating of the retardant coating, the thickness- and time-varying temperature field is formed in its subsurface layer, and gaseous products of thermal decomposition are emitted, and the frame hardens with increasing temperature, forming a layer of foam-coke that moves “towards” external heat flux [12]. Parameters such as the speed and order of reaction are characteristics which are called the effective parameters reflecting the amount of various chemical reactions during thermal degradation [13].

Given the above, a method for determining the kinetics of swelling of flame retardants, which is implemented by calculation of the thermal insulation properties according to the temperature measurement on the back surface and in front of the sample after exposure to heat flow. Along with this, the initial coating thickness and the thickness after the swelling process are additionally measured, and the kinetic parameter is calculated according to the dependency:

$$e_v = k_v \left(\frac{T - T_{ПС}}{T_{КС} - T_{ПС}} \right)^n, \qquad (1)$$

where k_v – a swelling coefficient:

$$k_v = \frac{\delta_1}{\delta_0}, \qquad (2)$$

where δ_0, δ_1 – the initial thickness and the thickness of the coating after the swelling process, respectively, mm; $T_{пс}$, $T_{кс}$ – the temperature in the beginning and the end of the swelling process, respectively, °C; T – the current blistering temperature, °C; n – the coating decomposition reaction order.

5. Experimental studies of the kinetics of swelling of the coating and the results

Fig. 2 shows the device for research.

Research by the above method is as follows. The prepared sample 5 with the flame retardant coating is placed in the sample 3 holder, which is attached to the door 4 and fixed so that the end of the control thermocouple 8 was pressed against the back surface of the sample, and inserted into the test chamber 1. The appropriate heating rate and temperature are set in the test cell by the block 7. The temperature recorder 11 for and the computer 12 are turned on, heating of the test chamber 1 by means of the radiation panels 2 is started, and the swelling process is controlled through the viewing window 6 by the ruler 10.

During testing, the temperature in front of and on the back surface of the sample is measured with the thermocouple 8, 9, and the coating swelling height sample is measured a the viewing window 6 by the rule 10.

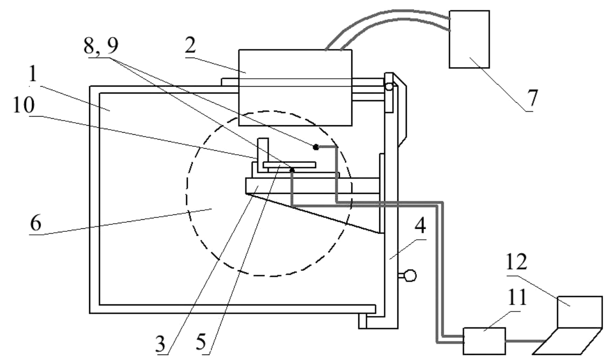

Fig. 2. Device to determine the kinetics of swelling of fire protective coatings: 1 — a test chamber, 2 — a radiation panel, 3 — a sample holder, 4 — a door of the test chamber, 5 — sample, 6 — the viewing window, 7 — thermoregulator, 8, 9 — a thermocouple, 10 — ruler, 11 — analog-to-digital converter, 12 — the computer

Upon reaching the temperature limit of 230 °C on the back surface of the sample 5, the study ends and heating of the test chamber 1 is turned off, and the time is recorded from the start of heating until the temperature is reached, and the swelling coefficient is determined at regular intervals of the temperature range of the heat flux.

Initially, tests were made of the organic-inorganic coating on a steel plate. On exposure of the samples to the heat flux for a short period of time at a temperature in front of the sample of about 100 °C, a slight swelling of the coating occurred, and at a temperature in front of the sample of about 190 °C an intense swelling of the coating and a slight rise in temperature on the back surface of the sample began, which lasted until the temperature about 360 °C was reached, and the height of the swollen layer of foam-coke increased to 32 mm. Upon further exposure to heat flux due to the foam-coke burnout, the expanded layer began to decrease, and when the steel plate temperature of 230 °C was reached after 1820 seconds of the test, the swelling coefficient was 48.0, respectively. Fig. 3 shows the process of swelling of the coating.

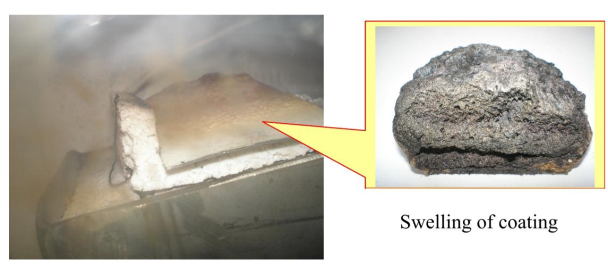

Fig. 3. The results of tests of the intumescent coating

To improve the heat resistance of foam-coke in the organic-inorganic coating, it was proposed to introduce the fillers and to investigate the stability of the foam-coke formed under the influence of heat flow (Table 2).

Table 2

The results of determining the stability of foam-coke to the action of heat flux for organic-inorganic coatings and with the addition of fillers

Sample of coating	Thickness, mm	The amount of the applied coating, g/m^2	The time to reach the limit temperature, s	The weight of the coating after test, g/m^2
Organic-inorganic without filler	0.6	10.2	1820	2.6
Organic-inorganic+(10 %) TiO_2	0.55	10.1	1932	4.4
Organic-inorganic+(10 %) talc	0.56	10.2	1958	4.6
Organic-inorganic+(5 %) TiO_2+(5 %) talc	0.6	10.2	1946	5.8
Organic-inorganic+(10 %) $Al(OH)_3$	0.54	10.1	1861	5.0
Organic-inorganic+(10 %) $Mg(OH)_2$	0.57	10.2	1848	5.1
Organic-inorganic+(5 %) TiO_2+(5 %) $Al(OH)_3$	0.56	10.2	1912	6.2

6. Discussion of the results of research of the kinetics of swelling of the coating

Fig. 4, 5 show the dependence of the swelling coefficient on the temperature, which was determined experimentally and processed with an exponential function of Microsoft Excel:

$$y = a \cdot x^b, \tag{3}$$

where a i b – empirical constants, swelling coefficient and reaction order.

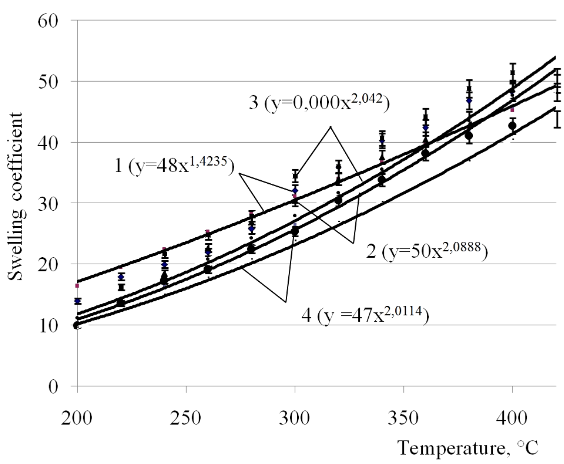

Fig. 4. The dependence of the swelling coefficient of the coating on temperature: 1 – organic-inorganic, 2 – organic-inorganic+(10 %) TiO_2 TiO_2 (10 %), 3 – organic-inorganic+talc (10 %), 4 – organic-inorganic+TiO_2 (5 %)+talc (5 %)

It was found that the dynamics of change in the swelling thickness, obtained experimentally, coincides with the theoretically calculated. The calculated reaction order for the organic-inorganic coating, is 1.42, and in the case of administration of fillers is increased to 2, which is in turn connected with the formation of heat-resistant compounds with a significant coke residue.

To confirm these studies, the corresponding thermogravimetric analysis was carried out, which showed the dependence of the weight loss for these compositions (Table 3), and the activation energy was calculated by the method of studying the kinetics of decomposition given in [12].

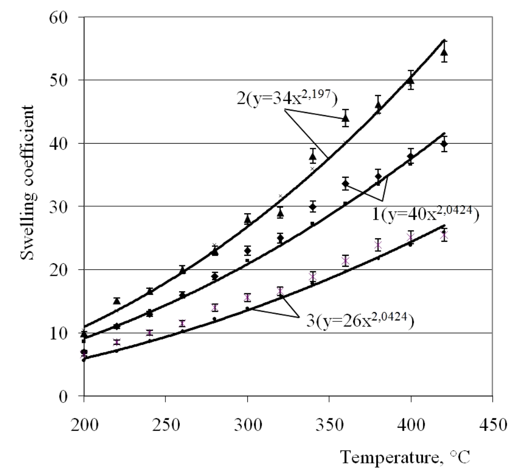

Fig. 5. The dependence of the swelling coefficient of the coating on temperature: 1 – organic-inorganic+$Al(OH)_3$ (10 %), 2 – organic-inorganic+$Mg(OH)_2$ (10 %), 3 – organic-inorganic+TiO_2 (5 %)+$Al(OH)_3$ (5 %)

Fig. 6 shows the graphical dependence of the speed of degradation of the coating on the reciprocal temperature.

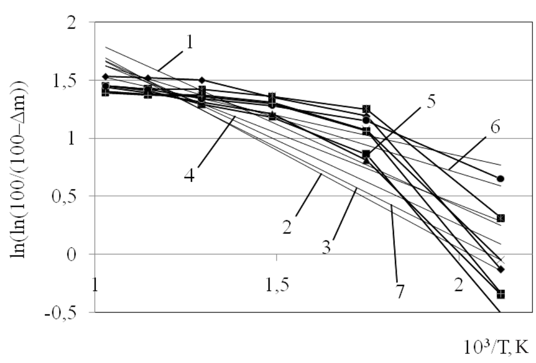

Fig. 6. Graphic dependence of the rate of destruction of the coating on the reciprocal temperature: 1 – organic-inorganic, 2 – organic-inorganic+$Al(OH)_3$ (10 %), 3 – organic-inorganic+TiO_2 (10 %), 4 – organic-inorganic+talc (10 %), 5 – organic-inorganic+$Mg(OH)_2$ (10 %), 6 – organic-inorganic+TiO_2 (5 %)+talc (5 %), 7 – organic-inorganic+TiO_2 (5 %)+$Al(OH)_3$ (5 %)

The activation energy (E) is calculated by the equation:

$$E = tg\phi \cdot R,$$

where R – gas universal constant, kJ/(mol·K).

Table 3

The results of the coating weight loss depending on temperature

t, ºC	Δm, %	Ln(Ln(100/100–Δm))
organic-inorganic coating		
200	2.4	–0.133
300	26.8	1.190402
400	47.1	1.348663
500	86.7	1.495699
600	94.9	1.515748
700	98.9	1.524775
organic-inorganic+TiO_2 (10 %)		
200	1.82	–0.51277
300	10.73	0.862993
400	25.91	1.181143
500	38.05	1.29132
600	59.71	1.408382
700	70.8	1.449236
organic-inorganic+talc (10 %)		
200	1.02	–0.35226
300	9.55	0.813833
400	28.65	1.210498
500	40.23	1.306876
600	54.66	1.386577
700	69.1	1.443514
organic-inorganic+TiO_2 (5 %)+talc (5 %)		
200	2.6	–0.04551
300	18.5	1.07082
400	40.0	1.305323
500	50.7	1.367602
600	52.5	1.376449
700	56.8	1.39613
organic-inorganic+$Al(OH)_3$ (10 %)		
200	3.9	0.308202
300	33.1	1.25263
400	49.1	1.359401
500	62.0	1.417583
600	63.57	1.423738
700	71.2	1.450558
organic-inorganic+$Mg(OH)_2$ (10 %)		
200	6.75	0.646864
300	23.4	1.148271
400	36.9	1.283212
500	44.9	1.336168
600	63.9	1.42487
700	71.5	1.451543
organic-inorganic+TiO_2 (5 %)+$Al(OH)_3$ (5 %)		
200	2.04	–0.33834
300	17.7	1.055553
400	38.8	1.297031
500	49.3	1.360444
600	51.4	1.371089
700	54.4	1.385385

Table 4 shows the values of the activation energy in the thermal decomposition of coatings without fillers and with them.

Table 4

The calculated values of the activation energy in the thermal decomposition of timber at various values of oxygen in the gas-air medium

№	The coating	The activation energy, E kJ/(mol·K)
1	organic-inorganic	18.79
2	organic-inorganic+$Al(OH)_3$ (10 %)	32.59
3	organic-inorganic+TiO_2 (10 %)	31.45
4	organic-inorganic+talc (10 %)	30.36
5	organic-inorganic+$Mg(OH)_2$ (10 %)	29.35
6	organic-inorganic+TiO_2 (5 %)+talc (5 %)	60.85
7	organic-inorganic+TiO_2 (5 %)+$Al(OH)_3$ (5 %)	65.10

It is found that the thermal decomposition of organic-inorganic coatings with fillers require considerably more activation energy than the decomposition of the organic-inorganic system without fillers. Thus, it is established that the organic-inorganic coating at high temperatures is capable of a significant loss of mass, and the introduction of fillers leads to the formation of refractory compositions which prevent burnout of the foam-coke formed, which increases the efficiency of the fire protection of building constructions.

6. Conclusions

These studies established the efficacy of the fillers in the mixture of organic and inorganic substances as flame retardants, in particular:

– a study of the process of swelling of fire protective coatings was carried out, the change in temperature and the kinetics of decomposition of the samples under the thermal action were determined by the proposed method for determining the kinetics of swelling of the coatings, the essence of which is the impact of heat flow on the sample for a certain period of time, measuring the temperature on the back surface and in front of the sample and determining the thermal insulation properties;

– tests on model samples of organic-inorganic coatings containing fillers showed that the coating based on organic-inorganic substances under the influence of heat forms a substantial swelling ratio, but eventually the process of the foam-coke burnout occurs and the swelling effect is reduced. But adding fillers to the organic-inorganic coating system favors the formation of refractory compositions, which prevents the foam-coke burnout and passage of heat to the material.

Further studies may be aimed at studying the processes of structure formation of the protective layer, establishing the relationship between the components and properties of coatings and their optimization.

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