Розглянуто основні критерії оцінки вогнезахисної ефективності покриттів інтумесцентного типу, що базуються на вивченні фізико-хімічних параметрів теплоізоляційного спученого шару. Досліджено термічні перетворення інтумесцентної системи (поліфосфат амонію, пентаеритрит, меламін, співполімер стиролакрилату) у температурному інтервалі 200–600 °С в присутності органомодифікованих монтморилонітів. Надано практичні рекомендації щодо складання рецептур вогнезахисних покриттів для будівельних конструкцій в залежності від межі вогнестійкості згідно з вимогами протипожежної безпеки

Ключові слова: органоглина, вогнезахист, монтморилоніт, інтумесцентні композиції, коефіцієнт спучення

Рассмотрены основные критерии оценки огнезащитной эффективности покрытий интумесцентного типа, основанные на изучении физико-химических параметров теплоизоляционного вспученного слоя. Исследованы термические превращения интумесцентной системы (полифосфат аммония, пентаэритрит, меламин, сополимер стиролакрилата) в температурном интервале 200–600 °С в присутствии органомодифицированных монтмориллонитов. Даны практические рекомендации по составлению рецептур огнезащитных покрытий для строительных конструкций в зависимости от предела огнестойкости в соответствии с требованиями противопожарной безопасности

Ключевые слова: органоглина, огнезащита, монтмориллонит, интумесцентные композиции, коэффициент вспучивания

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THE EFFECT OF ORGANOCLAYS ON THE FIRE-PROOF EFFICIENCY OF INTUMESCENT COATINGS

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1. Introduction

Fire protection of buildings and structures is, above all, in improving the bearing capacity of building structures (steel, concrete, wood) by applying special flame retardant coatings that inhibit reaching critical states by structures under fire conditions [1, 2].

The most common and uncontested in many cases means of fire protection are a thin-layer intumescent (swelling) coatings of traditional composition – ammonium polyphosphate (APP)/pentaerythrite (PE)/melamine (MA)/co-polymer. Despite the universality, manufacturability of application and aesthetic characteristics, coatings of the intumescent type have a basic drawback of high toxicity of combustion products due to the presence of halogen-containing components in the coating. Solving this problem by developing new flame retardant intumescent technologies with improved parameters of fire-protection efficiency and environmental safety is a relevant and important task.

2. Literature review and problem statement

Numerous studies of intumescent systems to find the optimum components for the purpose of improving the fireproof efficiency demonstrate that the range of these substances is constant and limited. Typically, these are ammonium phosphates, pentaerythrite and its close analogues, melamine and melamine derivatives, chloro-paraffins, titanium oxide, rheological additives [3].

One of the modern technologies of increasing fire resistance of the intumescent coatings with a decrease in the formation of toxic products of thermolysis is the application of nanostructural fire retardants – nanooxides [4–6], nanoclays [7, 8], boron nanocompounds [9] and others. Results of research into the influence of nanoadditives on the effectiveness of intumescent fire protection make it possible to highlight general peculiarities of nanoparticles effect under conditions of high temperatures: the strengthening of coke protective casing by structuring a polymer matrix with particles MeO or atoms B and Si [5, 7, 8], the reduction of release of toxic gases [7, 10], the improvement of thermal stability of the polymer component of a flame retardant coating [7, 8, 10–13].

It should be noted that despite the proven positive impact of nanooxides (titanium, magnesium, aluminum) [4–6] on the coating fire-retardant properties, their wide application at industrial scale is economically impractical due to the high price of nanostructural oxides.

As an alternative to nanooxides, bentonite clays – natural layered silicates – may be considered as additives to the systems of the intumescent type. The most examined and promising nanoclays are montmorillonite and its close analogues (smectite, attapulgite), which in the form of organomodified derivatives (organoclays) are widely used in nanotechnology and the synthesis of nanocomposites [7, 11].

The scientific literature presents studies of joint action of organoclays and the intumescent system (APP/PE/MA) to reduce flammability of polymers – polyolefins [8, 10, 11], polyamides [12], ethylene vinyl acetate (EVA) [10, 13]. However, the information on the application of identified synergy for designing flame retardant coatings of the intumescent type is limited, and sometimes controversial. On the one hand, organoclays take part in the processes of carbonization with the formation of a coke layer with increased strength and thermal stability [10–13], and on the other hand, they create barrier obstacles to the migration of outgoing gases and negatively affect swelling ratio [7, 14].

The closest ones to the problem of development of new formulations based on the system APP/PE/MA in the presence of organoclays are the studies [7, 10, 13] of thermolysis of the EVA co-polymer – a common film-forming agent of water-dispersion intumescent paints. Information about effect of the intumescent systems with additives of organoclays (or other nanocompounds) on the thermal decomposition of styrene acrylates (SA) is practically missing [7]. But fireproof organic solvent-based paints containing styrene acrylate co-polymers use up to 10 % of chlorine paraffin as fire retardant [14].

That is why a research into the influence of organoclays as an alternative to halogen-containing fire retardants on the fireproof efficiency of the intumescent organic solvent-based compositions is not only of scientific but of practical interest as well, connected to the minimization of environmental risks for humans and the environment in case of fires.

3. The aim and tasks of the study

The main aim of the research is to study the action of organomodified montmorillonite on the fireproof efficiency of the intumescent composition (IC) composed of ammonium polyphosphate/pentaerythrite/melamine/copolymer of styrene with butyl acrylate.

The set goal implies solving of two blocks of interconnected tasks:

– obtaining modified montmorillonite using, as a raw material, bentonite clay of the II-nd layer of the Dashukivsky deposit (Ukraine);

– research into the influence of the obtained organoclays on the formation and physical characteristics of a coke layer of intumescent composition in the range of temperatures 200–600 °C and under conditions of fire tests.

4. Materials and methods of research into the influence of organoclays on the formation and physical characteristics of a coke layer

4. 1. Materials and equipment used in the experiment

We used in the study ammonium polyphosphate of the type II CF-APP201 (Shifang Changfeng Chemical Co., Ltd., China), micronized pentaerythrite of the RN-P brand and melamine RN-M 40 (Roshal Group, Russia), copolymer of styrene acrylate Pliolite AC 80 (Omnova Solutions, USA), titanium oxide TiO_2 (Sumykhimprom, Ukraine), titanium nanooxide TiO_2-n in the form of nanopowder (Balti Kaubad ja Teenused AS, Estonia), bromide cetyltrimethylammonium (PanReac AppliChem, Spain), tallow bis-hydroxyethyl methyl ammonium chloride Corsaquat T2-50 (Corsitech , USA).

For the synthesis of organoclays we used a sample of bentonite clay from the Dashukivsky deposit (II-nd layer), which, according to technical documentation, contained 85–95 % of MMT and was crushed at a jaw crusher. The presence of impurities in the clay was controlled by IR spectroscopy at the IR Fourier spectrometer BX-11 (Spectrum) for the presence of calcite peaks.

The size, shape and microstructure of the obtained samples were investigated using the scanning electron microscope JSM-6490 LV.

4. 2. Modification of Na-MMT with tallow bis-hydroxyethyl methyl ammonium chloride

We dispergated 15 g of Na-MMT in 100 ml of isopropyl alcohol in a flask with capacity of 500 ml at room temperature for 30 min. Then, we added in the resulting suspension 5 g of tallow bis–hydroxyethyl methyl ammonium chloride (WEMC) and stirred for 5 hours using a reverse-refrigerator at temperature 70 °C. The sediment of montmorillonite modified with the cation of WEM was centrifuged; the sediment was washed three times with distilled water and once with isopropyl alcohol by decantation, centrifuged and dried at room temperature. We received 18 g of montmorillonite, modified with the cations of tallow bis-hydroxyethyl methyl ammonium (WEM-MMT).

4. 3. Preparation of intumescent composition

In a bead mill we put components of the intumescent system: ammonium polyphosphate, pentaerythrite, melamine, titanium oxide, the solution of copolymer AS-80 in a solvent in the required ratio, and a nanocompound of 0–3 % by weight. The mixture was stirred for 30 min, separated from the beads. From the finished composition, by the method of pouring into the boxes, we prepared samples of films from aluminum foil, dried them to constant mass at room temperature and then determined the swelling ratio.

4. 4. Fire tests in line with DSTU B V.1.1-14:2007

Testing the intumescent paints was carried out in accordance with the procedures provided by DSTU B V.1.1-14:2007, in the test center "Donstroytest". Thickness of the intumescent coating on the columns of resulting thickness 5.4 mm was (0,50±0,05) mm and (1,76±0,12) mm.

As a known intumescent paint (IP), we tested the organic solvent paint that has similar formulation to the examined IC, and contains, as a flame retardant, chloro-paraffins. The paints' formulations based on the examined IC that consists of APP/PE/MA/SA, containing TiO_2 in the amount of 6 % and 3 % of TiO_2-n or 1 % of WEM-MMT, have been compiled taking into account the results obtained in this study.

Methods of enrichment of bentonite clay, obtaining Na-form of montmorillonite, modification of Na-MMT with cetyltrimethylammonium bromide (CTA-MMT), determining swelling coefficient of the intumescent compositions (cm^3/g) and value of mass of the coke residue (CR), are described in detailed in paper [15].

5. Results of the modification of montmorillonite with quaternary onium cations and of the research into indicators of thermal transformations of intumescent composition

5. 1. Modification of montmorillonite with quaternary onium cations

To conduct the research, we used bentonite clay from the Dashukivsky area of the Cherkassky deposit, from which we obtained samples of MMT and its organomodified derivatives – CTA-MMT and WEM-MMT.

We obtained organoclays of MMT, modified with cations of cetyltrimethylammonium and tallow bis-hydroxyethyl methyl ammonium, by the substitution of Na^+ cations in the Na-form of montmorillonite with quaternary ammonium salts – cetyltrimethylammonium chloride and tallow bis-hydroxyethyl methyl ammonium chloride. The infrared spectra of CTA-MMT and WEM-MMT confirm the intercalation of the ammonium cation to the layered cationic silicate by the presence of absorption bands of 2921–2860 cm^{-1}, which correspond to the valent fluctuations of the group of $-CH_2-$ alkyl chain, and the bands of 1490–1470 cm^{-1}, characteristic for the R_4N^+cation.

Fig. 1 displays results of the scanning electronic microscopy, which allow determination of the size of the particles of the examined clays. It follows from these data that due to the procedure of MMT organomodification, there occurs a reduction in the size of the particles of natural nanosilicate by 3–4 times, and the organomodified montmorillonites (CTA-MMT and WEM-MMT) obtained from clay of the Dashukivsky deposit have the size of particles smaller by 2–3 times than the commercially-available product Organoclay 801D (tallow bis-hydroxyethyl methyl ammonium montmorillonite), which is used by the industry as a thickener for organic solvent-based paints.

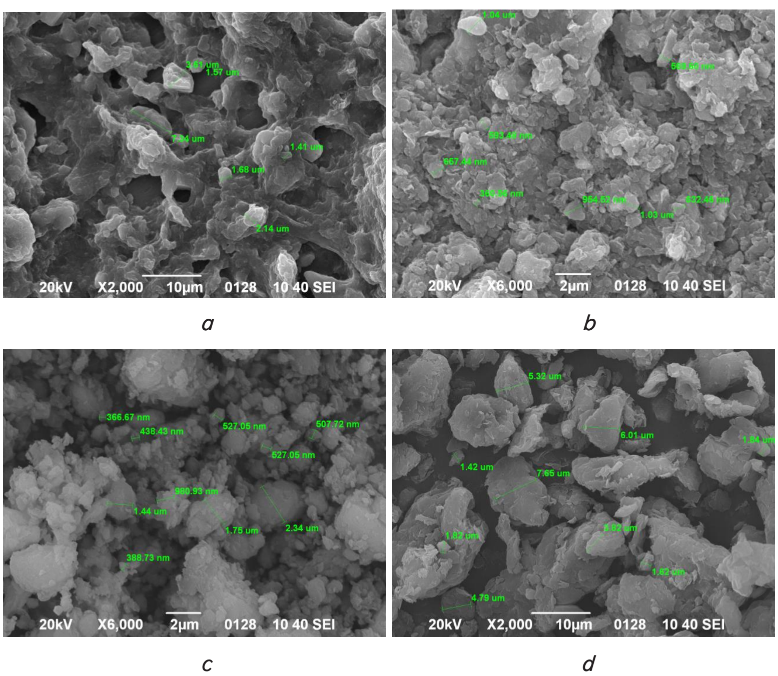


Fig. 1. SEM image: *a* — montmorillonite, *b* — montmorillonite cetyltrimethylammonium, *c* — willow bis-hydroxyethyl methyl ammonium of montmorillonite, *d* — nanoclay Organoclay 801D

The nanoclays MMT, CTA-MMT and WEM-MMT we received were used as additives to IC to study their effect on the formation and structure of the coke layer that is formed as a result of action on the intumescent coating of high temperatures.

5. 2. Determining the coefficient of swelling and loss of mass of intumescent compositions in the temperature range of 200–600 °C

The most common method of scientific research into flammability of polymeric materials is the cone calorimeter method [16], which allows obtaining information about the speed of heat release, effective combustion heat, induction period of ignition and other indicators for the evaluation of ignition behavior of polymers. A set of these parameters is used for the prediction of flame retardant properties of intumescent coatings. However, data received by the cone calorimeter method do not provide a full picture of the physical and mechanical properties (swelling ratio, temperature of destruction, density, adhesion to substrate) of the coke layer that is formed as a result of chemical interactions between the components of the intumescent system. And these particular characteristics are very important to provide for a long-term limit of fire resistance of building structures under fire conditions.

In this work, we applied a phased study of structure of the IC coke layer that implies the aging at certain temperature from 200 to 600 °C of the samples of intumescent compositions consisting of APP/PE/MA/SA with additives of nanocompounds.

In order to explore the properties of a coke layer of the composition APP/PE/MA/SA, we prepared samples by mixing a varnish of copolymer with dry ingredients and nanocompounds (1 % of nanoclay or 3 % of nanooxide) in a bead mill. Prepared samples were aged in a thermal cabinet at the set temperature for 10 min, then we determined coefficient of swelling (K, cm^3/g) and mass of a coke residue (CR, %), as described in the experimental chapter.

The given amounts of nanoadditives are optimal for the examined systems, which was determined experimentally. The examined IC is especially sensitive to the content of nanoclay – an increase in the amount of MMT and its derivatives by 3 % reduces coefficient of swelling (K) by 3–4 times, while the presence of nanoclay in IC above 5 % terminates the swelling processes almost completely.

Fig. 2 demonstrates dependences of the volumetric coefficient of swelling K of the intumescent compositions APP/PE/MA/SA with additives of titanium nanooxide and nanoclays on temperature.

The character of these dependences demonstrates that the basic chemical processes responsible for building a coke layer and, accordingly, fire-retardant properties of IC, start after 300 °C and proceed in the temperature range of 350–550 °C while the influence of nanoadditives on the process of swelling has a number of peculiarities:

– IC without additive, which contains copolymer SA in its composition, has a fairly high coefficient of swelling (K=55 g/cm^3), but it forms a coke residue that is not resistant to temperatures, as evidenced by the sharp reduction in parameter K at temperature >350 °C;

– at temperatures of 300–350 °C, the additives of TiO_2 and TiO_2-n practically do not affect the value of swelling coefficient K and greatly increase thermal stability of a coke layer in the temperature range of 350–500 °C;

– nanoclays, when heating a composition to 400 °C, significantly inhibit the swelling of IC and provide for a stable coke layer state during the interval of temperature from 400 to 600 °C.

Dynamics of change in parameter K (Fig. 2) demonstrates that IC with titanium nanooxide and nanoclays are characterized by a longer stabilizing section of stability of swelling coefficient K in the temperature range of 300–550 °C compared to the system that does not contain additives.

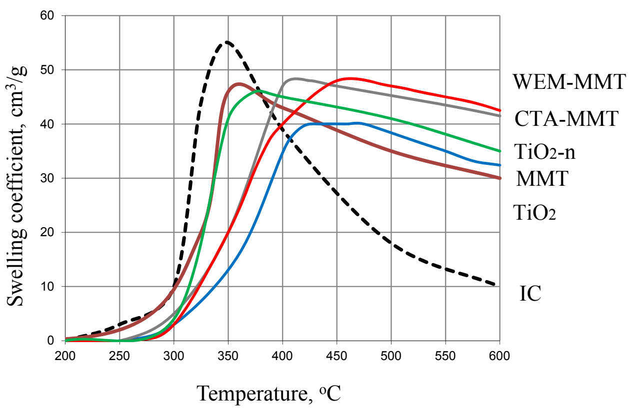


Fig. 2. Dependence of coefficient of swelling K (cm^3/g) of the intumescent compositions of APP/PE/MA/SA (IC) and IC with additives of oxides (3 %) and nanoclays (1 %) on temperature T (°C)

The values of mass of coke residues of the IC samples during heating in the temperature range of 200–600 °C are displayed in Fig. 3. It follows from these data that the addition of both titanium oxide TiO_2 and its nanostructural analog, as well as obtained organoclays, significantly increases the mass of CR of the swollen layer over the entire range of temperature influence. In the region of temperature above 400 °C, the lowest mass loss is characteristic for the intumescent systems containing organomodified clays CTA-MMT and WEM-MMT, indicating the building up of a thermally stable coke layer.

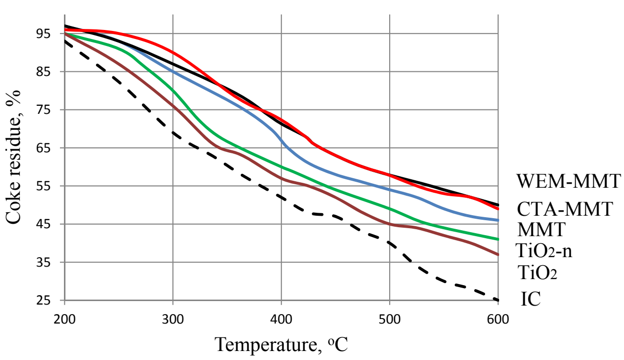


Fig. 3. Dependence of the values of magnitude of the coke residue (%) of the intumescent composition APP/PE/MA/SA (IC) and IC with additives of oxides (3 %) and nanoclays (1 %) on temperature T (°C)

Based on the results of determining the coefficient of swelling and loss of mass of the intumescent compositions in the temperature range of 200–600 °C with the additives of organoclays derived from bentonite clay of the Dashukivsky deposit, it is possible to draw at least two conclusions that are useful for the development of domestic nanotechnologies and nanocomposites:

– the bentonitic clay we examined may be applied as a starting raw material for obtaining organoclays – an important component of modern nanocomposites;

– the determined parameters of coke residue of IC consisting of APP/PE/MA/SA allow us to consider the addition of organoclays as a promising direction for improving formulations of the intumescent fire retardant coatings.

6. Discussion of results of research into the influence of nanocompounds on the structure of a coke layer

The obtained experimental results of determining coefficient of swelling for the intumescent compositions K have important practical significance because they allow us to state that there is a positive influence of nanoadditives on the thermal stability of a coke layer that is responsible for thermal insulation of a building structure. However, it should be noted that the impurities of montmorillonite and its organomodified analogues (CTA-MMT and WEM-MMT) is the cause of too late swelling of IC. That is why the intumescent coatings with nanoclays are not expedient to use to provide for the limit of fire resistance of the metal structures R 30, which is achieved at thickness of the original coating of 0.4–0.6 mm. In this case, the speed of metal reaching critical temperature of 500 °C might be higher than the rate of the formation of a swollen coke residue because of the coating layer being too thin.

Adding nanocompounds to IC significantly reduces the loss of mass of the samples compared to the unfilled IC, as well as to the composition containing regular titanium oxide in the amount of 3 % (Fig. 3). Almost over the entire range of temperature action, the mass of the IC coke residue, containing nanocompounds, at temperature of 600 °C, is 10–20 % larger than the mass of coke residue of the basic IC.

Table 1 displays the values of temperatures T_{20} and T40, at which there are 20 and 40 % losses of mass of the IC samples in the absence and in the presence of nanoadditives. It follows from these data that in comparison with the basic IC, the values of T_{20} for the samples with TiO_2-n, CTA-MMT and WEM-MMT increase by 40–90 °C, and the corresponding difference for T_{40} is in the range of 100–175 °C. If we compare the values of T_{20} and T_{40} with such values for IC with a regular TiO_2 oxide, which is a mandatory component of paints of the intumescent type, then it should be stated that the additives of nanoclays are able to significantly inhibit the loss of mass of an intumescent coating in the temperature range of 500–600 °C, which is critical for the strengthening or decomposition of a coke layer [5, 7].

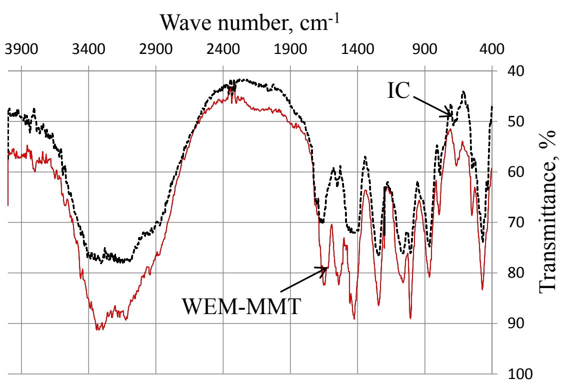
There is no doubt that the increase in the CR mass of intumescent composition in the presence of nanooxides and nanoclays is the result of participation of these compounds in the chemical transformations between components of the system and in the building of a coke layer. The mechanisms of chemical interactions in similar IC were examined in more detail earlier [17, 18], and the infrared spectrum of the IC coke residue with WEM-MMT at 350 °C (Fig. 4, *a*) allows us to state that the system with nanoclay is more thermally stable than the unfilled one. In the spectrum (WEM-MMT, Fig. 4, *a*), one observes clear functional groups absorption bands involved in the construction of a heat–resistant casing (3380–3100 cm^{-1} – –OH, $-NH_2$, =NH; 2920–2860 cm^{-1} – $-CH_2-$; 1248 cm^{-1} –P=O; 1180 cm^{-1} – –P–OH; 1087 cm^{-1} – –C–N–; 1012 cm^{-1} – –P–O–C– and others),) than in the spectrum of compositions without additives (IC, Fig. 4, *a*). More to the point, an analysis of infrared spectra of the intumescent composition APP/PE/MA/SA in the presence and absence of WEM-MMT (Fig. 4, *a*) enables us to determine clear absorption bands of amide groups for the systems containing nanoclay – 1658 cm^{-1} and 1558 cm^{-1}. These bands are characteristic and unequivocally point to the reaction proceeding between melamine and the SA copolymer, which, with great probability, is catalyzed by nanoclay.

Table 1

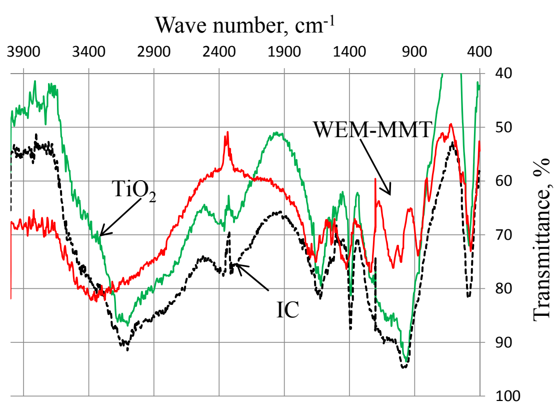
Data of gravimetric analysis of intumescent composition in the presence of additives in the temperature range of 200–600 °C

No.	Additive	T_{20}, °C	T_{40}, °C	CR, % 600 °C
1	–	258	301	25
2	TiO_2	279	377	37
3	TiO_2-n	300	399	41
4	MMT	338	426	46
5	CTA-MMT	349	475	50
6	WEM-MMT	351	475	49

Note: based on data in Fig. 3



a

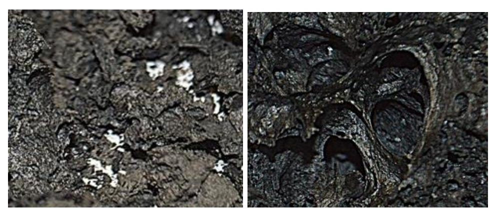


b

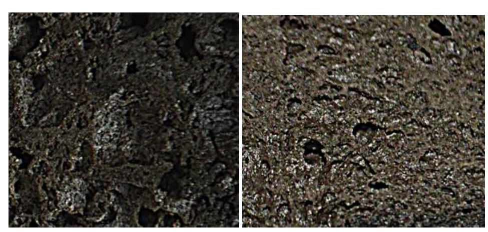
Fig. 4. Infrared spectra of coke residue of the intumescent composition APP/PE/MA/SA (IC) and IC with additive of WEM-MMT on temperature T (°C): *a* – 350 °C; *b* – 450 °C

With all common attributes of chemical transformations observed in an unfilled IC and the IC that contains additives of TiO_2 and WEM-MMT, the IR-spectra of coke residues at 450 °C (Fig. 4, *b*) demonstrate the difference in the structure of products of thermal destruction. Thus, titanium oxide, as IC filler, hardly changes chemical structure of the IC coke layer, which is why these compositions should be considered as more depleted for consequent endothermic processes in contrast to the IC with WEM-MMT, the IR-spectrum of which comprises the bands that correspond to active functional groups (Fig. 4, *b*). It is also worth noting that the IC coke residue at 350 °C is close in its structure to the coke residue of the modified with WEM-MMT composition that is formed at 450 °C. That is, one can state the fact of slowing down the processes of thermooxidative destruction of the intumescent composition in the presence of nanocompounds, at least in the temperature range of 200–450 °C.

Participation of nanooxides and nanoclays in the chemical transformations of IC may be varied and multifaceted – promotion and catalysis of oxidative reactions and the processes of dehydration, esterification, aminolysis, inter-molecular stitching that is implemented under conditions of the structuring of polymer matrix by the MeO particles, barrier effects created by layered silicates, etc. [7, 10]. In our opinion, the largest contribution to the growth in the IC thermal stability in the temperature range of 500–600 °C may be added by reactions associated with the introduction of atoms of metals and silicon to the structure of a polymer coke residue, as evidenced by comparison of the cross-sections of coke layers of the compositions APP/PE/MA/SA in the presence of oxide and nanooxide of titanium and WEM-MMT after exposing them to the flame of a gas burner for 15 min (Fig. 5).



a *b*

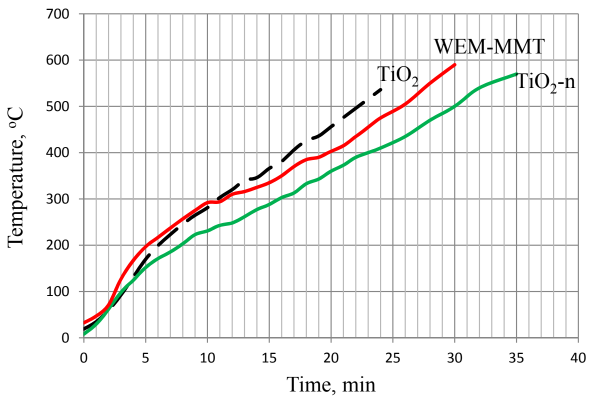


c *d*

Fig. 5. Cross-sections of coke layers of intumescent composition: *a* – APP/PE/MA/SA; *b* – IC with additives of TiO_2; *c* – TiO_2-n; *d* – WEM-MMT

Visual observations of the examined compositions demonstrate positive effect of nanoadditives on the mechanical, strength and adhesion properties of coatings. Structure of a coke swollen layer of the examined materials varies: the most solid, hard and fine-porous frame is observed when using the WEM-MMT nanoclay and titanium nanooxide as a flame retardant. Such a coke residue effectively protects substrate material from heat and flame, and allows us to expect high values of fire resistant efficiency of coatings and reduction in flammability of polymeric materials.

Conclusions and scientific hypotheses obtained in this study were tested by conducting full-scale fire tests in accordance with DSTU B V. 1.1-14:2007 [19]. Test results are shown in Fig. 6.



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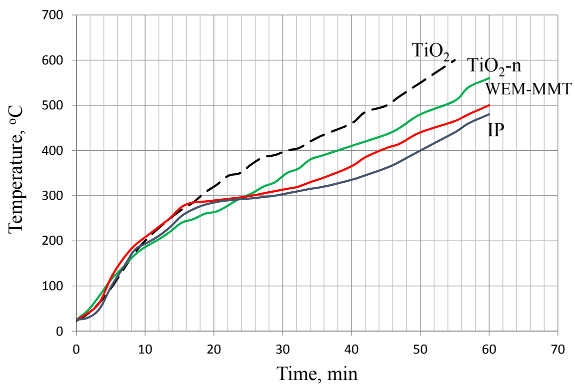

b

Fig. 6. Data of fire tests for the limit of fire resistance of metal columns, protected by intumescent coatings based on intumescent composition APP/PE/MA/SA (TiO_2, TiO_2-n, WEM-MMT) and a known intumescent paint (IP) in line with DSTU B V. 1.1-14:2007: *a* — thickness of the coating (0,50±0,05) mm; *b* — thickness of the coating (1.76±0.12) mm

These results demonstrate that when applying a coating by a thin layer (Fig. 6, *a*), the limit of fire resistance of metal column is reduced in row TiO_2 (22 min)<<WEM-MMT (26 min)<TiO_2-n (30 min), while at an increase in thickness of the coating (Fig. 6, *b*), the highest limit of fire resistance (60 min) is provided for by the coating with the WEM-MMT organoclay. This fact confirms the previous assumption that it is inappropriate to use organoclays, as additives to intumescent paints, for the protection of steel structures with the fire resistance limit requirements R 30 and possibly R 45. In turn, organoclays are an efficient additive to the paints, which should provide for the limit of fire resistance R 60 and above.

It should also be noted that the fire-resistant coating, with custom-fabricated additive of WEM-MMT, demonstrates almost the same fireproof efficiency as the sample of IP that contains 8 % of chlorine paraffin (Fig. 6, *b*). This fact attests to the prospects of research into replacing harmful halogen-containing components of intumescent compositions with organomodified montmorillonites with the possibility of implementation of new high-tech fire-resistant coatings at competitive price, the need for which grows in proportion to the development of construction industry.

7. Conclusions

1. Montmorillonite, obtained from bentonite clay of the II-nd layer of the Dashukivsky deposit (Ukraine, Cherkassy Region), can be used as a source raw material for obtaining nanoclays, modified with quaternary ammonium cations. The organoclays we received do not differ in their composition and structure from the commercially-available samples of manufactured abroad and can be used as modifiers and fire retardants for flame retardant compositions of the intumescent type.

2. Additives of organoclays to the intumescent composition consisting of ammonium polyphosphate/pentaerythrite/melamine/copolymer of styrene with butyl acrylate positively affect the formation of a coke layer in the temperature range of 400–600 °C. It is demonstrated that adding organoclays to the intumescent composition in the amount not exceeding 1 % leads to a shift in the temperature of oxidation of carbonized polymer residue to a higher temperature region at minimal reduction of volumetric coefficient of swelling and increase in the mass of coke residue by 10–25 %.

Results of the research allow us to recommend introducing montmorillonite, modified with quaternary ammonium cations, to the formulations of intumescent paints as an efficient and environmentally-friendly additive that should predictably improve effectiveness of fireproof coatings, designed for high limits of fire resistance of building structures – R 60–R 120.

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