

Thermal destruction of fire-retardant intumescent coating of the composition of ammonium polyphosphate (APP)/melamine (MA)/pentaerythrite (PE)/titanium oxide (TiO₂)/polymer, which can be applied for fire protection of steel structures, was studied. The influence of polymers of different nature – ethylene-vinyl acetate (EVA), vinyl acetate versatate (VAVV), styrene acrylates, and vinyl toluene acrylate on the processes of formation of a coke layer and fire-retardant effectiveness of appropriate coatings was determined.

Chemical transformations of polymers EVA and styrene acrylate in the intumescent system of ARR/MA/PE/TiO₂ in the temperature range of 200–800 °C were studied. It was established that the processes of the thermal destruction of vinyl acetate polymer are more harmonized with chemical reactions of the components of the intumescent system than similar processes for acrylate aromatic polymers.

Thermal-oxidation destruction of intumescent compositions at the temperatures of 200–800 °C was explored. It was shown that basic chemical processes with polymers of EVA and VAVV begin after 300 °C and flow in the temperature range of 350–600 °C. It was found that the noticeable degradation of the carbon-phosphorus frame of intumescent compositions with styrene acrylate polymers begins at 450 °C, which is almost by 150 °C below the temperature of degradation of the compositions containing vinyl acetate binders.

The conducted fire tests demonstrate that intumescent compositions with the use of acrylate aromatic polymers are more effective at the low coating thickness in ensuring the fire resistance boundary of 30 min. In order to ensure higher values of fire resistance, it is necessary to use intumescent coatings containing vinyl acetate co-polymers as the polymer component.

The study of the impact of polymers of intumescent coatings on the boundary of fire resistance of steel structures has scientific and practical significance for the development of differentiated fire protection means, oriented to the given class of fire resistance. Fire-retardant intumescent compositions examined in this study can be used as the basis for the formulations of materials for fire protection of building structures under conditions of a standard fire

Keywords: vinyl acetate, styrene acrylate, coefficient of swelling, intumescent coating, fire resistance boundary, standard fire

COMPARISON OF FIRE RESISTANCE OF POLYMERS IN INTUMESCENT COATINGS FOR STEEL STRUCTURES

K. Kalafat

Postgraduate Student*

E-mail: K.V.Kalafat@nas.gov.ua

N. Taran

PhD****

E-mail: N.A.Taran@nas.gov.ua

V. Plavan

Doctor of Technical Sciences*

E-mail: plavan.vp@knu.edu.ua

V. Bessarabov

PhD**

E-mail: drvib500@gmail.com

G. Zagoriy

Doctor of Pharmaceutical Sciences**

E-mail: Ph.G.Zag@gmail.com

L. Vakhitova

PhD****

E-mail: L.M.Vakhitova@nas.gov.ua

*Department of Applied Ecology, Technology of Polymers and Chemical Fibers***

**Department of Pharmaceutical Industry

***Kyiv National University of Technologies and Design Nemyrovycha-Danchenka str., 2, Kyiv, Ukraine, 01011

****L. M. Litvinenko Institute of Physical-Organic

Chemistry and Coal Chemistry of

the National Academy of Sciences of Ukraine

Kharkivske shose str., 50, Kyiv, Ukraine, 02160

Received date 02.07.2020

Accepted date 30.07.2020

Published date 25.08.2020

Copyright © 2020, K. Kalafat, N. Taran, V. Plavan, V. Bessarabov, G. Zagoriy, L. Vakhitova

This is an open access article under the CC BY license

(<http://creativecommons.org/licenses/by/4.0>)

1. Introduction

Thin-layer intumescent coatings are actively applied in fire safety practices as the best choice for the reactive fire protection of construction steel [1, 2]. Such popularity is the result of the ability of intumescent coatings to provide effective fire protection solutions while preserving aesthetic characteristics and architectural design of steel construction [3, 4].

However, there are a series of restrictions on the use of intumescent type means, the major of which should be considered:

– environmental hazard under fire conditions, due to the use of antipyrine admixtures containing halogens and heavy metal oxides;

– low resistance to the effect of moisture and other corrosive media, and, consequently, a short lifetime in comparison with other types of passive fire protection means;

– a significant price of flame retardant material especially for achieving a fire-resistance boundary of steel structures of 90–120 min (R90–R120).

The problem of the ecology of fire-retardant coatings of the intumescent type is intensively studied and maintained by the REACH norms [5], which prohibit the use in the construction industry of the reagents and raw materials that are harmful to humans. When it comes to the increased service life and a decrease in the cost of fire-retardant material, one of the variants of the solutions to this problem is the choice of the optimal polymer matrix of the intumescent composition (IC).

The necessity and the relevance of the development of new intumescent technologies are also determined by a series of global problems in the sphere of fire safety. First of all, these are the needs for the development of the construction industry and the safe operation of construction projects. In addition, the threats of terrorist attacks and the wars with the use of heavy and explosive weapons, the consequence of which is inevitable fires, have increased lately.

2. Literature review and problem statement

The technology of intumescent coatings for steel structures has almost remained unchanged in the last 40 years. The main reactive components of the traditional IC are [1, 2]: the acid donor is phosphates, ammonium polyphosphates (APP); the carbonizing agent is pentaerythrite (PE) or its analogs; the gas generating agent is the derivatives of melamine (MA), di-cyandiamide, urea. In the form of a fire-retardant paint, IC additionally contains a polymer binder, pigment, fillers, and rheological impurities.

By the nature of the polymer component, intumescent compositions for steel structures should be divided into two groups:

– paints containing water dispersions of polymers (most commonly co-polymers of vinyl acetate (VA): ethylene with vinyl acetate (EVA), vinyl acetate of vinyl versatate (VAVV), vinyl acetate with acrylate (VAA) [6, 7]);

– paints based on organosoluble polymers (styrene co-polymers with acrylate (SA), vinyl toluene with acrylates (VTAC) [8]).

In addition to the above polymer materials, epoxy resins, polyurethane, and silicone polymers are used in the firefighting practice. However, the fire-retardant coatings based on them belong to a higher price segment and are usually used for fire protection of structures under a hydrocarbon fire [6].

The main function of intumescent fire-retardant coatings is to provide the class of fire resistance of steel structures (R_{min}) [9] in accordance with the norms established by the national legislation. According to the data of research [10], thin-layer coatings confidently ensure the R60 fire resistance class for the thickness of metal $\delta \geq 4$ mm (cross-section coefficient $A_m/V \geq 250 \text{ m}^{-1}$) and R90 for $\delta \geq 12$ mm ($A_m/V \geq 80 \text{ m}^{-1}$). At the world market of firefighting means, there are also intumescent coatings, for which the R120 and R150 fire resistance class was declared [10]. However, in the open sources, there is no information regarding the effect of the polymer component IC on the value of fire resistance class R .

Patent research and information from the open sources make it possible to offer the sustainable intumescent bases of fire-retardant means, which are currently produced by the world industry (Table 1).

The data of Table 1 indicate that typical fire-retardant compositions have approximately identical composition both

by the list of components, and their ratio. That is why researchers, as a rule, do not pay attention to the role of a polymer in the structure of the insulation coke layer and thermal destruction of IC under conditions of the fire influence [12]. Typically, the choice between water dispersion or organosoluble intumescent paints and coatings is in comparison of their operational characteristics. There is a common belief that water-dispersive IC are more environmentally friendly, whereas organosoluble IC are more resistant to the action of moisture and other atmospheric and chemical factors [13].

Table 1

Composition (%) of typical formulations of modern flame retardant coatings [11]

Component	APP	MA	PE	Polymer	TiO ₂
Organosoluble IC	25–27	8–10	8–10	9–11	7–10
Water dispersive IC	23–25	8–10	8–10	12–14*	9–11

Note: * in conversion to non-volatile substances

It should be emphasized that the information about scientific and technical sources on the influence of the nature of polymers on the fire-retardant effectiveness of intumescent coatings is limited and not systematized [2, 6]. Assuming that at 200 °C, polymers, as a rule, are completely subjected to the destruction, ensuring the formation of the coating film and its adhesion to different substrates is accepted as the main function of a polymer binder. However, in research [14], it was shown that a polymer in the composition of an IC in thermolysis is capable of turn into in graphite-like regular layered structures that are built in the insulating coke layer. The existence of antipyrines in the IC ensures an increase in thermal stability of the polymer component, and accordingly, changes the chemical mechanisms of its thermal decomposition [15, 16]. In addition, it was proved that the binding component influences the rheological properties of the melted coke layer, which determines the effectiveness of the foam expansion process.

The literature presents the study of the influence of the intumescent mixture of APP/MA/PE on an increase in the flammability of co-polymers of the EVA [17, 18] and SA types [19, 20]. However, the results of these works do not make it possible to predict the firefighting efficiency of the studied polymers as a part of intumescent coatings. There is no comparative analysis and argumentation of the appropriateness of using water-dispersive or organosoluble paint to ensure the fire resistance class in the interval of R30–R120. The review of literary data gives reasons to believe that a variation of the polymer component of IC will enable the regulation of the firefighting efficiency of the coating for a particular fire resistance class (R30–45 or R90–150). This approach, which implies developing the IC of different composition of a polymer part, will allow a significant reduction of the thickness of the fire-retardant coating for the required fire resistance value, and accordingly, reduction of the cost of the fire-retardant treatment.

That is why the research into the impact of polymers on fireproof efficiency of intumescent compositions is not only of scientific but also of practical interest associated with the minimization of steel construction costs.

3. The aim and objectives of the study

The aim of this work is to study the action of water-dispersion vinyl acetate and acrylic co-polymers and organosoluble

co-polymers of styrene and vinyl toluene acrylate on flame-retardant effectiveness of the intumescent composition of ammonium/melamine/pentaerythrite/melamine/polymer polyphosphate in the composition of the flame retardant coating.

The set goal implies solving the following tasks:

– to study the effect of polymers on the regularities of the IC swelling and the physical-mechanical properties of the obtained coke layer;

– to test the fire-retardant effectiveness of intumescent compositions with different polymers under conditions of fire tests.

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

4.1. Materials and equipment used in the experiment

Ammonia polyphosphate Exolit AP 422 (Clariant, Germany), micronized pentaerythrite of the Charmor PM40 brand (Perstorp Holding AB, Sweden), melamine (Borealis Agrolinz Melamine GmbH, Austria), titanium dioxide Ti-Pure R-902 (DuPont, CIIIA), rheological admixtures of the BYK Additives & Instruments brand (Germany) were used in the research. Styrene co-polymer with acrylate Pliolite AC80 and vinyl toluene co-polymer with acrylate Pliolite VTAC (Omnova Solutions, the USA) were studied as organosoluble polymers. Water dispersions Mowilith LDM 1780, Mowilith DM 230 (Celanese, CIIIA) and Hydro Pliolite 211 (Omnova Solutions, CIIIA) were used in the research.

Table 2 shows the characteristics of the polymers that were used in the course of the experiment.

Table 2

Technical characteristics of polymers of different producers

Name	Shortened name	pH	Viscosity by Brookfield, mPa·s	Vitrification temperature, °C
Mowilith LDM 1780	EVA	4.5	500–3,500	12
Mowilith DM 230	VAVV	4.0	1,500–3,500	24
Hydro Pliolite 211	H211	8.0–9.0	>4,000	29
Pliolite AC80	AC80	–	–	52–56
Pliolite VTAC	VTAC	–	–	51–53

To identify the coatings and their thermolysis products, the methods of infrared spectroscopy with the application of the device Bruker Tensor 37 FT-IR were used. Thermogravimetric studies were carried out on the device «Thermoscan-2». To determine the rate of an increase in the temperature of elements, the automatic measuring-recording complex «TEST-1» (AVRK «TEST-1») was used. The swelling coefficient of intumescent compositions K (cm³/g) and the value of the weight of coke residue (m, %) were described in detail in [21].

4.2. Preparation of water-dispersion intumescent compositions

1.7 weight fractions of water and the components of the intumescent system were placed into the laboratory dissolver with the working cup volume of 1 dm³. APP, PER, MA, TiO₂

at the ratio of 3.0:1.1:1.1:0.7 (weight fraction) were used as components. The mixture was stirred for 60 minutes at the cutter rate of 900–1,000 rpm. 2.4 weight fractions of a water dispersion of the polymer were added to the resulting paste and stirred at the cutter rate of 500–600 rpm for 30 min. The finished IC was stored in a sealed container.

The water dispersion intumescent paint for fire tests was prepared in a similar way with the use of a disperser, a foaming agent, and a thickener in addition to IC2.

4.3. Preparation of organosoluble intumescent compositions

1.7 weight fractions of water and the components of the intumescent system were placed into the laboratory dissolver with the working cup volume of 1 dm³. APP, PER, MA, TiO₂ at the ratio of 3.0:1.1:1.1:0.7 (weight fraction) and 4.1 of weight fraction of 30 % solution of co-polymer Pliolite (Omnova Solutions, the USA) in an organic solvent were used as components. The mixture was stirred for 60 min at the cutter rate of 900–1,000 rpm. The finished IC was stored in a sealed container.

The organosoluble intumescent paint for fire tests was prepared in a similar way with the use of a disperser and a thickener in addition to IC4.

4.4. Fire tests using a «Bunsen burner» method

This test is applicable in accordance with the ASTM E-119 standard to compare the rate of an increase in the temperature of the steel plate, on which different IC are applied, under the influence of the gas burner flame (Fig. 1). The growth of the temperature on the reverse side of a steel plate is controlled and recorded using three thermoelectric converters (thermocouples) of the K-type (100–1,250 °C) and AVRK «TEST-1». A gas burner with the diameter of an ignition hole of 40 mm is used as a source of fire influence. The distance from the burner nozzle to the steel plate is 70 mm. Some experiments revealed that the burner flame temperature reaches the indicator of 950–1,000 °C.

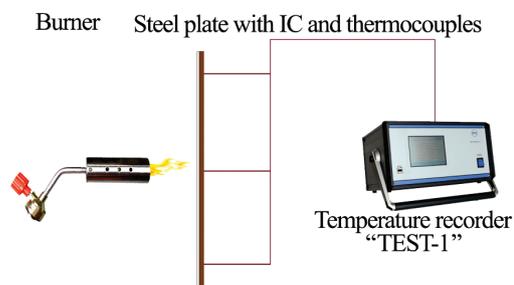


Fig. 1. Schematic of the device for fire tests using the «Bunsen burner» method

For the experiment under conditions of the «Bunsen burner», the steel plates of 150×150×3 mm with the mounted thermocouples were prepared. The priming coating GF-021 of the average thickness of 80±10 μm and IC, made according to formulations 4.2 and 4.3 of the thickness of 1.50±0.10 mm, were applied on the steel surface on the side of the flame influence. The plates were held at the temperature of 20±3 °C at least for 10 days. The thickness of coatings was measured with magnetic thickness gauge Qnix1500.

Under conditions of the «Bunsen burner», the IC swelling rate and the temperature increase on the backside of the plate were determined for some time.

4. 5. Fire tests in a mini furnace under the conditions of «a standard fire»

For the firing tests, a plate of the size of 300×300×5 mm is laid in the upper hole of the furnace. The control under the conditions of «a standard fire» and recording of the temperature on the reverse side of the plate is carried out with the use of K-type thermocouples and AVRC «TEST-1». The schematic view of the mini furnace is shown in Fig. 2.

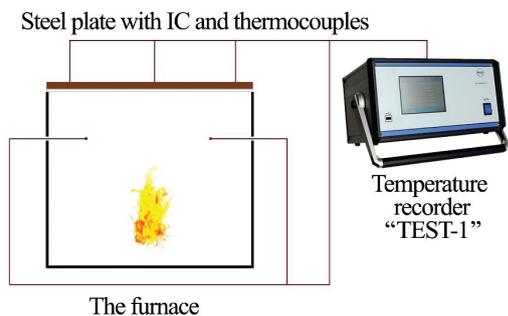


Fig. 2. Mini furnace for fire tests

Before fire tests, the steel plates were prepared according to the procedure described in the experimental part.

During the fire tests, the boundary of fire resistance of the steel plates was determined in the mode of «a standard fire» in the mini furnace.

4. 6. Determining the coefficient of swelling of the intumescent compositions K (cm³/g) and the weight of coke residue m (%)

To determine the swelling coefficient and the mass of coke residue, 0.5 g of the IC is placed in a metal foil cell of the dimensions of 30×30×10 mm. The samples are dried for 10 days to constant mass. The sample prepared in this way is put into a thermal chamber heated to the required temperature. The sample is kept in the chamber for 10 minutes and the volume and the mass of coke residue are determined.

5. Results of studying the influence of a polymer on the thermal properties and fire-retardant efficiency of intumescent compositions

5. 1. Studying the structure and physical-mechanical properties of a coke layer

During the development of new coatings for fire protection of steel structures, preliminary tests are needed to predict fire protective effectiveness. The following is used as a tool for such tests: determining the oxygen index (LOI), establishing V-rating (UL-94); methods of cone calorimetry, and pyrolysis calorimetry of combustion flow.

Cone calorimetry is considered the most versatile intermediate method for fire resistance tests [21], standardized by the international standard ISO 5660-1. The method makes it possible to obtain the value of heat release, effective heat of combustion, and other evaluative criteria for the thermal destruction of polymers in the IC composition. These characteristics can be used to forecast the fire-retardant properties of intumescent coatings in terms of the thermal effects of

the chemical processes between the coating components. However, the obtained parameters do not make it possible to foresee the physical and mechanical properties of the resulting heat-insulating coke layer, responsible, as a result, for the fire protection level.

This study uses the stage-by-stage exploration of the structure of the IC coke layer, which involves simulating the behavior of the intumescent coating in the temperature range of 200–800 °C. It should also be noted that it is appropriate to consider the temperature mode set in the thermal chamber as the temperature of the coating, rather than the temperature of fire exposure, such as a fire. The temperature of a fire, as a rule, significantly differs from the temperature in the swollen coating, which arises under the influence of heat factors of a flame.

Volumetric swelling coefficient (K , cm³/g) and the mass of coke residue (m , %) are proposed as the basic numerical indicators of the firefighting effect

Formulations of the studied IC samples with the involvement of water-dispersion (w) and organosoluble (s) co-polymers are given in Table 3.

Table 3

Composition of intumescent systems (%)

Sample	Type of polymer	Polymer	APP	PER	MA	TiO ₂
IC1	Ethylene with vinyl acetate (w)	12	30	11	11	7
IC2	Vinyl acetate with vinyl versatate (w)					
IC3	Styrene with acrylate (w)					
IC4	Styrene with acrylate (s)					
IC5	Vinyl toluene with acrylate (s)					

To determine the K and m parameters, the prepared samples were kept in a thermal chamber at the assigned temperature for 10 min as described in the experimental part. Fig. 3 shows the dependences of the volumetric coefficient of swelling (K) of intumescent compositions with different polymers (Table 3) on temperature.

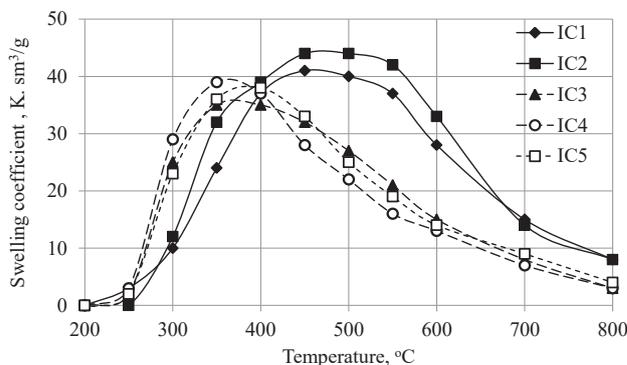


Fig. 3. Dependence of swelling coefficient K (cm³/g) of intumescent compositions on temperature T (°C)

The values of the weight of coke residues (m) of the IC samples during heating in the temperature range of 200–800 °C are shown in Fig. 4. Conditionally, the process of IC swelling can be divided into four main parts:

– 200–300 °C – the beginning of thermal degradation of the IC related to thermal destruction of individual components

of the IC, the course of chemical processes, the release of volatile components or products of reactions;

- 350–500 °C – active phase of chemical transformations, which is necessary for the formation of a heat-insulating layer;
- 500–650 °C – thermal decomposition of the primarily formed carbon frame, hardening and formation of difficultly fusible fire protective structures;
- 650 °C and above – burnout and destruction of a coke layer.

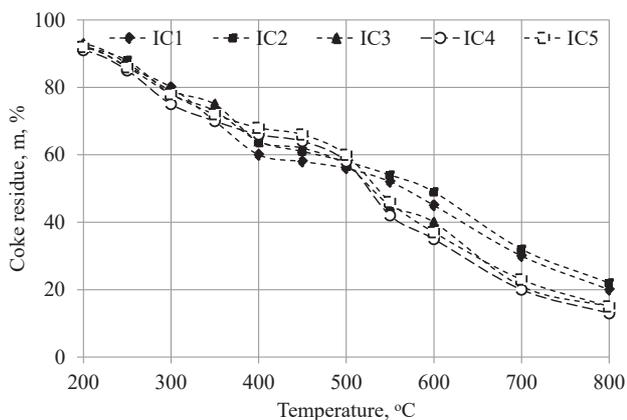


Fig. 4. Dependence of the values of coke residue m (%) of intumescent compositions on temperature T (°C)

To make a numerical comparison of the influence of a polymeric component on the formation of the fire protective layer of the IC, the calculation (based on the data of Fig. 3) of the rate of changing the value K ($v, \text{cm}^3/\text{g}\cdot^\circ\text{C}$) during a temperature increase was conducted (Table 4). Table 4 shows the results of the thermogravimetric research into the IC with different polymers (Table 4): the values of $T_{20\%}$, $T_{50\%}$, $T_{80\%}$ correspond to the weight loss of the sample by 20, 50 and 80 %, respectively. Table 4 also shows the results of the thermogravimetric analysis of the studied polymers with the use of the TG-analyzer «Thermoscan-2» under the atmospheric conditions: T_d and $T_{d\text{max}}$ are the temperatures of the beginning of thermal destruction and of maximal weight loss of a polymer.

Results of thermal analysis of polymers and intumescent compositions IC1–IC5

Sample	$v, \text{cm}^3/\text{g}\cdot^\circ\text{C}$		$T_{20\%}, ^\circ\text{C}$	$T_{50\%}, ^\circ\text{C}$	$\Delta T_{80\%}, ^\circ\text{C}$	$m, \% 700^\circ\text{C}$
	200–350 °C	550–700 °C				
IC1	0.22	0.059	300	568	799	30
IC2	0.26	0.052	291	592	804	32
IC3	0.33	0.071	292	502	708	21
IC4	0.36	0.069	275	460	701	20
IC5	0.34	0.079	288	490	727	23
	$T_d, ^\circ\text{C}$	$T_{d\text{max}}, ^\circ\text{C}$				
EVA	249	315	374	412	475	0
VAVV	256	313	339	375	491	0
H211	231	388	364	398	412	0
AC80	207	373	305	391	421	0
VTAC	210	391	368	401	428	0

The nature of the dependences (Fig. 3, 4) demonstrates the conformity of the stages of thermal transformations of the studied IC with the swelling mechanism proposed above. There is also a significant influence of the polymer nature both on the values K and m parameters, and on the shifts in temperature intervals of the implementation of a particular stage in the intumescent process. The obtained results make it possible to state that the main differences in the swelling process of IC correspond to two groups of polymers – vinyl acetate (IC1 and IC2) or aromatic acrylate (IC3–IC5).

Based on the data of Fig. 3, 4, it is possible to make some generalizations about the influence of the polymer component on the processes of formation of the IC coke layer:

- basic chemical processes in IC1 and IC2 (with vinyl acetate polymers EVA and VAVV, respectively) begin after 300 °C and flow in the temperature range of 350–600 °C. For IC3–IC5, visible chemical transformations begin from the temperature of 280 °C and last approximately to 500 °C (Fig. 3);
- thermal decomposition of the frame, formed in the mode of maximal swelling, for styrene co-polymers (Hydro Pliolite 211 (IC3), Pliolite AC80 (IC4)) and vinyl toluene (Pliolite VTAC (IC5)) is more rapid ($v, \text{cm}^3/\text{g}\cdot^\circ\text{C}$ at 550–700 °C, Table 4), than decomposition of the frame, formed by IC1 and IC2 (Fig. 4);
- IC with vinyl acetate co-polymers (ethylene with vinyl acetate (IC1), vinyl acetate with vinyl versatate (IC2)) in comparison with the systems IC3–IC5 are characterized by slower swelling ($v, \text{cm}^3/\text{g}\cdot^\circ\text{C}$ at 200–350 °C, Table 4), a longer stabilization section of the constancy of swelling coefficient K in the temperature range of 350–650 °C;
- the loss of 70 % of the weight for the IC with aromatic co-polymers (IC3–IC5) occurs on average at 640 °C, whereas the IC1 and IC2 lose 70 % of the weight at the temperature of 701 °C and 715 °C, respectively.

5. 2. Determining fire protective effectiveness of intumescent compositions under conditions of fire exposure

The results obtained above make it possible in the first approximation to predict fire protection effectiveness of the studied IC: $\text{IC2} \geq \text{IC1} > \text{IC3} > \text{IC5} > \text{IC4}$. Fig. 5 shows the data of fire tests (using the procedure of p. 4.4) of the coatings IC1–IC5 with the thickness (1.50 ± 0.13) mm (Table 5).

Table 4

The dependences of the temperature of a metal plate protected by a fire retardant coating on time prove that the effectiveness of the IC with vinyl acetate co-polymers exceeds the effectiveness of the IC with acrylate co-polymers of styrene and vinyl toluene. The determined magnitudes of the fire resistance boundary are shown in Table 5. The values of the linear coefficient of swelling of coatings K , which is determined as the ratio of the average thickness of a coke layer after the tests to the initial thickness of the intumescent coating before the tests, are also presented here.

The whole complex of the factors that can be determined as chemical and physical acts as responsible for the fire protection properties of the IC [2, 11]. The former include endothermic chemical reactions that ensure the absorption of

thermal energy and the construction of a coke layer. The role of the physical factors is determined by the thermal physical parameters of the formed coke layer, which are determined by its thermal conductivity, density, strength, and adhesion to the metal substrate.

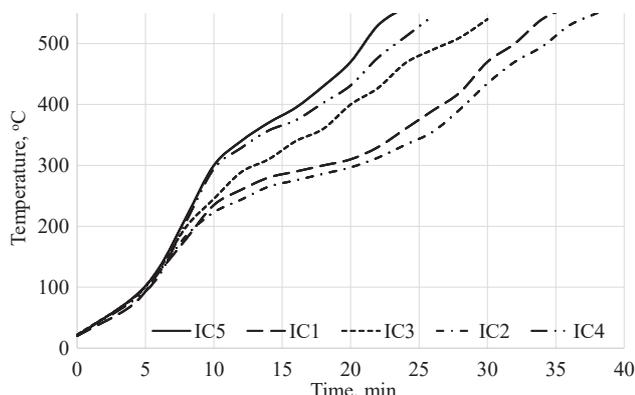


Fig. 5. Dependence of the temperature of metal plates (T , °C), protected by the intumescent coatings IC1–IC5 on time of the flame exposure (tests according to p. 4.4)

Table 5

The boundary of fire-resistance (the time of reaching the temperature of 500 °C) of steel plates, protected by intumescent coatings IC1–IC5 and the values of their linear coefficient of swelling

Thickness of the coating, mm	IC1	IC2	IC3	IC4	IC5
	1.61±0.04	1.58±0.09	1.63±0.07	1.64±0.10	1.59±0.08
Fire resistance boundary, min	32	35	27	23	21
K_l	25	28	18	15	17

Fig. 6 represents the appearance of the cuts of coke residues of the IC after 15 min of testing by the «Bunsen burner». According to Fig. 5, this time is determined as the average time of the stable phase of coke formation for both types of compositions. This experiment proves the key role of a polymer in the process of the formation of a heat-insulating layer of the IC.

Visual observations of the explored compositions IC1–IC5 (Fig. 6), together with the data in Fig. 4 and Table 5 demonstrate the influence of the polymer component on the swelling coefficient and the structure of a coke layer. The coatings formed with vinyl co-polymers (Table 5, Fig. 6) produce swelling that is an average by 1.5 times more than coatings with co-polymers of an aromatic type (IC3–IC5).

Significant differences are also observed in the structure of the coke swollen layer of the studied compositions. The regular, dense, and fine-porous frame is observed when using co-polymers EVA and VAVV in the IC (Fig. 6). In turn, the IC containing polymers H211 (IC3), AC80 (IC4) and VTAC (IC5) form lighter frames of the porous structure (Fig. 6). In this case, the process of coke formation (both as the beginning of formation and the beginning of decomposition of a coke layer) for IC3–IC5 flows at lower temperatures than the similar process for IC1 and IC2.

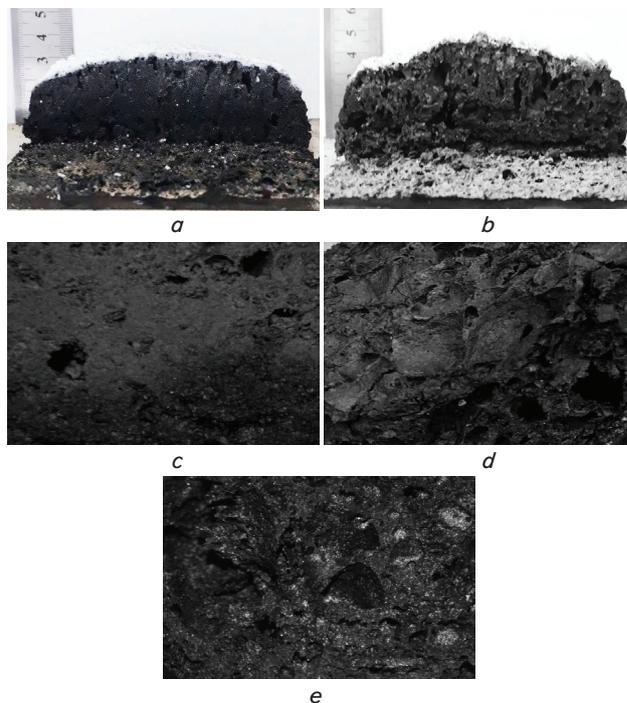


Fig. 6. Cuts of the coke layers of intumescent compositions after the effect of «Bunsen burner» for 15 min: a – IC2; b – IC3; c – IC1; d – IC4; e – IC5

Field fire tests were carried out in accordance with procedure 4.5. Two intumescent paints based on the compositions of IC2 and IC4 for the experiment were made based on compositions IC2 and IC4 (using procedures 4.2 and 4.3). These systems according to the data in Fig. 6 show the best and the worst results of fire-retardant effectiveness, respectively. The paints were applied on the steel plates with an average thickness of 0.4 mm and 1.8 mm.

The test results are shown in Fig. 7, 8, and Table 6.

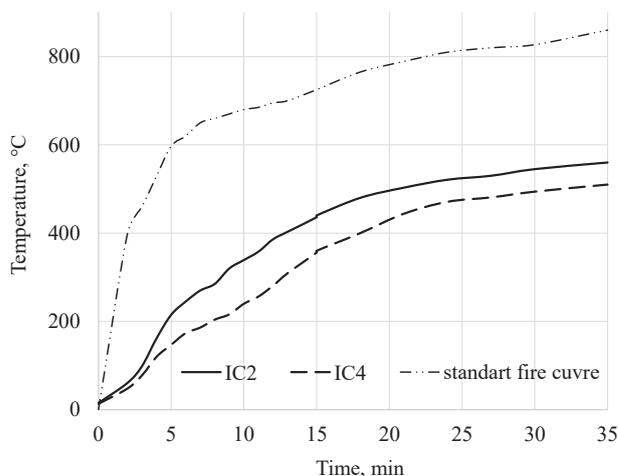


Fig. 7. Dependence of temperature on metal plates (T , °C), protected by intumescent coating IC2 and IC4 with the thickness of 0.4 mm on the time of flame exposure (tests by p. 4.5)

The data presented in Table 6 are somewhat unexpected: there is a reverse of fire-retardant effectiveness of intumescent coatings containing polymers of different nature, depending

on the thickness of a layer. The value of the fire resistance boundary of steel plates, protected by intumescent coating IC2 with the thickness of 0.41 mm is 20 minutes, which is significantly lower than the similar magnitudes for the IC4 coatings of the same thickness (31 min, Table 6), while the fire resistance value of the IC4 coating with the thickness of 1.82 mm is 47 minutes and of the IC2 coatings – 58 min.

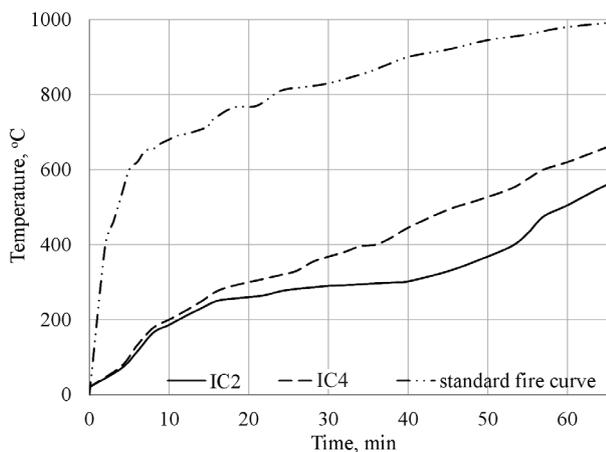


Fig. 8. Dependence of the temperature of metal plates (T , °C), protected by intumescent coatings IC2 and IC4 with the thickness of 1.8 mm on the time of flame exposure (tests according to p. 4.5)

Table 6

Fire resistance boundary of steel plates, protected by intumescent coatings IC2 and IC4 of different thickness

IC	IC2		IC4	
Thickness of coating, mm	0.41±0.04	1.79±0.12	0.40±0.03	1.82±0.08
Boundary of fire resistance, min	20	59	31	47
K_f	22	36	35	21

Based on the results of the conducted experiment, it is possible to make some preliminary conclusions that are important for the development of effective fire-retardant coatings for the standard fire conditions:

- variation of the polymer component of the intumescent coating under other equal conditions makes it possible to adjust the level and rate of swelling;
- vinyl acetate polymers in the IC composition ensure the creation of a stronger, regular and thermo-stable frame than acrylic aromatic polymers;
- the use of different polymers for fire retardant coatings is one of the ways of differential development of fire protection means, oriented to the given fire resistance class.

6. Discussion of results regarding the impact of polymers on coke formation and fire-retardant effectiveness of the intumescent coating

The results of the study, outlined in p. 5, undoubtedly indicate the key role of the polymer both in the process of swelling of a fire protection system and in the construction of the thermal insulation frame, and in the regulation of the

temperature mode of these processes. These features clearly indicate the significant impact of a polymer on a complex of chemical transformations, accompanying intumescent fire protection. As a consequence, they enhance the functional purpose of the polymer component on the conventional binding agent of the varnish and paint material to the active component of the intumescent system.

6. 1. Chemical transformations of polymers in the construction of a protective coke layer

The sequence of the chemical processes that occur in the IC of the APP/MA/PE composition depends on the temperature mode (T , °C) and generally looks as follows [22]:

- $T=150-215$ °C – the release of polyphosphoric acid and ammonia from the ARR;
- $T=215-280$ °C – etherification of the source of carbon PE by polyphosphoric acid and the formation of the structures of the future phosphorus- carbon frame;
- $T=280-350$ °C – re-grouping of polyphosphoric ethers with the further formation of a coke layer;
- $T>300$ °C – the beginning of the MA decomposition with the release of gases that foam the melting coke layer and organize the porous structure of the swollen coating;
- $T=550-600$ °C – hardening of the melted coke layer due to the formation of refractory compounds.

At higher temperatures, there is the thermal decomposition of coatings with the oxidation of the formed coke layer.

Usually, the presented intumescent mechanism has a rather simplified and abstract character. However, it makes it possible to predict the probable chemical interactions of the polymer, depending on its structure and the existing functional groups. The intumescent system, which includes the APP (electrophilic agent with the pentacoordinating atom of phosphorus), PE, and melamine (O- and N-nucleophiles, respectively), is a classic nucleophilic system. In this system, the parallel flow of alcoholysis with the formation of O=P-O-C bond and aminolysis with the formation of bond O=P-N-S are possible. The most informative for distinguishing the products of alcoholysis and aminolysis of phosphates is the IR-region of $1300-1000$ cm^{-1} . In this interval, the absorption of groups $(\text{RO})_3\text{P}=\text{O}$ ($1280-1250$ cm^{-1}), P-O-C ($1120, 1020$ cm^{-1}) and $(\text{RNH})_3\text{P}=\text{O}$ ($1300-1220$ cm^{-1}), P-N-C ($1050-930, 760, 630$ cm^{-1}) is recorded.

Fig. 9 shows the IR spectra of the IC1 compositions (with vinyl acetate polymer EVA) and IC4 (with styrene acrylate polymer AC80) after the exposure at specified temperatures in the interval of $350-700$ °C. These data make it possible to establish the basic chemical transformations occurring in the IC1 and IC4 samples at an increase in temperature.

At $350-420$ °C, the changes in the studied systems are manifested in the appearance of the bands of $1,245$ cm^{-1} (O=P-O-C) and 1020 cm^{-1} (O=P-N-C), which correspond to the valence fluctuations of group P=O. These bands indicate the etherification of PE with polyphosphoric acid, as well as aminolysis of MA or its derivatives of the fragments of phosphoric acid. More essential transformations occur in the system at 550 °C. On the one hand, there decrease the absorption bands in the region of $3,380-3,100$ cm^{-1} , which belong to OH-groups of PE and NH_2 -groups of MA, as well as the band of $1,275$ cm^{-1} , which corresponds to the fluctuations P=O of ammonia polyphosphate. On the other hand, the existence of the bands of $1210, 980, \text{ and } 750$ cm^{-1} (P-N) in the spectra indicates the benefits of the formation of phosphamide bonds in the system.

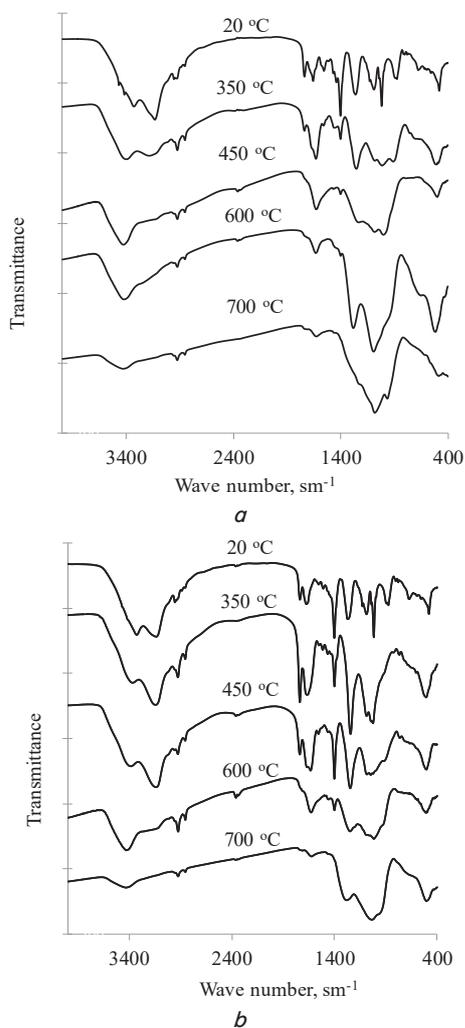


Fig. 9. IR-spectra of coke residues of intumescent systems at various temperatures: *a* – IC1; *b* – IC4

The results of the IR-tests of the thermal decomposition of EVA and AC80 do not contradict the commonly accepted mechanisms of thermal destruction of the studied types of polymers [23, 24]. According to the data of Fig. 9, the formation of acetic and acrylic acids ($1,650\text{--}1,630\text{ cm}^{-1}$, --C=O) are observed for IC1 and IC4. The appearance of new absorption bands in the region of $1,650\text{--}1,550\text{ cm}^{-1}$ is the result of the formation of amide bonds --C(O)NH_2 between the formed acids and ammonia and melamine ($1,580\text{--}1,490\text{ cm}^{-1}$, --C(O)NH). It is not possible to identify more distinctly the products of the polymer transformation by the IR-spectra. There are original amino- and hydroxyl-containing components and ammonia, water, and carbonic oxides are released under the influence of heat.

The data of the spectra of coke residues of IC1 and IC4 at 700 °C (Fig. 9) indicate that the chemical structure of cokes is typical by its chemical nature, regardless of the applied vinyl acetate or styrene acrylate polymer. However, in the IC1 spectrum at 700 °C , there is the band of $1,282\text{ cm}^{-1}$, which proves the existence in the system of the fragments of the undecomposed phosphorus-carbon frame (--P--O--C). In general, by the change in the characteristic absorption bands of the IC1 and IC4 compositions during a temperature increase, it is necessary to state the identity of the basic chemical stages within the mechanism (*a–e*). However, according to

the data of Fig. 9, for IC4 chemical transformations occur at lower temperatures and the coke residue at 700 °C is more exhausted and oxidized.

Probably the main reason for the earlier decomposition of a coke layer of the IC4 is the difference in mechanisms of thermal degradation of vinyl acetate and acrylate co-polymers. The thermal destruction of vinyl acetate polymers occurs at two stages. The first intensive one between 300 and 400 °C consists of the process of deacetylation and cutting-off the fragments at the end of the polymer chain with the formation of polyenes. At the second stage in the interval of $400\text{--}500\text{ °C}$, there is a degradation of the chain by double bonds.

In the case of styryl acrylic polymers, the thermal destruction takes place in one main step from 340 to 450 °C with the simultaneous separation of the fragments of acrylic acid, their decarboxylation and splitting the chain directly into volatile monomers.

This interpretation of the mechanisms of thermal destruction of polymers makes it possible to put forward a hypothesis about the influence of polymers on intumescence and the formation of a frame of fire retardant coatings: the most productive polymer binders for polymeric systems are the compounds with a complex and slow decomposition mechanism, which are capable to release the reactive products, which positively influence the building of a heat-resistant protective frame.

6. 2. The influence of a polymer on the fire protective effectiveness of an intumescent composition

The swelling coefficient (K , cm^3/g) is one of the main characteristics of the intumescent fire protection, the essence of which is the formation of the heat-insulating layer from the coating under the influence of fire. The nature of a change in value K for the system APP/MA/PE at an increase in temperature within the interval of $300\text{--}800\text{ °C}$ (Fig. 4) demonstrates the influence of the nature of a polymer in the following areas:

- the temperature of the beginning of swelling – the samples that contain acrylate co-polymers (Hydro Pliolite 211 (IC3), Pliolite AC80 (IC4)) and vinyl toluene (Pliolite VTAC (IC5)) begin swelling 50 °C earlier than samples IC1 and IC2 with vinyl acetate polymers – EVA and VAVV;
- noticeable degradation of carbon-phosphorus frame of styrene-acrylic compositions IC3–IC5 starts at 450 °C , which is almost by 150 °C lower than the temperature of the destruction of compositions IC1 and IC2;
- the length of the stabilization section – temperature interval, where the value of K has conditionally maximum values (the dashed line in Fig. 4) makes up on average 150 °C for IC3–IC5, and 250 °C for IC1 and IC2.

The beginning of the IC swelling, depending on the nature of a polymer is predictable, regarding the temperature of the beginning of the destruction T_d , °C (Table 4). A priori, it is necessary to expect the temperature of the beginning of IC swelling between 200 and 300 °C , related to the beginning of the polymer component and decomposition of APP on phosphoric acid and ammonia. In general, the data in Fig. 4, 5 are agreed with the flow of the necessary stages between the basic components IC – APP, PE and MA – the formation and the thermodestruction of a carbon-phosphorus frame from the ceramic-like material. However, it is worth paying attention to slowing down the rate of the weight loss of acrylate compositions IC4–IC5 in the temperature range of $400\text{--}500\text{ °C}$ at a significant decrease in coefficient of swelling K (Fig. 5).

It is possible that such a situation can be related to the isolation of the components of the inner part of a coke layer by a dense substance of the melted polymer on the surface.

Results on the weight loss (m , Table 4, Fig. 5) also testify that at 700 °C, value m for the IC with vinyl acetate polymers is 1.5–2 times as high as the values m for the IC with acrylate polymers.

The obtained results make it possible to conclude that the IC based on vinyl acetates are more effective and promising to solve the problems of fire protection.

The advantages of vinyl acetate binders are caused by both chemical and physical (rheological) peculiarities of behavior of these polymers in the IC. The slow and stage-by-stage degradation of the type EVA polymer (p. 6.1) makes it possible to maximally harmonize the chemical processes with the participation of the fragments of original polymer and other IC components. A certain role in the chemical transformations is played by acetic acid, which is the acid catalyst of reactions of alcoholysis and aminolysis that are necessary for building primary carbon-phosphorus compounds. It is noted for the similar mechanisms of thermal decomposition of vinyl acetate and acrylic polymers that the acids of the acrylic type tend to rapid decarboxilization under conditions of elevated temperatures [12]. This fact, along with the splitting of acrylate fragments into flammable volatile hydrocarbon, is explained both as a low-temperature swelling IC3–IC5, and as more low-temperature decomposition of the carbon-phosphorus frame.

The rheological properties of a coke layer in the process of elevated temperatures were not studied in this research. However, the obtained results, specifically, the value K and the nature of the coke layer foam (Fig. 7), are consistent with the results of research [12]. Vinyl acetate polymers create more elastic and rigid foams due to the cross-linking of the products of polymer degradation. Acrylic aromatic polymers, in turn, produce foam with higher viscosity. This is the key fact in the process of swelling – the formed gases concentrate inside the melt in large gas pockets, provoke ineffective expansion of foam, break, and destroy the coke layer.

Within this study, it is impossible to determine all differences in the behavior of vinyl acetate and acrylic aromatic polymers at the high-temperature destruction of the IC. However, the obtained results made it possible to determine the approach to the choice of a polymer component of the intumescent coating, which will reduce the cost of fire-retardant treatment of steel structures.

This conclusion is obtained from the results of fire tests of steel plates covered with the coatings with the boundary

average values of thicknesses of 0.40 and 1.80 mm (Fig. 8). This thickness ensures the fire resistance boundary of the usual construction steel structures of 30 and 60 minutes, respectively. It follows from the data of Fig. 8 that:

- to ensure a low fire resistance boundary (30 minutes), it is advisable to use acrylate intumescent coatings, such as polymer Hydro Pliolite 211 for water-dispersion paints, or polymers Pliolite AC80 or Pliolite VTAC (Omnova Solutions, USA) for organosoluble paints;

- for higher values of fire resistance (60 min and above), it is necessary to apply intumescent coatings of the vinyl acetate type with the use of water-dispersion polymers Mowilith LDM 1780 and Mowilith DM 230 (Celanese, USA) or similar polymer materials of other manufacturers (Table 6).

Thus, the optimal polymers that can be used to create the formulations of fire-retardant coatings for an assigned fire-resistance boundary were determined in this research. It should also be emphasized that these magnitudes of a fire-resistance boundary (Table 6) are not identical to those determined by natural fire tests according to the national standards. However, the obtained results clearly indicate the general tendencies on the effects of polymers on the thermal destruction of coatings of the intumescent type.

7. Conclusions

1. Polymers of the vinyl acetate type form with the components of the intumescent system ARR/MA/PE the thermostable coke layers with regular, dense foam, the intense thermal destruction of which begins after 600 °C. Thermal degradation of coke residue of styrene-acrylate compositions begins at 450 °C, and its weight is 1.5 times less than the weight of the coke layer formed with the participation of vinyl acetate polymers.

2. Fire retardant effectiveness of the intumescent coating depends on the chemical nature of the polymer component of the intumescent system, specifically, on the mechanisms of thermal destruction of the polymer. To ensure a low limit of fire resistance of 30–45 min, it is advisable to apply the intumescent coating with the use of styrene-acrylate or vinyl toluene acrylate polymers, the thermal decomposition of which occurs at one stage by the destruction of the polymer structure. Vinyl acetate polymers, which are characterized by gradual thermal destruction with the separation of end fragments, are optimal components of the intumescent coatings to ensure the fire resistance boundary of steel structures of 60 minutes and higher.

References

1. Yasir, M., Ahmad, F., Yusoff, P. S. M. M., Ullah, S., Jimenez, M. (2019). Latest trends for structural steel protection by using intumescent fire protective coatings: a review. *Surface Engineering*, 36 (4), 334–363. doi: <https://doi.org/10.1080/02670844.2019.1636536>
2. Puri, R. G., Khanna, A. S. (2016). Intumescent coatings: A review on recent progress. *Journal of Coatings Technology and Research*, 14 (1), 1–20. doi: <https://doi.org/10.1007/s11998-016-9815-3>
3. Bilotta, A., de Silva, D., Nigro, E. (2016). Tests on intumescent paints for fire protection of existing steel structures. *Construction and Building Materials*, 121, 410–422. doi: 10.1016/j.conbuildmat.2016.05.144
4. Mariappan, T. (2016). Recent developments of intumescent fire protection coatings for structural steel: A review. *Journal of Fire Sciences*, 34 (2), 120–163. doi: <https://doi.org/10.1177/0734904115626720>
5. Vakhitova, L., Drizhd, V., Taran, N., Kalafat, K., Bessarabov, V. (2016). The effect of organoclays on the fire-proof efficiency of intumescent coatings. *Eastern-European Journal of Enterprise Technologies*, 6 (10 (84)), 10–16. doi: <https://doi.org/10.15587/1729-4061.2016.84391>

6. Weil, E. D. (2011). Fire-Protective and Flame-Retardant Coatings – A State-of-the-Art Review. *Journal of Fire Sciences*, 29 (3), 259–296. doi: <https://doi.org/10.1177/0734904110395469>
7. Riva, A., Camino, G., Fomperie, L., Amigouët, P. (2003). Fire retardant mechanism in intumescent ethylene vinyl acetate compositions. *Polymer Degradation and Stability*, 82 (2), 341–346. doi: [https://doi.org/10.1016/s0141-3910\(03\)00191-5](https://doi.org/10.1016/s0141-3910(03)00191-5)
8. Magnet, S., Duquesne, S., Delobel, R., Jama, C. (2006). Pat. No. US7288588B2. Polymer binder for intumescent coatings. No. 11/473615; declared: 23.06.2006; published: 30.10.2007. Available at: <https://patentimages.storage.googleapis.com/2b/e8/1d/c98c4d5dee03a6/US7288588B2.pdf>
9. EN 1993-1-1 (2005). Eurocode 3: Design of steel structures – Part 1-1: General rules and rules for buildings [Authority: The European Union Per Regulation 305/2011, Directive 98/34/EC, Directive 2004/18/EC]. Available at: <https://www.phd.eng.br/wp-content/uploads/2015/12/en.1993.1.1.2005.pdf>
10. Kalafat, K. V., Vakhytova, L. N. (2019). Analiticheskiy obzor sredstv ognenezashchity stal'nyh konstruktsey 2019-2020. Kyiv: «UTSS», 200. Available at: <https://uscc.ua/uploads/page/images/publications/ognenezashchita/analiticheskij-obzor-sredstv-ognenezashchity-stalnyh-konstrukcij-2019-2020.pdf>
11. Nenakhov, S. A., Pimenova, V. P. (2010). Physico-chemical foaming fire-retardant coatings based on ammonium polyphosphate (review of the literature). *Pozharovzryvobezopasnost'*, 19 (8), 11–58. doi: <https://doi.org/10.18322/pvb.2010.19.08.11-58>
12. Pimenta, J. T., Gonçalves, C., Hiliou, L., Coelho, J. F. J., Magalhães, F. D. (2015). Effect of binder on performance of intumescent coatings. *Journal of Coatings Technology and Research*, 13 (2), 227–238. doi: <https://doi.org/10.1007/s11998-015-9737-5>
13. Anees, S. M., Dasari, A. (2017). A review on the environmental durability of intumescent coatings for steels. *Journal of Materials Science*, 53 (1), 124–145. doi: <https://doi.org/10.1007/s10853-017-1500-0>
14. Duquesne, S., Magnet, S., Jama, C., Delobel, R. (2005). Thermoplastic resins for thin film intumescent coatings – towards a better understanding of their effect on intumescence efficiency. *Polymer Degradation and Stability*, 88 (1), 63–69. doi: <https://doi.org/10.1016/j.polymdegradstab.2004.01.026>
15. Canosa, G., Alfieri, P. V., Giudice, C. A. (2011). Hybrid Intumescent Coatings for Wood Protection against Fire Action. *Industrial & Engineering Chemistry Research*, 50 (21), 11897–11905. doi: <https://doi.org/10.1021/ie200015k>
16. Hu, Y., Wang, X., Li, J. (2016). Regulating Effect of Exfoliated Clay on Intumescent Char Structure and Flame Retardancy of Polypropylene Composites. *Industrial & Engineering Chemistry Research*, 55 (20), 5892–5901. doi: <https://doi.org/10.1021/acs.iecr.6b00480>
17. Bourbigot, S., Sarazin, J., Samyn, F., Jimenez, M. (2019). Intumescent ethylene-vinyl acetate copolymer: Reaction to fire and mechanistic aspects. *Polymer Degradation and Stability*, 161, 235–244. doi: <https://doi.org/10.1016/j.polymdegradstab.2019.01.029>
18. Cai, Y., Hu, Y., Song, L., Lu, H., Chen, Z., Fan, W. (2006). Preparation and characterizations of HDPE–EVA alloy/OMT nanocomposites/paraffin compounds as a shape stabilized phase change thermal energy storage material. *Thermochimica Acta*, 451 (1-2), 44–51. doi: <https://doi.org/10.1016/j.tca.2006.08.015>
19. Chuang, C.-S., Sheen, H.-J. (2019). Effects of added nanoclay for styrene-acrylic resin on intumescent fire retardancy and CO/CO₂ emission. *Journal of Coatings Technology and Research*, 17 (1), 115–125. doi: <https://doi.org/10.1007/s11998-019-00246-x>
20. Beh, J. H., Yew, M. C., Yew, M. K., Saw, L. H. (2019). Fire Protection Performance and Thermal Behavior of Thin Film Intumescent Coating. *Coatings*, 9 (8), 483. doi: <https://doi.org/10.3390/coatings9080483>
21. Grexa, O., Lübke, H. (2001). Flammability parameters of wood tested on a cone calorimeter. *Polymer Degradation and Stability*, 74 (3), 427–432. doi: [https://doi.org/10.1016/s0141-3910\(01\)00181-1](https://doi.org/10.1016/s0141-3910(01)00181-1)
22. Bourbigot, S., Duquesne, S. (2007). Fire retardant polymers: recent developments and opportunities. *Journal of Materials Chemistry*, 17 (22), 2283. doi: <https://doi.org/10.1039/b702511d>
23. Zanetti, M. (2001). Synthesis and thermal behaviour of layered silicate–EVA nanocomposites. *Polymer*, 42 (10), 4501–4507. doi: [https://doi.org/10.1016/s0032-3861\(00\)00775-8](https://doi.org/10.1016/s0032-3861(00)00775-8)
24. Pieliowski, K., Njuguna, J. (2005). Thermal Degradation of Polymeric Materials. Shawbury: Rapra Technology.