



Research article

Improving the fire-retardant performance of industrial reactive coatings for steel building structures

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ABSTRACT

The main aim of this study was to determine key factors that regulate fire-retardant effectiveness of intumescent coatings comprising of ammonium polyphosphate, melamine, pentaerythritol, polymer binder. Fulfillment of the research objectives resulted in the development of a coating with R120 fire resistance. The expected service life of the coating is at least 15 years when applied at Z2 type of environmental conditions (indoor use). It was established that in order to provide fire resistance of around R30 it is advisable to use the styrene-acrylic polymers as binders for both water-based and organic-based intumescent systems. The ratio of target components ammonium polyphosphate/melamine/pentaerythritol in such systems should be close to 2/1/1. The coating thickness is to be 0.4–0.5 mm. To achieve higher fire resistance (R60 or more) the coating should include a vinyl acetate derivative as a binder (copolymers with ethylene or vinyl versatate). Target components ratio in this case is to be close to 3.5/1/1.5, while the coating thickness should be kept at 1.6–1.8 mm. If the required class of fire resistance is above R120, coating thickness is usually to be kept above 3.5 mm. In order to achieve higher fire resistance, it is advisable to use nano-clay additives and reinforcing fibers in intumescent compositions.

The obtained results were used in the development of intumescent coating, which is produced industrially and provides over R120 fire resistance of steel, which was confirmed in standardized full-scale fire tests.

Abbreviations

IFR	Intumescent fire-retardant system
IC	Intumescent coating
APP	Ammonium polyphosphate
MA	Melamine
PE	Pentaerythritol
EZ 3010	Vinyl acetate – ethylene
EZ3112	Vinyl acetate – ethylene – vinyl versatate
CEZ 3031	Vinyl acetate – ethylene – vinyl chloride
H211	Styrene acrylate
AC80	Styrene acrylate

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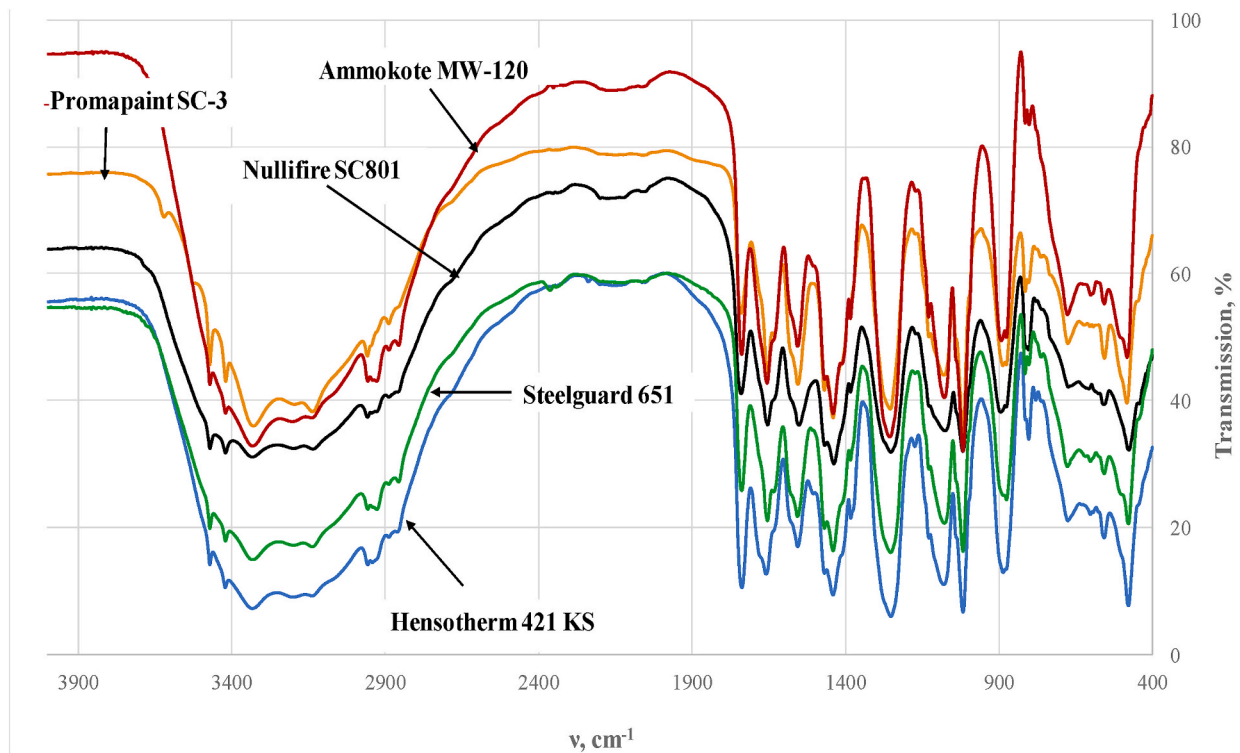
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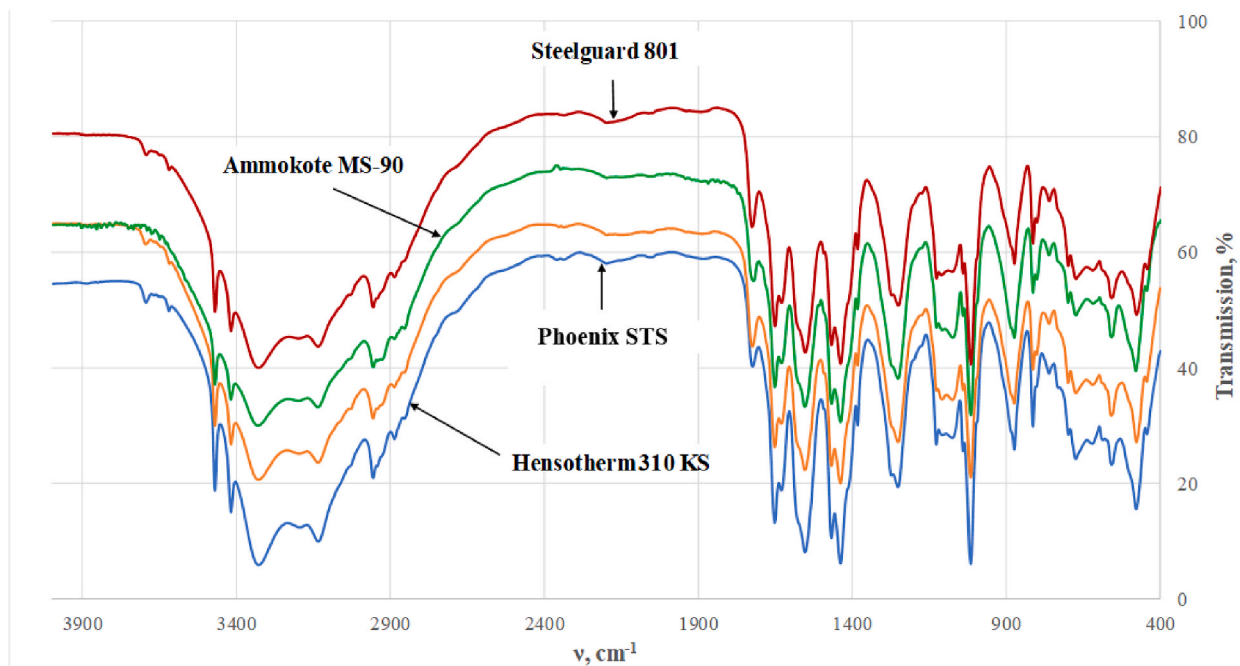
AC4

Styrene acrylate

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(a)



(b)

Fig. 1. IR-spectra of industrially produced intumescent paints: a) water-based, b) solvent-based.

(continued)

VAGH	Vinyl chloride – vinyl acetate – vinyl alcohol
VYHH	Vinyl chloride – vinyl acetate
R	Fire resistance rate for steel building structures

1. Introduction

The use of steel, wooden, and concrete structural members in construction is possible only if they are able to ensure the standardized levels of fire safety of buildings [1,2]. The main strategy for increasing fire resistance of building structures is the use of passive fire protection systems that increase their load-bearing capacity and integrity [3,4]. The following fire-retardant coatings were discussed in detail in scientific and technical sources as fire protection systems: cement and gypsum plasters [5,6], fire-retardant composite panels [7], boards and fibrous materials [8,9], reactive (intumescent) coatings [10–14].

Reactive coatings are scientifically the most studied type of passive fire protection in terms of the nature and ratio of both the main components and the auxiliary additives that can be introduced in order to increase fire-retardant efficiency. Throughout the history it is possible to distinguish certain milestones in the development of intumescent fire protection technology: development of the first prototype intumescent formulation in 1821 by J. L. Gay-Lussac [15]; the first patented formulation by Tramm et al. [16] dated 1938; publication in 1971 of the most comprehensive review on intumescence technology by Vandersall [17]. It is from 1970s that the development and wide use of modern intumescent fire-retardant coatings takes off in the US and Europe.

Over the past 50 years of studying various chemical and physical properties of a wide variety of IFRs, considerable amount of experimental data has been accumulated. It allows to build strong theoretical foundation for development and improvement of intumescent fire-retardant materials. In this context, several fundamental studies on the mechanisms of chemical interaction between IFR components at high temperatures by Camino et al. [18,19], Bourbigot et al. [20,21], Jimenez et al. [22] should be mentioned. Physical aspects of the intumescent char formation, the patterns of char expansion, the rheology of char during expansion were discussed in detail in Refs. [3,23–26]. The effects of various flame retardants [27,28], nano-additives [29,30] and other means of increasing fire-retardant efficiency of IFR [12,31] are the subject of numerous researches and discussions. The results of such studies were used as a basis for developing theoretical concepts, hypotheses, and generalizations. The general principles of creating effective intumescent fire-retardant compositions were outlined in review articles by Mariappan [11], Yasir et al. [12], Puri et al. [13], Vakhitova [29], Li [31], etc.

It is known that an average IFR includes three obligatory components, which can be categorized into three groups [3,11,29]: acid source – usually, salts of non-volatile inorganic acids, such as boric, sulfuric or phosphoric acid; carbon source – carbon-rich compounds with a large number of hydroxyl groups; blowing agent – a substance or mixture thereof which under the influence of elevated temperatures produces a large amount of non-combustible gaseous products. These gases contribute to the formation of foam from the carbonized melted material during the intumescent expansion.

Such set of three categories of IFR components can comprise various individual compounds or mixtures thereof, provided that collectively they contribute to all the described chemical processes [11,12]. However, it is only useable if we consider such IFR as an independent flame retardant the main function of which is to reduce the flammability of polymeric, composite or other flammable materials. When IFR is intended to be used as part of a fire-retardant intumescent coating (IC), polymer binder is to be considered as its fourth integral component. It should be emphasized that information published regarding the influence of the nature of polymer binder on the fire-retardant characteristics of intumescent coatings is limited and barely systematized [14,31]. As a general rule, researchers assume that the main function of a polymer binder in reactive coating is to provide adequate film-formation, sufficient adhesion to various substrates, required service life of the coating and environmental properties.

Nevertheless, certain studies [21,32–35] have shown that the binder makes, at times, critical contribution to the fire-retardant performance of the acid source/carbon source/blowing agent ternary system. In the required temperature range, polymers participate in the construction and viscosity regulation of the heat-insulating intumescent char, contributing to it having a satisfactory adhesion to the metal substrate [3,14,25]. The mechanism of char formation, the strength of its adhesion to the substrate, and the intensity of its thermal destruction during the fire exposure, all directly depend on thermal stability of the binder in intumescent composition [35]. This, obviously, predetermines specific requirements for a polymer, limiting the range of polymers that can be used in reactive fire-retardant coatings [34]. It should be noted that we were unable to find any published studies describing direct connection, or even correlations, between the nature of polymer binder in IFR and its actual fire-retardant characteristics obtained specifically by large-scale fire tests.

Industrially produced intumescent paints (IP) are either water- or solvent-based highly filled compositions with a fairly stable formulation in regards to the nature of their components [11,13]: ammonium polyphosphate (APP), melamine (MA) and pentaerythritol (PE). In practice, the mass use of these compounds in the industrial production of IP is confirmed by the IR spectra of water-based and solvent-based paints from well-known global brands (Fig. 1).

Obviously, having an identical IFR basis, the paints presented in Fig. 1 differ in their fire-retardant efficiency largely due to the use of different additives and modifiers. Such compounds, added in small amounts, are undetectable by IR spectroscopy. However, they are capable of drastically changing both fire-retardant and operational characteristics of the system. Among the methods of increasing the fire-retardant characteristics of intumescent materials the following should be highlighted: introduction of complex compounds – product of condensation of phosphorus (phosphonium) compounds with derivatives of melamine and pentaerythritol [36–39];

preliminary modification of IFR components with polymers or organic flame retardants [40,41]; introduction of dried composite hydrogels [42], nanocomposites [43], natural materials [44], halogen-free organic flame retardants [45], nano-compounds of various nature [30] to the formulations. Relatively new suggestions for improving intumescent fire protection imply the concept of ceramization of intumescent char [46], or the use of polymer flame retardants [47], organic and inorganic composites [48,49] in a fire-retardant coating. One popular trend is using natural raw materials, or recycled industrial waste, in passive fire protection [50,51]. These concepts and other results of scientific research can certainly be applied in the production of IP. However, most of the proposed solutions are not cost-friendly or simple in terms of their technological implementation.

Analysis of modern trends in the development of industrial intumescent fire protection makes it possible to formulate the main requirements for the quality of intumescent fire-retardant coatings, which are presented in Fig. 2.

Intumescent paints, based on the nature of their polymer binder, can be divided into the following main groups:

- water-based ones, usually containing dispersions of polyester polymers, e.g., vinyl acetate copolymers with either ethylene, vinyl versatate, acrylates or vinyl chloride [12,34,35,52,53];
- solvent-based ones, containing solutions of styrene acrylates, vinyl toluene acrylates, silicones, polyurethanes, copolymers of vinyl acetate with vinyl chloride in organic solvent [11,34,54,55];
- epoxy, polyurethane, silicone ones, designed to endure the conditions of hydrocarbon or jet fire [12,13,56–60].

The main direction of development and improvement of intumescent compositions in recent years is increasing fire-retardant performance of the coating in order to provide up to 180 min fire resistance to structural steel. At that, the necessary condition is a simultaneous reduction of the required coating thickness, the cost of fire-retardant paint, and, accordingly, the cost of fire-protective treatment of structures.

Some aspects of the practical implementation of the above tasks will be the focus of this study. The aim of the study is to identify the key factors that can increase fire-retardant efficiency of the reactive coating consisting of ammonium polyphosphate/melamine/

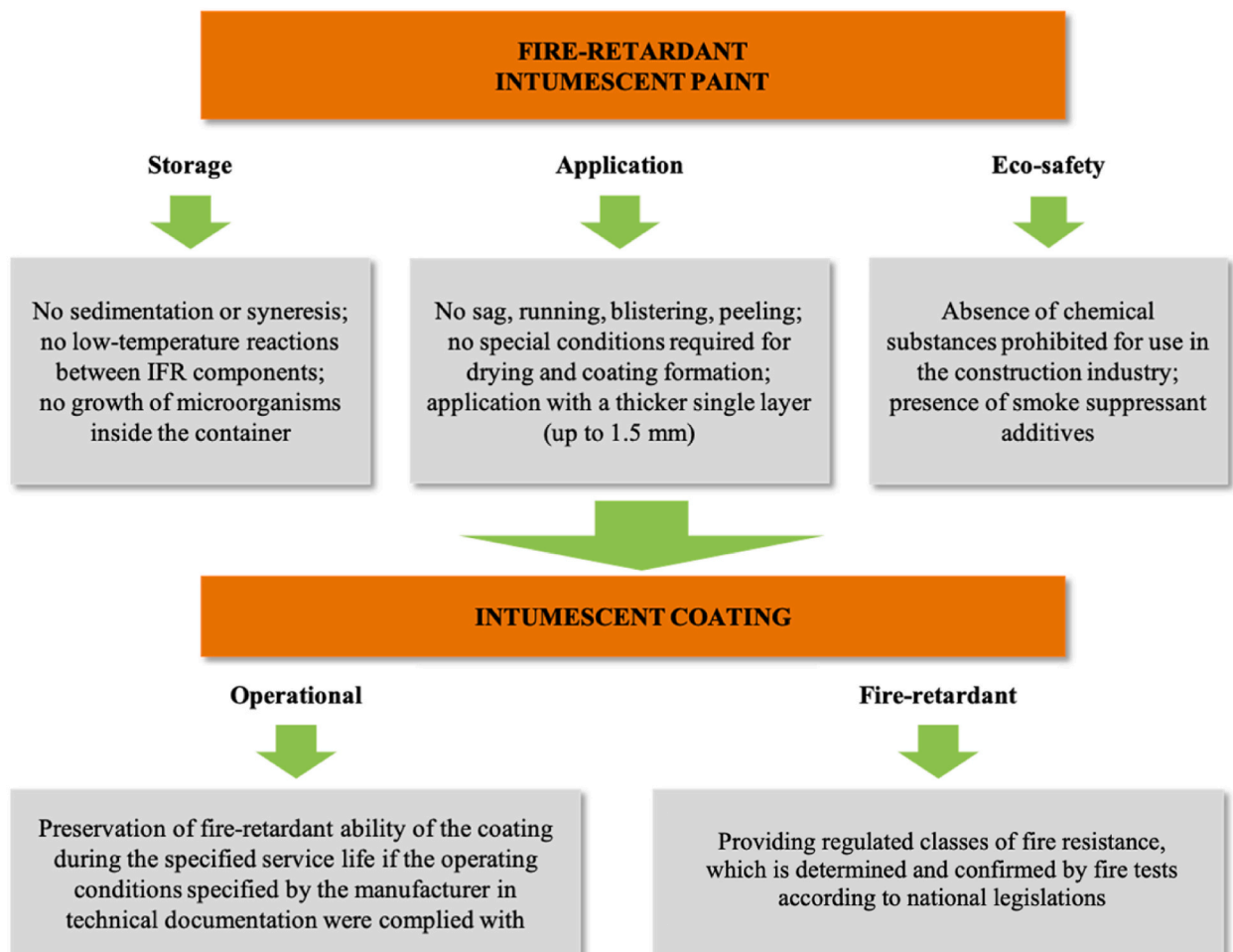


Fig. 2. Requirements for fire-retardant intumescent paints and coatings they form.

pentaerythritol/binder. The practical goal is to use theoretical findings to develop a formulation and production technology for a coating that provides at least 120 min fire resistance of steel structural members, and has an expected service life of at least 15 years. To achieve this, the following objectives were set.

1. Investigate the effects of the polymer binder present in an intumescent coating on the fire resistance of steel structures provided by said coating.
2. Determine the optimal ratio of target components: ammonium polyphosphate, melamine, pentaerythritol, polymer, which is specific to ensure a certain level of fire resistance of steel.
3. Determine the optimal amount of nano-clay and reinforcing fibers, and the directions of their influence on fire-resistant efficiency, water resistance and service life of fire-retardant coatings;
4. Develop a formulation of an intumescent coating with the fire-retardant efficiency of at least 120 min which, in terms of the availability of components and the technological aspects of its manufacturing, is suitable for industrial production and application.

The originality of this research consists in the fact that the results obtained in it represent an evolution from laboratory-scale test methods using physicochemical methods of fundamental science to the practical implementation of the formulations and technologies into production. The theoretical results obtained in current study were confirmed using large-scale fire testing of studied materials in accordance with national legislation and international standards.

2. Materials and methods

2.1. Materials and equipment used in experiment

Phase II ammonium polyphosphate FR Cros 484 (Budenheim, Spain), Exolit AP 422 (Clariant, Germany), micronized pentaerythritol Charmor PM40 (Perstorp Holding AB, Sweden), melamine (Borealis Agrolinz Melamine GmbH, Austria), titanium dioxide Ti-Pure R-902 (DuPont, USA) were used in the current research. Polymer binders used in the experiment are listed in Table 1.

The layered silicate additives are represented by nano-clays produced by BYK Additives & Instruments (Germany): Optigel WA – bentonite $\text{Si}_8\text{Al}_4\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$; Garamite 7305 – a mixture of montmorillonite $[\text{M} \cdot n\text{H}_2\text{O}](\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$ and sepiolite $\text{Mg}_4(\text{Si}_6\text{O}_{15})(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ modified with benzalkonium; Claytone HY – tallow-modified montmorillonite; Laponite EP – synthetic magnesium silicate, hectorite $\text{CaO}_3(\text{Cr}^{3+}, \text{Mg}^{2+}, \text{Fe}^{2+})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ analogue.

This section lists the materials and agents that were most used in the experiment. In case analogs manufactured by other companies were used in certain part of experiment, this will be additionally specified when discussing the results.

In order to improve the operational characteristics of intumescent coating materials, dispersing agents and defoamers produced by BYK Additives & Instruments (Germany) and Troy Corporation (USA) were used. Mergal K14 from Troy Corporation (USA) was used as a biocide in water-based compositions. Cellulose ethers Bermocoll EBM (Nouryon, Germany) and HEUR-thickeners e.g., Rheolate by Elementis (USA) were used to modify rheology of studied coating materials.

Specord 75 IR spectrometer was used to identify compositions of coating samples and their charred residues. Thermogravimetric studies were carried out on the «Thermoscan-2» derivatograph.

2.2. Preparation of fire-retardant intumescent compositions

Solvent-based compositions were prepared as follows. Necessary components of intumescent system: ammonium polyphosphate, pentaerythritol, melamine, titanium dioxide, required amounts of additives and rheology modifier, polymer (or a mixture thereof) solution in organic solvent (Table 1) were placed in a laboratory dissolver with a dispersing vessel volume of 1 dm^3 . Resulting mixture was continuously stirred for 60 min at 900–1000 rpm grinding discs rotation speed to obtain the average particle size of 30–50 μm . Finished intumescent compositions were transferred for storage to airtight containers.

Water-based compositions. Water, cellulose thickeners and nano-clay (where required) were placed in a laboratory dissolver with a dispersing vessel volume of 1 dm^3 . The mixture was stirred for 10–15 min until a translucent solution was formed. The rest of necessary

Table 1
Polymer binders used as part of the studied intumescent systems.

Nature of the polymer	Trade name	Abbreviated name	Solvent	Manufacturer
<i>Water-based polymer dispersions</i>				
Vinyl acetate – ethylene	Vinnapas® EZ 3010	EZ 3010	Water	Wacker, USA
Vinyl acetate – ethylene – vinyl versatate	Vinnapas® EZ 3112	EZ 3112	Water	Wacker, USA
Vinyl acetate – ethylene – vinyl chloride	Vinnapas® CEZ 3031	CEZ 3031	Water	Wacker, USA
Styrene acrylate	Hydro Pliolite 211	H211	Water	Omnova Solutions, USA
<i>Solvent-based systems</i>				
Styrene acrylate	Pliolite AC80 (Newtonian)	AC80	Xylene	Omnova Solutions, USA
Styrene acrylate	Pliolite AC4 (non-Newtonian)	AC4	Xylene	Omnova Solutions, USA
Vinyl chloride – vinyl acetate – vinyl alcohol	VAH-N VAGH	VAGH	Xylene/butanone	Dow UCAR, USA
Vinyl chloride – vinyl acetate	VYHH	VYHH	Xylene/butanone	Dow UCAR, USA

components: ammonium polyphosphate, pentaerythritol, melamine, titanium oxide, the required amounts of additives and rheological modifiers were then added to the solution. The mixture was stirred for 40 min at 900–1000 rpm grinding discs rotation speed to obtain the average particle size of 30–50 μm . Aqueous polymer dispersion was then added to the obtained paste and stirred for 10 min at 500–600 rpm followed by the addition of HEUR-thickener to the composition and final mixing that lasted approximately 30 min. All the compositions were stored in airtight containers.

The specific ratios of IFR components, as well as the composition of IFR formulations prepared for research, are described further in the text of this article.

2.3. Evaluation of volumetric intumescence factor

Fire-retardant intumescent compositions weighing 2 g each were placed into separate metal container (Fig. 3) and dried to constant weight at a temperature of 40°C or below. The containers with dried compositions (two parallel samples per each formulation) were placed in a laboratory oven preheated to 340 \pm 5°C, and conditioned for 20 min. The average height of thermally expanded material (h) was measured for each sample.

Based on the measurement results, the following equation was used to calculate volumetric intumescence factor, K_1 (cm^3/g), for each composition:

$$K_1 = 0.125 \pi d^2 (h_1/m_1 + h_2/m_2), \quad (1)$$

wherein d – diameter of the container, cm; h_1 , h_2 – average height of the expanded material for the first and second samples respectively, cm; m_1 , m_2 – weight of the first and second sample respectively, g.

The volumetric intumescence factor K_2 (cm^3/g), measured in laboratory furnace, is defined as the ratio of the volume of the intumescent char after fire exposure to the weight of the sample pre-exposure.

Linear intumescence factor K_i is determined as the height of intumescent char after fire exposure to that before the exposure.

A step-by-step study of the intumescent char formation in the temperature range of 200–800°C was carried out by exposing the same sample of intumescent coating to gradually rising set of temperatures. The duration of each exposure is 15 min. Intumescence factor K after each step is calculated using equation (1).

2.4. Bunsen burner fire test

This test is used to compare the rates of temperature increase for steel plates, coated with various ICs, under the influence of flame produced by a laboratory air gas burner (Fig. 4).

The increase in temperature on the uncoated side of steel plates is monitored and recorded using three K-type (100–1250°C) thermoelectric converters (thermocouples) and «TEST-1» temperature recorder. An air gas burner with a nozzle diameter of 40 mm was used as a source of ignition. The distance from the burner nozzle to the steel plate was 70 mm. Separate experiment was conducted in order to establish that the maximum temperature of the flame in the test setup was 950–1000°C.

For the purpose of this experiment 150 \times 150 \times 3 mm steel plates (Fig. 4) with thermocouples attached to one side were prepared. The fire facing side of each plate was primed with alkyd GF-021 primer with average dry layer thickness of 80 \pm 10 μm and coated with studied intumescent compositions to reach a specific dry layer thickness. The plates were then conditioned at 20 \pm 3°C for no less than 10 days. The thickness of dry coatings was measured using Qnix1500 magnetic thickness gauge.

The rate and level of coating expansion, as well as adhesion of the charred layer to the steel surface were evaluated during Bunsen burner fire test. Based on those factors and the temperature increase registered on the plate in the course of the experiment, a comparative assessment of intumescent compositions was performed.

2.5. Cellulose fire test using laboratory-scale furnace

Steel plate measuring 300 \times 300 \times 5 mm was inserted into the furnace opening. During the test the temperature inside the furnace as well as that on the outer surface of the plate were registered using K-type thermocouples and «TEST-1» temperature recorder. Test



Fig. 3. Visualization of the experiment to measure volumetric intumescence factor.

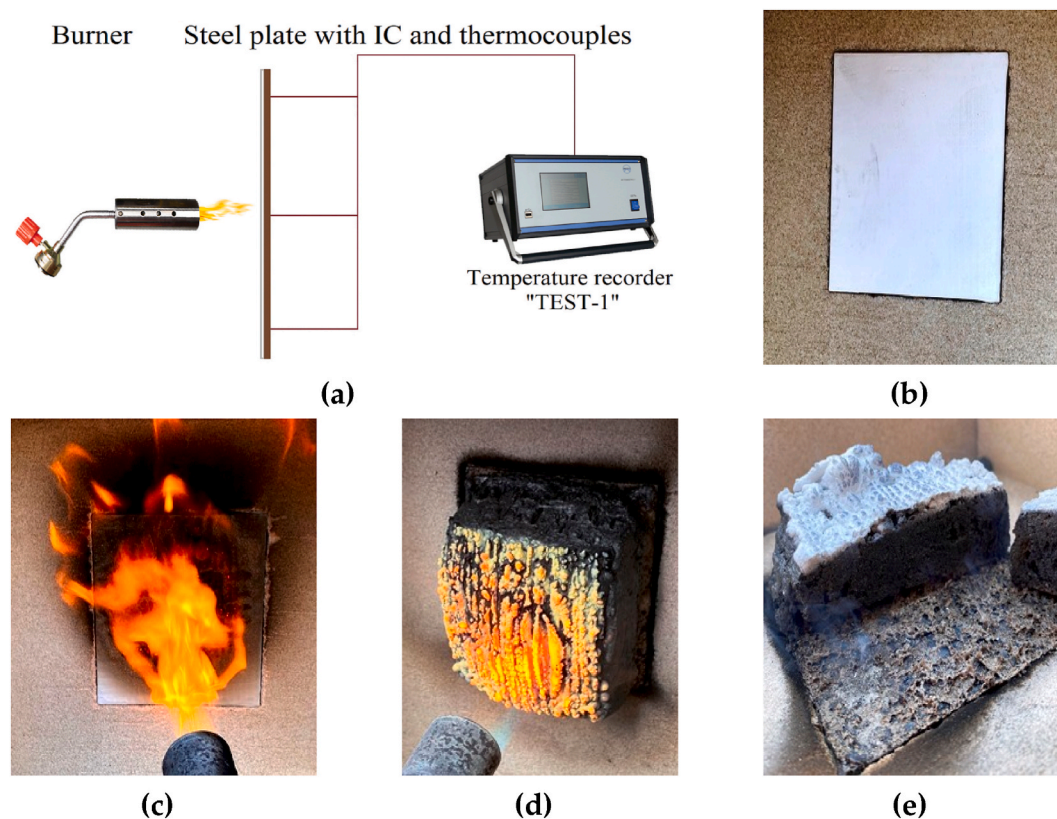


Fig. 4. Visualization and results of fire tests using Bunsen burner: a) test setup; b) sample before fire exposure; c) initial reaction to fire; d) expanded char during fire exposure; e) expanded char after the test.

setup is visually described in Fig. 5.

The inner surface (facing the flame) of the plates was coated with alkyd GF-021 primer with the average thickness of $80 \pm 10 \mu\text{m}$. The studied intumescent compositions were applied on top of it with a set dry coating thickness. Plates were conditioned at the temperature of 15°C , or above, for 21 days and later subjected to fire test.

The fire resistance determined for steel plates in standard fire tests using laboratory-scale furnace is, in most cases, in good accordance with the results of large-scale fire tests conducted according to national standards. Such factors as density, integrity and adhesion to the substrate of the intumescent char can also be used to predict fire-retardant performance of the coating.

2.6. Fire testing according to national standards

Large-scale fire tests for studied coatings were performed according to the procedures described in DSTU B V.1.1-14:2007 (EN 1365-4:1999 analog) on steel column samples and DSTU B V.1.1-13:2007 (EN 1365-3:1999 analog) on steel beams (Fig. 6).

To conduct fire tests, steel I-beams (Fig. 6) with three K-type thermocouples installed on each were used. I-beams were primed with GF-021 alkyd primer with a dry coating thickness of $60\text{--}80 \mu\text{m}$ and the studied intumescent compositions were applied to them until the specified thickness of the dry coating was obtained. Prior to being subjected to the fire tests, all the samples were conditioned at the temperature of no less than 15°C for 40–50 days.

3. Results and discussion

The main purpose of fire-retardant intumescent coatings is to provide a certain degree of fire resistance to building structures. Fire resistance of structural members can be classified based on the physical properties they are supposed to keep intact during fire: R – load bearing capacity; I – insulating property; E – structural integrity.

In this study, the main emphasis was placed on developing an intumescent fire-retardant coating for load-bearing steel building structures. Therefore, the evaluation of fire-retardant efficiency of the IC was carried out using R fire resistance rating. It is determined as a period of time (measured in minutes or hours) from the start of the fire test until the ultimate limit state of structural steel is reached due to the loss of its load bearing capacity. Other things being equal, R rate depends on the section factor and critical temperature of steel structure, test conditions, and the load applied to the structure [3,61,62]. In all the fire tests performed in current

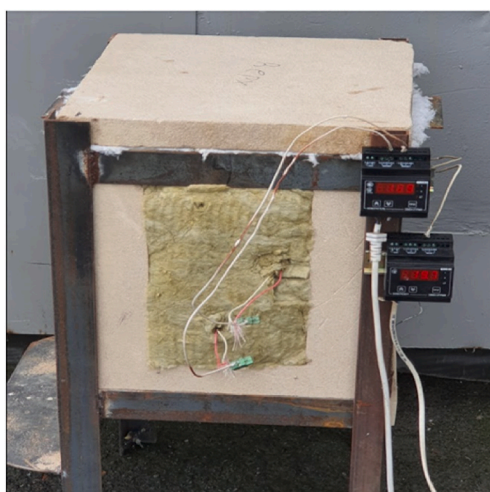
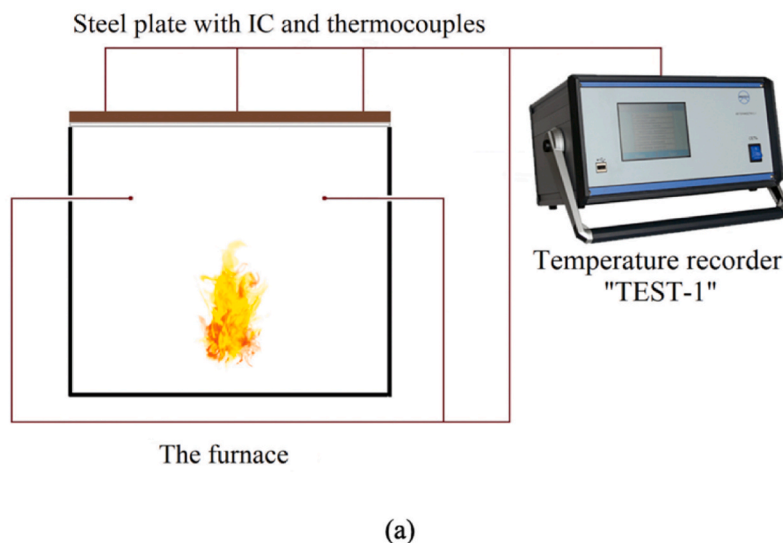


Fig. 5. Laboratory-scale furnace test at cellulose time-temperature curve: a) test setup; b) laboratory furnace; c) intumescent char after 120 min of fire test.

study, the ultimate limit state of steel structural members was determined by critical temperature method as the point where structural steel reaches an average temperature of 500 °C.

The R fire resistance rate is determined experimentally by large-scale fire tests (e.g., according to methods described in EN 13381-8:2013). The methods require complex equipment, long time in preparations, and are generally associated with significant monetary costs [3,29,61,62]. Therefore, computational methods, modeling and indirect experimental methods for determining fire resistance, such as cone calorimetry, TGA, loss on ignition (LOI), measuring the self-extinguishing time (UL-94), are gaining more popularity recently. Cone calorimetry is the most common research method used for prediction of IC fire-retardant properties. It is considered to be a universal intermediate test method [63] being presented in ISO 5660-1:2015 international standard. Nevertheless, an established opinion [3,35,64] exists that the conclusions drawn from cone calorimetry experiments are insufficient for the purpose of developing new formulations of intumescent coatings.

The criticism of indirect methods of predicting IC fire-retardant efficiency is related, first of all, to the fundamental difference between the thermal conditions of a real fire and the thermal influence on the coating, which can be achieved using laboratory equipment [64]. In addition, most indirect methods, like cone calorimetry or TGA, use minimum mass samples. Hence, they are not suitable to evaluate the properties and quality of the main source of fire-retardant ability of IFRs – the expanded intumescent char. Such methods provide no information regarding char's strength, inner structure, density, intumescence factor, adhesion to substrate, degree of thermal destruction.



Fig. 6. Fire test of intumescent coating according to DSTU B V.1.1-14:2007 (EN 1365-4:1999 analog): a) steel columns before test; b) steel columns after 120 min exposure to fire.

Therefore, in our opinion, modeling the behavior of each coating in increasing temperature conditions similar to those of real fire with the analysis of the intumescent char formed, using a sample with sizable mass and coating area, is a more reliable and direct method of predicting the fire-retardant efficiency of IC. The expansion process characterized by the formation of heat-insulating char is depicted in Fig. 7 and can be described by successive stages taking place at different temperature ranges. Temperature regime of each stage was determined by summarizing data provided in Refs. [3,25,65].

It should be noted that both the temperature ranges and the intumescence factor (K) values during the intumescent char formation process described above are conditional. They may shift significantly depending on the composition of IC, the nature of polymer binder, the effect of flame-retardant additives, etc.

In general, the experimental results regarding the fire-retardant properties of ICs were obtained in current study according to the algorithm described in Fig. 8.

It is this sequence of research stages that allows to develop formulations of effective intumescent coatings with a high probability of

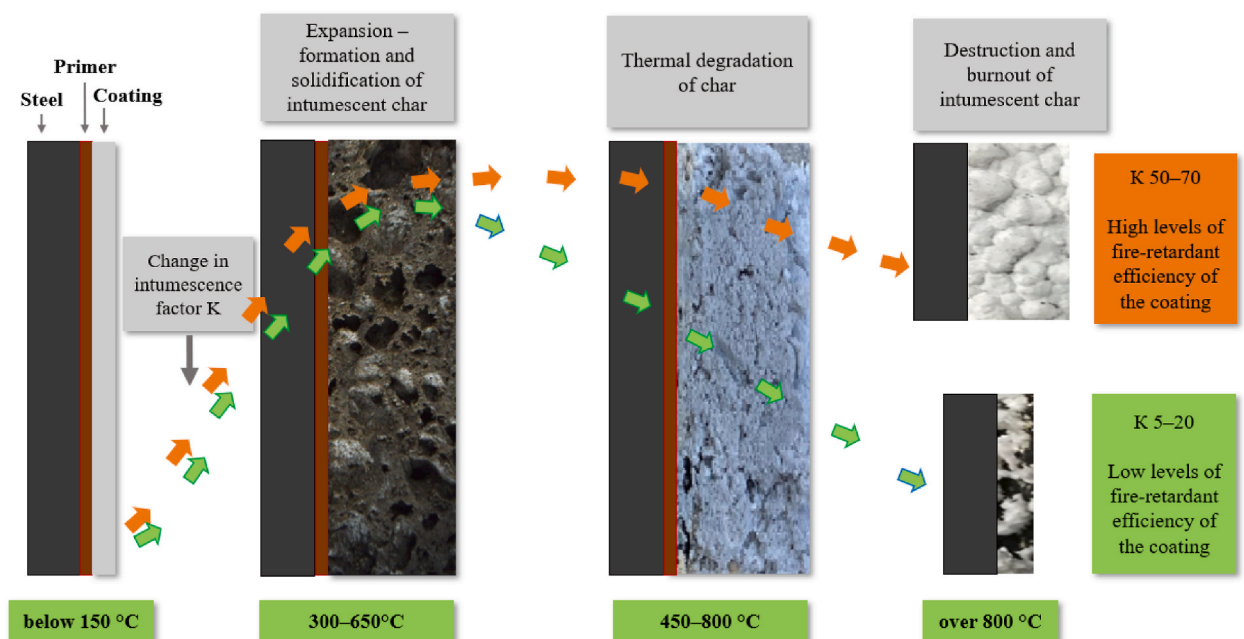


Fig. 7. Approximate temperature regime of intumescent char formation.

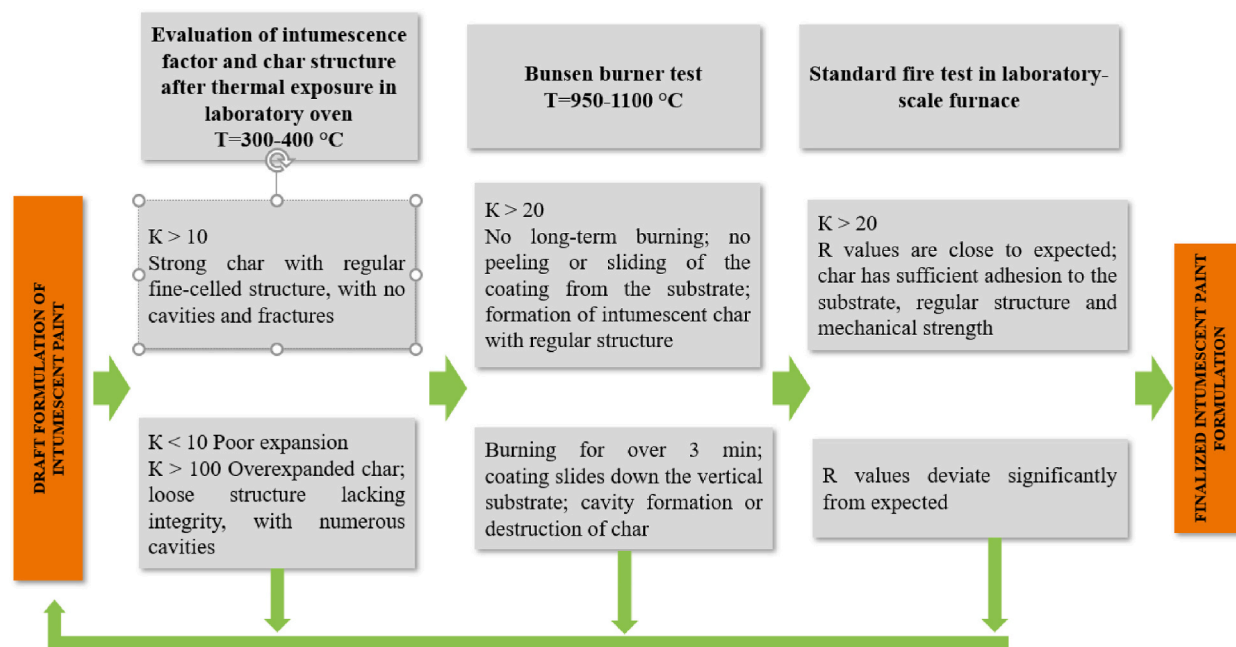


Fig. 8. Algorithm for testing fire-retardant efficiency in the process of designing new formulations of intumescent coatings.

obtaining a satisfactory result quickly and with no overbudgeting.

3.1. Influence of polymer binder on the intumescent char formation processes and fire-retardant efficiency of intumescent coating

In order to study the influence polymer binder has on the fire-retardant properties of intumescent coatings, water-based and solvent-based intumescent paints (Table 2) were prepared using polymers of various nature listed in Table 1. The following additives (Table 2) were used in water-based paint samples: Bermocoll EM 7000 FQ hydroxyethylmethyl cellulose thickener (2.5 %), Disperbyk 192 dispersant (1 %), Byk 1610 antifoaming agent (1 %), Mergal K 14 biocidal additive (0.5 %). The Disperbyk 108 dispersant (2 %) and Tixatrol ST thickener (1 %) were added to the solvent-based paint.

Fire-retardant efficiency of the coatings was investigated according to the algorithm proposed in Fig. 8: evaluation of the volumetric intumescence factor (K_1) in laboratory oven at 340°C; Bunsen burner fire tests; measuring fire resistance rate (R_1) and intumescence factor (K_2) in a laboratory furnace; large-scale fire tests according to DSTU B V.1.1-14:2007 and DSTU B V.1.1-13:2007 (R_2); evaluation of the linear intumescence factor (K_3).

Table 3 shows the results of these experimental studies, obtained for coatings with an average dry-layer thickness of (1.50 ± 0.15) mm. For the purposes of large-scale fire tests steel I-beam columns with section factor of 6.4 mm ($A_m/V = 156 \text{ m}^{-1}$) were used with fire exposure from four sides.

The results (Table 3, Fig. 9) demonstrate a significant effect the nature and structure of polymer binder have on achieving the ultimate result – providing certain fire resistance rate (R_2 , min) to structural steel.

The best result was obtained for IC2 coating containing a vinyl acetate-ethylene-vinyl versatate copolymer ($R_2 = 62$ min). Fire resistance of this composition almost 2 times exceeds that for IC5 coating with styrene acrylate binder (R_2 , Table 3). It should also be noted that Bunsen burner tests demonstrate a general tendency of coatings with styrene acrylate binders, i.e., IC4 and IC5, to melt and sag along the vertical steel surface (Fig. 10, a). This situation is somewhat leveled by using a mixture of AC80 (Newtonian) and AC4 (non-Newtonian) copolymers with 3:1 ratio (Fig. 10, b). It is obvious that in order to completely eliminate this defect, an additional modification of IC6 composition is required, aimed at increasing the viscosity of the molten intumescent layer before its charring.

To determine the tendencies of intumescence factor fluctuations in the temperature range of 200–800°C, a step-by-step study of the expansion of intumescent char was carried out. Fig. 9 demonstrates temperature dependences of volumetric intumescence factor (K)

Table 2

Intumescent paint components and their content (%).

IFR composition type	Polymer binder	APP	MA	PE	TiO ₂	Additives ^b	Solvent
Water-based	10 ^a	25	8	10	12	5	30
Solvent-based	10	26	10	10	9	3	32

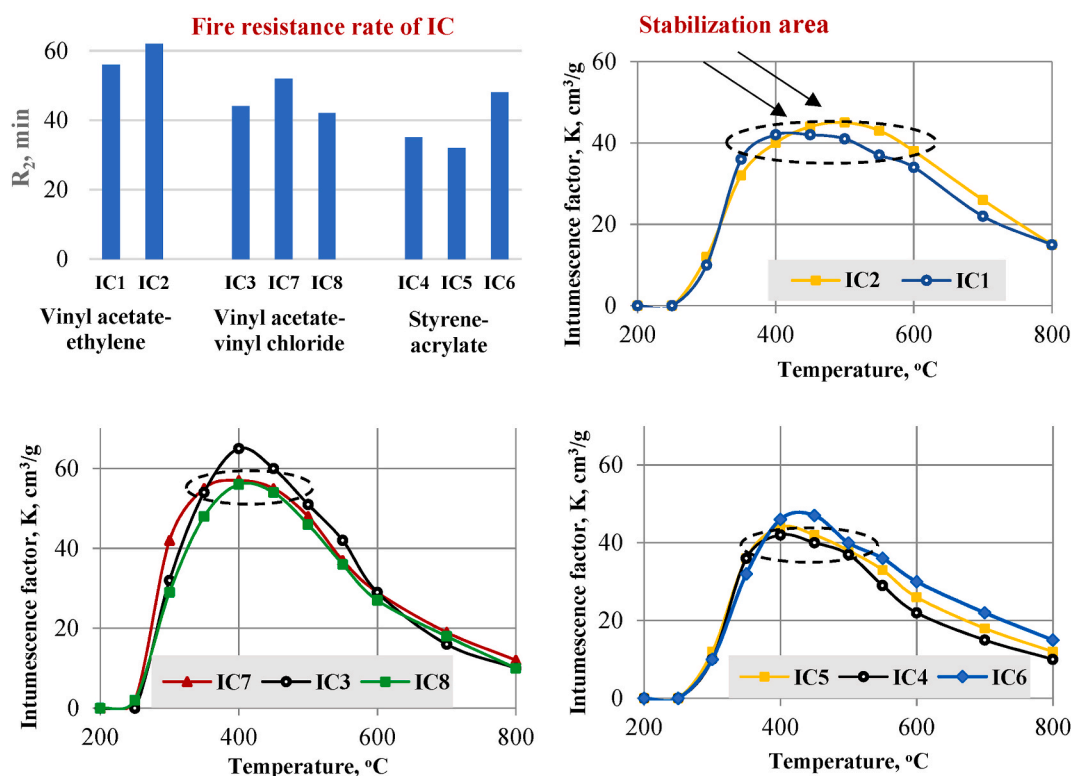
^aPure polymer content.

^bDispersant, thickener, defoamer, etc.

Table 3

The results of the study of fire-retardant characteristics for intumescent coating samples.

Intumescent coating	Polymer	K_1 , cm ³ /g	R_1 , min	K_2 , cm ³ /g	R_2 , min	K_1^a	T_d^a
Water-based							
IC1	EZ 3010	42	35	38	56	42	249
IC2	EZ 3112	45	41	40	62	46	256
IC3	CEZ 3031	64	30	24	44	23	211
IC4	H211	35	28	18	35	21	231
Solvent-based							
IC5	AC80	40	23	15	32	5	207
IC6	AC80+AC4	43	36	25	48	34	229
IC7	VAGH	56	41	46	52	38	200
IC8	VYHH	62	37	26	44	30	208

^aLinear intumescence factor.^bPolymer degradation onset temperature found by TGA.**Fig. 9.** Intumescence factor K (cm³/g) vs temperature T (°C) for studied intumescent compositions.

for ICs with various polymer binders (Table 3).

According to the experimental results (Fig. 9) studied polymer binders based on their influence on intumescence process, and hence on the main physical characteristics of the char formed during those processes, can be divided into three groups:

- 1) non-halogenated vinyl acetate copolymers used, for example, in IC1 and IC2. Based on the intumescent char formation progress (K , Fig. 9) the main complex of chemical reactions in IC1 and IC2 commences after the temperature reaches 350°C and happens mostly in temperature range 300–600°C. IC1 and IC2 coatings both are characterized by the presence of a significantly long flat area on the intumescence factor (K) vs temperature curve. That indicates the formation of thermally stable char (350–650°C range, Fig. 9);
- 2) halogenated vinyl acetate copolymers, which are present in IC3, IC7, IC8. These coatings are distinguishable due to their earlier expansion onset (<300°C) and rapid intumescence factor growth (K , Fig. 9) with a shortened stabilization area of K at 350–500°C;
- 3) styrene acrylates like the ones used in IC4, IC5, IC6 also demonstrate the tendency to have a shortened (350–500°C) stabilization area on K vs temperature curve.

Dependence of intumescence factor on temperature (Fig. 9) allows to state that non-halogenated vinyl acetates are the best choice

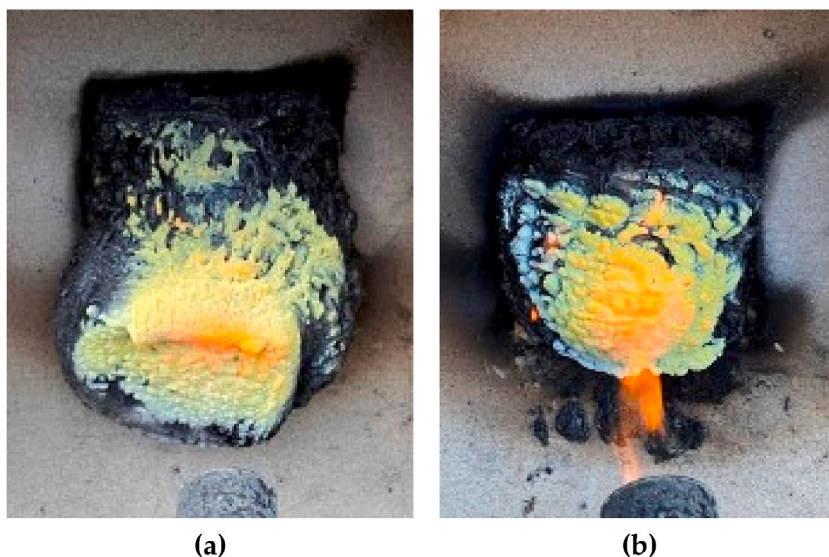


Fig. 10. Intumescent coatings during the Bunsen burner tests: a) IC5; b) IC6.

of binder for IC due to their contribution to the formation of thermally stable char. Such char is destroyed at higher temperatures compared to that of the rest (Table 3) of the studied ICs. It was established [35], that 70 % mass loss for ICs with aromatic styrene acrylates (IC4 and IC5) occurs, on average, at 640°C, while IC1 and IC2 suffer 70 % mass loss at 701°C and 715°C respectively.

Visual depiction of intumescent chars obtained during experimental part of this study for each of the specified groups of polymer binders is presented in Table 4.

A regular, dense frame with fine pore size is observed for ICs with non-halogenated vinyl acetates similar to EZ 3010. This trend persists in large-scale fire tests, as the I-beams after fire exposure are usually covered with a dense, evenly expanded char with strong adhesion to the substrate (Table 4). ICs containing AC80 styrene acrylates, in turn, tend to form lighter, foamy char with uneven porous structure that are unstable at temperatures above 600 °C. According to the results of fire tests based on DSTU B V.1.1-14:2007 standard, after 40–50 min of fire exposure, burnout with nearly complete destruction of the protective char can be observed for IC5. At the same time, significant defects can be registered in that for IC6 (Table 4). Intumescent chars formed by ICs with halogenated vinyl acetate binders generally show the highest values of intumescence factor. However, their structure is loose and includes large cavities. Coatings containing halogenated vinyl acetates (VYHH) also tend to form loose foamy chars characterized by local burnouts and partial destruction (Table 4).

The obtained results are yet another proof that the polymer binder in intumescent paints should not be regarded only in terms of film formation and providing certain shelf and service life. They are to be considered as the fourth integral component of IFR. As proved above, the binder directly influences fire-retardant characteristics of intumescent coatings.




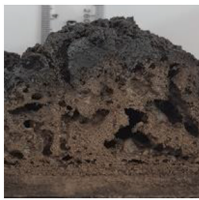








As shown in several studies [34,35,66–68], the main reason for the dissimilarity in fire resistance rates R obtained for the studied ICs is the difference in polymer binders thermal degradation mechanisms. It is known [66], that thermal degradation of vinyl acetates is a two-stage process. First, an intensive deacetylation process occurs at temperatures between 300 and 400 °C, where the polymer chain end fragments are cut off, resulting in polyenes formation. The second stage is characterized by thermal degradation which occurs on the double bonds of polymer chains at 400–500°C. For styrene acrylates their thermal destruction is a one-stage process that occurs at temperatures 340 to 450°C. It involves acrylic acid fragments being separated from the main chain and decarboxylated simultaneously with the main chain splitting directly into volatile monomers [67]. When it comes to halogenated vinyl acetates, an intensive release of acetic acid can be expected due to it being catalyzed by the formed hydrochloric acid. This provokes a decrease in the temperature at which polymer decomposition occurs. It oversaturates IC with volatile substances, which in turn leads to excessive expansion and subsequent mechanical weakness of intumescent char.

Fig. 11 shows IR-spectra for two compositions – IC1 (containing EZ 3010 vinyl acetate copolymer) and IC5 (with AC80 styrene acrylate copolymer), recorded after their exposure at different temperatures in the 350–700°C range. These data make it possible to identify the main chemical transformations that occur in IC1 and IC5 samples with a gradual increase in temperature.

At 350–450°C bands corresponding to stretching vibrations of $P=O$ group appear in the recorded spectra at 1245 cm^{-1} ($O=P-O-C$) and 1090–1000 cm^{-1} ($O=P-N-C$), while absorption bands present at 1020–1000 cm^{-1} are attributed to $P-N$ group ($O=P-N-C$). This indicates that esterification of PE with polyphosphoric acid, as well as aminolysis of phosphoric acid fragments by melamine or its derivatives, occur at this stage of thermal exposure. It is worth noting that the absorption band for carbonyl group in EZ 3010 vinyl acetate spectra (1734 cm^{-1}) disappears at 600 °C (Fig. 11, a). At the same time, the band corresponding to AC80 styrene acrylate (1734 cm^{-1}) cannot be detected at temperature as low as 450 °C (Fig. 11, b).

A broad band in the 3500–3350 cm^{-1} interval corresponds indicates the presence of ammonia (NH_3), which is generated during the thermal decomposition of MA. The intensity of absorption bands at 3380–3100 cm^{-1} , which belong to OH groups in PE and NH_2 in MA,

Table 4
Intumescent chars obtained in different test conditions.

Intumescent coating/polymer binder	Visualization of intumescent char		
	Thermal exposure in laboratory oven	Laboratory-scale furnace test	Large-scale fire test according to DSTU B V.1.1-14:2007 ^a
IC2, Vinyl acetate -ethylene- vinyl versatate			
IC5 Styrene acrylate (Newtonian)			
IC6 Styrene acrylates mixture (AC80+AC4)			
IC8 Vinyl chloride- vinyl acetate			

^aIntumescent paints used in large-scale fire tests contain additional flame retardants and are listed in [Table 2](#).

decreases at 600 °C, as does the intensity of the band at 1275 cm⁻¹, which corresponds to P=O vibrations in APP. The wide band at 1100–1000 cm⁻¹ can be attributed to the P–O–C vibrations in the formed intumescent char structure.

The IR spectra recorded for IC1 and IC5 intumescent chars after their exposure at 700°C ([Fig. 11](#)) indicate that the chemical structure of both chars is the same, regardless of the nature of polymer binder used. Additionally, based on the changes in the characteristic absorption bands registered for IC1 and IC5 compositions at each stage of temperature increase, a close similarity of the main phases within the mechanism of intumescent fire protection can be ascertained. However, as shown in [Fig. 11](#), for IC5 all chemical transformations occur at lower temperatures, and the char obtained at 700°C is much more exhausted and oxidized.

Further selection of polymer binders for intumescent fire protection, however, should unequivocally exclude halogenated ones, as they produce acutely harmful and carcinogenic substances when subjected to fire conditions. As for styrene acrylates used in solvent-based formulations, it should be noted that with the current situation on polymer binder market it is difficult to find similar budget-friendly substitutes. Most of the alternatives are not capable of forming highly concentrated (up to 30 % resin) semi-products which are a must to obtain highly filled (up to 80 % of non-volatile substances content) intumescent paints in the lower price segment.

The data presented below was obtained in the experimental determination of the scope of application of aromatic styrene acrylates in fire-retardant ICs. [Table 5](#) describes the results of large-scale fire tests conducted according to DSTU B V.1.1-13:2007 for IC1 and IC6 coatings with different dry film thickness. Steel beams with a section factor of 5.1 mm ($A_m/V = 196 \text{ m}^{-1}$) were used in fire tests. Depending on the thickness of intumescent coating, there is a reverse dynamic in fire-retardant efficiency of the system with vinyl acetate binder (EZ 3010, IC1) compared to one with styrene acrylate (a mixture of AC80+AC4, IC6). Fire resistance rate R_2 of steel beams with 0.45 mm IC1 coating is 22 min, which is significantly less than that for IC6 coating of the same thickness (34 min). At the same time, fire resistance of 1.95 mm thick IC6 coating was found to be 42 min, compared to 56 min for IC1. Visually the experiment is presented in [Fig. 12](#).

Thus, the use of different polymer binders for fire-retardant intumescent coatings can be a solid way for differential development of

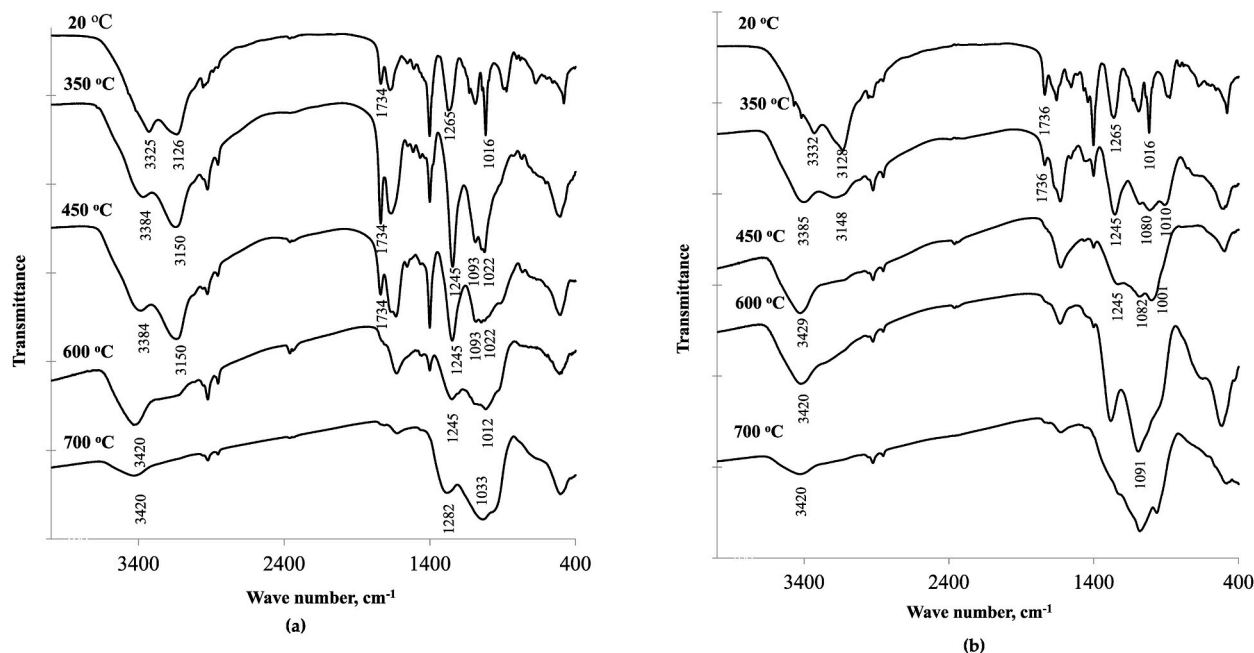


Fig. 11. IR-spectra recorded for intumescent chars formed at different temperatures: a) IC1; b) IC5.

Table 5

Fire resistance of steel beams with IC1 and IC6 intumescent coatings at different coating thickness.

Intumescent coating	IC1		IC6	
Coating thickness, mm	0.45 ± 0,04	1.92 ± 0,11	0.44 ± 0,05	1.95 ± 0,13
Fire resistance rate, R ₂ , min	22	56	34	42

fire-retardant materials focused on providing a certain predetermined class of fire resistance. In order to reach lower fire resistance (30 min) the use of acrylates-containing intumescent coatings is advisable, with for example H211 (Hydro Pliolite 211) polymer used for water-based systems or AC80+AC4 (Pliolite) polymers mixture for solvent-based ones. Whereas, acquiring higher fire resistance (60 min and above) is possible when vinyl acetates are used as binders in intumescent coatings, for example EZ 3010 or EZ 3112 polymer water dispersions, or similar materials produced by other manufacturers.

3.2. The influence of the ratio of main components in intumescent fire-retardant coating

One of the common ways to optimize fire-retardant intumescent compositions consisting of APP/MA/PE/TiO₂/binder is by experimentally selecting the best ratio of main ingredients (APP, MA and PE) in the system. Several researches were published describing the influence of the APP/MA/PE ratio on the fire-retardant properties of IC [69]. However, in those studies, the conclusions regarding the fire-retardant efficiency of coatings were drawn based on applying indirect preliminary test methods. Usually, those methods include cone calorimetry, Bunsen burner tests, LOI and UL-94 fire tests. Such tests are applicable for purely research purposes. They do not provide a clear understanding of which APP/MA/PE ratios in an actual intumescent coating can provide low (close to R30) or higher (close to R120) fire resistance of real structural members. This insufficiency can only be corrected by carrying out systematic fire tests to determine fire resistance of the coating in uniform temperature conditions similar to those of a cellulosic fire.

Table 6 lists the compositions for ICs with a wide varying content of main ingredients. In addition, it also includes fire-resistance rates R₁ obtained from tests in laboratory-scale furnace for steel plates coated with 1.5 ± 0,10 mm thick films of studied ICs. All the ICs listed in Table 6 contain 24 % of EZ 3010 vinyl acetate-ethylene aqueous dispersion and the required amounts of water as solvent. Additionally, intumescent paints contained rheological additives at 5 % amount. The ratios of different additives are specified in Section 3.1.

For each coating presented in Table 6 a step-by-step measuring of intumescence factor in the temperature range of 200–800 °C was carried out. The results of experimental study of the intumescent char characteristics for ICs are summarized in Table 7.

Based on the intumescence factors, the values of T_{max} (Table 7) and visual observations of the strength and density of intumescent char, coatings IC2-2, IC2-3, IC3-2, IC3-3, IC4-1, IC4-2 were deemed the best among the ones presented in Table 6. The content of the main IFR components in the mentioned ICs is: 19–33 % for APP, 12–17 % for PE and 6–10 % for MA.

Data obtained from thermogravimetric studies conducted in the oxidative environment of air for IC2–IC4 with different ratios of

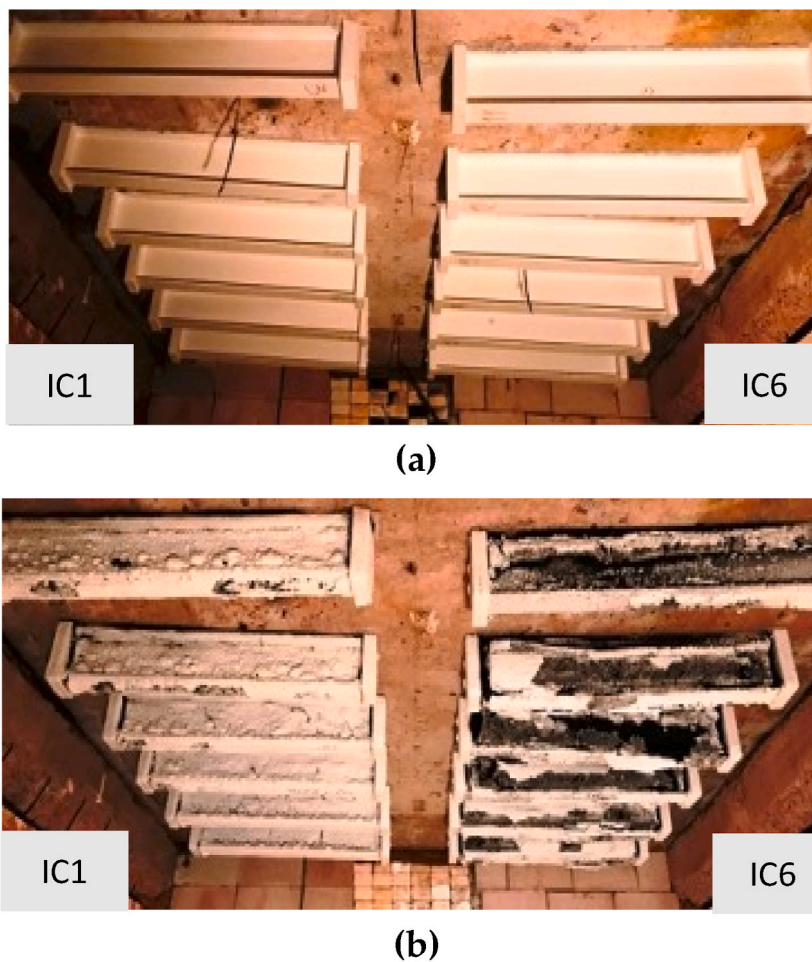


Fig. 12. Fire tests according to DSTU B V.1.1-13:2007 of I-beams with different thickness of IC1 and IC6 coatings: a) before fire exposure; b) after 60 min of exposure to cellulose fire conditions.

Table 6

Composition (wt. %) and fire resistance for studied IC variations.

Intumescent coating	APP	MA	PE	TiO ₂	R ₁ , min
IC2-1	12	19	19	12	21
IC2-2	19	16	16	10	31
IC2-3	33	11	14	8	37
IC2-4	42	11	12	7	34
IC2-5	49	10	10	7	25
IC3-1	38	9	6	9	37
IC3-2	35	9	12	9	41
IC3-3	33	8	17	9	36
IC3-4	31	8	21	8	31
IC3-5	30	8	25	7	26
IC4-1	38	6	9	9	35
IC4-2	35	10	11	8	38
IC4-3	35	12	9	9	31
IC4-4	32	21	8	7	26
IC4-5	30	25	8	7	22

APP, MA and PE are presented in Table 8, where T_d – temperature of thermal destruction onset; $T_{20\%}$, $T_{50\%}$, $T_{60\%}$ – the temperatures which correspond to 20, 50 and 60 % mass loss respectively [70].

Different thermal destruction onset temperatures (201–224 °C) and thermal stability of intumescent char upon temperature increase ($T_{50\%}$, $T_{60\%}$, Table 8) are observed for IC2–IC4 compositions. Mass loss for the chars (m, Table 8) at 700 °C significantly depend

Table 7
Intumescence factor K (cm^3/g) for ICs measured in temperature range 200–800 °C

Component	Content, %	K_{max}^a , cm^3/g	T_{max}^b , °C
APP	12	26	450
	42–49	32–46	420
	19–33	67–108	500
PE	6	60	400
	21–25	39–44	400
	12–17	48–52	450
MA	6	112	420
	10–12	78–88	500
	21–25	35–48	450

^aMaximum registered intumescence factor.

^bTemperature at which maximum value of K was registered.

Table 8
TGA results for intumescent coating samples.

Intumescent coating	T_d , °C	$T_{20\%}$, °C	$T_{50\%}$, °C	$T_{60\%}$, °C	m , %, 700 °C
IC2-2	204	304	400	458	24
IC2-3	210	331	475	538	35
IC3-2	224	345	503	523	31
IC3-3	210	329	497	563	24
IC4-1	201	327	505	505	25
IC4-2	208	325	537	593	37

on the ratio of APP, MA and PE in the coating. Noteworthy is also the difference in temperatures at which 60 % weight loss occurs for the studied ICs. For example, if we look at IC2-2 (APP – 19 %, MA – 16 %, PE – 16 %), $T_{60\%}$ for it equals 458 °C, whereas that for IC4-2 (APP – 36 %, MA – 8 %, PE – 12 %) is 593 °C, with the temperature difference between the two being 135 °C in favor of the latter.

According to the results of fire tests in laboratory-scale furnace (R_1 , Table 6), the following coatings should be listed as those with the highest fire-retardant efficiency: IC2-3 ($R_1 = 37$ min), IC3-1 ($R_1 = 37$ min), IC3-2 ($R_1 = 41$ min), IC3-3 ($R_1 = 36$ min), IC4-1 ($R_1 = 35$ min), IC3-2 ($R_1 = 38$ min). By analyzing the compositions of these ICs, it is possible to predict that intumescent coatings containing 30–32 % of APP, 8–10 % of MA and 12–14 % of PE are optimized to provide higher fire resistance (>60 min) of structural steel. In turn, when it comes to lower fire resistance, up to 30 min, it is advisable to use APP:MA:PE in ratios close to 2:1:1.

In order to confirm this hypothesis, fire resistance of steel columns was measured using the method provided in DSTU B V.1.1-14:2007. Columns with section factor $\delta = 5.4$ mm ($A_m/V = 185$ m⁻¹) with fire-retardant intumescent coatings IC9 (APP:MA:PE = 3.4:1:1.4) and IC10 (APP:MA:PE = 2.3:1:1.2) were subjected to the fire test. The results are given in Fig. 13.

Table 9 summarizes experimental data on the influence of EZ 3010 polymer binder content on the intumescent char formation in APP/MA/PE/TiO₂ system (the weight ratio of listed components is 3:1:1:0.8).

These results indicate that an excessive amount of binder in the system can significantly reduce its fire-retardant effectiveness due to the adverse effect on intumescence factor. Based on authors' observations, the optimal content of binder in IC for ethylene-vinyl acetate type polymers is approximately 9–11 % of pure polymer (or 18–22 % for most commercially available aqueous dispersions

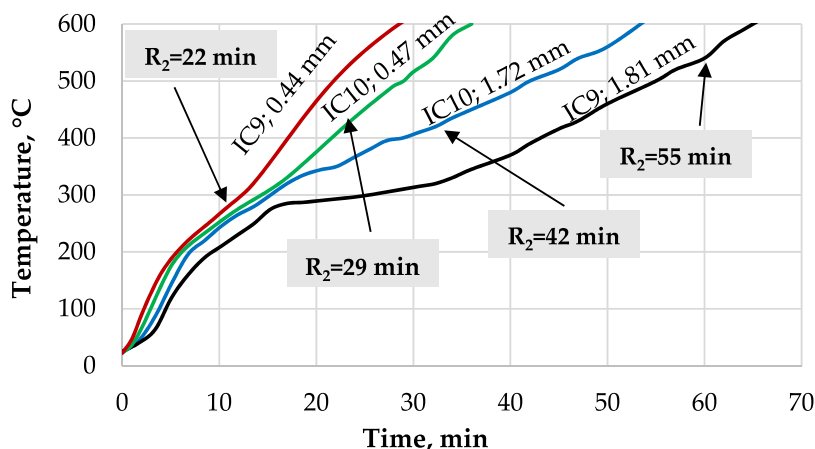




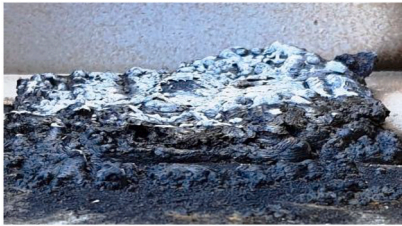



Fig. 13. Results of fire tests according to DSTU B V.1.1-14:2007 for steel columns with studied intumescent coatings.

Table 9
Intumescent chars formed by ICs with varied polymer content after fire tests in laboratory furnace.

[EZ3010] ^a , %	Laboratory-scale furnace ^b	K _i	R ₁ , min
5		25	19
7		28	21
9		36	37
11		34	34
13		21	28
15		7	13

^aContent (wt. %) of pure polymer.

^bCoating thickness (1.50 ± 0.19) mm.

of said polymers). If the polymer content is under 9 %, intumescent char formed by such coating would have a loose irregular structure. Mechanical strength and structural regularity of the char framework are lost as the polymer content in IC decreases. It happens due to the fact that polymer is the fourth component taking an essential part in the formation of the char by interacting with APP, MA as well as the already-formed compounds comprising the char framework [11,14,21,71]. At the same time, for systems with over 11 % of polymer binder intumescence factor would decrease with the increase of polymer content, up until the expansion would cease completely. This effect is explained by the fact that an excessive amount of polymer in the IC causes higher viscosity of the melted coating at high temperatures [3,11]. This, in turn, leads to the suppression of intumescent expansion, and formation of a dense char with increased thermal conductivity.

Analysis of the data obtained from experiments with varying the content and nature of the main components in IC makes it possible to draw conclusions practically applicable for future development of effective fire-retardant coatings. The ratio of the obligatory IC components – APP, MA, and PE, as well as their content in the composition, can both be used as regulators of the fire resistance of structural steel protected with said IC. IFRs based on the mixture of APP:MA:PE with their ratio being around 2:1:1 (20:10:10 wt% in intumescent paint) are more suitable to provide R30 fire resistance at an average dry coating thickness of 0.3–0.5 mm. The use of intumescent coatings where APP:MA:PE ratio is closer to 3.5:1:1.5 (35:10:15 wt% in intumescent paint) at 1.6–1.8 mm average dry film thickness is more likely to provide over 60 min fire resistance of structural steel.

This should be, of course, understood that any conclusions and generalizations regarding the correlations between fire-retardant efficiency of the system and any aspects of its composition, in terms of both the chemical nature of the components and their content in the IFR, are somewhat conditional. Such generalizations are to be used as a practical guideline rather than fundamental knowledge. The multicomponent nature of intumescent system, the multidirectionality of chemical interactions (including unpredictable ones) at high temperatures, the variety of thermal effects (fire spread conditions, atmospheric pressure, other environmental conditions) can critically affect intumescent processes during the formation of the heat-insulating char.

3.3. Modification of intumescent coatings with nano-clay additives

Some successful approaches to improving fire-retardant properties of intumescent paints, which were implemented into industrial production, will be discussed in this section of the research. According to authors opinion, the most successful approach to IC modification is the use of nano-clays. Such nano-additives simultaneously perform at least three functions. They have been proven to increase fire-retardant characteristics of IC, improve rheological characteristics of IP during its storage and application and increase environmental resistance of the coating.

The influence of hydrophilic and hydrophobic nano-clays on intumescence factor and fire resistance during exposure to laboratory-scale furnace conditions was studied for ICs listed in Table 10. The ratio of main components APP/MA/PE/TiO₂ for studied systems is 3:1:1:0.8. Water in the amount of 0.25 PBW was added to all water-based systems.

Fig. 14 demonstrates the dependence of intumescence factor (K_1 , cm³/g) on the amount of nano-clay additive. Studied IC11–IC15 coatings contain EZ 3010 ethylene-vinyl acetate copolymer (a), while IC16–IC20 include 3:1 mixture of Newtonian (AC80) and non-Newtonian (AC4) solutions of styrene acrylate in xylene (b).

The change in K_1 measured for ICs in the presence of nano-clays shows its significant dependence not only on the concentration and nature of added nano-clays, but also on the polymer they form nano-composites with [72]. The data presented in Fig. 14 makes it possible to highlight some general trends in the influence of the nature and amount of nano-clay additive on studied systems:

- in ICs with ethylene-vinyl acetate binders (Fig. 14, a), the most effective additives proved to be hydrophilic nano-clays Optigel WA, Claytone HY and hydrophobic organomodified nano-clay Garamite 7305 when their amount in the system is up to 2 % (best between 0.3 and 0.6 %). IC with synthetic hectorite Laponite EP in the amount of up to 1 % (0.3–0.6 % optimally) also shows good results of intumescent expansion;

Table 10
Composition (PBW) of intumescent coatings.

Intumescent coating	Nano-clay	APP/MA/PE/TiO ₂	Additives ^a	Binder ^b	
				EZ 3010	AC80+AC4 (3:1)
IC11	No nano-clay	1	0.08	0.27	–
IC12	Optigel WA	1	0.08	0.27	–
IC13	Garamite 7305	1	0.08	0.27	–
IC14	Claytone HY	1	0.08	0.27	–
IC15	Laponite EP	1	0.08	0.27	–
IC16	No nano-clay	1	0.05	–	0.61
IC17	Optigel WA	1	0.05	–	0.61
IC18	Garamite 7305	1	0.05	–	0.61
IC19	Claytone HY	1	0.05	–	0.61
IC20	Laponite EP	1	0.05	–	0.61

^aEach paint additionally contains rheological additives; their composition is provided in Section 3.1.

^bThe amount of polymer dispersion or solution.

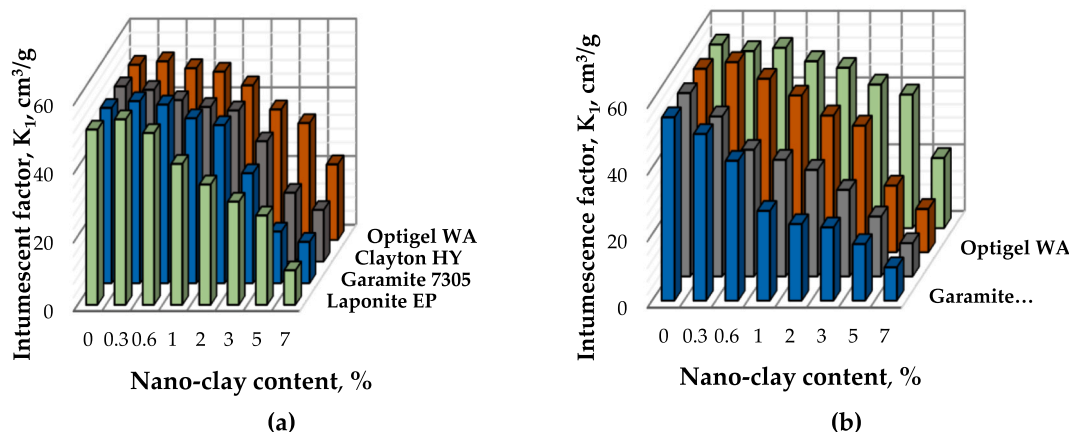


Fig. 14. Intumescence factor (K_1 , cm^3/g) for studied intumescent coatings vs nano-clay content (%) in IC: a) IC11–IC15; b) IC16–IC20.

- in ICs based on styrene acrylic binders (Fig. 14, b) organomodified hydrophobic nano-clay additives provide relative preservation of K_1 . Their concentrations should be kept at up to 0.3 % for Claytone HY and Garamite 7305, up to 5 % for Laponite EP and up to 3 % for Optigel WA.

It is obvious that the concentrations of nano-clay that can be added into intumescent composition without hindering its thermal expansion depend on the ability of each layered silicate to exfoliate in IC. If a certain nano-clay demonstrates high degree of exfoliation in a coating, it can be considered as “cognate” to that particular IC. The degree of exfoliation, in turn, correlates with the interlayer distance between nano-clay silicate mono-platelets (basal spacing, d). According to the results of XRD analysis [72], the basal spacing for Garamite 7305 is on average 2.37 nm, while for Optigel WA it is closer to 1.21 nm. Since the studied ICs are highly filled compositions, it is safe to assume that any influence the polarity of the medium (water or organic solvent) in such compositions might have on the exfoliation of nano-clays will be at least partially leveled. Therefore, the chemical nature of nano-clays does not have a decisive effect on the exfoliation of the additive in intumescent compositions. Study [73] claims that at the maximum of its exfoliation degree, nano-clay would structure the coating with oriented nano-platelets distributed throughout. At that, the structure formed by platelets is significantly less permeable to liquids and gases compared to regular intumescent coatings. Thereby, it is expectable that the expansion in such system will be suppressed.

In view of the obtained results, it is obvious that the possibility of use of nano-clay additives in ICs without reducing their fire-retardant efficiency depends on the selectivity of nano-clay choice for each specific composition. The nature of polymer binder and the type of solvent used in said intumescent composition should be taken into careful consideration. In case the structure of the used nano-clay and its amount were not harmonized with the IC composition of choice, it is highly probable that the intensity of intumescent expansion will come into conflict with the barrier effect of the additive. If the latter prevails, the mechanisms of fire-retardant action for the intumescent coating can be suppressed completely [74,75].

Comparison of fire resistance rates R_1 (Table 11) measured for studied ICs during fire tests in laboratory-scale furnace demonstrates an increase in fire resistance of the systems with nano-clay additives. The same Table shows fire resistance rates R_1^* measured for steel plates in the same test conditions after their exposure at a relative humidity of 80 % for 300 days.

The data in Table 11 demonstrate that coatings based on a mixture of styrene acrylates AC80+AC4 (IC16–IC20) are rather sensitive to the effect of nano-clay additives. For example, the fire resistance measured for IC19 (containing Claytone HY, $R_1 = 32$ min, Table 11) is 50 % higher than that for IC with no nano-clay added (IC16, $R_1 = 22$ min, Table 11). IC with EZ 3010 ethylene-vinyl acetate binder is less susceptible to such influence, therefore the difference between fire resistance rates for IC13 (Garamite 7305 additive, $R_1 = 44$ min, Table 11) and IC10 (no nano-clay added, $R_1 = 34$ min, Table 11) is merely 30 %.

The positive effect of nano-clay additives on the resistance of intumescent coating to environmental influences is evidenced by the data obtained in the following experiment. Fire resistance for steel plates with intumescent coatings was measured before (R_1 , Table 11) and after (R_1^* , Table 11) artificial aging at air humidity of 80 % for 300 days. Using the results of fire tests, authors were able to calculate the decrease in fire-retardant ability of the studied ICs caused by environmental influence: $\Delta R = R_1/R_1^* \times 100$ (%),

Table 11
Fire resistance of steel plates protected with studied intumescent coatings^a.

Intumescent coating	IC11	IC12	IC13	IC14	IC15	IC16	IC17	IC18	IC19	IC20
R_1 , min	34	41	44	39	37	22	27	29	32	25
R_1^* , min	30	38	44	37	33	20	25	28	31	23
ΔR , %	12	7	0	5	11	9	7	3	3	8

^aDry film thickness for all coatings close to 1 mm.

Table 11). It was established that with the organomodified Garamite 7305 and Claytone HY clays present in the intumescent coating, the decrease in fire resistance after aging is between 0 % (IC13, Table 11) and 3 % (IC18, IC19, Table 11). At the same time, IC11 and IC14, both with no nano-clay added, lose over 10 % of their fire-retardant efficiency in similar conditions.

It should be noted that assessing environmental durability of intumescent coatings according to EN 16623:2015 confirms the resistance of IC11 to environmental conditions specific to Z2 category of exposure. In such conditions fire resistance of the coating remains intact for 10–25 years of service, provided that the guidelines for the application, maintenance and repair of the coating were adhered to. Despite that, however, there is no denying that for IC11 the decrease in both, fire resistance during fire tests with steel plates and the linear intumescence factor, is more significant compared to that of the IC12 coating containing Optigel WA nano-clay (Table 12).

Numerous visual observations of the structure of intumescent char after fire tests conducted in both a laboratory-scale and a large-scale furnace makes it possible to draw a number of empirical conclusions, which might be of use for intumescent fire-retardant paints manufacturers. If correctly selected in terms of its nature and amount, nano-clay (a “cognate” nano-clay) radically alters both the structure and mechanical strength of intumescent char, making it denser and more evenly expanded (Fig. 15).

The presence of nano-clay additives in IC not only increases the adhesion of intumescent char to steel surface during the prolonged exposure to fire, it also prevents excessive flow of the paint on inclined or vertical surfaces [74], which is a typical defect for styrene acrylate-based coatings.

According to the statistics derived from the conducted fire tests, the authors consider it expedient to recommend only adding nano-clays “cognate” to a specific IC. Such approach can provide fire resistance of structural steel $R > 60$ min. Although, this might not be as important if lower fire resistance is to be obtained. At the same time, the optimal amount of nano-clay, in order for it to be able to effectively exfoliate and be evenly distributed throughout the coating, should not exceed 0.3–0.6 wt% of the total content of non-volatile components in the IC.

It should also be taken into account that nano-clays, even the chemically modified and properly processed ones, are natural materials and therefore do not have totally uniform chemical structure and elemental content. Therefore, when using any nano-clay in the production of IPs, it is necessary to carry out preliminary experiments to confirm the absence of any adverse effects on intumescent expansion.

3.4. The influence of reinforcement fibers on fire-retardant efficiency of intumescent coatings

When the thickness of IC layer is over 3 mm, which is usually required to provide $R \geq 90$ min fire resistance of steel structures, as well as during long-term exposure to fire, the intumescent char shall lose its adhesion and detach from steel surface, become brittle, and subsequently collapse due to inability to hold its own weight. This occurs regardless of the presence of nano-clay additives in IC. Visually the examples of such behavior in coatings during fire tests are presented in Fig. 16.

Strengthening of the heat-insulating intumescent char in this study was carried out by introducing two types of reinforcement fibers into the IC: mineral fiber (MS, trade name “Lapinus”) and glass fiber (GF, trade name “Cem-fil”). These types and brands of fibers were chosen based on the results of preliminary tests. Basalt, polypropylene, cellulose fibers, and wollastonites were studied in order to evaluate the effect of reinforcement additives on intumescent char formation. The required amount of individual fibrous materials, or mixture thereof, was chosen empirically, and was close to 3 % based on the weight of IC sample. That amount of fibers was beneficial for the formation of sturdy and structurally uniform intumescent char. When the content of fibers is closer to 5 %, it significantly lowers the level of intumescent expansion, as can be seen in Fig. 17.

The compositions of IC samples used in this experiment are provided in Table 13. In addition to the target components (Table 13), dispersant, antifoam agent, thickener and flame retardants were added into the ICs in amounts required for the production of marketable intumescent coatings. Additionally, 0.3 pbw of water were mixed into the ICs. Here and further the chemical structure and content of certain non-target components of ICs will be disclosed to a degree sufficient to understand the essence of the scientific idea of current research.

Fire resistance of structural steel protected by the studied ICs (Table 13) was measured by conducting fire tests according to DSTU B V.1.1-14:2007. Nullifire SC801-120 fire-retardant paint (produces by « Tremco Illbruck Trading as Nullifire», UK), which according to the Certificates of Conformity issued in numerous countries worldwide, provides 120 min fire resistance to steel structures, was used as a comparative sample in this experiment. All fire-retardant coatings were applied to I-columns with a section factor $\sigma = 4.2$ mm ($A_m/V = 238$ m⁻¹).

The results of this experiment, presented in Table 14 and Fig. 18, show that a 1:1 mixture of MF and GF fibers (IC24, Table 13) can be deemed the most effective reinforcement additive. IC containing MF + GF provides the best results in terms of fire resistance of structural steel sample – 62 min.

Based on the measured fire resistance (Table 14), as well as visual observations of the strength and adhesion of intumescent chars (Fig. 18) it can be concluded that IC24 intumescent coating, will be able to provide R120 fire resistance of steel load-bearing structures during large-scale fire tests. This coating contains a combination of mineral and glass fibers.

This statement is also supported by a comparison of time-temperature curves obtained for samples of structural steel protected by intumescent coatings IC24 and Nullifire SC801-120 during their exposure to cellulose fire conditions (Fig. 19).

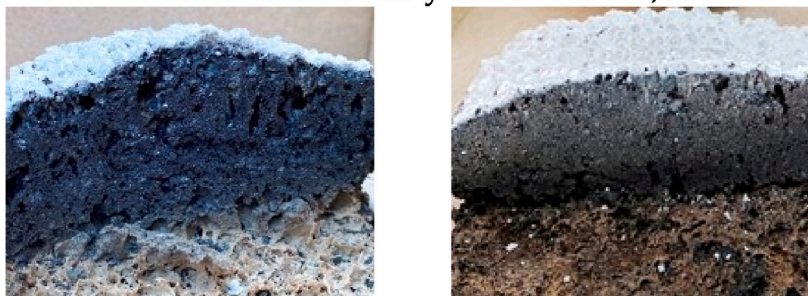
Only a limited number of basic approaches to improving the formulations of intumescent coatings are presented in this study. A heavy focus was on them being cost-friendly for mass production. In addition, the study provides an algorithm of direct laboratory methods that can be used to confirm and predict fire-retardant efficiency of ICs during its development. It was these preliminary laboratory test methods, as well as the above-mentioned approaches to increase fire-retardant performance of ICs, that allowed the

Table 12

Fire resistance class (R_1) and linear intumescence factor (K_i) registered for IC11 and IC12 before and after durability test (exposure conditions for type Z2) according to EN 16623:2015.

Intumescent coating	Sample #	Number of exposure cycles	R_1 , min	K_i
IC12	1	0	39	35
	2	0	41	39
	3	21	37	34
	4	21	39	36
IC11	1	0	35	35
	2	0	34	36
	3	21	30	31
	4	21	28	30

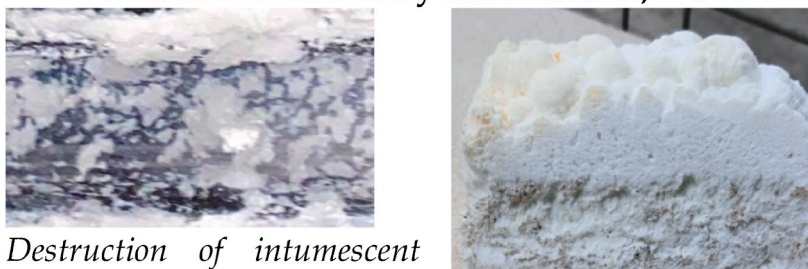
Fire test in laboratory-scale furnace, 45 min



Fire test according to DSTU B V.1.1-14:2007, 120 min



Fire test in laboratory-scale furnace, 150 min



Destruction of intumescent char

(a)

(b)

Fig. 15. Photos of vertical sections of intumescent chars obtained after fire tests at different exposure conditions for water-based IP consisting of APP/MA/PE/TiO₂/EZ 3112/additives and fillers: a) IP with no nano-clay; b) IP with Optigel WA nano-clay additive.

authors to develop and implement into production a formulation of an intumescent coating for structural steel which will be referred to as ICX. It provides fire resistance class of R120 and over, and is widely used for fire protection in Ukraine. Some indicators of the fire-resistant efficiency of the coating, which were confirmed by fire tests according to ENV 13381-4:2002 and reflected in the Certificate of Conformity, are listed in Table 15.

Table 15 contains data regarding the thickness of ICX coating, which was developed with the implementation of generalizations made in current study, required to provide R60–R150 fire resistant classes. The results are presented in comparison with similar data

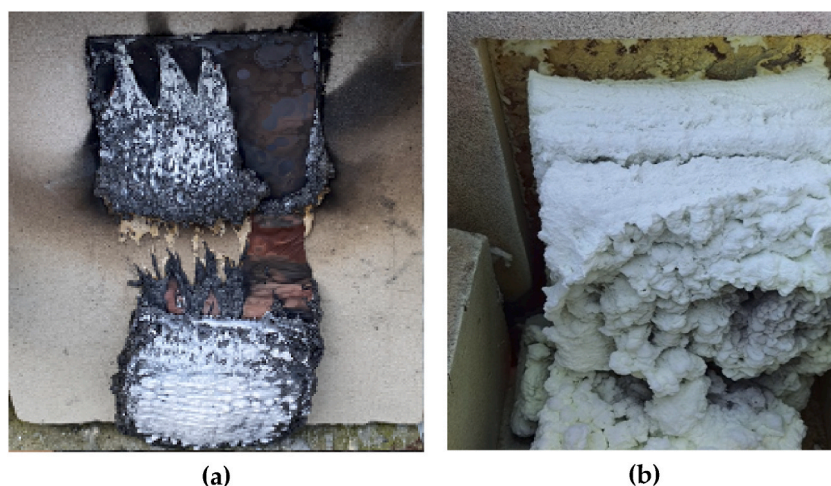


Fig. 16. Intumescent char obtained in: a – Bunsen burner flammability test; b – fire test in laboratory-scale furnace (the duration of test – 120 min, coating thickness – 4 mm).



Fig. 17. Intumescent char obtained for intumescent composition similar to IC2 (Table 3) during fire test in laboratory-scale furnace: a – MC fiber content at 2.8 %, expansion factor $K_1 = 34$, fire resistance $R_1 = 52$ min; b – MC fiber content at 5.2 %, expansion factor $K_1 = 14$, fire resistance $R_1 = 36$ min. Dry coating thickness 1.8 mm for both, a and b.

Table 13

The ratio (PBW) of intumescent coating components.

Intumescent coating	APP	PE	MA	EZ 3112	TiO ₂	Nano-clay	MC	GF	Additives ^a
IC21	3,5	1.6	1.1	2.2	1.0	0.1	–	–	0.5
IC22	3,5	1.6	1.1	2.2	1.0	0.1	–	0.3	0.5
IC23	3,5	1.6	1.1	2.2	1.0	0.1	0.3	–	0.5
IC24	3.5	1.6	1.1	2.2	1.0	0.1	0.15	0.15	0.5

^aAdditives include: Bermocoll EM 7000 FQ thickener (0.2); Disperbyk 192 dispersant (0.15); Byk 1610 antifoaming agent (0.1); Mergal K 14 biocidal agent (0.05).

for Nullifire SC801-120 intumescent fire-retardant coating by a globally-known manufacturer. Based on these data, it can be stated that the developed IC is not inferior in its fire-retardant characteristics to the Nullifier intumescent coating, and even surpasses it in providing R150 class of fire resistance. This purely practical result is the most significant achievement of this study, which emphasizes the correctness of the applied experimental approaches and a series of conclusions drawn during different stages of the research.

4. Conclusions

The development of new technologies of effective budget-friendly thin-layer intumescent coatings for building structures is an important task of fire protection industry. The reduction of fire protection contribution to the overall cost of structural steel is one of the best ways to promote metal as the material of choice for fast, most reliable and ergonomic construction.

In this research, the influence of the nature of polymer binder, the ratio of main components (ammonium phosphate/melamine/pentaerythritol/polymer) in intumescent composition, nano-clay additives and reinforcing fibers on fire-retardant intumescent

Table 14
Results of fire tests for studied intumescent coatings.

IC/coating thickness	Char characteristics	K_f	Fire resistance, min
IC21 2.1 mm	Brittle, with multiple cracks and visible signs of destruction	14	32
IC22 2.1 mm	Brittle, uneven, with multiple cavities, mostly detached from the substrate	26	44
IC23 1.9 mm	Strong, with multiple cracks, partially detached from the substrate	36	54
IC24 1.9 mm	Strong, even, no detachment from the substrate	32	62
Nullifire SC801-120 2.1 mm	Strong, even, partially detached from the substrate	38	59

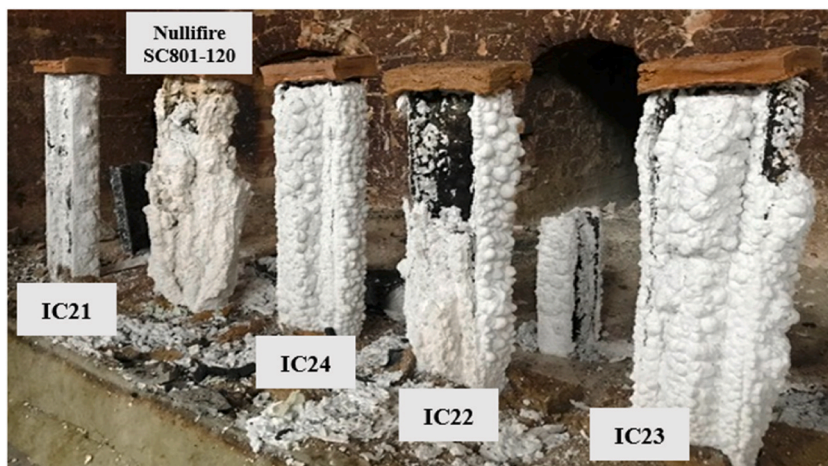


Fig. 18. Photo of the samples after fire test conducted according to the method described in DSTU B V.1.1-14:2007.

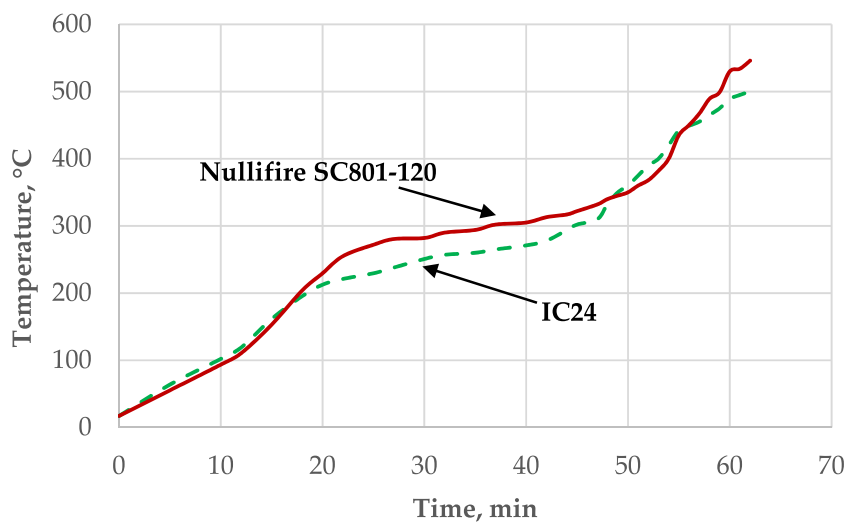


Fig. 19. Steel column temperature vs time of fire exposure at test conditions set in DSTU B V.1.1-14:2007.

coatings were studied. As a result, practical recommendations were provided for the improvement of reactive coatings formulations.

1. It has been shown that the nature of polymer binder in an intumescent coating is one of the regulators of its fire-retardant characteristics. In order to ensure lower fire resistance (close to R30), it is advisable to use acrylic polymers: ones similar to H211 (Hydro Pliolite 211) for water-based coatings, or a mixture of AC80 and AC4 (Pliolite AC80, AC4) for solvent-based ones. In turn,

Table 15

Data obtained from documents of conformity for the developed ICX intumescent coating and existing Nullifire SC801-120 coating [72,76].

Fire resistance, R, min	Section factor δ , mm	Section factor Λ_m/V , m ⁻¹	Minimum coating thickness, at which the temperature is lower than 500°C, mm	
			ICX	Nullifire SC801-120
60	10.0	100	1.12	1.02
	5.00	200	1.95	1.78
	3.10	324	2.27	2.32
90	10.0	100	2.33	2.24
	5.00	200	3.53	3.66
	3.10	324	4.19	4.66
120	10.0	100	3.65	3.20
	5.00	200	5.20	5.20
	3.10	324	6.10	N/A
150	10.0	100	4.91	N/A
	6.25	160	6.28	N/A

higher fire resistance (R60 or more) is better provided by coatings containing vinyl acetates (vinyl acetate-ethylene, vinyl acetate-ethylene-vinylversatate). Those can be either aqueous polymer dispersions by Vinnapas, Mowilith, etc., or similar polymer materials produced by other manufacturers.

- The dependence of fire resistance of steel structural members on the ratio of target components in the reactive coating was investigated. When APP:MA:PE ratio is close to 2:1:1 such intumescent coating can effectively provide R30 class of fire resistance of structural steel when applied at 0.4–0.5 mm thickness. With the use of APP:MA:PE at approximately 3.5:1:1.5 ratio and intumescent coating thickness being at 1.6–1.8 mm, fire resistance of R60 and above can be achieved with a high probability. In order to provide fire resistance of over R120, the dry coating thickness for a reactive coating is to be at least 3.5 mm.
- It was shown that in order to create fire-retardant coating formulation capable of providing R120 or higher fire resistance, the addition of “cognate” nano-clays or fibers in the required limited amounts is necessary to ensure the formation of strong and durable intumescent char. In general case, the required amount of nano-clay additive is approximately 0.6 % for water-based, or 0.3 % for solvent-based intumescent paints. Reinforcing fibers are to be added at around 1–2% content.
- The patterns outlined above were practically implemented to develop a reactive coating, which is currently put into industrial production, and provides R120 class of fire resistance of steel structural members. Fire-retardant efficiency of the developed coating has been proven by means of full-scale standardized fire tests according to national standards adapted to European ones.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Liubov Vakhitova: Writing – review & editing, Writing – original draft, Supervision, Project administration, Data curation, Conceptualization. **Kostyantyn Kalafat:** Validation, Methodology, Formal analysis. **Ramil Vakhitov:** Visualization, Validation, Investigation. **Varvara Drizhd:** Writing – review & editing, Writing – original draft, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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