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Reactive Fire-Retardant Nanocoatings for Steel Structures

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Abstract: Modern construction is characterized by an increasing use of steel structural members. This is due to their strength, durability, and their capability to ensure rapid structure assembly. One of the key requirements for such structures is ensuring an adequate level of fire safety, which is achieved through the application of reactive coatings. The most effective means in this regard are intumescent coatings, which form a thermal insulation layer at high temperatures. Such a layer preserves the load-bearing capacity of structures through thermal insulation. Recently, significant attention has been given to improving the properties of intumescent systems and enhancing their fire-retardant efficiency. A promising direction is the use of nanotechnology, which enables the creation of environmentally friendly, fire-resistant, and durable fire-retardant coatings. Fire-retardant coatings that contain nanomaterials are called nanocoatings. Among the most common and multifunctional nanofillers used in reactive coatings are layered nanoclays, LDH compounds, nanostructured carbon forms, silicon and metal nano-oxides. Nanomaterials play a key role in enhancing the fire-retardant properties of intumescent systems by participating in both chemical and physical fire protection mechanisms. An interesting research direction is the development of environmentally safe nanofillers, particularly the bio-based ones, which opens up opportunities for creating new materials with improved performance characteristics. Given these factors, nanomaterials continue to be a promising direction for the advancement of fire-retardant coatings.

Keywords: *Fire-Retardant Nanocoatings, Intumescent Coating, Nanomaterials, Layered Nanosilicates, LDH, Nanostructured Carbon, Nano Silica Oxide.*

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I. INTRODUCTION

One of the defining features of construction in recent years is prioritizing the high-rise multi-story buildings. Such structures require lightweight architectural forms and, thus, a search for alternatives to traditional concrete use [1, 2]. The increasing share of steel structures in the construction sector, while providing remediation for the issues of strength and durability, rapid assembly, the realization of non-conventional design concepts and solutions, imposes certain requirements on buildings and structures — necessary levels of fire safety.

One of the primary methods for enhancing the fire resistance of steel building structures is the application of passive fire protection. This includes materials and structural elements that extend the integrity, load-bearing capacity, or thermal insulation properties of building structures in fire [3, 4]. Among the various fire protection materials, reactive coatings (intumescent coatings — those that expand under heat) and solutions based on direct thermal insulation (fireproof plasters, mineral and fiber boards, etc.) are the most widely used in global practices. In recent years, intumescent fire-retardant coatings have become the preferred choice for steel construction, with their share steadily increasing in the global fire protection market (Figure 1). This trend is primarily due to the fact that thin-layer coatings preserve architectural forms and designs, which often rely on the aesthetic potential and advantages of steel [1].

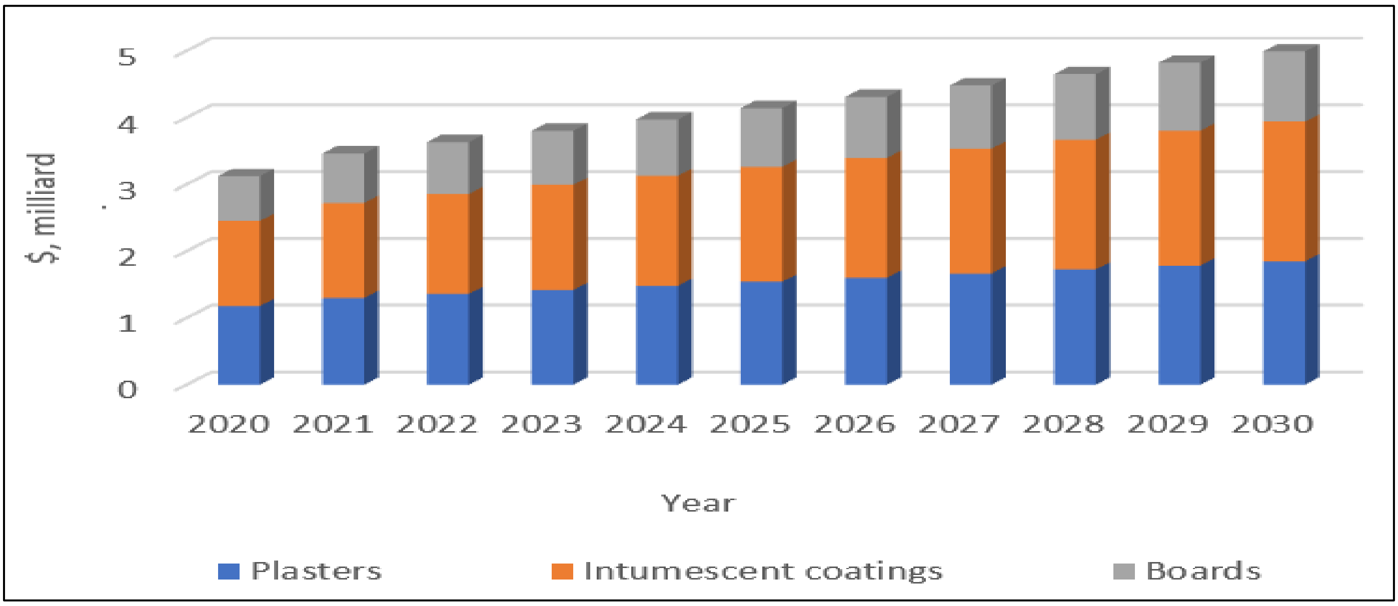

Fig 1 Passive Fire Protection Growth Dynamic and Prognosis in 2020–2030 [4]

Currently, scientific research in this domain is increasingly focused on the targeted improvement of intumescent systems, including enhancing fire-retardant efficiency, reducing the amount of the protective material required to achieve a specific fire resistance, and extending the service life of coatings by increasing their resistance to external factors.

One of the most promising trends in fire-retardant coating development is the application of nanotechnology. The use of nanomaterials opens up new possibilities for creating more efficient, compact, multifunctional, and environmentally friendly fire-retardant coatings. Those would not only effectively suppress combustion but also retain their properties during long-term use, while simultaneously offering improved mechanical characteristics without additional weight load. In the future, the integration of nanotechnology into fire protection may become the standard, ensuring a safer and more resilient living and working environment.

II. INTUMESCENT FIRE-RETARDANT COATINGS

Passive fire protection is a generalized term used to describe methods based on using the materials that prevent ignition, hinder the spread of fire, and enhance fire resistance of buildings, engineering systems, and structures [5-7].

Reactive fire-retardant (intumescent) coatings are a type of materials used in passive fire protection. Under high-temperature conditions, the components of such coatings undergo a series of chemical reactions that significantly increase coating thickness, change the geometric shape of the coating (expand), and provide fire protection via a combination of endothermic and thermal insulation effects [5, 7].

A number of published studies extensively examine various passive fire protection coatings, including cement- and gypsum-based plasters [8], composite fire-resistant panels [9-11], boards and fiber-based materials, ceramic coatings, and intumescent coatings [12-14].

A review of the literature indicates that thermal insulation fire protection (boards and plasters) is the material of choice for fire protection of steel columns and beams with a R > 150 minutes fire resistance. However, the considerable thickness of these materials (3–4 cm) compared to intumescent coatings (up to 5 mm) which impose less load on the structure, makes the latter a more practical choice [11].

An analysis of fire protection materials for steel building structures suggests that intumescent coatings are best suited for R30–R120 fire resistance [1, 3, 7, 15]. Key areas of improvement include achieving fire resistance of 150–180 minutes while minimizing thickness and associated costs, increasing resistance to moisture and environmental factors, and improving ecological characteristics.

Intumescent coatings have been actively used in the U.S. and Europe since the 1970s. Modern coatings are water-based or solvent-based compositions that can be applied using standard painting methods. A coating thickness of 0.2–6 mm provides protection by forming a coke-like charred insulating layer with low thermal conductivity [13]. The effectiveness of intumescent systems is determined by chemical and physical factors, which depend on the composition and ratio of components [12-14].

- *Intumescent Charring Mechnisms. Chemical Transformations.*

The fire-retardant function of an intumescent coating lies in the formation of a thermally insulating char as a result of chemical reactions between its components [14, 16, 17].

The classification of intumescent coating components based on their functional roles within an intumescent fire-resistant system (IFR) was first introduced in studies by Vandersall and Kay et al. [18, 19]. According to modern classification [14, 20-22], the main components of IFR have conventional names:

- acid source – typically phosphoric acid salts, such as ammonium polyphosphates (APP), which release acid at temperatures above 150°C;
- carbonization compound (carbon source) – polyhydric alcohols, such as pentaerythritol (PE), which form a carbon-rich char through esterification;
- blowing agent (foaming agent) – organic amines and amides (e.g., melamine (MA), urea) that release non-flammable gases to create foam;
- polymeric matrix (binder) – ensures the cohesion of components and significantly influences coating efficiency.

Modern intumescent coatings contain these components, supplemented with organic and inorganic additives to enhance fire protection and performance properties [23, 24]. A generalized list of components is provided in Table 1.

A review of scientific literature over the past 30 years on the composition of intumescent coatings confirms that the most commonly used components are ammonium polyphosphate (APP), melamine (MA), and pentaerythritol (PE) [11-14, 25]. These substances form the basis of modern industrial intumescent paints, and their combination provides an optimal fire retardancy.

The effectiveness of IFR depends on the interaction between its components, which determines the strength and structure of the char. In this aspect, the alignment of degradation temperatures for the acid source, carbonization agent, and blowing agent is critical. The acid source must decompose first, creating conditions for alcohol charring and subsequent foaming of the formed intumescent layer with non-flammable gases (NH_3, CO_2, etc.) [26, 27]. This process results in a multi-cellular protective layer that thermally insulates the steel structural member from heat exposure [28-30].

The mechanism of chemical transformations in IFR, suggested over 50 years ago [18], remains relevant. Studies on the ternary APP/MA/PE system confirm the effectiveness of its thermal degradation in forming a protective char [11, 31, 32].

- *The Mechanism of Char Formation in the APP/MA/PE/Inorganic Additives System Can Be Represented as Follows [33-35]:*

- ✓ T = 150–210 °C – decomposition of the acid source with the formation of polyphosphoric acid and ammonia. For example, ammonium monophosphate decomposes at 115°C, while the APP/PE system decomposes at 215°C;
- ✓ T = 210–280 °C – esterification of polyol (PE) by polyphosphoric acid, forming structures rich in phosphorus and carbon;
- ✓ T = 280–350 °C – decomposition of esters and formation of cyclic carbon structures which incorporate elements of inorganic fillers;
- ✓ T = 350-550 °C – active phase of chemical transformations: alcoholysis of APP fragments by hydroxyl groups of PE, formation of thermally unstable esters, their rearrangement into primary phosphorus-carbon frameworks, thermal decomposition of MA, aminolysis of unsaturated C and P atoms, etc.; gas release (NH_3, CO_2, H_2O) by blowing agents, which foams the layer and forms a porous structure;
- ✓ T = 450-650 °C – oxidation of unsaturated bonds, rearrangement of high-molecular-weight compounds formed in the previous phase into thermally stable cyclic structures;
- ✓ T ≥ 650 °C – combustion and degradation of the char.

According to the proposed mechanism, the decomposition temperature of the main IFR components should increase in the order: acid source < carbonization agent < blowing agent [11, 13]. The mechanism of these transformations remains a subject of continuous research, and the coordination of degradation temperatures for the components is key to optimizing IFR fire-retardant properties [35-38].

Table 1 Main Components of an Intumescent Fire-Retardant System [11, 14, 20]

Component	Function	Compounds
Acid source	Releasing an acid for esterification of hydroxyl groups of the carbonization compound.	Phosphoric acid, its ammonium salts and esters; melamine and urea phosphates; ammonium polyphosphates. Boric acid and its derivatives - borax, ammonium borates.
Carbon source	Esterification with acids, forming the carbon-rich material – the basis of the intumescent char	Polyhydric alcohols – pentaerythritol, dipentaerythritol, tripentaerythritol, arabitol, sorbitol, saccharides, polysaccharides, polyhydric phenols
Blowing agent	Thermal decomposition with the formation of non-flammable gases to produce a foamed structure in an intumescent char	Organic amines and amides – melamine, urea, dicyandiamide, guanidine and their derivatives, glycine, chlorinated paraffins
Binder	Coating formation and participation in charring processes	Vinyl acetate, acrylic, epoxy, polyurethane polymers and copolymers

Numerous studies have described the effect of inorganic fillers on chemical processes in IFR. It has been shown [39] that additive such as boric acid, zinc borate [40, 41], boron, phosphorus, and silicon compounds contribute to the formation of a mechanically stable char by strengthening its carbon-rich framework via the formation of refractory substances [42-44].

The most common inorganic fillers in known polymer intumescent coatings include titanium dioxide, aluminum hydroxide, talc, wollastonite, calcium carbonate, carbon black, silica (SiO_2), and kaolin [45, 46]. According to several studies [47-49], mineral fillers can be categorized based on their influence on the intumescent foaming process:

- those that promote the formation of a porous foamed char structure – titanium dioxide, barium and zinc borates, magnesium hydroxide, aluminum hydroxide, calcium carbonate;
- those that suppress the expansion – aluminum hydroxide, zeolite, sodium tripolyphosphate.

The most effective fillers for stimulating foam formation are titanium dioxide and magnesium hydroxide. Zinc borate, talc, kaolin, and fiberglass contribute to the formation of glassy and ceramic charred structures, strengthening the foamy framework [47, 48]. For example, at temperatures up to 600°C, APP reacts with talc to form crystalline products such as $Mg_2P_4O_{12}$, MgP_4O_{11}, SiP_2O_7, and $Si_5O(PO_4)_6$. At temperatures close to 1000°C, glass-like magnesium and silicon phosphates are formed [47].

➢ *Physical Aspects of Intumescent Char Formation.*

Intumescent fire protection is characterized by the coating's ability to expand and retain the char intact on the substrate surface. Intumescence proceeds through the following steps: thermal decomposition, expansion, charring, and degradation of the char framework [11, 50, 51].

Appropriate temperature spans for each of the foaming stages, as defined and generalized using data from different sources [39, 50], are presented in Figure 2. The temperature intervals for the char formation are approximate and may shift depending on the composition and the ratio of IFR components [52, 53].

The formation of the char is determined by the interaction of gases with the semi-liquid molten phase, which requires synchronization of the thermal decomposition of the main IFR components [33]. The viscoelastic properties of the molten phase affect the morphology of the char, while excessive foaming can reduce its mechanical stability [54, 55].

The intumescent char is heterogeneous in its composition. It consists of a condensed phase, whose carbonized cells contain trapped gases. The condensed phase, in turn, consists of solid and liquid phases (acidic resins), which contain both liquid and gaseous polymer decomposition products. The carbonized fractions of the condensed phase include polyaromatic fragments, which form layered structures, characteristic of graphitic systems [56, 57].

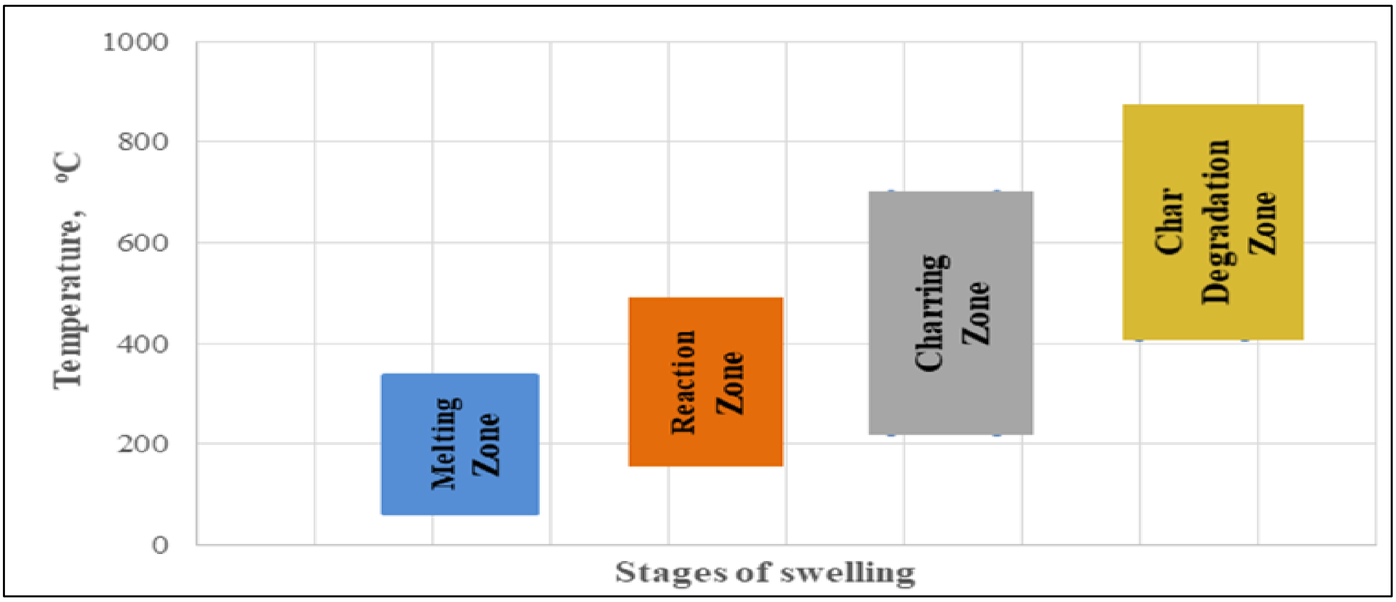

Fig 2 Temperature Profile of Intumescence Stages

Over time, distinct zones, composed of crystalline macromolecular polyaromatic layers, form within the material. These structures are made of crystalline particles linked by bridging bonds of polymer chains and phosphate groups (poly-, di-, or orthophosphate), and an amorphous phase, which is embedded within the crystalline zones [58, 59]. The amorphous phase consists of small polyaromatic molecules formed through the hydrolysis of phosphate fragments from alkyl chains, resulting from the decomposition of additives and polymer chain fragments. A phosphorous-containing carbonized char will exhibit fire-protective properties under the following conditions: this material must be sufficiently voluminous to cover the surface and strong enough to maintain integrity [59, 60].

The fire protection efficiency of the coating depends on the expansion factor, which does not necessarily correlate with other fire-retardant properties [12, 61, 62]. An excessively porous char, however well expanded, loses its mechanical stability, thus reducing its protective effectiveness [11, 12, 63].

The expansion factor of IFR is determined by gas bubble movement within a viscous melt, which affects the structural properties of the coating. Optimal viscosity ensures uniform expansion and the formation of a stable charred framework [12, 64].

Studies have shown that unmodified IFRs without stabilizing fillers do not provide sufficient fire protection efficiency, as the formed char has low strength, adhesion, and viscosity [65, 66]. Research on the effects of fillers (e.g., zirconium silicate [67], kaolin [68], boric acid [69], and basalt fiber [70]) confirms that their inclusion improves thermal characteristics and stability of the char. Additives such as titanium dioxide and boron compounds regulate rheological properties of the polymer melt and contribute to the reinforcement of the formed char [71-73].

Thermal conductivity of the char framework is a key parameter in fire protection and depends on the cellular structure of the char [12, 74]. At temperatures below 200°C, expansion is minimal, while at higher temperatures, increase in the char porosity reduces its thermal conductivity. Above 375°C, charred layer degradation stabilizes this parameter, limiting heat transfer to the substrate [75-77].

Thus, to enhance the efficiency of IFR, it is crucial to conduct comprehensive studies on the physicochemical properties of coatings, including their rheological characteristics, mechanical strength, and thermal stability. This approach can help systemically optimize formulations and develop more effective intumescent compositions.

III. FIRE-RETARDANT NANOCOATINGS FOR STEEL STRUCTURES

➢ *Fire-Retardant Coatings Containing Nanomaterials Can Be Conventionally Referred to as Nanocoatings [14]. Nanofillers Impart Several Additional Properties to Such Coatings [78, 79]:*

- improved fire resistance characteristics (increased decomposition temperature, reduced smoke formation);
- reduced weight and thickness (lightweight and thin coatings without loss of efficiency);
- environmental safety (no toxic emissions upon heating);
- multifunctionality (simultaneous improvement of multiple material properties).

➢ *Use of Nanocompounds for Enhancing the Efficiency of Fire-Retardant Reactive Coatings.*

The modification of intumescent coatings with nanoparticles of organic and inorganic nature, which results in the formation of nanocoatings, is a common research direction for improving the APP/MA/PE/polymer system. Nanocoatings are at their core multicomponent materials that may include nanoparticles of various types, including clay minerals, metal oxides, carbon nanomaterials, and hybrid nanostructures [13, 80, 81].

For example, to enhance the thermal stability of the intumescent char at high temperatures, three categories of nanocompounds have been habitually used: layered inorganic materials, nanofibers, and metal-containing nanoparticles [10]. The authors suggest that nanofillers in IFR can serve as substitutes for banned halogen-containing flame retardants. Several studies [48, 82, 83] have explored the positive effects of the following nanofillers in strengthening the intumescent char framework: metal oxides, layered silicates, layered double hydroxides (LDH), carbon nanotubes (CNTs), nanosilica gel, nanotitanium, nanoaluminum, fullerenes, and silsesquioxanes [48, 84].

Nanoclays are widely used as modifiers in passive fire protection [11, 12, 85]. Bentonite clay derivatives are employed in intumescent compositions as fire-retardant additives and rheology regulators. However, questions remain about the optimal amount and structure of nanoclay additives and their role in the overall fire protection mechanism of IFR. A study [86] examined the effect of Cloisite 15A nanoclay (oMMT, montmorillonite modified with quaternary ammonium salt) on fire resistance of the APP/MA/PE/styrene-acrylate (SA) system. TGA analysis of the intumescent coatings showed increased thermal stability in systems with nanoclay. This effect [86] results from the influence of oMMT on the copolymer stability, which in turn prolongs the overall stability of the char. The retention of a stable carbon-rich char structure lasts longer than for IFR formulations without additives. However, it was found that higher concentrations of organoclay do not enhance the thermal stability of the coating further.

The study [87] analyzed the impact of MMT and organically modified montmorillonite (oMMT) on the formation of the char produced by an intumescent system integrated into a styrene-butadiene-styrene (SBS) matrix. TGA analysis, IR spectroscopy, and X-ray diffraction demonstrated that both MMT and oMMT promote the formation of cross-linked structures within the char, improving its thermal stability.

However, further scanning electron microscopy (SEM) analysis combined with real-time layer resistance measurements revealed significant differences between these materials. oMMT significantly improves the expansion and continuity of the intumescent char, whereas MMT, on the contrary, causes char ruptures during expansion, negatively impacting the fire resistance of the material. Thus, the synergistic effect of oMMT with IFR surpasses that of MMT, mainly because oMMT disperses better within the SBS matrix, increasing the viscosity of the molten intumescent layer, preventing gas escape, and enhancing expansion and char integrity [87].

Studies on bentonite-based organoclays in intumescent APP/PE/MA systems have been conducted to reduce the flammability of polymers such as EVA [88], various polyolefins [89], polyamides and their derivatives [90], and other thermoplastic polymeric materials [91, 92].

Several examples of reducing polymer flammability using IFR or its components in combination with nanoclays are presented in Table 2.

Table 2 Combined Influence of Montmorillonite and Intumescent Systems on the Fire Resistance of Polymers [14, 78]

Polymer	MMT, wt%	Synergist, wt%	Effects
Polypropylene PP	MMT (4,0)	PE, APP, melamine polyphosphate (20,0)	78% reduction in PHRR
	Cetyltrimethyl ammonium bromide modified Fe-MMT (6,0)	PE (3,6), APP (8,1), melamine polyphosphate (6,3)	LOI value increase from 17.0% (pure PP) to 29.0% UL-94 V0 rating achieved
Polylactide PLA	N, N-dimethyl dehydrogenated tallow quaternary ammonium chloride modified MMT (5,0)	PE (3,0), APP (9,0), MA (3,0)	LOI value increase from 20.1% (pure PLA) to 27.5%
Low-density polyethylene LDPE ethylene-vinyl acetate copolymer EVA	Hexadecyltrimethylammonium bromide modified MMT (4,0)	Polypiperazine spirocyclic pentaerythritol bisphosphonate (16,0)	50 % reduction in PHRR

Examination of EVA/APP/PA-6 and EVA/APP/PA-6/MMT mixtures, where the nanoclay MMT content was 2 wt.% was conducted in the study [93]. Cone calorimetry showed a reduction in the peak heat release rate (PHRR) from 320 to 240 kW/m² in the presence of MMT, as well as a decrease in EVA flammability according to LOI and UL94 standards. However, above 200°C, MMT catalyzes EVA thermal degradation and increases the overall flammability of the EVA/APP/PA-6 IFR formulation.

In a similar study [83] that investigated the effect of oMMT on the thermal properties of the APP/PE/MA/styrene-methyl methacrylate copolymer (SMA) system, a positive effect of oMMT on the LOI value was also established. The LOI increased with the content of nanoclay in the investigated IFR. An extreme dependence of fire resistance on the amount of oMMT was found: a positive effect at oMMT content up to 1.5% and a negative impact at oMMT content of 3% or higher.

A synergistic effect was observed [94] between APP and imogolite, a silicate clay mineral with the general formula $Al_2SiO_3(OH)_4$, when studying the fire resistance of unsaturated polyester resin (UPR). Imogolite consists of a complex network of nanotubes with an outer diameter of approximately 2 nm and an inner diameter of about 1 nm. The inner part of the nanotube is composed of Si-OH, while the outer part consists of Al_2-OH. These nanotubes do not disperse easily in hydrophobic polymers, so they are priorly functionalized with ionic liquids. According to cone calorimetry, the PHRR of pure UPR is 666.25 kW/m², for UPR/APP it is 516.68 kW/m² (22.4% lower), and for the UPR/APP/imogolite nanotube composite, it is registered at 392.46 kW/m² (41.1% lower).

The synergistic effect of IFR combination with nanoclays on the intumescent fire protection mechanism is explained by their involvement in char formation in the condensed phase, leading to a stronger and more thermally stable expanded foam. It has been established that the introduction of nanoclays promotes the synthesis of crosslinked structures in the condensed phase, enhancing char's thermal stability and creating a barrier effect that improves the fire-retardant characteristics of IFR [92, 95].

Recently, the use of layered double hydroxide (LDH) nanoparticles has emerged as a trend in reducing polymer flammability and enhancing IFR efficiency [14, 96, 97]. Layered double hydroxides, with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}A^{n-}_{x/n}\cdot H_2O$, consist of metal cation layers (M) and hydroxyl groups, with inorganic or organic anions (A) and solvent molecules located between them to balance the positive charge. Due to their tunable structure, they can be used as environmentally friendly flame retardants [98] and smoke suppressants given the correct choice of metals and anions. The mechanism of LDH action is based on enhancing formation of a stable char, reducing oxygen availability, and decreasing the concentration of combustible gases through water molecule release. The concentration of this nanofiller is similar to that of clay-based nanoparticles, ranging from 0.1 to 10 wt.% [98].

Since inorganic hydroxides such as Al $(OH)_3$ or Mg $(OH)_2$ are effective flame retardants only at high concentrations, materials like LDH, which are more compatible with the polymer matrix and provide better dispersion due to lower hydrophilicity, have become an optimal choice for achieving the required level of fire resistance. A lower amount of LDH is needed to achieve the same physical barrier effect, but it must be used in combination with other flame retardants. In study [99], it was shown that the addition of tricresyl phosphate (TXP) and dodecyl sulfate intercalated with magnesium-aluminum nitrate LDH (MgAl DS LDH) to UPR increases the thermal stability of the nanocomposite. The decomposition of LDH into water and metal oxides catalyzes and enhances char formation from fragmented polymer chains during pyrolysis.

It was found that $CaAlCO_3$-LDH and MMT fillers increase the fire resistance threshold of metal by 20 minutes when applied in an intumescent coating. The authors attributed this effect to the chemical modification of the carbonaceous char layer through Si-alloying. The formation of Si-C structures with limited lattice deformation stabilizes the porous carbon layer, thereby improving its thermal protection properties [100].

Studies [97, 101, 102] examined the influence of two-dimensional LDH on the flammability of certain polymers in combination with various flame retardants. It was established that LDH compounds act synergistically with traditional flame retardants such as Mg $(OH)_2$, APP, and IFR [14, 101, 102]. The summarized results are presented in Table 3.

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Table 3 The Effect of LDH Combined with Flame Retardants on the Flammability of Polymers [14, 78, 102]

Polymer/ Copolymer	LDH, wt%	Synergist / flame retardant, wt%	Effects observed
Polyvinyl alcohol PVA	Zn-Al (0,7) Ni-Al (0,7) Ni-Fe (0,7)	APP (14,3)	LOI increased to 30,0% from 19,7%; UL-94 V0 rating obtained
EVA copolymer	Mg-Al (7,5)	$Mg(OH)_2$ (42,5)	LOI increased to 34,0% from 18,0%
	Mg-Al-Fe (32,5)	APP (17,5)	UL-94 V0 rating obtained
	Mg-Al-Fe (45,0)	MA (5,0)	LOI increased to 25,6% from 17,0%; UL-94 V0 rating obtained
	Mg-Al, Zn-Al, Mg-Fe (5,0)	$Mg(OH)_2$ (45,0)	pHRR decrease EVA/$Mg(OH)_2$ /$Mg(OH)_2$ -Al LDH (-88%); EVA/$Mg(OH)_2$ /Zn-Al LDH (-78%); EVA/ $Mg(OH)_2$ /Mg-Fe LDH (-85%); EVA/ $Mg(OH)_2$ (-70%).
Polylactide PLA	Zn-Al LDH (2,0)	IFR– PE (9,2), APP (9,2) MC (4,6)	PHRR decrease PLA/IC (-43%); PLA/IC/Zn-Al LDH (-59%).
Polypropylene PP	Mg-Al LDH (4,0); Mg-Zn-Al LDH (4,0)	APP (16,0)	PP/IC/Mg-Zn-Al LDH UL-94 V0 rating achieved

Several studies demonstrate that nanosized SiO_2, in combination with intumescent systems, enhances fire resistance and water resistance of coatings [103, 104, 105]. It has been proven [103, 104, 105] that the inclusion of nano-SiO_2 into the APP/MA/PE system positively affects the formation and charring of the intumescent foam. Nano-SiO_2 gel does not exhibit chemical activity, does not decompose with the release of water or gases, and does not promote polymer crosslinking. The fire resistance imparted to polypropylene and polyethylene oxide by various forms of silicon dioxide (silica gel, silica sol) has been examined in [106]. In the condensed phase, silica accumulates on the sample surface, acting as an insulating layer, creating a radiation shield and a mass transfer barrier. Additionally, under high-temperature conditions, Si can chemically interact with P or N, improving the thermal stability of the char and suppressing smoke formation [14, 106].

The modification of reactive coatings with nanoparticles of inorganic oxides and metal salts is one of the methods for creating fire-retardant nanocoatings with enhanced efficiency [14, 107]. Specifically, the positive effect of nano-MgO in the APP/MA/EG/boric acid/zinc borate/MgO/bisphenol A system has been reported in [108], nano-TiO_2 in the APP/PE/MA/polymer system in [109], and nano-oxides such as Fe_2O_3, ZnO, and TiO_2 in IFR with bicyclic phosphate in epoxy coatings in [110]. Additionally, nano-TiO_2 has been studied in epoxy-based intumescent fire-retardant coatings for hydrocarbon fire [14, 111, 112].

Carbon-based nanofillers are represented by a large group of compounds, including single-walled (SWCNT) and multi-walled (MWCNT) carbon nanotubes, graphite oxide, expandable graphite (EG), graphene, fullerenes, and others [113, 114, 115]. The mechanism of action for these nanofillers is based on the formation of a protective layer acting as a thermal barrier [114]. However, carbon-based nanofillers are typically used in combination with other flame retardants, as their effectiveness significantly increases in such formulations [114]. Their content can range from 0.1 to 25 wt.% [116, 117].

Studies have shown that carbon nanotubes (CNTs) serve as ideal fire-retardant fillers [118]. During combustion, they form a protective network structure that enhances the strength of the intumescent char, reduces voids and cracks, improves density, increases fire resistance, and reduces smoke formation [119]. However, some studies claim that when used as standalone fillers in coatings for steel substrates, MWNTs may cause cracking and hole formation in the char, showing no improvement to the fire resistance of the coatings [120].

The combination of graphene and carbon nanotubes has been shown to more effectively prevent the release of combustible gases from the intumescent layer during the combustion, thereby improving its expansion. Moreover, increasing the graphene content enhances the mechanical properties of the coatings [121, 122].

A study [123] found that introduction of MWCNT/$NiFe_2O_4$ nanofiller into the coating contributes to the formation of a protective barrier that reduces heat release. Specifically, the PHRR value of a nanocomposite based on UPS with 2 wt.% MWCNT/$NiFe_2O_4$ decreased from 1098 kW/m^2 to 335 kW/m^2. This reduction in PHRR compared to pure UPS was more significant than that for the composites containing individual fillers, which indicates a synergistic effect. These results also highlight the importance of achieving sufficient dispersion of nanofillers within the matrix [123].

TGA showed [124] that the addition of 0.5 wt.% MWCNT in an intumescent system based on epoxy polymer increases the residual char mass by 29.35 wt.%, reducing oxygen content by approximately 25 wt.%, which improves the fire resistance of the nanocoating.

Similar studies on fire-resistant polymer composites based on PP were conducted in [125], where expandable graphite, carbon black, MWCNT, and graphene were used as nanofillers. Graphene exhibited the highest reduction in PHRR (-76%).

It is known [126, 127] that the presence of graphene, during polymer combustion in cone calorimetery, reduces the heat release rate, however LOI values and UL-94 ratings may not necessarily improve. However, a synergistic effect is observed when graphene is combined with traditional flame retardants (Table 4 [14, 78]).

Table 4 Synergistic Effect of Graphene with Other Additives on Flame Retardant Properties of Polymer Composites [14, 78]

Polymer	Graphene content	Synergist / flame retardants	Observed effects
Poly (butylene succinate) PBS	2 wt%	APP (12 wt%) MA (6 wt%)	LOI value increased to 33.0% from 23.0% (pure PBS) UL-94 V0 rating achieved
PP	1 wt%	CNT (1 wt%) MPP (14.4 wt%) PE (3.6 wt%)	LOI value 31.4% UL-94 V0 rating PHRR decreased by 83%
Polyethylene PE	0.2 wt%	ATH (40 wt%)	PHRR decreased by 18% compared to PE/ATH composite
Polyurethane PU	2 wt%	APP (12 wt%) MA (6 wt%)	LOI value increased from 22.0% to 34.0% Excellent antidripping properties UL-94 V0 rating achieved
Poly (methyl methacrylate) PMMA .	1 wt%	LDH (5 wt%) 1,2-Bis (5,5-dimethyl-1,3,2-dioxyphospacyclohexane phosphoryl amide) ethane (10 wt%)	PHRR decreased by 45% UL-94 V-1 rating achieved

Expandable graphite (EG) retains the high-temperature resistance and corrosion resistance of graphite but possesses unique properties not found in natural graphite, including flexibility, elasticity, impermeability, and porosity [128]. One of its key characteristics is its synergistic interaction with other flame retardants. When used as a filler in combination with $MoSi_2$ [129], zirconium silicate [130], or dolomite [128], it demonstrates a synergistic effect in increasing the density and thermal stability of the intumescent char while also enhancing fire resistance and the overall mechanical properties of the coating.

Polyhedral oligomeric silsesquioxanes (POSS) are nanoscale structures that can be functionalized with reactive groups to create new organic-inorganic hybrids. The chemical structure of POSS can be represented by the general formula $(RSiO_{1.5})_n$, where n = 6, 8, 10, ..., and R is an organic radical, including the ones carrying a reactive group. The thermal and chemical stability of these materials is due to their inorganic framework, while other properties can be determined by the organic substituents. In addition to improving fire resistance, nanocomposites containing POSS exhibit lower viscosity, improved mechanical properties, and enhanced oxidation resistance [116].

In [131], a functionalized phosphorus-nitrogen-containing POSS (F-POSS) with a low oxidation state of phosphorus was developed. Its nanocomposite with polybutylene terephthalate (PBT), PBT/F-POSS, was obtained via melt blending, demonstrating improved thermal stability and thermo-oxidative resistance compared to PBT and PBT/POSS. In cone calorimetery, the peak heat release rate (PHRR), peak smoke production rate (PSPR), peak CO_2 production rate (PCO2P), and peak CO production rate (PCOP) in PBT/F-POSS decreased by 50%, 46%, 45%, and 35%, respectively, compared to pure PBT. The analysis of the charred residue showed that during expansion and carbonization, the phosphine groups of F-POSS can capture free radicals or decomposition products from PBT and form a stable $SiO_xC_yP_z$ network [131].

Currently, the demand for renewable and environmentally friendly materials is driving researchers toward the synthesis of bio-based flame retardants. Biomass conversion leads to the isolation of proteins, carbohydrates, lipids, and phenolic compounds. Saccharide-based products (cellulose, starch, and chitosan), bio-based aromatic compounds (lignin, gallic and ellagic acids), proteins (casein), and phytic acid are some examples of compounds that can serve as flame retardants either in their pure form or after specific modification. The flame-retardant action for most of these compounds is based on their ability to donate carbon to the forming intumescent char [132].

Phytic acid, polyphenol, and polydopamine are the three bio-based compounds widely used in fire-retardant coatings [133, 134, 135]. Phytic acid has multiple phosphoric acid groups capable of chelating transition metal ions, forming layered structures. Fire-retardant coatings containing phytic acid easily form compact char on the surface of burning materials, blocking mass and heat transfer. However, the acidity of phytic acid is too high for it to be compatible with the relatively hydrophobic surfaces. Due to its high acidity, alkaline compounds are usually added to improve compatibility with hydrophobic surfaces in reactive coatings.

The authors of [136] developed a multilayered fire-retardant coating based on polyvinyl alcohol (PVA) by incorporating a layer of phytic acid between two layers of melamine-doped polyethyleneimine. The resulting coating material is ultra-thin and transparent, incorporating only ~6 wt.% of the polyvinyl alcohol matrix (PVA). This modification increased the tensile strength of PVA and significantly reduced the PHRR (-37%) [136].

Other examples of bio-based nanoscale flame retardants include cyclodextrins and hydroxyapatite [137]. Among these bio-based compounds, some cellulose-derived materials can be obtained in nanoscale form. Cellulose nanofibers and nanocrystals can be used to enhance the thermal stability of composites [138].

Recently, compounds derived from waste recycling or other secondary resources have been used as nanofillers in fire-retardant coatings. For example, study [139] describes an intumescent fire-retardant coating based on a vinyl acetate copolymer loaded with 3 wt.% of eggshell-derived nanofillers.

- *Mechanisms of Fire-Retardant Action of Nanomaterials (Chemical Factors).*

The fire-retardant properties of nanomaterials are determined by their ability to influence combustion processes through physical and chemical mechanisms. The combination of these mechanisms significantly enhances the thermal stability of materials, reduces the decomposition rate of polymers, and minimizes the release of flammable gases [14, 140]. However, the distinction between chemical and physical factors is somewhat arbitrary, as they are interconnected and interact with each other [14].

The specific conditions under which reactions occur in IFR (high-temperature processes, uncontrolled combustion, and multicomponent systems) complicate the identification of exact interaction mechanisms between nanoparticles and other components of reactive coatings. Hypotheses about the involvement of nanoparticles in the intumescent process are based on analogies and general knowledge of the physical and chemical behavior of nanomaterials, such as nano-oxides, layered silicates, and carbon nanotubes [141].

Nevertheless, only a limited number of studies have successfully demonstrated the effect of nanofillers on specific stages of reactions pathways in intumescent systems. The following modes of action of layered nanomaterials were identified in study [101]:

- Participation in thermal decomposition processes: With increasing temperature, LDH releases water vapor and CO_2, which dilute flammable gases, reducing their concentration;
- Catalysis of polymer thermal degradation by metal ions, promoting the formation of non-flammable volatile products and preventing the generation of flammable radicals;
- Catalytic effect on the formation of graphene-like chars from polycyclic aromatic hydrocarbons;
- Prevention of oxidation reactions occurring in the gas phase by capturing free radicals (such as H• and OH•) generated during polymer decomposition;
- Synergistic effect with IFR flame retardants: Nanomaterials can interact with IFR components, enhancing their effectiveness and reducing the required concentration of flame retardants in the material [14, 142].

A general trend in the involvement of nanoscale compounds in IFR component reactions at high temperatures is the formation of cyclic aromatic compounds, which transform into thermally stable conglomerates of charred residues. These compounds ensure sufficient thermal stability of the intumescent char.

Numerous studies have investigated the thermal decomposition of EVA in the presence of MMT and other nanoscale compounds [143, 144, 145]. For example, in study [146], MMT was shown to catalyze the cyclization of polyenes (products of EVA deacetylation) into aromatic fragments, forming a charred ceramic surface on the expanded intumescent coating.

The influence of aluminosilicates (zeolite 4A, 13X, and mordenite) on the thermal transformations of the APP/PE system has been studied in [147]. Using TGA and X-ray photoelectron spectroscopy, the following mechanism of nanoclay involvement was established:

- T < 250 °C: catalysis of the esterification reaction between APP and PE;
- T 250-450 °C: catalysis of cross-linking reactions and incorporation of SiO_2 and Al_2O_3 oxides into the carbon structure;
- T > 600 °C: inhibition of the char degradation.

At high temperatures, SiO_2 and Al_2O_3 from MMT are highly likely to react with the phosphate degradation products of APP, forming thermally stable Si-O-P-O-Al-O-C structures, polyaromatic compounds, and metal-aluminophosphates [14, 142].

The hypotheses proposed by Tang et al. regarding the influence of nanofillers on intumescence, presented in study [148], generally align with the conclusions of study [147]. The role of MMT in the PA-6/APP/MMT/EVA system has been analyzed in terms of:

- the formation of thermally stable alumino-phosphate-ceramic compounds;
- acid catalysis of processes accompanying the thermal decomposition of EVA;
- the release and decomposition of acetic acid, elimination of polyenes, and their cyclization, leading to char formation.

Research shows that layered silicates improve the fire retardancy of nano-coatings, but their large-scale production is only feasible with a deeper understanding of the interaction mechanisms between nanofillers and traditional flame retardants. One of the key challenges is studying the chemical activity of silicate functional groups during combustion and their impact on fire protection effectiveness. Additionally, questions remain regarding the quantitative correlation between peak heat release rate (pHRR) reduction and the degree of nano-sized flame retardants dispersion in the polymer matrix.

- *Mechanisms of Fire-Retardant Action of Nanomaterials (Physical Factors).*

The physical influence occurs majorly via three different mechanisms [149, 150]: the cooling effect, fuel dilution, and the formation of a protective layer. In the first mechanism, temperature decreases during endothermic reactions; in the second, nanoparticles promote the release of non-combustible gases, which reduce the oxygen concentration in the combustion zone; while in the third case, they facilitate the formation of an impermeable protective layer on the surface of the expanded intumescent material.

The main physical factors of influence that nanomaterials create in polymeric intumescent systems under high-temperature conditions include:

- enhancing thermal insulation provided by the char by structuring it with nanofiller particles, which reduces heat transfer and slows down the thermal degradation of the polymer matrix;
- reducing toxic gases emissions;
- lowering the oxygen content in the combustion zone;
- formation of a scale layer during nanocomposite combustion, which reduces the maximum temperature and the rate of fire spread;
- increasing the adhesive strength of coatings;
- increasing the viscosity of the polymer melt, which complicates the diffusion of volatile combustible compounds and slows down their release into the flame zone [142, 151, 152].

The barrier effects of nanoparticles involve forming a glassy layer that prevents the release of volatile gases, hindering oxygen access to the substrate and protecting the material surface from high-temperature exposure [101, 151, 153]. The use of plate-like nanoparticles (usually in concentrations of less than 5 wt.%) allows the material to acquire a specific gas barrier and flame-retardant properties. In the first case, uniformly dispersed nanoparticles create a tortuous pathway that slows down the diffusion of gas molecules through the polymer matrix. In the second case, layered nanomaterials form an inorganic, non-combustible barrier on the polymer surface, reducing the burning rate [154].

It is also evident that the addition of nanofillers should not be considered a universal approach to improve fire-retardant properties or reduce the flammability of polymeric materials for all intumescent flame retardants (IFR). It is necessary to find methods to resolve the contradictions regarding the differing effects of nanomodifiers in IFR [14]:

- enhancing the positive effect, which involves forming a heat-resistant nanocomposite between the polymer and, for example, nanoclay, and the participation of silicon and metal atoms in the construction of an intumescent char structure with prolonged lifespan under high-temperature exposure;
- eliminating the reduction of the expansion factor, which occurs as a consequence of barrier restrictions on gas migration in the condensed phase, significantly limiting normal thermal behavior of an intumescent coating.

The individual contributions of both of these effects to the overall mechanism of nanofiller action determines the efficiency of fire-retardant nanocoatings.

The barrier effect poses a significant threat to the formation of the expanded layer under thermal impact on IFR. The formation of a hard, rigid surface that hindered the expansion of a nylon-6/MMT (5 wt.%) system was described in [155]. The authors of this study observed the formation of carbon capsules that completely blocked the release of gases formed during polymer thermal degradation. To eliminate the negative manifestations of the barrier effect, Alongi et al. propose a new concept for designing nanocoatings, which involves applying nanoparticles to the surface of the polymeric intumescent coating instead of direct introduction of those into the coating formulation [156].

IV. CONCLUSIONS

The most common and widely used intumescent system in industrial-scale production of fire-retardant reactive coatings for steel structures is the APP/PE/MA/polymer composition. Enhancing its fire-retardant efficiency and improving its environmental characteristics—particularly by significantly reducing smoke generation during fire—is possible through the use of nanomaterials. Among the most promising and multifunctional nanofillers are layered nanoclays, LDH compounds, nanostructured carbon forms, and nano-silicon oxides.

Nanomaterials play a key role in enhancing the fire-retardant properties of intumescent systems by utilizing both chemical and physical fire protection mechanisms. Physical effects, such as barrier protection and reduced thermal conductivity, contribute to the mechanical deceleration of combustion processes, while chemical mechanisms operate at the molecular level, altering the composition and mechanism of polymer thermal degradation.

The methods applied to incorporate nano-sized fire retardants into polymer coatings are crucial, particularly the chemical modification of these additives to improve their interaction with the polymer matrix. Replacing halogen-containing flame retardants with environmentally friendly nanocomposites is a promising direction that requires further research.

The effectiveness of fire-retardant nanomaterials depends on their uniform dispersion within the polymer matrix and their interaction with traditional flame retardants. Considering these factors, nanomaterials continue to be a promising research direction for the advancement of fire-retardant coatings.

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