INTRODUCTION TO INTUMESCENT FIRE RETARDANT COATING

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Introduction

This chapter describes a brief overview of Intumescent Fire Retardant Coating (IFRC), starting from the basics of fire leading to its impact on structural steel and how IFRC could protect it. Moreover, the control is confined to protect structural steel in uncontrolled fire, but it is widely used in other thermoplastic applications. However, much attention is paid to its application as a thermosetting polymer composite in the present context. Furthermore, titanium oxide (micron-sized) based IFRC coupled with Expandable Graphite (EG) and a range of additives is developed and applied on a sandblasted structural steel substrate. The coated substrates were tested using fire and other characterisation techniques to evaluate the char and degradation compounds. Large-scale industrial fire test as per BS 476 Part 20 was conducted on alumina-based IFRC. The results are offered in the upcoming chapter, where substrate thickness on coating performance is evaluated.

Fire and Prevention

Fire is the outcome of the combustion process and an exothermic reaction, which gives off heat and variable intensities. It could be either slow or fast, depending upon available oxygen. Significant elements of fire are fuel, oxygen, and energy, as shown in schematic Figure 1.

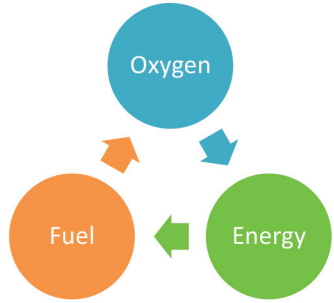


Figure 1 Fire triangle

A chemical reaction takes place on a combination of three components leading to the fire. Fuel could be in any form of matter like hydrocarbons, wood, paper, etc. However, at this point, it is worth mentioning that the fuel must be heated to its critical temperature before the fire takes place, and it lasts if the fuel, oxygen, and heat are present. Fuel is heated to an extent where fire occurs, and because of chemical reactions, the gases are released from the surface.

Types of Fire

Generally, fire can be divided into cellulosic, hydrocarbon, electric, and chemical fires, generally known as Class A, B, C, and D.

Cellulosic Fire

This type of fire involves ordinary combustible materials like cloth, paper, plastic, wood, etc. It usually occurs in residential buildings, offices, shopping malls, airports, warehouses, etc. Due to the slow heat rise rate and maximum temperature of 950°C in 60 mins, it can be extinguished quickly using dry or wet chemicals. However, Air Pressurised Water (APW) fire extinguishers are particularly designed to extinguish this fire class.

Hydrocarbon Fire

This type of fire is due to the burning of flammable liquids like hydrocarbons. It occurs at petrochemical plants, onshore and offshore structures, etc. It is fueled by flammable liquids, gases, or products

derived from hydrocarbons. It has a high heat rise rate and temperature, as shown in Figure 2. Dry chemical or carbon dioxide-based extinguishers are particularly designed to overcome this type of fire. For example, in the case of fire to the hydrocarbon storage tanks, the shell's temperature rises rapidly, so as the internal pressure. If the fire is uncontrolled, the internal pressure reaches its maximum value. If it exceeds the tank's design strength, a catastrophic failure in the form of BLEVE (boiling liquid expanding vapour explosion) occurs.

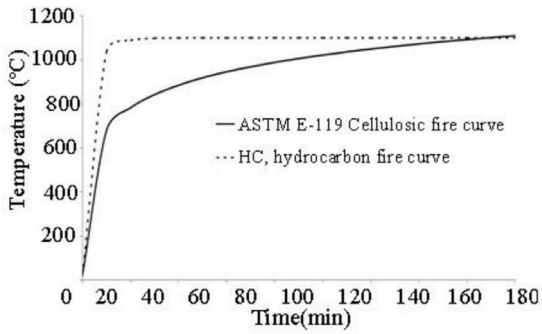


Figure 2 Comparison of cellulosic versus hydrocarbon fire curves [1]

Electric Fire

Electrical appliances like switch gears, short circuits, wirings, etc., are the major causes of this fire type. However, it can be extinguished quickly using dry chemicals like mono ammonium phosphate or carbon dioxide-based extinguishers.

Chemical Fire

This type of fire usually occurs in chemical laboratories that involve combustible metals like sodium, magnesium, or other alkali metals. It can be extinguished by using a dry powder that contains sodium chloride or graphite.

Stages of Fire

Fire ignition involved four stages: incipient, growth, fully developed, and decay [2], as shown in Figure 3 [3] and briefly described in the following section.

Incipient

It is the first stage that initiates with the combination of fuel, heat, and oxygen. A chemical reaction takes place, leading to the fire. Controlling a fire at this stage is relatively easy and can prevent major losses.

Growth

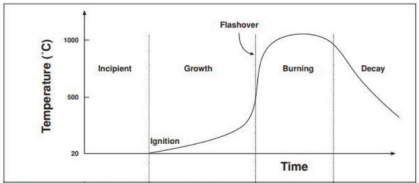
In the second stage, a fire starts affecting the environment, and during the early step of growth, heat is transferred due to convection. Later, the oxygen and structural fire load act as fuel for the fire.

Fully Developed/Burning

It is the severe stage of fire where the temperature and heat release rate reaches their highest value, and in some cases, the temperature may reach above 120°C. There is a plateau at maximum temperature, and afterward, it starts decreasing due to the severity of the fire, all the flammable material burns.

Decay

It is the final and extended stage of fire. Fuel or oxygen begins to decrease that ultimately leads to extinguishing the fire.



Stage	Incipient	Growth	Burning	Decay
Fire behaviour	Heating of fuel	Fuel-controlled burning	Ventilation -controlled	Fuel-controlled burning
Human behaviour	Prevent fire	Extinguish by hand, escape	Death	
Detection	Smoke detectors	Smoke detectors Heat detectors	External smoke and flame	
Active control	—	Extinguish by sprinklers of Fire Service, Smoke control	Control by Fire Service	
Passive control	Control of materials	Flammability, surface spread of flame	Fire resistance, containment, prevent collapse	

Figure 3 Time versus temperature profile for fire [3]

Structural Steel

Structural steel is a non-combustible material and an essential part of any construction. It is also commonly used in several products such as rails, beams and columns, plates and coils, angles and channels, structural elements, and reinforcing steel. The role of steel is vast, i.e., continual. It is highly resistant to extreme natural catastrophes in earthquakes due to its strength and ductility, and many seismic actions show it around the globe. For example, during the 1994 Northridge earthquake in California, 96% of all steel bridges remained undamaged. Like other construction materials such as wood, structural steel loses its mechanical properties above its critical temperatures. Strength and stiffness are two main mechanical properties of steel, which deteriorate with the increase in temperature. Strength can be expressed as the maximum stress per unit area which a material can bear. Stiffness is the force required per unit deflection. Both properties are usually taken as constant at normal temperatures, but these properties no longer remain unchanged at a higher temperature. It needs to insulate the steel at a higher temperature to conserve its load-bearing capacity. Besides the deterioration of steel's mechanical properties, thermal properties like thermal conductivity and thermal expansion are also affected by temperature rise. Although steel is a non-combustible material, it starts losing its load-bearing ability above the critical temperature, 500°C. According to the international building regulations implemented in most countries, an essential prerequisite is to conserve the veracity of steel for 1-3 h in case of fire when the fire temperature is more than 1100°C and to ensure the safe evacuation of people.

Heating the structural steel at 600°C for more than 15 mins reduces 50% of its load-bearing capability and leads to deforming, twisting, or buckling, and crystalline or metallurgical properties undergo deformation. Jimenez et al. [4] elaborated that the structural steel loses its structural properties at a minimum of 470°C. For safety reasons, in offshore structures, the failure temperature is kept as low as 400°C, but in other onshore sites, approximately 550°C. Studies have shown that on exposing structural steel members to fire, the following points were obtained,

1. The steel temperature has an inverse relation with the distance of steel from the center of the fire. As the distance from the center of the fire to the steel member increases, the steel temperature reduces.

2. The temperature of shielded steel members near the fire is significantly less than the unshielded steel member.
3. The temperature of steel members significantly reduces by using a proper fire compartment.

The structural steel member is heated up to 650°C; yield strength, tensile strength, and modulus of elasticity are decreased.
The types of structural steel are as follows,

1. Carbon-Manganese steel.
2. High-strength, low alloy steel.
3. High strength quenched and tempered steel alloy.

The major constituents for this type of steel are carbon and manganese other than iron. Materials for this type are relatively low cost and have sufficient strength and ductility. The most common is ASTM A36, and it is extensively used steel grade with a minimum yield stress of 248 MPa. A recent development in steelmaking reported higher strength ranges from 289 MPa to 448 MPa was attained by adding chemical components in a minimal amount. ASTM grade A572 and A588 are the most frequent high-strength steel.

Flame Retardant Materials

Flame retardant materials can be defined as materials incorporated into combustible materials that make them more resistant to an explosion. These are designed to reduce fire danger when in touch with ignition sources like candles, electrical circuits, cigarettes, etc. Also, these chemicals avert the fire from spreading out. These flame retardant chemicals ensure the safety of different combustible materials from fire for a limited time. We are surrounded by a range of combustible materials such as sofa, cloth, etc. It catches fire in the room and automatically starts developing and will burn other items placed nearby. If the fire is not controlled, the room temperature reaches a flashover point, making it impossible to escape from the room. There is a possibility that the fire will spread out to other places. In such an unfortunate case, flame retardants offer obstruction to ignition and prevent the fire from spreading. Thus, increasing the time to escape and even prevents flashover points. Nowadays, polymers are widely used in

everyday life in the aerospace and automobile industry due to their less weight and enhanced fuel economy, so it becomes mandatory to use flame retardants in these polymers as their melting point is relatively low.

In modern industrialised countries such as Canada, Japan, USA, and Germany, there are about 10 to 12 fire deaths per million inhabitants. The number of severe injuries amounted to 100 to 200 per million inhabitants. There are more than ten fire deaths and 100 severe injuries reported in Europe daily. Most fire deaths occur in residential buildings due to smoke production and less time to evacuate the space. Gases released during the fire are usually toxic due to the incomplete combustion of organic material such as polymer, textile, wood, etc. Carbon Monoxide (CO) is the primary precursor in causing fire deaths, and it is estimated that over 80% of fire deaths are due to toxicity. For example, 17 people were killed due to a fire caused by carbon monoxide poisoning in 1996 at Düsseldorf Airport. Hydrogen cyanide (HCN) is also formed besides carbon monoxide, which is also toxic.

History of Flame Retardants

In the nineteenth century, fireproofing polymer requirements became imperative due to cellulosic nitrate plastics' commercialisation because of their high flammability and fire danger. Conventionally cementitious coatings were used for fireproofing. These cementitious coatings were founded on Portland cement, gypsum, vermiculite material, and different minerals. Different fibrous fillers, additional binders were mixed with water on the desired location and applied by spraying with thickness more than one inch during steel construction. These are named spray fire-resistant materials (SFRM's) by Underwriter's Laboratories (UL). Some coatings were applied by using a roller on the substrate, which is to be protected. These coatings release water and have a thermal efficiency of up to half an hour. It was reported earlier that specific polymers such as melamine resin and polyvinyl chloride have inherently flame-retardant properties. Later, it was found that polyolefin, i.e., polyethylene (PE), polypropylene (PP), and polyesters, are more flammable compared to wood. In the early 1980s, the intumescent fire-retardant system was based on pentaerythritol, melamine, and additives like phosphates. Halogen compounds and aluminium trihydrate (ATH) were the foremost flame retardants. Antimony oxide was used as a synergistic agent with halogen-based compounds.

In the early 1990s, the flame retardant market started to move away

from halogen-based fire retardants. Although halogen-based flame retardants were helpful in some cases, they release hazardous gases during fire decomposition. Thus, in the early 2000s, aluminium tri hydroxide and halogen-based compounds were used as flame retardants. In the same way, the intumescent system as flame retardants is also increasing.

Properties of Flame Retardants

The ideal flame retardants are expected to have the following properties [5],

1. Reduce flammability of polymers and fire spreading
2. Must be thermally safe at the processing temperature
3. Helps to maintain the intrinsic properties of materials
4. Ecologically safe
5. Low cost
6. Long service life
7. Good surface finish

Working Principle of Flame Retardants

Flame Retardants (FR) act both physically and chemically. A physical mechanism-a protective layer is formed, and chemically, the gas-phase reaction is discussed in the upcoming section. FR either slows down or restrains the combustion process. Halogen-based FR releases halogen radicals during thermal decomposition and functions properly through gas free radical inhibition mechanism [6]. Certain flame retardants release non-combustible gases that dilute the quantity of fuel and oxygen delivered to the fire. Different mechanisms by which the flame retardants work is described below.

Inert gas dilution

Thermal decomposition of different additives occurs that liberate a high amount of non-combustible and inert gases. This leads to a reduction in oxygen concentration, which is one of the critical components of the fire triangle as presented earlier in this chapter, and combustible species, and eventually, the fire dies [6].

Thermal quenching

Different additives decompose endothermically, which reduces the coating surface temperature, which ultimately lowers the substrate temperature. A low number of combustible products are produced, and thermal degradation is delayed, due to which it takes longer to affect the fire to affect the substrate [7].

Physical dilution

In this mechanism, the overall quantity of combustible products is reduced by adding inorganic fillers used in large amounts such as glass fiber to reduce flammable material and eventually resistance to fire enhanced [8].

Protective char

During the thermal decomposition of additives, a protective char layer is formed. The substrate is protected with a solid char layer from heat and oxygen, which are the key elements of the combustion process [9].

Types of Flame Retardants

The following types of flame retardants are in use [10],

1. Halogen-based flame retardants
2. Phosphorous-based flame retardants
3. Nitrogen-based flame retardants
4. Inorganic-based flame retardants
5. Nitrogen and Boron-based flame retardants
6. Mineral-based flame retardants

Halogen based flame retardants

Different compounds that have carbon, hydrogen, and oxygen serve as fuel despite flame suppressants. However, these compounds become flame suppressants or gain the ability to quench flame by substituting with one or more halogen atoms [11]. Brominated and chlorinated are two common types of halogen-based flame retardants. In the 1970s,

halogen-based flame retardants were used widely, and during the 1980s, the Brominated flame retardants were dominant [6],[12]. 150000 Metric Tons (MT) of halogenated-based flame retardants were utilised annually worldwide in the 1990s, more than one-quarter of the total flame retardants market [13]. Touval et al. [14] presented an efficient synergistic effect between phosphorous and antimony-based halogen FRs. Brominated flame retardants are used in different electrical equipment such as printed circuit boards, wire, and cable compounds to avoid fire. The FR market has moved away from halogen-based flame retardants, especially in Europe since the 1990s, because of their acute toxic effects, releasing toxic and corrosive gases during the burning of halogen-based FRs [15]. Another environmental hazard faced by researchers is the difficulty in disposing of these flame retardants. Researchers are now focusing on non-halogen-based flame retardants, though less effective and costly than halogenated based. Still, proper optimisation makes it possible to have more effective flame retardants than halogenated-based FRs [16]. Based on their properties, these compounds are safe, low-cost, and environment friendly. Halogenated-based flame retardants act in the gas phase, and when they are incorporated into the substance, they produce radicals during decomposition, which acts as flame quenching as given in Equations 1-4 radicals released at the same time as that of bulk material [17].

$$CH_4 + X \rightarrow CH_3 + HX \quad (1)$$

$$H + HX \rightarrow H_2 + X \quad (2)$$

$$OH + HX \rightarrow H_2O + X \quad (3)$$

$$O + HX \rightarrow OH + X \quad (4)$$

Where X may be chlorine or bromine, iodide-containing compounds are also known, limiting their use due to low thermal stability.

Phosphorous based flame retardants

Phosphorous-based FRs are used widely due to their best thermal performance. Phosphate esters, red phosphorous, and ammonium polyphosphate are used widely in engineering applications, polyurethane foam, thermoset, textiles, and coating. These compounds act both in condensed and vapour phases [18]. Phosphorous and boron-based compounds inhibit the oxidisation of carbon. Phosphorous-based

FRs act as synergistic with other halogen and inorganic compounds. Intumescent-based formulations are much dependent upon phosphorous-based flame retardants. In the condensed phase, these FRs act by several mechanisms, including inhibition of flame, obstruction of a surface by the formation of char, condensed phases such as enhancement of char, and acid-catalysed dehydration polymers [19]-[20]. On exposure to heat, Phosphates or derivates of phosphoric acid decompose to form phosphoric acid with low volatility. It acts as a dehydration catalyst in the presence of rich compounds in hydroxyl groups or polymers. It converts into polyphosphoric acid if heated for a sufficiently long time. Polyphosphoric acid is a more robust dehydration catalyst as compared to phosphoric acid. Char formed acts as a heat shield or protecting material, and water vapours released to act as a heat sink during the decomposition step. The synergistic effect can be achieved by using nitrogen-based compounds to preserve the phosphorous in char. An initial cross-linking reaction in some polymers has also been studied using phosphorus-based flame retardants, thereby preventing the polymer from volatilising, resulting in fewer combustible products. The chemical reaction between hydrogen radicals and oxygen [20] forms the hydroxyl and oxygen radicals. These two radicals, such as hydroxyl and oxygen, effectively maintain the flame in reaction with fuel, as given in Equation 5.

$$H^{o} + O_2 \rightarrow OH^{o} + H^{o} \tag{5}$$

During thermal decomposition, volatile phosphorous compounds are formed, which are efficient flame retardants [20]. Mass spectrometry has been cleared that P_2, PO, PO_2, and HPO_2 formed from the thermal decomposition of triphenyl phosphate given in the following Equation (6-8).

$$HPO_2 + H^{o} \rightarrow H_2O + PO \tag{6}$$

$$HPO_2 + H^{o} \rightarrow H_2 + PO_2 \tag{7}$$

$$HPO_2 + OH^{o} \rightarrow H_2O + PO_2 \tag{8}$$

Red phosphorous is one of the examples of phosphorus-based FRs, an allotropy form of phosphorous and relatively non-toxic. It is thermally stable up to 450°C. Red phosphorous is exceptionally useful in providing flame retardant characteristics to polymers containing oxygen like

polycarbonates and polyethylene terephthalate. It is also significant to retard flame in nylon-based electrical equipment, especially in Europe. Its drawback is the formation of phosphine gas, which is toxic by reacting with moisture contents present in the atmosphere [21].

Nitrogen-based flame retardants

Nitrogen-based flame retardants attract the researchers' popularity due to their environmental-friendly behaviour. Melamine and melamine cyanurate are commonly used in polyurethane foam and nylon, respectively. Nitrogen-based FRs decomposed into non-combustible gases and showed low toxicity due to halogen acid [22]. These compounds showed a synergistic effect and enhanced yields or expanded char with phosphate-based flame retardants. Nitrogen-based compounds are frequently used in the intumescent system because they helped improve char and expand the carbon-rich char due to the chemical reaction. Melamine is extensively used in the intumescent fire retardant system due to its promising flame retardant effect [23]. Nitrogen-based have high decomposition temperatures and cannot react with hazardous products like dioxins. These compounds are used extensively in thermoplastics because these can be re-extruded many times without losing flame retardant or mechanical properties. They do not affect the operators because of their non-toxic nature, i.e., not evolving any toxic gas [23].

Inorganic based flame retardants

Some of the inorganic compounds have a flame retardant effect when incorporated into polymers. These compounds are not able to vaporise under the influence of heat like organic compounds. Instead, they decompose endothermically and release non-flammable gases like CO_2 and water [24]. One such example is Boron containing compounds such as Borax, barium metaborate, boron oxide, and zinc borate, used extensively in flame retardant applications for polymer and cellulose materials [1]. About 4500 MT of Boron-based flame retardants is used annually, among which zinc borate is most dominant in the USA. For example, zinc borate is used in PVC and formed zinc chloride during the pyrolysis of PVC, which has a smoke suppressant effect. Boric acid is also used in many fire retardant applications; it has two-step thermal degradation processes [25] as given in Equations 9 and 10,

$$H_3BO_3 \rightarrow HBO_2 + H_2O \quad \text{at } 100\text{-}140^\circ C \tag{9}$$

$$2HBO_2 \rightarrow B_2O_3 + H_2O \quad \text{at } 140\text{-}180^\circ C \tag{10}$$

Zinc borate is a widely used additive because of its flame retardant, smoke suppressants, and glow suppressant polymers' properties. Samyn et al. [26] had enhanced the residual weight of polypropylene by using zinc borate and ammonium polyphosphate due to the formation of boron and zinc phosphate compounds. Jimenez et al. [27] used boric acid as an additive along with APP that enhanced the fire protection time and the adhesion of char with a substrate, and better mechanical resistance of char was achieved. They concluded that Boronphosphate is a by-product of ammonium polyphosphate and boric acid responsible for all the properties. The thermal efficiency of intumescent fire retardant coating protecting steel was also increased by using zinc borate or a combination of zinc oxide and borate along with APP and melamine [28].

Keeping in view the above literature, the significance of inorganic flame retardants, especially Boron-containing compounds, cannot be denied because they enhanced char thermal insulation time and thermal stability. There is a need to include other inorganic compounds and Boron-containing compounds to enhance thermal stability and thermal insulation time. One such inclusion is the use of clay, and clay is used widely as a flame retardant. For example, using 5% montmorillonite clay in nylon-6-clay nanocomposite, the heat release rate was reduced to about 63%. The properties of the material do not degrade by using clay as an additive. Degradation of the matrix slowed down by adding clay in the polymer [29].

Nitrogen and boron-containing flame retardants

Ammonium Pentaborate is produced by the chemical reaction of ammonium polyphosphate and boric acid. Ammonium Pentaborate has high water solubility at room temperature. The chemical reaction has two steps of degradation. At first, it dehydrates at about 120°C by giving off a large number of water vapours. In the second step, it releases ammonia above 200°C. After 450°C, it is all converted into boric oxide, which is a glassy layer. It can be used as a flame retardant for cellulosic products. It is also used in polyurethane and epoxy-based intumescent coatings. Due to their high water solubility, its use is limited to polymer applications [21].

Melamine diborate is produced by the reaction between boric acid and melamine. It is partially soluble in water and is mainly used for cellulosic applications. It can be used in the intumescent system as well. It has low dehydration temperature, i.e., above 125°C, which limits its use in thermoplastic applications. When combined with ammonium polyphosphate, it is used to retard afterglow combustion in textiles [21]. Boron nitride is produced by the chemical reaction between the boric acid and urea. It is also known as "white graphite," as its structure resembles the graphite structure. It is converted to a cubic-like structure, i.e., a diamond upon heating at a high temperature above 1600°C and high pressure. Recently, single-walled boron nitride nanotubes were also prepared to be more resistant to oxidation than carbon nanotubes [21]. Combined nitrogen and Boron-based fire retardants have a wide range of applications from thermoplastic to intumescent systems. However, their thermoplastic usage is limited due to their low dehydration temperature, and some of its compounds are highly water-soluble.

Intumescent Fire-Retardant Coating

Intumescent comes from the word "intumescence," meaning "swelling of substance." Intumescent fire-retardant coatings expanded into a multi-cellular char layer with thickness much more significant than its original thickness upon heating, which acts as a thermal barrier protecting the substrate from fire or heat source, mass loss from the substrate heat source, and spreading of flame. It is one of the former and straightforward methods of protecting the material from fire. The earliest intumescent formulations were based upon phosphate-based compounds, i.e., ammonium polyphosphate and nitrogen-containing compounds [30]. The intumescent coating's principal purpose is to protect the underlying material such as structural steel from fire. The flow chart for the development of char is shown in Figure 4. For any intumescent coating, there are three essential components,

1. Acid source or dehydrating agent such as ammonium phosphate, ammonium polyphosphate, diammonium diphosphate, etc.
2. Carbon sources such as pentaerythritol or polymers carbonise under heat.
3. Blowing agents such as melamine.

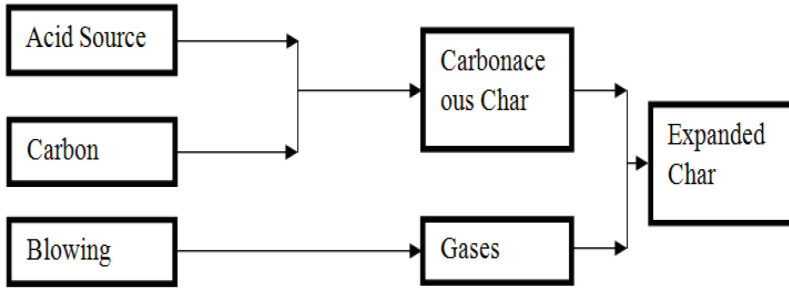


Figure 4 Flow chart of intumescence mechanism

For intumescent formulations, it must contain ingredients that fulfilled all three functions. Compounds can also act in multiple ways. For example, ammonium polyphosphate, used as an acid source, also acts as a blowing agent. The decomposition under the flame's heat releases ammonia other than the corresponding acid during its decomposition [10]. The widely accepted mechanism of intumescent formulation begins with the decomposition of an acid source that gives mineral acid. The resulted mineral acid reacts with the carbonific compound to form a carbonaceous or carbon-rich char layer. Finally, the blowing agent decomposes and releases non-combustible gases like carbon dioxide and ammonia, which causes the carbonaceous char layer to swell and form an insulating layer. Continuous heating of char for a long time causes the char to decompose [10].

Vandersall [30] presented a review of the classical development of commercial intumescent coating. It was composed of mineral acid, char forming material, and a spumific or blowing agent bound together with resin's help, which was the basic idea to develop the new, improved formulations. During the early 1980s, some polymers used ammonium polyphosphate, pentaerythritol, and melamine as a flame retardant. The foaming or intumescence action of char material is due to gaseous degradation products [31]. If the material's melt viscosity is high or low, the charring material's poor intumescence or foaming is obtained. Intumescent fire retardants can be categorised into two types. The first is the conventional intumescent fire-retardant coating, and the second is expandable graphite-based intumescent fire retardant coating [32]. The expandable graphite-based intumescent fire-retardant coating consists of three significant ingredients; the role of these ingredients is explained in the following subsections.

Acid Source

The acid source is a dehydrating agent, and for this Ammonium, polyphosphate is widely used as an acid source. It decomposes above 200°C and releases phosphoric acid, which increases the formation of carbonaceous char. Due to ammonia gas release, it acts both as an acid source and as a blowing agent, which improves the swelling process [25]. Jimenez et al. [27] proposed the degradation mechanism of APP. APP is degraded into three steps. The first step occurred between 200-300°C, with a weight loss of 20%. The second step occurred between 300-400°C, with a weight loss of 20%. The third degradation step occurred at 400-600°C. The final residual weight at 800°C is 10%. The degradation of the APP between 600-800°C is prolonged.

Besides acting as an acid source and a blowing agent, it also acts as a carbon source when coated with THEIC tris-(2-hydroxyethyl) isocyanurate. For the intumescent system, three components are mandatory: an acid source, a carbon source, and a blowing agent. In this case, the coated APP fulfilled all three requirements. It releases phosphoric acid, formed carbon char, and releases ammonia gas [27]. Wang et al. [33] investigated the effects of polymerisation degree of APP on intumescent fire retardant coating. By increasing the polymerisation degree of APP, the fire protection of the steel substrate was increased. Besides increasing fire protection performance, the intumescent factor and anti-oxidation property of char was also increased. On exposure to the fire, the release of gases from the acid source help to increase the carbonaceous char.

Carbon Source

The carbon-rich compound is used in an intumescent coating, forming a carbonaceous char during an intumescent reaction. This char acts as a thermal barrier protecting the substrate from fire. In traditional intumescent coating, pentaerythritol PER was used as a carbon source. PER began to dehydrate in the temperature range of 300-360°C through esterification on an acid attack [34]. Expandable graphite is also known as intumescent flake graphite, used as a flame retardant. It is a type of graphite intercalation compound. It is formed by treating flake graphite with intercalated acid such as sulfuric or nitric acid. Various advantages, such as reducing ignition and heat release rate and suppression of flame, can be achieved by using it in intumescent formulations [35]. On exposure to heat, the intercalated compound changes its phase from

solid or liquid to the gaseous phase, resulting in increased volume and pressure, as shown in Figure 5 [36].

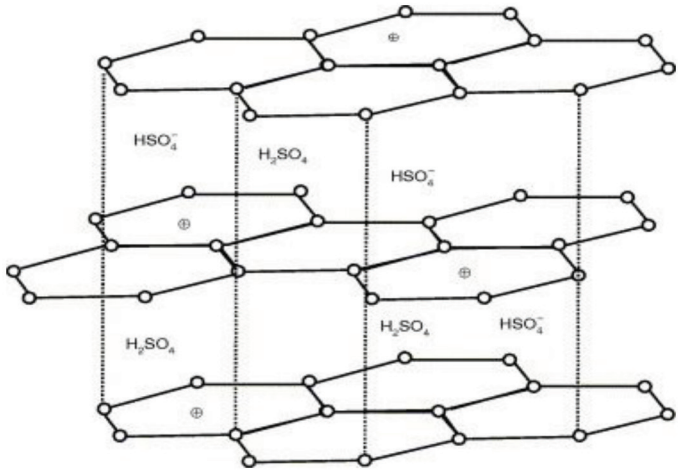


Figure 5 Expandable graphite intercalated by H_2SO_4 [36]

Blowing Agent

A blowing agent is used to blow the char formed by an acid source's chemical reaction with the carbon source to form an expanded multi-cellular char layer having thickness better than its original thickness. Melamine is widely used as a blowing agent in the intumescent system. Besides, melamine and its derivatives are non-halogen-based flame retardant. Its thermal decomposition forms nitrogen-containing compounds like ammonia, which can dilute combustible gases [37]. Its reaction process is given in equation 11 [34];

$$\mathbf{C_3N_3(NH_2)_3} \xrightarrow{\Delta} \mathbf{NH_3} \uparrow \tag{11}$$

Thermoset Epoxy Resin

Thermoset epoxy resins are extensively used in different areas, from small to large scale industries like aerospace, automobile, marine, coating, electrical equipment, etc. Epoxy resins have excellent adhesion

properties to numerous substrates and can be cured using amines, producing no volatiles during curing. These are rigid, stiff, 3-D cross-linked polymers due to irreversible curing reactions. Thermosets are more flammable and combustible as compared to thermoplastics. Upon removal of the combustion source, these can sustain burning on their own. Upon heating, a smaller number of gaseous products is formed. Epoxy resins, phenolic resins, polyurethane, etc., are the different types of thermoset resins. Thermoset epoxy resins alone do not provide any fire protective effect. When applied to the steel substrate, the time of failure of the epoxy resin-coated substrate was close to the time of failure of the uncoated steel substrate. Thermoset resins decompose via exposure to heat and produce various volatile products. By incorporating Boron and phosphorus-containing flame retardants, the time of failure considerably increases compared to without the inclusion of any flame retardant [25]. The incorporation can make the flame retardants of FRs like nitrogen or phosphorus-containing flame retardants. Horold et al. [7] illustrated that halogen-based epoxy resins like tetrabromide-bisphenol A are used in printed circuit boards (PCB) for electrical equipment. Still, during a fire or smoldering process, highly corrosive gases evolve. These corrosive gases are not produced by incorporating phosphorus-based flame retardants.

Protection via Intumescence

The fire retardancy of the polymer matrix can be enhanced by using an intumescent system. These are incorporated into the polymers to disrupt their self-sustained burning at the initial stage. During thermal degradation, a polymer releases gaseous fuel. By incorporating the intumescent system, they swell, and multi-cellular char layers are formed on its surface, thus protecting them from heat and mass loss, as shown in Figure 6.



Figure 6 Intumescence char

In addition, this physical barrier (char layer) prevents the diffusion of combustible gases released during the burning of the polymer at an elevated temperature to feed the flame and oxygen that maintain the combustion process. The intumescent system interferes with all three segments of the fire triangle [38], as shown in Figure 7. The thermal insulation of the coating depends on the intumescent factor. A lower value of the intumescent factor could not protect the substrate effectively, thus aiding in the flame's heat penetration to the substrate. This also leads to the non-uniform microstructure of char.

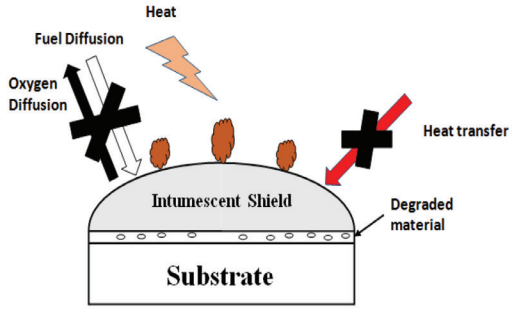


Figure 7 Schematic diagram of intumescence of char [39]

Synergistic Effect

A synergistic effect is commonly used in fire resistance coating, which is the added effect of incorporating some substance or compound into

the system. The synergistic agent in flame retardancy has increased due to its additional effects or enhanced flame retardant properties. The number of flame retardants can be reduced by adding synergistic agents resulting in enhanced polymer properties. Bourbigot et al. [38] used zeolite as a synergistic agent with the intumescent system, resulting in enhanced fire-retardant properties. The fire performance was considerably increased up to 35% compared to conventional APP/PER by adding zeolite.

Chen et al. [40] had used Hydroxyl Silicone Oil (HSO) as a synergistic agent in the polypropylene-based flame retardant composites by incorporating HSO, silicon phosphate, and the ceramic-like layer formed by the chemical reaction with the APP. As recorded by digital photography, a compact and uniform char layer was formed on the burning polymer's surface. Estevao et al. [41] used spent oil refinery catalysts as synergistic agents in the intumescent system with APP and PER. The fire-retardant property of polymer, i.e., polyethylenic matrix, was greatly enhanced by incorporating it with other intumescent systems. Without using APP and PER, it does not enhance the flame retardant property. Table 1 shows the synergists used with hydrated fillers such as aluminium hydroxide (ATH) and magnesium hydroxide (MH) [21].

Table 1 Synergists used with hydrated fillers [21]

Hydrated Fillers	Co-Additives	Polymer	Results
ATH	Antimony trioxide / zinc borate	PVC	Reduced the overall amount of filler
ATH	Zinc borate / Calcium borate	EVA	Flammability resistance improved with the lower amount of additive
ATH	Silicon-containing compounds	Polyolefins	Flammability resistance improved. Less smoke produced

Table 1 *(cont.)*

Hydrated Fillers	Co-Additives	Polymer	Results
ATH / MH	Metal oxides	Polyolefins	Reduced the overall amount of filler. Toxic in nature
ATH / MH	Melamine	PP	Enhanced fire retardancy
ATH	Copper nitrate / Iron nitrate	EVA	Flammability resistance improved by using a small amount of additive
ATH / MH	Nano clays	EVA	Heat release rate decreased Time to ignition increased

Effect of Added fillers on IFRC

The presence of fillers in polymers has presented excellent effects on the enhancement of thermal insulation properties. They reduced the overall flammability, resistance to combustion, and emission of toxic gases from polymers. They dilute the concentration of flammable gases, reduce oxygen diffusion rate, and even melt the dripping polymers. Most of the fillers decomposed endothermically and slowed down the rate of combustion. The inorganic residue left after the decomposition of fillers acts as an insulator between the substrate and heat source, reducing smoke suppression. The properties associated with the fillers are as follows,

1. It decomposed endothermically by releasing water and carbon dioxide in the temperature range from 100-300°C
2. Readily available with low cost
3. Low toxicity

Some inorganic fillers also can reduce the flammability by endothermic decomposition, sending out non-flammable gases like carbon dioxide, suppressing the radicals such as H and OH, and reducing the overall flammability of polymer if present in very high quantity.

Aluminium hydroxide, which is also known as aluminium trihydrate ($Al(OH)_3$), is produced from the bauxite mineral, which contained about 40-70% of aluminium-containing compounds [42]It endothermically decomposed within the temperature range of 190-200°C, releases water, and is converted into aluminium oxide [12], following Equation 12. ATH is the least expensive flame retardant material requiring more than 60% loading in polymers because the flame retardant mechanism is based on water release. In 1990-1991, about 66000 tons and 110000 tons of ATH were used as flame retardants.

$$\mathbf{2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O} \qquad (12)$$

ATH is a widely used FR material with polymers. It decomposes endothermically and releases water vapours to blanket the combustion process on exposure to a heat source. The limitation of the use of ATH is its low decomposition temperature. Most of the thermoplastic resins had a decomposing temperature higher than ATH. Stinson et al. recommended the modified ATH to enhance its decomposition temperature [43]. Aluminium oxalate is formed as a result of the reaction between ATH and oxalic acid. Aluminium oxalate has many applications in specific polymers, i.e., polyamides and thermoplastic polymers due to its enhanced thermal stability, i.e., thermally stable up to 330°C and loses about 51% of its total mass above 450°C. It has been used as a flame retardant due to endothermic decomposition; the polymer and aluminium oxide formed on the substrate has a protective effect. ATH has found many applications to be used in PVC and polyolefin. Magnesium hydroxide is the second most widely used halogen-free non-toxic flame retardant filler. It acts in the same way as aluminium tri hydroxide, except it decomposes at higher temperatures, i.e., above 300°C, as given in Equation 13. It can be used in polymers with high processing temperatures like polypropylene (PP), polyamides, etc. [12].

$$\mathbf{Mg(OH)_2 \rightarrow MgO + H_2O} \qquad (13)$$

Magnesium oxide (MgO) is an active oxide formed on the surface of

polymers during decomposition of $Mg(OH)_2$ and effectively contributed to the suppression of smoke [44]. The drawback is using a high amount of polymers, which sharply reduced the other properties like mechanical properties of the polymer [45].

Magnesium carbonate is a mineral filler that releases above 70% water and carbon dioxide. These are non-flammable gases, but it decomposes at a lower temperature, i.e., about 70°C, limiting their use to cellulosic materials like wood and paper. Another FR filler named hydromagnesite is a mixture of magnesium carbonate and magnesium hydroxide. It decomposes in the range starting from 210°C with a total weight loss of about 55%. Although it is an admirable fire retardant filler in many polymers, it is costly, limiting its use [21]. Hydrotalcite is the chains of magnesium aluminium hydroxy carbonates having differing magnesium to aluminium ratios. Their flame retardant properties are the same as ATH, but these are extremely expensive, limiting their use [21]. Table 2 shows the different fire-retardant fillers.

Table 2 Details of flame retardant fillers and degradation [21]

Fillers	Decomposition temperature (°C)	Volatile content (%w/w)		
		H_2O	CO_2	Total
Nesquehonite $MgCO_3.3H_2O$	70-100	39.0	32.0	71.0
Aluminium hydroxide	180-200	34.5	0.0	34.5
Hydromagnesite $4MgCO_3.Mg(OH)_2.4H_2O$	220-240	19.0	38.0	57.0
Magnesium hydroxide	300-320	31.0	0.0	31.0
Calcium Hydroxide $Ca(OH)_2$	430-450	24.0	0.0	24.0
Gypsum $CaSO_4.2H_2O$	60-130	2.0	0.0	21.0

Wang et al. [46] studied the effect of nano-size organic-modified montmorillonite (OMMT) on conventional intumescent fire retardant coating's thermal performance. By modifying the coating with 1% of OMMT and 6.5% of titanium oxide, the backside temperature of the steel substrate was reduced to 288°C from 304°C compared to coating without nano-OMMT. The residual weight was enhanced to 41.7% from 38.3%, and less weight loss occurred in the range of 500°C-800°C, which means that OMMT decreases the weight loss at a higher temperature. Zhao et al. [47] studied the effect of Halloysite nanotube (HNT) on flame retardancy of low-density polyethylene polymer. By modifying with 2% of HNT, the flame retardancy and LOI value were enhanced compared to without HNT. Besides, thermal stability and residual weight were also enhanced, providing a compact microstructure of char. Dong et al. [48] had demonstrated the effect of boron nitride of different particle sizes on thermal protection and the anti-oxidation property of the water-borne intumescent coating. The substrate's backside temperature was dropped after modification with micron-size boron nitride filler and further dropped with nano-size filler. The anti-oxidation property is also enhanced by modification with a nano-size filler. Weight loss was reduced in the temperature range of 500°C-750°C. Also, a more uniform char structure was obtained.

Huang et al. [49] studied the combined effect of carbon nanotubes (CNT's) with graphene on intumescent fire retardant (IFR) based polypropylene (PP) nanocomposites. Results showed that the addition of 1% CNT, 1% graphene, and 18% IFR effectively enhanced the onset and maximum weight loss temperature of PP composites. Further, the heat release rate was reduced with a compact and denser microstructure of char obtained. Zhang et al. [29] had suggested the fire behaviour of nano clay polypropylene composites. Nano clay with ammonium polyphosphate as flame retardant with amine stabiliser was used to prepare the PP nanocomposite. It has been seen that the flammability of the polymer was reduced. Limiting oxygen index and char residue was significantly enhanced by using nano clay with flame retardants.

Wang et al. [50] investigated the thermal degradation, fire performance, and anti-oxidation property of intumescent coating using different fillers of varying particle sizes such as micron-size sodium silicate nano-size silica. Sodium silicate does not provide better fire protection to the substrate compared to nano-silica. The fire performance and thickness of char were enhanced by using nano-silica due to the Si-O-Si network formation. Using a high amount of nano-size particles, i.e., 4.5%, helps reduce the fire performance and thickness of char due to the formation

of intense nanoparticles, a cross-linking network obstructing the carbon dioxide from swelling and producing a negative lamp wick effect.

Qui et al. [45] had prepared $Mg(OH)_2$/ethylene-vinyl acetate nanocomposite and investigated its flame retardant properties. They reported that by using nano-size $Mg(OH)_2$, the flame retardant properties effectively increased compared to micron size $Mg(OH)_2$. The limiting oxygen index value had noticeably increased from 24 to 38 by using nano size. The enhancement in flame retardant properties was due to the proper dispersion of nano-size $Mg(OH)_2$ in the EVA matrix. Also, a compact char structure was obtained, as examined through SEM. This char structure is fundamental as it blocks the gaseous products produced during combustion and the flame's heat to penetrate, thus preventing the material from burning.

Wang et al. [34] modified the conventional intumescent fire retardant coating using nano magnesium-aluminium double-layer hydroxide (nano-LDHs). In the heat, nano-LDH absorbs heat and releases water vapours and carbon dioxide during burning, ultimately protecting the substrate from fire. The steel substrate was primed (primer paint used to enhance the coating adhesion) with red epoxy iron oxide coating to enhance the coating's adhesion. Results showed that the fire performance, char layer thickness, and anti-oxidation property of the coating were significantly enhanced using 1.5% nano-LDH. Also, the microstructure of char showed a small hole diameter in the range of 10-30 μm. Deodhar et al. [51] reduced polypropylene's burning rate from 25-70% by using the APP with nano calcium carbonate. Results showed that β-calcium metaphosphate was formed due to a chemical reaction between polyphosphoric acid and calcium carbonate, which acts as a thermal barrier and dilutes the oxygen concentration by releasing carbon dioxide and ammonia. The heat release rate of polypropylene was also reduced above 50% with nano calcium carbonate and montmorillonite.

Ullah et al. [52] studied the effect of multi-wall carbon nanotubes (MWCNTs) on expandable graphite-based intumescent fire retardant coating. Results showed that the char expansion, char strength, and residual weight were increased by increasing the percentage of MWCNTs. MWCNTs act as bridges and overlap the pores created during the coating's thermal degradation and between the char layers. It joins the cracks produced in the char layer leading to enhancement in char strength and heat shielding effect. Gibson et al. [53] found that halloysite-based IFRC provides better thermal resistance to the steel substrate than graphene and carbon Nanotubes due to improper dispersion. Puri [54] has found a reduction in more than 80°C in

substrate temperature after using zirconium silicate (ZS) in their formulation, suggesting that ZS forms a silicate-based protective layer that is highly efficient in providing a thermal barrier.

Titanium oxide is a naturally occurring oxide (TiO_2). It occurs in nature as anatase, brookite, and rutile and is widely used in the paints industry. It is used as filler in the intumescent fire-retardant coating. Wang et al. [55] had investigated that 2% of nano-size TiO_2 (205 nm) enhanced the thermal stability of the acrylic polymer. 1.6% of nano-size TiO_2 enhanced the anti-oxidation property of flame retardant coating due to forming a ceramic-like layer on the char surface, which is to be protected. Titanium oxide reacts with APP's degradation products to form titanium pyrophosphate, a thermally stable compound, preventing the char from oxidising at a higher temperature.

Aluminium oxide is the chemical compound of aluminium and oxide, having the chemical formula Al_2O_3. It is a ceramic material that is widely used for heat-resistant applications. It is an inert and relatively inexpensive filler that provides better fire protection due to its low thermal conductivity, high mechanical strength, and enhanced thermal stability. Morgan et al. [56] showed that polyimide's thermal stability improved using aluminium oxide as filler. The nanocomposite of aluminium oxide, silicon dioxide, and carbon nanofibers has shown low flammability, but cracks appeared. Wei et al. [57] investigated silica and alumina's synergistic effect in the PP/APP-PER-based intumescent fire retardant system. The LOI value, thermal stability, and less heat release rate were achieved using silica and alumina. Mohamad et al. [58] studied alumina's effect on intumescent coating's thermal stability and char morphology. Thermal stability was increased by increasing the percentage of alumina as an inorganic filler, but the pore size diameter was increased.

Magnesium oxide is produced by the calcination of magnesium carbonate and magnesium hydroxide. It is a ceramic material that is stable at high temperatures and can be used as flame retardant fillers. Muller et al. [59] studied the effect of nano-magnesium oxide (particle size not mention) with ammonium polyphosphate in the polyurethane matrix. Magnesium phosphate was formed due to a chemical reaction between MgO and APP. However, the heat release rate was lowered by incorporating nano-MgO. The fire-retardant properties were enhanced by incorporating nano-MgO with APP due to the uniform dispersion of bubbles and homogenous char structure. Kazmina et al. [60] formulated an eco-friendly fire retardant coating and found that hydromagnesite is more effective in providing thermal insulation to the substrate than

brucite magnesite. Based on this discussion, the addition of nano magnesium oxide in the intumescent coating resulted in magnesium carbonate and magnesium hydroxide at a high temperature, reducing the emission of toxic gases and developing a uniform char enhancing fire protection.

Characterisation Techniques for Intumescent Fire retardants

Different methods have been presented to estimate the thermal efficiency of IFRC. The furnace test and Bunsen burner test are widely used to determine the char expansion and thermal performance of IFRC. The integrity of the expanded multi-cellular char layer is fundamental because it prevents the flame's heat from penetrating inside the char to the substrate required to be protected. The ultimate goal of the IFRC is to increase the time of failure of the steel substrate [61]. The load-bearing capacity of structural steel starts to decline with the increase of time due to its high thermal conductivity and deterioration of mechanical properties, and structural steel starts to twist and buckle. The structure will collapse after crossing its critical value, which is 550°C.

Grigonis et al. [62] investigated a relationship between the thickness of the intumescent coating and the time at which the temperature of steel plates reaches a critical temperature. All the plates were primed with alkyd anticorrosive primer and coated with three different commercial intumescent coating. Two methods were employed, i.e., one side heating of steel plate and volumetric heating where both sides were coated and exposed to heat. Results showed that fire resistance time increased or time to reach critical temperature was increased by applying the thicker coating. Jimenez et al. [25] presented the performance of IFRC protecting structural steel. Results showed that by incorporating FR, the time of failure was significantly enhanced. The time of failure of the bared steel plate was only 5 min. The failure time increased from 5 to 11.3 mins, and with BA increased to 18.2 mins by incorporating APP. By incorporating both APP and BA, the failure time was appreciably increased to 29.5 mins compared to the bared or uncoated steel plate, which was only 5 mins.

Wang et al. [36] presented the intumescent fire retardant's fire resistance by incorporating expandable graphite. The exposed or unshielded steel substrate's temperature reached 500°C only after a few mins of the fire test. By adding expandable graphite (74), the fire resistance time or fire performance considerably increased, and the final temperature of the steel substrate was 262°C after 100 mins of the fire

test. Wang et al. [63] presented the effect on fire performance by using nano clay. The heat release rate and fire performance are effectively enhanced using nanoscale fillers in the intumescent fire-retardant coating. By using 1.5% nano clay, the fire-resistant time was 87 mins. By increasing the percentage of nano clay from 1.5% to 3.0%, the protective layer thickness, i.e., char reduces.

Other characterisation techniques include estimating residual weight and microstructure of char, which are considered two important factors in analysing the coating's effectiveness. Higher residual weight indicates the high anti-oxidation property of coating so that the char withstands higher temperatures for a longer time. A dense, compact, and open cellular char structure prevents heat transference to the substrate [36]. The open cellular structure was formed due to EG's expansion and effectively protects the flame from penetrating the substrate. Li et al. [64] illustrated the thermal degradation of ammonium polyphosphate, pentaerythritol, melamine, a mixture of ammonium polyphosphate, and pentaerythritol and binder. APP started to decompose above 250°C by eliminating water and ammonia. PER started melting and decomposed in the temperature range of 186-334°C. It is clear that both ingredients' decomposition is in the same temperature range, so they interact to form char. Melamine started to decompose in the temperature range of 200-350°C by eliminating ammonia, which caused the char to swell, as shown in Figure 8 [64]. The residual weight of coating containing APP-PER-MEL was only 4.85% at 800°C [64]. Wang et al. [33] claimed that the residual weight also increased by increasing the polymerisation degree (PD) of APP. The final residual weight of APP with PD of 184 was 42.20% at 800°C.

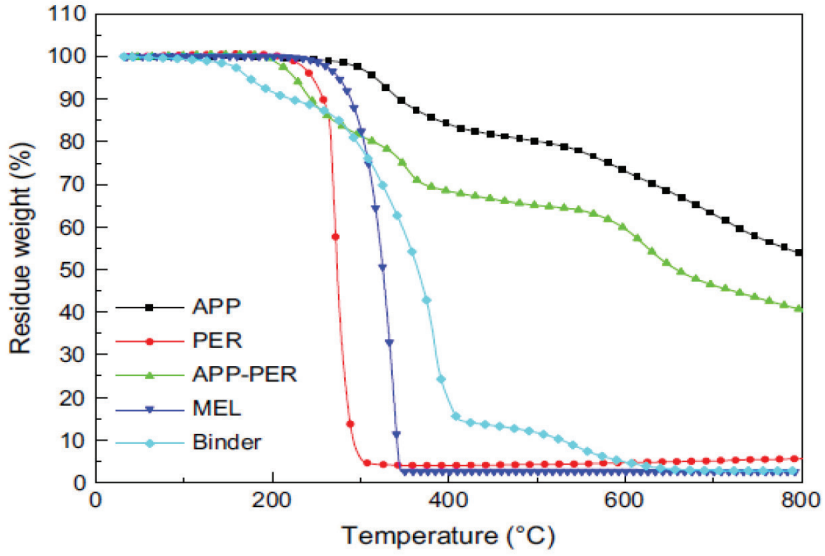


Figure 8 Residual weight of different ingredients of IFRC [64]

X-ray Diffraction (XRD) is used to study the residual char composition. Li et al. [64] had used expandable graphite and molybdenum disilicide to improve the anti-oxidation property of APP-PER-MEL coating. The chemical reaction occurred between molybdenum disilicide and oxygen to form a protective layer that enhanced the anti-oxidation of APP-PER-MEL and prevented the thermal oxidation of char of EG. The figure shows the XRD pattern of coating modified with EG and $MoSiO_2$. Different peaks are allocated to silica and molybdenum disilicide ($MoSiO_2$). The peaks at 0.4255 and 0.3342 are assigned to silica. The peaks at 3.9276, 3.9684, 2.2663, and 2.0265 are allocated to molybdenum disilicide.

Gu et al. [65] had used expandable graphite as a synergistic agent with APP-PER-MEL with titanium oxide. They found that after burning, white material was formed on residual char. The white material was composed of titanium oxide and titanium pyrophosphate, which improved the fire performance and reinforced the strength of the char layer. Li et al. [66] improved APP-PER-MEL's thermal performance by modifying molybdenum trioxide and ferric oxide. The residue was found to be composed of molybdenum oxide and iron phosphate. Iron phosphate was formed due to the chemical reaction between the phosphate and ferric oxide. Wang et al. [67] had used a glass flake and

analysed the elemental composition of the residue char layer through XRF. Using the glass flake, they elaborated an increase in phosphorous content and decreased oxygen content, but carbon content remains almost unchanged. The ratio of oxygen to carbon was decreased. Still, the ratio of phosphorous to carbon increased by adding glass flake, enhancing the anti-oxidation property.

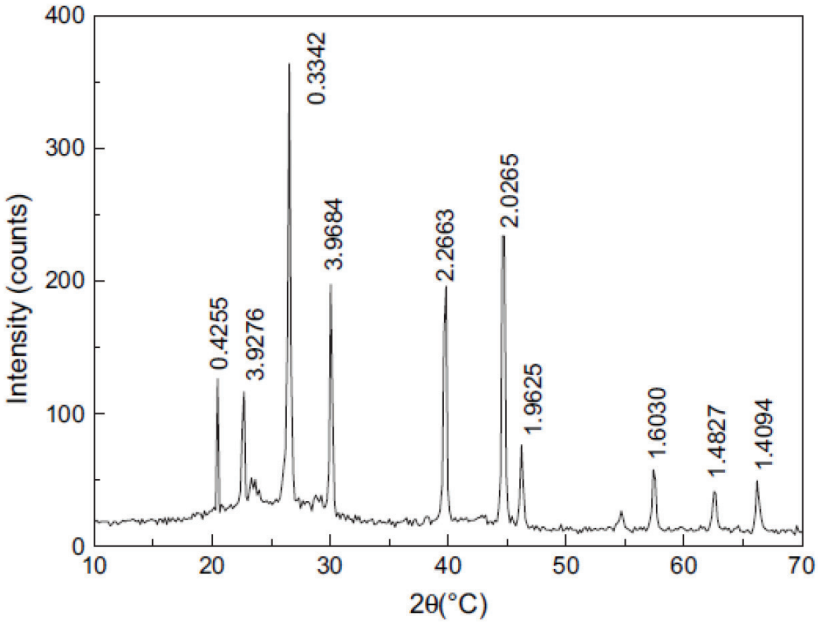


Figure 9 XRD curve of residue char showing SiO_2 and $MoSiO_2$ [64]

The microstructure and char morphology were analysed by using FESEM. Char plays a very crucial role in enhancing the thermal efficiency of the coating. During thermal degradation of coating, a multi-cellular char layer is formed. A thermally stable char layer acts as a thermal barrier that prevents the flame's heat from penetrating inside the char and preventing the mass loss from the substrate to the fire. Expanded multi-cellular char layers were formed due to the slow diffusion of gases inside the char structure while blowing agents played significant parts. Effective char structure also depends upon the viscosity of the coating. During thermal degradation of the coating, a multi-cellular char layer was formed. If the viscosity is too high, the gases do not form an effective char layer, leading to a rupture of the

char structure. Contrary to it, the gases will escape the flame [68]. The intumescence process is shown in Figure 10 describes the slow diffusion of gases into the char structure to form thermally stable material that provides a protective effect.

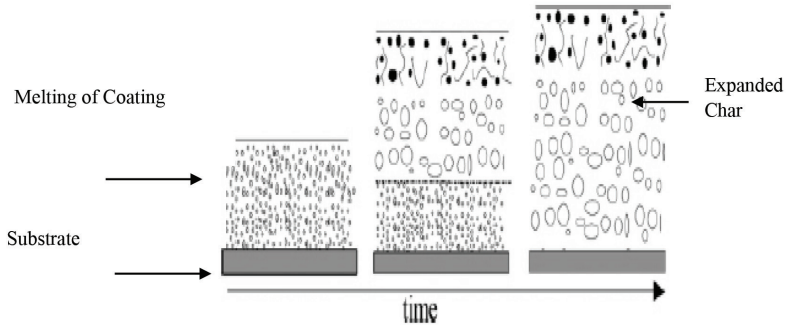


Figure 10 Intumescence process [68]

Gu et al. [65] suggested a model for the char layer. For an effective char layer, the decomposition temperature of all essential ingredients of intumescent coating must be within the same range. If APP>> PER decomposition temperature, pentaerythritol will entirely be decomposed before the decomposition of APP and not an effective char layer formed in this case. If the decomposition temperature of APP >> MEL, all the gases will escape, feeding the flame and not playing any role in intumescence. If the MEL >> APP, all the gases will blow off and not contribute to an effective char layer.

Summary

Intumescent fire-retardant coating (IFRC) is more efficient than any other technique to protect structural steel members from an uncontrolled fire. The market of flame-retardant coating is expected to increase to above US$1.0 billion by 2024. The fundamental components of IFRC are acid, carbon, and gas source (blowing agents). However, its fire protection efficiency is limited. Therefore, researchers are trying to increase thermal protection time by incorporating various flame retardant additives and fillers of different sizes. The flammability of polymers is reduced by incorporating mineral fillers. Due to endothermic decomposition, they absorb heat and keep the surrounding

polymer cooler. They also produce inert gases during decomposition and form an inert layer on the polymer's surface, protecting it from heat and oxygen to reach the polymer. This logic is valid to some extent, but with the increase of the char's expansion, the cohesion and adhesion factor of the char is seriously compromised.

Furthermore, many researchers also consider nanoparticles, but the problem involves the dispersibility of nanoparticles, making them difficult to mix and apply to the substrate. Thus, proper dispersion of nanoparticles is important to achieve desired thermal protection. More research is needed in this area to further the thermal protection of IFRC using nanoparticles. However, a higher weight percentage of mineral fillers is required in polymers to be effective flame retardants [69]. The expansion of char is an important factor in providing thermal insulation. It is suggested that only the height of the char plays a significant role as the thermal barrier [70].

References

[1] M. Jimenez, S. Duquesne & S. Bourbigot, "High-throughput fire testing for intumescent coatings", *Industrial and Engineering Chemistry Research,* 45, 22, pp. 7475-481, 2006.

[2] H.F. Spreads, "Stages of fire", *Effective Physical Security,* p. 277, 2012.

[3] A.H. Buchanan, "Fire Engineering Design Guide*",* Place*: Centre for Advanced Engineering, University of Canterbury*, 2001.

[4] M. Jimenez, S. Duquesne & S. Bourbigot, "Multiscale experimental approach for developing high-performance intumescent coatings", *Industrial and Engineering Chemistry Research,* 45, 13*,* pp. 4500-508, 2006.

[5] J. Green, "Mechanisms for flame retardancy and smoke Suppression - A review", *Journal of Fire Sciences*, 14, 6*,* pp. 426-442, 1996.

[6] G.J. V. Esch, Bilthoven ,B.J. Sutker, "environmental health criteria for flame retardants: a general introduction"*,*1997 .

[7] S. Hörold, "Phosphorus flame retardants in thermoset resins", *Polymer Degradation and Stability,* 64, 3*,* pp. 427-431, 1999.

[8] S. Bourbigot & S. Duquesne, "Fire retardant polymers: Recent developments and opportunities", *Journal of Materials Chemistry,* 17, pp. 2283-300, 2007.

[9] S. Bourbigot, M. Le Bras, S. Duquesne & M. Rochery, "Recent advances for intumescent polymers", *Macromolecular Materials and Engineering,* 289, 6*,* pp. 499-511, 2004.

[10] C.A. Wilkie & A.B. Morgan, "Fire retardancy of polymeric materials", *CRC Press*, 2010.
[11] R.E. Tapscott, R.S. Sheinson, V. I. Babushok, M.R. Nyden & R.G. Gann, "Alternative fire suppressant chemicals: A research review with recommendations", *US Department of Commerce, National Institute of Standards and Technology*, 2001.
[12] R. Wolf & B. Kaul, "Plastics, additives", *Ullmann's Encyclopedia of Industrial Chemistry,* 2002, Wiley & VCH Verlag.
[13] R.G. Gann, "Flame retardants overview", *Kirk Othmer's Encyclopaedia of Chemical Technology,* John Wiley and Sons, New York, 2000.
[14] I. Touval, "Antimony and other inorganic flame retardants", In *Kirk-Othmer Encyclopedia of Chemical Technology,* John Wiley & Sons, 1993.
[15] P.O. Darnerud, "Toxic effects of brominated flame retardants in man and in wildlife", *Environment International,* 29, pp. 841-53, 2003.
[16] R. Mount, "The three sisters of intumescence", *Proceedings of the FRCA Conference*, pp. 33-34, 1992.
[17] G. Avondo, C. Vovelle & R. Delbourgo, "Guide to manuscripts in the national agricultural library*Technical Information System (U.S),* 31, pp. 7-16, 1979.
[18] J. Green, "A review of phosphorus-containing flame retardants", *Journal of Fire Sciences, 10*, 6,pp. 470-487, 1992.
[19] S.V. Levchik & E.D. Weil, "A review of recent progress in phosphorus-based flame retardants", *Journal of Fire Sciences,* 24, 5, pp. 345-364, 2006.
[20] B. Schartel, "Phosphorus-based flame retardancy mechanisms – old hat or a starting point for future development?", *Materials*, 3, 10, pp. 4710-745, 2010.
[21] C.A. Wilkie & A.B. Morgan, *Fire Retardancy of Polymeric Materials,* Second edition", *CRC Press*,2012.
[22] G.E. Zaikov & S.M. Lomakin, "New aspects of ecologically friendly polymer flame retardant systems", *Polymer Degradation and Stability,* 54, 2-3, pp. 223-233, 1996.
[23] H. Horacek & R. Grabner, "Advantages of flame retardants based on nitrogen compounds", *Polymer Degradation and Stability,* 54, 2-3 pp. 205-215, 1996.
[24] W. Horn, "Inorganic hydroxides and hydroxycarbonates: their function and use as flame-retardant additives", In A.F. Grand & C.A. Wikie, *Fire Retardancy of Polymeric Materials,* Boca Raton: CRC Press, pp. 285-352, 2010.

[25] M. Jimenez, S. Duquesne & S. Bourbigot, "Characterization of the performance of an intumescent fire protective coating", *Surface and Coatings Technology,* 201, 3-4, pp. 979-987, 2006.
[26] F. Samyn, S. Bourbigot, S. Duquesne & R. Delobel, "Effect of zinc borate on the thermal degradation of ammonium polyphosphate", *Thermochimica acta,* 456, pp. 134-144, 2007.
[27] M. Jimenez, S. Duquesne & S. Bourbigot, "Intumescent fire protective coating: Toward a better understanding of their mechanism of action", *Thermochimica Acta,* 449,1-2, pp. 16-26, 2006.
[28] R.M. Nugent , T.A. Ward, P.P. Greigger & J.A. Seiner, "Flexible intumescent coating composition", US5108832A, Google Patents, 1992.
[29] S. Zhang, A.R. Horrocks, R. Hul & B.K. Kandola, "Flammability, degradation and structural characterization of fibre-forming polypropylene containing nanoclay–flame retardant combinations", *Polymer Degradation and Stability,* 91, pp. 719-725, 2006.
[30] H. Vandersall, "Intumescent coating systems, their development and chemistry", *Journal of Fire and Flammability,* 2, 1971.
[31] G. Camino, L. Costa & L. Trossarelli, "Study of the mechanism of intumescence in fire retardant polymers: Part I – Thermal degradation of ammonium polyphosphate-pentaerythritol mixtures", *Polymer Degradation and Stability,* 6, 4, pp. 243-252, 1984.
[32] J. Hao & W. Chow, "A brief review of intumescent fire retardant coatings", *Architectural Science Review*, 46, 1, pp. 89-95, 2003.
[33] G. Wang, Y. Wang & J. Yang, "Influences of polymerization degree of ammonium polyphosphate on fire protection of waterborne intumescent fire resistive coating", *Surface and Coatings Technology,* 206, 8-6, pp. 2275-280, 2012.
[34] Z. Wang, E. Han & W. Ke, "Influence of nano-LDHs on char formation and fire-resistant properties of flame-retardant coating", *Progress in Organic Coatings,* 53, 1, pp. 29-37, 2005.
[35] D. Krassowski, D. Hutchings & S. Qureshi, "Expandable graphite flake as an additive for a new flame retardant resin", *GrafGuard Fire Retardant,* GrafTech International, pp. 1-10, 2012.
[36] Z. Wang, E. Han & W. Ke, "Influence of expandable graphite on fire resistance and water resistance of flame-retardant coatings", *Corrosion Science,* 49, pp. 2237-253, 2007.

[37] D. Chattopadhyay & D.C. Webster, "Thermal stability and flame retardancy of polyurethanes", *Progress in Polymer Science,* 34, pp. 1068-133, 2009.

[38] S. Bourbigot, M.L. Bras, P. Bréant, J.M. Trémillon & R. Delobel, "Zeolites: New synergistic agents for intumescent fire retardant thermoplastic formulations – criteria for the choice of the zeolite", *Fire and Materials,* 20, pp. 145-154, 1996.

[39] M. Le Bras, G. Camino, S. Bourbigot & R. Delobel, "Fire retardancy of polymers; The use of intumescence", *Cambridge: Royal Society of Chemistry,* 1998.

[40] X. Chen & C. Jiao, "Synergistic effects of hydroxy silicone oil on intumescent flame retardant polypropylene system", *Fire Safety Journal,* 44, pp. 1010-014, 2009.

[41] L.R. Estevão, M. Le Bras, R. Delobel & R.S. Nascimento, "Spent refinery catalyst as a synergistic agent in intumescent formulations: Influence of the catalyst's particle size and constituents", *Polymer Degradation and Stability,* 88, pp. 211-227,, 2004.

[42] A.R. Horrocks & D. Price, *Fire Retardant Materials*, Cambridge: Woodhead Publishing, 2001.

[43] J.M. Stinson & W.E. Horn, "Flame retardant performance of a modified aluminum trihydroxide with increased thermal stability", *Journal of Vinyl Technology,* 1, pp. 94-97, 1995.

[44] P.R. Hornsby, "The application of magnesium hydroxide as a fire retardant and smoke□suppressing additive for polymers", *Fire and Materials,* 18, pp. 269-276, 1994.

[45] L. Qiu, R. Xie, P. Ding & B. Qu, "Preparation and characterization of Mg $(OH)_2$ nanoparticles and flame-retardant property of its nanocomposites with EVA", *Composite Structures,* 62, pp. 391-395, 2003.

[46] J. Wang & G. Wang, "Influences of montmorillonite on fire protection, water and corrosion resistance of waterborne intumescent fire retardant coating for steel structure", *Surface and Coatings Technology,* 239, pp. 177-184, 2014.

[47] J. Zhao, C.L. Deng, S.L. Du, L. Chen, C. Deng & Y.Z. Wang, "Synergistic flame□retardant effect of halloysite nanotubes on intumescent flame retardant in LDPE", *Journal of Applied Polymer Science,* 131, 201.

[48] Y. Dong & G. Wang, "Influence of nano-boron nitride on fire protection of waterborne fire-resistive coatings", *Journal of Coatings Technology and Research,*11, pp. 1-8.

[49] G. Huang, S. Wang, P.A. Song, C. Wu, S. Chen & X. Wang, "Combination effect of carbon nanotubes with graphene on intumescent flame-retardant polypropylene nanocomposites", *Composites Part A: Applied Science and Manufacturing,* 59, pp. 18-25, 2014.

[50] Z. Wang, E. Han & W. Ke, "An investigation into fire protection and water resistance of intumescent nano-coatings", *Surface and Coatings Technology,* 201, pp. 1528-535, 2006.

[51] S. Deodhar, K. Shanmuganathan, Q. Fan, C.A. Wilkie, M.C. Costache, N.A. Dembsey & P.K. Patra, "Calcium carbonate and ammonium polyphosphate□based flame retardant composition for polypropylene", *Journal of Applied Polymer Science,* 120, pp. 1866-873, 2010.

[52] S. Ullah & F. Ahmad, "Enhancing the char resistant of expandable graphite based intumescent fire retardant coatings by using multi-wall carbon nano tubes for structural steel", *Solid State Phenomena,* 185, pp. 90-93, 2012.

[53] A.G. Gibson, W.N.B.Wan-Jusoh & G. Kotsikos, "A propane burner test for passive fire protection (PFP) formulations containing added halloysite, carbon nanotubes and graphene", *Polymer Degradation and Stability,* 148, 2018.

[54] R.G. Puri & A.S. Khanna, "Influence of heat-stable filler on the thermal shielding performance of water-based intumescent fire-resistive coating for structural steel applications", *Journal of Coatings Technology and Research,* 14, pp. 323-331, , 2017.

[55] Z. Wang, E. Han, F. Liu & W. Ke, "Thermal Behavior of Nano–TiO2 in Fire–Resistant Coating", *Journal of Materials Science and Technology*, 23, 4, pp. 547-550, 2007.

[56] A.B. Morgan & S. Putthanarat, "Use of inorganic materials to enhance thermal stability and flammability behavior of a polyimide", *Polymer Degradation and Stability,* 96, pp. 23-32, 2011.

[57] P. Wei, J. Hao, J. Du, Z. Han & J. Wang, "An investigation on synergism of an intumescent flame retardant based on silica and alumina", *Journal of Fire Sciences,* 21, pp. 17-28, 2003.

[58] W.F. Mohamad, F. Ahmad & S. Ullah, "Effect of inorganic fillers on thermal performance and char morphology of intumescent fire retardant coating", *Asian Journal of Scientific Research,* 6, pp. 263-271, 2013.

[59] M. Muller, S. Bourbigot, S. Duquesne, R. Klein, G. Giannini, C. Lindsay & J. Vlassenbroeck, "Investigation of the synergy in intumescent polyurethane by 3D computed tomography", *Polymer degradation and stability,* 98, pp. 1638-647, 2013.

[60] O. Kazmina, E. Lebedeva, N. Mitina & A. Kuzmenko, "Fire-proof silicate coatings with magnesium-containing fire retardant", *Journal of Coatings Technology and Research,* 15*,* pp. 719-724, 2018.

[61] S. Duquesne, P. Bachelet, S. Bellayer, S. Bourbigot & W. Mertens, "Influence of inorganic fillers on the fire protection of intumescent coatings", *Journal of Fire Sciences,* 31, 3, pp. 258-275, 2013.

[62] M. Grigonis, R. Mačiulaitis & D. Lipinskas, "Fire resistance tests of various fire protective coatings," *Materials Science,* 17, pp. 93-98, 2011.

[63] Z.Y. Wang, E.H. Han & W. Ke, "Fire□resistant effect of nanoclay on intumescent nanocomposite coatings", *Journal of Applied Polymer Science,* 103, pp. 1681-689, 2006.

[64] G. Li, G. Liang, T. He, Q. Yang & X. Song, "Effects of EG and $MoSi_2$ on thermal degradation of intumescent coating", *Polymer Degradation and Stability,* 92, pp. 569-579, 2007.

[65] J.-W. Gu, G.-C. Zhang, S.-L. Dong, Q.-Y. Zhang & J. Kong, "Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings", *Surface and Coatings Technology,* 201, pp. 7835-841, 2007.

[66] G. Li, J. Yang, T. He, Y. Wu & G. Liang, "An investigation of the thermal degradation of the intumescent coating containing MoO_3 and Fe_2O_3", *Surface and Coatings Technology,* 202, pp. 3121-128, 2008.

[67] G. Wang & J. Yang, "Influences of glass flakes on fire protection and water resistance of waterborne intumescent fire resistive coating for steel structure", *Progress in Organic Coatings,* 70, pp. 150-156, 2011.

[68] S. Duquesne, S. Magnet, C. Jama & R. Delobel, "Intumescent paints: Fire protective coatings for metallic substrates", *Surface and Coatings Technology,* 180-181, pp. 302-307, 2004.

[69] T.R. Hull, A. Witkowski & L. Hollingbery, "Fire retardant action of mineral fillers", *Polymer Degradation and Stability,* 96, 8, pp. 1462-469, 2011.

[70] S. Murat Unlu, U. Tayfun, B. Yildirim & M. Dogan, "Effect of boron compounds on fire protection properties of epoxy based intumescent coating", *Fire and Materials,* 41, pp. 17-28, 2017.