Advances in Fire Retardant Coatings

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Edited by

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PREFACE

Fire safety remains an essential concern across industries, public infrastructure, and residential sectors worldwide. With the increasing complexity of modern materials and constructions, the demand for innovative, effective, and sustainable fire-retardant technologies has never been more critical. This book, Advances in Fire Retardant Coatings, is a timely and comprehensive contribution to the rapidly evolving field of fire protection. It is part of the book series entitled Advances in Functional Coatings, which brings together pioneering developments in advanced coating technologies for diverse applications.

This book comprises seven carefully curated chapters, each exploring a specific facet of fire-retardant coatings. Chapter 1 introduces the foundational principles and critical role of these coatings in contemporary fire safety frameworks. Chapter 2 delves into recent advances in fire-resistant polymer formulations, laying the groundwork for enhanced thermal performance. In Chapter 3, the focus shifts to multifunctional coatings that not only provide fire resistance but also address mechanical and environmental challenges.

Chapter 4 examines novel application techniques that improve coating efficiency and adaptability across substrates. Chapter 5 highlights the real-world industrial applications of advanced fire-retardant coatings in construction, transportation, and electronics. Environmental considerations and sustainability, an increasingly vital topic, are covered in Chapter 6, addressing ecological impact and green formulation strategies. The book concludes with Chapter 7, which explores future trends and emerging innovations poised to transform fireproofing technologies in the years ahead.

We extend our heartfelt gratitude to all the authors and contributors who have enriched this book with their deep expertise, rigorous research, and valuable insights. Their collaboration has been instrumental in shaping this book into a reliable and forward-looking reference for researchers, engineers, and industry professionals.

We are deeply thankful to our families for their unwavering support, patience, and encouragement throughout the development of this project. Their belief in our work has been a source of constant motivation.

Our sincere appreciation goes to Ms. Amanda Millar, Typesetting Manager at Cambridge Scholars Publishing, UK, for her meticulous attention to detail and professionalism during the production of this book. We are especially grateful to Ms. Alison Duffy, Commissioning Editor at Cambridge Scholars Publishing, UK, whose guidance, approval, and commitment were vital for the timely completion of this publication.

We hope this book will serve as a valuable resource for those seeking to understand, innovate, and implement fire-retardant coating technologies for a safer and more sustainable future.

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CHAPTER 1

INTRODUCTION TO FIRE-RETARDANT COATINGS AND ITS ROLE IN FIRE SAFETY

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Abstract

Fire-retardant coatings play a vital role in mitigating the devastating impacts of fires by inhibiting or delaying the ignition and spread of flames. These coatings are designed to inhibit or delay the ignition and spread of flames, thereby providing valuable time for evacuation, firefighting, and minimizing property damage. This work explores the comprehensive overview to fire-retardant coatings: their principles, types, applications, and significance. This work also involves comprehensive review of recent advancements in fire-retardant coatings, including their future prospects. The significance of fire-retardant coatings cannot be overstated. Beyond protecting property, they play a critical role in safeguarding lives by

slowing down the spread of fire and providing vital escape time during emergencies. Furthermore, they contribute to sustainability efforts by reducing the environmental impact of fires and minimizing the need for resource-intensive rebuilding and reconstruction. With ongoing advancements in materials science and technology, these coatings continue to evolve, providing increasingly effective solutions for fire prevention and protection. As our understanding of fire dynamics deepens, so too will the efficacy and versatility of fire-retardant coatings in safeguarding lives and property.

Keywords: Fire-retardant coatings, fire safety, Process industries, Environment, Coatings

1.1 Introduction

The destructive power of fire can cause immense damage, leading to significant loss of lives and assets, as well as serious human suffering and financial setbacks. Catastrophes caused due to fires are exacerbated by the increased and extensive use of flammable materials in the industry, such as polymers (Davesne et al. 2021). Industries today are more vulnerable to fires due to the increasing use of combustible materials, compact manufacturing layouts, and the sheer scale of modern operations. Industrial fires can arise from numerous sources, such as electrical faults, overheating machinery, human error, or chemical reactions. Not only can fires destroy physical infrastructure and critical equipment, but they can also lead to widespread environmental pollution, long-term health risks, and severe economic disruptions. In industries dealing with chemicals, petrochemicals, textiles, and plastics, fires pose an even higher risk due to the flammability of materials and the presence of explosive atmospheres. Historically, the consequences of industrial fires have been catastrophic. For instance, the 1984 Union Carbide plant disaster in Bhopal, India, resulted not only in chemical leakage but also in a fire that amplified the damage, killing thousands and causing long-term health issues. Fires can also occur due to the ignition of combustible dust, as seen in the West Pharmaceutical plant explosion in 2003. These incidents underscore the need for robust fire protection methods (Varma and Mulay, 2009).

Traditionally, fire protection in industrial environments involved passive and active systems. Passive methods, such as fire-resistant building materials (e.g., concrete or gypsum board), aim to contain fires and slow their spread. Active systems, such as water-based sprinklers, foam extinguishing systems, and fire alarms, actively combat fire by either extinguishing flames or alerting personnel. However, these traditional methods have limitations. Water sprinklers, for instance, are not always effective on oil or chemical fires, and can sometimes cause damage to sensitive electrical equipment or industrial products. Furthermore, in environments where fire spreads rapidly—such as in chemical plants or warehouses filled with flammable materials—these systems may not react quickly enough to prevent significant damage. As a result, substantial efforts have been made to create effective fire protection methods to prevent casualties and minimize economic damage from fires to an acceptable level (Giudice et al. 2017). The use of fire-retardant-coatings has come out as an effective and convenient means of fire protection which can isolate and control the spread of fire in an efficient way (). While fire-retardant coatings offer significant protection, several challenges remain in their widespread adoption. One challenge is the need to balance fire-retardant properties with the functional requirements of materials. For example, adding too much fire-retardant coating can affect the mechanical properties or weight of a material, limiting its use in certain applications. Additionally, the cost of fire-retardant coatings can be a barrier for some industries, especially small businesses with tight budgets. Ongoing research is focused on developing cost-effective solutions without compromising fire safety. The future of fire-retardant coatings will likely involve greater integration with smart technologies. For example, smart coatings that can change properties in response to fire or heat stimuli are under development. These coatings could provide real-time feedback, alerting personnel or activating firefighting systems based on the severity of the fire. Furthermore, sustainability will continue to drive innovation, with more emphasis on eco-friendly fire-retardants that minimize environmental impact during production and in the event of a fire.

1.2 Fire-retardant coatings

Fire-retardant coatings are protective substances applied to materials to slow down or prevent the spread of fire. These coatings provide a critical layer of protection by creating a barrier that delays the ignition and combustion processes. They are commonly used on various materials such as wood, steel, plastics, and textiles, helping to minimize damage, structural failures, and potential loss of life during a fire incident. By controlling fire spread, these coatings allow for more time to evacuate and take other emergency actions (Soares et al. 2024). The fire protection system is usually of two types; active fire protection (AFP) which consists of motion and a quick response to extinguish fire such as fire extinguishers, fire fighters, fire alarms, sprinklers. Secondly, we have passive fire protection (PFP) which aims to mitigate or retard the effects of fire, and consists of fire-retardant coatings, firewalls, chopped fire sprays, fire doors, and fire dampers (Yasir et al. 2019). Fire-retardant coating stands out as one of the simplest, oldest, and most effective methods for safeguarding materials against fire without altering the intrinsic properties of materials. Materials such as wood, plastics, steel, electric cables, polymer composites, and foams are protected by fire-retardant coatings. Optimal fire-retardant coatings should exhibit minimal flame propagation, release negligible or low quantities of smoke and hazardous gasses, be easy to apply, adhere to the underlying substrate, and remain cost efficient (Mariappan et al. 2017).

1.2.1 Mechanisms and Importance of Fire-Retardant Coatings in Fire Protection

Fire-retardant coatings function by reducing the flammability of materials and slowing down the spread of fire. The mechanisms vary, but the core principles involve insulating the material from heat, reducing the availability of oxygen, or forming protective layers that prevent the material from igniting. Intumescent coatings expand to form a thick foam that insulates the surface, while non-intumescent coatings may release gases that dilute flammable components or disrupt chemical reactions involved in combustion. The ignition of fire invariably commences on the surface, underscoring the importance of prioritizing the protection of materials. Hence fire-retardant coatings are majorly focused on the protection of flammable as well as non-flammable materials occurring before the fully developed phase of fire called flashover. Material properties such as flame spread, release of heat, gases and smoke, and ignition are taken into consideration by fire-retardant coatings which play a huge role prior to the flashover period (Perez Ulises. et al. 2009). Although achieving indefinite protection of materials against fire through coatings is unattainable, these coatings can effectively delay fire propagation or preserve structural integrity and stability during fire exposure. This allows sufficient time for the implementation of safety measures.

1.2.2 Standards and Regulations

Fire-retardant coatings must comply with stringent safety standards and regulations, which vary by region and application. Organizations such as ASTM International, NFPA (National Fire Protection Association), and UL (Underwriters Laboratories) set guidelines for the performance, testing, and certification of these coatings. Building codes also dictate the required fire ratings for various construction materials, ensuring that fire-retardant coatings meet minimum safety requirements for residential, commercial, and industrial settings. Especially the NFPA 703- Standard for Fire retardant Treated Wood and Fire Retardant Coatings for Building Materials defines requirements for fire-retardant treatments and coatings used to reduce the flame spread of combustible materials. NFPA 703 offers enforcers, engineers, and architects the most up-to-date and comprehensive criteria for defining and identifying fire-retardant-treated wood (FRTW) and fire-retardant coatings for building materials. This standard ensures that these materials are rigorously tested and properly classified, providing a clear framework for their use in construction. By adhering to NFPA 703, professionals can have greater confidence that fire-retardant materials meet the necessary safety requirements, effectively reducing the spread of flames and contributing to overall fire safety. The standard not only specifies the performance criteria but also ensures that the products maintain their fire resistance properties throughout their lifespan, even under environmental stressors like humidity and temperature changes. As a result, NFPA 703 plays a critical role in enhancing building safety and ensuring compliance with fire safety regulations (FSP Books 2018).

1.3 Importance of Fire-Retardant Coatings in industrial safety

As fire safety rules become increasingly strict, there is a growing need to reduce the risk of fires caused by combustible materials including wood, plastics, and fabrics. An appropriate flame retardant (FR) treatment may delay ignition and reduce flame spread, reducing the risk of fire, loss of life, and property damage. The only barrier between the fire source and the fuel is fire resistance coating. Throughout the combustion of a material this coating will withstand the fire spread. This helps to delay the ignition by diminishing the thermal and material exchange between the gas medium. Intumescent or non-intumescent are the types of retardant coatings which are classified in the FR mechanism. When the substance is exposed to fire the three-dimensional carbonized layer forms on the top of the substance. A traditional intumescent char formation forms with the help of carbon sources, an acidic source employed to form dehydrating catalyst and a porous barrier forms with the help of blowing agent. Hinder flame spread and flame-retardant additives are the two this non-intumescent coating contains (Liang et al. 2013).

Polymers are chemical compounds or combinations of chemicals made up of a high quantity of repeating structural units. Polymerization is a process to obtain this smaller molecular binding. Polymers are the formation of linked chain components. A homopolymer is a material with all structural units corresponding to the same monomer. Copolymers, on the other hand, have diverse structural units. Polymers are highly combustible materials due to their molecular arrangements. These polymers will decompose when they are exposed to sufficient heat. The material characteristics of the polymer will determine the sufficient heat needed for decomposition of the polymer. The heat storage capacity of the polymer correlates with the energy stored by the polymer when it is exposed to heat sources (Kiliaris et al. 2014).

The flame retardant will help to keep the heat supply of the material below its critical flame stability. This fire restriction can be obtained by the changes in the rate of the chemical and physical burning process. This flame retardant will perform a blanket action above the volatile materials to avoid burning of products. Create an insulation between the surface of burning material to limit the mass and heat transfer across the surface layer. To evaluate flame retardant systems, it's important to consider their inherent toxicity and environmental impact, which is becoming increasingly important in current industrial chemistry (Camino et al. 1991).

1.3.1 Cost Effectiveness

Cost effectiveness is a key consideration when evaluating and implementing fire-retardant (FR) systems. The type of flame retardant used significantly impacts overall costs. Intumescent coatings, which form a protective char layer when exposed to heat, tend to be more expensive than non-intumescent coatings due to their complex formulation. However, the additional protection they provide might justify the higher initial investment by reducing the long-term risk of fire, loss of life, and property damage. Moreover, the installation and application of FR systems can involve labor costs, equipment, and surface preparation. While advanced FR technologies may offer superior protection, the cost of labor and materials must be balanced with the benefits they provide. This analysis includes considering the lifespan of the coatings and their maintenance requirements, as some may need to be reapplied or repaired over time, contributing to overall costs. Training and awareness also play a significant role in cost-effectiveness. Investing in proper training for staff responsible for applying and maintaining FR systems ensures these materials are used correctly, maximizing their protective capabilities. This approach can minimize costly errors that might lead to inadequate fire protection or the need for costly reapplication. Regular maintenance and inspection are vital for ensuring the continued efficacy of FR coatings. While this adds to the cost, it is a necessary investment to prevent more severe financial losses due to fire incidents. A proactive maintenance program can extend the life of the coatings and ensure they remain effective, ultimately leading to greater cost savings in the long run.

1.4 Types of Fire-Retardant Coatings

Fire-retardant coatings can be divided into two primary categories: non-intumescent and intumescent coatings. Intumescent coatings demonstrate significant expansion by the formation of a char layer and provide effective fire protection when exposed to combustion (Hu et al. 2017). These coatings, also referred to as reactive coatings, have become a widely accepted method of protecting load-bearing structural steel during fire events. One of the key advantages of intumescent coatings is their minimal impact on the architectural appearance of exposed steel structures; they maintain aesthetic integrity while providing crucial fire protection. Furthermore, these coatings are lightweight, which is beneficial for maintaining the structural load of buildings. Their versatility allows for application both on-site and off-site, making them a convenient choice for various construction scenarios (Lucherini et al. 2019). On the other hand, non-intumescent coatings are primarily decorative and architectural coatings infused with flame retardant additives. These additives are designed to slow down the speed of flames and reduce the production of smoke on combustible substances (Giudice et al. 2017). While they do not expand like intumescent coatings, non-intumescent options offer a level of fire protection suitable for less critical applications where aesthetics are paramount. They are often utilized in residential and commercial interiors, where maintaining the visual appeal of surfaces is essential while still providing a degree of fire safety. Non-intumescent coatings can effectively shield against ignition and limit fire spread on exposed surfaces, making them an important component of a comprehensive fire safety strategy.

Overall, both intumescent and non-intumescent coatings play vital roles in enhancing fire safety across various applications, balancing functional performance with aesthetic considerations. The choice between these two types of coatings ultimately depends on the specific requirements of the structure, including fire safety regulations, design preferences, and the desired level of protection. By selecting the appropriate coating, builders and architects can ensure that their designs meet safety standards without compromising on aesthetics or functionality.

1.5 Flame-Retardant Polymers

The widely used fire-retardants are halogen-based compounds, phosphorus-based compounds, and nitrogen-based compounds. To enhance a polymeric material's fire resistance, successful solutions entail halting the combustion process at specific phases to prevent ignition, reduce burning rate, and/or alter the combustion mechanism. The basic goal is to remove one of the three necessary components of fire. The combustion process involves three components: (1) fuel, (2) external or internal heat, and (3) oxidizing gases (Kiliaris et al. 2014).

1.5.1 Halogen-based additives

The volatile combustion product, which has a concentration within the flammability limit and a temperature higher than the ignition temperature, then undergoes combustion. Flame stability of the polymer can be maintained below the critical level with the help of fire-retardants. These halogen-based compounds are widely applicable and among the most effective flame-retardant compounds available. During the polymer process, the thermal stability of iodine compounds is lower than required; however, fluorine components exhibit comparatively high stability during processing. Flame-retardant polymer materials can be prepared by adding halogenated structures into the polymer chain through copolymerization. The flame-retardant properties of halogenated compounds can be significantly improved without the addition of any metal compounds. The active species formed in the halogen compounds play a major role as an essential flame retardant mechanism in the condensed phase (Wilkie and Morgan 2009). Halogenated compounds are the most commonly used flame retardants due to their low cost, availability, and substantial industrial experience. Their effectiveness stems from their ability to disrupt combustion by scavenging free radicals and preventing flame propagation in the vapor phase. During combustion, oxygen and fuel are converted into stable combustion products through thousands of chemical reactions. The most significant reactions include the formation of highly reactive hydroxyl (OH) radicals, with reactions such as $O + H_2 \rightarrow OH + H$ and $H + O_2 \rightarrow OH + O$ being essential to the combustion process. A simplified model of combustion chemistry demonstrates how the formation of OH radicals contributes to flame propagation. However, the primary source of energy for the flame arises from the exothermic processes, including $OH + CO \rightarrow CO_2 + H$ (Kiliaris et al. 2014). The use of halogenated flame retardants, such as iodine, fluorine, chlorine, and bromine compounds, can be strategically designed to enhance fire safety in various applications. Their effectiveness in reducing flammability and limiting flame spread can provide significant benefits in terms of safety and compliance with fire regulations. However, it is essential to consider environmental and health impacts associated with halogenated compounds, as some may release toxic byproducts upon combustion. As a result, there is ongoing research into developing safer and more sustainable flame retardant alternatives that can provide similar protective qualities without the associated risks. This research is crucial as industries increasingly prioritize fire safety alongside environmental sustainability. By optimizing the use of halogenated flame retardants and exploring new formulations, manufacturers can enhance the performance of polymeric materials while ensuring safety and compliance with environmental regulations.

1.5.2 Phosphorus-based additives

Many reactive and additive methods to phosphorus-containing compounds are becoming more and more successful, leading to their proposal as halogen-free flame retardants for a range of polymeric materials and applications with distinct mechanisms and efficiencies attained. Phosphorus can function in the gas phase through flame suppression and in the condensed phase by promoting char, yielding intumescence, or through the creation of inorganic glass. The flame-retardant coating containing phosphorus will act in the gas phase. In the gas phase the radical recombination are harmless due to the replacement of less effective hydrogen and hydroxy radicals. Flame inhibition is the process of slowing down or stopping the branching and chain reactions that result from the oxidation of hydrocarbons in the gas phase, which lowers the amount of heat produced. Here the PO radicals play a major role in reducing heat release by lowering the heat releasing rate. Some important reactions are, (Schartel et al. 2010).

$$PO + H \rightarrow HPO$$
$$PO + OH \rightarrow HPO_2$$
$$HPO + H \rightarrow H_2 + PO$$

Depending on the qualities required of the plastic in terms of the performance of the final product, phosphorus flame retardant can either be blended with polymers or be reactive, that is, chemically bound into the plastic molecules at polymerization. Epoxy resins, polyurethane foams, and polyethylene terephthalate fibers are the primary applications for reactive phosphorus flame-retardant compounds. In polyolefins and engineering plastics, additive phosphorus flame retardant is frequently used. (Hörold 2014).

1.5.3 Nitrogen-based additives

The gas or vapor emitted from the nitrogen-based compound has low toxicity. The cone calorimeter results indicate that nitrogen compounds have the maximum efficiency. It emits much less corrosive gas when compared to hydrogen chloride or hydrogen bromide. This type of flame retardant has the advantages of low smoke and absence of dioxins. They can be recycled by re-extrusion because of their high decomposition temperature. Ammonium polyphosphate is among the most widely used nitrogen compounds in fire retardants, they can also act as a fertilizer due to their chemical composition. Another important compound used as a flame retardant is called melamine. Melamine phosphate is a flame-retardant compound mainly used in textile fibers (Horacek et al. 1996).

Nitrogen-containing compounds are among the most environmentally friendly flame retardants, emitting minimal smoke and no dioxin or halogen byproducts after combustion. Polymeric material combined with the nitrogen-based flame retardant will help to facilitate recycling. The performances of polyamides and polyolefins are improved using the nitrogen-based flame-retardant coating. Organic and inorganic acid comes to react with the weak base melamine to form thermal salt. Melamine cyanurate and melamine phosphate are often utilized to improve polymer fire behavior due to their flame-retardant properties and melamine pyrophosphate. The bulk of melamine salts function in the condensed phase. Using N-alkoxy or cycloalkoxy derivatives as flame retardants results in the formation of radical species during breakdown, providing a unique mode of action (Kiliaris et al. 2014).

1.5.4 Advantages of Flame-Retardant Polymers

The main advantage of flame-retardant polymers is to slow down the combustion of material. The halogen-based, phosphorous-based, and nitrogen-based components are used to slow down the combustion of materials. Halogen radicals are formed when the flame retardant is exposed to high temperature. Flame retardants form a protective layer on the surface of the combustion material. When the inorganic compound undergo combustion, this layer forms a non-volatile layer on the surface. This flame retardant will create a physical barrier on the surface with the help of dense protective layer. A flame retardant containing bromine compounds will not emit toxic gas to its surroundings. The phosphorus-based flame retardants are very active in the gas or condensed phase. Active radicals H and OH can be deactivated during the decomposition of halogen radicals. Fire protection of electrical products is produced by specially processed red phosphorus called polyamides. (Zaripov et al. 2022).

1.5.5 Disadvantages of Flame-Retardant Polymers

Toxicity is the major disadvantage of flame retardant, during the large-scale fire the chemically produced flame retardants will emit high toxicity. Only the smaller fire can help to achieve the environmental benefit. Use of polyaromatic hydrocarbons as a flame retardant in the furniture can create a huge impact on the environment. The flame retardant and non-flame retardant does not have any significant difference between toxicity of combustion gases. There is a high need for environmentally safe and recyclable flame-retardant thermoplastics. (Levchik et al. 2007).

1.6 Thermal Barrier Coatings

Thermal barrier coating (TBC) systems are usually made up of duplex, consisting of a metallic bond coat and a ceramic topcoat. The bond coat protects substances from oxidative and corrosive harm. Enhance the connection between the ceramic topcoat and the substrate. When compared with metallic coating, ceramic topcoats have low thermal conductivity and can also form a significant temperature decrease across the ceramic layer. This will help to improve the operation efficiency and durability of the metallic substance by reducing its temperature. These thermal barrier coatings have played a major role in industrial development since the 1950s; at first these enamel coatings were used in military engine components. In the past decade, yttria-stabilized zirconia (YSZ) has been accepted as a superior ceramic topcoat material and has become the norm. There are two well-established deposition procedures. There are two processes: electron beam physical vapor deposition and atmospheric plasma spraying (Vaßen et al. 2010).

Thermal barrier coatings are used on components that use air channels to cool themselves. Designs with TBC-coated parts consider portions. The system engineers determine the configuration, thickness, heat flow, heat transfer coefficients, combustion and turbine inlet temperatures, and total cooling air allowed. Thinner coatings are recommended to reduce bulk and improve cooling hole sealing. Yttria-stabilized zirconia has a high melting point, moderate thermal conductivity, high oxygen permeability, and considerably $Y2O_3$ has a higher coefficient of thermal expansion than other oxides, and its 6-8 wt-% composition remains constant at high temperatures (Darolia et al. 2013).

YSZ TBCs with 6 to 8 wt.% yttria content are commonly used due to their high fracture toughness, which is achieved by a unique method. Adding more stabilizer can result in fully stabilized cubic zirconia with lower durability. A decreased amount of stabilizing additive causes a higher durability at room temperature and can lead to detrimental phase transitions after heating. Other materials, such as aluminates, are being investigated. These materials are often deposited partially amorphously. Heat treatment causes crystallization and shrinkage, resulting in fracture formation. Controlled crystallization can provide complex strain-tolerant microstructures with an attractive lifespan. Recent improvements in TBC systems include enhanced processing pathways and modern TBC materials. New TBC materials in a double-layer structure, using YSZ as the first layer, provide advantages over YSZ. Double-layer systems using pyrochlore and YSZ are particularly efficient (Vassen et al. 2009).

1.6.1 Advantages of Thermal Barrier Coatings

Coatings should have a high melting point to sustain high working temperatures without melting down. The coating exhibits low thermal conductivity, resulting in a significant temperature reduction being seen throughout the covering. To lower the payload, the coating material should be lightweight and low density, and resistant to oxidation and chemical exposure. The coating should protect the underlying metal from oxidation and corrosion. The coating's strong emissivity reflects the majority of incident heat being released away. Coatings should withstand mechanical erosion. The combustion chamber's exhaust gas contains numerous particles. The coating material has a higher coefficient of expansion under heat relative to the substrate. It can withstand high temperatures without cracking or failing. It also resists high thermal shock. Depending on the conditions, it produces coatings of varying thicknesses and deposition speeds (Sankar et al. 2014).

1.6.2 Disadvantages of Thermal Barrier Coatings

Thermal barriers will undergo phase changes at 1170°C. They have the nature of corrosion and oxidation diffusion. Thermal barriers will get crystalized at 700 to 1000°C. These thermal barriers have very low thermal expansion coefficient. Some materials of thermal barriers have the characteristic nature of high sintering rate. Alumina-based thermal barriers have some limitations such as very low thermal expansion and phase transformation above 1000°C. CeO_2 + YSZ-based thermal barriers have limitations of high sintering rate, CeO_2 precipitation at temperature above 1100°C, and loss of CeO_2 while spraying. (Avci et al. 2018).

1.7 Intumescent Coatings

The term "intumescent flame retardant" refers to the mode of flame retardancy used during fires. During a fire, they form a protective carbon foam that rises in response to heat (intumesce). This class of flame retardants is rigidly condensed in their activity, and either provides and produces its own carbon char or utilizes the polymer as a carbon char source. Intumescent typically consist of three components that generate carbon char. A thermally stable form of carbon was formed by the carbon source of an acidic catalyst. The gas form helps to convert carbon source to carbon foam. These compounds are combined to provide high protection when the material is exposed to fire. The intumescent system has ammonium polyphosphate that acts as the acidic source, pentaerythritol which acts as the carbon source, and a gas form which acts as a melamine source. These are the three compounds combined to form an intumescent formulation, but the formulation of intumescence varies with its structure. Graphite is another source of intumescence with its own carbon content with no requirement of acidic catalyst. Intumescent flame retardants are commonly used to protect fire barriers, steel, and wall holes, as well as other applications that require excellent fire safety. Intumescents are typically applied to another substrate as a paint or barrier, providing thermal protection for a set length of time (Morgan et al. 2012).

When heated, intumescent polymeric systems produce a significant amount of thermally stable carbonaceous residue. The charred layer serves as a physical barrier, slowing heat and mass transfer between the gas and condensed phases. The intumescence phenomena has a direct use in protecting metallic elements in construction. Fire can bend materials, causing building structures to collapse. Using intumescent paint to create a heat barrier can protect these interests. It reacts with free radicals produced during polymer breakdown. These species may contribute to the end of free radical reactions. Pyrolysis of polymers and deterioration of protective materials occurs in the condensed phase. It supports acidic catalytic species that react with oxidized products from thermo oxidative degradation of materials. Intumescence is a method of achieving flame retardancy that maintains the polymer's inherent qualities while meeting fire requirements (Bourbigot et al. 2004).

Intumescent coatings form a multicellular cushion to prevent combustion of material when it is exposed to fire, it prevents penetration of oxygen and heat into the material. A 'catalyst' must be high in phosphorous and degrade to produce phosphoric acid below the decomposition point of the other ingredients. Typically, ammonium or organic phosphates like melamine phosphate are used. The carbonific is a carbon-containing compound with numerous 'phosphorous esterifiable' groups, usually hydroxyl groups. The ester then the breakdown process produces a substantial amount of carbon, water, carbon monoxide, and other gases. Phosphorus is released for further esterification. This approach minimizes the amount of flammable tars and gases produced during carbonific decomposition, yielding a carbon-rich char instead. When choosing a carbonific, achieve a balance between the number of carbon and hydroxyl groups present. Carbohydrates, proteins, and polyfunctional alcohols are all suitable materials. The blowing agents disintegrate, releasing significant amounts of non-flammable gases. This causes the carbon-rich bulk to bubble and froth, creating a dense insulating coat. Many combinations use two blowing components with somewhat variable degradation temperatures to increase the gas release duration. In general, lower temperature blowing agents are amides or amines, while higher temperature blowing agents are chlorinated paraffins. The binder creates a skin over the foam, containing it and ensuring a consistent structure throughout. The resin might be deformable or transformable and it hardens by oxidization or polymerization (Rhys et al. 1980).

1.7.1 Advantages of Intumescent Coatings

Intumescent coatings are a type of non-mineral coating which undergo thermal expansion to swell into a thick insulative foam when heated above a critical temperature (Weil et al. 2011). This prevents the temperature increase of a material such as steel by swelling to form a low-density, low-thermal conductivity foamed char (Lucherini et al. 2019). Intumescent coatings have the ability to expand up to 100 times their original thickness when exposed to heat, transforming from a 1-mm layer into a 10-cm thick foam (Puri et al. 2016). These coatings can be easily applied by professional painters, and can offer pleasing appearance and robust surfaces (Weil et al. 2011). Due to their substantial void content and considerable thickness, these act as an effective thermal insulator protecting the underlying substrate against heat and flame. These coatings exhibit exceptional thermal insulation properties in the presence of flame by depleting the heat transfer rate to the underlying material. These coatings can be considered advantageous as they are highly effective in delaying combustion, moderating heat release, inhibiting flame propagation, and decreasing the density of smoke in composite materials (Mohd Sabee et al. 2022). Owing to their visual appeal and functional efficacy, organic thin intumescent coatings are widely gaining popularity. Thin intumescent coatings consist of organic intumescent coatings which provide high-quality finish and can be top-coated for enhanced durability in an outdoor environment. They offer numerous advantages including ease of application, aesthetic appeal, and flexibility. These are frequently used today in sports complexes, shopping malls, skyscrapers, hotels, and modern-day airports. (Puri et al. 2016)

1.7.2 Disadvantages of Intumescent Coatings

The impact of heating conditions on intumescent coatings’ performance is quite significant. Some researchers have demonstrated that low heating regimes or slow-heating fires may potentially cause melting and/or delamination of the coatings along with incomplete swelling. These conditions reduce the efficiency of the intumescent coatings, compromising the insulation properties. Certain climatic factors such as humidity, temperature changes, thawing and freezing, ultra-violet radiations, and/or acid polluted environments result in the potential aging and deterioration of the intumescent coatings (Häßler et al. 2024). Constant exposure of the coatings for an elongated period of time to the atmosphere causes the alteration of the internal structure of the coatings, weakening the factors which are of utmost importance for the formation of the char layer. Due to this, it cannot be guaranteed that the coating properties will still be effective for fire protection (Puri et al. 2016). Many commercially used coatings exhibit poor adhesion to the underlying substrate and hence often detach during swelling, because of which the composite material is directly exposed to the flame. Additionally, these coatings present some incompatibility with certain manufacturing processes, have poor durability, limited susceptibility to erosion, and poor aesthetics (Mohd Sabee et al. 2022).

1.8 Non-Intumescent Coatings

Non-intumescent coatings are primarily decorative or architectural finishes that incorporate additives to diminish the propagation of flames and reduce smoke production (Mariappan et al. 2016). Unlike intumescent coatings, these do not swell, but instead employ a dissimilar mechanism of activity when exposed to heat. These coatings release active species into the gas phase which inhibits flame propagation through chemical interactions. These active compounds catalyze the decomposition of substrate material to produce char layers, or help in preventing the radiational heat transfer from heat source to the substrate (Liang et al. 2013). Usually, these are liquid-based saturants and penetrate deep into the wood, ensuring thorough coverage and protection. Upon exposure to high heat and elevated temperatures, these retardants simultaneously release water vapor along with increasing the charring level of the wood. This mechanism reduces the woods capacity to sustain combustion, leading to a “self-extinguishing effect” once the external source of flame is removed. Hence, propagation of fire further along the wood surface is prevented. Another type of non-intumescent coating is paint. Instead of expanding when heated, this type of retardant undergoes chemical transformation, forming a tough, protective layer which acts as a barrier for flames to penetrate and reach the underlying substrate. Moreover, it dissipates the heat across the layer of paint, reducing the risk of ignition. These retardants are frequently available as paint additives (Zybina and Gravit 2020). These coatings are categorized into Class A, B, or C based on their efficacy in minimizing fire contribution and smoke emission (Mariappan et al. 2016). These normally offer a high flame-resistant concentration on the surface area of the substance, therefore keeping the bulk qualities of the substance that is coated (Liang et al. 2013).

1.8.1 Advantages of Non-Intumescent Coatings

These coatings can penetrate deeply into porous materials such as wood, hence they provide protection throughout the material rather than just protecting the surface; with proper application they provide protection uniformly across the area. Traditional non-intumescent coatings incorporate flame proof additives that obstruct the fire propagation. These coatings are durable and do not require frequent re-application and hence require less maintenance cost compared to other types of fire-retardants. Various forms of non-intumescent coatings such as paints and saturants are available, which can be used on a variety of materials depending on the suitability of application (Liang et al. 2013).

1.8.2 Disadvantages of Non-Intumescent Coatings

These lack in providing substantial volumetric protection to the underlying substrate that the intumescent coatings offer, hence the effectiveness of using only flame-retardant compounds in non-intumescent coatings is inadequate for some applications (Liang et al. 2013).

1.9 Fire-retardant Additives, Binders, and Fillers

Many existing flame retardants pose significant health and environmental risks due to their harmful formulations, and are not environment friendly or sustainable, as they are synthetically developed. Hence, the development of sustainable and non-toxic alternatives is significant to overcome problems created by the synthetically produced flame retardants. For this purpose, numerous research groups are dedicated to creating new bio-based flame-retardant additives for synthetic polymers such as lipid, chitosan, proteins, polysaccharides, chitosan, microfibrillated cellulose, fly ash, and clay. Essentially, additives are employed to enhance the flame resistance of flammable materials. Additives are incorporated into combustible materials to delay ignition, supress flames, and reduce the spread of flame when exposed directly to flames. Moreover, these are not chemically bonded to the surrounding material. However, ongoing research aims to graft additional chemical groups onto these additives, enabling their integration without compromising their flame-retardant effectiveness. Additives that can be used to formulate effective intumescent flame-retardant coating systems are ammonium polyphosphate, pentaerythritol phosphate alcohol, melamine, and boric acid/borate (Mohd Sabee et al. 2022).

Binders in intumescent flame-retardant coatings are of utmost importance as they bind together the ingredients of the coatings. They play a huge role in the main degradation step of the coating by aiding in the development of a consistent foam structure and facilitating the expansion of the char layer. Binders like alkyd resin, acrylic resin, cellulose, polyamide, polyvinyl acetate emulsion, vinyl chloride latex, epoxy resins, polyurethane, ethylene-vinyl acetate paints, and phenolic or amino resins are commonly utilized in the formulations of intumescent flame-retardant coatings. Although these binders effectively combat flames, their chemical compositions typically release a substantial amount of smoke and toxic gases when exposed to flame. Water-soluble binders, such as epoxy emulsion, are recommended to limit the amount of smoke and harmful fumes. They avoid pollution while keeping the effectiveness and quality of intumescent fire-retardant coverings that provide flame protection (Mohd Sabee et al. 2022; Yasir et al. 2019).

Fillers are quite popular and have been extensively used in industry for many years, and are crucial components in all polymeric systems, typically making up 20-40% of the intumescent coatings mass. These are found in various shapes and sizes to increase the mechanical stability and thermal integrity at a lower cost, and may be used as active or synthetic fillers (Yasir et al. 2019). Incorporating any particulate filler into a polymer has a substantial impact on its combustion behavior, including its resistance to ignite, the kind and quantity of smoke, and the release of poisonous gases. These modifications can be due to the dilution of the ignitable substance, which reduces the speed of diffusion of both oxygen and combustible pyrolysis products and alters the melt rheology of the polymers, thereby impacting its potential to drip (Hornsby et al. 2001). Generally, no filler can be classified as truly inert with respect to their effect on flame-retardant combustion. Although, fillers such as carbonates, hydroxides, and some metal hydrates can present additional smoke suppression and flame retardancy properties. These fillers undergo an endothermic breakdown reaction, which chills the solid or condensed phases and the release of gases that dilute and cool combustible combustion products in the vapor phase is observed. This procedure not only helps with overall smoke suppression, but it also leaves an inorganic residue as the filler decomposes. This residue forms a thermally isolating barrier between the base polymer substrate and the outside heat source. For commercial use, these fillers should not only be effective flame retardants, but also be non-toxic, cost-effective, readily available, and free of conductive contaminants. The thermal decomposition of the fillers should generally occur near to the onset of flame-retardant degradation, while subsequently releasing flammable volatile compounds, to maximize the fire-retarding effect. Some commonly used fillers in the formulation of intumescent flame-retardant coating systems are aluminum tri hydroxide, magnesium carbonate, magnesium hydroxide, titanium dioxide, fly ash, expandable graphite, and cenospheres (Mohd Sabee et al. 2022).

1.10 Comparative Analysis between Fire Retardant and Fire Resistant

Fire-retardants can affect the various stages of combustion. Depending on their nature, flame retardants can work chemically or physically; physically in the solid, liquid, or gas phase. They disrupt combustion during specific stages, including heating, breakdown, ignition, and flame spread. It is well accepted that flame retardants that prevent burning by chemical action are more effective than those that act by physical means. The distinction between chemical and physical impacts is sometimes unclear, making it challenging to assess their contributions. Synergistic combinations of retardants are increasingly being used, resulting in greater effectiveness at lower doses. Different modes of action for flame retardants can be distinguished from synthetic polymers. Intumescent protective coatings create foams. They protect combustibles. Materials that prevent heat release and temperature rise. The polymer matrix may also include intumescent components. Key characteristics for estimating the behavior of retardant materials include ignitability, heat release, flame spread, smoke production, and toxicity. Elevated temperatures can affect corrosive gas production, charring rate, and mechanical qualities (Mikkola et al. 2000).

In addition to fiber properties and fabric quality, various clothing features have an impact on thermal protection. Lower density correlates with increased thermal resistance for a given fabric thickness. This applies to fibers like cotton and wool that form insulating char when heated. Hence, heavier textiles were produced. Cotton, wool, and other non-melting fibers provide good thermal protection, while thicker thermoplastic-fibre materials cause more severe burns (Bajaj et al. 1992).

Fire resistance is employed to restrict the burning of material for certain hours. Fire barriers and supporting structures must have enough fire resistance. To assess fire resistance, exposures (time-temperature connections) must be identified. Exposures are classified as either standard fires or real fires. The stability fire rating determines how long an element can sustain a conventional fire test and maintain its load-bearing capacity while permitting a degree of the load is placed. The tightness of an element's joints limits smoke and gas, determining how long it can maintain its fire separation capabilities. Insulation refers to heat shielding given by either primary or secondary elements. It is used for fire separations where heat can be transmitted. This could threaten passengers on the non-exposed side and spread fire to neighboring fire compartments. The fire rating refers to the maximum permitted temperature rise on the non-exposed side. Fire resistant can continue to work normally in the presence of fire. Flame retardant will not operate normally during a fire, but will actively avoid the fire from spreading (Zybina and Gravit 2020).

1.11 Methods of applying fire-retardant coatings

Fire-retardant coatings can be applied using various methods, each with its advantages and disadvantages based on application requirements and surfaces involved. The brush application is particularly suitable for small areas or intricate details, allowing for precise application but can be time-consuming for larger surfaces. For flat and expansive surfaces, roller application is preferred, as it allows for quick and even coating, significantly speeding up the application process, though it may lack the precision of brushes. The spray method, utilizing a spray gun, excels for both large and complex surfaces, ensuring an even coat while reaching difficult areas. However, it requires proper equipment and safety measures to avoid inhalation of fumes. Dipping involves immersing the object in the fire-retardant coating, providing thorough coverage, especially for small items, but is generally impractical for large structures. Proper preparation of the substrate is crucial for achieving the best results with fire-retardant coatings. Cleaning the surface thoroughly is essential; it should be dry and free from dust, grease, or contaminants, accomplished using a damp cloth or appropriate cleaning agents. Sanding is necessary for wooden surfaces, creating a smooth finish and improving adhesion, while metal surfaces may require sandblasting to remove rust and create a rough texture for better bonding. Applying a primer enhances adhesion, particularly on porous surfaces like wood or concrete, acting as a binding layer that improves performance and longevity. Any existing cracks, holes, or imperfections should be repaired before applying the coating to ensure a uniform finish and prevent failure due to underlying defects. Several factors can impact the quality and effectiveness of fire-retardant coatings. The condition of the surface is critical for ensuring good adhesion and effectiveness; a clean, smooth, and properly prepared surface results in better performance. The chosen application method can significantly influence the thickness and uniformity of the coating, making it essential to select the right one for optimal results. Environmental conditions, such as temperature and humidity during application and drying, greatly impact performance; thus, following the manufacturer's recommendations regarding optimal conditions is advisable. Finally, applying the correct thickness of the fire-retardant coating is crucial, as a layer that is too thin may fail to provide adequate protection, while an overly thick layer can lead to issues such as cracking or peeling. Careful attention to coating thickness will ensure the longevity and effectiveness of the fire-retardant properties.

1.12 Significance of fire-retardant coatings

Fire-retardant coatings are significantly used across various sectors, including building construction, electrical appliances, electronics, and transportation. These coatings provide essential fire resistance, enhancing safety and durability in these critical industries (Liang et al. 2013)

Wood being a sustainable, versatile, and an aesthetically pleasing material, is used in making various products such as laminated timbers, flooring, cladding, structural timbers, solid wood panels, and widely used in construction and furnishing. However, wood has some inherent deficiencies such as poor dimensional stability, flammability, and low resistance to microbial decay which needs to be addressed for construction purposes. Hence, the fire retardation of wool is typically achieved by applying flame retardant chemicals through spraying, dipping, or impregnation techniques. Some of the compounds used in improving the fire retardancy of wood are mineral acids, boron compounds, and inorganic salts (Mariappan et al. 2017). Fire-retardant coatings also have significant application in textiles. Typically, a reactive fire-retardant or polymer-coated matrix provides fire resistance when applied to textile surfaces. The polymeric matrix consists of polyacrylates, epoxides, silicones, polyvinyl chloride (PVC), or polyurethanes (PUs). The wide use of PVC-based coatings is observed for textiles because of their effective flame retardancy and durability even under adverse environmental conditions (Hu et al. 2017). In the transportation and building industry, flame retardancy is often achieved by incorporating flame retardant additives into paints and lacquers used for surface coatings. These formulations typically include components like antimony trioxide, chlorinated paraffins, and titanium dioxide which are used for FR latex and alkyd-based paints. These additives help to reduce flame spread in the gas phase and promote the formation of nonvoluminous char on the surface of the material in the condensed phase, enhancing fire resistance. In electrical applications, flame retardant coatings are commonly applied to cables and wires to impact necessary fire-resistant properties (Liang et al. 2013).

1.13 Recent Advancements in Fire-Retardant Coatings

The recent advancements in this field are focused on producing non-halogen flame retardant additives such as nitrogen containing compounds, phosphorous containing compounds, or metal hydroxides. The halogen-based retardant additives usually produce a huge amount of smoke and toxic gases, hence the use of non-halogen-based retardants can easily replace the role of halogen-based additives. Nitrogen-based coatings are becoming increasingly popular due to their reputation as environmentally secure and harmless alternatives to typical halogen compositions. Additionally, the substance containing nitrogen-based flame retardants is appropriate for recycling. Common nitrogen-based compounds utilized for flame retardant applications are melamine derivatives, which demonstrate flame inhibition in both gas and condensed phases. However, the exclusive use of nitrogen-based systems for effective protection of surface is still being evaluated. Phosphorus-based coatings in comparison with other flame-retardants are known to produce less smoke and toxic gases after undergoing combustion. Similar to nitrogen-based flame retardants, these also exhibit flame retardancy in the gas and condensed phase. Even though these are thought to be more favorable than halogen-based coatings, they do pose certain environmental risks, such as pollution caused by compound hydroxylation, acidic erosion, and even cancerous activity (Liang et al. 2013). Studies state that the incorporation of both the compounds, nitrogen, and phosphorous work effectively as radical trappers along with exhibiting efficient charring properties and can act as efficient flame retardants in both the condensed and gaseous state (Pham et al. 2024). Hence, the use of phosphorous-nitrogen-based coatings are more effective compared to the hypothetical impact of individual phosphorous and nitrogen added separately, and are great alternatives for the halogen-based coatings (Liang et al. 2013). Silicon-based coatings, generally made up of silicates, silsesquioxanes, silicones, and organosilanes as the main polymeric matrix, or as filler and copolymer into the entire matrix, have been developed in recent years. Similar to the above-mentioned alternatives, these coatings do not release corrosive during combustion (Liang et al. 2013).