



Contents lists available at ScienceDirect

## Journal of Cultural Heritage

journal homepage: [www.elsevier.com/locate/culher](http://www.elsevier.com/locate/culher)

## Review

## Fire-retardant and fire-resistant coatings: From industry to the potential use on cultural heritage

Inês Soares<sup>a,c,\*</sup>, Joana Lia Ferreira<sup>b</sup>, Helena Silva<sup>c</sup>, Maria Paula Rodrigues<sup>c</sup><sup>a</sup> LAQV-REQUIMTE, Department of Conservation and Restoration, NOVA School of Science and Technology, Universidade NOVA de Lisboa, 2829-516, Caparica, Portugal<sup>b</sup> CIUHCT - Interuniversity Center for the History of Sciences and Technology, Department of Conservation and Restoration, NOVA School of Science and Technology, Universidade NOVA de Lisboa, 2829-516, Caparica, Portugal<sup>c</sup> Materials Department - Organic Materials Unit, National Laboratory for Civil Engineering (LNEC), 1700-066, Lisboa, Portugal

## ARTICLE INFO

## Article history:

Received 19 October 2023

Accepted 28 June 2024

Available online 13 July 2024

## Keywords:

Heritage

Fire-retardant

Fire-resistant

Intumescent

Non-intumescent

Coatings

## ABSTRACT

Fire is one of the most damaging deterioration agents in a short time of action. It can cause considerable damage, leading to the loss of lives and possessions. Concerning fire safety recommendations, buildings must be protected by an integrated system of passive and active measures. Two passive measures widely used in many industries are fire-retardant and fire-resistant coatings. These systems provide a fire-protective layer to the surfaces of flammable and non-flammable materials, delaying or preventing their ignition, reducing the heat transfer from the source to the substrate and decreasing the flame spread and the release of smoke and toxic gases. When exposed to fire, according to the different mechanisms of action, fire-protective coatings (FPC) can be classified as non-intumescent and intumescent. Despite being widely mentioned in heritage fire safety guidelines, studies on their application in the field are still scarce. Namely, research on the safety and efficacy of their application near collections (in support materials) and systematic studies comparing different formulations. Therefore, this research assembles interdisciplinary studies on the use of FPC to deepen knowledge and theoretically identify the feasibility of their application in collection support/storage materials or exhibition furniture (bookshelves, cabinets, plinths) in heritage environments.

© 2024 The Author(s). Published by Elsevier Masson SAS on behalf of Consiglio Nazionale delle Ricerche (CNR).

This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>)

## 1. Introduction

Fire is one of the most destructive disasters, even in a short time of action. It can cause considerable damage to health and nature, leading to loss of lives and possessions, and it is no exception for cultural heritage. Fire risk awareness is usually only considered after a tragedy occurs. These moments are crucial for raising questions such as “what has caused it?”, “why did it happen?” and “how can we avoid it from happening again?”, which can prevent future disasters, be they human or material. Still, sometimes awareness comes too late, and many losses have already happened.

Several heritage fires have been reported over the years, confirming that heritage remains highly vulnerable despite the enormous socio-cultural, technological and economic development [1]. Notwithstanding the growing awareness of the protection and

preservation of cultural heritage, whether historic buildings or collections, several highly destructive fires have occurred in the previous years [2–5]: in September 2018, a fire destroyed the most extensive anthropological collection of 20 million artefacts from Rio de Janeiro's 200-year-old National Museum [6,7]; in April 2019, the 850-year-old landmark Notre Dame Cathedral (Paris, France) was partially destroyed [8,9]; in October 2019, the 500-year-old UNESCO World Heritage Site in Okinawa (Japan), the Historic Shuri Castleburned for the third time [10]; followed by the fire at the UNESCO World Heritage Site Tomb of Buganda Kings at Kasubi (Uganda) on June 2020, which burnt for the second time [11]. Such events can raise concerns about whether heritage professionals are doing enough.

Fire safety guidelines mention that buildings must be defended by an integrated system of active (equipment inserted in the building) and passive (physical and/ or architectural barriers) fire prevention and protection measures, and the same must apply to heritage [4,12,13]. Active measures will respond to extinguish the fire (requiring either manual or automatic activation), whilst passive

\* corresponding author.

E-mail address: [i.soares@campus.fct.unl.pt](mailto:i.soares@campus.fct.unl.pt) (I. Soares).

measures will act to contain the fire, preventing it from spreading or resisting the initial ignition (do not require activation to function) [4,14–16]. Still, according to Rio de Janeiro Declaration on Fire Risk Reduction in Cultural Heritage [17], most heritage fires could have been prevented or significantly reduced by proper maintenance and safety procedures, demonstrating that the challenge to reduce heritage fires goes beyond knowledge or recommendations. Guidelines for the mitigation of fire hazards in heritage were also described highlighting the importance of gathering research comparing and compiling alternative fire protection and prevention measures that can fulfil the needs of a wide range of heritage facilities with diverse resources [17].

A passive measure efficiently implemented in multiple domains (automotive, electrical and electronics, transportation, aerospace industry) to reduce fire hazards is the application of fire-retardant and fire-resistant coatings; the latter has significant relevance in the construction sector, for structural steel [18–23], particularly after the tragic collapse of the World Trade Center towers. Nowadays, architects, designers, and engineers use them to construct public spaces and commercial buildings [24–26].

Fire-retardant and fire-resistant coatings are some of the most convenient, economical, and efficient ways to protect materials from fire hazards [18,21,27,28]. By *fire-retardant coatings* (or *flame-retardant coatings*), it is understood coatings formulated to protect the substrate, delaying their ignition, preventing the spread of flames, and not contributing as fuel to the fire. The coating will reduce the heat flow in the substrate, which can inhibit or retard the propagation of thermal degradation, ignition or combustion. Whilst the term *fire-resistant coatings* (also called *fire-resistive* and *fireproofing*) defines coatings capable of withstanding a fully developed fire - after flashover (the simultaneous ignition of most combustible materials) - preventing the substrate from collapsing (usually applied to structures or structural elements). This coating will prevent the substrate from catching fire under extreme heat and flames, having varying degrees of resistance ranging from minutes to hours [19–21,29]. When exposed to fire, according to the different fire-protection mechanisms, these coatings can be classified as intumescent and non-intumescent [18,27,30]. Intumescent coatings undergo thermal degradation, resulting in an expanded carbonaceous layer on the surface of the substrate, acting as a non-flammable physical and thermal barrier [21,29,31–33]. Regarding non-intumescent coatings, in the gas phase, radicals are released, acting as flame inhibitors and catalyse the decomposition of the coating to form a non-voluminous insulating layer [29,34–36]. Although widely mentioned in heritage fire safety guidelines, only a few rehabilitation and conservation teams are aware of the potential of fire-protective coatings (FPC), having already used them in heritage environments. Mainly applied directly to heritage, namely to structures of historic buildings and items with historical and artistic value associated [37–41], some studies report its application on support/ storage materials [42–45]. However, to the authors' knowledge, there are no systematic studies evaluating the potential benefits and challenges of applying FPC near the wide range of collections nor studies assessing their efficacy and performance by comparing different formulations.

### 1.1. Research aim

Following the previously outlined premises, this investigation aims to contribute to a deeper knowledge of Fire Protection Coatings (FPC), being divided into two distinct parts. The first part focuses on assembling studies and systematise the extensive data on the application of FPC, addressing the main sectors of activity incorporating these systems, the substrates to which they are applied, the different mechanisms of action and the main formulations (for intumescent and non-intumescent). In order to un-

derstand the possibility of safely applying fire-retardant and fire-resistant coatings in support/storage materials or exhibition furniture (such as bookshelves, cabinets, plinths) within museum and storage environments, the second part of the study addresses heritage fires. A brief description of fire protection measures, the leading causes of fires and contributing factors to the flame spread are given, followed by a brief review of the few existing studies on the application of FPC in heritage.

## 2. Fire-retardant and fire-resistant coatings: an overview

In the past, the application of materials such as concrete, brick, tile and asbestos (already banned for health reasons) [46] was frequent to give a fire-proof protection effect to structural elements, such as steel [19–21,46]. Traditional passive fire protection is categorised as dense concrete and lightweight cementitious coatings. These traditional methods are based on Portland cement, vermiculite, magnesium oxychloride cement, gypsum and other materials [19–21,46,47]. In addition, fillers, binders, density and rheology-controlling additives are mixed with water on the construction sites and applied by spraying [19,20,46]. Higher thickness increases the time until the heat reaches the steel [46]. These non-reactive fire protection systems avoid direct exposure of the substrate to the heat source by thermal insulation (materials with low thermal conductivity) and water release from minutes to several hours, increasing heat transfer time from the source to the structural element [19,20,46]. This cementitious protection is low cost, easy to apply, and some may resist weathering [19–21,47]. However, they have some drawbacks related to: the unappealing aesthetics, which limits the design and the architectural project; thickness, which may take up valuable space around structural elements; time-consuming application method and the surface finish is poor, which provides moisture penetration, promoting corrosion; weight, handling the materials is difficult and increases the weight of the building; and durability to fire, the cementitious paste is susceptible to cracks and displacement, decreasing the fire-proof performance [19–21,46].

The industries' scientific and technological development has followed the needs of an increasingly demanding society, which led to the growth in the production and the use of flammable materials. As a result, fire protection and safety regulations have become more stringent, providing the development of new passive protection systems to minimise the risk of fire [18,20]. Currently, there is an increasing interest in the research and development of fire-retardants products which, when suitable, can be crucial to prevent loss of life and property in a fire hazard [18,20,21].

Regarding the protection of substrates with fire-retardants, some authors support that three approaches can be considered [20,48,49]. The first approach is categorised by the additive type of fire-retardants, which are incorporated into the materials mechanically during the transformation or production process. It is an economical and fast blending approach. Nevertheless, fire-retardant additives can migrate to the surface. To be effective, it requires a high load of fire-retardant, which can impact the compatibility and mechanical properties of the material [22,28,50,51]. The second method involves the chemical modification of the substrate to create fire-rated materials, which results in higher efficiency and more extended durability, even with relatively low loadings. However, it requires specific production processes and may be inappropriate for some materials, such as fibres and flexible foams, as it can lead to changes in physical properties (melting point and glass-transition temperatures) and mechanical behaviour (tensile strength, recovery) [23,49–52]. The last approach to reduce flammability concerns surface modification by applying thin fire-retardant or fire-resistant coatings to the surface of materials. They are considered an efficient way to provide fire protection with-

out affecting the physical and mechanical properties of materials [50,53,54]. A strategy already employed in several commercial and industrial applications as it is the most efficient approach [50–52,55].

Fire-retardant and fire-resistant coatings provide a fire-protective layer to the surfaces of flammable and non-flammable materials without modifying the intrinsic properties of the substrate [19,21,28,56]. Regarding flammable materials, sometimes these coatings are the only barrier between the fuel and the fire. Therefore, they must be able to: delay the ignition of the substrate or prevent it and cause self-extinguishment (fire-retardant and fire-resistant coatings, respectively); reduce the heat transfer from the source to the substrate and the mass transfer from the substrate to the heat source; decrease the flame spread and the release of smoke or toxic gases; present good resistance to abrasion; and be easy to apply [18,27,29,57]. It also has the advantage of being low cost and having an attractive aesthetic [20,25,30,52,55]. Besides, these protective systems are available in the market as solvent-based and water-based transparent varnish or coloured paint (pigments, driers, and thinners are included as in conventional paints) [19,55,56], making them more versatile for the application to different materials (metals [20,25,53,58], polymers [22,27,49,59], textiles/ fibres [60–63] and wood [54,64–68]). When exposed to fire, they respond differently according to the fire retardation mechanism as these systems can still be classified between intumescent and non-intumescent [18,19,27,28,30,69], described in sections 3.1 and 3.2. respectively.

### 2.1. Intumescent coatings

The intumescent concept is based on the coating's response when exposed to a heat source. The coating thermal degradation results in the formation of an expanded porous carbonaceous layer on the surface of the substrate to which it is applied, acting as a non-flammable insulating physical and thermal barrier [20,25,30,70]. This carbonaceous layer reduces the heat and mass transfer (oxygen and pyrolysis products) between the source and the substrate, thus preserving the underlying material for some time [29,50,56,71]. This multicellular layer can expand in a controlled way from 2 to 100 times its original thickness [31,32,72].

Inorganic intumescent water-soluble silicate coatings were widely used due to their performance and low cost [19–21]. However, they have some limitations concerning outdoor exposure and ageing; coatings tend to lose adhesion, become brittle and have low water resistance [19,20,73,74]. In this way, organic intumescent coatings become more popular [20,21] and typically rely on the interaction of the following main components:

- (i) an acid source, acting as a dehydrating agent (usually a source of phosphoric acid, e.g. ammonium polyphosphate (APP), diammonium phosphate);
- (ii) carbon source operating as a char former (a carbon-rich polyhydric compound, e.g. pentaerythritol (PER), starch, glucose);
- (iii) and a blowing/foaming agent (the gas source) responsible for the expansion process and the formation of a porous multicellular layer (usually nitrogen- or halogen-releasing compound, e.g. melamine (MEL), urea, chlorinated paraffins, dicyandiamide) [21,25,75,76].

These components are further bounded by a solvent- or water-based polymeric binder (e.g. poly(vinyl acetate), acrylic, epoxy) [20,29,72]. This essential element, upon heat, promotes cross-linking reactions, contributing to the expansion and formation of a hardened structured and uniform carbonaceous layer. Overall, thermoplastic binders have better char-forming behaviour compared to thermosets [31,33,75,76].

The intumescent coatings protection mechanism is described by the complex physical and chemical phenomenon resulting from exposure to a heat source. First, the acid source decomposes into a mineral acid, acting as a catalyst for dehydration and esterification of the carbon source, producing a carbon char. Then, the blowing agent decomposes, releasing a large amount of non-flammable gases products from which some fraction is trapped in the molten viscous matrix, causing the char to swell until the blowing agent is exhausted or the solid matrix is insufficiently elastic [21,29,31,32]. The performance of these fire protective coatings relies on the components selected for the formulation, considering the synergistic effects resulting from the mixture of compounds, the optimal ratio between all components, and the loadings [72,75,76].

These organic intumescent coatings are known to provide fire protection to structural steel in civil buildings such as airports, hospitals, shopping malls, and residence constructions [21,55,58]. Weathering can be a challenge for these coatings, especially for water-based coatings, which can experience leaching, affecting their durability. Nevertheless, organic systems are more weather-stable and water-resistant than alkali silicate-based coatings, and if required for the outdoor environment, a top coat can be applied [31,77–79]. Also, for some materials with a characteristic appearance and texture, such as wood, it may be necessary to preserve their original aesthetics. In this case, due to the required loads, intumescent coatings may be too viscous, hiding some of those characteristics [31,55]. To overcome some of the limitations of intumescent coatings, studies were developed considering the intended function and performance. Nowadays, it is possible to find numerous combinations of formulations for these systems based on the traditional and mainly used hydrophilic system of APP-PER-MEL intumescent coating [20,31,54,76]. Ammonium polyphosphate (APP) is the mainly used acid source, yet studies reveal some limitations of this compound, such as water sensitivity (hydrolyses) and low compatibility with the binder [77,79–83]. Laoutid et al. [50] and Puri & Khanna [20] state that the chain length ( $n$ ) of this polymeric compound is variable and that APP short linear chains ( $n < 100$ ) are more sensitive to water and less thermally stable than longer chains ( $n > 1000$ ). Other salts, such as melamine phosphate and melamine pyrophosphate also found to be used due to their low water solubility [20]. Techniques such as microencapsulation of coating compounds have been developed to improve this issue [84]. Microencapsulation of APP (MCAPP) with water-insoluble polymers, such as melamine-formaldehyde resin, urea-formaldehyde resin and polyurethane, is commonly used to reduce water absorption, providing a more water-resistant APP and higher thermal stability [80,83–85]. Also, polyvinyl alcohol, hydroxyl silicone oil, and epoxy can be used to microencapsulate APP [84,86]. Regarding fire protection, Wang et al. [87] studied the influence of the degree of polymerisation (DP) of APP, concluding that fire protection increases with the increase in DP ( $> 100$ ).

Starches, sugars, carbohydrates and proteins are often mentioned in carbon source substances lists for the formulations, besides being low cost, the number of carbons will influence the char formation, and the number of hydroxyl ions will regulate the degree of char formation [19,33,53]. Pentaerythritol (PER) is the most widely used char forming agent yet, as APP is highly susceptible to water [19,20,88,89]. Andersson et al. [89] compared formulations containing pentaerythritol, di-pentaerythritol, and tri-pentaerythritol. The study has shown that di- and tri-pentaerythritol are less soluble, and pentaerythritol is the most effective at swelling earlier and keeping the substrate temperature low for longer. Tris(hydroxyethyl) isocyanurate is another well-known and efficient char former agent by the synergistic interaction with APP, although its low resistance to water [19,20,30]. Studies show the use of alkali lignin as a char forming agent for intumescent coatings as an efficient option. Jiao & Wu [90] com-

pared formulations using alkali lignin and PER; it was observed that alkali lignin coating provides better fire-retardant performance than the formulation containing PER. Zhang et al. [91] compared formulations containing alkali lignin and urea modified lignin, concluding that modified lignin provides better fire-retardancy and thermal stability. Puri & Khanna [20] also refers Poly-hexa methylene terephthalamide and Bi(4-methoxy-1-phospha-2, 6, 7-trioxabicyclo[2.2.2]-octane-1-sulfide) phenylphosphate as efficient carbon agents to produce a uniform and compact char layer.

Concerning the blowing/ foaming agent, MEL is the typical component of intumescent coating formulations; it decomposes at high temperatures and releases many efficient fire-retardant gaseous products, such as ammonia, causing the char to swell [20,30,33,76]. Urea, dicyandiamide, glycine, guanidine, chlorinated paraffin, and expandable graphite (EG) are efficient blowing agents for intumescent coatings [25,76,92]. EG has been extensively studied because it improves the fire-retardant properties by expanding to a greater degree than the traditional intumescent coatings, providing better insulation to the underlayer substrate. It is thermally more stable, less sensitive to water, could be efficient enough to provide corrosion resistance to steel and reduce the emission of smoke and volatile organic compounds (VOC) or toxic gases of these reactive systems [33,77,93].

Recent research shows the efficiency of new additives with synergistic effects and new formulations. Xu et al. [94] studied different intumescent phosphorus-boron fire-retardants (BPEAs) successfully synthesised by introducing boric acid (BA) into cyclic phosphate ester acid (PEA) via esterification to create transparent fire-retardant coatings. It was observed that the transparency gradually decreases with increasing BA loading; however, higher loads led to reduced flame spread rating, mass loss, heat release rate and smoke production rate. Furthermore, as the decomposition of the phosphorous compounds can catalyse a char formation (as in intumescent formulations), the authors suggested that BA contributed to generating dense phosphorus cross-linked and aromatic structures, such as those in intumescent formulations. In the research developed by Yan et al. [95], a series of novel intumescent phosphorus, boron, and zinc-containing fire-retardants (ZPEAs) that were synthesised by the esterification of cyclic phosphate ester with different contents of zinc borate (ZnB) and then incorporated into amino resin to produce transparent fire-retardant coating. It was observed that higher ZnB content: reduces the transparency of the ZPEAs (although exhibiting a high degree of transparency); increases the thermal stability and smoke suppression properties; decreases the flame spread rate and the mass loss; and promotes a more compact char, rich in phosphorus-containing cross-linked and aromatic structures. Wang et al. [96] prepared APP-PER-MEL intumescent coating with waterborne epoxy resin as a film-forming polymer and a varying amount of Conch shell bio-filler (CSBF). The results suggested that the introduction of 3 wt% CSBF enhanced the coating's flame-retardancy and smoke suppression properties. CSBF also contributed to forming more cross-linking and aromatic structures during the combustion process, exhibiting higher thermal stability and residual weight. Another recent study refers to enhancing the fire safety of poly(methyl methacrylate) (PMMA) by transparent flame-retardant coating. A hyperbranched poly(urethane-phosphine oxide) (HPUPO) coating synthesised from 4,4'-diphenylmethane diisocyanate (MDI) and trihydroxymethylphosphine oxide was prepared to be applied onto PMMA transparent surface. The results showed that the transparency of coated PMMA is as high as pure PMMA. HPUPO demonstrates excellent transparency, adhesion, flame-retardancy, smoke suppression and toxicity reduction properties [97]. Li et al. [98] developed a study on eco-friendly fire-retardants to improve viscose fabrics' flame-retardancy and antibacterial properties. Ammonium phytate and chitosan (CS) demonstrate the enhanced

fire behaviours of viscose fabrics; the addition of CS decreased the total smoke production. Fire-retardant viscose fabrics release less flammable and volatile substances and more water (indicating that the flame-retardant fabric can generate ammonia or some substances containing hydrogen bonds), form stable char residues (composed mainly of graphite) and perform well in the antibacterial property for *S. aureus* and *E. coli*. Rao et al. [99] reported a fire-retardant coating without halogen and formaldehyde via a one-pot sol-gel approach derived from ammonium polyphosphate (APP), sodium alginate (SA), and tetraethoxysilane (TEOS). SA (char forming agent) works as a negatively charged stabiliser to inhibit APP agglomeration (both acid and blowing agent) and further co-gelatinise with TEOS (a silicon source); together create a highly transparent P/N/Si-containing hybrid intumescent system. The coating showed highly fire-retardant efficiency for cotton fabric at an ultralow loading of 10 wt%. The analysis of the coated cotton fabric confirmed that the dense P/N/Si-containing graphitised char layer decreases the flammability, heat release and total smoke production, while the mechanical property remained almost unchanged. As for plywood substrate, several silicon-containing epoxy/PEPA (caged bicyclic phosphate 1-oxo-4-hydroxymethyl-2,6,7-trioxo-1-phosphabicyclo[2.2.2] octane) phosphate flame retardants (EPPSi) have been tested, varying the ratios of silicon-containing epoxy 1,1,3,3-tetramethyl-1,3-bis(3-(oxiran-2-ylmethoxy)propyl)disiloxane (TMSEP) and 1,4-butanediol diglycidyl ether (BDE) [100]. The findings revealed that the ratio of TMSEP/BDE influences the coating fire protection. An efficient ratio identified was 20/100 (TMESP/BDE), as higher concentrations of TMESP decrease fire protection once excessive silicon produces thin char layers. Nevertheless, in balanced amounts, silicon plays a vital role as silicon-containing compounds migrate to the surface of the char layer, protecting the inner char residue and improving the coating fire protection. In addition, silicon decreases the coating intumescence ratio and improves the foam structure (the char layers' compressive strength is improved). Moreover, it enhances the thermo-oxidation resistance of coatings. In 2022, Qi et al. [101], investigated polydopamine-polyphosphonamide (PDA-PPA) coatings for fabric and foam materials (such as cotton, polyethylene terephthalate, poly (lactic acid), polyamide, polypropylene fabrics, and flexible polyurethane foam). The coating revealed excellent intumescent charring ability for all substrates except for polypropylene. Overall, it significantly increased the flame-retardancy of the substrates and improved the breaking strength of the fabrics and the compression stress of the foam.

The fire-retardancy of intumescent coatings is highly influenced by the expansion and compaction degree of the char layer. Several authors have been studying the introduction of nano-materials with insulating effects to improve char ability and increase char compaction [102–107]. Yan et al. [102] prepared transparent silica-modified cyclic polyphosphate (SPEAs) based coatings to improve the fire-retardancy of plywood. The coating was obtained by mixing melamine formaldehyde resin, cyclic phosphate ester acid (PEA) and SPEAs (introducing nano-silica into the structure of PEA). The results showed that nano-silica significantly decreases weight loss, flame spread, heat release, smoke production, and so on; increases the thermal stability of the coating; and improves the formation of a compact and intumescent char layer. Also, Wang et al. [108] designed an intumescent nano-coating with P/N/Si constructed by layer-by-layer assembly from colloidal silica and polyphosphates to reduce the flammability of polyester/cotton blends. The nano-coating was successfully deposited on the surface of the polyester/cotton blend, it decreased the heat release and produced an intumescent char, endowing the blends with superior fire-retardancy. Hu & Sun [103] studied a novel intumescent nano-coating prepared by doping inorganic fillers (CaAlCO<sub>3</sub>-LDH) into an APP/PER/MEL system in amino and acrylic resins binders

to apply on plywood. It was observed a formation of a cellular porous honeycomb char layer chelated with metal ions (Ca and Al) at high temperatures and higher oxidation resistance. Wang et al. [104] produced multifunctional phenylboronic acid-decorated zirconium phosphate (ZrP-M) nano-sheets to enhance structural steel fire-resistance. It was observed that ZrP-M nano-sheets mainly promote the formation of highly intumescent and compact chars, increasing the fire-resistance. In addition, it enhanced the smoke suppression, thermal stability, and water/acid/alkali tolerance of intumescent coatings. Xu et al. [105] investigated the potential of using carbonaceous nano-materials to create an environmentally friendly flame-retardant nano-coating for cotton fabrics. The combination of single-walled carbon nano-horns (SWCNHs) and APP has a synergistic effect which improves the fire-retardancy of the fabric, promotes char formation, and enhances the volatiles suppression.

## 2.2. Non-intumescent coatings

Upon heat exposure, non-intumescent fire-retardant coatings exhibit different retardation mechanisms to disrupt the combustion process. They work mainly in the gas phase, releasing specific radicals (scavengers/ trappers, such as  $\text{Cl}^\bullet$  and  $\text{Br}^\bullet$ ) that will act as flame inhibitors and react with highly reactive species, such as  $\text{H}^\bullet$  and  $\text{OH}^\bullet$ , to form less reactive or inert molecules to interrupt the exothermic processes and consequent decrease in temperature [18,23,50]. They can also act in the condensed phase by decomposing the coating surface (chemical transformation of the degrading polymer chains) to form a non-luminous glassy/char layer, which will act as an insulating physical barrier against radiation from the heat source (thermal shielding effect) [34–36]. The main compounds of traditional non-intumescent formulations contain halogens (bromine, chlorine), phosphorous, or inorganic compounds. Note that combinations of the aforementioned compounds can coexist in the same system for synergistic interaction in the formulation [18,109,110].

Halogen-based formulations present a very popular fire protection system; they are low-cost and highly efficient [35,111–113]. The retardation mechanism of these compounds has been explained by the radical trap theory and/or by forming a glassy protective surface (contrary to the voluminous char formed in intumescent coatings) [18,23,29,50]. Depending on the type of halogen used, they can present exceptional efficiency; bromine and chlorine are the most used due to their low bonding energy with carbon atoms, which can be released in the combustion process [29,50,51]. Also, the increase of halogen atoms in the formulation leads to better performance in fire protection [50]. Synergistic agents can be incorporated to improve the fire-retardant action of halogen-based formulations. Antimony oxide ( $\text{Sb}_2\text{O}_3$ ) reacts with the hydric acids (HCl or HBr) produced by the halogenates to form volatile antimony oxyhalide ( $\text{SbOX}$ ) and/or antimony trihalide ( $\text{SbX}_3$ ) in the condensed phase and transport the halogen into the gas phase. Since they are heavier than native hydric acids, they remain longer in the flame [29,50,110]. Other known synergistic agents are antimony trioxide (ATO), metal borates, specifically zinc borates [22,50,114]; their synergistic effect has been compared to the zinc stannate (ZS) and zinc hydroxystannate (ZHS) effect in PVC coatings by Horrocks et al., exhibiting great potential [115].

Inorganic compounds can be present in a fire-retardant system as a synergistic co-additive, enhancing fire performance. These compounds can also be present as the main component in coatings (aluminium or magnesium hydroxides are examples) [27,29]. Therefore, the combustion process is usually inhibited by endothermic/cooling effects on the surface, with the release of water vapour or non-flammable gases [50,116]. However, the high loads required can affect the physical properties of the coatings adversely. Also,

the inorganic (insoluble) additives increase viscosity, which may be incompatible with the required low viscosities of the binder used for most UV-curable coatings, leading to unwanted effects [18,109,117].

Research concerning the safety of halogen compounds reveals that their use has become more restrictive due to the emission of toxic gases and corrosive smoke during combustion (strong acidic gases such as HCl and HBr) [111,112]. Halogenated fire-retardant (FR) coating formulations have been the focus of public health concerns for decades, nowadays, these materials' production and application are increasingly being restricted in the European Union and the United States of America [118]. Their bioaccumulative properties and toxicity to the environment, animals and humans stimulated the development of halogen-free formulations, providing the introduction of phosphorus-based FR coatings [119–122]. Like in the halogen-based fire-retardant coating, phosphorus-based coatings operate in the gas- and condensed-phase to suppress combustion [123,124]. The phosphorous components are mainly present in the coating formulation as phosphate esters, phosphonates, and phosphinates. Some examples of these elements are tributyl phosphate (TBP), triphenyl phosphate (TPP) and triphenylphosphine oxide (TPPO), which have many applications, including textile coatings [118,124,125]; ammonium polyphosphate (APP), allyl diphenylphosphine oxide (ADPPO) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), which are widely used in epoxy resin and polyurethane coating systems [123,126–128]. Despite the growing interest in phosphorus-based coatings, halogens are sometimes added to formulations for synergistic effects, as the transition to halogen-free coatings is not yet complete. In addition, these compounds have the advantage of increasing the lifetime of the coating [23,118,126]. Phosphorus-based FR coatings generally release less smoke and toxic products than halogen-based FR coatings, however, studies have shown that also phosphorous-based compounds can potentiate environmental and health concerns. During their lifetime, they can release products that will accumulate in the settled dust in the surrounding environment, which can be harmful to human health [118,129,130].

Other halogen-free formulations developed and with a growing trend towards their application contain nitrogen [59,131,132] and silicone [133–136]. Nitrogen-based FR coatings formulations are known to be more “environment friendly”; they release fewer smoke particles and toxic gases than the previously referred coatings formulations. There are no dioxin and halogen acids by-products and they have low smoke production during combustion [131,132,137]. Nitrogen-based formulations also act in the gas- and condensed-phase; they can absorb heat and produce non-combustible gases to dilute the concentration of combustible gases during the matrix decomposition [18,35,50]. Melamine or derivatives are the most important and widely used compounds in the coatings formulation [131,137,138]. However, which concerns FR efficiency, these formulations are not as efficient as phosphorus-based FR formulations. To overcome this limitation, nitrogen FR compounds are usually combined with phosphorous FR compounds for a synergistic effect upon heat [113,137,139]. The FR efficacy of the mixture is more significant than the compounds individually, providing higher thermal and chemical stability. A recent research by Zhang et al. [132] synthesised a novel star-like phosphoramidate salt flame-retardant with high P–N content, the tris(2-aminoethyl)amine phosphoramidate salt (TAEAPA), to modify lyocell fibres. The results showed improvements in thermal stability and fire-retardancy of the coated fibres, a decrease in heat release and the production of char residues.

Silicon-based systems formulations release lower amounts of, to none, toxic gases and withstand high temperatures [133,134]. Silicon compounds are known for their flexibility, good thermal stability, and versatile reactivity [128]. The main compounds

present in the formulations are silicones, silicates, organosilanes or silsesquioxanes, and they can be incorporated as fillers and copolymers or as the main polymeric matrix in the system [133,135]. Upon heat, these FR systems can act by the dilution effect of the more combustible organic components and, mainly, through the condensed-phase with the formation of an insulating layer obstructing the oxygen transmission and the heat and mass transfer [35,134,135,140]. However, the fire-retardant effect of these compounds alone is also very low, so it is usually used, as in nitrogen-based systems, together with phosphorus compounds [128,141–143]. Cui et al. [128] synthesised 4- DOPO-((3-hydroxypropyl) imino) methyl phenol (PHID) flame-retardant to be used as a copolymeric component for preparing a water-based polyurethane (WPUR) FR coating with phosphorus (P) and silicon (Si) units. Compared with pure WPUR, the synergistic mechanisms of P (via PHID) and Si (via hydroxyl silicone oil, HO-Si) can efficiently decrease the flame spread and produce a denser char, providing a significant improvement in flame-retardancy and smoke suppression. As mentioned in the literature, also in the study it was found that Si-based flame retardants can form a stable thermal insulating protective layer and, due to the Si flexibility, the coating can also exhibit tuneable cold resistance and mechanical properties. Jhajharia et al. [143] focused on chemically modified shellac using P- and Si-containing precursors blended with an epoxy resin to obtain a thermally stable shellac-epoxy coating for application on mild steel panels. The coating with both precursors increased the thermal stability and presented better fire-retardant properties than unmodified shellac coating. However, the precursors negatively influenced the film's mechanical properties, as films turned brittle; nevertheless, according to the authors, this drawback may be overcome by optimising the precursors' ratio in the coating.

Coating formulations are under constant development and due to the synergistic effects that the different components can have when combined, it is common to find studies of multi-element formulations [23,126,142], namely the one by Jiao et al. [144]. A UV-curable N-P-S-containing flame-retardant was prepared from N-P-S-containing acrylate and thiol-containing silicone hyper-branched polymers by UV-initiated thiol-ene click reaction. The results showed that Si aids the production of a fine and dense char (white SiO<sub>2</sub>), and the N and P the formation of honeycomb char structures that efficiently act as a barrier to heat, oxygen and other flammable gases, thus increasing fire-retardancy.

### 3. Fire protection and safety systems: the cultural heritage outlook

Cultural heritage can be found in World Heritage Sites, monuments, museums, galleries, theatres, palaces, cathedrals, archives, storages, industries, and historic buildings, almost anywhere. Among the ten deterioration agents threatening cultural heritage, identified by Michalski (physical forces, criminals, fire, water, pests, contaminants, light and UV radiation, incorrect temperature, and incorrect relative humidity) [145,146] and Waller (custodial neglect) [146,147] fire is one of the most destructive, even in a short time of action [148]. Both buildings and the incorporated collections are highly vulnerable to fire hazards. They are mainly composed of flammable materials such as wood (floors, stairs, furniture), textiles (curtains, clothes, tapestries), paper (documents, books) and plastic (furniture, electronic devices), which can be present as artistic/authored works, support/ storage materials or exhibition furniture (bookshelves, cabinets, plinths) [146,149]. Therefore, the effects of fire can lead to the partial or total destruction of several collections. Even small fires can cause irreparable damage; the flames, heat, smoke, residue deposition and the released gases can indirectly affect heritage. In extreme cases, fire can cause the collapse of the building's structure [146,148–150].

Fire protection measures in buildings are classified into active fire protection (AFP) and passive fire protection (PFP) [4,15,16,151]. AFP systems include fire alarms, smoke and heat detectors, fire blankets, sand buckets, portable extinguishers and automatic fire sprinklers. These measures act after the fire has already started, with detection and suppression systems, to extinguish the fire. To work, they require activation, either manual or automatic. Some challenges associated with using AFP are related to failures in the activation of the system (due to lack of human resources, maintenance or incorrect equipment positioning) and accidental discharges of suppression measures (water, foam or powder-based) [1,37,152]. On the other hand, some examples of PFP systems are: building compartmentation, fire-resistive doors and walls, fire-retardant materials, ventilation, emergency lighting and signs. These measures operate to contain the fire and its by-products, preventing the fire from spreading, minimising the potential damage and allowing the occupants time to escape safely. As these measures do not need activation, they are less likely to malfunction. PFP require less maintenance and less vigilance to ensure proper operation. AFP and PFP measures have specific functions contributing to achieving the overall fire safety goal, making them equally indispensable - they operate as complementary systems and should not be considered individually [37,53,54].

Nowadays, despite the knowledge of fire risk assessment, regulations and integrated fire protection measures, such events still happen, and most of them could have been controlled and prevented [17,148,149,153]. A 1998 note from the Canadian Conservation Institute [148] reports the museum community's propensity to keep the information of a fire hazard to themselves out of fear or embarrassment—noting that the dissemination of such events may be essential to prevent it from happening again. Furthermore, Marrion [154] stated that studying these disasters provides information about how fires started, how they progressed, what failed and what worked so that better response and mitigation plans can be prepared to prevent future fires or limit the extent of the damage.

Over the years, several reports and studies have been published exposing the most common causes of fire and contributing factors to the spread of fires in heritage [37,148,155,156]. Regarding the leading causes of fires, arson (the crime of intentionally starting a fire), defective systems or electrical installations, electrical appliances (wiring, heaters, candles, and lighting fixtures) close to flammable materials, unsafe construction and renovation activities causing open flames (welding, soldering, brazing, cutting, etc.) and unsafe practices and use (cooking and smoking types of equipment) are the most prevalent causes reported [44,153–155]. Additional factors contributing to the spread of fire in heritage are delayed discovery and notification to fire brigades, limited fire safety awareness, knowledge and professional training, lack of building compartmentation allowing the fire and smoke to spread, and fire protection systems not in place or deactivated (namely, automatic fire detection and automatic suppression systems). In fact, sometimes the building becomes a major challenge, especially when addressing heritage facilities listed in historic buildings, where the integration of fire protection measures is not always possible as it requires structural modifications (compartmentation and automatic suppression systems are some examples) [1,44,154,156]. Even so, it is also the thoughts/doubts of heritage professionals that limit the mitigation of fire hazards. The deactivation of protection measures such as sprinklers to prevent false alarms under renovation, or to avoid accidental sprinkler discharges for fear of water damage, are some examples. This divisive subject has been rooted in many heritage institutions for years, believing that water damage is more significant than fire damage [149,153,157]. Therefore, just as it is necessary to clear up misgivings through sharing knowledge, finding alternative fire

protection strategies that complement the heritage institutions' needs and the already integrated measures, is also of utter value.

Most of the guides for good practices for risk management and fire safety in cultural heritage refer to the use of fire-retardant, fire-resistant coatings and intumescent fire-rated materials [37,151,158,159], especially when addressing historic buildings [1,38,160–162]. In these buildings, the areas of greatest concern are those containing wooden panelling or objects (with many layers of paint/varnish) and textiles (usually large). While often considered structural or decorative, these elements can have tremendous historical value. It is in this context that fire-retardant and fire-resistant coatings are addressed in the recommendations, as a strategy to provide fire protection to both these and other materials, mainly being applied directly to heritage (on ceilings, doors, panelling walls, floors, stairs, joints, beams, columns, insulation, interior and exterior structure, among others) [37–39,159–161,163–165].

The fire protection of wooden buildings has been investigated and reported over the years [40,41,166,167]. Through the study of potential fire hazards in heritage buildings, Fei et al. [166] perceived that the materials and surrounding environment could influence the fire development in a fire event. Therefore, the authors proposed using fire-retardant coatings, both on historic building wooden panels and heritage textiles - since the latter are rarely used and washed - so that, in a fire event, they do not contribute as fuel. In the case study of Du et al. [167], the local government and the people's building improvement response to multi-hazard risk, and the locals' response difficulties in Dali Dong Village, were investigated. Among the residential buildings, originally constructed with highly flammable China fir wood, 71% have retained the traditional features and original materials (highly vulnerable to fire hazards), and 29% have incorporated non-combustible materials to enhance the buildings' fire resistance (bricks, cement mortar and ceramic tile). However, these alterations were mainly carried out on the ground level, while the upper floors still retain wooden components. In response to these exterior alterations and the resulting change in the buildings' architectural characteristics and landscape, the local government opted to cover several modified houses with wood, effectively reversing the earlier fire-resistance enhancements. In this context, and among other recommendations, the authors proposed the application of transparent fire-resistant coatings to both the interior and exterior of the buildings, even for those structures with other materials already applied. Although regulations or technical guidelines also suggest using non-combustible or fire-retardant materials when renovating wooden buildings, the action plan for enhancing the overall fire resistance of the village remains unclear. In addition, limited financial resources, restricted access to building technology, and the perception that technical guidance is unnecessary have proven to be limitations to building improvement. With a well-devised plan, the fire resistance of the village would be significantly improved. In a ground-breaking study, Zhang et al. [40], investigated the fire risk of Dong wind and rain bridges in Hunan using fire dynamics simulator and modelling software to simulate the fire conditions; the bridge Huilong was selected as the case study. Four fire mitigation strategies were created according to the architectural characteristics, the cultural environment and the combustion patterns of wind and rain bridges. The studied measures were automatic fire suppression, intumescent transparent fire-resistant coatings (organophosphate-based coatings or phosphorus-nitrogen), suspended ceiling in fire-proof glass and skylights. The fire resistance effectiveness of the proposed measures was evaluated, revealing that the coating was the most effective measure. Automatic suppression and skylights were also able to reduce the fire risk, but not as the fire-resistant coatings; the suspended ceiling ended up increasing the risk of fire. Finally,

the authors made a note recommending the use of fire-resistant coatings in wind and rain bridges, highlighting that, in addition to being an effective protection measure, it does not hide the traditional features of the structure. A recent research by Pokrovskaya & Pakhomov [41] investigated the influence of flame retardants on the thermal decomposition of wood samples collected from several Russian monuments built between 1720 and 1892. Two fire-retardant coatings were tested: a commercial product from Senezh and a mixture of phosphonic acid (amino trimethylene - 30%) and carbon nanotubes (0.1%) - compounds that have been used in cultural heritage for conservation treatments, as reviewed by Gomez-Villalba et al. [168]. The results showed a significant reduction in thermal decomposition for all samples treated with either coating despite variations in the thermal decomposition rate (possibly associated with the different stages of sample degradation) [41].

Despite the wide application of fire protection coatings directly to heritage, a study by Kučerová et al. [169] addresses how coating composition influences timber degradation. In this research, severely deteriorated roof timber samples from several historical buildings in the Czech Republic, were assessed. Ammonium phosphate and ammonium sulphate-based coatings have been applied for several years, leading to the accumulation of salts in the timber. Examination of the wooden samples revealed that damages are extended to the central lamella (predominantly formed by lignin) and the cell walls (mainly composed of cellulose), affecting the wood's stability. Furthermore, wood degradation causes the loss of surface information, including traces of tool work. A recently published *Guide on Historic Buildings and Fire in War-affected Countries* emphasises the application of such coatings directly to heritage, stating that they should not be applied to historical wood or objects [170]. Mentioning that ammonia-, phosphorus- or silicon-containing retardants can result, respectively, in the defibring of historical wood, a decrease in wood stability due to efflorescence (in high humidity conditions) and a significant reduction in the timber's strength. Moreover, wood preparation for the coating application may destroy historical features. Nonetheless, the authors make a distinction between application to historic wood and fresh wood, noting that the commercialised products are developed to be used on the latter [170].

Regarding using fire-retardant coatings as surface modification treatments on textiles, there are reports of their use directly in artworks and on support textiles for restoration practices. According to the literature and some fire protection laws in public spaces, textiles hung in public buildings must be treated with flame-retardants, which encouraged the study of these materials in textile artworks [171–174]. According to Bannerman et al. [171] and Bergstrand et al. [173], linen, wool and cotton are adversely influenced by the flame-retardants applied by spraying or dipping. Fire-retardant coatings minimally enhanced the flame resistance of the fabrics. Yet, it also resulted in an increase in weight and acidity (decreased in pH). Moreover, a decrease in tensile strength and an increase in stiffness was observed, changing the textiles' shape and, thereby, their aesthetics. The colour of the textiles was significantly altered by the fire-retardant coatings, and in some cases, these coatings caused metal corrosion and salt migration. Nonetheless, light exposure appeared to contribute to the degradation and colour change of treated textiles [171,173]. A review from 1995 by Halvorson [174] states that spray retardant finishes are very successful in polyester and cotton but are highly problematic for nylon, acetate, and acrylic fibres, further warning that its general application in historic textiles and textile art pieces is not recommended [37,174].

Concerning the use of fire-retardants in support fabrics, Atia et al. [42] studied a paste composed of silica nano-particles (from waste agriculture products such as rice husk (RH-SNP))

**Table 1**  
Summary of the results from the application of fire protection coatings in the heritage context.

	WOOD	TEXTILE		OTHER MATERIALS
	Directly on heritage	Directly on heritage	In support materials	In support materials
Successful application	Fir [40,166], pine and camphor [166]	Polyester and cotton [174]	Linen [42]	Paper [45]
Unsuccessful application	Timber [168,170]	Linen, wool and cotton [171,173]; and nylon, acetate and acrylic fibres [174]	–	Polyethylene [43]

impregnated with organic borate and mixed with a binder in different compositions; a paste intended to be spread on the back surface of linen fabrics to be used as inner support to historical textiles. The results have shown a significant decrease in the burning rate for the back-coated samples and an improvement in the tensile strength and elongation of the treated samples compared to blank linen. As for the flame-retardancy properties after thermal ageing, there were no changes [42]. Leikach [43] also approached fire-retardants in support materials in heritage environments. In this case, polybrominated diphenyl ethers (PBDEs) were studied as a fire-retardant additive for polyethylene (PE) sheets to protect copper collections. Although the use of PBDEs is controversial, it is mentioned that in a fire event, fire-retardant plastics may slow the flame spread, which can be the difference between a minor fire and a catastrophe, giving the example of the National Air and Space Museum. To assess the metal corrosion, electrochemical measurements were performed. ZnBr<sub>2</sub> was used to represent the brominated fire-retardant plastics, keeping in mind that bromine ions are more easily released than when extracted from the plastic (after boiling and exposure to heat and humidity, bromine was not easily released from the plastic). Comparisons were made between known damaging materials, such as wood/plywood and cellulose acetate, and a trusted material as PE. Results revealed that the fire-retardant plastics were found to be slightly more corrosive than pure PE, but not as corrosive as plywood or cellulose acetate – showing some of these materials' potential. In 2022, Grkman et al. [45] developed a multicomponent fibre box with improved fire resistance and barrier properties to protect objects from mechanical damage (during transportation, storage and handling), moisture, and possible fire hazards. The base material of this box consists of a pH-neutral acid-free paper (for the outer layers) coated with various combinations of water barrier agents and fire-retardant coatings (on the inside). After assessing these combinations, four have stood out for the lower water vapour transmission rate (WVTR) and reliable fire retardancy. The best performance was achieved using an aqueous dispersion of styrene-acrylic copolymer (for moisture barrier) and a coating of sodium silicate and aluminium hydroxide mixture (for fire-retardant protection). This combination resulted in a fourfold reduction in the WVTR compared to uncoated samples, and the fire-retardant efficiency was confirmed by the minimal burn area (without penetrating the material). These findings demonstrate the packaging's potential for storing museum objects [45].

Table 1 compiles the main findings from the reviewed articles on the successful/ unsuccessful application of fire protection coatings on different cultural heritage and storage support materials (including studies simulating the application). As it is possible to see, these coatings have been applied mainly directly to heritage assets, rather than to support materials. To the authors' knowledge, there are no reports evaluating the potential benefits and challenges of applying fire-retardant and fire-resistant coatings to support/storage materials or exhibition furniture for a wide range of museum and storage environments, nor studies assessing their efficacy and performance by comparing different formulations.

#### 4. Discussion and conclusion

Several heritage fires have been reported over the years, confirming that heritage remains highly vulnerable. Although sporadic, the occurrence of such events can be enough to cause the total loss of collections. According to fire protection standards, heritage must be protected by an integrated system of active and passive protection measures.

The application of fire-retardant and fire-resistant coatings as a passive measure has shown great potential in several domains. According to the literature, some rehabilitation and conservation teams have already applied these coatings to protect heritage, being aware of some of the benefits and drawbacks of its use. However, most of the research carried out in this context mentions using fire-retardants as additives in materials and as coatings applied directly to heritage. Hence, this investigation aimed to identify, through the literature, whether fire-retardant and fire-resistant coatings can also be a valuable tool to mitigate heritage fire hazards, assessing the potential of its application in collection support/storage materials or exhibition furniture (bookshelves, cabinets, plinths). In this way, the ethical issues associated with reversibility and compatibility between the coating and artefacts would be minimised, as the coatings would not be applied to heritage items, so in a less invasive way.

The main benefit of using these fire-protective coatings (FPC) comes from being a passive fire protection measure, so they are less prone to malfunction, are less invasive and can be tailored to the facility's needs. In a fire event, fire-retardant coatings may slow down the ignition of coated materials, resulting in more time to act. In contrast, fire-resistant coatings may prevent ignition or even cause fire self-extinguishment. In addition, FPC can be a complementary strategy for historic buildings where sometimes, the integration of protection measures is limited or even not possible for requiring changes in the building structure.

Within the numerous studies with different halogen- and phosphorus-free formulations and the openness to developing new environmentally friendly coatings, the main commercialised and commonly used formulations are still halogen and phosphorous-based compounds. The safety of these compounds has been questioned due to the harmful effects they can induce on the user and the environment. Since many heritage institutions do not have the resources to acquire new fire-rated support materials and exhibition furniture, FPC could be a valuable addition to protecting collections in fire-prone locations or for institutions more susceptible to fire-related events. Furthermore, it is an alternative available on the market, is low-cost and encourages the reuse and upgrade of existing materials. Therefore, it would be essential to conduct more research on their application in heritage facilities in support materials, including formulations comparison, exploring the safety near collections and assessing their long-term effectiveness and safety. Furthermore, continuing research on user- and environment-friendly formulations is essential so they may be available on the market in the near future.

To further this investigation, a questionnaire named "Fire prevention and protection systems in museums and storage environ-

ments” was carried out to explore the fire safety strategies currently integrated into the wide variety of heritage institutions. The enquiry findings will be subsequently disseminated.

## Funding

This work received financial support through national funds from Fundação para a Ciência e a Tecnologia, **Ministério da Ciência, Tecnologia e Ensino Superior (FCT/MCTES)** under a PhD grant awarded to Inês Soares (**SFRH/BD/147015/2019**) and through Laboratório Associado para a Química Verde - LAQV (UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020).

## CRediT authorship contribution statement

**Inês Soares:** Conceptualization, Funding acquisition, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. **Joana Lia Ferreira:** Funding acquisition, Writing – review & editing. **Helena Silva:** Funding acquisition, Writing – review & editing. **Maria Paula Rodrigues:** Funding acquisition, Writing – review & editing.

## References

- L.G.F. Salazar, X. Romão, E. Paupério, Review of Vulnerability indicators for fire risk assessment in cultural heritage, *Int. J. Disast. Risk Reduct.* 60 (2021) 102286, doi:10.1016/j.ijdr.2021.102286.
- P. Drury, A. McPherson, *Conservation principles: policies and guidance*, English Herit. (2008) 78.
- A.P. Borgese, *Why preserve history?* The Enterprise, 2013.
- Fire Protection in Historical Buildings and Museums: Detection, Alarming, Evacuation, Extinguishing*; Siemens Switzerland Ltd, Building Technologies Division.; 2015.
- R. Mason, *Fixing historic preservation: a constructive critique of “significance, Places 16* (2004) 9.
- Phillips, D. Brazil museum fire: ‘incalculable’ loss as 200-year-old Rio Institution Gutted available online: <https://www.theguardian.com/world/2018/sep/03/fire-engulfs-brazil-national-museum-rio> (accessed on 18 August 2020).
- T. Roche, M. Lima, It’s time to protect our heritage and stop burning it, *FM Glob.* 8 (2019).
- Wu, J.; Arkin, D.; Muccari, R. Notre Dame fire: what was damaged available online: <https://www.nbcnews.com/news/world/notre-dame-fire-what-was-damaged-n995371> (accessed on 18 August 2020).
- C.E. Marrion, *Protecting our cultural icons from fire: lessons from Notre Dame and beyond*, AIANY Historic Buildings Committee and World Monuments Fund (WMF), 2020.
- Shiraishi, S. Shuri Castle: fire destroys 500-year-old world heritage site in Japan available online: <https://www.bbc.com/news/world-asia-50244169> (accessed on 18 August 2020).
- UNESCO’s heritage emergency fund supports firefighting measures for Uganda’s Kasubi Tombs World Heritage Site available online: <https://en.unesco.org/news/unescos-heritage-emergency-fund-supports-firefighting-measures-ugandas-kasubi-tombs-world> (accessed on 15 September 2021).
- Portaria n. 1532/2008 de 29 de Dezembro.
- D. Diamantes, *Principles of Fire Prevention*, 3rd ed., Jones & Bartlett Learning, 2014.
- D. McDaniel, J. Hunter, T. Knapp, S. Floray, S.J. Wolf, Chapter 9: museum fire protection, in: D.R. Shore (Ed.), *NPS Museum Handbook, Part I: Museum Collections*, 2019, p. 78.
- Heritage under fire: a guide to the protection of historic buildings*, in: S. Kidd (Ed.) *FPA for the UK Working Party on Fire Safety in Historic Buildings*: London, ISBN, 1995 978-0-902167-90-2.
- S. Kincaid, The upgrading of fire safety in historic buildings, *Hist. Environ.: Policy Pract.* 9 (2018) 3–20, doi:10.1080/17567505.2017.1399972.
- Rio de Janeiro declaration on fire risk reduction in cultural heritage 2019.
- S. Liang, N.M. Neisius, S. Gaan, Recent developments in flame retardant polymeric coatings, *Prog. Org. Coat.* 76 (2013) 1642–1665, doi:10.1016/j.porgcoat.2013.07.014.
- E.D. Weil, Fire-protective and flame-retardant coatings - a state-of-the-art review, *J. Fire Sci.* 29 (2011) 259–296, doi:10.1177/0734904110395469.
- R.G. Puri, A.S. Khanna, Intumescent coatings: a review on recent progress, *J. Coat. Technol. Res.* 14 (2017) 1–20, doi:10.1007/s11998-016-9815-3.
- T. Mariappan, Recent developments of intumescent fire protection coatings for structural steel: a review, *J. Fire Sci.* 34 (2016) 120–163, doi:10.1177/0734904115626720.
- C.M.C. Pereira, M.S.S. Martins, Flame retardancy of fiber-reinforced polymer composites based on nanoclays and carbon nanotubes, in: D. Constantine, Papaspyrides, Kiliaris Pantelis (Eds.), *Polymer Green Flameretardants*, Elsevier, 2014, pp. 550–595. ISBN 978-0-444-53808-6..
- S.Y. Lu, I. Hamerton, Recent developments in the chemistry of halogen-free flame retardant polymers, *Prog. Polym. Sci.* 27 (2002) 1661–1712, doi:10.1016/S0079-6700(02)00018-7.
- J.G. Speight, Chapter 4: sources and types of organic pollutants, *Environmental Organic Chemistry for Engineers*, Elsevier, 2017 ISBN 978-0-12-804492-6..
- C. Zhang, *Reliability of Steel Columns Protected by Intumescent Coatings Subjected to Natural Fires*, Springer Theses; Springer Berlin Heidelberg, Berlin, Heidelberg, 2015 ISBN 978-3-662-46378-9.
- J. Han, G.Q. Li, Y.C. Wang, Q. Xu, An experimental study to assess the feasibility of a three stage thermal conductivity model for intumescent coatings in large space fires, *Fire Saf. J.* 109 (2019) 102860, doi:10.1016/j.firesaf.2019.102860.
- E.D. Weil, S.V. Levchik, *Flame Retardants for Plastics and Textiles: Practical Applications*, 2nd edition, Hanser Publishers, Munich, 2016 ISBN 1-56990-454-5.
- G.C. Tesoro, Chemical modification of polymers with flame-retardant compounds, *J. Polym. Sci. Macromol. Rev.* 13 (1978) 283–353, doi:10.1002/pol.1978.230130106.
- J. Green, Fire-retardant/fire-resistive coatings, in: Arthur A. Tracton (Ed.), *Coating Technology Handbook*; CRC Press Taylor & Francis Group, Boca Raton, 2006, p. 99. -1-99-5.
- Mariappan, T. Fire retardant coatings. In *New Technologies in Protective Coatings*; Giudice, C., Canosa, G., Eds.; InTech, 2017; pp. 101–122 ISBN 978-953-51-3491-6.
- N. Amir, F. Ahmad, P. Megat-Yuso, Study on the fibre reinforced epoxy-based intumescent coating formulations and their char characteristics, *J. Appl. Sci.* 11 (2011) 1678–1687, doi:10.3923/jas.2011.1678.1687.
- D.B. Dahm, Reformulation of fire retardant coatings, *Prog. Org. Coat.* 29 (1996) 61–71, doi:10.1016/S0300-9440(96)00663-7.
- J. Hao, W.K.A. Chow, Brief review of intumescent fire retardant coatings, *Archit. Sci. Rev.* 46 (2003) 89–95, doi:10.1080/00038628.2003.9696967.
- H. Yang, B. Yu, P. Song, C. Maluk, H. Wang, Surface-coating engineering for flame retardant flexible polyurethane foams: a critical review, *Compos. Part B: Engineering* 176 (2019) 107185, doi:10.1016/j.compositesb.2019.107185.
- X. Qiu, Flame retardant coatings prepared using layer by layer assembly\_ a review, *Chem. Eng. J.* (2018) 15.
- E.M. Pearce, R. Liepins, Flame retardants, *Environ. Health Perspect.* 11 (1975) 59, doi:10.2307/3428325.
- S. Kidd, Guide for practitioners 7: fire safety, *Management in Traditional Buildings, Part 2, Historic Scotland*, Edinburgh, 2010 ISBN 978-1-84917-035-2..
- McClean, R. *Sustainable management of historic heritage guidance series: fire safety and heritage places*; New Zealand Historic Places Trust Pouhere Taonga.; 2012; ISBN 978-1-877563-08-9.
- R. Benešová, M. Rusinová, L. Sibilla, Analysis of fire protection with focus on the specific conditions of the historic roofs, *AMM* 861 (2016) 120–128, doi:10.4028/www.scientific.net/AMM.861.120.
- F. Zhang, L. Shi, S. Liu, J. Shi, C. Shi, T. Xiang, CFD-based fire risk assessment and control at the historic Dong wind and rain bridges in the Western Hunan Region: the case of Huilong Bridge, *Sustainability* 14 (2022) 12271, doi:10.3390/su141912271.
- Pokrovskaya, E.; Pakhomov, A. Influence of flame retardants on the thermal decomposition of wood of the monuments of wooden architecture in 1720–1892.; Moscow, Russian Federation, 2023; p. 030018.
- N. Attia, H. Ahmed, D. Yehia, M. Hassan, Y. Zaddin, Novel synthesis of nanoparticles-based back coating flame-retardant materials for historic textile fabrics conservation, *J. Ind. Text.* 46 (2015) 1379–1392, doi:10.1177/1528083715619957.
- D.C. Leikach, *An Assessment of the Use of Flame Retardant Plastics for Museum Applications*, Master of Science degree, Faculty of the Graduate School of the University of Maryland: College Park, 2007.
- M.J. Kilby, in: *Managing Fire Risk in Cultural Properties - a Holistic Approach*. Presented at the International Seminar - Heritage on fire: Who’s next? Fire Risk Management For Cultural Heritage, June, Rio de Janeiro, Brazil, 2019, pp. 26–28.
- J.J. Grkman, U. Kav, I. Karlovits, Development of multicomponent fiber box with improved fire resistance and barrier properties, *Cellulose Chem. Technol.* 56 (2022) 159–163, doi:10.35812/CelluloseChemTechnol.2022.56.15.
- M.G. Goode, in: *Fire Protection of Structural Steel in High-Rise Buildings*, National Institute of Standards and Technology (NIST): Building and Fire Research Laboratory, Gaithersburg, Maryland, 2004, pp. 1–88.
- A. Lucherini, J.P. Hidalgo, J.L. Torero, C. Maluk, Influence of heating conditions and initial thickness on the effectiveness of thin intumescent coatings, *Fire Saf. J.* (2020) 103078, doi:10.1016/j.firesaf.2020.103078.
- R. Anastácio, *Especificação De Protecção Fogo Para Estruturas De madeira*. Master dissertation, Faculty of Engineering, University of Porto, Porto, 2010.
- S. Bourbigot, S. Duquesne, Fire retardant polymers: recent developments and opportunities, *J. Mater. Chem.* 17 (2007) 2283, doi:10.1039/b702511d.
- F. Laoutid, L. Bonnaud, M. Alexandre, J.-M. Lopez-Cuesta, Ph. Dubois, New prospects in flame retardant polymer materials: from fundamentals to nanocomposites, *Mater. Sci. Eng.: R: Reports* 63 (2009) 100–125, doi:10.1016/j.mser.2008.09.002.
- V. Cádiz, J. Ronda, G. Lligadas, M. Galíá, Chapter 32 - polybenzoxazines with enhanced flame retardancy, in: *Handbook of Benzoxazine Resins*, 2011, pp. 556–576, doi:10.1016/B978-0-444-53790-4.00077-1.

- [52] S. Duquesne, P. Bachelet, S. Bellayer, S. Bourbigot, W. Mertens, Influence of inorganic fillers on the fire protection of intumescent coatings, *J. Fire Sci.* 31 (2013) 258–275, doi:10.1177/0734904112467291.
- [53] M. Yasir, F. Ahmad, P.S.M.M. Yusoff, S. Ullah, M. Jimenez, Latest trends for structural steel protection by using intumescent fire protective coatings: a review, *Surf. Eng.* 36 (2019) 334–363, doi:10.1080/02670844.2019.1636536.
- [54] J.J. Kwang Yin, M.C. Yew, M.K. Yew, L.H. Saw, Preparation of intumescent fire protective coating for fire rated timber door, *Coatings* 9 (2019) 738, doi:10.3390/coatings9110738.
- [55] X. Hu, G. Wang, Y. Huang, Study on the preparation and properties of novel transparent fire-resistive coatings, *J. Coat. Technol. Res.* 10 (2013) 717–726, doi:10.1007/s11998-013-9475-5.
- [56] M. Jimenez, S. Duquesne, S. Bourbigot, Multiscale Experimental approach for developing high-performance intumescent coatings, *Ind. Eng. Chem. Res.* 45 (2006) 4500–4508, doi:10.1021/ie060040x.
- [57] ASTM D16 - 98b: standard terminology for paint, related coatings, materials, and applications.
- [58] Q. Xu, G.Q. Li, Y.C. Wang, L. Bisby, An experimental study of the behavior of intumescent coatings under localized fires, *Fire Saf. J.* 115 (2020) 103003, doi:10.1016/j.firesaf.2020.103003.
- [59] D. Enescu, A. Frache, M. Lavaselli, O. Monticelli, F. Marino, Novel phosphorus–nitrogen intumescent flame retardant system. Its effects on flame retardancy and thermal properties of polypropylene, *Polym. Degrad. Stab.* 98 (2013) 297–305, doi:10.1016/j.polydegradstab.2012.09.012.
- [60] A.R. Horrocks, M.Y. Wang, M.E. Hall, F. Sunmonu, J.S. Pearson, Flame retardant textile back-coatings. Part 2. effectiveness of phosphorus-containing flame retardants in textile back-coating formulations, *Polym. Int.* (2000) 13.
- [61] F. Carosio, J. Alongi, G. Malucelli, Layer by layer ammonium polyphosphate-based coatings for flame retardancy of polyester–cotton blends, *Carbohydr. Polym.* 88 (2012) 1460–1469, doi:10.1016/j.carbpol.2012.02.049.
- [62] S. Chen, X. Li, Y. Li, J. Sun, Intumescent flame-retardant and self-healing superhydrophobic coatings on cotton fabric, *ACS Nano* 9 (2015) 4070–4076, doi:10.1021/acs.nano.5b00121.
- [63] G. Malucelli, Sol-gel and layer-by-layer coatings for flame-retardant cotton fabrics: recent advances, *Coatings* 10 (2020) 333, doi:10.3390/coatings10040333.
- [64] Koo, J.H.; Wootan, W.; Chow, W.K.; Yeung, H.W.A.; Venumbaka, S. Flammability studies of fire retardant coatings on wood. In *Fire and Polymers*; Nelson, G.L., Wilkie, C.A., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2001; Vol. 797, pp. 361–374 ISBN 978-0-8412-3764-3.
- [65] N.K. Saxena, D.R. Gupta, Development and evaluation of fire retardant coatings, *Fire Technol.* 26 (1990) 329–341, doi:10.1007/BF01293077.
- [66] L.C. Ferle, G.H.D. Santos, L.M.R. Mesquita, Mechanical properties of wood based panels with and without fire retardants, *Revista da Associação Portuguesa de Análise Experimental de Tensões - Mecânica Experimental* 30 (2018) 35–42.
- [67] L.LeVan Susan, E. Jerrold, Winandy effects of fire retardant treatments on wood strength: a review, *Wood Fiber Sci.* 22 (1990) 113–131.
- [68] A. Lucherini, Q.S. Razaqae, C. Maluk, Exploring the fire behaviour of thin intumescent coatings used on timber, *Fire Saf. J.* 109 (2019) 102887, doi:10.1016/j.firesaf.2019.102887.
- [69] H. Lu, L. Song, Y. Hu, A review on flame retardant technology in China. Part II: flame retardant polymeric nanocomposites and coatings: flame retardant technology in China, *Polym. Adv. Technol.* 22 (2011) 379–394, doi:10.1002/pat.1891.
- [70] S. Bourbigot, M.L. Bras, S. Duquesne, M. Rochery, Recent advances for intumescent polymers, *Macromol. Mater. Eng.* (2004) 13.
- [71] H.L. Vandersall, Intumescent coating system, their development and chemistry, *Fire Flammability* 2 (1971) 97–140.
- [72] M.C. Yew, Fire-resistive performance of intumescent flame-retardant coatings for steel, *Mater. Des.* (2012) 6.
- [73] D.E. Veinot, K.B. Langille, D. Nguyen, J.O. Bernt, Soluble silicate-based coatings for fire protection, *Fire Technol.* 25 (1989) 230–240, doi:10.1007/BF01039780.
- [74] K.B. Langille, D. Nguyen, J.O. Bernt, D.E. Veinot, M.K. Murth, Mechanism of dehydration and intumescence of soluble silicates. Part II effect of the cation, *J. Mater. Sci.* (1991) 704–710.
- [75] S. Duquesne, S. Magnet, C. Jama, R. Delobel, Thermoplastic resins for thin film intumescent coatings – towards a better understanding of their effect on intumescent efficiency, *Polym. Degrad. Stab.* 88 (2005) 63–69, doi:10.1016/j.polydegradstab.2004.01.026.
- [76] Y.H. Ng, A. Dasari, K.H. Tan, L. Qian, Intumescent fire-retardant acrylic coatings: effects of additive loading ratio and scale of testing, *Prog. Org. Coat.* 150 (2021) 105985, doi:10.1016/j.porgcoat.2020.105985.
- [77] Z. Wang, E. Han, W. Ke, Influence of expandable graphite on fire resistance and water resistance of flame-retardant coatings, *Corros. Sci.* 49 (2007) 2237–2253, doi:10.1016/j.corsci.2006.10.024.
- [78] J. Wang, The protective effects and aging process of the topcoat of intumescent fire-retardant coatings applied to steel structures, *J. Coat. Technol. Res.* 13 (2016) 143–157, doi:10.1007/s11998-015-9733-9.
- [79] D.T. Hoang, D. Schorr, V. Landry, P. Blanchet, S. Vanslambrouck, C. Dagenais, Preparation and characterisation of flame retardant encapsulated with functionalised silica-based shell, *J. Microencapsul.* 35 (2018) 428–438, doi:10.1080/02652048.2018.1521477.
- [80] L. Sun, Y. Qu, S. Li, Co-microencapsulate of ammonium polyphosphate and pentaerythritol in intumescent flame-retardant coatings, *J. Therm. Anal. Calorim.* 111 (2013) 1099–1106, doi:10.1007/s10973-012-2494-0.
- [81] C.S. Chou, S.H. Lin, C.I. Wang, Preparation and characterization of the intumescent fire retardant coating with a new flame retardant, *Adv. Powder Technol.* 20 (2009) 169–176, doi:10.1016/j.apt.2008.07.002.
- [82] K. Cao, S. Wu, K. Wang, Z. Yao, Kinetic study on surface modification of ammonium polyphosphate with melamine, *Ind. Eng. Chem. Res.* (2011) 5.
- [83] J. Ni, L. Song, Y. Hu, P. Zhang, W. Xing, Preparation and characterization of microencapsulated ammonium polyphosphate with polyurethane shell by in situ polymerization and its flame retardance in polyurethane, *Polym. Adv. Technol.* 7 (2009).
- [84] B. Wang, H. Sheng, Y. Shi, W. Hu, N. Hong, W. Zeng, H. Ge, X. Yu, L. Song, Y. Hu, Recent advances for microencapsulation of flame retardant, *Polym. Degrad. Stab.* 113 (2015) 96–109, doi:10.1016/j.polydegradstab.2015.01.008.
- [85] K. Wu, Z. Wang, H. Liang, Microencapsulation of ammonium polyphosphate: preparation, characterization, and its flame retardance in polypropylene, *Polym. Compos.* (2008) 854–860, doi:10.1002/pc.20459.
- [86] L. Liu, Y. Zhang, L. Li, Z. Wang, Microencapsulated ammonium polyphosphate with epoxy resin shell: preparation, characterization, and application in EP system: microencapsulated app in ep system, *Polym. Adv. Technol.* 22 (2011) 2403–2408, doi:10.1002/pat.1776.
- [87] G. Wang, Y. Wang, J. Yang, Influences of polymerization degree of ammonium polyphosphate on fire protection of waterborne intumescent fire resistive coating, *Coat. Technol.* 6 (2012).
- [88] M.L. Bras, S. Bourbigot, B. Revel, Comprehensive study of the degradation of an intumescent EVA-based material during combustion, *J. Mater. Sci.* 34 (1999) 5777–5782.
- [89] A. Andersson, S. Lundmark, F.H.J. Maurer, Evaluation and characterization of ammoniumpolyphosphate–pentaerythritol-based systems for intumescent coatings, *J. Appl. Polym. Sci.* 104 (2007) 748–753, doi:10.1002/app.25588.
- [90] L.Y. Jiao, Z.J. Wu, Alkali Lignin as a carbonization agent on the thermal degradation and flame retardancy of intumescent flame retardant coating, *AMR 750–752* (2013) 1385–1388, doi:10.4028/www.scientific.net/AMR.750-752.1385.
- [91] R. Zhang, X. Xiao, Q. Tai, H. Huang, Y. Hu, Modification of Lignin and its application as char agent in intumescent flame-retardant poly(lactic acid), *Polym. Eng. Sci.* 52 (2012) 2620–2626, doi:10.1002/pen.23214.
- [92] S. Ullah, F. Ahmad, A.G. Al-Sehemi, M.R. Raza, M.A. Assiri, A. Irfan, E. Oñate, G.H. Yeoh, Effects of expandable graphite on char morphology and pyrolysis of epoxy based intumescent fire-retardant coating, *J. Appl. Polym. Sci.* 138 (2021) 51206, doi:10.1002/app.51206.
- [93] S. Duquesne, M.L. Bras, S. Bourbigot, R. Delobel, H. Vezin, G. Camino, B. Eling, C. Lindsay, T. Roels, Expandable graphite: a fire retardant additive for polyurethane coatings, *Fire Mater.* 27 (2003) 103–117, doi:10.1002/fam.812.
- [94] Z. Xu, Z. Chu, L. Yan, Enhancing the flame-retardant and smoke suppression properties of transparent intumescent fire-retardant coatings by introducing boric acid as synergistic agent, *J. Therm. Anal. Calorim.* 133 (2018) 1241–1252, doi:10.1007/s10973-018-7201-3.
- [95] L. Yan, Z. Xu, X. Wang, Synergistic flame-retardant and smoke suppression effects of zinc borate in transparent intumescent fire-retardant coatings applied on wood substrates, *J. Therm. Anal. Calorim.* 136 (2019) 1563–1574, doi:10.1007/s10973-018-7819-1.
- [96] F. Wang, H. Liu, L. Yan, Y. Feng, Comparative study of fire resistance and anti-ageing properties of intumescent fire-retardant coatings reinforced with conc shell bio-filler, *Polymers* 13 (2021) 2620, doi:10.3390/polym13162620.
- [97] K. Zhang, C. Ma, Y. Zheng, F. Zhou, Y. Xiao, W. Xing, Y. Hu, A novel coating of hyperbranched poly(urethane–phosphine oxide) for poly(methyl methacrylate) with high fire safety, excellent adhesion and transparency, *Prog. Org. Coat.* 161 (2021) 106481, doi:10.1016/j.porgcoat.2021.106481.
- [98] P. Li, C. Liu, B. Wang, Y. Tao, Y.J. Xu, Y. Liu, P. Zhu, Eco-friendly coating based on an intumescent flame-retardant system for viscose fabrics with multifunction properties: flame retardancy, smoke suppression, and antibacterial properties, *Prog. Org. Coat.* 159 (2021) 106400, doi:10.1016/j.porgcoat.2021.106400.
- [99] W. Rao, J. Shi, C. Yu, H.B. Zhao, Y.Z. Wang, Highly efficient, transparent, and environment-friendly flame-retardant coating for cotton fabric, *Chem. Eng. J.* 424 (2021) 130556, doi:10.1016/j.cej.2021.130556.
- [100] Y. Shi, G. Wang, The novel silicon-containing epoxy/PEPA phosphate flame retardant for transparent intumescent fire resistant coating, *Appl. Surf. Sci.* 385 (2016) 453–463, doi:10.1016/j.apsusc.2016.05.107.
- [101] P. Qi, Y. Li, J. Sun, X. Wang, K. Wang, D. Meng, X. Gu, H. Li, S. Zhang, Flame retardant and anti-dripping surface treatment through a co-deposition of polydopamine/polyphosphonamide for fabric and foam materials, *Compos. Part B: Engineering* 247 (2022) 110262, doi:10.1016/j.compositesb.2022.110262.
- [102] L. Yan, Z. Xu, X. Wang, Influence of nano-silica on the flame retardancy and smoke suppression properties of transparent intumescent fire-retardant coatings, *Prog. Org. Coat.* 112 (2017) 319–329, doi:10.1016/j.porgcoat.2017.07.017.
- [103] X. Hu, Z. Sun, Nano CaAlCO<sub>3</sub>-layered double hydroxide-doped intumescent fire-retardant coating for mitigating wood fire hazards, *J. Build. Eng.* 44 (2021) 102987, doi:10.1016/j.jobbe.2021.102987.
- [104] C. Wang, S. Huo, G. Ye, Q. Shi, Z. Fang, H. Wang, Z. Liu, Phenylboronic acid-decorated ZrP nanosheets for enhancing fire resistance, smoke suppression, and water/acid/alkali tolerance of intumescent coatings, *Colloids Surf. A: Physicochem. Eng. Asp.* 655 (2022) 130292, doi:10.1016/j.colsurfa.2022.130292.
- [105] J. Xu, Y. Niu, Z. Xie, F. Liang, F. Guo, J. Wu, Synergistic flame retardant effect of carbon nanohorns and ammonium polyphosphate as a novel flame retardant

- system for cotton fabrics, *Chem. Eng. J.* 451 (2023) 138566, doi:10.1016/j.cej.2022.138566.
- [106] T. Marzi, 11 Nanotechnologies for reinforcement and protection of timber structures: innovative nano-coatings, in: A.M. Harte, P. Dietsch (Eds.), *Reinforcement of Timber Structures: A State-of-The-Art Report*, 2015.
- [107] S. Sfamini, G. Rando, M.R. Plutino, Sustainable secondary-raw materials, natural substances and eco-friendly nanomaterial-based approaches for improved surface performances: an overview of what they are and how they work, *IJMS* 24 (2023) 5472, doi:10.3390/ijms24065472.
- [108] B. Wang, Y.J. Xu, P. Li, F.Q. Zhang, Y. Liu, P. Zhu, Flame-retardant polyester/cotton blend with phosphorus/nitrogen/silicon-containing nano-coating by layer-by-layer assembly, *Appl. Surf. Sci.* 509 (2020) 145323, doi:10.1016/j.apsusc.2020.145323.
- [109] T. Randoux, Halogen-free flame retardant radiation curable coatings, *Prog. Org. Coat.* 9 (2002).
- [110] A.R. Horrocks, Flame retardant challenges for textiles and fibres: new chemistry versus innovative solutions, *Polym. Degrad. Stab.* 96 (2011) 377–392, doi:10.1016/j.polyimdeggradstab.2010.03.036.
- [111] H. Järnström, S. Vares, M. Airaksinen, *Semi Volatile Organic Compounds and Flame Retardants. Occurrence in Indoor Environments and Risk Assessment for Indoor Exposure*, Research notes; VTT Technical Research Centre.; VTT TIEDOTTEITA, Finland, 2009 ISBN 978-951-38-7299-1.
- [112] H.M. Stapleton, S. Klosterhaus, S. Eagle, J. Fuh, J.D. Meeker, A. Blum, T.F. Webster, Detection of organophosphate flame retardants in furniture foam and U.S. house dust, *Environ. Sci. Technol.* 43 (2009) 7490–7495, doi:10.1021/es9014019.
- [113] Y.L. Li, C.F. Kuan, S.W. Hsu, C.H. Chen, H.C. Kuan, F.M. Lee, M.C. Yip, C.L. Chiang, Preparation, thermal stability and flame-retardant properties of halogen-free polypropylene composites, *High Perform. Polym.* 24 (2012) 478–487, doi:10.1177/0954008312443391.
- [114] C.A. Gúdice, J.C. Benítez, Zinc borates as flame-retardant pigments in chlorine-containing coatings, *Prog. Org. Coat.* 42 (2001) 82–88, doi:10.1016/S0300-9440(01)00159-X.
- [115] A.R. Horrocks, G. Smart, S. Nazaré, B. Kandola, D. Price, Quantification of zinc hydroxystannate\*\* and stannate\*\* synergies in halogen-containing flame-retardant polymeric formulations, *J. Fire Sci.* 28 (2010) 33, doi:10.1177/0734904109344302.
- [116] J. Alongi, M. Ciobanu, G. Malucelli, Thermal stability, flame retardancy and mechanical properties of cotton fabrics treated with inorganic coatings synthesized through sol-gel processes, *Carbohydr. Polym.* 87 (2012) 2093–2099, doi:10.1016/j.carbpol.2011.10.032.
- [117] W. Xing, G. Jie, L. Song, S. Hu, X. Lv, X. Wang, Y. Hu, Flame retardancy and thermal degradation of cotton textiles based on UV-curable flame retardant coatings, *Thermochim. Acta* 513 (2011) 75–82, doi:10.1016/j.tca.2010.11.014.
- [118] I.van der Veen, J.de Boer, Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis, *Chemosphere* 10 (2012) 1119–1153, doi:10.1016/j.chemosphere.2012.03.067.
- [119] S. Shaw, Halogenated flame retardants: do the fire safety benefits justify the risks? *Rev. Environ. Health* (2010) 25, doi:10.1515/REVEH.2010.25.4.261.
- [120] G. Martinez, J. Niu, L. Takser, J.P. Bellenger, J. Zhu, A review on the analytical procedures of halogenated flame retardants by gas chromatography coupled with single quadrupole mass spectrometry and their levels in human samples, *Environ. Pollut.* 285 (2021) 117476, doi:10.1016/j.envpol.2021.117476.
- [121] C. Zhang, X.W. Cheng, J.P. Guan, G. Chen, Preparation of nano-Mg(OH)<sub>2</sub> for surface coating of silk fabric with improved flame retardancy and smoke suppression, *Colloids Surf. A: Physicochem. Eng. Asp.* 625 (2021) 126868, doi:10.1016/j.colsurfa.2021.126868.
- [122] T.R. Hull, R.J. Law, Å. Bergman, *Environmental drivers for replacement of halogenated flame retardants*, in: *Polymer Green Flame Retardants*, Elsevier, 2014, pp. 119–179. ISBN 978-0-444-53808-6.
- [123] Greiner, L.; Kukla, P.; Eibl, S.; Döring, M. Phosphorus Containing polyacrylamides as flame retardants for epoxy-based composites in aviation. 2019, 25.
- [124] Thomas, A.; Arun, M.; Moinuddin, K.; Joseph, P. Mechanistic aspects of condensed- and gaseous-phase activities of some phosphorus-containing fire retardants. 2020, 17.
- [125] Horrocks, A.R.; Davies, P.J.; Kandola, B.K.; Alderson, A. The potential for volatile phosphorus-containing flame retardants in textile back-coatings. 2007, 19.
- [126] P. Joseph, S. Tretsiakova-Mcnally, *Reactive modifications of some chain and step growth polymers with phosphorus containing compounds: effects on flame retardance a review*, *Polym. Adv. Technol.* (2011) 12.
- [127] M.V. Kahraman, N. Kayaman-Apohan, N. Arsu, A. Güngör, Flame retardance of epoxy acrylate resin modified with phosphorus containing compounds, *Prog. Org. Coat.* 51 (2004) 213–219, doi:10.1016/j.porgcoat.2004.07.014.
- [128] M. Cui, J. Li, X. Chen, W. Hong, Y. Chen, J. Xiang, J. Yan, H.A Fan, Halogen-free, flame retardant, waterborne polyurethane coating based on the synergistic effect of phosphorus and silicon, *Prog. Org. Coat.* 158 (2021) 106359, doi:10.1016/j.porgcoat.2021.106359.
- [129] A. Davis, P.B. Ryan, J.A. Cohen, D. Harris, M. Black, Chemical exposures from upholstered furniture with various flame retardant technologies, *Indoor. Air.* (2021) 1473–1483.
- [130] J. Feiteiro, M. Mariana, E. Cairrão, Health toxicity effects of brominated flame retardants: from environmental to human exposure, *Environ. Pollut.* 285 (2021) 117475, doi:10.1016/j.envpol.2021.117475.
- [131] C.-E. Wilén, R. Pfaendner, Design and utilization of nitrogen containing flame retardants based on n-alkoxyamines, azoalkanes and related compounds, in: *Polymer Green Flame Retardants*, Elsevier, 2014, pp. 267–288. ISBN 978-0-444-53808-6.
- [132] Q. Zhang, X. Liu, Y. Ren, Y. Zhang, B. Cheng, Fabrication of a high phosphorus-nitrogen content modifier with star structure for effectively enhancing flame retardancy of lyocell fibers, *Cellulose* 27 (2020) 8369–8383, doi:10.1007/s10570-020-03333-0.
- [133] W. Zhou, H. Yang, *Flame retarding mechanism of polycarbonate containing methylphenyl-silicone*, *Thermochim. Acta* (2007) 6.
- [134] X. Cheng, W. Shi, UV-curing behavior and properties of tri(di)acryloyloxyethylphenoxy phenyl silane used for flame-retardant coatings, *Prog. Org. Coat.* 69 (2010) 252–259, doi:10.1016/j.porgcoat.2010.06.002.
- [135] S.A. Kumar, *Thermal properties of siliconized epoxy interpenetrating coatings*, *Prog. Org. Coat.* 8 (2002).
- [136] Q. Wu, Q. Zhang, L. Zhao, S.N. Li, L.B. Wu, J.X. Jiang, L.C. Tang, A novel and facile strategy for highly flame retardant polymer foam composite materials: transforming silicone resin coating into silica self-extinguishing layer, *J. Hazard. Mater.* 336 (2017) 222–231, doi:10.1016/j.jhazmat.2017.04.062.
- [137] H. Horacek, R. Grabner, Advantages of flame retardants based on nitrogen compounds, *Polym. Degrad. Stab.* 54 (1996) 205–215, doi:10.1016/S0141-3910(96)00045-6.
- [138] H. Liang, A. Asif, W. Shi, Thermal degradation and flame retardancy of a novel methacrylated phenolic melamine used for UV curable flame retardant coatings, *Polym. Degrad. Stab.* 7 (2005), doi:10.1016/j.polyimdeggradstab.2004.10.006.
- [139] D. Bakoš, M. Košík, K. Antoš, M. Karolyová, I. Vyskočil, The role of nitrogen in nitrogen-phosphorus synergism, *Fire Mater.* 6 (1982) 10–12, doi:10.1002/fam.810060104.
- [140] M. Gao, W. Wu, Z. Xu, Thermal degradation behaviors and flame retardancy of epoxy resins with novel silicon-containing flame retardant, *J. Appl. Polym. Sci.* (2012) 1–6, doi:10.1002/APP.37909.
- [141] X. Wang, Y. Hu, L. Song, W. Xing, H. Lu, Thermal degradation behaviors of epoxy resin/POSS hybrids and phosphorus-silicon synergism of flame retardancy: epoxy resin/POSS hybrids, *J. Polym. Sci. B Polym. Phys.* 48 (2010) 693–705, doi:10.1002/polb.21939.
- [142] J. Li, H. Wang, S. Li, A novel phosphorus-silicon containing epoxy resin with enhanced thermal stability, flame retardancy and mechanical properties, *Polym. Degrad. Stab.* 164 (2019) 36–45, doi:10.1016/j.polyimdeggradstab.2019.03.020.
- [143] V. Jhahharia, R. Patil, S. Mestry, S.T. Mhaske, P- and Si-modified shellac for flame-retardant epoxy-based coatings, *Iran. Polym. J.* 30 (2021) 907–916, doi:10.1007/s13726-021-00941-w.
- [144] X. Jiao, Y. Song, N. He, S. Shi, L. Xie, X. Wang, D. Hu, M. Li, G. Lai, X. Yang, Preparation and performance of nitrogen-phosphorus-silicon-containing flame retardant UV-curable coatings with high transparency, *Prog. Org. Coat.* 173 (2022) 107169, doi:10.1016/j.porgcoat.2022.107169.
- [145] S. Michalski, *An overall framework for preventive conservation and remedial conservation*, in: *ICOM Committee for Conservation, Preprints of the 9th Triennial Meeting, Dresden*; Kirsten Grimstad, ICOM Committee for Conservation, 1990, pp. 589–591.
- [146] J.L. Pedersoli Jr., C. Antomarchi, S. Michalski, *A Guide to Risk Management of Cultural Heritage*, ICCROM, Canadian Conservation Institute, 2016 ISBN 978-92-9077-248-4.
- [147] R. Waller, *Conservation risk assessment: a strategy for managing resources for preventive conservation*, *Stud. Conserv.* 39 (1994) 12–16, doi:10.1179/sic.1994.39.Supplement-2.12.
- [148] P. Baril, *CCI Notes 2/7: Museum Fires and Losses*, Canadian Conservations Institute, 1998.
- [149] P. Baril, *CCI Notes 2/6: Fire Protection Issues for Historic Buildings*, Canadian Conservations Institute, Canada, 1998.
- [150] E. Garcia-Castillo, I. Paya-Zaforteza, A. Hospitaler, Fire in heritage and historic buildings, a major challenge for the 21st century, *Dev. Built Environ.* 13 (2023) 100102, doi:10.1016/j.dibe.2022.100102.
- [151] D.R. Shore, *Museum Handbook Part I, Chapter 9: Museum Fire Protection*, 2019, p. 78.
- [152] P. Baquedano Juliá, T.M. Ferreira, H. Rodrigues, Post-earthquake fire risk assessment of historic urban areas: a scenario-based analysis applied to the historic city centre of Leiria, Portugal, *Int. J. Disast. Risk Reduct.* 60 (2021) 102287, doi:10.1016/j.ijdr.2021.102287.
- [153] Pedersoli Jr., J.L. My museum is on fire! Presented at the ICCROM lectures series - global voices: heritage and pandemics., Online, 2020.
- [154] C.E. Marrion, More effectively addressing fire/disaster challenges to protect our cultural heritage, *J. Cult. Herit.* 20 (2016) 746–749, doi:10.1016/j.culher.2016.03.013.
- [155] J. Tétreault, *Fire risk assessment for collections in museums*, *J. Canadian Assoc. Conserv.* 33 (2008) 20.
- [156] Maxwell, I. *Built Heritage: Fire Loss to Historic Buildings – The Challenge Before Us*; Edinburgh, Scotland; 2004.
- [157] T.A. Graham, *A Preventive Conservation Guidebook*, The Graduate School, University of Akron, Akron, Ohio, 2009.
- [158] B. Wedvik, K. Storesund, *FRIC Fire Research & Innovation Centre*, 2020, p. 34. Unpublished.
- [159] *Practice guidebook for adaptive re-use of and alteration and addition works to heritage buildings 2012* (2019 Edition) 2019.
- [160] A.C. Parnell, *The Historic Buildings and Monuments Commission for England*, Elsevier, The Architectural Press Ltd., 2013 ISBN 978-1-4831-4149-7.

- [161] G. Bernardini, Fire safety and building heritage: the occupants perspective, in: *Fire Safety of Historical Buildings*; SpringerBriefs in Applied Sciences and Technology, Springer International Publishing, Cham, 2017, pp. 7–43. ISBN 978-3-319-55743-4.
- [162] P. Barker, *Fire safety and heritage buildings*, NBS (2010).
- [163] Forecast, A. The building conservation directory: intumescent products available online: <https://www.buildingconservation.com/articles/intumescent-products/intumescent-products.htm> (accessed on 21 June 2020).
- [164] Devi, K.S.; Sharma, T.D. Innovations in conservation of heritage museums and libraries from fire hazards.; Madhya Pradesh, India, 2019; p. 020005.
- [165] B. Zhou, H. Yoshioka, T. Noguchi, X. Wang, C.C. Lam, Experimental study on fire performance of weathered cedar, *Int. J. Architect. Herit.* 13 (2019) 1195–1208, doi:10.1080/15583058.2018.1501115.
- [166] Y. Fei, Z. Shun-bing, H. Xue-feng, Analysis and flame retarding design of combustibles in Nanjing typical historical buildings, *Procedia Eng.* 11 (2011) 625–633, doi:10.1016/j.proeng.2011.04.706.
- [167] F. Du, K. Okazaki, Building improvement responses to multi-hazard risk in the historic Dali Dong Village, Guizhou, China, *Int. J. Disast. Risk Reduct.* 19 (2016) 64–74, doi:10.1016/j.ijdr.2016.08.014.
- [168] L.S. Gomez-Villalba, C. Salcines, R. Fort, Application of inorganic nanomaterials in cultural heritage conservation, risk of toxicity, and preventive measures, *Nanomaterials* 13 (2023) 1454, doi:10.3390/nano13091454.
- [169] I. Kuerová, M. Ohlídalová, M. Novotná, A. Michalcová, Examination of damaged wood by ammonium phosphate and sulphate-based fire retardants, in: *Proceedings of the Wood Science for Conservation of Cultural Heritage – Florence 2007: Proceedings of the International Conference held by COST Action IE0601 in Florence (Italy)*, 8–10 November 2007; Uzielli, L., Ed., Firenze University Press, Florence, 2007.
- [170] R. Teijgeler, N.K. Jernaes, *Guide on Historic Buildings and Fire in War-Affected Countries*; Maidaan Museum and The Heritage Emergency Response Initiative, Blue Shield International, ICON, Fundacion Fuego: Oslo, 2022.
- [171] J. Bannerman, M. Bergstrand, G. Lagnesjö, H. Degerblad, in: *Flame Retardants and Wool – Long Term Effects 2: Evaluating Fabrics for the ECOSOC Curtain*, Swedish National Heritage Board, Visby, Sweden, 2014, p. 42.
- [172] P. Vashist, S. Basak, W. Ali, Green flame retardants – keeping out fires, *Sci. Rep.* (2019).
- [173] M. Bergstrand, K.H. Degerblad, K. Thuresson, T. Winther, Fire! A twofold risk for textile art. An investigation into the consequences of flame retardant treatments, in: *Critério Artes Gráficas, Lda.; ICOM Committee for Conservation: Lisbon*, 2011, p. 10.
- [174] Halvorson, B. Flame retardants finishes for textiles in textile conservation newsletter 1995.