Treatments and modification to improve the reaction to fire of wood and wood based products—An overview

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SUMMARY
Wood and wood-based products are widely used for structural building elements, but due to their composition, they are susceptible of combusting if exposed to fire. Fire safety is an important issue of building safety, especially when the building’s fire load contents enhance the risks of fire spread. Therefore, the involved materials are very important to address the fire safety requirements. When existing timber structures are involved, the most usual way to improve its reaction to fire is to treat wood with fire retardant materials.

The idea of this paper is to give an overall overview, on the existing fire-retardant and intumescent coating materials, modification, and treatments that can be applied to wood and wood-based products in order to improve their reaction to fire.

KEYWORDS
fire retardant, intumescent systems, reaction to fire, wood modification, wood treatment

1 INTRODUCTION

Wood is widely used as a building material and in some areas as the main construction material, due to its unique combination of properties, like easy of processing, maintaining a sustainable life cycle, good physical and mechanical properties, esthetic, environmental and health aspects (minimal environmental pollution), and providing a good strength/weight ratio. In particular, according to the latest global trends in increase in living standards and growing concerns about environmental protection for people, wood is attracting gradually more attention. However, the use of wood can be restricted by safety requirements and regulations concerned with its ignitability and fire spreading characteristics.

The combusting of wood can be divided into three consecutive processes. The first one consists in the evaporation of water as an endothermic process. In a second phase, since the specific heat of the wood is relatively low (depending on its moisture content), no large quantities of heat are required to bring the wood to a temperature of about 150°C, where the degassing with the formation of combustible degradation products from the main constituents of wood, combined with a flame formation, starts. Thus, combustion takes place as a reaction between oxygen and the gases released from the material. If sufficient degradation products are formed, this process takes place exothermically. The elimination of the volatile constituents is terminated at a temperature around 800°C. Finally, the exothermic annealing of the carbon takes place.

Substances employed (as fire retardants) to protect wood against fire can reduce the surface combusting characteristics. They protect the underlaying material without deteriorating its bulk properties, by acting as barrier between fire source and substrate. They enhance the fire performances of the wood by reducing the amount of heat released during the initial stages of fire, by retarding the spread of flame and by limiting the production of smoke and flammable volatiles. Moreover, the used fire retardants must be harmless to humans and animals and should not release toxic substances in the course of normal exploitation of the material. Their most important properties are time to ignition, heat release rate, extinction flammability index and thermal stability index, mass loss, smoke toxicity, limiting oxygen

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index, surface spread of flame, and fire resistance. Each retardant works in a different manner, increasing mass residue while decreasing onset temperature of charring stage and mass loss rate.

Nevertheless, all these materials present disadvantages, like insufficient efficiency and limited applications, and they are susceptible to leaching when exposed to outdoor conditions. Therefore, the durability of fire retardant treatments, when exposed to humid conditions, is closely linked to the water solubility of the used chemicals. Here, one risk is high moisture content due to the retardant and the migration of the fire retardant chemical within the wood product and crystallization on the product surface. A second case is loss of retardant chemicals by leaching. Therefore, a European system with Durability of Reaction to Fire performance (DRF) classes and an analog North American system were developed. Both systems consist of a classification system for the properties over time of fire retardant treated wood exposed to different humid conditions and suitable test procedures. Due to this, they may have limited use or are recommend to be used in specific applications. Exceptions are, of course, fire retardants that react and thus form more complex and insoluble substances in the wood structure. In addition, wood modification approaches are increasing in their industrial spread.

The aim of this paper is to evaluate the existing fire retardant and intumescent coating materials and also to examine the potential of wood modification for their reaction to fire. It gives overall information about the potential materials to be used for fire safety or to improve the reaction to fire of wood and wood-based products.

2 | FIRE RETARDANT AND INTUMESCENT SYSTEMS, MECHANISM OF ACTION, AND THEIR APPLICATION FOR WOOD

2.1 | Fire retardant systems

2.1.1 | General remark on fire retardants used for wood

The presented fire retardant solutions act by interfering with a particular stage of wood combustion process (i.e., during heating, decomposition, ignition, or flame spread) through mechanisms and submechanisms that may either act chemically or physically to inhibit or suppress wood combustion process. In order to make the treatment more efficient, some fire retardant systems combine several mechanisms of action. Therefore, the mechanisms of action to reduce combustion include

- changing the pathway of pyrolysis of wood,
- isolating surface layer,
- changing the thermal properties of wood, and
- diluting pyrolysis gases.

Most commercial fire retardants for wood function by enhancing the pyrolysis reaction of cellulose, via through the pathway that leads mainly to char formation. It may also slow down the pyrolysis reactions and stabilize the chemical structures of wood against decomposition.

The isolating surface layer delays the temperature rise and also reduces the release of pyrolysis gases and the access of oxygen on the surface. These effects can be accomplished using intumescent fire retardant surface treatments as they expand when temperature increases and form a thick, porous, carbonaceous layer that will protect wood surface from fire.

The principal chemical fire retardant coatings for wood typically use compounds that contain halogens (i.e., chlorine or bromine), phosphorous, nitrogen, boric acid, borax, or inorganic metal compounds, as main component in the formulation. It is known from literature that their presence helps inhibit the flame spread via radical quenching and/or by forming glassy or foamy protective layers.

Traditionally, the fire retardants were divided into two types:

- The additive type dominates the market because of its low price, high availability, and wide application; these chemicals are added to the product, and as a drawback, a high loading of additive type fire retardant is required
- The reactive type is mainly used to bond the fire retardant segments into a polymer backbone.

According to literature, e.g., Liang et al and Unlu et al these systems work via two different mechanisms: in gas phase or in solid phase. In gas phase, the evolved gases from the fire retardants induce first a reduction in temperature, followed by a reduction in the amount of combustible gases. Finally, the combustion process is completely suppressed. In the case of reactions in the solid phase, the fire retardants usually form a carbon layer or ceramizing organic substances on the surface. This leads to a reduction in the heat conduction and thus the combustion progress of the wood.

2.1.2 | Halogen-based fire retardant compounds

Halogen (chlorine or bromine) based systems are popular and largely used in coating formulations, due to the cost effective solution for fire retardant applications. As it is mentioned in an extended review by Liang et al, most of the halogen-based compounds work in the gas phase by the action of the free radical scavengers. During the fire conditions, the combustion process is interrupted by the release of oxygen and hydroxyl radicals. In the last years, only few publications evaluated the development of new halogen-based systems for applications in fire retardant coatings, and most of them analyze different compounds as synergists for halogenated fire retardant systems. For example, antimony oxide combined with 2-decaboromediphenoxyide works via an intermediate formation of antimony trihalide that acts as a strong flame quencher in the gas phase, or aluminum hydroxide and zinc borates in chlorinated alkyd coatings act as inhibitors of the flame spread by endothermic/cooling effects on the surface. A combination of nanoclay with 1,2-bis(pentabromophenyl) and ethylene bis(tetramethylenimide) lowered heat release rate and total heat
release of the composites, leading to significantly improved flame performance.\textsuperscript{15}

Although these compounds present high efficiency, their applications are restricted due to a growing global concern about the possible health impacts. Upon combustion, the halogenated compounds release toxic and/or highly corrosive gases, which are harmful to both humans and environment. There are extensive studies concerning their persistence in the environment and the impact on human and animal health. For example, the brominated fire retardants were divided into three groups: poly brominated biphenyls and diphenyl ethers, hexabromocyclododecanes, and tetrabromobisphenol A. These groups of components were analyzed according to their presence in the environment or food,\textsuperscript{16-20} their accumulation in humans or animals,\textsuperscript{19,21-23} and their toxicological properties and biodegradation.\textsuperscript{21,24,25} The authors concluded that the exposure to these chemicals can indicate neurotoxicity,\textsuperscript{26} have effect on thyroid functioning\textsuperscript{27} or even infertility.\textsuperscript{28} All of these depend on the amount and type of chemicals and on their presence in the environment.\textsuperscript{16,19,21}

### 2.1.3 Inorganic salts–based fire retardant compounds

The inorganic compounds (hydroxides, phosphates, carbonates, and sulfates) present environmentally friendly properties, good thermal stability, and less release of smoke and corrosive toxic gases. They are mostly used as synergistic co-additives, helping to increase the involved fire retardant efficacy of a coating system. The main drawback of these solutions is their high water solubility. Therefore, they are used mostly for interior applications. Used in exterior applications or subjected to repeated cleaning actions, their leaching becomes an issue due to the migration of the salts with the movement of water in the wood. Wooden materials treated with inorganic salts are usually more hygroscopic.\textsuperscript{11}

As a synergistic co-additive, aluminum or magnesium hydroxyl are the most used elements within the coating system.\textsuperscript{29,30} They act by cooling the fuel source and diluting the gases, but to be effective, a large quantity is required.\textsuperscript{11} For example, aluminum trihydroxide (Al(OH)$_3$) and mica added in a polyurethane binding medium indicated enhanced fire retardant properties.\textsuperscript{31} Another principal chemical compound in the fire retardant preparation is potassium carbonate (K$_2$CO$_3$), which has a high fire retardant efficiency. Among its advantages one can mention fungicidal properties, low iron corrosiveness, and complete absence of (or very low) harmful effects on humans and animals (both, in the form of solution and as combustion products).\textsuperscript{13} Used in combination with silica sol (SiO$_2$ sol) potassium carbonate (K$_2$CO$_3$), indicates improved fire retardancy and leaching resistance.\textsuperscript{32} In their study, He et al (2017)\textsuperscript{32} suggested that K$_2$CO$_3$ catalyzed the degradation of wood at lower temperatures inducing the increase of water and carbon dioxide, while SiO$_2$ sol formed a compact and melted barrier on the surface of the char residue. Huntite (Mg$_3$Ca(CO$_3$)$_4$) and hydro-magnesite (Mg$_{6}$[CO$_3$]$_4$(OH)$_2$4H$_2$O) have been suggested as an alternative to health and environmental concerns.\textsuperscript{9} Zinc oxide (ZnO) and titanium dioxide (TiO$_2$) showed significant reduction in the amount of heat release and delayed ignition time for the coated wood.\textsuperscript{6} The impregnation of wood with Al$_2$O$_3$ and SiO$_2$ lead to an increase in the char formation and lower thermal conductivity of the surface.\textsuperscript{33} Na$_2$WO$_4$, Na$_2$SnO$_3$, and Na$_2$MoO$_4$ treated wood indicated a decrease of the decomposition temperature, a weight reduction, and the increase of the char amount.\textsuperscript{34}

Vargun et al\textsuperscript{35} studied the effect of (NH$_4$)$_2$HPO$_4$, K$_2$HPO$_4$, NH$_4$Cl, and (NH$_4$)$_2$SO$_4$ salts and their mixtures on the thermal properties of beech wood. They observed that the impregnated wood with (NH$_4$)$_2$HPO$_4$ and K$_2$HPO$_4$ mixture presented remarkable effects on thermal stability, resulting in higher char yields, while the beech wood impregnated with NH$_4$Cl salt indicated lower decomposition temperatures and char yield.

In order to present high efficiency against fire, the inorganic fillers need to be added in high amounts. This might influence negatively the coatings physical properties, or the incompatibility between them and the binder system might cause blooming and other similar effects.\textsuperscript{7}

Several studies, ie, Merk et al,\textsuperscript{36,37} indicate the mineralization of the wood with CaCO$_3$ in order to create a structured organic-inorganic hybrid material as a green alternative to conventional fire retardant systems with highly improved fire retardancy properties of wood. Inorganic salts are considered environmentally friendly fire retardant materials, having very low harmful effects on humans and animals in the form of solutions or as products, which result after the combustion process.\textsuperscript{13}

### 2.1.4 Boron-based fire retardant compounds

Boron compounds are widely used as fire retardants for wood and wood-based products, providing high thermal and biological resistance, being nontoxic, having low cost, being ease of handling and treatment, and giving a long lasting protection due to their deep penetration into wood.\textsuperscript{38} They also present low melting point and form glassy films, when exposed to high temperatures in fires. Because of their non-fixed characteristics, boron preservatives are normally recommended for use in protected environment and are not for use in ground contact.

The most common boron compounds, which have found many application areas in the wood preservation industry, are the boric acid and borax.\textsuperscript{1,38-42} Boric acid increases the dehydration reaction in the cellulose component of wood, leading to increased amounts of char and reduced amounts of volatile organic compounds, reduces smoldering and glowing combustion, but has little effect on flame spread.\textsuperscript{38} On the other hand, borax tends to reduce fire spread, but can promote smoldering or glowing. Therefore, these compounds are normally used together providing an excellent reaction to fire as well as efficiency against both fungi and insects.\textsuperscript{1,43,44}

They also can be used in combination with other compounds. For example, boric acid added to trimethylol melamine and dicyandiamide
coatings were found to be resistant to decay even after severe weathering conditions, due to the possible synergistic properties and compatibility of the mixed chemicals.\textsuperscript{39} Boron salts, such as disodium octaborate tetrahydrate, act by releasing water and forming a protective and insulating glaze on the wood surface and catalyzing dehydration and esterification. Same salt used in combination with guanyl urea phosphate showed a significantly improved thermal stability (reduced weight loss, increased char formation, and lowered pyrolysis temperature), indicating synergistic flame retardant and smoke suppression effect.\textsuperscript{45} In combination with tannin-based formulations, this salt can be suitable for outdoor fire protection.\textsuperscript{40} Boric acid was also used for the synthesis of boric-phenol-formaldehyde resin in order to impregnate fast-growing wood species.\textsuperscript{46} The authors indicated that comparing with control samples, the treated samples presented improved mechanical and fire performance properties.

The known effect on health upon exposure to high concentration of boron and boron-based compounds is the acute respiratory irritation and teratogenic effect.

2.1.5 | Phosphorous-based fire retardant compounds

Phosphorus is usually the main element in fire retardants for wood due to its particular effectiveness. Phosphorous-based fire retardants are predominantly represented by phosphate esters, phosphonates, phosphinates, polyphosphonate, or phosphonic acid salts. They are regarded as one of the best choices as additive for coatings of wood to reduce flammability, due to their good fire properties.\textsuperscript{7,47,48} They can exhibit both condensed phase (char enhancement, intumescence, and formation of inorganic glass) and/or gas phase (flame inhibition) fire retardant modes of action.\textsuperscript{49} Compared with other fire retardants, phosphorous compounds generate fewer toxic gases and smoke during combustion. Because the materials generate no toxic or corrosive gases upon combustion, they are considered to be environmentally friendly. As a drawback, the phosphorus compounds increase the moisture content of wood in humid conditions, promoting fungal decay; therefore, they are more suitable to interior applications.\textsuperscript{11}

A series of novel fire retardant waterborne polyurethanes with a phosphorus-containing fire retardant diamine (bis(4-aminophenoxy)phenyl phosphine oxide) were synthesized by the method of post chain extension technique.\textsuperscript{50}

Even they are considered promising alternatives to halogen free additives, some of the phosphorous-based compounds present potential environmental and health concerns. For example, the organophosphate fire retardants (structurally similar to organophosphate pesticides) can be hazardous for the respiratory health and allergic asthma especially in children.\textsuperscript{51} A recent study in Japan\textsuperscript{52} demonstrated that two compounds (tributyl phosphate and tris(1,3-dichloroisopropyl)phosphate) are associated with asthma, allergic rhinitis, and atopic dermatitis.

2.1.6 | Nitrogen-based fire retardant compounds

Nitrogen-based fire retardants are also considered environmentally friendly and nontoxic substitutions for existing formulations. Melamine and its derivatives are among the most used nitrogen-based fire retardant compounds. As the previous class, they can exhibit both gas and condensed phase flame inhibition.\textsuperscript{7,53}

Their mechanisms include vaporization in a fire situation and dilution of the fuel gases and oxygen near the combustion source. Besides melamine, melamine-formaldehyde resins, urea, and dicyandiamide are other nitrogen compounds used in fire retardant formulations.\textsuperscript{11} Another compound, methacrylated phenolic melamine, works only in the vapor phase by releasing non-flammable gasses with no increase in char formation.\textsuperscript{54}

The ammonium salts decrease fire intensity and the rate of spread, but the fire retardants containing ammonium salts may be potentially toxic to the environment.\textsuperscript{8}

To our knowledge, there are no studies concerning the health and environment risks related to these compounds.\textsuperscript{7}

2.1.7 | Phosphorous-nitrogen–based fire retardant compounds

Combined phosphorus and nitrogen fire retardant systems are used together for wood because of their synergistic effect.\textsuperscript{7} The phosphorous-nitrogen–based fire retardants were developed on the basis of mono and di-ammonium phosphate, ammonium polyphosphate, polyl, amide, and aqueous-organic dispersion with addition of oxide and organic compounds. The phosphorus acts to protect the combusting surface by forming a char, while the nitrogen is released as a gas and dilutes the wood combustible volatile products. As an example, the mechanism of monoammonium and diammonium phosphate includes cooling down of the condensed phase, inhibiting the access of oxygen and thus ignition, and formation of a carbon char on the surface, which protects the remaining condensed combustible layer.\textsuperscript{55}

Novel cyclic phosphazene derivative, aziridinyl phosphazene, was synthesized by reacting hexachlorocyclotriphosphazene with aziridine. This compound was reported to serve as a cross-linker and reactive fire retardant for the aqueous-based polyurethane curing system.\textsuperscript{56} A series of hyperbranched phosphorous-nitrogen containing fire retardant coatings have been developed based on UV curable technology.\textsuperscript{57} Using bio-based materials like castor oil, a series of phosphorous-based fire retardant polyurethanes have been also prepared.\textsuperscript{58} Various phosphorous containing polyester polyols was reacted with multiple diisocyanates in order to obtain superior fire retardant coatings. During the fire exposure, it is believed that the phosphorous compounds decompose and release active species that act in gas phase and further produce phosphoric acid derivatives that catalyze and improve the char formation.\textsuperscript{7} A novel fire retardant based on ammonium phosphate polymer, guanyl urea phosphate, and phosphonic acid as main components has been synthesized.\textsuperscript{59}
Lignin is considered to have certain fire retardant properties; therefore, Zhu et al.\(^6\) used lignin as the starting material. They firstly chemically grafted it with phosphorus-nitrogen containing fire retardants to generate lignin-based phosphate melamine compound (LPMC). Then they used it to substitute parts of polyols and copolymerize it with isocyanate to produce lignin-based foams.\(^6\) The combustion process of simple polyurethane (PU), in a concentration of oxygen of 19.2%, indicates a quick ignition with a rapid flame propagation, while the PU-LPMC, tested at an oxygen concentration of 26.7%, slowed down the flame propagation. The flame becoming smaller and extinguished within 49 s.

Wang et al.\(^6\) synthesized a phosphorus nitrogen containing fire retardant system via thiol-ene UV click reaction by using Triallyl orthophosphate, \(\text{NN-dimethylacrylamide, pentaerythritol tetraakis (3-mer-capto} \text{propionate), and pentaerythritol triacrylate. They found that the best coating for wood was the one that had 2:4 the molar ratio of phosphorus and nitrogen monomer.}

### 2.1.8 Silicon containing fire retardant compounds

Silicon-based compounds are another class of chemicals used as an alternative of environment friendly fire retardants.\(^7,6\) They form silica layers with high thermal stability, therefore protecting the substrate decomposition at high temperatures.\(^6\) This class of compounds includes silicones, silicates, organosilanes, or silsesquixoxanes as fillers or copolymers or as main polymeric matrix into a system.\(^7\)

In the last years, different silicone containing epoxies that can be cured on their own or mixed with other epoxy components were developed. Hydroxyl-terminated polydimethylsiloxane was used as a chemical modifier to effectively introduce silicon into an epoxy coating, of which the thermal stability and anticorrosive properties were significantly improved.\(^6\)\

These compounds can also be incorporated into the phosphorus containing fire retardants in order to improve their effect. The silicon groups give high thermal stability, while phosphorus groups improve the char forming ability.\(^10\) Their synergistic effect improves the fire protection of the transparent intumescent fire resistant coatings.\(^6\) A novel silicon containing hyperbranched polyphosphonate acrylate was synthesized via the Michael addition polymerization, and further, a series of UV-curable fire retardant coatings were prepared.\(^6\)

Siloxane derivatives exhibit a good synergic effect with phosphorus compounds when applied in epoxy resins. Polysiloxanes synthesized inside the wood pores through the sol-gel process, by using aminopropyl methyl diethoxysilane, aminopropyl triethoxysilane, and aminopropyl methyl diethoxysilane/aminopropyl triethoxysilane mixture as precursors, proved to be efficient as fireproof impregnants. It is considered that the formation of condensation bonds such as \(\text{Si-O-Si} \) within the inorganic polymer and \(\text{Si-O-C} \) at the polysiloxane-wood interface is responsible of the high thermal stability of treated wood.\(^5\)

Polysiloxane-based copolyesters and copolyamides have great potential as fire retardant materials. Polysiloxane copolyimides synthesized enzymatically and copolyamic acids synthesized by a simple environmentally friendly method were found to be thermally stable and exhibit enhanced flame retardant properties. Moreover, it has been found that the incorporation of small amounts of boronic acid, through covalent linkages in these polymers, improved the nature and amount of char formed during combustion.\(^6\)\

Cheng et al.\(^6\) synthesized a silsesquioxane-based hybrid urethane acrylate by modifying silsesquioxane hybrid polyol with isophorone diisocyanate and 2-hydroxyethyl acrylate. After that, this was mixed with a phosphorus containing monomer tri-(acryloyloxyethyl) phosphate in different ratios to form a series of UV curable resins.

This class of fire retardants is considered to be environmentally friendly, and no additional studies about their potential health risks were found.

### 2.1.9 Nanocomposite fire retardant compounds

Nanocomposites constitute a new development in the idea of fire retardancy.\(^7\) The use of nanomaterials to enhance the properties of conventional materials has been extended during the last decades. The small size and great surface area of nanomaterials make them more effective at low concentrations than other conventional compounds.\(^7\) However, their efficiency is still insufficient in providing adequate fire retardancy when used alone in the coatings. Therefore, their combination with other conventional fire retardant systems can give superior properties to the substrate. It has been reported that nanocomposite-based coatings represents a promising system that protects the oxidation of the char structure once formed and thus reinforce the fire resistant properties of the coatings.\(^7\)

Typically, nano-sized inorganic fillers such as layered silicates,\(^7\) silsesquioxane derivatives,\(^7\) and \(\text{TiO}_2, \text{SiO}_2, \) and carbon nanotubes have been extensively used.\(^7\)

Nanocomposite systems of very high silica/alkali molar ratio were prepared from a commercial sodium silicate colloidal solution and nanosilica solution to be used as fire retardant impregnants. The significant advantages of the alkaline silicates for the treatment of wood are the high fire retardant efficiency, the reduced generation of smoke during the conflagration, and their low cost. The most essential disadvantage of the inorganic silicates is the high alkalinity of the solutions that demands special care for their manipulation.\(^7\)

Wood samples coated with vermiculite and various vermiculite-sodium silicate composites exhibited a solid foamy layer, which was effective in delaying of ignition and decreasing the heat release rate and the total heat release. The incorporation of vermiculite clay mineral into the commercial sodium silicate improved fire properties.\(^\)\

Cellulose nanofiber/clay nanocomposites, with unique brick and mortar structure, were proposed by Carosio et al.\(^7\) as sustainable and efficient fire protection coating for wood.
### 2.2 Intumescent fire retardant systems

Recently, a more important role in fire retardancy has been played by intumescent coatings. When exposed to high temperatures, they swell and increase their volume by 50 to 200 times, forming a thick porous charred layer as a protective barrier and providing resistance to both heat and mass transfer.\(^{13,77}\) They have low weight, and a relatively thin coat can be applied. This can be obtained by a heat insulating effect for a specified period of time\(^ {78}\) by comparative ecological safety.\(^ {79}\)

The intumescence process is a combination of charring and foaming at the surface of the gas and condensed phase. An effective char is formed during a semiliquid phase that coincides with the formation of the gas and the expansion of the surface. The gases released are trapped and diffuse slowly in the highly viscous melted degraded material. At the same time, cross-linking reactions and charring cause the matrix to harden thereby. Therefore, in making a formulation, components with certain melting points and composition are chosen in such a way that they react in a specific order and create conditions for the transformations of coatings under the action of flame.\(^ {79}\)

The porosity of the char is extremely high, and the resulting structure has extremely low thermal conductivity. Another important parameter is the stability of the intumescent char, which depends on the structure and porosity of the foamed intumescent material.\(^ {78,80-82}\)

The usual chemistry of intumescence involves composition containing: an inorganic acid or a material yielding acidic species, a char former, and a component that decomposes to enable the volume increase of the system by frothing.\(^ {80}\) Typical examples of components used in intumescent systems are presented in the Figure 1.

During the process of combustion, the following sequences of events takes place\(^ {81}\):

- the decomposition of dehydrating agent, followed by the formation of acid from its ammonium salt, amine, or ester at temperatures depending on its source and the other components;
- the acid reacts further with hydroxyl groups of carbonizing substance to form a thermally unstable ester at temperatures slightly above the acid release temperature;
- the mixture of materials melt prior to or during esterification;
- the decomposition of ester is accompanied by the decomposition of a pore forming substance resulting in the formation of considerable amounts of non-flammable gases;
- released gases cause foaming of carbonaceous material created as a result of the ester decomposition, which leads to the appearance of a thick insulating layer;
- at the end gelation and solidification occurs, resulting a solid multicellular foam.

Intumescent fire retardant coatings have the advantage of low price, simple preparation and high availability. They are usually obtained by the addition of the intumescent fire retardants directly into a resinous matrix with high concentration, which usually give rise to problems of opacity, difficulties in curing, and precipitating from the matrix.\(^ {83}\)

The phosphorus-nitrogen containing intumescent fire retardant systems are most widely used for wood due to the effect of their composition on the protective action and thermal decomposition and stability of phosphorus-nitrogen-containing compounds in fire retardant treated wood elements.

The most important components of a fire retardant intumescent formulation are polyphosphates (especially ammonium salts of polyphosphoric acid). Ammonium polyphosphate acts as an inorganic polymer favoring formation of a strong foam and acts as an effective high temperature provider of gases. As a main second component, the most used one is melamine. Its role consists in that it combines a capacity for intense gas evolution after its involvement in the formation of a cross-linked polymeric structure and function as a reinforcement matrix of the foamed carbonized layer. The third main component of the fire retardant intumescent formulations is pentaerythritol, which is actively involved in the formation of foamed layer.\(^ {84,85}\) In addition to the proportion of reactive components in the formulation, the performance of an intumescent coating is also affected by the type of polymeric

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**FIGURE 1** Design and examples of typical components used in intumescent systems [Colour figure can be viewed at wileyonlinelibrary.com]
binder; therefore, it can be a key issue in an intumescent coating formulation.\textsuperscript{84} Titanium dioxide pigment is also present in some formulation, acting as an opacifier of the paint film and a reinforcing filler of the foam.\textsuperscript{84}

Other formulations have been also reported in literature:

- an intumescent fire retardant synthesized from phosphoric acid, pentaerythritol, urea, and trolamine in water solution\textsuperscript{86};
- water borne intumescent fire retardant varnish based on phosphate resin acid cold cured amino resin\textsuperscript{87};
- an intumescent phosphorus containing polyether synthesized using phosphorus oxychloride to react with caged bicyclic phosphate1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane and water soluble oligomer polyethylene glycol 200\textsuperscript{88};
- pentaerythritol phosphate-containing polyether fire retardants with high water solubility were synthesized by pentaerythritol phosphate, phosphorus oxychloride, and polyethylene glycol with different molecular weights\textsuperscript{88};
- a new cyclic polyphosphate synthesized by the reaction of polyphosphoric acid and pentaerythritol was used to synthesize a reactive type fire retardant by introducing polyethylene glycol into the molecular structure\textsuperscript{89};
- an intumescent waterborne fire retardant coating for wood was synthesized from urea-formaldehyde resin blended with polyvinyl acetate resin, guanyl-urea phosphate, ammonium polyphosphate, pentaerythritol, and melamine.\textsuperscript{3}

- The core-shell organic modified montmorillonite/epoxy resin/styrene-acrylic emulsion was prepared using semicontinuous seeded emulsion polymerization and used as the binder of the water-borne intumescent fire retardant coating to improve the reaction to fire performance and other basic performance (such as water resistance, anti-yellowing, and adhesion to substrates).\textsuperscript{89}

To achieve high performance painted film, all these components of the intumescent fire retardants need to be balanced perfectly.\textsuperscript{87}

Conventional intumescent coatings have some drawbacks; for example, the char structure formed from the intumescent coating is easily damaged at high temperature, and the intumescent coating is vulnerable to aging. Moreover, the adhesion to substrates of most of waterborne intumescent fire retardant coatings is poor, resulting in sagging and loss at high temperature; thereby, its fire protection is greatly reduced.\textsuperscript{89}

A new class of intumescent coatings with potential application to wood and wood-based products is based on clay-organic hybrid systems.\textsuperscript{90,91} Kim et al\textsuperscript{90} used polyethylene vinyl acetic acid combined with ammonium phosphate monobasic, mono-pentaerythritol, melamine, and a cationic nanoclay (Pristine clay). They observed that “the active sites on layered silicates and acidic sites created by the decomposition of organoclay can catalyse the dehydrogenation, crosslinking, and charring of the nanocomposite.”

### 3 | INFLUENCE OF WOOD MODIFICATION APPROACHES ON THE REACTION TO FIRE PERFORMANCE OF WOOD MATERIALS

#### 3.1 | General remark on chemical modification of wood

Wood chemical modification by impregnation with different solutions is known as an efficient process to improve its dimensional stability and durability, especially in fast-growing plantation species. Generally, the chemicals used for this treatment are anhydrides, furfuryl alcohol, phenol-formaldehyde, and melamine-formaldehyde resins (produced by reaction of phenol or melamine with formaldehyde).\textsuperscript{92}

#### 3.2 | Phenol/melamine formaldehyde and DMDHEU wood modification

Phenol-formaldehyde resins are a significant group of wood binders and are used for wood modification. Especially low molecular weight phenol-formaldehyde and melamine-formaldehyde resins exhibit adequate permeation into wood and can be used to modify its properties. Their chemical reaction in wood occurs as a result of condensation between methylol groups in the resin and etherification between methylol groups and hydroxyl groups in the cell wall polymers, forming a three-dimensional stiff network.\textsuperscript{93}

Beyond that, the production of compressed laminated wood is technically established. Compressed laminated wood is a material consisting of beech veneers and synthetic resins. A homogeneous material is produced by impregnation and pressing under high pressure and temperature. The fixing of the compaction is realized by the synthetic resin, which acts as an adhesive. Phenol-formaldehyde (PF) condensation resins are usually used as the synthetic resins. Unmodified novolacs and phenolic resins are intrinsically very fire resistant and can meet requirements for reaction to fire well. PF combusts with low smoke emission and low toxicity; hence, they exhibit very favorable fire retardant characteristics under fire conditions. Since phenolics are mainly composed of carbon, hydrogen, and oxygen, their combustion products are water vapor, carbon dioxide, carbon char, and moderate amounts of carbon monoxide depending on combustion conditions. The toxicity of the corresponding combustion products is, therefore, relatively low.\textsuperscript{94,95}

The rigid three-dimensionally cross-linked structure resists thermal stress without softening or melting. Since resorcinol has far more reactive sites than phenol, more cross-linking occurs with the phenol formaldehyde/resorcinol formaldehyde resins, than the unmodified phenol formaldehyde resins. This additional cross-linking will render the phenol formaldehyde/resorcinol formaldehyde treated wood more impervious to water and more chemically stable. The increased chemical stability also reduces the risk of formaldehyde emissions from the treated wood or other cellulosic products that favor the decomposition and volatilization. The cross-linking of the phenol formaldehyde/resorcinol formaldehyde resins provides more bonding.
with the cellulose, which in turn entraps in the treated wood the water soluble additives that enhance wood preservation and fire retardancy, even after the treated wood is cured. These water soluble additives can penetrate deeply into the heartwood for greater protection of the wood. As the phenolic material is heated to ignition temperature, it is transformed into a char forming material. The phenolic structure facilitates the formation of a high carbon foam structure (char) that radiates heat and functions as an excellent heat insulator.96,97

Treated Scots pine (Pinus sylvestris L.) sapwood with phenol-formaldehyde and melamine-formaldehyde resins was found to be more resistant to fire. Incorporation of aromatic phenol-formaldehyde resins into the wood (cell wall bulking) did not substantially changed the heat release, but caused an increased smoke and carbon monoxide production due to incomplete combustion. Also, new compounds in the smoke from the treated wood were identified as phenols, and its derivatives resulted from incorporation of phenol-formaldehyde resin. Compared with the untreated wood, wood modified with melamine-formaldehyde resin exhibited significant smoke suppression, and reduction in carbon monoxide yields and resulted in a greater heat release due to complete combustion.93

In order to improve their efficiency, fire retardant additives are used in phenolics mainly if moderately flammable fillers or reinforcing fibers, eg, cellulose, wood particles, and textile fibers, are employed. Satisfactory additives include tetrabromobisphenol-A (TBB) and other brominated phenols, p-bromobenzaldehyde, organic and inorganic phosphorous compounds, red phosphorus, melamine, and melamine resins, urea, dicyandiamide, boric acid, and borates and other inorganic materials.98,99

Modification of oak wood with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) also enhances the flammability of this wood, although the incorporated DMDHEU may release incombustible nitrogen gas.100,101

### 3.3 Acetylation of wood

Durability of wood can be improved considerably by acetylation process that may increase the hydrophobicity of wood and decreases dimensional changes when modifications in the relative humidity take place, as well as protects it against biological damage.72,102 This modification can also change the reaction to fire performance of acetylated wood products. Morozovs and Bukans103,104 investigated the reaction to fire performance of acetylated ash wood and observed that wood acetylation decreases the reaction to fire performance and the appropriate modified wood reaction to fire class. Wood modification with acetic anhydride decreases smoke production when combusting in comparison with natural wood. Further, Mohebby et al105 studied the influence of acetylation on the reaction to fire of beech plywood. The research showed that the acetylation influenced the time to ignition and to glowing and also charring surfaces in the plywood. The glowing was reduced; however, the time to ignition was increased in the acetylated plywood. The acetylation of plywood leads to an extension of the ignition time, shortening the glowing time, combusting with short flames and increasing the charred surfaces.105

### 4 NEW TECHNIQUES TO INCREASE WOOD REACTION TO FIRE

#### 4.1 Surface charring

Already archeological discoveries from around the year 5000 BC from the Nile Valley show the use of charred piles for pile dwellings. Caesar and Vitruvius also mentioned carbonization to increase the service life of bridges and fortification fences. Modifications of the method are also known. Thus, on the Hamburg Alster, Venice, Amsterdam, and other towns built on and in the water, piles were found in the soil without carbonization, but the space was generously filled with coal.106 In Japan, “Shou Sugi Ban” is understood as a traditional production method for surface pyrolysis of wood. Here, the wood surface is charred on the surface with a directly acting flame.107 A first scientific study of the pyrolysis was carried out by Graham108 on exposed fence posts. The formation of a hydrophobic surface during carburizing is already described here. This effect can be explained by the formation of oily and tarry substances during the coalization.108

More recently, this technique is used as “fire retardant” for wood materials.109,110 The improved fire protection effect arises because the surface pyrolysis reduces the outgassing of volatile combustible components and the carbon layer acts as a heat insulator. Orienting fire reaction tests according to DIN 4102-1111 show a significantly improved reaction to fire behavior of surface pyrolyzed oak wood.

#### 4.2 Ionic liquids as fire retardants

Ionic liquids are salts that have melting points around ambient temperature and unique characteristics, such as high solubility, extremely low volatility, incombustibility, and low viscosity. Application of ionic liquids in wood processing technology has attracted attention and is expected to promote further use of wood. They are considered to be effective as preservation agents to enhance decay-resistance and also improve reaction to fire of wood.111 For example, wood treated with ionic liquids 1-ethyl-3-methylimidazolium bromide, 1-ethyl-3-methylimidazolium tetrafluoroborate, and 1-ethyl-3-methylimidazolium hexafluorophosphate was tested using thermogravimetric analysis.112 Here, the wood treated with the latter chemical exhibited the highest reaction to fire, was more resistant against flaming and the subsequent glowing at higher temperatures compared with the former chemical. The untreated wood was almost entirely combusted, whereas that treated with ionic liquid was combusted only at the portion directly contacting the fire, and flames did not spread. This enhanced reaction to fire was interpreted by dehydration in the presence of the ionic liquids under observation.112,113
5 | CONCLUSIONS

The aim of this paper was to give an overview on existing fire retardant and intumescent materials and potential chemical modification methods that may improve the reaction to fire of the wood material. Therefore, we showed the possibilities given by the treatment of the wood with different fire protection materials (fire retardant or intumescent coatings) but also the potential of various wood modification approaches (chemical treatments) to improve the reaction to fire. Apart of the possible materials to be used, the review also presents the advantages and the health and safety risks of these materials and also the possible application methods and their action mechanisms.

It was found that the pure wood modification is not entirely suitable for significantly improving the reaction to fire of wood. Therefore, combined strategies of wood modification and the use of fire retardant chemicals will provide higher protection.

New approaches such as surface pyrolysis or the use of ionic liquids have also been described.

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