JOURNAL of QASSIM UNIVERSITY FOR SCIENCE
©2023 Qassim University [E-ISSN: 1658-9610]
Vol. 2, Issue 1, pp 161-186 (July 2023)
JQUS

Flame retardant applications-based coating cotton fabric

M. M. Abd El-Hady[a,b]

[a]Department of Chemistry, College of Science, Qassim University, Buraidah-51452, Saudi Arabia
[b]National Research Centre (Scopus affiliation ID: 60014618), Institute of Textile Research and Technology, 33 El-Behoth Street, Dokki, P.O. Box 12622, Cairo, Egypt.

Abstract

This review discusses recent advances in flame retardancy achieved in the field of cotton textiles through the deposition of novel coatings able to enhance the flame retardant properties of cotton fabrics. There are a variety of methods for creating these new coatings, including nanoparticle adsorption, layer-by-layer assembly, sol-gel and dual-cure techniques, and plasma treatments. In most cases, these concerns center on the usage or combination of ceramic protective coatings or flame retardant species. Different mechanisms of flame retardant systems were also examined. This article concludes with a discussion of the various approaches to developing flame retardant coatings based on halogens, phosphorus, nitrogen, silicon, and polymer nanocomposites.

Keywords: Flame retardant; Coating; Cotton; Nanocomposite; Sol gel; LBL assembley

Contents :

1. Introduction

Since many fires and flames are ignited by the burning of textile materials, which can cause severe burns or even death, flame-retardant textiles are necessary in many settings to protect against fire and protect human life. The flammability of synthetic fibres, which are naturally flame resistant, is very different from that of cellulosic fibers, which can burn easily. When exposed to an open flame, untreated natural fibers like cotton, linen, and silk burn quickly and easily. The density and structure of a fabric have a greater impact on its flame-spread rate than the fibres themselves. Fabrics that are thin and voluminous can easily burn up [1].

Because synthetic fibres like nylon, acrylic, and polyester are resistant to combustion, it is believed that blended textiles are less flammable and spread flames more slowly. The rapidity with which synthetic textiles burn and their tendency to melt make them far more hazardous. It is possible that blended fabrics, rather than those made entirely of synthetic or cellulosic fibers, pose a greater fire risk. Reducing the flammability of cellulosic fibres has been a major challenge for the textile industry [2]. Cotton is both the most popular and most flammable textile material. Cotton fabrics should be treated with flame retardant materials for the protection of consumers in the military and ~~the~~ aerospace industries. Since the introduction of Pyrovatex CP and Pyrovatex CP New, phosphorous compounds like tetrakis hydroxymethyl phosphonium chloride (THPC) and N-methylol dimethylphosphono propionamide have become the standard for making long-lasting flame retardant finishes for cotton (MDPA).

The fiber surface may undergo a reaction, or cross-linking structures may be formed [5, 6]. These chemicals act as an efficient flame retardant for cellulose because they prevent the formation of levoglucosan and flammable volatiles when heated, boost the production of char, and reduce the rate of combustion [7]. The phosphorus content of the treated cellulose has been found to play a crucial role in the effectiveness of the flame retardant. To rephrase, more flame retardant was better at decreasing the flammability of cellulose fiber [8]. One major drawback of these chemicals is that they emit formaldehyde during curing and consumer use. Since formaldehyde is considered to be a carcinogen agent efforts should be made to develop effective flame retardants that do not contain it [8].

Nanotechnology has gotten a lot of attention from both industry and academic research because of the surprising and positive results that have come from using nano-sized devices in many fields over the last 20 years. People have come up with and used different ways to improve the finishing qualities of textiles, yarns, and fibers [9, 10]. Nanostructured synthetic fibres [11], nanoparticles in the standard back-coating [12, 13], and deposition of (nano) coatings [14, 15] are three of the most interesting ways to make something flame resistant.

The current review examines recent developments in flame-retardant cotton fabric. First, we investigate coating techniques and mechanisms. In addition, the development of flame retardant coatings based on halogens, phosphorus, nitrogen, silicon, and polymer nanocomposites is reviewed and discussed

2. Coating Technology

Coating is the application of a polymeric layer to one or both surfaces of the fabric. When applying the viscous polymer coating, it is necessary for it to attach to the fabric using a blade or other aperture [16]. Inter-layer adhesion must consequently be high, which can be achieved by applying consecutive layers of coating. An additional top layer may be applied for aesthetic purposes or to enhance the coating [16]. Flame retardant coatings have become a common way to protect a surface from fire. It is easy to use and can be used on a wide range of materials [17], such as metal, polymers, fabrics, and wood, because it doesn't change the material's basic properties, like its mechanical properties. By putting nanoparticles into the component fibers or on their surfaces, including those of yarns and fabrics made from them, the textile industry has recently come up with a new way to deal with flammability and combustion.

These nano-objects can move to the surface of the fibre during combustion and protect the polymer by acting as a "thermal shield" [18, 19]. The first is predicated on the potential for melt spinning to incorporate various nanoparticle types into thermoplastic fibers. The term "nanostructuring" refers to this efficiency. Alternatives include the deposition of innovative and intelligent coatings, such as ceramic protective layers or flame retardant species alone or in conjunction with ceramic protective layers, on the surface of the fabric to impart flammability resistance (Figure 1). New techniques, including nanoparticle adsorption, layer-by-layer assembly, sol gel processes, dual curing procedures, and plasma deposition, have been created for this purpose

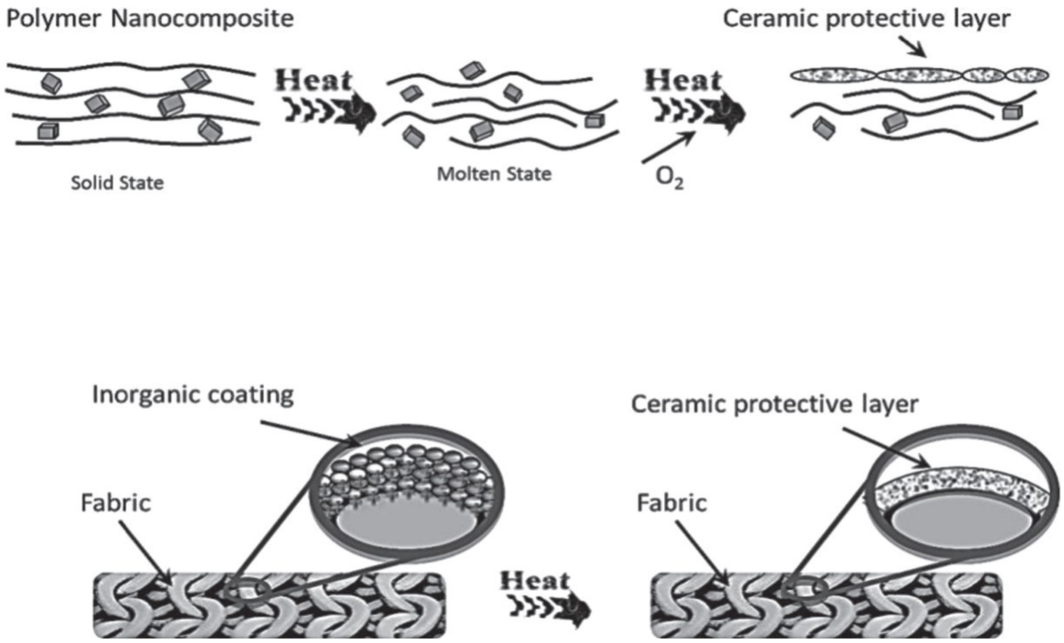


Figure 1: Schematic diagrame of flame-retardancy properties to fibres and fabrics [19]

Depending on how they suppress flames, "flame-safe" coatings are categorized as intumescent or non-intumescent. An intumescent coating is a substance that, when exposed to heat, can expand and form a char layer in three dimensions. Traditional intumescent systems [20] consist of pentaerythritol, an acid source that serves as a dehydrating catalyst, polyphosphate, and a blowing agent that aids in the formation of the porous barrier. This carbonaceous, cellular/porous residue protects the underlying substrate from further degradation by blocking the passage of heat, air, and pyrolysis products [21]. Bourbigot's team has conducted extensive research on such systems [22–24], and Weil has just released a state-of-the-art review of the literature [25].

2.1. Coatings from nanoparticle adsorption

Adsorption of nanoparticles is the most straightforward method for modifying a surface with nanoparticles. The fabric is simply submerged in an aqueous suspension of nanoparticles, which aids in their adherence to the fabric's fibre surface. The flame retardancy of synthetic (such as polyester) and natural (such as cotton) fabrics and their blends can be improved by applying a nanoscale coating, as was recently demonstrated. The polymer beneath the fibre may be shielded from heat, oxygen, and fire by coating it with an inorganic shield. The nanocoating can actually serve as a thermal insulator by sucking in ambient heat and oxygen and blocking their transfer to the surrounding polymer. Coatings can aid in fire spread by entrapping the substrate's volatile substances. The substrate is prevented from burning and instead undergoes pyrolysis. It has been shown that, unlike polyester, cotton fabrics treated with hydrotalcite and silica have effective flame retardancy [26].

To adsorb nanoparticles, a combination of simple immersion and surface pretreatment with cold oxygen plasma was used. The primary goal of this study was to examine how immersion time and pre-treatment affected nanoparticle uptake on cotton fibers and the resulting cotton properties. Silica nanoparticle uptake was highest after 30 minutes of immersion, while hydrotalcite showed no significant differences between 30 and 60 minutes of immersion. The time required to ignite (TTI) was lengthened and the peak heat release rate (PHRR) was decreased when using either nanoparticles alone or in tandem, as revealed by scanning electron microscopy. Adsorption of nanoparticles has also been used to add carbon nanotube functionality to cotton fibres [27]. The mechanical properties, flame resistance, UV protection, and water resistance of the treated fibres have all been improved.

2.2. Coatings from layer by layer (LbL) assembly

Nanoparticle adsorption can be seen as having evolved into the layer-by-layer assembly of nanoparticles [28]. It was first developed in 1991 for polyanion/polycation couples to obtain so-called polyelectrolyte multilayers [29] and was later applied to inorganic nanoparticles by taking advantage of interactions other than electrostatic repulsion (such as covalent bonds, hydrogen bonds, etc.) Substrate immersion in a polyelectrolyte (typically water) solution with an oppositely charged polyelectrolyte is all that's needed for the LbL assembly via electrostatic interactions (or dispersion). Utilizing a total surface charge reversal after each immersion step [30], an assembly of positively and negatively charged layers is accumulated on the surface of the substrate. Figure. 2 depicts an overview of the process. Very recently, this strategy proved to be extremely advantageous when applied to the flame retardancy of nano-coatings containing phosphorus/nitrogen/silicon [31] and SiO_2-PEI/PA [32].

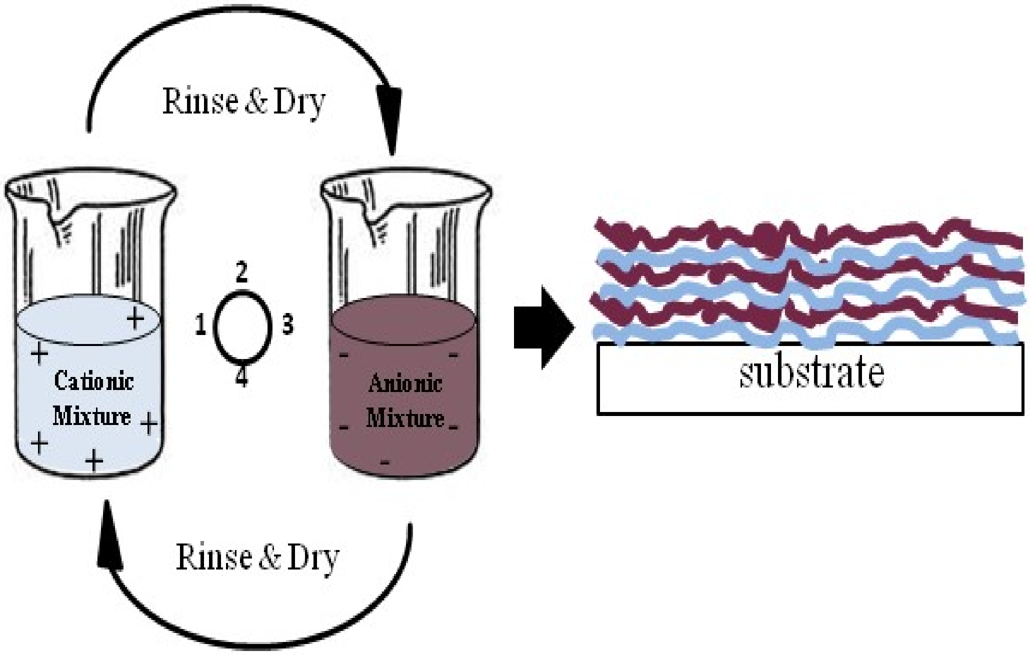


Figure 2. Schematic representation of LbL assembly [30].

According to the chemical nature of the deposited coatings, the LbL assemblies applied to fabrics will be thoroughly evaluated.

2.2.1. Inorganic LbL coatings

Recently, several research teams have looked into inorganic LbL coatings with the goal of developing a thermal insulator system for the fabric's outer layer. A barrier of this type may act as a thermal shield for the surrounding substrate, encouraging phenomena like char formation and discouraging the production of volatile species that can fuel the combustion further. Cotton's main component, cellulose, is a great illustration of this. In fact, a thermal insulator barrier can encourage cellulose dehydration, resulting in the formation of char, and inhibit cellulose depolymerization, resulting in the production of volatile species like levoglucosan and furan. The first attempt at depositing such architectures was made by Grunlan and work colleagues, who built structures on cotton fabrics out of laponite nano-platelets (the negative layer) and branched poly(ethylenimine) (the positive counterpart).

Although the coated fabrics' afterglow occurred 10 seconds earlier than the uncoated fabrics', vertical flame tests revealed that the addition of ten bilayers did not significantly improve the properties of flame retardancy of cotton in terms of ignition and after flame times. However, the residue on the treated fabrics varied in appearance and was fragile (Table 1) [33].Sodium montmorillonite has been used as a partial solution to this problem by replacing laponite [34]. Colloidal silica (silica (+) / silica (-)) [35] is a completely inorganic coating that has shown promising results when applied to cotton fabrics.

Table 1: Results on inorganic LbL coatings [36].

Positive counterpart	Negative counterpart	Main results
Natural fibers (namely, cotton)		
Polyethylenimine	Laponite	Afterglow of 10BL-coated cotton fabrics occurred 10 s earlier with respect to the uncoated fabrics
Polyethylenimine	Sodium montmorillonite	Final residue of 10 BL-coated cotton fabrics after vertical flame spread tests is coherent and not-fragile
Alumina-coated silica	Silica	10 BL-coated fabrics exhibit a PHRR reduction of 20%, assessed by micro-combustion calorimetry
Octa-3-ammoniumpropyl chloride POSS_	Octakis (tetra methyl ammonium) Penta cyclo octasiloxane octakis (cyloxide) hydrate POSS_	Afterglow time is reduced and the fabric weave structure and shape of the individual fibres are highly preserved
Synthetic fibers (namely, polyester)		
Alumina-coated silica	Silica	5BL-coated fabrics exhibit a PHRR reduction of 20% and a TTI increase of 45%, assessed by cone calorimetry. The same coatings reduce the burning time by 95% and eliminates melt dripping phenomena
Poly diallyl dimethyl ammonium chloride (PDAC)	Zr phosphate nano-platelets	PDAC-based assemblies increase TTI up to 86%, assessed by cone calorimetry
Octa-3-ammoniumpropyl chloride POSS_		POSS-based assemblies decrease PHRR down to 26%, assessed by cone calorimetry
Alumina-coated silica nanoparticles		Silica nanoparticles promote a significant reduction in the smoke production rate (25%), together with a strong pkCO decrease (30%), assessed by cone calorimetry

2.2.2 Intumescent coatings

Fires could not be extinguished by depositing a completely inorganic coating, despite the initial encouraging results; consequently, viable alternatives, such as those provided by intumescent systems, have been explored (Table 2). A carbonaceous multi-lamellar structure (char) forms on the surface of an ignitable substance when it is subjected to a heat flow. This char is a physical barrier that can reduce the amount of heat, fuel, and oxygen that can pass through the polymer into the flame. When heated, the acid source, carbon source, and blowing agent in a typical intumescent system release copious amounts of expandable or noncombustible gases **[37]**.

Table 2: Results on hybrid organic-inorganic LbL coatings deposited by dipping [36]

Positive counterpart	Negative counterpart	Main results
Chitosan	Ammonium polyphosphate (APP)	Suppression of the afterglow phenomenon for cotton-rich (70%) - polyester blend; 20BLs are able to reduce the THR (_22%) and PHRR (_25%), assessed by cone calorimetry
Alumina-coated silica nanoparticles	Ammonium polyphosphate (APP)	Suppression of the afterglow phenomenon for cotton-rich (70%) -polyester blend; 10BLs are able to increase the TTI (þ40%) and reduce the THR (_15%), assessed by cone calorimetry
Poly(allylamine)	Poly(sodium phosphate)	10BLs induce a significant decrease of the THR and PHRR when deposited on cotton fabrics (_80 and _60%, respectively), assessed by microcombustion calorimetry
Chitosan	Phytic acid	30BLs applied to cotton were able to block the flame propagation on cotton and to reduce PHRR of 50%, as assessed by microcone calorimeter
An amino derivative of poly (acrylic acid)	Sodium montmorillonite	20BLs favour an increase of TTI (ca. þ40%) and a reduction of THR and PHRR when applied to cotton fabrics (_50 and _18%, respectively)
A derivative of polyacrylamide	Graphene oxide	20BLs favour an increase of TTI (ca. þ56%) and a reduction of PHRR when applied to cotton fabrics (_50%)

2.3. Sol-gel and dual-cure coating processes

New materials with remarkable molecular homogeneity and physical and chemical properties have been developed using sol-gel synthesis [38]. Starting with (semi) metal alkoxides, this versatile synthetic route then proceeds to form either entirely inorganic or hybrid organic-inorganic coatings via a two-step reaction (hydrolysis and condensation) at or near room temperature. Process parameters include the type of semi-metal atom and alkyl/alkoxide groups present, the structure of the of semi- metal alkoxide, the water/alkoxide ratio, the pH (basic or acidic conditions), the temperature, the time required for the reaction, and the presence of co-solvents. Oxidic network structure and morphology are established by these factors [39]. A simplified diagram of this procedure is shown in (Figure 3).

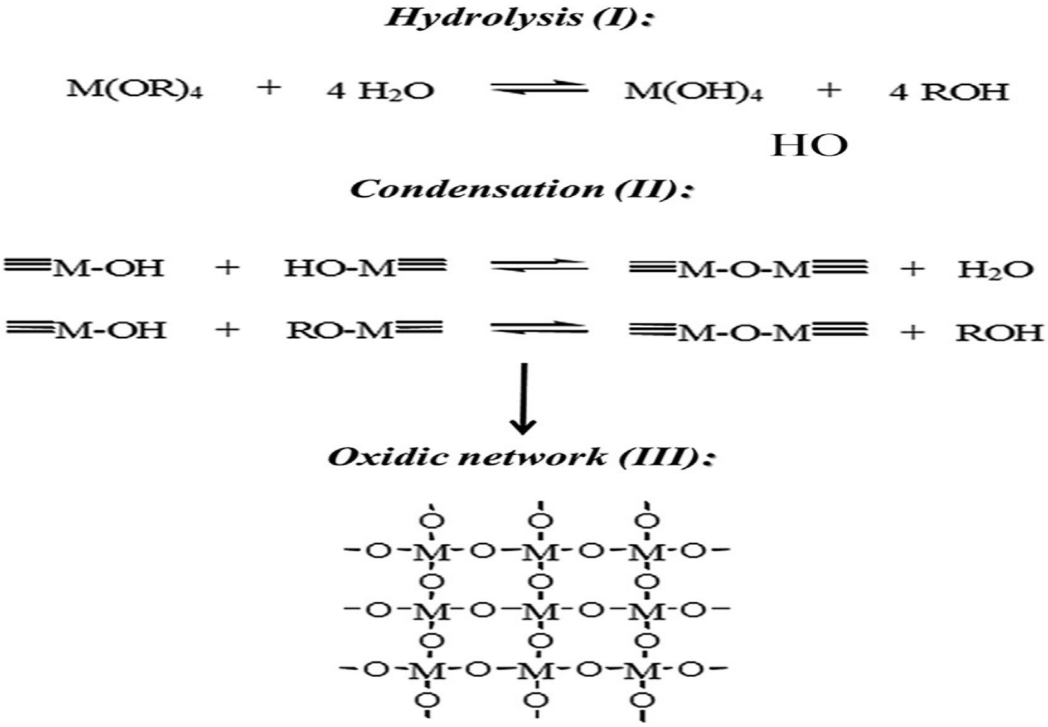


Figure 3: Sol-gel processes [39]

Although sol-gel processes have been around since the 1950s, it is only recently that they have been used to improve the flame retardancy of textiles. This is because, in recent years, sol-gel derived hybrid architectures have been able to protect the polymer surface by exerting a thermal shielding effect, thereby improving the flame retardancy of the treated fabrics. As a matter of fact, these architectures can prevent the formation of volatile species that fuel further degradation and promote the formation of char [41] by absorbing heat from the surrounding atmosphere and creating a physical barrier to oxygen and heat transfer. For this reason, the flame retardancy promoted by the sol-gel derived coatings is only effective when they operate in synergy or combined effects due to the fabric's limited thickness and the protective coating's limited shielding effect on the underlying polymer. Other flame retardant active species, such as those containing phosphorus and/or nitrogen, have been combined with sol-gel oxidic phases (typically silica). These progressions are discussed in the following paragraphs.

2.3.1. Inorganic architectures

Pure silica particles or coatings make up the majority of inorganic architectures fabricated using the sol-gel technique. Common precursors include tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate, (3-aminopropyl)triethoxysilane and 3-glycidoxypropyltriethoxysilane. Recently, reactive -aminodiphosphonate siloxane (TTPBD) was synthesized successfully, and flame-resistant cotton fabric was prepared using sol-gel coating technology [41]. When it comes to TTPBD, researchers have looked into the effects of using a variety of silica or other oxidic phase precursors and explored a number of process aspects that have a direct bearing on the morphology of the coating that is deposited on the fabrics. The following factors were specifically considered: - Process parameters (specifically, precursor to water molar ratio, temperature and time of thermal treatment [42], and moisture [43]), Chemical structure of the sol-gel precursors (specifically, chain length and number of hydrolysable groups [44], precursor Type [45].

2.3.2. Phosphorus-doped silica architectures

Previous discussion has established that synergistic or combined effects are required for sol-gel derived architectures to be considered effective flame retardant systems [46-48]. This goal can be accomplished through one of three methods:

1- Combining an alkoxysilane precursor with a phosphoric acid source yields precursors with silane and phosphate functional groups.

2-Utilizing a silane- and phosphate-functional alkoxysilane precursor.

3-Combining P- and N-containing chemicals with an alkoxysilane precursor that possesses silane and phosphate functionality.

2.4. Plasma treatments based coating

In recent years, plasma's popularity has skyrocketed due to its accessibility at room temperature [46]. Electrons, ions, and neutral species in both their ground and excited states make up plasma, a gaseous medium. So-called "atmospheric plasma" has attracted a lot of attention because it can be used economically and industrially and does not necessitate a vacuum. Moreover, after an impregnation-based treatment, plasma treatments rarely necessitate additional energy-intensive thermal curing to finish reactions or remove solvent. Plasma treatment increases the fire resistance of substrates because ions and radicals are produced during the process. Contact between monomers and a plasma-treated substrate causes the monomers to undergo surface reactions, which can result in the creation of new functions or the initiation of polymerization. After being ionized, charged polymers and nanoparticles adhere more strongly to a charged substrate. Plasma-based surface modification takes place in a gaseous rather than liquid phase, in contrast to more conventional surface treatments.

In 1990 [47], Reports have surfaced suggesting plasma could be used to increase fire resistance. In order to polymerize the treatment on the surface, we used a treatment system that generated plasma around the substrate and directly monomer deposited onto the substrate. researchers in one study were able to successfully polymerize a siloxane on the surface of polyamide-6 [48]. The treated substrate ignited sooner than the untreated substrate did, despite the treatment reducing the peak HRR. Exposure to argon ions and radicals, the agents of surface functionalization and polymerization, was found to cause damage to the substrate and speed up its degradation. Cotton can be made flame-, water-, and oil-proof with a plasma coating [49]. With the addition of energy sources that can modify and form covalent bonds, plasma-based treatments have been brought to the commercial market. A UV laser that can break the covalent bonds in fabrics is included in multiplexed laser surface enhancement (MLSE) systems, for instance (such as, C–C bonds or C–N bonds). Since MLSE processes can be scaled up, factories can now mass-produce fabrics with special finishes like hydrophobic or antimicrobial coatings, or coatings that enhance dye uptake. Flame-retardant coatings can be applied to fabrics using these MLSE systems without the use of any liquid processing steps [50]. This discovery is a game-changer for the widespread implementation of plasma-based surface treatments for flame-retardant coatings, and it suggests that this will be a topic of ongoing research for some time to come.

3. Mechanism of flame retardants

In textiles, flame retardants are used to inhibit or even suppress the combustion process by interfering with one or more burning stages, including heating, decomposition, ignition, and flame spread. The two broad categories of action, chemical and physical, in the solid, liquid, and gas phases of textile flame retardants, are further subdivided into the mechanisms detailed below [51, 52].

3.1 Physical action

3.1.1 Coating theory (the principle of intumescence).

During chemical finishing or when the flame retardants and substrate are heated, the flame retardants form a protective layer with low thermal conductivity on the fibre's surface. This shield prevents the transfer of heat, oxygen, and mass. This category of agents includes carbonates, inorganic borates, and phosphorus additives, among others. The pyrolysis of the latter results in the formation of vitreous pyrophosphoric or polyphosphoric compounds that are thermally stable.

3.1.2 Dilution of the gas phase.

Water vapor, carbon dioxide, sulphur dioxide, and ammonia are just some of the non-flammable gases released during flame retardant decomposition. These gases diffuse and mix with the oxygen present around the combustible cellulose, preventing it from igniting. As an example of this mode of action, consider the decomposition and subsequent evaporation of alumina trihydrate (ATH) and magnesium hydroxide. Melamine also sublimes, and its nitrogen-rich vapors act as a benign diluent in the fire [53] .

equations 1 and 2 (Please added reference)

$$2\mathrm{Al(OH)_3} \xrightarrow{180\text{-}240^\circ\mathrm{C}} \mathrm{Al_2O_3} + 3\mathrm{H_2O} \qquad (1)$$

$$\mathrm{Mg(OH)_2} \xrightarrow{330\text{-}460^\circ\mathrm{C}} \mathrm{MgO} + \mathrm{H_2O} \qquad (2)$$

3.1.3 Cooling.

An endothermic change, like fusion or sublimation, in the retardant can dissipate the heat input from a source. As a heat sink, the flame retardant prevents the substrate from heating to a point where combustion can continue.This mechanism also applies to Alumina trihydrate (ATH) and magnesium hydroxide, as their decomposition (equations 1 and 2) is endothermic [53] .

3.2 Chemical action

3.2.1 In the gas phase.

Flame retardants and their breakdown products hinder the gas-phase radical mechanism of combustion by replacing highly reactive hydroxyl and hydrogen radicals with less energetic species. Especially in the case of organo halogen compounds like decabromodiphenyl oxide, flame retardants containing halogens (primarily brominated and chlorinated) work via the gas-phase mechanism and are often combined with metal oxides (antimony oxide, Sb_2O_3). In addition, certain phosphorus flame retardants (such as triphenylphosphate) can be effective in the gas phase by producing phosphorus-containing radicals that can combine with hydrogen radicals to extinguish the flame [53].

3.2.2. In the condensed phase.

Flame retardants chemically stop the solid substrate from burning and change the chemical reactions that happen during decomposition so that protective char is made instead of CO or CO_2. For example, cellulose's pyrolysis process takes place in two stages that compete with each other between 200 and 400 °C. First, cellulose loses its water and turns into char, CO_2, and water. Second, levoglucosan is made at low temperatures [53], which then dehydrates and polymerizes to make tars, gases that can catch fire, liquids, and other solids. Flame retardants or their decomposition products dehydrate cellulose without forming levoglucosan. Changing the cellulose decomposition path reduces flammable tars and gases and increases char. Dehydrating flame retardants include phosphorus and sulphur derivatives. Upon heating, they decompose into polyacids, which catalyze char formation via cellulose esterification and pyrolytic ester decomposition (equation 3) or carbonium ion charring (equation

4). Ciba's Pyrovatex® CP, a dialkylphosphonopropionamide flame retardant, is important (bought currently by Huntsman) [53].

$$
\begin{aligned}
&\mathrm{R_2CHCH_2OH + ROH\ (acid) \rightarrow R_2CHCH_2OR + H_2O} \\
&\quad \mathrm{\rightarrow R_2C = CH_2 + HOR\ (acid)} \qquad (3) \\
&\mathrm{R_2CHCH_2OH + H^+ \rightarrow R_2CHCH_2OH_2^+} \\
&\quad \mathrm{\rightarrow R_2CHCH_2 + H_2O \rightarrow R_2C = CH_2 + H^+} \qquad (4)
\end{aligned}
$$

Intumescence-based flame retardant fabrics are a special case of a condensed-phase mechanism. Combining charring and foaming at the surface of a burning substrate, intumescent systems (IFRs) protect the surface from flame. Foaming agent, acid source, and carbonific agent are the three main components of IFRs. The fiber in cellulose serves as a carboniferous agent and is one of the incendiary components. One example of an IFR is the ammonium polyphosphate-pentaerythritol system; however, spirocyclic pentaerythritol diphosphoryl chloride and melamine reacting to form a trifunctional molecule is preferable [53]. One major drawback of these systems is that even water-insoluble intumescents do not fare well in the washing machine unless they are either bonded to a hydrophobic resin or incorporated into the molecular structure of the textile fiber, both of which are impractical in practice. Relevant research has been conducted by phosphorylating polyol phosphoryl chloride with cellulose [53,54].

4. Flame retardant chemistry for application in coating

4.1. Halogenated flame retardants

Halogenated flame retardants have molecules made up of chlorine, bromine, and fluorine. The most effective flame retardant additives for polymers are organohalogen compounds [55]. However, flame retardant additives can have a wide range of chemical structures, from aliphatic to aromatic carbon substrates that have been per-halogenated (all hydrogen replaced with halogen) or come in inorganic forms. Organobromine compounds are much more common than those containing organochlorine or another halogen [56]. The C-Br bond is perfect for extinguishing flames, which is why organobromine compounds are widely used in fire safety. Although the bond is strong enough to withstand the elements, it is easily broken by high temperatures, releasing the bromine to counteract free radical reactions in a fire. To illustrate the variety of chemical reactions that can occur in the vapor phase of bromine to prevent combustion, see (Figure 4). Due to the halogens' unique ability to suppress combustion in the vapor phase, halogen-based flame retardants are limited to that application. In order to increase the efficacy of halogenated flame retardants in the vapor phase, they are sometimes mixed with synergists like antimony oxide, zinc borate, or chemistry based on phosphorus.

$$H\cdot + O_2 \rightarrow HO\cdot + O\cdot \qquad HO\cdot + H\cdot \rightarrow H_2O \qquad HO\cdot + CO \rightarrow CO_2 + H\cdot$$

$$R\text{-}Br \rightarrow R\cdot + Br\cdot \qquad Br\cdot + R\text{-}H \rightarrow HBr + R\cdot \qquad H\cdot + Br\cdot \rightarrow HBr$$

$$HO\cdot + HBr \rightarrow H_2O + Br\cdot \qquad H\cdot + HBr \rightarrow H_2 + Br\cdot$$

$$SbBr_3 + 3H\cdot \rightarrow Sb + 3HBr$$

$$Sb + HO\cdot \rightarrow SbOH$$

$$SbOH + HO\cdot \rightarrow SbO + H_2O$$

Figure 4 : Bromine free radical combustion reaction [55]

4.2. Phosphorus flame retardants

Some flame retardants, both inorganic and organic, contain phosphorus in their chemical makeup [57]. Since direct phosphorus-carbon bonds are often prohibitively expensive or technically challenging to achieve, most phosphorus-based flame retardants instead feature phosphorus-oxygen bonds with organic groups attached to the oxygen. Some believe that the effectiveness of these flame retardants is greatly enhanced in oxygen-containing polymers (e.g., cellulose and rigid polyurethane foam). Some typical phosphorus-based flame retardant structures are shown in (Figure 5).

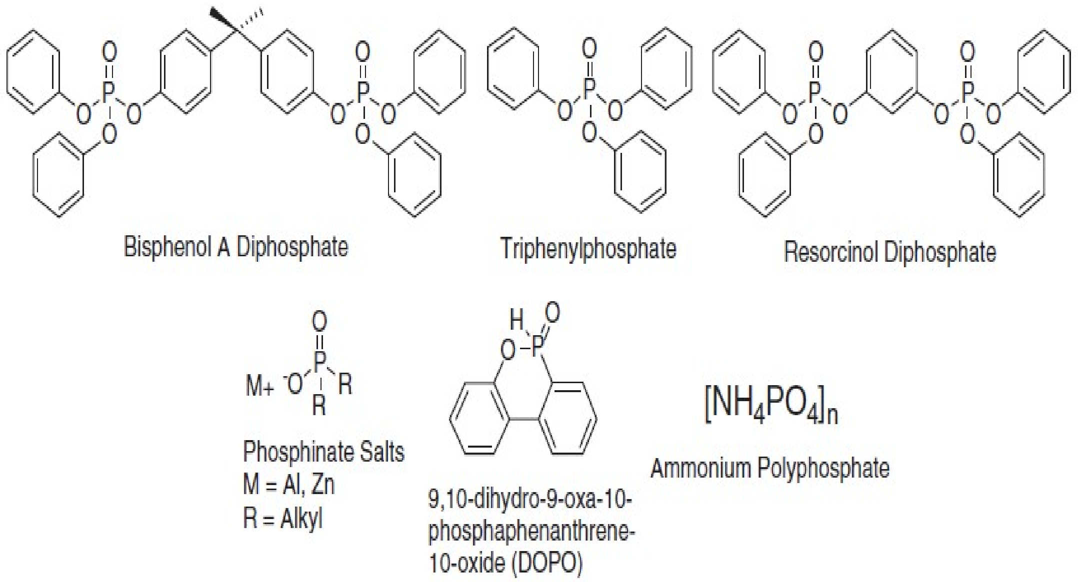
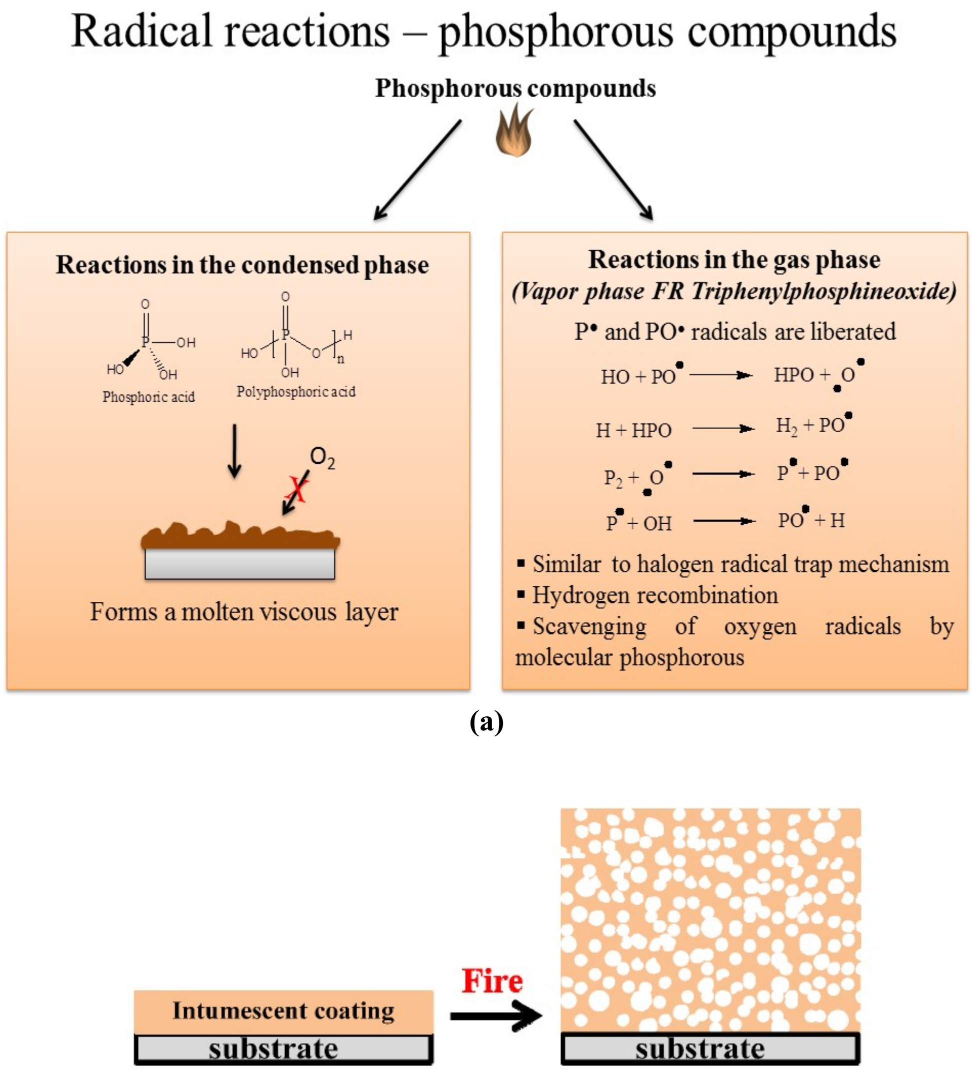


Figure 5: Common phosphorus-based flame retardants [57]

Phosphorus compounds are distinctive in that, depending on their chemical structure and their interaction with the polymer under fire conditions, they can be vapor phase or condensed phase flame retardants [58]. Figure 6 depicts some examples of phosphorus chemistry in the vapor phase. They are also effective in the condensed phase of polymer combustion [59]. As shown in (Figure 6), phosphorous reacts with heat to produce phosphoric acid derivatives. This acid is responsible for the formation of a glassy layer, which inhibits the spread of flames. One other category of flame retardants that makes use of phosphorus compounds is intumescent systems [60]. Lack of reactive groups in polymers necessitates the use of coadditives to generate a thick, swollen char that will shield the polymer from damage.

Char-forming agents (polyhydric compounds like starch, dextrins, and pentaerythritol) that can be phosphorylated; an acid source (a precursor for catalytic acidic species like ammonium polyphosphate and melamine phosphate, etc.); and a blowing agent (like urea or melamine, which decomposes into gaseous nitrogen and water). The reactions that result in the formation of char are thought to be catalyzed by amines and amides. There are drawbacks to using these, as there are to all flame retardant technologies. They aren't as effective when used alone in polystyrene or polyolefin, and they aren't as widely applicable as halogenated flame retardants. Furthermore, because they inhibit polymer combustion, they generate more smoke and carbon monoxide in the event of a fire, and their environmental impact is starting to draw regulatory scrutiny [55].



(a)

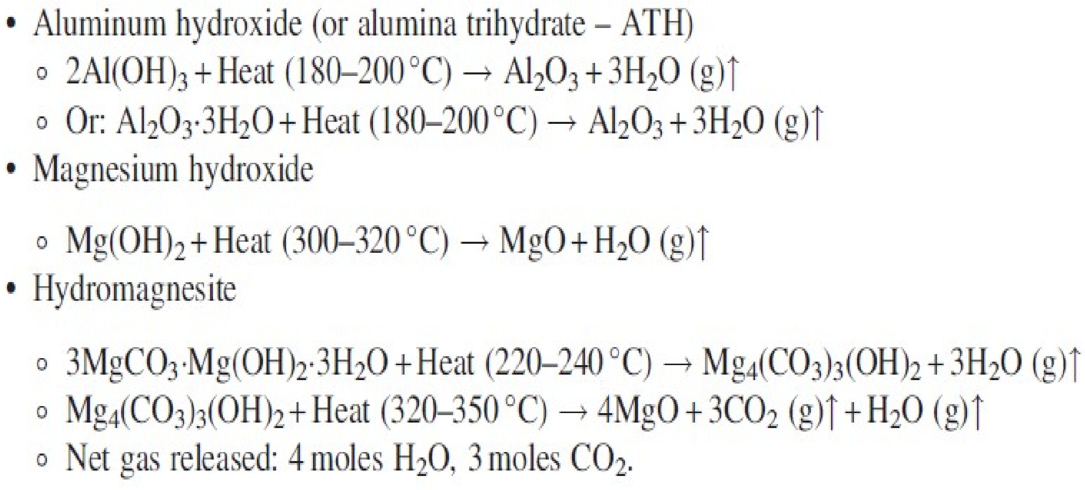
(b)

Figure 6: a) Mechanisms of flame retardant reactions based phosphorus and b) schematic of intumescent coating [61]

4. 3. Mineral filler flame retardants

As part of the endothermic cooling mechanism of flame retardancy, the vapor/condensed phase activity of flame retardants containing mineral fillers is easily distinguishable. It is now common practice to use mineral fillers as flame retardants, with metal hydroxides and metal carbonates being the most popular examples [62]. For the hydroxide or carbonate to be effective, it must be able to release its water or carbon dioxide at elevated temperatures without causing the polymer to decompose first. Hydroxides and carbonates that decompose between 180 and 400 degrees Celsius are therefore the only additives commonly used as flame retardants today. Aluminum ($Al(OH)_3$) and magnesium ($Mg(OH)_2$) hydroxides are two examples of hydroxides that are frequently used.

Because the water is hydrated on the aluminum oxide surface rather than being predominated by Al-OH bonds, alumina trihydrate ($Al_2O_3.3H_2O$) is a more common name for this compound. However, the net stoichiometry is the name, and both structures are used interchangeably when discussing flame retardant chemistry [63]. Calcium carbonate, along with other fillers (silicone) and activating materials, is used to make wire and cable compounds flame retardant [64]. Magnesium carbonate is also occasionally used for carbonates. Hydromagnesite, a slightly modified form of magnesium carbonate, is also put to use because it can emit water and carbon dioxide at milder temperatures. While synergists and mineral fillers rarely work together, there are cases where the two are used together as flame retardants. Some of these common mineral fillers are provided below :



- Aluminum hydroxide (or alumina trihydrate – ATH)
  - $2Al(OH)_3 + \text{Heat } (180\text{–}200\,°C) \rightarrow Al_2O_3 + 3H_2O\ (g)\uparrow$
  - Or: $Al_2O_3{\cdot}3H_2O + \text{Heat } (180\text{–}200\,°C) \rightarrow Al_2O_3 + 3H_2O\ (g)\uparrow$
- Magnesium hydroxide
  - $Mg(OH)_2 + \text{Heat } (300\text{–}320\,°C) \rightarrow MgO + H_2O\ (g)\uparrow$
- Hydromagnesite
  - $3MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O + \text{Heat } (220\text{–}240\,°C) \rightarrow Mg_4(CO_3)_3(OH)_2 + 3H_2O\ (g)\uparrow$
  - $Mg_4(CO_3)_3(OH)_2 + \text{Heat } (320\text{–}350\,°C) \rightarrow 4MgO + 3CO_2\ (g)\uparrow + H_2O\ (g)\uparrow$
  - Net gas released: 4 moles H_2O, 3 moles CO_2.

Figure 7: Some schemes on main classes of mineral fillers [55]

4.4. Nitrogen flame retardants

As environmentally friendly and non-toxic alternatives to existing halogen formulations, nitrogen-based flame retardants are becoming increasingly popular. In addition, nitrogen-based flame retardants can be recycled along with the materials they are used in. Most melamine derivatives, which are nitrogen-based compounds, are used as flame retardants because they extinguish flames both in the gaseous and condensed phases [65].

4.5. Silicon flame retardant

Silicon-based flame retardants are seen as a good alternative to halogenated flame retardant compounds because they don't produce corrosive smoke when they burn [66, 67] and can be used in coatings without harming the environment. Silicon-based coatings are mostly made by adding silicones, silicates, organosilanes, or silsesquioxanes as filler sand copolymers or as the main polymeric matrix to the whole system. "Network armor" made of silicon dioxide (SiO_2) has also been used to make flame retardant coatings. Hydrolysis and condensation of the precursor tetraethyl orthosilicate (TEOS) was followed by cross-linking on the surface of fibers (sol-gel process) to create this "armor" [67].

4.6. Polymer Nanocomposite (PNC) based coating systems

In terms of enhancing the flame retardant properties of a number of polymermatrices, research and development on various polymer nanocomposites over the past two decades has shown great promise. A few examples of typical nano-sized inorganic fillers are layered silicates, silsesquioxane derivatives, layered materials (2D) like montmorillonite clay (MMT), layered double hydroxides (LDH), and layered zirconium phosphate, tubes/rods (1D) like carbon nanotubes, and spherical/colloidal solids (0D) like polyhedral oligosilsesquixane [68,69]. The degradation of nanocomposites is significantly influenced by the interaction between polymer and particle at the interface. By acting as restriction sites for a polymer chain's motion, particles can be made to interact strongly, which shifts the material's degradation temperature and makes the scission chain harder at lower temperatures [70]. The most prominent nanoparticles used in commercial nanocomposite formation are carbon nanotubes/ nanofibers and clay nanoparticles (organically treated layered silicates).

Due to thermal instability issues associated with the organic treatment of the clay's surface, the polymers into which they can be incorporated are restricted [71]. When compared to other nanomaterials, carbon nanotubes and nanofibers don't experience the same degree of thermal instability, but they can be difficult to work with because of their high cost or poor interface with many polymers. Overall, the nanoparticles slow polymer pyrolysis, which lowers the rate of heat release during polymer combustion and, thus, reduces the rate of mass loss. The decomposition of polymer nanocomposites forms a protective barrier, which accounts for the decreased mass loss rate. The nanopartices are driven upward toward the polymer matrix surface by the numerous bubbles of degradation products. Because of this, the composite surface is insulated from the condensed phase's temperature by an inorganic barrier [72]. To incorporate nanoscale inorganic particles into an organic matrix, sol-gel processing is one of the most well-known methods [73,74].

5. Future outlook and conclusion

Nanotechnology is now an important part of making new flame-retardant systems and is being used in more industries. The most recent innovation in fire-safe materials is polymer nanocomposites. and there is a lot of hope that they will lead to new fire-safe materials that can be used in both commercial and noncommercial settings. The benefits of nanocomposites are much more important than their cost. It can allow flexible coating architecture and microstructural design to meet a wide range of needs, such as precise control of physical, chemical, and mechanical properties and the creation of assemblies with multiple functions. Combining nanoparticles with other systems that already contain flame retardants seems like a good way to give the substrate better flame resistance.

Biomacromolecules in general have been investigated as a new, green approach to flame retardancy from an ecological standpoint. Research in both industry and academia is being driven by the possibility that environmentally friendly flame retardant systems could one day replace conventional chemicals. In particular, using flame retardant systems based on natural macromolecules like proteins or nucleic acids could be an unorthodox but highly effective strategy because they do not contain halogens or formaldehyde.

6. References

[1] Lam Y. L., Kan C. W., Yuen C. W. M. "Effect of titanium dioxide on the flame-retardant finishing of cotton fabric", *Journal of Applied Polymer Science*, 2011, 121, 267-278.

[2] Abd El-Hady M. M., Farouk A., Sharaf S. "Flame retardancy and UV protection of cotton based fabrics using nano ZnO and polycarboxylic acids", *Carbohydrate Polymers,* 2013, 92, 400-406.

[3] Wu W., Yang C. Q. "Comparison of different reactive organophosphorus flame retardant agents for cotton: part I. The bonding of the flame retardant agents to cotton", *Polymer Degradation and Stability,* 2006, 91, 2541-2548.

[4] Schindler W. D., Hauser P. J. "Chemical Finishing of Textiles", Woodhead Publishing Limited, Cambridge, UK, 2004, 98-107.

[5] Wu W., Yang C. Q. "Comparison of different reactive organophosphorus flame retardant agents for cotton. Part II: Fabric flame resistant performance and physical properties", *Polymer Degradation and Stability,* 2007, 92, 363-369.

[6] Gaan S., Sun G. "Effect of phosphorus and nitrogen on flame retardant cellulose: A study of phosphorus compounds", *Journal of Analytical and Applied Pyrolysis,* 2007, 78, 371-377.

[7] Cheng X., Yang C. Q. "Flame retardant finishing of cotton fleece fabric: Part V. Phosphorus-containing maleic acid oligomers", *Fire and Materials*, 2009, 52, 246-253.

[8] Wu X., Yang C. Q. "Flame retardant finishing of cotton fleece fabric. II. Inorganic phosphorus containing compounds", *Journal of Applied Polymer Science,* 2008,

[9] Gulrajani M. L., Gupta D. "Emerging techniques for functional finishing textiles", *Indian Journal of Fibre* & Textile *Research,* 2011, 36 (4), 388-397.

[10] M. Afshari, R. Kotek and A. E. Tonelli (Ed. Brown P. J., Stevens K). "Nanofibers and nanotechnology in textiles", Woodhead Publishing Limited, Cambridge, UK, 2007, 71-73.

[11] Alongi J., Carosio F., Horrocks A. R., Malucelli G., "Update on flame retardant textiles: State of the art, environmental issues and innovative solutions". Puplished by Smithers Rapra Limited, Shropshire, UK, 2013,239

[12] Bourbigot S., Le Bras M., Flambard X., Rochery M., Devaux E., Lichtenhan J. D. (Ed. Le Bras M, Wilkie CA, Bourbigot S, Duquesne S, Jama C) "Fire retardancy of polymers: New applications of mineral fillers", Royal Society of Chemistry, Cambridge, UK, 2005, p. 189.

[13] Solarski S., Benali S., Rochery M., Devaux E., Alexandre M., Monteverde F., Dubois P. "Synthesis of a polyurethane/clay nanocomposite used as coating: Interactions between the counterions of clay and the isocyanate and incidence on the nanocomposite structure", *Journal of Applied Polymer Science,* 2005; 95(2), 238-344.

[14] Alongi J., Frache A., Malucelli G., Camino G. (Ed., F. Selcen Kilinc), "Handbook of fire resistant textiles". Woodhead Publishing Limited, Cambridge, UK, 2013. p. 63.

[15] Alongi J., Carosio F., Horrocks A. R., Malucelli G., "Update on flame retardant textiles: State of the art, environmental issues and innovative solutions". Puplished by Smithers Rapra Limited, Shropshire, UK, 2013,259-260.

[16] Singha K., "A Review on Coating & Lamination in Textiles: Processes and Applications", *American Journal of Polymer Science,* 2012, 2(3): 39-49.

[17] Lu H., Song L., and Hu Y., "A review on flame retardant technology in China. Part II: Flame retardant polymeric nanocomposites and coatings", *Polymers for Advanced Technologies,* 2011, 22, 379–394.

[18] Alongi, Jenny, and Giulio Malucelli. "Cotton flame retardancy: state of the art and future perspectives." *Rsc Advances,* 2015, 5.31, 24239-24263.

[19] Horrocks, A. Richard, Ahilan Sitpalan, and Baljinder K. Kandola. "Design and characterisation of bicomponent polyamide 6 fibres with specific locations of each flame retardant component for enhanced flame retardancy. Polymer Testing, 2019, 79 , 106041.

[20] Wang Z., Han E., Ke W. "Effect of acrylic polymer and nanocomposite withnano-SiO_2 on thermal degradation and fire resistance of APP–DPER–MEL coating", *Polymer Degradation and Stability,* 2006, 91, 1937–1947.

[21] Gu J. W., Zhang G. C., Dong S. L., Zhang Q. Y., Kong J., "Study on preparation and fire retardant mechanism analysis of intumescent flame-retardant coatings", *Surface and Coatings Technology*, 2007, 201, 7835–7841.

[22] Jimenez M., Duquesne S., Bourbigot S., "Fire protection of polypropylene and polycarbonate by intumescent coatings", *Polymers for Advanced Technologies*, 2012, 23, 130–135.

[23] Gardelle B., Duquesne S., Rerat V., Bourbigot S. "Thermal degradation and fire performance of intumescent silicone-based coatings", *Polymers for Advanced Technologies*, 2013, 24, 62–69.

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

[25] Weil E. D., "Fire-protective and flame-retardant coatings - a state-of-the-art review", *Journal of Fire Sciences* , 2011, 29, 259–296.

[26] Khandual, Asimananda. "Green flame retardants for textiles." *Green fashion*. Springer, Singapore, 2016. 171-227.

[27] Kolar, Tjaša, and Vanja Kokol. "Synergistic Effect of Screen-Printed Single-Walled Carbon Nanotubes and Phosphorylated Cellulose Nanofibrils on Thermophysiological Comfort, Thermal/UV Resistance, Mechanical and Electroconductive Properties of Flame-Retardant Fabric." *Materials* ,2021, 14.23 ,7238.

[28] El-Hady, Abd, S. Sharaf, and A. Farouk. "Highly hydrophobic and UV protective properties of cotton fabric using layer by layer self-assembly technique." *Cellulose* , 2020, 27.2, 1099-1110.

[29] Richardson, Joseph J., et al. "Innovation in layer-by-layer assembly." *Chemical reviews,* 2016, 116.23 ,14828-14867.

[30] LIU, Hengrao, et al. Rapid preparation of Tannic acid (TA) based zwitterionic nanofiltration membrane via a multiple layer-by-layer (mLBL) assembly strategy for enhanced antifouling performance. *Separation and Purification Technology*, 2020, 253: 117519.

[31] Wang, Bin, et al. "Flame-retardant polyester/cotton blend with phosphorus/nitrogen/silicon-containing nano-coating by layer-by-layer assembly." *Applied Surface Science* 509 (2020): 145323.

[32] Li, S., Ding, F., Lin, X., Li, Z., & Ren, X.. Layer-by-layer self-assembly of organic-inorganic hybrid intumescent flame retardant on cotton fabrics. *Fibers and Polymers*, 2019,*20*(3), 538-544.

[33] Li Y. C, Schulz J., Grunlan J. C. "Polyelectrolyte/nanosilicate thin-film assemblies: Influence of pH on growth, mechanical behavior, and flammability". *ACS Applied Materials & Interfaces,* 2009, 1(10), 2338-2347.

[34] Li Y. C, Schulz J., Mannen S., Delhom C., Condon B., Chang S., Zammarano M., Grunlan J. C. "Flame retardant behavior of polyelectrolyte clay thin film assemblies on cotton fabric", *ACS Nano*, 2010, 4(6), 3325-3337.

[35] Laufer G., Carosio F., Martinez R., Camino G., Grunlan J. C. "Growth and fire resistance of colloidal silica-polyelectrolyte thin film assemblies", *Journal of Colloid and Interface Science,* 2011, 356(1), 69-77.

[36] Alongi, Jenny, Federico Carosio, and Giulio Malucelli. "Current emerging techniques to impart flame retardancy to fabrics: an overview." *Polymer Degradation and Stability* 106 ,2014, 138-149.

[37] Liu, Y., Xu, B., Qian, L., Chen, Y., & Qiu, Y. Impact on flame retardancy and degradation behavior of intumescent flame-retardant EP composites by a hyperbranched triazine-based charring agent. *Polymers for Advanced Technologies*, 2020,*31*(12), 3316-3327.

[38] Owens, G. J., Singh, R. K., Foroutan, F., Alqaysi, M., Han, C. M., Mahapatra, C., & Knowles, J. C.. Sol–gel based materials for biomedical applications. *Progress in materials science*, 2016, *77*, 1-79.

[39] Sakka S. "Handbook Sol-gel science and technology. Topics and fundamental research and applications. Norwell (Massachusetts): Kluwer Academic Publishers; 2003.

[40] Alongi J., Ciobanu M., Carosio F., Tata J., Malucelli G. "Thermal stability and flame retardancy of polyester, cotton and relative blend textile fabrics subjected to sol-gel treatments". *Journal of Applied Polymer Science*, 2011, 119 (4), 1961-1969.

[41] Xu, D., Gao, Z., Xu, B., Ren, H., Zhao, X., Zhang, Y., & Zhu, P.. A facile and effective flame-retardant coating for cotton fabric with α-aminodiphosphonate siloxane. *Polymer Degradation and Stability*, 2020, *180*, 109312.

[42] Alongi J., Ciobanu M., Malucelli G. "Sol-gel treatments for enhancing flame retardancy and thermal stability of cotton fabrics: optimization of the process and evaluation of durability", *Cellulose*, 2011 ;18 (1), 167-177.

[43] Alongi J., Malucelli G. "Heat and moisture transfer in sol-gel treated cotton fabrics". *Journal of Thermal Analysis and Calorimetry*, 2013, 11(1), 459-465.

[44] Alongi J., Ciobanu M., Malucelli G. "Sol-gel treatments on cotton fabrics for improving thermal and flame stability: effect of the structure of the alkoxysilane precursor", *Carbohydrate Polym*ers, 2012, 87(1), 627-635.

[45] Alongi J., Ciobanu M., Malucelli G. "Thermal stability, flame retardancy and mechanical properties of cotton fabrics treated with inorganic coatings synthesized through sol-gel processes", *Carbohydrate Polymers,* 2012; 87(3), 2093-2099.

[46] Tendero, C., Tixier, C., Tristant, P., Desmaison, J. & Leprince, P. Atmospheric pressure plasmas: a review. *Spectrochim. Acta. B At. Spectrosc.,* 2006, 61, 2–30.

[47] Akovali, G. & Gundogan, G. Studies on flame retardancy of polyacrylonitrile fiber treated by flame-retardant monomers in cold plasma. *J. Appl. Polym. Sci.* ,1990, 41, 2011–2019.

[48] Bourbigot, S. et al. New approach to flame retardancy using plasma assisted surface polymerisation techniques. *Polym. Degrad. Stab.* ,1999, **66**, 153–155.

[49] Tsafack, M. J. & Levalois-Grützmacher, J. Towards multifunctional surfaces using the plasma-induced graft-polymerization (PIGP) process: Flame and waterproof cotton textiles. *Surf. Coat. Technol.* 2007**, 201**, 5789–5795 ().

[50] Horrocks, A., Eivazi, S., Ayesh, M. & Kandola, B. Environmentally sustainable flame retardant surface treatments for textiles: the potential of a novel atmospheric plasma/UV laser technology. *Fibers* , 2018, **6**, 31.

[51] Weil, E. D. and Levchik S. V. "Flame retardants in commercial use or development for textiles", *Journal of Fire Sciences*, 2008, 26, 342–281.

[52] Weil, E. and Levchik, S. Current practice and recent commercial developments in flame retardancy of polyamides. *Journal of Fire Sciences*, 2004, 22, 251–264.

[53] Papaspyrides, C. D., Pavlidou, S., Vouyiouka, S. N., "Development of advanced textile materials: Natural fibre composites, anti-microbial, and flame-retardant fabrics", *Journal of Materials: Design and Application*s, 2009, 223, 91–102.

[54] Guin, T., Krecker, M., Milhorn, A. & Grunlan, J. C. Maintaining hand and improving fire resistance of cotton fabric through ultrasonication rinsing of multilayer nanocoating. *Cellulose* , 2014, 21, 3023–3030.

[55] Alexander B. Morgan, and Jeffrey W. Gilman, "An overview of flame retardancy of polymeric materials: application, technology, and future directions", *Fire and Materials*, 2012, 37(4), 259–279.

[56] Shen, K. K. in Non-Halogenated Flame Retardant Handbook (eds Morgan, A. B. & Wilkie, C. A.) 201–241 (Wiley, 2014).

[57] Levchik S. V., Weil E. D. "A review of recent progress in phosphorus-based flame retardants", *Journal of Fire Sciences*, 2006, 24, 345–364

[58] Salmeia, K., Fage, J., Liang, S. & Gaan, S. An overview of mode of action and analytical methods for evaluation of gas phase activities of flame retardants. Polymers , 2015, 7, 504–526.

[59] Schartel, B. et al. Flame retardancy of polymers: the role of specific reactions in the condensed phase. Macromol. Mater. Eng. 301, 2016, 9–35.

[60] Bourbigot S., Duquesne S. (Eds. Morgan, A. B.; Wilkie, C. A.). "Intumescence and Nanocomposites: A Novel Route for Flame-Retarding Polymeric Materials. In *Flame Retardant Polymer Nanocomposites*", John Wiley & Sons Inc., Hoboken, 2007, 131–162.

[61] Huo, S., Song, P., Yu, B., Ran, S., Chevali, V. S., Liu, L.,.& Wang, H. Phosphorus-containing flame retardant epoxy thermosets: Recent advances and future perspectives. *Progress in Polymer Science*, 2021, *114*, 101366.

[62] Morgan, Alexander B., and Jeffrey W. Gilman. "An overview of flame retardancy of polymeric materials: application, technology, and future directions." *Fire and Materials* , 2013, 37.4: 259-279.

[63] Prabhakar, M. N., Atta Ur Rehaman Shah, and Jung-Il Song. "A review on the flammability and flame retardant properties of natural fibers and polymer matrix based composites." Composites Research 2015, 28.2: 29-39.

[64] Kramer K. H., Blomqvist P., Hees P. V., Gedde U. W. "On the intumescence of ethylene–acrylate copolymers blended with chalk and silicone", *Polymer Degradation and Stability,* 2007, 92, 1899–1910

[65] Klatt, M., Nitrogen-Based Flame Retardants, in Non-Haloge- nated Flame Retardant Handbook (eds A. B. Morgan and C. A. Wilkie), John Wiley & Sons, Inc., Hoboken, NJ, USA (2014)

[66] Liang H., Asif A., Shi W. "Thermal degradation and flame retardancy of a novelmethacrylated phenolic melamine used for UV curable flame retardant coatings", *Polymer Degradation and Stability*, 2005, 87, 495–501.

[67] Zhou W., Yang H. "Flame retarding mechanism of polycarbonate containing methylphenylsilicone", *Thermochimica Acta*, 2007, 452, 43–48.

[68] Totolin V., Sarmadi M., Manolache S. O., Denes F .S. "Atmospheric pressure plasma enhanced synthesis of flame retardant cellulosic materials", *Journal of Applied Polymer Science*, 2010, 117(1), 281–289.

[69] Smith, R. J. et al. Environmentally benign halloysite nanotube multilayer assembly significantly reduces polyurethane flammability. *Adv. Funct. Mater.* **28**, 1703289 (2018).

[70] Yang F., Nelson G. L., "Polymer/Silica Nanocomposites Prepared Via Extrusion", *Polymers for Advanced Technologies,* 2006, 17, 320-326.

[71] Holder, K. M., Huff, M. E., Cosio, M. N. & Grunlan, J. C. Intumescing multilayer thin film deposited on clay-based nanobrick wall to produce self-extinguishing flame retardant polyurethane. *J. Mater. Sci.* **50**, 2451–2458 (2015).

[72] Zanetti M., Kashiwagi T., Falqui L., Camino G. "one Calorimeter Combustion and Gasification Studies of Polymer Layered Silicate Nanocomposites", *Chemistry of Materials,* 2002, 14, 881-887.

[73] Castellano, A., Colleoni, C., Iacono, G., Mezzi, A., Plutino, M. R., Malucelli, G., & Rosace, G.. Synthesis and characterization of a phosphorous/nitrogen based sol-gel coating as a novel halogen-and formaldehyde-free flame retardant finishing for cotton fabric. *Polymer Degradation and Stability*, 2019, *162*, 148-159.

[74] Skorodumova, O., Tarakhno, O., Chebotaryova, O., Bezuglov, O., & Emen, F. M.. The Use of Sol-Gel Method for Obtaining Fire-Resistant Elastic Coatings on Cotton Fabrics. *Materials Science,* 2021, 1038, 468-479.