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Recent Developments in the Sustainable Flame-retardants for Textiles: A Review

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Abstract: In response to increasing environmental concerns, the development of sustainable flame retardants for textiles has become a critical area of research. This review paper comprehensively examines the fundamentals and recent advancements in sustainable flame retardants, highlighting the shift from traditional halogenated and phosphorus-based chemicals to more eco-friendly alternatives. It delves into the underlying principles of flame retardancy, including the mechanisms by which these materials inhibit combustion. The paper discusses the limitations and environmental impact of conventional flame retardants, leading to the exploration of green alternatives such as natural polymers, bio-based compounds, and non-toxic additives. Recent innovations, including using renewable resources like plant extracts, biopolymers, and inorganic materials, are analyzed for their efficacy and sustainability. By synthesizing current research and technological developments, this review aims to provide a clear understanding of the progress made in the field and identify future directions for the development of effective and environmentally benign flame-retardant systems for textiles.

Keywords: *Biomaterials, Ecofriendly, Flame retardant, Green-chemicals, Sustainable, Textile*

I. INTRODUCTION

In today's world, the demand for flame retardant textiles is crucial for ensuring safety in various applications, from clothing and furnishings to industrial materials. The need for flame-retardant textiles covers a wide range of application areas, as shown in Figure 1. Fire safety is necessary for a variety of items, including firefighter uniforms, kid's clothing, cooking aprons, workers in the gas and petroleum industries, and furnishings and upholstery in homes, hospitals, and public spaces. Additionally, it is crucial for the interior design of automobiles, buses, trains, and airplanes, as well as for military protective clothing, tents, and tactical gear, as well as seat covers, roof linings, and floor carpets [1, 2].

The combustion behavior of textile fibers varies significantly, affecting their suitability for different applications. Cotton, a natural fiber, ignites at relatively low temperatures and burns rapidly with a bright flame, leading to quick flame spread and a high heat release rate. This makes untreated cotton less ideal for fire-prone environments [1,3]. Polyester, a synthetic fiber, ignites at a higher temperature and burns with a slower flame spread compared to cotton; however, it melts and drips when exposed to flames, which can exacerbate fire spread. Nylon shares similar ignition characteristics with polyester but also tends to melt and drip, posing similar risks. In contrast, wool, another natural fiber, has a higher ignition temperature and burns more slowly, often self-extinguishing and producing a compact char that helps resist flame spread. Aramid fibers, such as Kevlar and Nomex, are highly flame-resistant, igniting at much higher temperatures and forming a protective char that prevents flame spread while avoiding melting and dripping. Understanding these diverse combustion behaviors is crucial for selecting the appropriate textile for specific safety requirements and applications [4].

The most common chemicals are borax and boric acid, phosphorous, and halogen-based flame retardants, due to their synergistic effect, to be used over the fabrics which protect the textiles from catching fire when come in contact with the flame. Subsequently, for the previous 30 years, flame retardants based on the composition of phosphorus, nitrogen, and halogen, such as Tetrakis (hydroxy methyl) phosphonium chloride i.e THPC and tetrakis (hydroxy methyl) phosphonium hydroxide i.e THPOH, are widely ruling the commercial scenario [4]. Also, antimony while combined with halogen might impart good flame-retardant properties mainly on synthetic fabrics but there are some bad effects of halogen on the environment. Three halogenated products are presently banned: penta- and octa-bromo diphenyl ether and hexabromocyclododecane. The researchers found that the continuous use of halogenated flame retardants affects the health of humans linked to cancer, and reproductive problems and decreases brain development also. Furthermore, during burning there is an increase in smoke and toxic gases which increase the pollution in the air and pollute the surroundings [4,5].

Figure 1. Application areas for fire-retardant textiles

Therefore, traditional flame retardants often contain hazardous chemicals that can pose risks to both human health and the environment. As awareness grows about the negative impacts of these substances, there is an urgent need to develop and adopt sustainable and eco-friendly flame-retardant textiles. This review briefly explains the concept of flame retardancy, the different strategies employed in achieving this in textiles, and the classification of conventional and sustainable flame retardants. Researchers and investigators found there is the possibility of increasing the flame retardancy of cellulosic and synthetic materials by using plants that contain phosphorous, silicate, and other mineral salts. These innovative materials not only enhance safety but also minimize environmental impact, aligning with broader goals of sustainability and ecological responsibility. By focusing on green chemistry and alternative approaches, we can achieve effective fire resistance while protecting our planet and its inhabitants [5,6]. According to previous research, numerous efforts were made to expand the flame-retardant property of cotton fabric using extracted spinach juice, chicken eggshell powder, and banana pseudostem sap, chitosan with natural lignin [7].

II. CONCEPT OF FLAME RETARDANCY IN TEXTILES

Three essential phases are involved in the combustion of textiles: heating, pyrolysis (thermal breakdown), and ignition. At pyrolysis temperature fiber undertakes permanent chemical changes, emitting the non-flammable gases carbon dioxide, nitrogen, sulfur, carbon chars, tars, and fuels [8,9,10]. While combustion is an exothermic process that requires three components heat, oxygen, and fuel, at this temperature flammable gases combined with oxygen is called combustion [11,12]. They produce a sequence of gas phase free radical reactions that produce large amounts of heat and light.

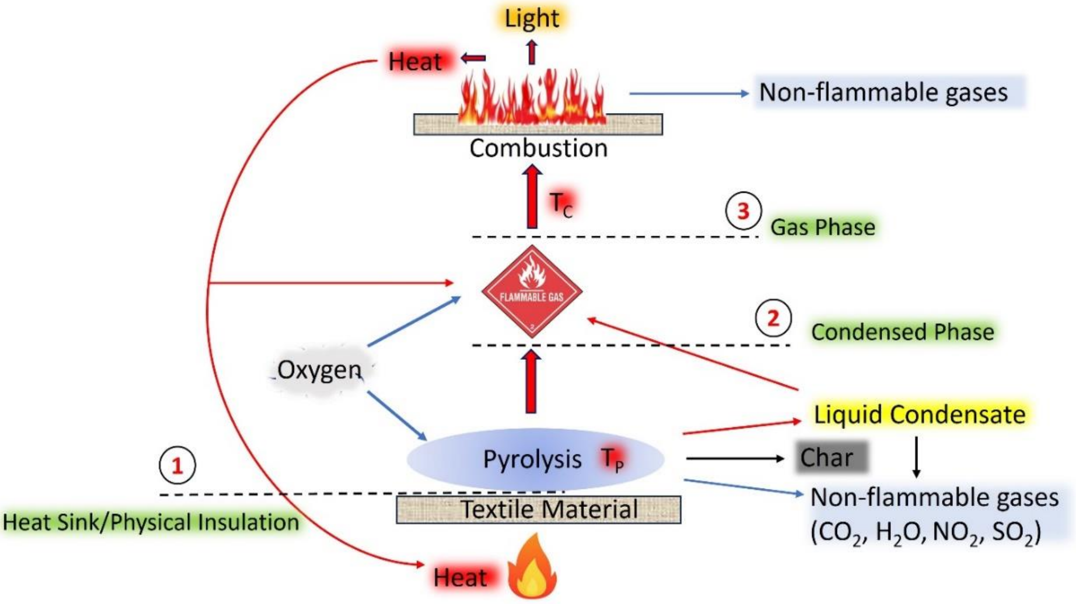

Figure 2: Burning cycle of textile & strategies to achieve flame retardancy

Figure 2 illustrates how a combustion cycle is formed after ignition occurs, either spontaneously (auto ignition) or as a result of an external source, such as a spark from a flame or a burning flame. In order to achieve flame retardancy in textile materials, we must interrupt this burning cycle. The general flame-retardant mechanism may be split into three different modes of action: (1) heat absorption or insulating layer (2) gas or vapor phase mechanism; and (3) solid or condensed phase mechanism.

The heat absorption phenomenon is related to applying a physical coating on the textile substrate featuring chemicals that effectively absorb the heat applied to the textile fibers, preventing them from reaching the temperature required for pyrolysis. The gas phase process does not involve any alteration in the thermal breakdown of a polymeric substrate. Instead, the flame-retardant substrate undergoes decomposition and produces free radicals which interact with oxygen and act as a means to quench the burning cycle. In the condensed phase, the flame-retardants modify the structure of the substrate by cross-linking, resulting in char, which acts as an insulating barrier between the flame zone and the substrate [13,14]. Achieving flame retardancy in textile materials involves various mechanisms that work to disrupt or inhibit the combustion process.

III. STRATEGIES EMPLOYED FOR THE FLAME-RETARDANCY IN TEXTILES

The different methods employed for flame-retardancy in textiles can be broadly categorized into physical, chemical, and structural modifications.

3.1 Physical Modifications

Char formation: In this mechanism, during combustion, the flame retardants promote the formation of a char layer on the surface of the textile. This char layer acts as an insulating barrier, slowing the transfer of heat to the underlying fibers and reducing the material’s flammability.

Intumescent coatings: Intumescent flame retardants expand when exposed to heat, forming a thick, insulating foam layer. This foam layer protects the underlying material from heat and oxygen, thus impeding the combustion process.

Coating and surface treatments: Applying flame retardant coatings or finishes to the surface of textiles can create a protective layer that either inhibits ignition or slows down the burning rate. These coatings can be based on various chemicals, including those that form a protective char layer or create an oxygen barrier [14,15].

3.2 Chemical Modifications

Halogen compounds: Halogenated flame retardants, such as brominated or chlorinated compounds, work by releasing halogen radicals when heated. These radicals disrupt the chemical reactions occurring in the flame, particularly the formation of reactive free radicals that sustain combustion. This effectively reduces the flame's intensity and can even extinguish it [16].

Phosphorus compounds: Phosphorus-based flame retardants operate through several pathways: Char Formation: Phosphorus compounds promote the formation of a protective char layer on the surface of the textile. This char layer acts as a barrier, insulating the underlying material from heat and oxygen. Acid-Base Reactions: Some phosphorus compounds generate phosphoric acid during combustion, which catalyzes the formation of a char layer and dilutes flammable gases. Gas Phase Mechanism: Phosphorus compounds can release non-flammable gases that dilute the combustible gases in the flame, thereby reducing the flame’s intensity.

Nitrogen compounds: Nitrogen-based flame retardants, such as melamine and its derivatives, release nitrogen gas when heated. This gas dilutes the oxygen and combustible gases in the flame, slowing down the combustion process and reducing the flame’s heat [17,18].

Inorganic compounds: Inorganic flame retardants, like alumina hydrate and magnesium hydroxide, work by: Endothermic Reactions: These compounds release water vapor when heated, which absorbs heat and cools the textile. Dilution of Flammable Gases: The released water vapor and non-combustible gases dilute the combustible gases, making it harder for the flame to sustain itself.

3.3 Structural Modifications

Fiber modification: Inherently flame-resistant fibers, such as aramid (e.g., Kevlar), modacrylic, or melamine, have molecular structures that make them less likely to ignite and burn. These fibers can withstand high temperatures and have low flammability.

Blending with flame-resistant fibers: Combining flame-resistant fibers with conventional fibers enhances the overall flame retardancy of the textile. For example, blending cotton with aramid fibers improves the textile’s resistance to ignition and burning.

Nanotechnology: Incorporating nanoparticles, such as silica or alumina, into textiles can enhance flame resistance. These nanoparticles can promote char formation, improve the thermal stability of the textile, or create a physical barrier to flame propagation.

Heat treatment and stabilization: Certain processing techniques, like heat-setting, can stabilize synthetic fibers, reducing their flammability. By altering the molecular structure of the fibers, these treatments enhance their resistance to ignition and burning [18,19,20].

Many flame retardancy strategies employ a combination of the above mechanisms to achieve optimal performance. For instance, a textile might be treated with both phosphorus-based chemicals and an intumescent coating to maximize its flame resistance through multiple pathways.

IV. DEVELOPMENTS IN THE FLAME-RETARDANT CHEMICALS FOR TEXTILES

Research into textile flame retardancy has a long history. Early studies date back to 1783 when the Montgolfier brothers first used alum to reduce fire hazards in textiles. In the 18th century, Gay-Lussac developed methods to protect theater fabrics using clay and plaster of Paris. Perkins made notable advances in the 19th century by treating cotton with sodium stannate and ammonium sulfate to create flame-retardant fabrics [8,9,21]. The 20th century marked significant progress, particularly in the 1950s, with the development of durable phosphorus-based flame retardants for cotton. This era saw the creation of new chemicals, including phosphorus-based and phosphorus halogen-based compounds by Ed Weil. Researchers like Hendrix et al. also studied the effects of triphenyl phosphate on cellulose pyrolysis and flammability.

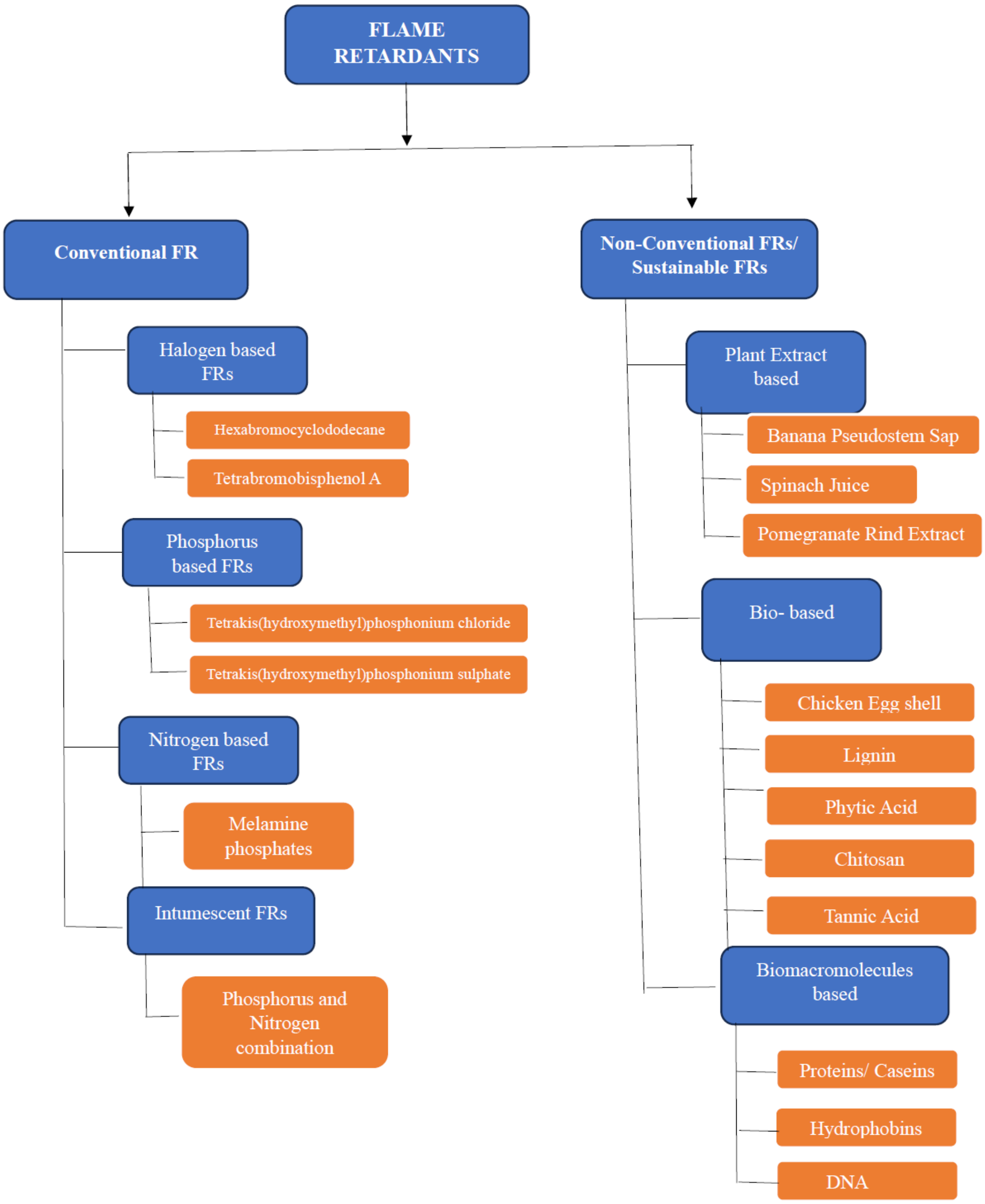

Figure 3. Classification of Flame-retardants

From 1980 to 2000, research focused on understanding the mechanisms of burning and degradation in textiles. This period highlighted unresolved issues and prompted the exploration of various flame-retardant materials, including those combining phosphorus and nitrogen. Additionally, the rise of nanotechnology showed promise for enhancing flame retardant properties through nanoparticles with different aspect ratios [9,10,22]. Since 2010, there has been a shift towards sustainable flame retardants. Traditional flame retardants have been criticized for health risks, such as respiratory issues and skin allergies, as well as environmental concerns due to the emission of formaldehyde and halogenated gases. Consequently, there is growing interest in developing eco-friendly and sustainable flame-retardant solutions [10,11,23]. The recent flame retardants employed in textiles can be classified into two major categories conventional and sustainable, depicted in Figure 3.

4.1 Conventional Flame Retardant for Textile

4.1.1 Halogenated Flame-retardant Compounds

They are the most common flame-retardant compounds used in gas/vapor phase mechanisms inhibited by free radical mechanisms based on chlorine and bromine chemistry [12,13]. The most common BFRs are brominated phenols, hexabromocyclododecane (HBCD), polybrominated diphenyl ethers, tetrabromobisphenol A (TBBPA), and tetrabromophthalic anhydride. But these flame retardants are very toxic and contaminate the environment as well as health hazards also [15,16,24].

4.1.2 Phosphorus Compound Flame-retardants

They can be inorganic as well as organic compounds, they chemically bond to compounds and physically incorporate as an additive. Phosphorous-containing flame-retardants are rather versatile because the element exists in several oxidation states, such as phosphate, phosphines, phosphine oxides, phosphite's, phosphonates and phosphonium salts for example THPC, THPS, and THPOH [17,18,19]. It's better to use several flame-retardant elements in combination with antimony, boron, nitrogen, and phosphorus is a better method than using only one [21,22,25]. The usually reactive phosphorus flame retardant is Pyrovatex CP, utilized in industries but releases formaldehyde toxic chemical that is dangerous to human being health [23,26].

4.1.3 Nitrogen-containing Compounds Flame-retardants

Nitrogen-containing flame retardants are those which contain nitrogen in their structure. Nitrogen compounds are a fast-growing flame retardant concerning eco-friendly materials. The most used nitrogen-containing flame-retardant compounds are Melamine-based products. The combination of nitrogen-containing flame retardants with phosphorus-containing compounds is frequently used because they either form an intumescent mixture or produce phosphorus/nitrogen synergistic effects [17,27].

4.1.4 Intumescent Flame-retardants (IFR)

They are the most commonly eco-friendly materials in the conventional one. When connected to heat, these IFRs enlarge to create a fire-resistant and insulation layer on the substrate, layer foamed char acts as a barrier against heat spread and oxygen diffusion. Phytic acid (PA) is a main storage form of high phosphorus content in plants; it is a talented bio-based flame-resistant product for polymeric textile and plastic materials [15,19]. IFRs are composed of three chief components, an acid source, a carbon source, and a foaming or blowing source melamine [24,25,28].

4.2 Sustainable Flame-retardants

Flame retardants based on phosphorus, nitrogen, and halogen compounds and their derivatives have widely dominated the commercial state for the last 50 years [29]. However, due to their harmful effects on health and the environment, their alternatives are tried to originate by the researchers like bio-based flame retardants, plant extract materials, waste materials of plants, etc [28,30]. However, an inadequate application of waste plant bio-molecules has been made for reporting flame retardant finishing to textile materials. The plants contain phosphorus, nitrogen, potassium, chloride, silicate, and other minerals and mineral salts, which have the potential to be applied to impart flame retardancy to cellulosic and non-cellulosic textiles.

4.2.1 Plant-based Flame-retardants

Banana Pseudostem Sap (BPS)

Recent studies by researchers and investigators found that the Banana Pseudostem Sap (BPS) shows the effects of FR on cellulosic materials and silk fabric [29,31]. When applied on bleached cotton, it was first mordanted with 5% tannic acid, and 10% alum, then it was dipped with BPS water solution either diluted or non-diluted for 30 min at an alkaline pH, afterward treated fabric was dried at 110°C for 5 min [6,32]. The plant stem contains potassium chloride, sodium chloride, and metal phosphate. BPS is found easily in India as well as Bangladesh abundantly that considered to be waste. It is easy to apply on cellulose with a wide range of pH with the help of mordants. Therefore, in textiles, the application of BPS for coloration and functionalization will give the advantages of value addition using natural products [1,5].

Spinach Juice

One more important study shows that spinach juice acts as a fire retardant on textile materials. It contains sodium, magnesium, silicates, and other constituents. The spinach juice was applied on the cotton material at boiling temperature with MLR 1:15 with the help of soda ash to maintain pH and applied by pad-dry-cure technique. When compared to the untreated and treated fabric, the FR-treated fabric shows good flame retardancy. After applying spinach juice to the fabric, the LOI value of the treated cotton fabric is increased [1,2,33].

Pomegranate Rind Extract

This wastage agriculture product contains nitrogen, inorganic metallic salts, metallic oxides, etc which act as FRs for textiles mainly for jute and cotton applied by pad-dry-cure technique. The test was carried out on jute, firstly jute fabric was impregnation for 30 min separately with pomegranate rind extract solution with 1:20 MLR at different pH values i.e. 4,7,10. Then treated fabric was dried at 110°C for 5 min [6]. The treated cotton and jute showed multifunctional properties like antiseptic, Ultraviolet protection, antioxidant properties, and enhanced thermal stability [12,34].

4.2.2 Bio-based Flame-retardants

Chicken egg shells

This is considered to be waste lightweight materials, have high thermal stability, and are cost-effective in fire fire-resistant coating business contain 95% calcium carbonate and 5% organic materials like sulfated polysaccharides, aluminum oxide, silicon dioxide, manganese oxide, etc. Upon fire contact, the eggshell coating fabric forms a multi-cellular insulating foam that acts as an effective barrier to the conduction of heat. Chicken eggshell-treated fabric is used as flame retardant material for a different area of application such as ceilings, and carpets for persons who wear in soldierly, aircraft, ships, and kitchen areas. This is also called a novel eco-friendly bio-filler to develop intumescent flame-retardant coatings [30,35].

Lignin

Biomacromolecules act as novel green flame-resistant materials for the textile also. Lignin is the second most abundant after cellulose found in plants, studies say that using lignin is one of the best ways to combine with intumescent FRs due to its strong heat resistance nature [30,36]. Thermal degradation of lignin creates a very large amount of char that forms the protecting layer over the surface of the cotton fabric over the action of heat. There are many methods to approach lignin formulation back coating, layer by layer, and padding methods.

Phytic acid

Eco-friendly flame retardants free from formaldehyde release and halogen-containing compounds are becoming popular day by day. It is obtained from the plant tissues like cereal, oilseeds, and beans [12]. One of the most common FR compounds that recently became the most popular among researchers is phytic acid because of its excellent, environmental friendliness, renewability, and biodegradability, containing 28% phosphorus in its structure, an organic phosphonic acid produced from plants applied on cotton, nylon and wool fabrics [32,33,34,37]. Compared to the conventional, Phytic Acid represented as the best fume suppressant, reduced the heat release capacity, and gave the best catalytic char-forming effect.

Chitosan

Chitosan is an eco-friendly natural source obtained from the deacetylation of chitin to impart flame retardancy to cellulosic textiles. The use of chitosan in flame retardant applications relies on its carbohydrate structure, which can be exploited as an effective carbon source. Furthermore, the chemical modification of chitosan agrees with its straight use as a resourceful flame retardant [35,36]. Chitosan, when added to the citric acid solution containing butane tetracarboxylic acid (BTCA), diammonium hydrogen phosphate (DAHP), and sodium hypophosphite (SHP) acted as a nitrogen source in synergy with phosphorus during the phosphorylation process. Certainly, chitosan formed a thin film of coating on the phosphate layer on the cellulose textile after drying and enhanced the wash durability of soluble phosphate-treated cotton fabric [37,38].

Tannic acid

A natural polyphenolic compound acts as an intumescent flame retardant on cellulose. To improve the LOI value concentration of sodium hydroxide is added to it. Sodium ions directed to increased adsorption of tannic acid on the cotton fabric, and catalyzed the decarboxylation of tannic acid, and dehydration of cellulose. The intumescent char layer obtained resulted in a reduction of heat release by 82% and improved LOI to 30 [12]. Natural tannic acid also has been used for the manufacture of fire-retardant protein, steel, ceramic, epoxy, and synthetic polymers like polyester, nylon, polylactic acid, etc. [38,39].

4.2.3 Biomacromolecule-based Flame-retardants

Whey proteins and Caseins

Some other biomacromolecules are Whey proteins and Caseins that show an intumescent-like behavior contain phosphate groups that form the char and make the substrate flame retardant [10,23,39,40]. Whey the bioproduct of cheese helps in forming a coating on the cotton textile to impart flame retardancy. Whey proteins isolate act as an oxygen barrier property. They improve the burning time of the materials and reduce the burning rate of cellulose [40,41]. Caseins is a milk protein obtained from skimmed milk consisting of phosphorus-rich proteins. These proteins encourage the dehydration of cellulose and form a char, which improves the burning rate [42].

Hydrophobins

Hydrophobins consist of small cysteine-rich proteins, produced by filamentous fungi containing N and S atoms show eight cysteine residues originating from four non-sequential disulfide bonds, due to the decomposition of these disulfide bonds release the sulphuric acid responsible for dehydration reaction and responsible for protective char layer. They form the char layer over the textile to make it a flame-retardant material [43,44].

Deoxyribonucleic Acid (DNA)

DNA is the most common well-known biomacromolecules that act as an intumescent flame retardant and contain phosphate group, deoxyribose or blowing agent, and nitrogen-containing compounds. The structure and chemical compositions of DNA are very interesting in flame retardancy behavior, The phosphate group contains phosphorus that degrades the fabric and forms a protective layer of char, and the deoxyribose unit contains a carbon source that helps to release water and formation of char, and nitrogen contains base which release ammonia [6,12,45].

V. APPLICATION TECHNIQUES FOR FLAME-RETARDANT CHEMICALS

There are many techniques for the effective application of flame-retardant chemicals on textile materials.

5.1 Flame Retardancy Using Nano-Technology

Nanotechnology is one of the most auspicious avenues of technology development due to its small size of nanoparticles, which are used to control matter at the atomic scale. Nano clay is to be used as a flame retarding agent that gets deposited on the surface and acts as an oxygen barrier for the fabric. It forms a protective layer of the char when combined with other conventional FRs. Nano clay is considered to be eco-friendly, biodegradable cost-effective, and obtained from natural resources [45,46]. The application of nanoclays such as attapulgite, hectorite, kaolin, Laponite, mica, montmorillonite (MMT), saponite, smectite, and vermiculite to various applications, including textile. The other nanoparticles zinc oxide, titanium dioxide, and silicon oxide are combined with the other sustainable FRs giving promising results in the flame retardancy sector. Zinc oxide combines with polycarboxylic acids like BTCA with sodium hydrogen phosphate via the pad dry cure method giving flame-resistant fabric. Applying TiO2 and SiO2 nanoparticles with chitosan and phytic acid the LOI and char yield increased especially in polyamides. Joining TiO2 and protein systems applied using a dip-pad-dry-cure method reports flame retardancy to the cotton fabric [47].

5.2 Layer-by-Layer Flame-retardant Techniques

This technique was discovered in 1966 but practical application was found first in 1992. This method has a less detrimental effect as compared to other methods on the fabric as well as on the environment. This method is a very simple and water-based method to form a multilayer film on the surface of the substrate which influences the combustion cycle. The LBL deposition process includes submerging the substrate into the solutions of oppositely charged polyelectrolytes or spraying the substrate with charged solutions [14]. Researchers find out the application of these methods on cationic chitosan with anionic ammonium polyphosphate and anionic phytic acid with excellent intumescent flame-retardancy [44,45,48]. The 20-30 layers of this technique are enough for the self-extinguish behavior, more layers result in the stiff fabric. With proper control of this method, the fabrication of multilayer films can be accepted. The thickness, function, and composition of the layer can be controlled and used for fabrication. As thickness can be controlled at the nanoscale level, deposition of nanoparticles is also possible by this method.

5.3 Plasma-assisted Flame-retardant Finishing

The technology of plasma is known as water-free and environmentally friendly, but it is a costlier process for making flame-retardant textiles. Atmospheric pressure dielectric barrier discharge plasma has been experimented with by researchers. The plasma-treated fabric is further treated with flame retardants through the conventional pad-dry-cure method. It is reported that to achieve an LOI value of 25, the time was 90 sec, and the temperature was 160 using plasma. Researchers also reported atmospheric pressure plasma as a pre-treatment on the cotton fabric to enhance post-finishing (flame retardant properties). Plasma pre-treatment is reported to expand the flame retardancy of cellulosic fabric treated with phosphoric acid (fire retardant) with melamine acting as a cross-linker, phosphoric acid acting as a catalyst, and zinc oxide. The results are not very effective through this technique [46,47,49].

5.4 Sol–Gel Technique

The latent sol-gel technology for consulting flame retardancy has been verified very recently though this method has been consumed for different special textile finishing such as UV protection, wrinkle resistance, and antimicrobial. The sol-gel technique involves two steps hydrolysis and condensation in its synthetic route. This reaction led to either completely inorganic or organic-inorganic hybrid coating formation at or near room temperature [49,50]. The silicon hydrogel resulting from this sol-gel process may be collected with phosphorus and/or nitrogen-containing additives to communicate flame retardancy to textiles [50,51].

VI. CONCLUSION AND FUTURE PERSPECTIVE

This study reviews both conventional and non-conventional flame retardants used for cellulosic and non-cellulosic textile materials, examining their applications, benefits, and limitations. Halogen-based flame retardants are known to pose significant health and environmental risks. Transitioning to sustainable flame retardants is a complex and lengthy process, as there are currently no specific standards for these eco-friendly alternatives. Typically, eco-friendly finishes must first meet certification criteria from standards like GOTS or the ECO mark scheme before they become commercially available. Research into sustainable flame retardancy remains limited; however, recent advancements over the past 5 to 10 years have introduced promising biomacromolecules and bio-derived products with effective flame-retardant properties. Natural extracts containing key elements such as phosphorus, nitrogen, and metals have shown the potential to enhance flame resistance in textiles. Ongoing progress in this field suggests that scaling up these green flame-retardant technologies to an industrial level may be achievable in the future.

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