Handbook of Sustainable Apparel Production

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Sustainable Flame-Retardant Finishing of Textiles Advancement in Technology

Publication details
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Published online on: 28 Apr 2015

Accessed on: 17 Dec 2018
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Advancement in Technology

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3.1 INTRODUCTION

Among the various functional finishing of textile substrates, flame-retardant finishing is important as it directly relates to human health and hazards. Cellulosic, lignocellulosic, and protein-based natural fibers, such as cotton, flax, ramie, jute, silk, and wool, are mostly used in apparels and home furnishings. Thermoplastic synthetic fibers, such as polyester, nylon, acrylic, and even to some extent polypropylene, are also used for similar applications. Unlike in the case of natural fibers, the situation is more complex for such thermoplastic fibers, as they shrink, melt, and burn in contact with the flame. Although their combustion temperatures are quite high (450°C–550°C), however, they, being thermoplastic in nature, first shrink and then melt in the temperature range of 165°C–265°C. The shrinking of a fabric and dripping of molten polymer can cause different degrees of skin burning. Besides their apparel and home-furnishing applications, both natural and synthetic fibers are also used in hotels, hospitals, automobiles, railways, and airways as tapestries and upholstery. For apparel and home textiles, mostly cotton is preferred due to its advantages of
soft feel, good moisture regain, and adequate thermal insulation. But being cellulosic in nature with a low limiting oxygen index (LOI) of 18, cotton catches flame readily and burns vigorously in an open atmosphere, which is difficult to extinguish, and also sometimes causes accidental death. Though cotton and regenerated cellulose (viscose) have combustion temperatures of 350°C and 420°C, respectively, during real-time burning, the temperature can go as high as 400°C–450°C, producing hardly any residual mass. It may be noted that textiles with an LOI ≤ 21 catches flame readily and burns in an open atmosphere rapidly. The samples with an LOI ≥ 21 to ≤ 27 also catch flame and, however, burn slowly in an open atmosphere. On the other hand, the sample with an LOI ≥ 27 is generally considered to be a flame-retardant textile. The major requirement of any textile material to be considered as a flame retardant is that it should have an LOI of more than 27. The situation is slightly better with the lignocellulosic textiles, such as jute with the LOI of 21 or more, making them suitable for packaging of agricultural crops and food products and upholstery and home-furnishing applications. Wool and silk being protein fibers, the situation are still better due to their higher combustion temperature of 600°C (wool) along with higher LOI value of 23.5–25. As the majority of the natural as well as the man-made fibers or fabrics has LOI values <25, there is a need for imparting flame-retardant finishes either during their manufacturing (e.g., polymerization, spinning) or in their final finishing stages making them suitable for various end applications as stated earlier.

The flame-retardant finishing of textiles can be categorized as nondurable, semidurable, and durable based on their efficacy in performance after successive washing cycles. The simple and well-known nondurable flame-retardant chemicals available in the market are inorganic salts, borax and boric acid mixture, diammonium phosphate, and urea. Phosphorous-based flame retardants along with nitrogenous compounds due to their synergistic effect provide the most effective treatment for all kinds of textiles as has been reported in the literatures. Chlorine- and bromine-based halogen compounds either alone or with an antimony compound providing synergism have also been introduced in the market in the middle of the nineteenth century. In the last six decades, flame-retardant formulations based on the composition of phosphorous, nitrogen, and halogen, like Tetrakis phosphonium salt and N-alkyl phosphopropionamide derivatives, have been widely used for commercial application. However, when such formulations are applied to cotton textiles, the fabric tear and tensile strength get reduced significantly, besides the fabric becoming stiffer. This mainly happened due to the requirement of an acidic condition for application of the aforementioned formulations and involvement of high-temperature drying or curing operations. Although the process is effective for different kinds of fiber, it has the disadvantages of being toxic, hazardous, and costly. To address these drawbacks, quite a few environmentally friendly and cost-effective formulations have been developed in the last few decades, to reduce the amount of formaldehyde release from the treated fabric using butane tetracarboxylic acid (BTCA) as the binding agent. Attempts have also been made to develop halogen-free phosphorus–nitrogen-based flame retardants to promote more char formation during burning of the cellulosic substrate. Recently, due to the rapid growth of nanoscience and technology, nano-zinc oxide (ZnO) particles, TiO₂, different clay compounds, and polycarboxylic acid have been reported on cotton and other textiles in an eco-friendly manner. Similarly, plasma treatment has been reported either as a pretreatment for increasing the uptake of fire-retardant chemicals, or for graft polymerization of acrylate phosphate and phosphonate derivatives, or as a posttreatment for better reaction. Due to constantly increasing awareness on human health, hygiene, and fashionable textiles with functional values, the demand for cellulosic textiles, processed and finished with natural products, such as natural dyes, enzymes, and aromatic and medicinal plant extracts for antimicrobial, mosquito-repellent, and well-being textiles, is getting importance in academic research and industrial product development for both the traditional and promising upcoming markets. Thus, cellulosic textiles have been finished with biomacromolecules, such as DNA from herring sperm and salmon fish, to improve their thermal stability. Whey proteins, casein, and hydrophobins have also been explored for similar such applications. In the last few years, efforts have also been made for utilization of agro-residues...
and other plant molecules for flame-retardant finishing of cellulosic and lignocellulosic textiles. In this regard, applications of banana pseudostem sap (BPS) and spinach extracts for flame-retardant finishing of cotton and jute fabrics due to their advantages of being environmentally friendly, cost effective, and sustainable materials produced from renewable sources are worth mentioning.13

The functional flame-retardant finishing of fibrous materials is an emerging area of research and sustainable product development. In this context, this chapter discusses in detail the mechanism of flame-retardant finishing of various textile substrates and the development of various chemical formulations over the years along with their merits and demerits. Further, it describes the application of emerging nano- and plasma technology for imparting flame-retardant finishing of textiles. A special reference to the recent developments on eco-friendly, cost-effective, and sustainable flame-retardant formulations from plant- and animal-based resources has also been made.

### 3.2 MECHANISM OF FLAME-RETARDANT FINISHING OF TEXTILES

The mechanism of imparting flame-retardant finishing to textiles is related to the combustion process of a fiber or fabric in contact with flame. It makes a difference between the untreated and flame-retardant-treated textiles in terms of LOI, heat required for combustion, burning rate, rate of heat release (RHR), and formation of flammable and nonflammable gases, char, and tar. On application of heat energy to a textile, its temperature goes up and finally reaches to the pyrolysis temperature. At that time, several chemical changes occur in the polymer structure, such as formation of nonflammable gases, like carbon dioxide, water vapor, carbon char, and tar, and flammable gases like carbon monoxide, hydrogen, and many other oxidizable organic volatiles. With further increase in temperature, the fiber reaches to its combustion temperature, when the flammable gases in the presence of oxygen burn rapidly and produce more amount of heat energy. Some portion of this heat energy again accelerates the pyrolysis of the polymer that successively produces more flammable gases, resulting in an intense combustion. Hence, to formulate an effective flame-retardant chemical, the points to be taken care of are either to increase the pyrolysis temperature of the fiber and formation of char and nonflammable gases or to decrease the formation of flammable gases and masking the availability of oxygen. A few approaches followed for the purpose are described in the following:

1. Use those chemicals that thermally decompose through a strong endothermic reaction to ensure less heat production.
2. Alter the pyrolysis temperature of the polymer to ensure formation of more char and less flammable volatile gases.
3. Dilute or replace the surrounding oxygen in the burning microclimate with inert or nonflammable gases to reduce or stop combustion.
4. Apply a suitable chemical that will form a glassy/foamy insulating layer on the textile substrates during combustion to restrict the flow of heat and/or oxygen.

### 3.3 TRADITIONAL FLAME-RETARDANT FINISHING OF TEXTILES

In the sixteenth century, Sabbatini et al. reported that clay or gypsum pigments could be added in the paint for a theater scenery to impart flame retardancy.14 Obadiah Wyld et al. published a patent in the seventeenth century on the flame-retardant formulation by a mixture of borax, alum, and ferrous sulfate. In the eighteenth century, Gay Lussac et al. developed fire-retardant jute and cotton fabrics with a mixture of ammonium phosphate, ammonium chloride, and borax.14,15 Later on, some other research group reported the use of aluminum hydroxide and calcium carbonate as fillers in textiles or polymers. These chemicals thermally decompose on heating through the strong endothermic reactions. Here the pyrolysis temperature of the fiber is not reached and no polymer combustion takes place. Inorganic salts also have been known for a long time for imparting flame retardancy to the cellulosic textiles that will not come in contact with water, rain, or perspiration.
With the advent of synthetic fibers during the period 1935–1980, many flame-retardant formulations and their application mechanism have been developed to impart flame retardancy in polyester, nylon, and polypropylene textiles, either by co-/graft polymerization (modacrylic LOI 29) or by using additives in the fiber-spinning bath. In the middle of the 1960s, many synthetic fibers with high LOI value and thermal resistance have also been developed, for use by the fire-fighters and in high-performance industrial applications, where the sample has to sustain its existence at an elevated temperature for a longer duration. Such high-performance fibers are basically made of aromatic-structured polymeric chains with a high strength-to-weight ratio and modulus. Some of the examples of these kinds of fibers are poly(para-aramid), better known as Kevlar, and poly(meta-aramid), known as Nomex. These fibers have LOI values of 28–30 and combustion temperature > 500°C. Being their LOI values >27, they are intrinsically considered as flame-retardant fibers/fabrics. A few more fibers in this category are carbon, poly(p-phenylene benzobisoxazole) (PBO-Zylon), polybenzimidazole (PBI), poly(tetrafluoroethylene) (PTFE), polyimide, and Fyrol (diethyl N,N-bis(2-hydroxyethyl aminomethyl phosphonate)). These fibers can sustain very high temperatures in the range of 500°C–700°C and for a longer duration compared to the maximum temperature ≈ 350°C at a shorter duration in the case of most apparel-grade fibers.

### 3.3.1 Imparting Flame Retardancy to Cotton

#### 3.3.1.1 Borax and Boric Acid Mixture

Borax and boric acid mixture with about 10% add-on are the most well-known chemicals commonly used for the flame-retardant finishing of fibrous material. Borax is used to lower down the melting temperature of boric acid, and on heating, it releases water vapor. Besides, it produces a thick glassy layer of boron trioxide on the substrate surface before reaching to its pyrolysis temperature. The mechanism is to insulate or cover up the textile fully or partially, from heat and surrounding oxygen. However, as these chemicals do not form any chemical bond with the substrates, they lose their efficacy after the laundering operation.

#### 3.3.1.2 Nitrogen- and Phosphorous-Based Chemicals

Diammonium phosphate along with urea and ammonium salts of phosphoric acid can be used as a fire retardant for cellulosic substrates. They act in the condensed phase mechanism. When a nitrogen- and phosphorous-based chemical is applied to improve the thermal stability of the cellulosic substrate, it reduces the pyrolysis temperature and promotes production of more residual char and less flammable volatiles. This happened due to the fact that phosphorous-containing flame retardants produce phosphoric acid at an elevated temperature, which then cross-links with the hydroxyl group of the cellulose, thus causing early dehydration. In such type of formulations, nitrogen acts in synergism with phosphorous and depicts a better efficiency. The interaction between phosphorous and nitrogen also alters the thermal decomposition pathway of cellulose. Possibly, it delays the thermal decomposition of cellulose by depolymerization. As a result, the LOI of the cellulosic fabric is enhanced through accelerated dehydration on heating. In this regard, the synergistic effect of trimethyl melamine (TMM) and dimethyl dihydroxy ethylene urea (DMDHEU) as a nitrogen provider with an organophosphorus compound has been reported in the literature. The TMM serves as a better nitrogen donor compared to DMDHEU, depending on the measurement of improvement in the LOI after the application. A group of researchers reported that probably organic nitrogen helps in controlling the pH during the cross-linking reaction of phosphoric acid. Here, nitrogen gets protonated, thus reducing the amount of available acid required for cross-linking. It also might have been converted into phosphorous acid amide that can catalyze the dehydration and carbonization of cellulose. The water-insoluble ammonium polyphosphate (APP) is also known as an effective flame retardant, when it is applied to binder systems in the coating. However, the majority of the aforementioned formulations are not durable to washing.
Sustainable Flame-Retardant Finishing of Textiles

The most successful durable flame retardant for cellulosic textiles is based on phosphorous- and nitrogen-containing chemicals that can directly react or cross-link with the fiber. Tetrakis hydroxy-methyl phosphonium chloride (THPC) is one of those compounds, which in mixture with urea forms an insoluble structure on the cellulose. The process is commonly known as Proban process. THPC is made of phosphine, formaldehyde, and hydrochloric acid. It can be applied to the cotton fabric with urea by pad-dry-cure method. Approximately 25% of THPC along with 15% urea formulation was found to yield 4%–5% phosphorous add-on in the cotton fabric. However, as discussed earlier, the treatment of cotton textile with such chemicals increases the stiffness of the sample with a simultaneous decrease in tensile and tear strengths. Further, it releases formaldehyde, a carcinogenic chemical during the processing. To overcome this drawback, THPC-urea-treated fabric was dried at 15% moisture content and then exposed to the ammonia vapor in an enclosed chamber, followed by oxidation with hydrogen peroxide. The finish achieved by this method resulted in imparting a good fire retardant to the textiles with better retention of fabric physicomechanical properties. However, the process is sensitive to dye molecules and the formulation affects different dye classes, such as reactive, direct, and acid. Therefore, it is recommended that in the fire-retardant finishing of cellulosic textile with THPC-urea, vat dyes should be used. Consequently, in the last five decades, flame retardants based on the composition of phosphorous, nitrogen, and halogen like Tetrakis phosphonium salt and N-alkyl phosphopropionamide derivatives have been widely used for commercial application. In this regard, N-methylol dimethylphosphopropionamide (Pyrovatex CP) in combination with trimethylol melamine and phosphoric acid is applied to the cotton fabric by pad-dry-cure process with an add-on of around 20%–25%. After the treatment, a wash with alkali is given to remove the residual phosphoric acid from the treated fabric surface. Unlike in the earlier Proban process, the main advantages of this process are durability to 50–60 wash cycles and low release of formaldehyde (below 40 ppm). It may be noted that melamine formaldehyde has a dual function, namely, as a resin to cross-link Pyrovatex to cellulose and as an additional nitrogen donor to accelerate the dehydration of cellulose. The restriction on choice of dye classes is less in this process compared to the Proban process and the treated fabric remained comparatively softer. Presently, most of the textile industries use N-methyl dimethylphosphopropionamide (Pyrovatex) with a melamine resin for fire-retardant finishing of cotton textile with the following recipe:

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Chemicals</th>
<th>Dosage (gpl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Softener</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Wetting agent</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>Melamine resin</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>Pyrovatex</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>Phosphoric acid</td>
<td>25</td>
</tr>
</tbody>
</table>

The fabric is padded with the aforementioned recipe, followed by drying at 100°C for 5 min and curing at 150°C for another 5 min, and then washing in alkali water for neutralization. Though the process is quite advanced and popular in textile industry, but it suffers from higher cost of application and unpleasant odor of formaldehyde emitted during the processing. Besides, the chemicals cited earlier are hazardous, non-eco-friendly, and nonbiodegradable. Due to the release of significant amounts of formaldehyde, the finishing process poses hazard to industrial workers, as it causes mucous and breathing problems. Considering the disadvantages, the Pyrovatex-finished flame-retardant textile is not recommended for home furnishing applications.

3.3.1.3 Antimony- and Halogen-Based Chemicals

Unlike other finishing areas of textiles using nano-, bio-, and plasma technology, very little research has been reported on the flame-retardant finishing of textiles using antimony compounds in the last decade of the twentieth century. Thereafter, the lead was taken by the U.K. home-furnishing industries due to the requirement of fabric to be resistant to cigarette ignition. The same was met
by providing halogen-containing back coatings to the upholstered fabrics. This coating prevents the combustion of the substrate by free radical reactions that provide the heat required for the flame propagation. The halogen-containing compounds work in the gas-phase mechanism and, those on heating, release hydrogen halide, which forms long-lived and less reactive free radicals. The formation of free radicals reduces effectively the heat available for fire propagation in concurrent with the dilution of oxygen in the burning microclimate. The main advantage of this process is that it can be applied to both natural as well as synthetic textiles, as it involves radical transfer reactions. Antimony chloride and antimony bromide are the few examples of this category. Linked to it, antimony oxide (Sb₂O₃) with stannous chloride provides a synergistic effect of flame retardancy into textiles. Here, the synergistic effect of antimony comes from the volatility of antimony trihalides and the effectiveness of antimony compounds in scavenging the free radicals. However, when these chemicals are applied to textiles with a binder for better fixation and durability, the fabric drape and handle get affected due to the presence of the binder. Also, there is a possibility of generation of toxic polyhalogenated dioxins and furanes during processing.

Due to the environmental issues associated with halogen compounds and the increasing demand for flame-retardant textiles, one new mechanism of flame retardancy, that is, intumescent technology, has come into the market in 1996. Intumescent chemicals provide a foamlike insulating layer on the fabric surface. This thick coating protects the underlying polymeric material from heat and flame. Successively on heating, the material gets expanded to increase in volume but decrease in density. Consequently, there was a production of porous carbonaceous foamlike char mass that masks the substrates from available oxygen. The reduction in smoke generation and toxic gas formation are the other two main advantages of this process. During exposure of the treated material to flame (i.e., at high temperatures), the temperature of the intumescent material is raised causing melting of the thermoplastic matrix. As the temperature corresponds to the approximate value for the viscosity of the melt, an endothermic gas-producing reaction is triggered. The gas is collected in small bubbles, thus turning the material to be foam. The formation of solid multicellular carbonaceous foamy char provides an insulating layer that slows down the heat and the mass transport required for the flame propagation. The intumescence property of a material depends on the ratio of carbon, nitrogen, and phosphorous atoms. APP is an example of intumescent that is applied as a coating in rigid polyurethane (PU) foams. Melamine is another example of a nitrogen-containing intumescent applied as a fire retardant for varnishes and paints. Few more such examples are ammonium polyphosphate, ammonium pentaborate, and melamine and its salts for flame retardancy of polyamide fiber (Nylon 6). All these chemicals work in the condensed phase. It was found that APP interacts with nylon 6 and produces alkylpolyphosphoric ester that acts as a precursor of the intumescent char. An APP add-on level of 10%–20% provides an LOI of 23–24, which was found to increase to 41–50, when the add-on was increased to 40%. Though this is a promising technology, it has the limitations of water solubility, brushing, and high cost associated with a higher add-on.

### 3.3.2 Imparting Flame Retardancy to Jute

In lignocellulosic fibers, cellulose, being the major constituent (70%–95%), also catches flame readily and is quite difficult to extinguish, thus posing risks to human health and damage to textile products. The lignocellulosic textile (jute) has a higher LOI value (≈21) compared to cellulose textiles (e.g., cotton and viscose) with an LOI of 18–19. In the past, significant efforts have been made to improve the flame-retardant property of jute textiles using various inorganic salts and commercially available synthetic chemicals. Inorganic salt, like sodium potassium tartrate (Rochelle salt), had been used as a fire-retardant agent for jute fabrics during the 1980s. The process could be considered environment friendly and the treated fabric showed good thermal stability while maintaining the mechanical strength of the fabric. However, the main issue with this process is the loss in efficacy after rainwater washing or soap washing. Similar to cotton textiles, the application of common borax and boric acid mixture has also been reported in the literature. Boron-based
derivatives provide better stability of finish due to their deeper penetration into the fiber, yarn, and fabric structure. Furthermore, boron compounds have fungicidal and insecticidal properties that are very much beneficial to jute products, as they are used in packaging of agricultural crops and for backing carpets.\textsuperscript{18} Similar to the application in cotton as discussed earlier, phosphorous-based flame retardant in combination with nitrogenous compound is also very successful in imparting flame retardancy in jute due to their synergistic effect and formation of more nonflammable products.\textsuperscript{19} In this regard, a research group on jute has developed a durable flame-retardant jute fabric with diammonium phosphate, urea, and resin with an LOI of 34, when the add-on percentage was kept at 7%. However, the durability of the imparted finish was not satisfactory and the treatment process had environmental effects. Sulfur along with nitrogen synergism has also been attempted to improve the flame-retardant property of the jute fabric. Sulfur- and nitrogen-based thiourea and thiourea resin has been applied on the jute fabric and it has been found that thiourea-treated fabric showed a fire-retardant behavior.\textsuperscript{20} It might have happened due to the fact that thiourea \([\text{SC-(NH}_2)_2]\) is an organosulfur compound, and upon heating, it releases ammonia, nitrogen oxide, sulfur oxide, and water that protect the substrate from getting \(\text{O}_2\) supply, thus improving the LOI value.\textsuperscript{19,22} Furthermore, sulfur oxide formed on heating reacts with the atmospheric oxygen \((\text{O}_2)\) at elevated temperatures and produces highly reactive sulfur trioxide \((\text{SO}_3)\), which further reacts with water vapor or water to produce sulfuric acid.\textsuperscript{22} Similarly to phosphoric acid in phosphorous-based flame retardants, the carbonium ion mechanism might have also helped in the dehydration of cellulose in lignocellulosic fibers resulting in increased char formation.

In a similar line, a thiourea resin was applied to the jute fabric to improve flame-retardant and mosquito-repellent functionalities.\textsuperscript{23} The treated fabric showed a higher LOI of 45 at 10% add-on compared to an LOI of 21 measured in the untreated jute sample as indicated in Table 3.1. In the treated sample after the flame was stopped, the afterglow remained for a longer duration and continued the fire propagation. In the control sample, no char length was observed as the sample burnt completely with flame, whereas in the urea- and resin-treated samples, 12.5–20 cm char length was observed depending on the concentration of the applications. They have also studied the temperature profile in the untreated and the thiourea-treated samples during the burning of samples in real time using an infrared thermometer in noncontact mode as shown in Figure 3.1.

It can be seen from the figure that the untreated sample burnt completely very fast with flame within 60 s with temperature as high as 400°C–450°C. In contrast, the treated sample burnt only at 100°C for the initial 10 s with an afterglow. Later, after 20 s, the afterglow stopped and the fabric temperature rapidly falls down to the ambient temperature within 20–30 s. In contrast, the control fabric burnt with flame, and a small extent of the afterglow with temperature 250°C–300°C could be seen at the edges of the sample holder. The thiourea-treated sample also showed the mosquito-repellent property, in addition to its flame retardancy. The mosquito repellent was tested quantitatively by the cage test and it has been reported that out of 25 mosquitoes in the cage, 10 mosquitoes were present on the control jute fabric after 1 h, whereas only 3 mosquitoes sat on the treated fabric. Thus, the treated fabric was 70% mosquito repellent. After 90–120 min, some of these mosquitoes were found surrounding the treated fabric sample, but none of them landed on the fabric. In contrast, in the control sample, the number of mosquitoes that landed increased with time. The mosquito-repellent effect in the treated fabric was possibly attributed to the strong odors of thiourea sulfur dioxide and ammonia.\textsuperscript{24,25}

The same research group also tried to improve the durability of the thiourea-treated samples with the DMDHEU resin. It was found that with increasing the resin concentration, the LOI of the treated fabrics was also increased due to the presence of more nitrogen, triggered by the DMDHEU resin. However, the thiourea process has the limitation of imparting yellowness to the fabric and reduction in mechanical strength, as the application is done in acidic condition.

To improve the durability of the imparted flame-retardant finish to the water, reactive halogen-based chemicals have been developed. Antimony in combination with various halogen compounds, a well-known formulation for cotton textile, has also been applied to the lignocellulosic substrate.
### TABLE 3.1
Flame-Retardant Parameters in Control, SMSN-, and Thiourea-Treated Jute Samples

<table>
<thead>
<tr>
<th>Flammability Parameters</th>
<th>Control</th>
<th>SMSN Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add-on (%)</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>LOI</td>
<td>21</td>
<td>29</td>
</tr>
<tr>
<td>After flame time (s)</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>Afterglow</td>
<td>Completely burnt with flame in 60 s</td>
<td>Completely burnt initially with flame followed by afterglow for 10 min</td>
</tr>
<tr>
<td>Char length (mm)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Burning rate (mm/min)</td>
<td>250</td>
<td>250</td>
</tr>
</tbody>
</table>

**Thiourea-Treated Samples**

<table>
<thead>
<tr>
<th>Flammability Parameters</th>
<th>Thiourea (80 gpl) + Different Resin Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add-on (%)</td>
<td>Control</td>
</tr>
<tr>
<td>LOI</td>
<td>21</td>
</tr>
<tr>
<td>Flashing over the fabric surface</td>
<td>Yes</td>
</tr>
<tr>
<td>Flame time (s)</td>
<td>Completely burnt with flame within 60 s</td>
</tr>
<tr>
<td>Afterglow (s)</td>
<td>80</td>
</tr>
<tr>
<td>Char length (mm)</td>
<td>20</td>
</tr>
<tr>
<td>State of fabric</td>
<td>Completely burnt</td>
</tr>
</tbody>
</table>

**Control**

| Add-on (%) | 0 |
| LOI        | 21 |
| After flame time (s) | 60 |
| Afterglow | Completely burnt with flame in 60 s |

**Thiourea-Treated Samples**

| Add-on (%) | 0 | 40 | 80 |
| LOI        | 21 | 43 | 45 | 45 |
| Flashing over the fabric surface | Yes | No | No | No |
| Flame time (s) | Completely burnt with flame within 60 s | Nil | Nil | Nil |
| Afterglow (s) | 80 | 60 | 50 |
| Char length (mm) | 20 | 15 | 12.5 |
| State of fabric | Completely burnt | Fire retardant | Fire retardant | Fire retardant |


![FIGURE 3.1](image)

**FIGURE 3.1** Temperature profile in control and thiourea-treated jute fabrics during burning. (From Basak, S. et al., *J. Text. Assoc.*, 74(5), 273, 2014.)
Similar to cotton, this particular process was not well accepted commercially due to its anticipated negative impact of halogen compounds on the environment and the requirements of the large quantum (15%–30%) of chemicals to achieve a satisfactory level of flame retardancy. One of the most efficient methods of protecting such lignocellulosic textile from fire is the use of intumescent-based fire-retardant coating, so as to reduce the percentage add-on to achieve a similar degree of fire protection. For example, carbonizing compounds, such as polyhydric alcohols, polyphenols, carbohydrates, and resins; dehydrating compounds like diammonium phosphate, urea, melamine, ammonium sulfate, and foam forming agents like dicyandiamide; and melamine have been reported to enhance more carbonaceous char formation. Similar to this principle to some extent, sodium silicate nonahydrate (SMSN) has been applied on jute fabric and various thermal, mechanical, and other functional properties were evaluated. It has been reported that SMSN not only improves the thermal stability of the samples but also ensures better antimicrobial efficacy. It can be seen (Table 3.1) that the LOI value linearly increased from 21 in the untreated sample to 29 and 32 in the 2% and 4% treated samples, respectively. With an increase in quantity of SMSN, burning with flame time gradually decreased and burning with afterglow time increased from 10 to 30 min in the 2% and 4% treated samples, respectively. In the 8% treated sample due to its high LOI value of 43, it did not burn with flame and also the afterglow was self-extinguishable within 30 s and produced a char length of 7 mm. The total burning time of a similar sample was possible to increase from 60 s in the untreated sample to 610 and 1805 s in the 2% and 4% treated samples, respectively. The SMSN possibly formed a silicate coating on the jute fabric that acted as an intumescent. It also serves as a hydrated plaster and a similar report has been reported in the literature for nontextile substrates. Upon exposure to a high temperature, it swells and increases in volume and forms an insulating carbonaceous foamlike glassy layer on the treated fabric surface. The insulating layer contains char-producing polyl that normally burns to produce nonoxidizable gases, like CO, H₂O, and CO₂. These generated gases might have diluted the major flammable gas concentration, such as levoglucosan and pyroglucosan produced during the pyrolysis of the lignocellulosic material in the burning microclimate. Furthermore, the chemically attached nine molecules of water with SMSN absorbed a significant amount of heat during burning, which is also hindered in faster fire propagation. Many of the existing flame-retardant formulations reduce the tensile strength of the fabric up to 30%, as they are applied in acidic condition. As this particular process was applied in alkaline condition, there was only a marginal loss in tensile strength. In the 2% SMSN-treated sample, there was only 3.7% and 7.5% reduction of tensile strength in the warp and weft directions, respectively. In the case of 8% SMSN-treated sample, there was 6% and 15% loss in the tensile strength in warp and weft directions, respectively.

From the thermogravimetric (TG) analysis, it was found that pure SMSN showed 60% mass loss in the temperature range of 50°C–200°C, possibly due to the loss of unbound and bound water molecules in different ways. Beyond 200°C and till 800°C, there was no significant change in the mass. On the contrary, the 4% and 8% SMSN-treated jute fabrics lost more mass below 150°C compared to the control jute fabric due to the loss of nine molecules of water of SMSN along with the water molecules present in the fabric. In the second stage, both the 4% and the 8% treated jute fabrics started to lose its mass due to its earlier pyrolysis from 230°C, which was about 35°C lower than the pyrolysis temperature of the control fabric (265°C). It was inferred that the presence of SMSN in the jute fabric had reduced the pyrolysis temperature of the lignocellulose and increased the overall thermal stability. Additionally, dilution of flammable volatile gases by the generation of nonoxidizable CO₂ and H₂O at relatively lower temperatures might have also contributed in providing flame retardancy. In spite of having several advantages, like good fire protection, eco-friendliness, low cost, marginal effect on mechanical strength, ease of application, and stability to weathering, the SMSN-based intumescent technology has not got commercial success, because of its lack of durability in repeated laundering. As a result, Pyrovatex-based technology is widely used in the industry till today due to its main advantages of repeated wash durability and little or no adverse effect on the fabric physical properties, though the processing condition is not so eco-friendly.
Besides the excellent flame-retardant functionality, the SMSN treatment was also found to exhibit good antimicrobial efficacy against both gram-positive and gram-negative bacteria. It was observed that the antibacterial activity was increased gradually from 62% in the 2% SMSN-treated sample to 99.9% in the 8% SMSN-treated sample against *Staphylococcus aureus* (Sa). A slightly better result was obtained against *Klebsiella pneumonia* (Kp) bacteria. Hence, SMSN can be used for dual functional finishing of the lignocellulosic textile. The antibacterial activity in the treated samples may be attributed to the higher pH of SMSN and breakage of the membrane integrity of bacteria and disruption of the cytoplasmic membrane.32–34

### 3.3.3 Imparting Flame Retardancy to Wool

It is known that protein fiber, like the wool, has a higher LOI of 25. It means that wool fiber is to some extent flame retardant due to the presence of nitrogen-based protein molecule in the wool keratin polymer. Despite this, wool fiber requires an additional flame-retardant treatment in order to meet the flammability standards required for some specific end applications. The well-known process for the same is commonly known as Zirpo, in which a mixture of hexafluorozirconate with titanate salt is applied by exhaust or padding method under acidic conditions. The process helps to attain an LOI as high as 35. Flame retardancy takes place in the condensed phase through zirconium ions that enhance or catalyze the carbonaceous char formation. This finish can withstand dry cleaning and aqueous washing at 40°C at neutral pH. Moreover, it has no significant adverse effect on the fabric strength unlike other flame retardants as described earlier. The only bothering issue is that with time the treated fabric slowly turns yellowish, whose degree increases with increasing light exposure. Alternatively, tetrabromophthalic anhydride (TBPA)-based flame retardant with an add-on of 10% in acidic condition also provides effective textile flame retardancy. The imparted finish is durable to mild laundering and dry cleaning, but it generates poly(brominated dioxins) under burning conditions.1

### 3.3.4 Imparting Flame Retardancy to Thermoplastic Fibers

Thermoplastic fibers, such as polyester, nylon, and polypropylene, are subjected to flame-retardant finishing depending upon their end applications. In case of nylon and polyester, the flame-retardant formulation can be applied, either in the polymerization stage (e.g., during polymerization) or as a spinning bath additive or grafting with a suitable monomer at the fiber stage or even in the later stage similar to an application done in the case of a traditional chemical finishing. Phosphorous and bromine–containing compound is the most effective fire-retardant formulation for the polyester fabric. Bromine-containing phosphate ester composition can be applied to polyester by both the padding and exhaust methods to achieve the desired fire retardancy. The only issue that needs to be tackled is their adverse carcinogenic effect that has resulted in their withdrawal from the market. In the recent time, the most commonly applied fire retardant for polyester is the mixture of cyclic phosphate/phosphonates. With an add-on of 3%–4% by pad-dry-heat steps, it could provide a durable flame retardancy to a wide range of polyester fabrics. Hexabromocyclododecane is another example of a durable flame-retardant agent for the polyester fabric. The material is fully water insoluble and a good flame retardant, when the add-on percentage is kept about 8%.

Similar to polyester, phosphorous and bromine–containing compound is also preferred and commonly used for nylon. Thiourea with the mixture of urea and formaldehyde also exhibited excellent fire-retardant effect on the nylon fiber. The effect of such fire retardant is possibly due to the lowering of the melting point of nylon by 40°C–50°C and also allowing the fiber to drip away from the ignition source. A back coating of nylon fabric with a mixture of antimony trioxide with bromine also provides an excellent fire-retardant effect. Other synthetic fibers, like polypropylene, can also be made flame retardant with the mixture of the aforementioned phosphorous and bromine–containing compound. However, to achieve a satisfactory level of flame retardancy, more quantum of flame-retardant agent needs to be applied.
3.4 ENVIRONMENT-FRIENDLY FLAME-RETARDANT FINISHING

Since year 2000, some of the major issues related to environment friendliness, toxicity, and sustainability of various traditional flame-retardant compounds have become a serious issue with increasing global awareness of sustainable eco-friendly green textile chemicals, auxiliaries, and textile products. Some of the adverse effects of the well-known existing flame-retardant formulations are mentioned in the following:

- Release of formaldehyde during the curing process that is hazardous to the worker and the surrounding environment.
- Toxicity of some of the halogen-based compounds and presence of heavy metals, as they produce toxic dioxins and furanes.
- Phosphorous, halogenated compounds, antimony, and zirconium compounds increase the toxicity of the wastewater and environment.
- A majority of the flame retardants reduce the fabric tensile and tear strengths and increase stiffness, making the fabric harsh in feel, yellow in color, and nondurable. Although industries are mostly using softener and easy-care chemicals to mitigate with such shortcomings in the fabrics, however, it increases the number of processing steps and cost due to the additional requirements of chemical and process, besides the effluent generation.

Thus, there is a need of development of environment-friendly, natural, and biomolecule-based sustainable flame-retardant formulations. As such, containing formaldehyde release, toxicity and reduction in fabric physicomechanical properties are the key challenges associated with many of the existing flame retardants. To address them, significant researches are being carried out both in the academic and the industrial sectors. A research group from the United States has reported a fully formaldehyde-free flame-retardant chemical from the char-forming polycarboxylated species, such as BTCA. The functional groups of BTCA get attached to the hydroxyl group of cotton cellulose and thus develop flame retardancy. Another research group has utilized BTCA as a cross-linker between the hydroxyalkyl organophosphorus oligomer and the cellulose polymer. Researchers have also developed Noflan, a mixture of phosphorous and nitrogen compound, mainly based on alkyl phosphoramidate. It can be applied with salt containing ammonium chloride that may react with the cellulosic substrate through the phosphoramidate NH$_2$ group. This formulation can be applied with methylated resin for improved durability of cotton and polyester–cotton blended textiles. Similarly, the Swiss-based research group has developed organophosphoramidate-containing flame retardants for cellulosic substrates. Researchers from the USDA Southern Regional Laboratory have synthesized two (2) new monomers, (2-methyl oxiranymethyl)-phosphonic acid dimethyl ester and [2-(dimethoxy-phosphoryl methyl)-oxyranylmethyl]-phosphonic acid. These two monomers along with dicyanamide and citric acid can provide LOI of more than 28. Similarly, the particular finish is also suitable for cotton and its blended fabrics. In our laboratory, eco-friendly flame-retardant formulations have been developed using BPS, an agro-waste plant residue, and spinach juice (SJ), a vegetable extract. After application of these two plant extracts on cellulosic cotton and lignocellulosic jute textiles, the LOI was found to increase over 30 from a value of about 21 in case of their untreated samples. The applications have been discussed in details in Section 3.7.

3.5 FLAME-RETARDANT FINISHING USING NANOTECHNOLOGY

Nanotechnology, an emerging science, has gained profound interest within the research community because of its various industrial applications, such as in the fields of textile, material, medicine, electronics, plastics, energy, aerospace, biotechnology, and agriculture. The novel material properties and low chemical consumption associated with nanoparticles have attracted global interest, across disciplines and industries including the textile industry. Nanotechnology endeavors at
manipulating atoms and molecules in a controlled manner in order to build up a new material with novel properties that can be used to produce smart and intelligent textiles, such as water-repellent, oil-repellent, hydrophilic, UV-protective, and flame-retardant properties. Nanomaterials, like nanoparticles, nanoclay, nanofibers, and nanocoating, are applied in textile substrates in order to improve such functionalities.\cite{35}

The antimony nanoparticles have been synthesized using potassium antimony tartrate precursor with particle sizes in the range of 350–550 nm.\cite{36} The x-ray diffraction (XRD) peaks at different 20 values of 27.7, 32, 35, 45.9, and 57.1 have confirmed the crystal structure of the antimony oxide. Similarly, the wave number in the region of 400–800 cm\(^{-1}\) depicted the symmetric and asymmetric vibrations of Sb\(_2\)O\(_3\) as observed in the Fourier transform infrared spectroscopy (FTIR) spectrum. After the application of antimony oxide nanoparticles on a cotton fabric along with zinc chloride, the sample was found not to catch the flame, whereas the untreated sample burnt completely within 18 s at a maximum temperature of 450°C. The LOI value was found to increase significantly from 18 in the untreated sample to 24 in the nanoparticle-treated sample. With further increase in the add-on percentage of antimony oxide, the LOI was found to increase. The thermal gravimetric analysis (TGA) curve of the treated sample showed the starting of pyrolysis of cotton at 230°C at a slower rate than the untreated cotton, where a sharp degradation was observed with pyrolysis starting at 330°C. It was further observed that the untreated cotton loses most of its mass before 350°C, whereas it was 500°C in the case of the nanoparticle-treated sample. After washing of the sample with soap solution, the LOI was found to reduce to 21 from 24 noted in the treated sample.

Yet in another study, the ZnO nanoparticle was used to impart dual flame-retardant and UV-protective functionalities in cotton and 65/35 cotton/polyester blended textiles.\cite{6} The size of the synthesized ZnO particles was 30 nm. The nanoparticles were applied in the textile by the conventional pad-dry-cure method with a mixture of different polycarboxylic acids, such as succinic acid (SA) and BTCAs, and sodium hypophosphite (SHP) catalyst. The effect of catalyst concentration of SHP on flammability was studied in details. It was observed that char length was much more in case of the treated samples (pure and blended fabrics) compared to the untreated sample.

An improvement in the mechanical property of polyamide 6 (PA6) has been reported with nanoclay-added fibers. The incorporation of nanoclay into the PA6 fibers leads to the enhancement in the fire-resistant properties also, thus offering a new technology proposition for imparting highly durable fire-retardant finishing to the PA6 textiles at a lower cost.\cite{37} The presence of nanodispersed montmorillonite (MMT) clay in polymeric matrices showed a significant improvement in the fire-retardant property. This research group has also developed hybrid polymeric materials, including organomodified clays, TiO\(_2\) nanoparticles, silica nanoparticles, and carbon nanotubes (CNTs).\cite{38} These materials exhibited improvement in the fire-retardant property in terms of the heat release rate (HRR). It was found that the peak of HRR was decreased by 50%–70% in a cone calorimeter experiment. In a similar line, the nanoclays and poly(silsesquioxanes) can reduce the peak HRRs in PU-coated cotton and knitted polyester fabrics. However, the presence of these nanoparticles alone reduced the time to ignition and prolonged the time of burning.\cite{39} MMT clay and polyhedral oligomeric silsesquioxanes (POSSs) have been added to PU for coating of cotton and polyester fabrics for improvement in flame retardancy.\cite{40} After application of PU/clay and PU/POSS coating, the polyester or cotton fabrics showed better flame retardancy properties in terms of cone calorimetry and TG analysis. Similarly, the flame-retardant property of the polyester fabric was improved by a novel layer-by-layer nanocoating.\cite{41} Instead of direct application of the silica nanoparticle, the same layer-by-layer technique was applied to impart a multilayer coating. Five bilayers of positively and negatively charged colloidal silica with <10 nm average thickness were found to increase the time to ignition of the PET fabric by 45% and decrease the HRR peak by 20%. In the vertical burning test, this nanocoated polyester sample showed a drastic reduction in the burning time, besides the elimination of more dangerous melt dripping. In another study, the flame-retardant coating of the cotton fabric was carried out with branched polyethyleneimine (BPEI) and sodium MMT clay by the layer-by-layer technique.\cite{42} Four different coating recipes were formulated by changing the
pH and clay loading (0.2 or 1 wt%). The BPEI at pH 10 produced the thickest films, whereas 1 wt% MMT gave the highest clay loading. The performance was evaluated for the 5 and 20 bilayers. TG analysis showed that the coated fabrics left as much as 13% char after heating to 500°C, which was nearly double in magnitude compared to the uncoated fabric. Additionally, it reduced the afterglow time in the vertical flame tests and could maintain the weave structure of the fabric after burning as observed in SEM images. The calorimeter data showed that for all the coated fabrics, both the total heat release and the heat release capacity reduced. Unlike the traditional finishing of textiles, here the fibers could retain their mechanical strength after coating.

### 3.6 FLAME-RETARDANT FINISHING USING PLASMA TECHNOLOGY

Wet-chemical processing of textiles is important for its improvement in aesthetic and functional value. However, the process remains water, chemical, and energy intensive due to the involvement of multistep operations, such as padding, drying, curing, and postwashing. Several developments have taken place in the textile sector in the last five decades from a cost and environmental point of view, such as application of enzymes, natural dyes, digital printing, low material to liquid processing, spray and foam finishing, infrared dyeing and drying, ultrasound dyeing and dispersion, and water-free plasma processing.\(^{42-44}\) Plasma, a partially ionized gas composed of many types of species, such as positive and negative ions, electrons, neutrals, excited molecules, photons, and UV light, can be used for nanoscale surface engineering of textile substrates without altering the major inherent bulk properties. Plasma reaction with a small nonpolymerizing molecule causes surface activation, cleaning, oxidation, change in surface energy, an increase in surface roughness/area, and etching. Similarly, plasma reaction with a bigger molecule leads to plasma polymerization, coating, deposition, and creation of nanostructures. These altogether improve the aesthetics and functional value of the textiles in terms of improvement in water absorbency, water repellency, oil absorbency, oil repellency, UV protection, antimicrobial, flame retardancy, dyeing, desizing, antistatic, adhesion, and antifelting of wool.\(^ {44-48}\) Low-temperature plasma, also known as nonthermal plasma with a bulk temperature of 50°C–250°C, is used for such surface modification of textiles. Plasma is an energetic chemical environment, where the generation of plasma species opens up diverse reactions resulting in various end applications in apparel, home, and technical textiles.

A single-step multifunctional finishing of the cotton textile to impart water repellency as well as flame retardancy has been reported using argon (Ar) plasma.\(^ {49}\) Argon plasma has been used for graft copolymerization of monomers of acrylate phosphate and phosphonate derivatives in combination with carbon tetrafluoride (CF\(_4\)) gas. The CF\(_4\) gas was responsible for imparting water repellency, and the fire-retardant chemicals had no opposing effect on it. The same research group from the national textile center has also developed monomers like cyclotriphosphazene and hexachlorocyclotriphosphazene to be deposited on the plasma preactivated cotton surface followed by polymerization by passing the fabric through the plasma zone to ensure formation of a grafted flame-retardant nanolayer on the fabric. They have also studied the low-temperature argon plasma–induced graft copolymerization of monomers like phosphorous diethyl phosphate and diethyl-2-(methacryloyloxyethyl) phosphate (DEMEP) on poly(acrylonitrile) fabrics. Different metal and/or metal oxide mixtures, such as aluminum oxide, nanosilver, and titanium dioxide, have been applied in the argon plasma–preactivated polyester fabric.\(^ {50}\) The treated fabric showed improvement in flame retardancy and thermogravimetry. Besides, the treated fabric showed good antimicrobial property. Similar to plasma treatment, the graft copolymerization of methacrylamide on the UV-irradiated cotton fabric was carried out using benzophenone as a photosensitizer so as to react easily with phosphorous-containing compounds, and the treated fabric showed improvement in thermal stability.\(^ {51}\)

Cotton fibers were coated with silicon dioxide (SiO\(_2\)) layers using atmospheric pressure plasma (APP) treatment. The SiO\(_2\) network armor was obtained through hydrolysis and condensation of the precursor TEOS, and it was successively cross-linked on the cotton fiber’s surface. Due to the protective effects of SiO\(_2\) network armor, the modified cellulosic fibers exhibited enhanced thermal
properties and improved flame retardancy. The scanning electron microscope (SEM) images have confirmed the presence of SiO₂ network on the fabric surfaces, even after intense ultrasound washes. The SiO₂-APP-coated flame-retardant cotton textiles will have numerous applications in the development of upholstery furniture, clothing, and military applications. A dense, thin film was obtained from the tetramethyldisiloxane (TMDS) monomer premixed with oxygen by plasma treatment. The flame-retardant properties of polyamides and polyamide nanocomposites could be improved using such deposit. The LOI of the coated PA6 nanocomposites was greatly improved when the film thickness was equal to 0.6 mm. The mechanism was attributed to the fact that under the burning condition, the nanocomposite structure of the polymer led to the formation of a surface protective layer. The presence of carbonaceous and silica-like layer acts as a barrier, thus preventing heat and mass transfers in the burning zone. Additionally, the polymer slows the toxic gas formation. A recent patented process has demonstrated the use of atmospheric plasma for flash-fire-resistant finishing of pure cotton, flame-retarded cotton, and poly(meta-aramid) fabrics using clay and a silicon-containing monomer such as hexamethylene disiloxane (HMDSO) in various combinations. It was found that at relatively low heat flux of 35 kW/m², the cone calorimetry showed that for pure cotton, both the time-to-ignite (TTI) and the time-to-peak (TTP) values increase for argon plasma–treated fabrics. It was observed that ArClayAr-Cotton showed significantly more TTP value. The effect of the presence of clay was clearly seen in this experiment. Low-pressure cold plasma was used to deposit a thin film on PA6 substrates for fire-retardant finishing by plasma polymerization of the 1,1,3,3-tetramethyl disiloxane (TMDS) monomer and oxygen gas mixture. The presence of oxygen during the polymerization process of TMDS promoted the formation of more thermally stable coatings with efficient fire-retardant properties. The coatings formed a thermal barrier that decreased the RHR of the coated PA6 by 28% and increased ignition time from 105 s in the untreated sample to 219–315 s in the treated samples. Another study on PA6 using low-pressure microwave plasma has described the graft polymerization of fluorinated acrylate monomer 1,1,2,2-tetrahydroperfluorodecyl acrylate (AC8). The deposit showed efficient fire-retardant properties in terms of decreased RHR peak value by 50% compared to the uncoated PA6. This was possibly due to the reaction of CF₂ radicals in the gas phase with different fragments of polymer generated during the thermal degradation, resulting in dilution of the combustible gases. Joëlle et al. reported the use of some monomer along with the diethyl(acryloyloxyethyl)phosphoramidate (DEAEPN) monomer, photo-initiator, and ethylene glycol diacrylate (EGDA) for multifunctional finishing of cotton textiles, with special emphasis on a simultaneous improvement in dyeing and flame retardancy. A flame-retardant agent (RF) of an organic phosphorus compound in combination with a melamine resin (cross-linking agent, CL), phosphoric acid (catalyst, PA), and zinc oxide to nano-ZnO (cocatalyst) could impart effective durable flame-retardant properties. In the study, an APP jet was applied as a pretreatment to improve the postfinishing operation (e.g., the flame-retardant finishing) of the cotton fabric. By application of FR-CL-PA in the presence of a ZnO/nano-ZnO cocatalyst to cotton fabrics, it was possible to impart flame-retardant properties. Both the plasma pretreatment–added and the ZnO/nano-ZnO (cocatalyst)–added flame-retardant formulations could improve the cross-linking between the flame-retardant chemical and the cotton fabric, thus minimizing the drawbacks of the existing acid-based flame-retardant formulation. To improve the durability to washing or to harsh weather conditions, the flame-retardant chemicals must be firmly attached to the surface of the textile. It could be most efficiently achieved through the covalent bonding. In this regard, the simultaneous grafting and polymerization of fire-retardant monomers on cotton and polyacrylonitrile (PAN) fabrics induced by argon plasma with four acrylate monomers containing phosphorus, such as diethyl (acryloyloxyethyl) phosphate (DEAEP), DEMEP, diethyl (acryloyloxymethyl) phosphonate (DEAMP), and dimethyl (acryloyloxymethyl) phosphonate (DMAMP), is worth mentioning. The treated samples showed an improved flame-retardant property in terms of the LOI and the thermogrametry. An APP jet was used as a pretreatment to enhance the flame-retardant property of the cotton fabric by either the sputtering or etching effect. The flame-retardant agent (FR) N-methyl dimethylphosphonopropionamide, in combination with a melamine resin,
cross-linking agent (CL), and a catalyst of phosphoric acid (PA), was used. Titanium dioxide (TiO$_2$/nano-TiO$_2$) cocatalyst was added to the FR formulation in order to improve the cross-linking of the FR-CL-PA components. Similarly, it has been reported that the plasma containing a phosphorus compound can be used for flame-retardant finishing of acrylic, cotton, and viscose rayon fibers.

### 3.7 FLAME-RETARDANT FINISHING USING PLANT EXTRACT

In the last few decades, due to the stringent pollution norms and the government legislation that have come into force, various technologies have been developed and implemented in the textile production and processing arena so as to reduce the consumption of water, energy, processing costs, and/or effluent load. Some of these technologies are as follows: (1) low material to liquid processing, (2) spray and foam finishing, (3) use of enzymes, (4) natural dyes, (5) digital printing, (6) infrared dyeing and drying, (7) radiofrequency drying, and (8) ultrasound for dyeing and dispersion. Few more promising and emerging technologies have also been explored in laboratory to industry, such as (1) supercritical carbon dioxide for dyeing, (2) plasma technology for water-free processing, and (3) UV- and laser-based processing and finishing. All these developed technologies are related to pre- or postprocessing of textiles or textile processing machineries. In spite of such developments, textile chemical processes still remain energy and water intensive, besides adding to pollution due to the use of various non-environment-friendly chemicals and auxiliaries. As discussed earlier, many of the present-day flame-retardant formulations, such as those based on phosphorus and nitrogen, antimony–halogen, diammonium phosphate, Pyrovatex, urea, and melamine formaldehyde, have an adverse effect on the environment, human body, and fabric physical, mechanical, and aesthetic properties. In this context, environment-friendly chemicals, such as BTCA, BTCA-hydroxyalkyl organophosphorus compound, Noflan, organophosphoramidates compound, and a few more, have also been demonstrated for commercial applications. Emerging plasma and nanotechnology have recently been explored to impart flame retardancy to the natural as well as synthetic textiles with an aim to partially or fully avoid the usage of water and reduce the number of processing steps and the quantum of chemicals required. However, the same has not met with much commercial success, and the processes still use the traditional types of flame-retardant chemicals. It may also be noted that till date, a very limited research work has been carried out on the development of textile chemicals and auxiliaries utilizing natural resources.

In this context, there is a need to develop sustainable green-flame-retardant chemicals preferably produced from renewable sources that will be easy to apply; cost effective; environmental friendly; limited to no adverse effect on fabric mechanical properties; versatile to cellulosic, lignocellulosic,
and protein textiles; and semidurable to durable. In recent years, a few researches have been reported on flame-retardant finishing of cellulosic cotton textiles using biomacromolecules, such as DNA from herring sperm and salmon fish. It has been reported that the DNA consists of phosphate, carbonaceous deoxyribose units of polysaccharide dehydrate and some essential amino acids, which are responsible for the formation of more carbonaceous char and ammonia release to enhance the thermal stability of the cotton fabric. Efforts were also directed to make cotton fabric flame retardant with whey proteins, casein, and hydrophobins, as these are rich in phosphate, disulfide, and protein that can influence pyrolysis by early char formation. As some of the plants (i.e., the plant molecules) contain phosphorous and other minerals, in our laboratory, two such plant extracts have been utilized for flame-retardant finishing of cellulosic and lignocellulosic textiles. In this regard, BPS, an agro-waste plant extract, and SJ, a vegetable extract, have been utilized, as they are rich in phosphorous, nitrogen, chlorine, silicate, and other many metallic compounds. A recent study on BPS reported that potassium chloride, sodium chloride, and metal phosphate are the major composition of salts of the BPS. Furthermore, the BPS is abundantly available in many of the countries and could be considered as a green, cost-effective flame-retardant chemical for jute and cotton textiles.

### 3.7.1 THERMAL ANALYSIS

The BPS was applied on premordanted (5% tannic acid + 10% alum) cellulosic and lignocellulosic textiles by the pad-dry method in an alkaline condition. The flame retardancy of the samples was measured in terms of LOI, burning rate, total heat production, differential scanning calorimeter (DSC), and TGA. As discussed earlier, a textile with LOI ≤ 21 burns rapidly in an open atmosphere and a sample with LOI ≥ 27 is generally considered to be flame retardant. It can be seen from Table 3.2 that the untreated cotton and jute have the LOI values of 18 and 21, respectively. However, when both samples were treated with the BPS, the LOI was found to become more than 27 and, hence, can be considered as flame-retardant textiles. From Figure 3.2, it can also be seen that the BPS-treated fabrics showed a better thermal stability in contact with flame compared to the control fabric.

<table>
<thead>
<tr>
<th>Flammability Parameters</th>
<th>Control Cotton</th>
<th>Control Jute</th>
<th>Plant Extract–Treated Textiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add-on (%)</td>
<td>Control Cotton</td>
<td>Control Jute</td>
<td>BPS on Cotton</td>
</tr>
<tr>
<td>LOI</td>
<td>18</td>
<td>21</td>
<td>4.5</td>
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<td><strong>Horizontal flammability</strong></td>
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<tr>
<td>Warp way burn rate (mm/min)</td>
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<td>62</td>
<td>7.5</td>
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<tr>
<td><strong>Vertical flammability</strong></td>
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<td></td>
</tr>
<tr>
<td>Burning with flame time (s)</td>
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<td>60</td>
<td>4</td>
</tr>
<tr>
<td>Burning with afterglow time (s) after flame stopped</td>
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<td>900</td>
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<td>Total burning time (s)*</td>
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<td>60 + 0</td>
<td>4 + 900</td>
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<tr>
<td>Observed burning rate (mm/min)</td>
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<td>250</td>
<td>16.6</td>
</tr>
</tbody>
</table>

*Total burning time = burning with flame time + burning with afterglow time.

The BPS-treated cotton fabric burns with flame only for 4 s followed by burning with an afterglow (after the flame is stopped) for 900 s. Hence, the total burning time of a 250 mm × 20 mm sample becomes 904 s, whereas the untreated sample of same size burnt completely within 60 s with the flame as shown in Figure 3.2.

Therefore, it can be expected that the rate of heat production would also be more in case of the control sample compared to the BPS-treated sample. It is important to note that the available time either to escape from the fire zone or to extinguish the fire was much more (904 s) in the treated sample compared to only 60 s in the case of the untreated sample. In the treated sample, the observed burning rate was only 16.6 mm/min, which is significantly lower than the 250 mm/min in the untreated sample. Compared to cellulosic cotton textiles, lignocellulosic jute shows a bit higher LOI value. The treated fabric showed an LOI of 33 and the flame time was only 5 s compared to the untreated sample, where the corresponding values were 21 and 60 s for the complete burning. Though the flame stopped after 5 s in the treated sample, it burnt at a very slow rate of 24.8 mm/min.

The advantages of this process are that the flame is self-extinguishable in 4–5 s and the application process is quite simple. It has been reported that the total heat of combustion measured in terms of the gross calorific value (GCV) measured in the oxygen bomb calorimeter was found to reduce from 16.4 to 13.1 MJ/kg in the untreated and BPS-treated cotton fabrics, respectively. The durability to soap washing of this particular finish was also investigated, and it was found that on washing, the LOI value reduced to 24 from 30 in the as-prepared sample. This implies that the treated fabric could retain some part of the imparted functionality after washing, and hence, it can be considered as a semidurable finish. After application of the BPS finish, there was no significant adverse effect (<5% change) in either the tensile or the tear strength of the treated fabrics, whereas most of the flame-retardant finish causes 10%–30% loss of the tensile strength.4

TG analysis was carried out to study the thermal stability of the BPS-treated fabric over a temperature range compared to the control sample.13 Figure 3.3 shows the TG curves of both the samples in air atmosphere at a heating rate of 10°C/min. Four distinct stages were observed in the BPS-treated sample. In the initial stage at temperatures below 200°C, the mass loss occurred mainly due to the removal of absorbed moisture from the fabric.30 In the second stage, the main pyrolysis occurred over the temperature range of 200°C–350°C with a sharp first derivative peak at 300°C. Above 380°C, that is, in the third stage, dehydration and char formation happened due to the formation of water and CO$_2$, and the sample showed one more first derivative peak.
In contrast, the TG curve of the control sample showed a rapid decomposition in a narrow temperature range of 320°C–340°C with the sharp first derivative peak at 340°C. It lost around 98% of its mass at below 500°C. The BPS-treated samples started to lose mass, that is, the pyrolysis from temperature of 215°C, which is 85°C lower than the degradation temperature of the control sample. In the last stage of the TG curves, both the untreated and the treated fabrics showed char formation and the quantity of char residue remained higher in the treated sample compared to the untreated samples. A similar result was also observed in the BPS-treated jute fabric. The result showed that the BPS could be effectively used for flame-retardant finishing of cellulosic and lignocellulosic textiles.

DSC analysis was carried out to understand the flame-retardant mechanism of the control and BPS-treated lignocellulosic textiles. It was observed that unlike the control sample, the treated sample showed a steep endothermic peak in the initial region, which corresponds to the evaporation of water. The control fabric showed small endothermic peak, corresponding to the depolymerization and degradation of cellulose at 387°C. On the other hand, the treated sample showed a strong exothermic peak at 326°C with onset at 291°C and followed by an endothermic hump at 365°C. This signifies that similar to TG analysis, the degradation of cellulose has shifted toward the lower temperature by 22°C due to the presence of BPS. Further, the large exothermic peak in the treated fabric exhibits an extensive dehydration and char formation.

### Chemical Analysis

Figure 3.4 shows the negative and the positive time-of-flight secondary ion mass spectra (ToF-SIMS) of the pure BPS. The different molecules that were detected have been calculated based on their mass/charge (m/z) ratio. The negative ToF-SIMS of BPS showed the presence of major molecules at different mass units, such as $\text{H}^-$ (1 amu), $\text{C}^-$ (12 amu), $\text{CH}^-$ (13 amu), $\text{N}^-$ (14 amu), $\text{O}^-$ (16 amu), $\text{OH}^-$ (17 amu), $\text{F}^-$ (19 amu), $\text{Cl}^-$ (35,37 amu), $\text{Cl}_2^-$ (70,71 amu), $\text{PO}_2^-$ (62,63 amu), $\text{PO}_3^-$ (79 amu), and $\text{KCl}^-$ (74,76 amu). On the other hand, the positive ion mass spectrum of the sample showed
mostly the presence of various metal ions, such as Mg\(^+\) (24, 25 amu), Al\(^+\) (27 amu), K\(^+\) (39 amu), Ca\(^+\) (40, 41 amu), Mn\(^+\) (55), and Fe\(^+\) (55, 56). Similar elemental peaks have also been detected in energy-dispersive x-ray spectroscopy (EDX) analysis of pure BPS.\(^{13}\) Therefore, the flame-retardant properties in the BPS-treated sample in terms of higher LOI value and more char formation in cotton and jute fabrics were due to the presence of free metal ions and various metal salts like potassium chloride, potassium fluoride, calcium chloride, and phosphate.\(^{13}\)

Similar to the BPS, the SJ, a vegetable extract, has also been utilized for flame-retardant finishing of the cotton textile.\(^{63}\) This plant (Spinacia oleracea) is available in many countries and it is rich in phosphorous, nitrogen, and other metallic constituents. Unlike the BPS on cotton, the SJ was applied to cotton textile directly without any premordanting. In the 8% add-on sample, the LOI was found to increase to 30 from 18 in the control cotton sample. It was interesting to note that the sample did not catch flame and the afterglow was present only for 400 s, whereas as discussed earlier, the control sample completely burnt within 60 s with a high-temperature range of 400°C–450°C. As the sample burnt slowly, the warp way burning rate decreased from 75 mm/min in the control sample to 10 mm/min in the SJ-treated sample. There was a reduction in LOI from 30 to 22 after washing of sample with soap solution. Hence, like in the BPS treatment, this particular finish can also be considered as a semidurable finishing. There was no significant change either in the fabric tensile or tear strength after the application of this plant extract–based finish. The developed finish is cost effective compared to any other synthetic flame-retardant chemicals, as it is abundantly available and produced from renewable sources.

A single-step multifunctional finishing process for textiles is important to reduce the cost of processing. In this context, the BPS and the SJ, in addition to flame retardancy, can also impart effective UV-protective functionality and natural color. It was observed that the plain-woven bleached cotton fabric showed a poor UPF value of 10. As a result, the majority of the incident UV rays can easily pass through the fabric structure. After mordanting with tannic acid and alum, the UPF value did not improve much. When the mordanted fabric was treated with BPS in alkaline condition, the UPF value was found over 100, that is, a UPF rating of 50+ (excellent category). Furthermore, the UVA and UVB transmittance percentages reduced drastically from 9.5% and 7.2% in the untreated sample to 1.2% and 1.0%, respectively, in the BPS-treated sample. On the other hand, if the bleached fabric was directly treated with an alkaline BPS without any mordant, it showed quite a lower UPF value (40). From these two facts, it can be said that the improved UPF value, that is, the lowering of UV (A and B) transmission percentage, is arising mainly due to the synergistic effect of the BPS and the mordant. The UV protection of the BPS was possibly attributed to the presence of \(N,N\)-alkyl benzeneamine, as confirmed by the GC-MS analysis of BPS.\(^{64-66}\) The UPF value of the treated fabric was 70 after the first ISO-1 washing and 55 after the second washing. Unlike the flame retardancy finishing, the fabric sample could easily retain the imparted UV protection functionality after washing. Similarly, the SJ-treated cotton fabric in alkaline condition showed the UPF value of 125 (rating ≥ 50), which may be due to the presence of organic color and silicate molecules. In the SJ-treated sample, the significant reduction in UVA and UVB percentage has also been reported in comparison with the untreated sample.

It has also been reported that after application of the BPS in the premordanted cotton fabric, the sample color changed from white to khaki. This color was only developed in the premordanted fabric in alkaline condition. The mordant has helped in exhaustion of the BPS and the color formation. In the treated fabric, the K/S value (color depth) improved from 0.04 for the control to 0.80 for the BPS-treated samples. With further increase in the concentration of the BPS, the depth of color increased linearly. Similarly, after the application of SJ on the bleached cotton fabric, the color of the sample changed to white to dark green. Therefore, from various results, it can be said that the BPS and the SJ can be used for imparting multifunctional flame retardance, UV protection, and natural color to textiles in a single step.
3.7.3 MECHANISM OF FLAME-RETARDANT FINISHING

The flame-retardant functionality imparted by the BPS may be due to the presence of phosphate and other mineral salts in the BPS. Different metals that are present in the form of metal chloride and phosphate were detected in positive and negative ion mass spectra. In addition, the elemental peaks of chlorine, phosphorous, magnesium, aluminum, sodium, potassium, calcium, etc., were also detected in EDX analysis. The FTIR analysis of pure BPS sample confirmed the presence of inorganic salts. One recent study on pure BPS reported that 10.5 g inorganic salts was obtained by evaporation of 500 mL aqueous ash extract collected from burning the banana pseudostem. It was found that potassium chloride, sodium chloride, and metal phosphate are the major components of that salt. On the other hand, the flame-retardant property of the SJ-treated cotton fabric was possibly due to the presence of silicate and phosphate, which have also been detected by elemental EDX and FTIR analysis. From the various characterizations, it was presumed that phosphate, silicate, chloride, and other mineral salts present in the BPS and SJ might have increased the thermal stability of the cotton and jute fabrics by forming more char and producing less flammable gases. A similar mechanism has also been reported in the literature wherein the presence of organometallic additives in cellulosic textiles could increase char formation while reducing formation of tar, that is, the volatile gases.

As far as the flame retardancy mechanism is concerned, the BPS mainly acts in the condensed phase. It might be due to the fact that it contains phosphate, phosphite, and other metallic constituents that help influence the pyrolysis of the cellulose polymer resulting in earlier char formation as supported by TGA. From the SEM pictures of the treated fabric, it was also observed that the BPS produced a thick protective coating on the surface of the cotton fiber. When this treated cotton fabric was exposed to flame, it favored the formation of a stable and protective char that limited the exchange of oxygen and combustible volatile substance, resulting in disappearance of flame and reduction in the burning rate. It has also been reported that the BPS coating might have also acted as an intumescent that swells on heating and increase its volume, thus protecting the underlying cellulose polymer from the heat or flame.

3.8 SUSTAINABLE FLAME-RETARDANT FINISHING

As discussed earlier, many of the present-day flame-retardant formulations, such as thiourea, THPC-urea, Pyrovatex–urea–melamine formaldehyde, antimony–halogen, phosphorus–nitrogen, and diammonium phosphate, have adverse effects of formaldehyde release and environmental impact in addition to the reduction in fabric physical, mechanical, and aesthetic properties. For the development of sustainable textiles, it is preferred that the textile should be made of natural fibers and to be processed and finished with eco-friendly chemicals and auxiliaries, preferably with natural products. As far as flame-retardant chemicals and fabrics are concerned, it should not be biologically harmful, and it should not have any detrimental effect on fabric properties. In this regard, formaldehyde- and halogen-free formulations have also been developed, but those are not very successful in the market. Till date, the most popular flame-retardant formulation for commercial application is Pyrovatex, which releases 330 and 550 ppm formaldehyde, when applied either alone or in combination with melamine formaldehyde to cotton fabrics. Even after five home launderings, it releases more than 25 ppm of formaldehyde that is harmful to the end user. To mitigate this problem, BTCA along with citric acid (cross-linker) has also been explored instead of using melamine formaldehyde. This has helped to reduce the formaldehyde release level below 20 ppm after 5 home launderings. Additionally, more substantive intumescent products, nanoparticle additives, and blends with inherently flame-retardant fibers have also been developed to provide environment-friendly durable textiles. Recently, eco-friendly green-flame-retardant chemicals from the plant extract and other biomolecules, such as DNA, whey protein, BPS,
SJ, have been applied on cotton and other lignocellulosic textiles for the development of sustainable textiles. As these materials are mostly produced from agricultural or other residues, they are renewable, cost effective, easy to apply, and free from any formaldehyde release. Such applications were found not to affect the mechanical properties of fabrics and can also be suitably used for natural coloration of textiles.

3.9 SUMMARY

Wet-chemical processing of textiles is important to improve its aesthetic and functional value. Among the various functional finishes of textiles, flame-retardant finishing is important, as it is directly related to the protection of human beings and other valuable products from fire hazards. Natural and synthetic fibers are used for apparel and home-furnishing applications. Due to the several advantages of natural fibers in terms of biodegradability, produced from renewable sources, good moisture regain, soft feel, adequate to fair strength, and good appearance after chemical treatment, natural fibers are preferred over their synthetic counterparts for apparel and home-furnishing applications. Both natural and synthetic apparel-grade fibers have a low LOI value <25; therefore, a flame-retardant finishing is essential for these fibers to make them suitable in apparels, baby products, hospital curtain, tent, automobiles, railways, and for protection of workers who are engaged in oil, gas, and petroleum industries. Although the combustion temperature of such fibers is quite high (450°C–550°C), but they degrade at a much lower temperature through pyrolysis and/or melting. Significant efforts have been made in the past to improve the flame retardancy of cotton and other textiles during their manufacturing or in the finishing stage. The most commonly used chemical for the same is a mixture of borax and boric acid, inorganic salts, diammonium phosphate, and urea. Phosphorous along with nitrogenous compounds and antimony with halogen compounds due to their synergism are also quite popular. Later on, environment-friendly flame retardants, such as urea and ammonium sulfamate, BTCA-hydroxyalkyl organophosphorus, and SMSN, have been developed. The emerging nanotechnology has been explored for similar applications using a number of nanoparticles, such as silica, ZnO, TiO₂, nanoclay, and CNTs. These materials were applied in the textile by layer-by-layer technique or as a polymer coating. Plasma technology has also been used to impart flame retardancy in the textile without usage of water or to accomplish multifunctional finishes in a single step. For example, monomers of acrylate phosphate and phosphonate derivatives in combination with carbon tetrafluoride (CF₄) were used to impart flame-retardant and water-repellent functionalities simultaneously. A majority of present-day flame-retardant formulations have the following disadvantages: (1) formaldehyde release during processing, (2) toxicity from some of the halogen-based compounds, (3) presence of heavy metals, (4) reduction in fabric tensile and tear strength, (5) increase in fabric stiffness and coarseness, (6) yellowing of color, and (7) nondurability. To address some of these issues and in the context of environmentally friendly, sustainable product development in recent years, various biomolecules have been used for flame-retardant finishing of textiles, such as DNA from herring sperm and salmon fish, whey proteins, casein, and hydrophobins. Similarly, BPS, an agricultural residue, and SJ, a vegetable extract, have also been applied on cotton and jute fabrics due to their advantages of low cost and being produced from renewable sources. After application of these plant molecules, the LOI was found to increase to over 30 from 18 and 21 in the untreated cotton and jute samples, respectively. In addition to flame retardancy, they could also impart UV protection and natural color to the textiles. The flame-retardant textiles will provide much longer time either to extinguish the flame or to escape from the fire zone. In spite of several such developments, the majority of flame-retardant formulations still lack the requisite durability to rainwater and/or soap washing, which needs to be addressed on priority. It is felt that the extraction and application of various plant molecules and other biomolecules for flame-retardant finishing of textiles will help to develop eco-friendly green textile products while ensuring much needed value addition to agro-residues.
REFERENCES


