Abstract: This chapter is a brief review of research and developments in the field of flame retardant textiles. The review focuses mainly on the currently available flame retardant solutions for different kinds of textiles. It gives insights into the general mode of action of flame retardants, types of flame retardant fibers, flame retardant additives for fibers and surface treatments and standard test methods for flame retardant textiles. The existing commercial flame retardant treatments for textiles are over 50 years old and some of them have created environmental concerns. Over the past few decades there have been considerable developments in inherently flame retardant synthetic fibers but effective and environmentally friendly flame retardant coatings or finishing solutions for textiles still elude us.

Key words: flame retardant, inherently flame retardant fiber, textile, phosphorus, polymer.

5.1 Introduction

Textiles are manufactured from fiber forming natural polymers such as cellulose and protein and a wide variety of synthetic polymers such as polyesters, polyolefin, polylactide, polyamides, polyaramids, polyetherketones, polyacrylonitrile and cellulose acetate. All of these polymers are suitable for use in textiles because of excellent fiber-forming properties, but they share a common problem, namely that most of them are combustible under normal environmental conditions and pose serious fire hazards in case of fire accidents. These organic polymers are a rich source of hydrocarbons and thus they are an excellent source of fuel during the burning process. The term ‘flame retardant textiles’ usually refers to textiles or textile-based materials that inhibit or resist the spread of fire. The hazards and risks associated with textiles are well documented elsewhere (Horrocks, 2001) and will not be discussed in this review. Flame retardant textiles find use in various areas such as (a) manufacturing of uniforms for fire fighters (Prezant et al., 1999), military/police personnel (Adanur and Tewari, 1997; Duran
et al., 2007; Rodie, 2008) and industrial workers; (b) high-performance sports applications (Stegmaier et al., 2005); (c) upholstery for home furnishing (Kamath et al., 2009), office/commercial infrastructure and transportation (Flambard et al., 2005); and (d) sleepwear for children and elderly people (Horridge and Timmons, 1979; Horrocks et al., 2004). Flame retardant (FR) textile materials help save lives, prevent injuries and property losses and protect the environment by helping to prevent fires from starting and limiting fire damage. Flame retardant textiles can be constructed from inherently flame retardant fibers such as Nomex, Kevlar, wool, Trevira CS, modacrylics, melamine fibers and polyvinyl chloride (Marsden, 1991; Weil and Levchik, 2008). Alternatively, flame retardant textiles can also be manufactured either by surface treatments with flame retardant compounds with various chemistries or by incorporating fire retardant additives in polymer bulk before fiber spinning.

5.2 Factors affecting flammability and thermal behavior of textile fibers and fabrics

The flammability of a textile material is a very complex phenomenon and depends on many factors such as the polymer itself, construction of the textile (i.e. weave/knit of fabric, yarn construction), weight/unit volume, additives in the fiber, the type of chemical treatments and the test conditions (Nair, 2000; Ozcan et al., 2003). All textiles can burn provided they are exposed to the right conditions of flame, heat, oxygen concentration and time of exposure to flame.

5.2.1 Fabric construction

In flammability tests, the inherent resistance of polymers to burning was the major factor affecting fabric performance with weight, weave and thickness being secondary. Fabric structure, weight and thickness were more important when measuring thermal protective capability. A combination of fiber non-flammability and optimum fabric structure should be used to achieve maximum non-flammability with the lightest weight for the specific fabric application (Barker and Brewster, 1982; Ross and Stanton, 1973).

Availability of oxygen is a critical factor in determining the flammability of a fabric. The construction of a fabric can play an important role as it determines the amount of air present, the active surface area and the flow of air through the fabric (Hendrix et al., 1972). Fabrics with open constructions may be more combustible and the flame propagation will also be faster. A fabric with raised surface (e.g. fleece-style fabrics, flannelettes and terry toweling) and containing fiber protruding out to the surface needs special care during processing and use. The flammability hazard with raised fiber
surface fabrics involves the phenomenon called ‘surface flash’ whereby a flame can travel rapidly over the fabric surface, singeing the fiber ends. This flash, in itself, may not be dangerous unless the intensity of the flame is sufficient to ignite the base fabric. In testing, this is known as timed surface flash with base burn. The twist of a yarn may also affect the porosity of the fabric. A tightly woven fabric with higher density, constructed from yarns with high twist will provide better flame protection. Fabric blends can also play a crucial role in defining the flammability of fabrics. Blends of fabric made from two different fibrous polymers may show flammability characteristics quite different from what is exhibited by each component of blend independently. For example, fabrics made from polyester are less flammable than cotton fabrics, but polyester/cotton blended fabrics burn more rapidly. This is because of the ‘scaffolding’ effect, where the charred cotton in the blend acts as a support for the polyester fibers. The melting polyester in the blend does not drip away as it may do in 100% polyester fabrics, and continues to burn (wicking effect). The flammability and thermal shrinkage are relatively independent of the fabric weight and weave design and primarily dependent on the thermal stability of component fibers (Minister of Health, 2009; Stepnica and Dipietro, 1971).

5.2.2 Type of textile fiber

The fibers used in textiles may be broadly classified based on natural polymers or synthetic polymers. Cotton, wool, silk and flax are some of the major natural textile fibers while viscose, Tencel™ and cellulose acetate are derived from natural polymers. The synthetic textile fibers owe their origin to several polymer classes such as polyester, polyamide, polycrylonitrile, polyolefins, polylactide, polyaramid, melamine based, polyurethane, etc.

The flammability properties of the textile fibers differ and can be grouped based on their burning characteristics into the following (Minister of Health, 2009):

- Readily flammable: these fibers ignite readily and burn rapidly, leaving a light ash residue (e.g. cotton acetate, triacetate, rayon and ramie).
- Moderately flammable: these fibers are more difficult to ignite. The synthetics tend to melt and drip, sometimes self-extinguishing upon removal of the ignition source (e.g. acrylic, nylon, polyester, olefin and silk).
- Relatively non-flammable: in general, these fibers will not support combustion after removal of the ignition source (e.g. wool, modacrylic, vinyon and aramids).

Burning behavior of fibers is related to the thermal transition temperatures and thermodynamic parameters such as glass transition temperature ($T_g$)
and melting point ($T_m$). Chemically related transitions such as temperature for onset of pyrolysis ($T_p$) and combustion ($T_c$) are also very important. The lower the $T_c$ values and the higher the flame temperature, the higher is the flammability of a fiber. The limiting oxygen index (LOI) of fibers is also an important property which determines the flammability of the fibers. Fibers with LOI values greater that 21% burn slowly and LOI values of 26–28% are sufficient to pass small burning tests. The thermal and flammability properties of fibers are discussed in detail elsewhere (Horrocks, 2001; Stegmaier et al., 2005). All cellulose-based fibers have very low LOI values (<19%) and are thus easy to burn. Among the natural fibers wool has relatively high LOI value (approx. 25%) and is a common component in manufacturing flame retardant clothing for firefighters in some countries such as Australia. Another criterion which determines the flammability of fibers is the heat release rates of fibers (i.e. the speed at which the heat is released during thermal decomposition) (Horrocks, 2001; Yang et al., 2009). Peak heat release rates of some common fibers like cotton, rayon, cellulose acetate, silk, nylon, polyester, polypropylene, acrylic fibers, Nomex and Kevlar have been recently measured using micro-scale combustion calorimetry. Cellulose-based fibers, polypropylene, nylon and polyester have relatively high peak heat release rates (>200 W/g) whereas m-aramid (Nomex), a commonly used fiber in manufacturing flame retardant fabrics, has very low values (~80 W/g) (Yang et al., 2009).

### 5.2.3 Thermal behavior of polymers

The polymer composition of the textile materials is the most important factor determining their flammability. Understanding the thermal behavior of polymers alone and in the presence of additives is useful in designing an effective flame retardant system. Subjecting polymers to elevated temperatures may lead to several physical and chemical changes which are related to the physical and chemical structure of the polymer. Physical changes like $T_g$ and $T_m$ are quite important in case of thermoplastics and may also influence the flammability of the polymers. Details of physical changes for polymers commonly used in textiles are discussed elsewhere (Hirschler, 2000; Horrocks, 2001). Thermoplastic polymers like polyesters have $T_m$ values much lower than the decomposition temperature ($T_d$) values, and thus tend to become fluids before they start to decompose. This physical property of the polymer greatly influences its fire performance. Under certain fire tests where the flame source is static, such as LOI and vertical flammability tests, once the polymer is subjected to flame the polymer melts away from the flame and stops burning. Thus one has to be careful in determining the real fire performance of polyester-based textiles.
Thermal decomposition of polymers leads to extensive changes in the chemical structure of the polymer, whereas the thermal degradation of a polymer may lead to the loss of physical, electrical or mechanical properties of the polymer. When a polymer is subjected to a temperature greater or equal to $T_p$ or $T_c$, the polymer chains start to break up into smaller fragments, some of which could be volatile flammable products. These flammable products break down further to finally release hydroxyl (OH$^\cdot$) and hydrogen (H$^\cdot$) radicals, which will combine with oxygen to release heat and light. The resultant heat could be released to the environment or could feed back into the burning cycle to cause further decomposition of the polymer. The burning process is a feedback process and will continue until the whole polymer has been consumed. The presence of flame retardant additives or absence of oxygen could interrupt this feedback process. The thermal decomposition of polymer is a very complex phenomenon and could lead to formation of several products such as flammable volatiles, non-flammable volatiles and solid residues. The flammable volatiles could be low molecular weight alkanes, alkenes, alkynes, aldehydes, ketones, ethers, etc. Water vapor and carbon dioxide are commonly formed non-combustible gases. The solid residue could be carbonaceous or inorganic in nature or even a combination of both (Horrocks, 2001). Some polymers like cellulose (wood), protein (wool) or aramids (Kevlar) tend to form carbonaceous chars upon heating. Some, like olefins, polyester and polyamides, do not leave any residues. Presence of additives may influence the amount of residue formed during the thermal decomposition process. Some phosphorus-based compounds would react with the substrate to accelerate formation of char. Presence of inorganic additives like silica derivates can form protective glassy layers which could insulate the inner layers from further decomposition.

Thermal decomposition of polymers can happen via one or more of the following routes (Hischler, 2000):

(a) random-chain scission where chain breakage happens along the chain length at random places;
(b) end-scission: the scission of polymer happens at the chain end mainly in the form of monomers;
(c) chain stripping: the main polymer chain remains more or less intact with removal of atoms or groups linked to the backbone;
(d) cross-linking: new bonds are formed between functional groups of adjacent chains.

Most of the vinyl polymers break down via routes (a) and (b) whereas route (c) is more common for halogenated olefins and acrylonitriles.
5.3 Types, chemistry and mode of action of flame retardant additives

Flame retardant additives used in textiles can be classified according to their elemental composition or their mode of action. Flame retardant additives are typically made up from compounds containing elements such as (i) phosphorus (in various organic and inorganic forms); (ii) halogens (brominated, chlorinated organics, fluorides of zirconium); (iii) silicon (organic or inorganic forms); (iv) boron; (v) metals (hydroxides of Al, Mg, Ca, phosphates of Al, Zn and Ca and Zinc borates, fluorides of zirconium); (vi) nitrogen (either alone or together with phosphorus, inorganic or organic); (vii) antimony (oxides together with halogens).

Flame retardant additives can also be grouped by their mode of action, i.e. gas-phase action and condensed phase action.

(a) Gas-phase action is characterized by evolution of reactive species during the burning process. This action is mostly exhibited by halogen (Georlette et al., 2000) and phosphorus-based flame retardants (Brauman, 1977; Huang et al., 2008). The reactive species could be radicals of halogen (X•) or phosphorus derivatives which act as free radical scavengers in the vapor phase. Halogen-based flame retardants may release halogen radical which may form hydrogen halide (HX) by abstracting hydrogen from the flame retardant (RX) or the polymer (PH). The hydrogen halide may react further with the hydrogen and hydroxyl radicals (reactions 5.1 and 5.2, respectively) formed from decomposition of polymers and thus interfere with the burning cycle.

\[
\text{HX} + \text{H}^\cdot \rightarrow \text{H}_2 + \text{X}^\cdot \quad \text{[5.1]}
\]

\[
\text{OH}^\cdot + \text{HX} \rightarrow \text{H}_2\text{O} + \text{X}^\cdot \quad \text{[5.2]}
\]

Flame retardant activity of halogen compounds can be further enhanced (synergistic interaction) by addition of antimony compounds (Sb₂O₃). This may be because of the formation of volatile antimony halogen compounds such as SbX₃, which act as an efficient inhibitor of the gas-phase oxidation in the flame (Camino et al., 1991).

Certain phosphorus species have also been found to have gas-phase action. Using direct mass spectrometric investigations of flames, researchers have identified phosphorus species like PO, HPO₂, PO₂ and P₂ with PO being the major constituent. On the molecular basis, the phosphorus species act by third-body mechanism, catalyzing the recombination of hydrogen atoms according to equations [5.3] and [5.4] (Granzow, 1978).

\[
\text{PO}^\cdot + \text{H}^\cdot \rightarrow \text{HPO} \quad \text{[5.3]}
\]

\[
\text{HPO} + \text{H}^\cdot \rightarrow \text{H}_2 + \text{PO}^\cdot \quad \text{[5.4]}
\]
More recently the gas-phase mechanisms of trimethyl phosphate and triphenyl phosphate derivatives have been studied using Fourier-transform infrared spectroscopy (FTIR). Acidic intermediates (phosphoric acid and its derivatives) formed during the thermal decomposition could also have gas-phase action (Clive and Ed, 2000).

(b) Condensed phase action is characterized by the formation of a protective barrier between the pyrolyzing polymer and the heat source. This protective barrier/char is mostly formed by reaction of the flame retardant additive with the polymer during the thermal decomposition of the polymer. The reaction of flame retardant additive with the polymer is catalytic in nature and causes the decomposition of the polymer at lower temperatures. The action of flame retardant is such that it either changes the pyrolytic pathways of thermal decomposition or it could change the rate of formation of combustible materials. In case of hydroxyl-containing polymers such as cellulose, a large amount of water molecules are released by reaction of phosphorus acidic species with the cellulose. In some instances the phosphorus compounds decompose to form a polyphosphoric acid which forms a thermal insulation barrier on the surface of decomposing polymers (Granzow, 1978; Horrocks, 1983, 2006). The condensed phase action of phosphorus flame retardants could be further enhanced (P-N Synergism) in presence of external nitrogen additives such as urea, guanidine and melamine. The enhanced action of phosphorus flame retardant was attributed to possible chemical reactions between decomposed products of nitrogen additive and phosphorus compound to form a protective coating on the surface of char (Gaan et al., 2008).

(c) Other actions like intumescent and heat sink effects are also mechanisms by which some flame retardant systems work. Intumescent systems are characterized by formation of a foam-like thermal insulation barrier when exposed to flame. A typical phosphorus–nitrogen-based intumescent system consists of a blowing agent (nitrogen-containing compounds like urea, guanidine and melamine), acid source (phosphorus-based flame retardants capable of forming phosphoric acid during thermal decomposition) and char former (generally polyhydroxyl compounds such as pentamerithritol are used). The intumescent effect is due to the combined effect of charring (reaction of phosphorus flame retardants with polyhydroxy compounds), and foaming (evolution of gases like ammonia from nitrogen source) (Camino and Lomakin, 2006). During the burning process the gases evolving from the thermal decomposition of blowing agent get trapped in the char, which is being formed simultaneously, thus forming foam of char on the surface of the material. A heat sink effect is commonly exhibited by additives such as metal hydroxides (aluminum hydroxide) which decompose to release water at elevated temperatures. The heat sink effect could be due to several factors such as endothermic decomposition, heat absorption by
water formed and dilution of gases formed due to pyrolysis of polymers (Weil and Levchik, 2009).

5.4 Flame retardation of textile materials

Flame retardant textiles can be manufactured via the following routes:

(a) Using inherently flame retardant fibers

(i) Fibers from inherently flame retardant polymer. These kinds of flame retardant fibers owe their flame retardant property to the polymer. Aramids, polyimide, melamine, glass, basalt, halogen-containing olefins, oxidized polyacrylonitrile and polyphenylene sulfide-based fibers are some examples of inherently flame retardant polymers. Figure 5.1 shows chemical structures of inherently flame retardant polymers.

(ii) Fibers from polymers containing special flame retardant co-monomers. Modified polyester such as Trevira CS and modacrylics are common examples of fibers containing special monomers with flame retardant characteristics.

(iii) Fibers containing special non-reactive flame retardant additives. Viscose fibers such as Viscose FR® and Visil® are flame retardant cellulosic fibers containing very high concentration of flame retardant additives (~30%).

(b) Finishing or coating

Application of flame retardants at fabric stage by a finishing process and subsequent fixation by various techniques such as thermal and ammonia curing, UV and plasma polymerization, etc.

5.4.1 Fibers from inherently flame retardant polymers

Aromatic polyamides or aramids, which were first developed in 1960s, are one of the most commonly used polymers for developing flame retardant textiles now. These fibers find usage in manufacturing firefighters’ uniforms, uniforms for industrial workers, military clothing and accessories. Dupont, USA (Nomex® and Kevlar®), Teijin, Japan (Twaron®, Technora®, Teijiconex®) and SRO Group, China (X-Fiper®), Yantai Spandex Co. Ltd, China (Newstar®), Kermel, France (Kermel®) are some major manufacturers of different kinds of aramid fibers. Para-aramid fibers have high tenacity and tensile modulus, heat resistance and dimensional stability and find applications mostly in automotive brake pads and other friction materials, tire cords and protective clothing and are also used as alternatives to asbestos. Meta-aramid fibers are characterized by their long-term heat and flame resistance, and are favored for such applications as heat-resistant filters and
5.1 Inherently flame retardant polymers.
other industrial materials and fireproof clothing for firefighters. Details of aramid fiber production, application and properties can be found elsewhere (Rebouillat, 2001; Yang, 1993).

Melamine fibers are produced by Basofil Fibers LLC, Enka, NC and marketed under the trade name Basofil® Fiber (TNC Global Inc, 2010). Melamine fibers are manufactured from fiber-forming synthetic polymer composed of at least 50% by weight of a cross-linked melamine polymer. The cost of melamine fiber is comparatively low for similar properties. These fibers can operate at high temperatures; they have high LOI values and typically target hot gas filtration and safety and protective apparel markets. Melamine fibers are weak and generally need blending with stronger fibers such as aramids to improve their processing. The major application of melamine fibers is in areas of the bedding industry, upholstery manufacturing of seats for automobiles and aircrafts, protective clothing for firefighters and industrial workers and in the filtration industry involving high temperature applications.

While there are different kinds of commercial polyimide polymers, only some are used in manufacturing textile fibers. P84 is a polyimide fiber manufactured by Evonik fibers GmbH, Austria (Weinrotter, 1988). The polymer structure of this fiber is shown in Fig. 5.1. P84 polyimide fiber is derived from aromatic dianhydrides and aromatic diisocyanates and exhibits outstanding thermal stability. The polymer is non-melting and has a glass transition temperature of 315°C. This fiber finds application in different areas such as high temperature filtration, protective clothing, braided packing and insulating material (Evonik Industries, 2010). Fibers based on polyetherimide resin (Ultem®) have been recently developed by General Electric (Dris et al., 2008). GE’s Ultem® resin is an amorphous, high-performance polymer that exhibits outstanding high heat resistance, strength, modulus and broad chemical resistance. This fiber has a high glass transition temperature of 217°C, a relative thermal index (RTI) of 170°C, is inherently flame resistant and has a very low smoke evolution.

Polybenzimidazole (PBI) is an organic fiber with excellent thermal resistant properties and a good hand. The Federal Trade Commission definition for PBI fiber is ‘A manufactured fiber in which the fiber-forming substance is a long chain aromatic polymer having recurring imidazole groups as an integral part of the polymer chain’. PBI does not burn in air and does not melt or drip. PBI Performance Products Inc. is the world’s only producer of high-performance PBI fiber (Performance Products Inc, 2010). The high LOI coupled with its good chemical resistance and good moisture regain makes PBI an excellent fiber for fire blocking end uses such as safety and protective clothing and flame retardant fabrics. Its physical properties are relatively inferior, but PBI can be processed on most types of textile equipment. It blends well with other materials such as carbon and aramid fibers and is most often done for performance reasons as well as cost. PBI has
had significant success in the firefighters’s apparel market, where, blended in a 60/40 para-aramid/PBI mixture, it has become the standard ‘premium’ material. PBI’s characteristic gold color blends well with other materials for a pleasing appearance.

Glass fibers are made up on a basis of inorganic amorphous polymer and were commercialized in the late 1930s. They find application in insulation (glass batts in home insulation and industrial insulation in mats and fabric form) and are widely used in reinforcing thermoplastic composites in products from circuit boards to boat hulls. They are also used in the manufacturing of barrier fabrics for furniture and military applications and high temperature filtration applications.

Halogenated fibers based on modacrylics and polyvinyl chlorides find specialized uses in the development of home furnishings and industrial applications which need fire protection and excellent chemical resistance. These fibers owe their flame retardancy to the presence of chlorine and may liberate large amount of toxic gases during the burning process. Shrinkage problems in the presence of heat, corrosive monomers and environmental regulations make them less attractive nowadays.

Polyphenylene sulfide fibers are known for their moderate temperature resistance and excellent chemical resistance. The polymer is produced by several manufacturers such as Chevron Phillips Chemical Company LP (Ryton®) (Chevron Phillips Chemical Company LLC, 2008), Toboyo (Procon®), Toray (Toray PPS®) (Toray Industries, 2006) and Celanese (Fortron®). The low moisture regain of PPS often prevents its use in protective apparel; the fiber has an uncomfortable hand, but the good chemical resistance makes it very attractive for industrial applications, especially for filtration.

Poly-phenylene benzobisoxazole is a new high-performance organic fiber first introduced by Toyobo in 1999 as Zylon® (Zylon-Department, 2010). It possesses outstanding thermal properties and has almost twice the tensile strength of conventional para-aramid fibers. Its high modulus makes it an excellent candidate for composites reinforcement. PBO has a very high LOI value, more than twice the LOI of meta-aramid fibers.

Oxidized polyacrylonitrile fibers are partially carbonized fibers which can be further converted into carbon or graphite fiber when subjected to further carbonization in an inert atmosphere at high temperature (Rahaman et al., 2007). These fibers do not burn, melt or drip; instead, they char and self-extinguish. Oxidized polyacrylonitrile fiber is relatively weak and has limited abrasion resistance and is thus often blended with other high-performance fibers such as aramid, polyvinyl halide, PBI, flame retardant rayon and polyester fibers creating a strong durable product with excellent flame resistance (Smith, 2007). Zoltek corporation (PYRON®) manufactures oxidized polyacrylonitrile in different forms such as fibers, fabrics and felts (Zoltek Corporation, 2010).
Inherently flame retardant polyesters are commercially available from various manufacturers such as Trevira GmbH (Trevira CS®), Invista (Avora®) and Toyobo (Heim®). These kinds of fibers contain reactive organophosphorus additives based on phosphonic acid derivatives. Structures of various reactive co-monomers used in manufacturing commercial flame retardants are shown in Fig. 5.2. A phosphorus content of 0.7–1% is sufficient to achieve satisfactory levels of flame retardancy. The mechanism of flame retardant action of these phosphorus compounds may be due to reduction in melt viscosity caused by acid hydrolysis. The phosphorus atom in these polyesters could be an integral part of the main backbone or it could be present as a pendant group to the main chain. The positioning of phosphorus atom in the polyester does not have any effect on the flammability of the fiber, but it does affect the hydrolysis stability of the polymer. Studies have shown that the main-chain-type hydrolyzes about two times faster than the side-chain type (Maki et al., 2000). Further studies on reaction kinetics have shown that main-chain-type phosphorus-containing monomer like 3-(hydroxymethyl phosphinyl) propanoic acid (HMP) and 3-(hydroxyphenyl phosphinyl) propanoic acid (HPP) are effective flame retardants. The phosphorus-containing monomer 9,10-Dihydro-9-oxa-10-(2,3-dicarbonylpropyl)-10-phosphophenanthrene-10-oxide (DI) is also effective in flame retardancy.
phosphinyl) propanoic acid (HMP) showed higher chemical reactivity in esterification reactions than the side-chain-type monomer, 9,10-dihydro-9-oxa-10,2,3-dicarbonylpropyl)-10-phosphophenanthrene-10-oxide (DI).

In addition, for production of polyester having the same phosphorous content in commercial scale, it is more beneficial to apply HPP than DI, because of low input of FR due to low molecular weight (Seung-Cheol and Jae Pil, 2007). Polyesters with HPP in the backbone had a higher amount of ethylene glycol in the main chain, thus resulting in lower thermal stabilities. Highly sterically hindered DI was more stable against thermal degradation and alkaline attack, and the DI polyester showed similar stability to that of the normal polyester. For higher phosphorous content polymer production, it is profitable to adopt main-chain-type phosphorous FRs rather than pendant types, because of their lower molecular weight and higher reactivity (Yang and Kim, 2007). The polymer chain of main-chain-type polyester fiber is more flexible than that of pendant type; it adsorbs the dyestuff at lower temperatures and reaches exhaustion more quickly (Seung-Cheol and Jae Pil, 2008). More recently Neopentyl glycol and 3-(hydroxyphenylphosphinyl) propionic acid have been used as the third and fourth co-monomers to synthesize phosphorus-containing poly[(ethylene terephthalate)-co-(neopentyl terephthalate)] (PENT) with both flame retardancy (LOI, 25–34%) and low melting temperature (170°C) properties (Xin-Ke et al., 2009).

Fully aromatic polyester fiber (Fig. 5.3) developed by Celanese Acetate LLC and now manufactured by Kuraray Co., Ltd (Vectran®) (Kuraray America Inc, 2010) is one of the newest high-performance polymers used for manufacturing textile materials where high thermal and flame protection is important. Vectran HT® and Vectran UM® fibers exhibit high LOI values of 28% and 30%, respectively. These fibers are characterized by low smoke generation and don’t drip in vertical flammability tests (Beers and Ramirez, 1990).

Important physical and flame retardant properties of the above-mentioned high-performance synthetic fibers are given in Table 5.1. A detailed review of these properties can be found elsewhere (Greer, 2000-2002).
Melt additives

Adding flame retardants during polymer processing is the most widespread and efficient method of FR protection of polymeric materials, since this method does not require new equipment and is economically efficient. However, application of this method is limited by the requirements for an additive: it should be thermally stable up to 300°C under mechanical force for considerable time, should dispense easily and have a suitable melting point and a high degree of dispersion, without degrading or reacting detrimentally with the polymer (Lawton and Setzer, 1975). Halogen-containing organic compounds and organophosphorous compounds are the most commonly used flame retardant additives for poly(ethylene terephthalate) (PET) fibers. Halogen compounds are inert to polyesters under thermal conditions. All phosphorous organic compounds can produce phosphorus-containing acids like $\text{H}_3\text{PO}_4$, $\text{H}_2\text{PO}_3$, $\text{H}_3\text{PO}_2$, which can cause degradation of the polyester by hydrolysis, leading to reduction of mechanical stability. If phosphinates or other P-compounds are used alone or in combination with other flame retardants in polyesters, there is generally some degree of polymer degradation, and this has an adverse effect on the mechanical properties of the polymer system. The melt viscosity of PET is lowered by addition of these compounds. Halogen compounds, typically
hexabromocyclododecane (HBCD), were mainly used as a flame retardant for polyester fibers. However, the use of these compounds is being regulated, because they are persistent and bio-accumulative in nature. Use of many types of halogenated flame retardants, especially brominated compounds (2,2',4,4',5,5'-hexabromobiphenyl), are banned due to toxicity and environmental issues. Some cyclophosphazene derivatives have been developed in the past as melt additives for polyester fibers. Cyclophosphazene phenyl and phenoxy derivatives were incorporated (5–10%) into polyester fibers before spinning to impart flame retardancy without harming their dyeing properties. PET chips were melted at 280°C, combined with 60% hexaphenylnylcyclotrimiphosphazene and spun into yarn which was self-extinguishing in nature (Clutter, 1975). Salts of phosphinic acid have been developed as an additive for thermoplastic polyester (Schlosser et al., 2008; Yao et al., 2006). The FR polyester fibers have been produced by the incorporation of FRs using blending or copolymerization (Levchik and Weil, 2004, 2005). A dialkylphosphinate salt has been recently introduced as a melt spinning additive in polyester (Weil and Levchik, 2008). The availability and commercial success of most of these phosphorus-based non-reactive melt additives are not known yet. Flame retardant polyester fibers are manufactured mostly from reactive additives or monomers containing a phosphorus component.

Unlike polyester fibers there are no inherently flame retardant fibers from polyamides that are commercially available. There are different kinds of polyamide in commercial use. They vary in their melting points: PA6 (220°C), PA6.6 (260°C), PA6.10 (240°C), PA6.12 (218°C), PA11 (198°C) and PA12 (178°C). There is a temperature range of about 60°C between the melting points which gives the possibility to use different thermo-stable flame retardant additive systems for melt-spun fibers. Other polyamides like thermoplastic fibers, even when flame retarded using either co-monomeric, modifications or additives introduced during polymerization and/or fiber extrusion stages, melt drip and/or form holes when exposed to flame. They cannot, therefore, be used in applications such as protective clothing and barrier textiles, where sustained thermal protection via char formation is an essential requirement (Horrocks, 1996). Some additives like low molecular weight phosphorous compounds, chlorinated polyethylene, brominated pentaerythritol, boric acid and antimony oxide have been used in the spinning dope of polyamides. Calcium zinc molybdate (KemGard 425, Sherwin-Williams Company) and a mixture of brominated pentaerythritol, antimony oxide and boric acid were introduced to nylon 6 melt without change of physical mechanical properties. Melt extrusion of nylon 6 at 230°C with red phosphorous has been reviewed elsewhere (Subbulakshmi et al., 2000). Compounds such as phosphorylated pentaerythritol, lead methylphosphonate and a complex compound of an alkylphosphonic acid and antimony have been investigated as thermally stable flame retardant additives for
fibre spinning (Butylkina et al., 1989). Ammonium polyphosphate (APP) has been applied on different kinds ofnylons and thermal decomposition and flame retardant behavior have been studied in detail. During the burning process APP acts as an intumescent agent and also forms a thermally stable polyphosphoric acid layer on the surface of decomposing polymer (Levchik et al., 1994, 1995). Resorcinol bis(diphenyl phosphate) and bisphenol A bis(diphenyl phosphate) have been used as fire-retardant additives on nylon 6 and nylon 6,6. It was shown that aromatic phosphates promoted charring of the nylons, but the char yield was insufficient to rapidly extinguish the flame (Levchik et al., 2001).

Recently phosphinic acid derivative additives have been developed as melt additive for application on nylon fibers (Yao et al., 2006). In spite of much research and development in flame retardant melt additives, there exist no successful commercial flame retardant additives for nylon melt spinning.

Polyolefin fibers are traditionally made flame retardant by adding brominated additives containing antimony or phosphorus (Zhang and Horrocks, 2003). These brominated flame retardants may adversely affect the light stability of olefins and also have shown to have adverse environmental effects. Tris (tribromoneopentyl) phosphate is a thermally stable, effective flame retardant additive for polypropylene fibers. More recently halogen- and phosphorus-free flame retardant has been introduced by Ciba (Flamestab® NOR™ 116). It requires an addition of 1–1.5% to achieve some degree of flame retardancy (Weil and Levchik, 2009).

**Additives for wet spun fibers**

Flame retardant viscose fibers such as manufactured by Lenzing, Austria (Viscose FR®) and Sateri International Group (Visil®) are the only inherently flame retardant fibers developed from cellulose. Both these fibers use different technology to achieve flame retardant property. Viscose FR® is made by incorporating ~30% organophosphorus-based pigment additive whereas Visil® fiber contains up to 35% SiO₂ as a flame retardant additive. The development of flame retardants for viscose is very challenging as the flame retardant has to withstand severe alkaline and acidic conditions during the fiber manufacturing process. Studies on several kinds of phosphorus-based flame retardants have shown that 1,3,2-dioxaphosphorinane, 2,2’-oxybis 5,5-dimethyl-, 2,2’-disulfide (Fig. 5.4) is the most suitable flame retardant additive for viscose fiber (Wolf, 1981). This compound is a white pigment, practically insoluble in water and very stable to acid and alkaline hydrolysis. It is currently manufactured by Clariant and sold under the trade name Exolit 5060. Visil fibers are manufactured by adding sodium silicate in the alkaline spinning solution and regenerating it as polysilicic acid in the coagulating bath.
5.4.3 Application of flame retardants on fabrics by finishing treatments

Application on synthetic fiber fabrics

Synthetic fabrics made from nylon, polyester and acrylic fibers are difficult to ignite but once ignited they exhibit severe melting and dripping. Nylon fabrics are commonly used in manufacturing of fabrics for military applications, upholsteries and carpet, because of their excellent mechanical property. Several flame retardant treatments based on brominated compounds, thiourea formaldehyde resins (Horrocks, 2003) and cyclic phosphonate esters have been discussed in the literature (Weil and Levchik, 2004). Back coating formulations containing polyvinyl chloride, chloroparaffin wax emulsions, brominated flame retardants and antimony oxides with polymeric binders were also suggested in the literature (Weil and Levchik, 2004). Treatments of nylon–cotton blended fabrics with hydroxyfunctional oligomers have also been reported. Durability of the treatments (up to ten laundry cycles) was ensured by the use of melamine- and urea-based cross-linkers. The treatments improved the char formation and reduced the decomposition temperature and heat release rates of the fabrics (Yang et al., 2009). Treatments with urea formaldehyde resin and brominated compounds lead to very high LOI values, but the treated fabrics could not pass vertical flame tests due to enhanced dripping effect. Non-durable anti-dripping flame retardant treatments of nylon 6,6 fabrics have been obtained by the use of intumescent formulations containing pentaerythritol and melamine (Li et al., 2009). Hydroxymethylation of nylon 6 fabrics with formaldehyde and subsequent treatments with N-methylol-3-(dimethoxy)phosphonopropioamide resulted in increased LOI values (Kang De et al., 1992).

Polyester fabrics owing to unavailability of reactive functional groups are difficult to make flame retardant by conventional finishing treatments. The most common method for making flame retardant polyester is by applying either phosphorus or halogen-based flame retardants by the thermosol method (Weil and Levchik, 2008). The fabrics are generally treated with aqueous solutions of flame retardants (2–15%), dried at around 100°C and cured at 185–195°C (knitted fabrics) or 190–205°C (woven fabrics).
for 120–160 s. Durable flame retardant treatments can be obtained by this method. The flame retardants are believed to diffuse into the soft polymer during the curing operation. Once the fabrics are cooled, the flame retardant gets trapped and excess flame retardant on the surface is washed off. A common phosphorus flame retardant composition for polyester fabric is a mixture of cyclic phosphonate compounds (Fig. 5.5) and is sold as Kappaflam P 31 by Kapp-Chemie GmbH, Germany. Diphosphonate products are also available from Thor (Afflamit) or Zschimmer & Schwarz (Flammex). They are slightly acidic in nature, therefore an application solution needs buffering of the pH to 6.5. Usually a final fixation of 1.5% of the compound is quite sufficient to achieve satisfactory flame retardancy. Halogen-containing novel organophosphorus compound such as dichlorotribromophenyl phosphate (DCTBPP) has been synthesized and applied to polyester fabrics by thermosol method to obtain self-extinguishing fabrics with durability up to 50 laundry cycles (Yoo-Hun et al., 2001). A novel anti-dripping flame retardant, poly(2-hydroxypropylene spirocyclic pentaerythritol bisphosphonate) (PPPBP) was synthesized and applied by the thermosol method to impart flame retardancy and dripping resistance to PET fabrics (Chen et al., 2005). Polyester fabric has also been treated with inorganic salts like sodium polymetaphosphate (Mostashari, 2007) and ammonium chloride to achieve non-durable treatments which could pass vertical flammability tests (Mostashari and Mostashari, 2008).

Polyacrylonitrile fabrics unlike modacrylics are rarely used for manufacturing fabrics which might be of use in areas that require flame protection. Nevertheless, one can find several research articles related to flame proofing.

5.5 Cyclic phosphonate compounds for thermosol application.
of polyacrylonitrile fabrics with various phosphorus- and halogen-containing compounds. Several compounds such as decabromodiphenyl oxide and ammonium bromide, urea and phytic acid, hydrazine hydrate, hydroxylamine sulfate, and metal salts have been used as flame retardants (Bajaj et al., 2000). More recent investigations have shown that polyacrylonitrile fabrics can be made flame retardant by grafting of acrylic-based organophosphorus compounds using environmentally friendly plasma technologies. In this research argon plasma-induced graft polymerization of four acrylate monomers containing phosphorus, diethyl(acryloyloxyethyl)phosphate (DEAEP), diethyl-2-(methacryloyloxyethyl)phosphate (DEMEP), diethyl(acryloyloxymethyl) phosphonate (DEAMP) and dimethyl(acryloyloxymethyl)phosphonate (DMAMP) was performed. The treatments resulted in moderate flame retardant properties for the fabrics with limited durability to several laundry cycles (Tsafack and Levalois-Grützmacher, 2006).

**Application on natural fiber fabrics**

Attempts to impart flame retardant properties to cellulose- and protein-based natural fibers have been made since the early nineteenth century. Since then considerable efforts have been made to develop newer flame retardant solutions for these natural fibers. Production of flame retardant cellulose-based textiles has been the most challenging task. Cellulose is a natural polymer and exists in different fibrous forms such as cotton, jute and linen. The only way to produce fire-resistant cellulosic textiles from these fibers is via a chemical finishing treatment. The intrinsic properties of textiles like the tensile strength, tactile properties, air permeability and dyeability should not be affected by the treatment. Moreover, the flame retardant should meet health requirements and not produce toxic gases when burned. It is also important that the flame retardant treatment should last at least 50 industrial washing cycles. These requirements make the development of flame retardants for cellulosic fibers very challenging. Textiles made from natural fibers like cotton and silk are highly flammable whereas wool-based textiles are self-extinguishing in nature. The LOI values of untreated cotton, silk and wool are 18.4, 22.8 and 25, respectively (Horrocks, 2001).

Finishing treatments for *cellulose-based textiles* can be grouped into the following:

(a) **Finishes with inorganic phosphates**

Examples of inorganic salts that are used as flame retardants for cellulose are ammonium phosphates, polyphosphates (Fig. 5.6), bromides and borate-boric acid mixtures.

Typically, 1–2% of the phosphorus content relative to the weight of the fabric is enough to obtain flame retardant cotton. Ammonium bromide can also be used in combination with ammonium phosphates to provide
some vapor-phase flame retardant action, particularly helpful for blends (Chellapa and Shah, 1989; Davies et al., 2002). Ammonium sulfamate or sulfate is also included in some ammonium phosphate formulations (Weil and Levchik, 2009). The use of APP is reviewed in the literature (Davies et al., 2005; Horrocks, 2003). Attempts have also been made to achieve durable coatings on cellulose by using these organic salts (Hawkes et al., 2009; Webb et al., 2007). Monoguanidine dihydrogen phosphates (Fig. 5.7) and diguanidine hydrogen phosphate are further examples of phosphates used for non-durable cotton treatment (Vroman et al., 2004). Some flame retardants like Flovan® CGN (Ciba), Flammentin® FMB (Thor Specialities) and Pyrovatim® PBS (Weil and Levchik, 2009) have been used to produce semi-durable coatings. Treatments with these flame retardant agents will survive water soaking or leaching to various degrees, but have poor stability to laundering. Semi-durable finishes with these inorganic phosphates are not durable to alkaline laundering conditions. When phosphoric acid groups are chemically attached and neutralized by ammonium cations, the finish can become fairly durable to water washing.

(b) **Finishes with organophosphorus compounds**

The two most successful products with more than 60 years’ history for flame retardation of cellulose are Pyrovatex® CP (Ciba) and Proban® CC (Rhodia). The basic molecule in Pyrovatex formulation is 3-(dimethylphosphono)-N-methylolpropionamide (DMPMP) (Fig. 5.8), and in Proban – tetra-kis (hydroxymethyl) phosphonium chloride (THPC) (Fig. 5.8). Durable
treatments of DMPMP on cellulose-based fabrics are generally obtained by the use of a formaldehyde-based cross-linker such as melamine formaldehyde. Presence of formaldehyde in DMPMP and the cross-linker creates environmental problems during the application process due to the release of formaldehyde fumes. Formaldehyde may also be released during the subsequent use of the treated fabric. Fixation of THPC on cellulosic textiles requires the use of patented ammonia curing process which limits its widespread usage. These compounds are presently the best solutions for flame retardant finishing of cellulose-based textiles.

Recent studies on the flame retardant action of DMPMP have shown that it has superior action to some phosphates and phosphoramidate compounds. The superior action of DMPMP has been attributed to the formation of acidic intermediates during the thermal decomposition process, which could further catalyze the char formation of cellulose (Gaan and Sun, 2007a). DMPMP treated cotton has higher activation energy of decomposition, higher char content, lower heat of combustion and forms a protective coating on the char surface (Gaan and Sun, 2007b). Application of THPC as a flame retardant on cellulose-based textiles has been extensively investigated by many researchers. THPC was applied together with urea and melamine on cotton, cotton–polyester blends and viscose to obtain finishes which could withstand 20 laundering cycles (Donaldson et al., 1973, 1975; Guthrie et al., 1955; Hamalainen et al., 1956; Reeves and Guthrie, 1953, 1954; Reeves et al., 1957).

Recently the use of oligomeric hydroxyl functional organophosphorus compound has been investigated in durable flame retardant finishing of cellulose (Fig. 5.9). HFPO has been used to make flame retardant cotton and cotton/nylon blends (Yang and Wu, 2006). In this study HFPO was shown to significantly lower the thermal decomposition temperature of cotton and increases the amount of char formed during the burning process. HFPO was used in combination with various cross-linkers such as trimethylolmelamine and dimethyloldihydroxyethyleneurea. The cotton fabric treated with this system maintained satisfactory flame retarding performance (LOI more than 29%) after 40 home laundering cycles (Stowell and Yang, 2003; Yang

5.8 Organophosphorus flame retardants for durable treatment on cellulose.
Numerous studies have been performed in order to improve the durability of the chemical finishing to washing. Eco-friendly cross-linkers such as multifunctional carboxylic acids (phosphorus-containing maleic acid, polycarboxylic acids) have also been used as finishing agents for cotton since the late 1980s (Blanchard and Graves, 2002, 2005; Welch, 2001; Wu and Yang, 2008).

Developments in organophosphorus flame retardants for cellulose have focused on novel phosphoramidate compounds (Gaan et al., 2009b). Phosphoramidates have been shown to have superior flame retardant action to the analogous phosphates (Gaan et al., 2009a). Phosphoramidates with hydroxyl terminating alkyl groups (Gaan et al., 2009a; Rupper et al., 2010) and methyl ester phosphoramidates have been shown to have superior flame retardant action (Gaan, 2008).

(c) Flame retardancy with sulfur derivatives

The sulfur derivatives are used mainly for treating cellulosics with ammonium, aluminium or other metallic sulfates and produce limited non-durable flame retardant coatings. Sulfation treatments with urea sulfamates yielded fabrics that withstood 50 hard and soft water launderings. However, the treatments suffered from drawbacks like reduced tensile strengths and after-glow effect (Lewin, 2005).

(d) Grafting flame retardant monomers to cellulose

Some attempts have been made to develop flame retardant cellulose by chemical graft polymerization techniques. Methacyrloyloxyethyl orthophosphotetra ethyl diamidate was used as flame retardant for graft polymerization on cellulose. Durability to about 50 washing cycles has been achieved by varying the parameters of graft polymerization (Abdel-Mohdy, 2003). Other researchers have used radiation graft polymerization technique to flame retard cotton fabrics. Orthophosphoric acid was used as a flame retardant, where the treatments had limited durability (Reddy et al., 2005). 4-Vinyl pyridine has been used as flame retardant with benzophenone as photoinitiator for grafting onto cellulose fabrics using UV radiation.
technique. The thermogravimetric analysis (TGA) of the grafted fabrics showed lower decomposition temperatures with slight increase in char yield (Kaur et al., 2007a). Methacrylamide has also been grafted onto cotton with the use of low energy UV irradiation technique to introduce functionalities that can react with phosphorus-containing compounds to impart flame retardancy. Subsequent phosphorylation of grafted fabric showed improved flame retardant behavior in comparison to grafted fabric (Kaur et al., 2007b). More recently plasma technology has been used as an environmentally benign technique to produce flame-resistant textiles. Grafting and polymerization of fire-retardant monomers on the cotton fabrics have been carried out using microwave argon plasma to produce durable flame retardant coatings (Tsafack and Levalois-Grützmacher, 2006, 2007). It is postulated that the flame retardant properties of treated cotton depend primarily on the structure of the FR monomer and not on the phosphorus content of the fabrics. The durability of the coatings obtained has been attributed to the covalent bond formed between flame retardant molecule and cellulose during plasma-induced polymerization. Sodium silicate has been applied onto cellulose textiles using radio frequency low pressure non-equilibrium oxygen plasma to produce phosphorus-free fire-resistant fabrics. It was observed that samples treated in plasma withstood 50 laundering cycles due to the cross-linked structure of the coatings (Totolin et al., 2009).

Wool textiles have the highest inherent non-flammability and pass the required flame-retardancy tests untreated, because of its highly cross-linked chemical structure, high amino- and amido-nitrogen content (16%) and moisture content (10–14%). Hexafluorozirconate (Zirpro® treatment) has been the basis for the widely used and commercial flame retardant system for wool textiles, which was developed by Benisek in the early 1970s. The Zirpro® treatments act in the solid phase by producing char around the fibers. A detailed review of flame retardant treatments for wool is discussed elsewhere (Horrocks, 1986). In 2005 a new flame retardant for wool was introduced (Noflan®). It is based on amidoalkylophosphonic acid and contains about 14% phosphorus. It is claimed, that Noflan® enhances char formation in the solid phase, thus minimizing smoke and toxic gas emissions (Benisek and Andrews, 2004, 2005). In addition, Noflan® is an environmentally benign flame retardant, and can be applied by continuous pad-dry technique.

Silk is widely used in apparel and home furnishing for its luxurious appearance, soft handle, high wearing comfort and other desirable aesthetic appearances (Currie, 2001; Robson, 1998). Treatment of silk with a mixture of phosphoric acid resulted in high level flame retardancy (LOI more than 28%) with limited wash durability (Achwal et al., 1987). Pyrovatex CP has also been used to render silk flame retardant. Treated silk is claimed to have LOI values greater than 30%. The flame retardant properties were retained...
to some extent even after 50 washing cycles (Guan and Chen, 2006). Graft copolymerization of a vinyl phosphorus-based monomer such as DEMEP has also been carried out on silk fabrics. Treated silk fabrics were found to be stable to 30 hand washing cycles (Guan and Chen, 2008). Hydroxyfunctional organophosphorus polymer in combination with 1,2,3,4-butane tetracarboxylic acid has been used as a formaldehyde-free flame retardant finishing system for silk. Treated fabrics were claimed to be stable to 15 washing cycles (Guan et al., 2009). Metal oxides and salts such as antimony oxide, lead monoxide, manganese dioxide and ammonium chloride have also been used in flame retardant treatments on silk fabrics. Antimony oxide has been shown to have better flame retardant effect than lead monoxide (Tarafder and Singh, 2007).

5.5 Environmental issues related to flame retardants

During the last few decades the knowledge about toxicity and environmental impact of chemicals has rapidly grown and people have become more aware of potential dangers associated with them. A large number of flame retardant compounds are on special lists of national or international environmental committees because of their harmful properties. Many of these substances are either banned or their use has been restricted. Currently tetrabromobisphenol A (TBBPA), decabromodiphenyl ether (DecaBDE) and HBCD are the most widely used brominated flame retardants worldwide. DecaBDE is mainly used as flame retardant for plastic casing of electrical and electronic equipments, for furniture and textiles. TBBPA is mainly used in manufacturing circuit boards and plastics. HBCD is mainly used in expanded and extruded polystyrene insulations, textiles and to a lesser extent for plastic casings of electrical and electronic equipments (Ittershagen, 2008).

Scientific and political discussions have focused on these products because of their growing worldwide presence in sediments, dust in buildings, microorganisms, fish and animals such as polar bears, seals, raptors and their eggs and even in human blood, tissues and breast milk (D’Silva et al., 2004; Hardy et al., 2009; Kang et al., 2009; La Guardia et al., 2007; Lilienthal et al., 2009; Schecter et al., 2009; Smolarz and Berger, 2009; Stapleton et al., 2009; Uddin, 2003).

Environmental risks associated with pentabromodiphenyl ether (PentaBDE), octabromodiphenyl ether (OctaBDE) and DecaBDE, have been assessed in the recent past and resulted in an EU Directive (Official Journal of the European Union, 2003). This Directive prohibits the application and use of PentaBDE and OctaBDE. More recently (2008) the use of DecaBDE in electrical and electronic devices has been banned in Europe. In Norway and Sweden there are national prohibitions for the use of DecaBDE. The US EPA has recently (2009) reached an agreement
with three manufacturers of DecaBDE to voluntarily phase out its production and use in all consumer products by the end of 2013. Studies have shown that DecaBDE persists in the environment, potentially causes cancer and may impact brain functions. DecaBDE can also degrade to form more toxic by-products which are frequently found in the environment (Environmental Protection Agency, 2009). According to the new European REACH-Regulation, all persistent, bio-accumulating and toxic compounds will be assessed and their substitution by less hazardous chemicals encouraged. The basic goal of REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) is the protection of human health and the environment from the risks posed by chemicals (Kemmlein et al., 2009).

The following halogenated flame retardants for fireproofing garments are restricted (European Commission, 2008):

- tris(2,3-dibromo-1-propyl)-phosphate
- tris-(aziridinyl)-phosphinoxide
- polybrominated biphenyls.

The use of antimony trioxide as synergist together with halogenated-based flame retardants (e.g. in textile back coatings, flame retarded paints, rubber, textiles) is also under review within the European Union Commission. The International Antimony Association opposes the ban of antimony oxides under the European Union’s Restriction of Hazardous Substances (RoHS) regulation as there is no conclusive evidence regarding the toxicity or environmental impact of antimony oxides (International Antimony Association, 2009).

Local legislations in some countries may not be able to induce a broad sustainable protection of mankind and the environment as many chemicals remain unchanged in nature for a long period of time and may also spread over large regions of the planet. The Stockholm Convention with more than 160 member states will decide on the possible ban of POPs (persistent organic pollutants) which have shown toxicity and environmental risks (Secretariat of the Stockholm Convention, 2009). Thus stronger cooperation between countries and international organizations is required to tackle the problems associated with the use of harmful chemicals.

### 5.6 Test standards for flame retardant textiles

There are several kinds of standard test methods to determine the fire risks of textile materials. The use of any particular standard test method is based on the end use of the textile material and the country where the material is to be used. The test method generally outlines various specifications such as the type and size of a sample, source of the flame/heat, and duration of the application of the flame/heat to the substrate. Table 5.2 outlines several important test methods for various kinds of textiles.
### Table 5.2 List of standard test methods for flame retardant textiles

<table>
<thead>
<tr>
<th>Textile type</th>
<th>Standard test methods</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnishing fabrics</td>
<td>BS 5852: Pts 1 and 2: 2006</td>
<td>Cigarette and simulated match flame (20 s ignition)</td>
</tr>
<tr>
<td></td>
<td>BS EN 1021–1: 2006</td>
<td>Cigarette</td>
</tr>
<tr>
<td></td>
<td>BS EN 1021–2: 2006</td>
<td>Simulated match flame (15 s ignition)</td>
</tr>
<tr>
<td></td>
<td>BS 6807: 2006</td>
<td>Ignitability of mattresses or divans</td>
</tr>
<tr>
<td>Nightwear</td>
<td>BS 5722: 1991 AS1249</td>
<td>Small flame Australian Standard for children’s nightwear</td>
</tr>
<tr>
<td></td>
<td>BS ISO 12952–1/4: 1999 BS ISO 12952–2/3: 2001</td>
<td>Ignitability of bedding items by cigarette and small flame sources</td>
</tr>
<tr>
<td></td>
<td>France Decree 2000–164</td>
<td>French Standard for bedding (cigarette resistance)</td>
</tr>
<tr>
<td>Protective clothing</td>
<td>EN 533, NF P92 503 (M1), BS 7175 Crib 5</td>
<td></td>
</tr>
<tr>
<td>Carpet</td>
<td>DIN 4102(B1), FAR25–853</td>
<td></td>
</tr>
<tr>
<td>Non-woven</td>
<td>NF P92 503</td>
<td></td>
</tr>
<tr>
<td>Textiles in aircrafts</td>
<td>ASTM E 906 1983, uses Ohio State University heat release calorimeter</td>
<td>Irradiate under 35 kW/m² with small flame igniter</td>
</tr>
<tr>
<td></td>
<td>NF P 92501: 1995 French ‘M test’</td>
<td>Irradiate with small burner</td>
</tr>
</tbody>
</table>

## 5.7 References


