Update on Flame Retardant Textiles: State of the Art, Environmental Issues and Innovative Solutions

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Preface

This volume presents a view of flame-retardant textiles that several recently published texts on flame-retardant textiles and materials have not covered adequately although, of course, there will be some overlapping areas. The main differences lie in its detailed presentation and analyses of the strengths and weaknesses of the well-established commercial, durable flame-retardant technologies that exist in the textile sector. This major focus provides a platform against which current legislation and regulations that relate to specific flame-retardant textile applications are reflected with pressures from within the environmental sustainability areas. Furthermore, possible (and more realistic ways) of addressing these issues are considered instead of merely presenting comprehensive literature reviews within relevant areas.

Flame retardancy applied to textiles by various means is a ‘hidden’ property with respect to the user, unlike other value-adding treatments that promote advantageous and obvious properties during use (e.g., water repellency, crease resistance and soil release). Flame retardancy also differs in that, not only should its presence on a fabric or textile be virtually unobservable during normal textile or product use during the whole service life, but also its presence is usually because of legislation and/or regulation rather than customer demand.

Thus, in **Chapter 1**, we consider the need for flame retardancy *via* fire fatality and injury statistics and the legislation and/or regulations that follow at international and national levels. Several high-risk areas are identified, such as children’s nightwear, domestic and contract furnishings (including bedding) and textiles used in transport (where passenger safety and means of escape are clearly defined). This chapter concludes with a glossary of terms and their definitions that relate to flame retardancy.

However, if fire regulations are to be applied *via* standard test methods, an understanding of the basics of the fire-science principles of fibre-forming and related polymers must be presented, as well as those of flame retardancy. **Chapter 2** provides grounding in these principles for most textile fibres in use along with the generic mechanistic behaviours of the different types of flame retardants and their applicability to various textile fibre types.

The areas of application of flame-retardant textiles identified in **Chapter 1** coupled with an understanding of the fire science of textile materials in **Chapter 2** leads to **Chapter 3**, which reviews the most important and current legislation and regulations as they relate to products such as nightwear and furnishings at international (e.g., European Union (EU)) and national (e.g., EU member states, USA) levels. Fire regulations for textile materials in transport systems are considered within those defined by the relevant international bodies, such as the International Maritime Organisation and International Civil Aviation Authority. The standard test methods at international (e.g., International Organization for Standardization), European (e.g., European Standards (CEN)) and national (e.g., British Standards, American Society for Testing and Materials, Deutsche Institüt für Norms) levels required are discussed in terms of the regulations and applications that they serve. These same standards are also discussed in terms of the typography of their methodologies where, for example, simple fabric-burning tests are contrasted with composite tests, with tests in which additional radiant heat is applied, and with those tests designed specifically for thermal protection.

Chapter 4 reviews, in detail, durable flame-retardant finishing technologies used for cotton, wool and synthetic fibres and their blends. The strengths and weaknesses of each are considered alongside recent and planned changes made as a consequence of current regulatory (e.g., Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)) and environmental pressures.

Chapter 5 similarly reviews fibres (conventional and high-performance) that possess some level of inherent flame retardancy (and even fire resistance). Thus, commercial examples of additives or copolymeric modifications of the conventional man-made fibres are reviewed together with high-performance organic fibres that have chemical structures possessing inherent resistance to heat and fire. A final section reviews inorganic fibres that, while possessing some textile properties, find use in applications in which ambient temperatures may be >500–1000 °C.

The environmental as well as health and safety aspects of flame-retardant chemical treatments alluded to in **Chapter 4** are expanded further in **Chapter 6**. Here, in particular, recent research results only are considered that, in the authors' opinions, are more likely to lead to commercial solutions with regard to alleviating the more immediate concerns of use of formaldehyde and halogen in current flame-retardant formulations. Recent developments in risk analyses and their reduction as well as the effects of current regulations such as REACH are also considered.

Finally, the possible roles of nanotechnology in providing novel and environmentally sustainable flame-retardant textile solutions are considered in terms of nanostructured fibres (**Chapter 7**) and nanosurface treatments (**Chapter 8**). These are discussed in detail with regard to the recent research undertaken in these areas.

This whole composite work is designed, therefore, for those with a current professional interest in any aspect of flame-retardant textiles and fibres. These include textile and fibre technicians, technologists, scientists as well as legislators and regulators. Other potential users include those professionals involved in patent drafting, legislation and assessment, fire insurance and product design. Finally, this book will be invaluable to students at bachelor and postgraduate levels, as well as their teachers, lecturers and supervisors.

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1 Burning Hazards of Textiles and Terminology

A. Richard Horrocks

1.1 Introduction

The particular hazard posed by burning textiles, especially those based on the natural cellulosic fibres cotton and flax (as linen), was recognised during early civilisations. Salts such as alum have been used since those times to reduce their ignitability and so confer flame retardancy. These risks remain with us to this day as a consequence of the intimate character of most textiles, primarily as clothing, and in the immediate domestic environment, coupled with the high specific surface area of the fibre-forming polymers present, which enable maximum access to atmospheric oxygen.

Thus, the need for flame-retardant textiles has been recognised for many years. The significant patent of Wyld [1] in 1735, which described a finishing treatment for cellulosic textiles using alum, ferrous sulphate and borax, as well as Gay-Lussac's first systematic study of the use of flame retardants in 1821 [2], have formed the basis for the more recent and modern approaches to developing heat- and fire-resistant textiles.

The most significant developments have occurred since World War II (WW2), especially with the need to confer durability to laundering as a significant feature in addition to the underlying flame-retardant character. The period up to the late-1940s was significantly reviewed by Little [3] with an obvious focus on flame-retardant cotton because the newer synthetic fibres were still under development.

Between 1950 and 1980, there existed significant literature that was reviewed comprehensively during the mid-1980s [4, 5]. Hence, individual references during this period will not otherwise be referred to unless essential to the arguments within this chapter. It was in this post-WW2 period that the need to reduce fire-related fatalities and injuries became of greater importance as greater consumer safety awareness increased and governments took notice of the human and financial costs of fire in domestic and work environments. Coupled with this was the fact that greater personal wealth in the post-WW2 society enabled far greater use of textiles in the home and public buildings. with a consequential increase in their fuel loadings and fire hazard. These factors were the drivers for developing flame-retardant textiles for use in the domestic, public and work environments.

Since then, several comprehensive reports have critically reviewed research during this period and since then. This has led to the current armoury of commercial flame retardants available [6–8].

Even more recently, Horrocks has presented a historical perspective to reflect the challenges posed by the current socio-economic environment with the underlying research challenges addressed during the previous 70 years [9].

Analyses of the reviews mentioned above suggest that, up to 1970–1980, the established durable and flame-retardant treatments for cotton and wool fibres as well as those additives and comonomers introduced into regenerated fibres (e.g., viscose) and synthetic fibres (notably polyester, polypropylene and the modacrylics) during manufacture were synthesised and developed into commercially acceptable products. In fact, most of the currently available flame retardants for textiles and fibres reviewed very recently by Weil and Levchik [8] derive from chemical developments before 1980. These may now be termed ‘traditional’ flame-retardant textile technologies, and are discussed fully in **Chapter 4**.

1.2 Hazards of Burning Textiles

The need for fire-retardant textiles is related directly to the hazard posed by textiles and regulations imposed by governments. Hence, it might be said that the whole field is driven by regulation. Legislation and regulation are complex not only within a given country but often differ significantly between countries, even if similar textile fire hazards are being assessed. These will be considered in a general sense in **Chapter 2** because they relate to those textiles deemed to be particularly hazardous and so require levels of flame retardancy and fire resistance that deliver defined and acceptable levels of safety to humans and property in the 'developed' world. However, before regulations can be drafted, there is the need for reliable and comprehensive statistics relating to the cost of fire in terms of human life and property.

Across the world, very few comprehensive fire statistics exist, especially those that attempt to relate deaths and injuries to cause, such as the ignition and burning-propagation properties of textile materials. World Fire Statistics, for example, concentrate on the loss of life and financial losses caused by fire, and rarely consider the major causes at the material level [10]. National statistics are available for many nations. However, their mode of collection and details of substances differ from nation-to-nation, and larger politico/economic groups such as the European Union (EU) do not collate them. Nevertheless, it is by analyses of these statistics that nations and international groups can demand and frame legislation and/or regulations for those textiles seen to be the most hazardous and which pose the greatest risk to life. An outline of the areas posing the greatest risk and hence where legislation is more commonly adopted by several countries in Europe and the USA is presented below.

The annual UK Fire Statistics [11] are some of the most comprehensive available and attempt to provide information representative of a European country with a population of ≈60 million. These statistics are collected from the local and regional fire-brigade records using a standard format, and so relate only to fires to which the fire services have been called. There are other, smaller fires (especially in the home) that may involve fire casualites to which the fire services have not been not called because the victims are taken directly to hospital. Such records are collected from UK hospital admission records by the Home Accident Surveillance Scheme (HASS) which, until 2002, was administered by the former UK Department of Trade and Industry. Since then, the HASS has been accessible *via* the Royal Society of Prevention of Accidents website [12]. With regard to textile burning hazards, clothing fires and the ensuing burn casualties are those which are most likely to involve attendance at a hospital without involvement of the fire services. Recently Horrocks, Nazaré and Kandola analysed data regarding the incidence of clothing burns using several sources [13], including HASS data for 1995–1998 [14] and from other sources on accidents involving burns and scald injuries for 1992–1996, which enabled 108 clothing fire accident data for 1990–2000 to be more understood effectively. Almost 50% of the incidences of clothing fires involved nightdresses, followed by those involving dressing gowns and pyjamas. The prevalence of accidents caused by ignition of nightdresses and dressing gowns taken together add up to a far greater total (70%) than pyjamas (20%). Moreover, 50% of fires involving pyjamas are considered to have been caused by the ignition of bedding. It has also been observed that burns involving the ignition of clothing (loose-fitting garments in particular) usually prove to be more severe because of the intimate nature of such textiles. **Figure 1.1** presents data on fatalities related to ignition of nightwear in graphical form. In clothing fires, as in other UK domestic fires [11], the victims are predominantly the very young and very old, as shown in **Figure 1.2** for clothing fatalities from 1990 to 1998 [13, 14].

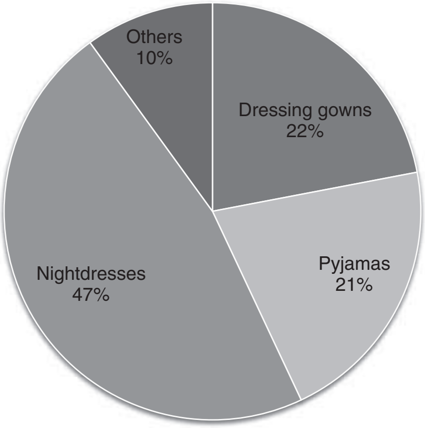

Figure 1.1 Garment types involved in incidences of nightwear clothing fires (compiled from HASS data for 1990–1998) [13]

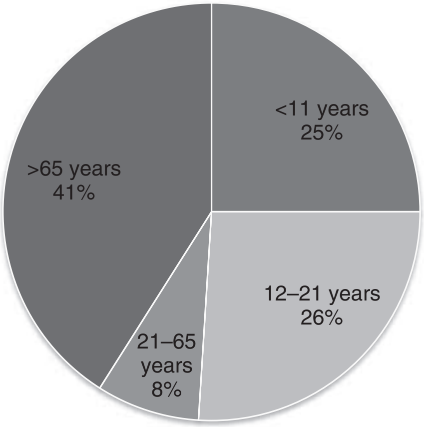

Figure 1.2 Age-based distribution of clothing fatalities (compiled from HASS data for 1990–1998) [13]

More generally and up to 2007, UK statistics have demonstrated that, whereas ≈20% of fires in dwellings are caused by textiles being the first ignited material, >50% of the fatalities are caused by these fires. **Figures 1.3** and **1.4** present typical data during the last 17 years, during which UK legislation related to furnishings [15] has prescribed minimum criteria for ignition on outer covers and fillings (including polyurethane foam) in terms of cigarette ignition and match ignition.

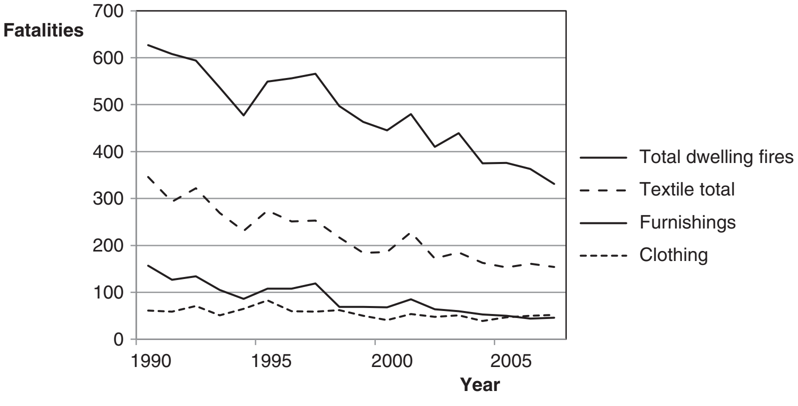

Figure 1.3 Fire death statistics in dwellings in the UK from 1990 to 2007 [11]

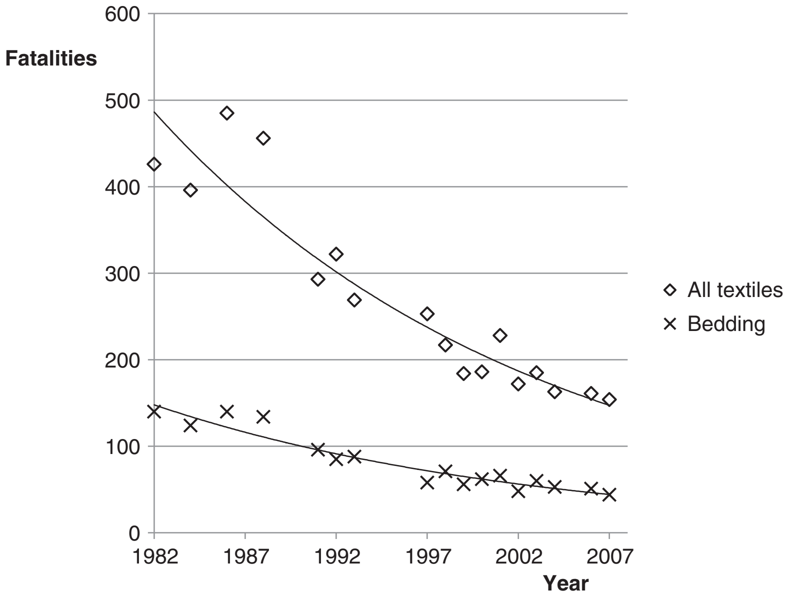

Figure 1.4 Bedding-related fatalities in the UK from 1988 to 2007 [11]

The trends show that, in general, deaths from fires in UK dwellings *per annum* have fallen from ≈600 in 1990 to ≈350 by 2007 although, from 1982 to 1988, the level was ≈700 p*er annum*. The trend shown in **Figure 1.3** for all textile materials shows an even more dramatic reduction from 346 *per annum* in 1990 to 154 *per annum* in 2007. This trend is reflected in parallel decreasing trends for furnishings and bedding (*see* **Figure 1.4**) caused by the need for defined levels of fire protection to cigarette and match ignition of fillings and cover materials (and of mattresses and ticking in the case of bedding) as a consequence of 1988 UK furnishing regulations [15]. Fatalities related to furnishings as the first ignited material in UK dwelling fires have decreased from 157 *per annum* to 46 *per annum* over the same period. After furnishings, bedding-related fires give rise to the next most hazardous textile in terms of fatalities and fire injuries. As the UK statistics for bedding show in **Figure 1.4**, the high levels of 130–140 fatalities *per annum* occurring in the early 1980s have reduced to ≈40–50 *per annum* during the period 2000–2007. Comprehensive UK statistics were not published for 2008 and 2009, but those for 2010/11 suggest that the pattern described above has been maintained.

In terms of being able to quantify the impact of current UK furnishing regulations [15] on these statistical reductions and while within the UK mandatory installation of smoke alarms in new and refurbished dwellings has increased over the same period, Stevens and co-workers showed that ≈140 lives are saved each year as a consequence of the introduction of ignition furnishing cover fabrics and fillings (primarily polyurethane foam) [16, 17]. Stevens and co-workers estimated that, between 1988 and 2002, the number of lives saved for upholstery as the first item ignited in UK dwellings fires was 1,150, and the number of injuries saved over the same period was 13,442 [17].

No other country publishes fire statistics as rigorously as the UK, and these singularly fail to identify those fire hazards related specifically to the various textile materials apart from furnishing and bedding. Kobes's analyses of European fire statistics [18] presented fire data for 18 of the EU nations in terms of fire and incidence of fire death, and could not find any data for Belgium, Cyprus, Italy, Luxembourg, Malta, Portugal, Romania or Spain. In terms of textile sources of fire ignition, statistics for the Netherlands in 2008 indicated that 29% of dwelling fire fatalities were caused by furnishings and 10% by bedding. These figures compare with the respective UK percentages of 13.9% and 13.3% for 2007.

In the USA, the National Fire Protection Agency stated that over the period 2006–2010, smokers materials (24%), candles (5%) and ‘playing with heat sources’ (4%) accounted for about one-third of all domestic fire deaths, for which the current total is 2,590 deaths *per annum* [19]. Furthermore, whereas only 7% of fires start in bedrooms, they cause 25% of fire deaths and 20% of injuries. Similarly, whereas living areas are associated with only 4% of fires, they are responsible for 24% of fire deaths. It is obvious that many of these fires will involve a textile material (although this is not stated directly). The US Fire Administration has published its research into bedding and mattress fires [20]. Even though it is >10 years' old, this research shows that of the total 20,800 fires that occur due to mattresses and bedding, they cause ≈2,200 injuries and ≈370 fatalities.

Children playing and smoking were responsible for 25% of these fires, with cigarettes accounting for 26% of cases and matches and lighters accounting for 31%. Furthermore, whereas 67% of injuries occurred to persons fighting to control the fires, 43% fatalities occurred while the victims were sleeping. As a consequence, there are now US federal regulations relating to the flammability of mattresses and bedding as defined in Consumer Products Safety Commission (CPSC) 16 (Code of Federal Regulations) (CFR) Part 1632 for cigarette ignition resistance [21]. The CPSC published regulation 16 CFR Part 1633 for open flame-source resistance [22] which came into effect on 1 July 2007.

The impact of furnishings in the US is also significant, and has prompted much debate over the last 10 years. Currently, there is no US federal flammability regulation for residential upholstered furniture, but the CPSC has proposed a regulation (CPSC 16 CFR Part 1634) [23] that defines criteria for minimum smouldering and open-flame ignition for these products. This has prompted considerable development into blocking fabrics for furnishings and mattresses, as reviewed recently by Nazaré and Davis [24]. These same authors very recently reviewed the entire area of regulations and testing as they relate to soft furnishings with a focus also on the underpinning US fire-related statistics [25].

In addition to the strong position of the UK with regard to regulations on domestic furnishing, most of the original 12 EU Member States, while appearing to lack detailed fire statistics, have legislation in place defining fire safety standards for bedding, mattresses and seats, and these have been reviewed extensively by Sainrat [26] and Guillaume [27].

Bearing in mind the above discussion on clothing fire hazards, **Figure 1.3** shows that the fatality rate associated with clothing has changed little over 15 years where neither of these factors would be expected to have influence. UK deaths *per annum* as recorded in the UK Fire Statistics [11] involving clothing (which ignore the HASS statistics emphasising the importance of nightwear-related fatalities [13, 14]) usually fluctuate within the 39–83 range and, as a group, have largely been ignored by the government and textile industry outside of the areas of nightwear [28] and protective clothing [29]. Clothing fires tend to be of an individual nature. Therefore, they receive little public attention and hence legislative pressure unless common groups of hazards are identified. The USA is unique in having a fundamental minimum flammability requirement which all consumer apparel textiles should conform to and defined in the standard CFR 1610 [30] (45°, 1 s ignition). This regulation falls under the US Flammable Fabrics Act 1953, which covers clothing, children's nightwear, carpets, rugs and mattresses [31].

Legislation and regulation usually occur only if considerable loss of life or property occurs. In the USA and UK, legislation for nightwear in particular has been recognised for >50 years and other countries have since adopted similar regulations, especially for nightwear worn by children, as reviewed by Horrocks and co-workers [13]. The impact of fire-related incidents and their impact on UK legislation have been reviewed to illustrate how the need for increasing safety levels (and hence fire-retardant textiles) is related [32].

However, more generally in the EU, the potential safety of textiles exposed to fire hazards falls within the General Product Safety Directive of 2001, which is the primary instrument to protect the health and safety of consumers with regard to products (although it does not consider effects on the environment). If there are no specific national regulations, the safety of a product is assessed in accordance with any one of the following: relevant European standards; Community technical specifications; codes of good practice; or 'the state of the art and the expectations of consumers' [33]. This does not replace existing national regulations such as UK 1988 furniture regulations [13] but acts as a 'safety net' for non-regulated items. However, at the present time, no previously non-regulated textile items in the UK have been identified for special treatment. In the USA, the Consumer Product Safety Act of 1972 has a similar overarching function with regard to the fire safety of consumer textiles – this has now subsumed the US Flammable Fabrics Act 1953 [31].

In many large-scale fires, the textiles present at each scene have functioned as the material ignited first by the relevant igniting source, as indicated in **Figure 1.1**. Secondly and subsequently, the speed with which this causes the fire to grow and spread to adjacent materials was and continues to be a significant feature in the inability of victims to escape or the fire fighters to bring fires under control. Therefore, these catastrophic fires initially serve to demonstrate more obviously the ignitability of textiles followed by the associated speed with which the resulting fire can grow. It is rarely the direct causes of the fire, such as burn severity, which are the prime causes of death. Instead, it is the effects of smoke and emitted fire gases that cause disorientation and impede escape, followed by incapacitation, asphyxiation and death [11]. Only in clothing-related fires are injury and death caused primarily by burns, especially if they are loose-fitting and worn directly over the body, such as nightwear and summer dresses.

Last but not least are the fire hazards of textiles used under conditions where the hazard is particularly high. These include contract furnishing in public buildings and textiles in defence, civil emergency and first-response sectors as well as industrial, aerospace and transport sectors. In these environments, textiles are designed not only for personal protection against specific fire hazards, but also comprise major structural elements, including textile-reinforced composites. It is within these areas, reviewed in detail elsewhere [34–37] as well as domestic and contract furnishing sectors (see **Chapter 3**), where flame-retardant textiles find greatest use. They also require the greatest level of sophistication in that, in addition to conferring the desired level of durable flame retardancy, they must also have minimal effects on the other desirable properties required of the product.

1.3 Glossary of Terms

Textile and other material burning hazards and their related risk-reducing methodologies use terms that, in some cases, may be confusing to the non-specialist within the fields of fire science and fire resistance. The list of terms shown below is taken from Lewin [4] and includes several additions and variations relating to flame-retardant fabrics and the literature.

- *Pyrolysis*: Irreversible chemical decomposition due to non-oxidative heating.

- *Combustion*: Self-catalysed exothermic reaction involving fuel and oxidiser.

- *Flames*: Combustion processes in the gas phase accompanied by emission of visible light.

- *Ignition*: Initiation of combustion.

- *Autoignition*: Spontaneous ignition of a material in air.

- *Ignition time or time to ignite*: Time taken for a sample to ignite if subjected to an ignition source, direct heat flux, or both.

- *Flammability*: Tendency of a material to burn with a flame.

- *To char*: Carbonaceous residue that can form during pyrolysis or combustion.

- *Afterglow*: Glowing combustion in a material after cessation (natural or induced) of flaming.

- *Afterglow time*: The time the flame continues to burn after the ignition flame is removed.

- *Smouldering*: Combustion without flame and without prior flaming combustion, but usually with incandescence and smoke.

- *Smoke*: Fine dispersion in air of particles, individually invisible, of carbon and other solids and liquids resulting from incomplete combustion. Opaque due to scattering and/or absorption of visible light.

- *Flame propagation*: Spread of flame from region to region in a combustible material (burning velocity = rate of flame propagation). In textile fabrics, the time to burn a specified length of fabric is defined.

- *Self-extinguishing*: Incapable of sustained combustion in air under the specified test conditions after removal of an external heat source.

- *Residual flame time*: The time burning fragments ('melt drip') falling from the fabric burn on the bottom of the test cabinet.

- *Fire resistance*: Capacity of a material or structure to withstand fire without losing its functional properties.

- *Flame resistance*: Property in a material of exhibiting resistance to ignition and/or minimal flammability; the term is often synonymous with *flame retardance* but may be considered to relate to fabrics which do not ignite under a flame but may be damaged by it.

- *Flame retardance or retardancy*: Resistance to ignition and reduced flammability; the term is often synonymous with *flame resistance* but may be considered to relate to fabrics which ignite under a flame.

- *Flame retardant*: Chemical compound capable of imparting flame resistance to (reducing the flammability of) a material to which it is added or combined with.

- *Effectiveness*: Ability of flame retardant to decrease flammability of the polymer substrate in which it is present.

- *Synergism*: Observed effectiveness of combinations of compounds greater than the sum of the effects of individual components.
- *Antagonism*: Observed effectiveness of combinations of compounds smaller than the sum of the effects of individual components.
- *Limiting Oxygen Index*: Minimum percentage oxygen in the environment that sustains burning under specified test conditions.
- *Vertical, horizontal, 45° angle (strip) test*: Orientation of the test specimen during a flammability test under specified conditions.
- *Flame spread*: Extent of propagation of flame in space or over specimen surface under specified test conditions.
- *Char length*: Difference between original length and remaining unburned length of material after testing the specimen by exposure to a flame.
- *Damaged length*: Extent of damage produced over the specimen by an ignition source and subsequent substrate ignition. It may include char, formation of a hole, discoloured region, or a zone having reduced tensile properties, or a combination thereof.
- *Rate of heat release*: Amount of heat released per unit time at a given time by a specimen burning under specified test conditions.
- *Peak heat release rate*: Maximum rate of heat release after ignition of a sample.
- *Comonomer*: Compound added in polymer synthesis and becoming a part of the polymer molecule.
- *Additive*: Compound added after the polymer has been synthesised but before or during its conversion to the final form (e.g., fibre, plastic) not covalently bound to the polymer substrate.

- *Finish*: Compound or combination of compounds added after conversion to the end product (e.g., fibre, yarn, fabric). May be chemically bonded or deposited on fibre, yarn and/or fabric surfaces.

- *Coating*: A layer of secondary material comprising a flame retardant and a binder or a flame-retardant resin deposited on the fabric surface or within the fabric surface.

- *Back-coating*: A coating applied to the reverse face of a fabric in a manner that does not affect the aesthetics or other properties of the face.

1.4 Hazard Assessment and Testing Methodologies for Flame Retardance

Terminology that relates to the testing of textiles is shown below [38], some of which overlaps with the terms defined above:

- *Ignition*: Flaming of the test specimen for ≥1 s after removal of the igniting flame.

- *Flaming*: Combustion in the gaseous phase with light emission.

- *Glowing*: Combustion of a material in the solid phase without flame but light emission from the combustion zone.

- *Smouldering*: Combustion of a material with or without light emission which, in general, is evidenced by smoke.

- *Melting*: Liquefaction of material when exposed to heat to the extent of forming a hole in its structure by shrinking and/or dripping away under the specified test conditions.

- *Flame spread time*: Time taken by a flame on a burning material to travel a specified distance measured from when the igniting flame is applied or after it has been removed.

- *Flaming debris*: Materials separating from the specimen during the test procedure and falling below the initial lower edge of the specimen and continuing to flame as they fall.

- *Afterglow time*: The time for which a material continues to glow (under specified test conditions) after cessation of flaming or after removal of the ignition source, ignoring glowing debris.

- *Surface flash*: Rapid spread of flame over the surface of a material without ignition of its basic structure.

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2 Fundamental Aspects of Flame Retardancy

A. Richard Horrocks and Jenny Alongi

2.1 Introduction

Materials such as plastic and textiles, which play an important part in everyday life, consist mainly of organic polymers, which are flammable and potentially dangerous species. Flame retardants have been developed to reduce the risk of fire by inhibiting the possibility of the material igniting or reducing the rate of flame spread if it is necessary. Flaming combustion is a gas-phase oxidative process requiring oxygen (or air) from the atmosphere. Thus, before undergoing flaming combustion, the polymer first degrades, giving rise to combustible species that can mix together with atmospheric oxygen and fuel a flame (**Figure 2.1**). Because of the exothermicity of the flame, if sufficient heat is transferred to the material surface, it may cause further degradation, and a self-sustaining combustion cycle can be promoted.

On the basis of these considerations, the next three sections will discuss briefly the thermal degradation and oxidation of polymers to describe thoroughly the direct consequences of such phenomena on the further combustion of a polymer [1].

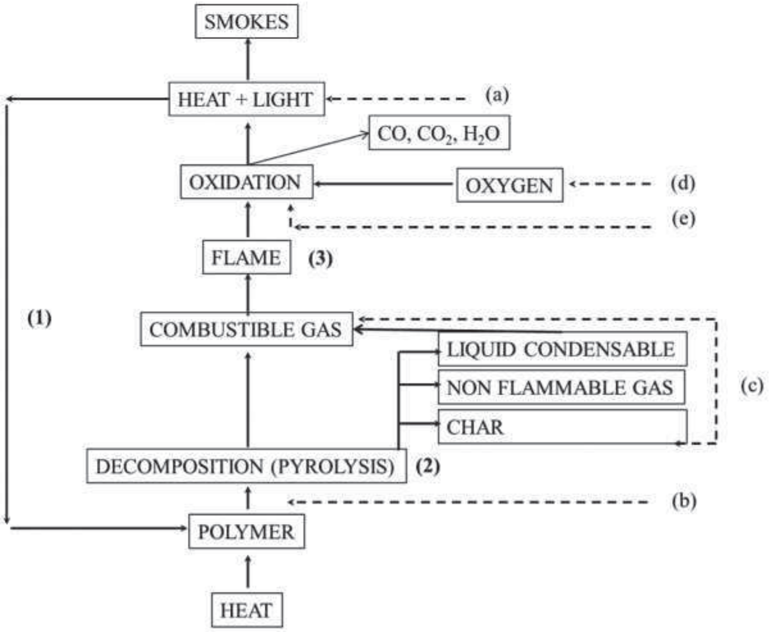

Figure 2.1 Thermal degradation of polymers (schematic)

2.2 Thermal Degradation of Polymers

When a polymer is heated, several thermal decomposition steps can occur at different transition temperatures that may influence the ultimate flammability of the fibre and hence of the textile. **Table 2.1** [1] lists the commonly available fibres with their physical glass transition temperature (T_g) and melting temperature (T_m), which can be compared with their degradation temperature (T_d), pyrolysis temperature (T_p) and ignition flaming combustion temperature (T_c). **Table 2.1** also presents the typical values of flame temperature and heats of combustion (ΔH_c). In general, the lower the respective T_c (and usually T_d) and the hotter the flame, the more flammable is the fibre. This generalisation is typical of natural cellulosic fibres such as cotton, viscose and flax as well as some synthetic fibres such as acrylics. Furthermore, the respective limiting oxygen index (LOI) values, the minimum volumetric concentration of oxygen (expressed as the percentage that will support combustion of a polymer) are also included in **Table 2.1**.

Table 2.1 Significant temperatures of the more commonly used fibres [2, 3]

Fibre	T_g [ºC]	T_m [ºC]	T_d [ºC]	T_c [ºC]	ΔH_c [kJ g^{-1}]	LOI [%]
Natural fibres/fibre-forming polymers						
Wool	–	–	245	600	27	25
Cotton	–	–	350	350	19	18.4
Viscose	–	–	350	420	19	18.9
Synthetic fibres						
Polyamide 6	50	215	431	450	39	20–21.5
Polyamide 6.6	50	265	403	530	32	20–21.5
Polyester	80–90	255	420-447	480	24	20–21
Acrylic	100	>220	290 (with decomposition)	>250	32	18.2
Polypropylene	–20	165	470	550	44	18.6
Modacrylic	<80	>240	273	690	-	29–30
Poly(vinyl chloride)	<80	>180	>180	450	21	37–39
Oxidised acrylic	–	–	^{3}640	–	45	–
Meta-aramid (e.g., Nomex®)	275	375	410	>500	30	29-30
Para-aramid (e.g., Kevlar®)	340	560	>590	>550	–	29

In general, fibres with a LOI ≤21.0% (natural oxygen content of air) are very flammable. They become moderately flammable if the LOI is 21.0–25.0%, and show limited flammability if the LOI is >25.0%, and start to pass various national and international standard tests for flame-retardant textiles [2, 3].

Before a polymer can undergo flaming combustion, it must first decompose to evolve flammable volatiles. Pure polymeric materials degrade *via* one or more of the following processes:

- End-chain scission: individual monomer units successively cleave from the chain end, usually leading to significant formation of volatiles.
- Random chain scission: scissions occur at random locations along the polymer chain.
- Chain stripping occurs if atoms or groups belonging to the polymer backbone are cleaved off.
- Crosslinking occurs if bonds are formed between adjacent polymer chains. Such reactions often lead to formation of carbonaceous char.

Synthetic polymers fall into three physical types, each of which decompose in a different manner upon heating. Thermoplastic polymers soften and melt before decomposing. Thermosets (crosslinked) do not melt and decompose, yielding char and evolving volatiles. Elastomers are rubber-like materials.

Polymers are rarely ‘pure’ in the ‘true’ chemical sense, so the intrinsic characteristics of thermal degradation of any commercial polymer or textile can be influenced by impurities. Impurities can be (i) those already present in monomeric feeds to polymerisation plants, (ii) polymerisation initiation or catalyst residues, (iii) thermally derived degradation products generated during polymerisation and processing, and (iv) contaminants introduced during processing (including atmospheric oxygen and metallic ions released from equipment in processing plants).

2.3 Thermo-oxidative Degradation of Polymers

Polymer degradation is almost always much faster in oxygen (or air) due to the accelerating reactions between oxygen and carbon-centred radicals (e.g., RO•) released from the initial degradation products. These interactions with oxygen result in an increase in the concentration of polymer alkyl radicals (R•), thereby leading to higher levels of scission products and crosslinked products. Furthermore, fragmentation reactions of oxygen-centred radicals yield new oxidation products with structures not found under an inert atmosphere. These radicals can undergo abstraction, fragmentation and combination reactions with the original polymer and other products from the decomposition. Such reactions can affect the polymer during processing (particularly if the required temperature is high) and also derived fibre and textile performance during end use.

In particular, the so-called Bolland and Gee reaction scheme [4] (**Figure 2.2**) and its subsequent developments have been applied to explain the characteristics of the chain reaction involved in the thermal-oxidation of polyolefins, as well as of many other fibre-forming polymers comprising aliphatic polyamides, polyesters and polypropylene (PP).

Initiation: $RH \xrightarrow{\Delta} R\cdot + \cdot H$

Propagation: $R\cdot + O_2 \rightarrow RO_2\cdot$

$RO_2\cdot + RH \rightarrow ROOH + R\cdot$

Termination: $R\cdot + R\cdot \rightarrow R\text{-}R$

$RO_2\cdot + R\cdot \rightarrow ROOR$

$RO_2\cdot + RO_2\cdot \rightarrow \text{Products}$

Chain branching: $ROOH \rightarrow RO\cdot + \cdot OH$

Figure 2.2 Bolland and Gee reaction scheme [4]

2.4 Degradation of Individual Fibre-forming Polymer Types

If polymers are heated, usually the weakest bonds that break first will determine the overall character of the subsequent degradation pathways. Flammability is associated with the availability and ease of oxidation of volatile degradation products. Hence, the degradation pathways that lead to the formation of volatiles are of great importance in the early stages of the degradation process. Crosslinking reactions usually eventually give rise to char (i.e., a thermally stable carbonaceous, multilamellar structure) formation and thus may minimise the formation of volatiles (**Figure 2.1**). Condensed-phase flame retardants facilitate such char formation and reduction of evolution of flammable volatiles.

2.4.1 Natural Fibre-forming Polymers

2.4.1.1 Cellulose

Of greatest importance is cotton, a natural form of cellulose, which comprises ≈50% of the textile markets of the world. Thus, the decomposition of cellulose has been studied extensively [5, 6]. Other, more detailed mechanisms have been reported [7], but the basic processes proposed are in accordance with that first described by Shafizadeh and Bradbury [8]. They suggested the formation, during the early degradation stages, of 'cellulose*' (i.e., an 'activated' cellulose species), which then undergoes further reactions depending on the temperature regimen as presented in stage I of the reaction schemes in **Figure 2.3**.

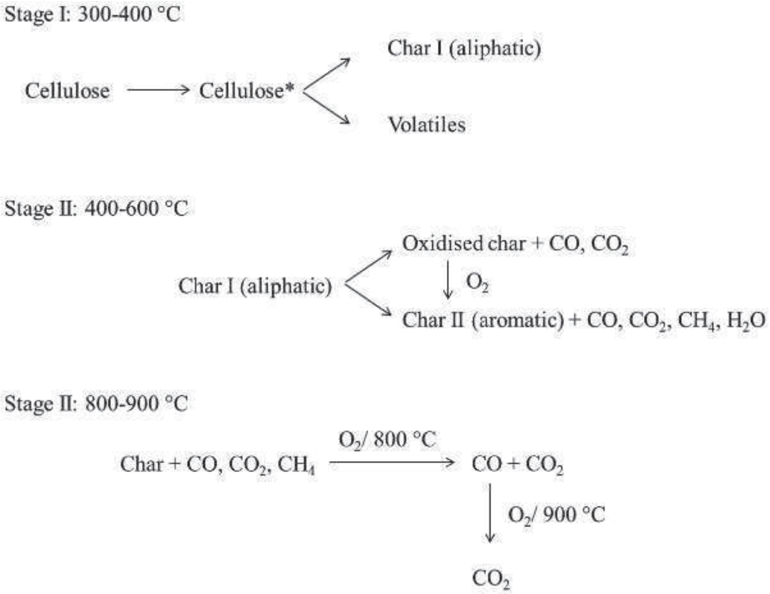

Figure 2.3 Model for the thermal degradation of cellulose as proposed by Shafezadeh and Bradbury

The existence of the cellulose* species is controversial, but experimental evidence of a free radical for the cellulose* species has been assessed by Price and co-workers [6]. At lower temperatures, oxygen plays a dominant part in cellulose degradation because pyrolysis has been shown to be faster in an oxidative atmosphere than in inert conditions (although at higher temperatures degradation products are little affected) [8]. Oxygen catalyses the evolution of volatiles as well as of char-promoting reactions [9, 10]. Recently, this mechanism has been shown to be dependent upon very high heating rates (100–300 °C/min) [11]. Essentially, the balance between the two subsequent competitive processes at 300–400 °C in stage I (i.e., depolymerisation and dehydration, as schematised in **Figure 2.3**) determines the ease of ignition. It is primarily this balance that condensed-phase flame retardants influence in that they usually enhance the dehydration and char-promoting reactions at the expense of formation of volatile fuels (see below).

Depolymerisation is initiated by the scission of acetal bonds between the chain glycosidic units, followed by successive splitting of volatile fuel-forming levoglucosan (the cyclic monomer of cellulose) from the ensuing chain ends [12]. Competing dehydration reactions lead to thermally stable aliphatic structures (char I), which subsequently are converted *via* stage II into aromatic structures (char II), with evolution of water, methane, carbon monoxide (CO) and carbon dioxide (CO_2) (400–600 °C). Char II (≈18%) is thermally stable at ≤800 °C.

As a consequence, the overall degradation process is the result of several competing reactions. Furthermore, the yield of volatiles as well as the yield and thermal stability of the final char are dependent upon the kinetic control exerted by the chemical degradation reactions and therefore on the adopted heating rate. Thus, the char produced by cotton degradation in nitrogen (N) at 10 °C/min is thermally stable ≤800 °C whereas, at very high heating rates, it decomposes at much lower temperatures.

If the degradation occurs in atmospheric oxygen, a further heating-rate effect is found that is dependent upon the sensitivity to oxygen of the chemical degradation reactions occurring in the polymer condensed phase (in which oxygen diffusion is dependent upon the heating rate). For example, cotton heated at low heating rates in air gives a larger char yield than at high heating rates with variable thermal stability.

2.4.1.2 Protein Fibre-forming Polymers

Proteins or poly(α-amino acids) contain the amide bond common to polyamides, and can be considered to be α-carbon substituted polyamides. Thus, their potential behaviour regarding thermal degradation might be expected to be similar to that of the aliphatic polyamides except that the α-substituents or -R groups are often quite reactive because of their functionalities, which significantly influence the overall thermal-degradation behaviour and potential flammability.

The most important protein fibre-forming polymers that require flame retardation are *silk* and *wool* [1–3, 13]. Silk comprises 16 α-amino acids, among which glycine (R= -H), alanine (R= -CH_3) and serine (R= -CH_2OH) are the most abundant. If heated, silk starts to decompose >250 °C and forms a char. Charring can be increased by the application of phosphorus-containing species [14].

Wool, which also comprises a large number of α-amino acids (18), some of which are present in silk, is uniquely identified by sulfur-containing α-substituents: in particular, cystine (R = -CH_2-S-S-CH_2-) comprises nearly 10 wt% of the entire fibre and provides crosslinks between adjacent polypeptide chains. This high sulfur content (3–4 wt%) coupled with the high N content (15–16 wt%) present in chain and side groups contribute to the inherently low flammability of wool. If this fibre is heated, it first gives off its adsorbed moisture at ≥100 °C. Its thermal degradation starts at >200 °C and rapidly produces gaseous species such as H_2S due to the cleavage of disulfide bonds at >230 °C [15], and gives rise to char formation [16]. The crosslinking and dehydrating tendencies of its α-substituents induce the evolution of non-flammable volatiles coupled with char formation. Their overall effect is responsible for a relatively high ignition temperature (≈570–600 °C) and low flame temperature (≈680 °C). The reducing character of the cystine disulfide bond encourages subsequent oxidation during pyrolysis/combustion.

2.4.2 Thermoplastic Fibre-forming Polymers

2.4.2.1 Polyolefins

For polyethylene (and its many copolymers) and PP, the main routes of thermal degradation follow the initial random chain scission mechanism. These reactions are affected only slightly by differences in physical structure (e.g., crystallinity) but are influenced by impurities (although these have little or no effect on flammability).

In the case of PP, pyrolysis is dominated by the initial chain scissions, usually at the carbon-carbon bond adjacent to the labile tertiary hydrogen atom in the repeating unit. Heating various forms of the polymer (including waste PP) generates a mixture of quite clean hydrocarbon fuels [17, 18] and other valuable products such as lubricants [19]. This efficient fuel-forming tendency explains the high flammability of PP and the difficulty of generating high levels of flame-retardant properties.

The complete absence of crosslinking reactions ensures that char-forming reactions are not favoured in the presence of conventional condensed-phase flame retardants. Thus, the most effective flame retardants for polyolefins are usually halogen-based (primarily *via* addition of organobromine compounds) so that flame inhibition occurs in the gas phase or is intumescent-based whereby char-promotion arises from the flame retardant itself.

2.4.2.2 Aliphatic Polyamides (Nylons)

Thermal degradation of all linear, aliphatic polyamides is substantially influenced by two major factors: (i) the strength of the weakest chain bonds around the amide group, and (ii) the actual bond cleavages that occur and which involve the $–NH.CH_2–$ and $–NH.CO–$ scissions [20]. These occur randomly and give rise to gaseous products such as ammonia (NH_3), CO and CO_2, low-molecular-weight fragments and subsequent degradation products from the latter. Among these simple gases, only CO is flammable but the volatiles generated from the shortest polymer chain fragments are the major fuel components. Thermal decomposition of nylon 6 involves depolymerisation to its monomer caprolactam, the rate of which increases with temperature. Thermal lability of aliphatic nylons can also be influenced by the potential for ring formation during chain degradation. In nylon 6.6, the adipate repeating units enable the formation of six-membered intermediates along the polymer chains with the eventual formation of cyclopentanone and its derivatives [21]. These are considered to be the precursors leading to gel formation. nylon 6.6 is particularly prone to this action and justifies the reason for which melt extrusion processes often require more interruptions because of potential gel blockages than is the case of other polyamides, such as nylon 6. Gel-formation mechanisms are not well understood but, in nylon 6.6, the formation of cyclopentanone derivatives and their subsequent reaction products are believed to be involved.

The overall flammability of the simple nylons is determined by their relative propensities to shrink and melt away from an ignition source, as well as by the nature of the produced volatiles. Indeed, the produced volatiles will have a reduced fuel value if NH_3 and CO_2 are present in significant quantities. Any strategy for flame retardation should address the possibility of reducing the amount of non-fuel gases in the volatile products or enhance gel formation, which may then lead to char formation. Unfortunately, to date, few efficient flame retardants have been commercialised for nylon 6 and nylon 6.6, partly because of the reactivity of nylon melts toward additives based on bromine-containing retardants with the adverse effects of acid-generating, phosphorus-containing species on the molecular weight of melts during processing. Weil and Levchik [22] reviewed this area and showed that certain melamine salts could be used as flame retardants.

2.4.2.3 Polyesters

The principal linear fibre-forming polyester is poly(ethylene terephthalate) (PET), so this will be the principal example chosen in this group [23–25]. Studies of the thermal degradation behaviour of PET mirror those of the aliphatic polyamides in that the basic research work was undertaken during the commercial development of PET during the 1950s and 1960s. Some crosslinking tendency has been identified [24] but, in the main, random chain scission dominates thermal degradation, with the major product (acetaldehyde) being formed at ≤290 °C along with smaller amounts of CO, CO_2 and ethane as well as very small amounts of other fuels, such as methane and benzene [25].

A simplified version of the primary stage appears to be:

$$\begin{aligned} &-C_6H_4.\ CO.O.\ CH_2.\ CH_2.O.\ CO- \quad \xrightarrow{\Delta} \quad -C_6H_4.\ CO.OH\ + \\ &\qquad\qquad\qquad\qquad\qquad\qquad CH_2 = CH_2.O.\ CO.\ C_6H_4.\ - \\ &-C_6H_4.\ CO.O.\ CH_2 = CH_2 \ + \ HO.\ CO.\ C_6H_4.\ - \ \rightarrow \ CH_3.\ CHO \ + \\ &\qquad\qquad\qquad\qquad\qquad\qquad -C_6H_4.\ CO.O.\ CO.\ C_6H_4.\ - \end{aligned}$$

in which it is seen that acetaldehyde is formed as the major initial flammable volatile. Further heat causes polymerisation of the vinyl ends coupled with loss of CO and CO_2 as the anhydride links undergo further scission. Crosslinking ensues from this reaction, but it cannot be considered to be a significant char-forming reaction.

Thus, any flame retardant must counteract the effect (or reduce the amount) of acetaldehyde formed. The actions of bromine- and phosphorus-containing species have achieved varying degrees of success. However, no flame retardant has managed to confer a significant char-forming character to the degradative mechanism. This phenomenon is perhaps an indication of the challenges involved with flame-retarding linear polyesters effectively.

A similar non-charring tendency occurs with aliphatic polyesters such as poly(3-hydroxy butyrate) (PHB), poly(ε-caprolactone) (PCL) and poly(lactic acid) (PLA). For PHB, random chain scission dominates whereas, for PCL, ‘unzipping’ is the major thermal degradation route [26]. PLA has a more complex set of concurrent degradative mechanisms which give rise to smaller oligomeric and potential fuel-forming products [26, 27].

2.4.3 High Temperature-resistant Fibre-forming Polymers

High temperature-resistant fibre-forming polymers tend to be highly aromatic with rigid polymer chain backbones to yield polymers having very high T_g values, absence of achievable melting transitions, and decomposition temperatures rarely <400 °C. Principal members are the well-established poly(*meta*- and *para*-phenylene amides) as typified by the respective commercial examples Nomex® and Kevlar® (Du Pont). These and other examples are discussed more fully in **Chapter 5**. Usually, in such polymers, the lower the aliphatic content, the lower is the hydrogen-to-carbon ratio (H/C), and hence the lower is the flammability of any polymer. Polymers bearing aromatic units have, in general, H/C ratios <1, so their ability to generate volatile and flammable degradation products at <500 °C is very limited. Consequently, they have LOI values >30% and are deemed to be sufficiently flame resistant for their specific applications [12].

2.5 Polymer Combustion

A polymer fire is fuelled by the products of combustible pyrolysis escaping from its surface due to heat being transferred from the flame in contact with the polymer surface and also radiated from the flame itself, which is the significant cause of flame spread (**Figure 2.1**). This process can be modelled on a laboratory scale by the cone calorimetry method (International Organization for Standardization 5560:1990 [28]). The oxygen required for sustaining the flaming combustion diffuses inwards from the surrounding air environment. Various solid particles escape from the flame as smoke, which is accompanied by gaseous species, some of which can also be toxic [29]. The significant polymer degradation reactions occur normally within one millimetre of the interface between the flame and solid polymer, where the temperature is high enough for condensed-phase degradation reactions to occur. These involve the polymer and any additive systems included in the formulations or external surface treatments. The volatile species formed escape into the flame zone whereas heavier species remain to undergo further reaction and may eventually transform into char. This is where the significant condensed-phase chemistry occurs. Experimental studies of this region have been undertaken by Price and co-workers [30] as well as by Marosi and coworkers [31, 32]. **Figure 2.4** provides a schematic representation of the various zones involved as a polymer fire spreads across a horizontal textile surface (e.g., a carpet).

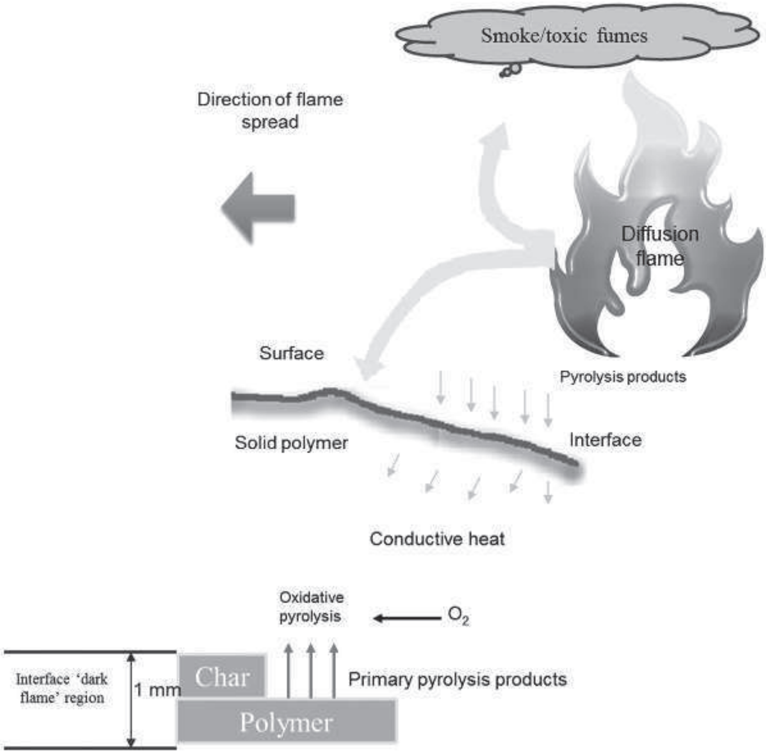

Figure 2.4 The various zones involved as a polymer fire spreads across a horizontal textile surface (schematic)

2.6 Influence of Polymer Degradation on Subsequent Combustion

The combustion cycle of a polymer can be referred to the schematic representation given in **Figure 2.1**. To enable a polymer material undergo flaming combustion, it must first degrade to evolve combustible volatiles, which mix together with an oxidative atmosphere. Once the ignition temperature is achieved (in the presence or not of a suitable ignition source, such as a spark), this mixture will ignite. The flames will yield gaseous products such as smoke and fumes as well as heat; some of the evolved gases may be toxic. Some of the heat will be conducted or radiated back to the original polymer to cause further degradation. Provided this heat is sufficiently intense, a combustion cycle will be established (**Figure 2.1**).

For a given polymer, the strategy to be adopted will be dictated largely by the respective chemistry of the thermal degradation process.

2.7 Mechanisms of Flame Retardancy

2.7.1 Chemical and Physical Mechanisms

Figure 2.1 shows the combustion process as a feedback system which can be interrupted at various points to create flame retardancy. Thus, the common flame retardants may be considered to function according to one or more of the following ways:

- Removal of heat.
- Enhancement of T_d (or T_p), at which significant generation of volatiles occurs.
- Reduction of volatiles and associated formation of combustible gas and char promotion.

- Preventing access to oxygen, or dilution of the flame.
- Enhancing the temperature at which the gaseous fuels ignite.

Figure 2.1 presents the three major modes (**1–3**) proposed for flame-retardant behaviour by which flame retardants may function. Mechanism (**1**) consists of a heat-barrier effect *via* formation of char or other residues and/or a heat sink effect whereby heat is removed (or prevented) from returning to the polymer. Examples of such flame retardants include those having high heats of fusion and/or degradation and/or dehydration (e.g., inorganic and organic phosphorus-containing agents, aluminium hydroxide or 'alumina hydrate') as well as those with intumescent properties. When an intumescent material is subjected to heat flow, it develops a carbonaceous shield (*char*) on its surface. This protection acts as a physical barrier that can limit the transfer of heat, fuel and oxygen between the flame and polymer. Usually, the intumescent material consists of three components: (i) an acid source (e.g., ammonium phosphates or polyphosphates, which release phosphoric acid); (ii) a carbon source (e.g., pentaerythritol, arabitol, sorbitol, inositol, saccharides, and polysaccharides); and (iii) a blowing agent (guanidine and melamine). The blowing agent releases considerable amounts of expandable and non-combustible gases (NH_3 or CO_2) upon heating [33–37]. The simple borates, however operate by forming glassy surface deposits that act as a heat barrier to the underlying textile substrate.

Mechanism (**2**), i.e., reduced formation of volatiles and enhanced formation of char, is exemplified by most phosphorus (P)- and N-containing flame retardants in cellulose (e.g., cotton) and wool as well as heavy metal complexes in wool.

Char formation is more difficult to achieve in common thermoplastic fibres that do not crosslink during thermal degradation. Polyacrylic fibres represent an exception, however, as shown by their well-known ability to be transformed into carbon fibres [38]. This inherent tendency to form char is enhanced in the presence of P- and N-containing flame retardants such as ammonium polyphosphate, despite their low durability [38], which precludes their use in textile fibre applications. Mechanism (**3**) occurs if flame evolution is influenced by species that terminate the chemistry of the chain reaction of the flame or physically dilute the reacting species. Such 'chain terminators' are radical species generated from the flame retardant present, as exemplified by the effectiveness of Cl• and Br• radicals generated by halogen-containing species (if present) [39]. Halogen-containing flame retardants (more usually as organobromine compounds) are used, typically in combination with antimony oxides as synergists (see **Section 2.7.2**) and these formulations are particularly useful for textile coatings and back-coatings [40]. The only commercial, inherently flame-resistant acrylic fibres are 'modacrylic fibres' (see **Chapter 5**), which include vinyl or vinylidene comonomers within the copolymeric acrylonitrile structure. Nowadays, antimony III oxide is also often included as a synergist in coating and modacrylic formulations. Physical dilution of the flame occurs if water-releasing flame retardants such as hydrated retardants and some char-promoting retardants are used, as well as halogen-containing retardants that release hydrogen halide during the formation of the chain-breaking species Cl• and Br• radicals.

From the information given above, it is clear that some generic flame retardants function in more than one mode. In addition, some flame-retardant formulations produce liquid-phase intermediates. These liquid-phase intermediates wet the fibre surfaces, thereby acting as thermal and oxygen barriers, as in the case of mixtures of borate/boric acid, which can also promote char formation *via* their acidic properties.

To simplify the classification of the different modes of behaviour of chemical flame retardants, the terms 'condensed-' and 'gas- or vapour-phase' activities may be used (**Figure 2.5**). Both are composite terms. The former includes modes (**1**) and (**2**) and the latter mainly mode (**3**) but with some contribution from mode (**2**) because the release of acidic hydrogen halides may catalyse char formation in some fibres, such as cellulosics.

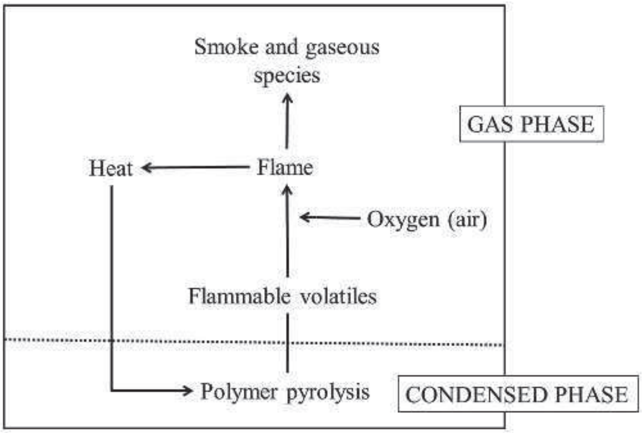

Figure 2.5 Simplified scheme of polymer combustion

Besides the physical mechanisms mentioned above, such as flame dilution and barrier formation, the effect of thermoplasticity must also be considered.

Whether or not a fibre softens and/or melts (as defined by the physical transitions shown in **Table 2.1**) determines whether it is a thermoplastic or not. Thermoplasticity can influence considerably how a flame retardant behaves because of the associated physical change.

Conventional thermoplastic fibres such as polyamide, polyester and PP will cause fabrics to shrink away from an ignition flame and avoid ignition. This action can give the appearance of flame retardancy when, as a matter of fact, if the shrinkage could be prevented, these fibres would burn intensely. Such shrinkage can give rise to apparently high LOI values because during this test the vertical sample is ignited from the top and molten drips flow away from the ignition front, causing premature extinction; therefore, higher oxygen concentrations are required to offset this. As an example, polyamide (PA) fabrics may yield LOI values as high as 24% if unsupported but the LOI reduces to ≈21% if the fabrics are supported on a glass fibre scrim, which prevents melt dripping [41]. This *scaffolding effect* is also seen in polyester-cotton and corresponding blends, where the molten polymer melts onto the non-thermoplastic, charring cotton and ignites, thereby making the blend much more flammable than one or both of the component fibres individually.

In addition to the considerations stated above, molten and often flaming drips represent a serious problem which, while removing heat from a flame front and encouraging flame extinction, can lead to burns or secondary ignition of underlying surfaces (e.g., carpets or moquette).

Most flame retardants applied to conventional synthetic fibres during manufacture or as finishes usually act by increasing melt dripping and/or promoting the extinction of flaming droplets. None to date have successfully reduced their thermoplasticity and promoted significant formation of char as is the case of flame-retarded cellulosics, including viscose fibres [42]. However, flame-retardant back-coatings and coatings applied to thermoplastic fibre-containing textiles comprise char-forming resin binders and so reduce overall fabric shrinkage and can even prevent hole formation in otherwise fusible fibre-containing fabrics. These resins, combined with a bromine-containing species and antimony III oxide, are effective for extinguishing flame independently of fabric composition (see **Chapter 4**).

2.7.2 Retardant Additive and Interactive Effects

In many textiles, especially those comprising more than one fibre type (e.g., blends), more than one flame-retardant system may be present or one of the fibres may be inherently flame-retarded, whereas the other(s) requires application of a flame retardant. Such combinations may exert additive or reactive effects. Reactive effects include antagonistic effects, in which the combination of flame retardants may not only have a less than additive effect but also yield enhanced substrate flammability relative to the absence of either! A typical example refers to the combination of the inherently flame-resistant polyester Trevira CS® with wool flame-retarded with hexafluoro zirconate (Zirpro®) [43]. However, the desirable reactive effect when flame retardants are combined is synergistic, i.e., the resulting flame-retarding effect is greater than the sum of those of the singly flame retarded component fibres.

The most well-known synergistic combination involves P-N flame retardants for cellulosics [3, 44]. For example, the well-established organophosphorus- and N-containing durable finishes for cotton based on tetrakis (hydroxymethyl) phosphonium salt-urea condensates (e.g., Proban®) or *N*-methylol dimethyl phosphonamide derivatives (e.g., Pyrovatex®) require respective N/P molar ratios of ≈2–2.5 and ≈1.5–2 for optimal flame-retarding effectiveness (see **Chapter 4**).

High levels of synergy are essential if halogen-containing flame-retardant formulations are to be exploited fully, where the addition of antimony III oxide, which by itself has a little or negligible flame retardant effect, significantly enhances that of halogen-containing flame-retardant formulations. Antimony III oxide/halogen-based formulations act primarily in the vapour phase by mode (**3**) and flame chemistries for different fibres are essentially very similar [39]. For textile back-coatings, most antimony-halogen systems comprise antimony III oxide and bromine-containing organic molecules such as decabromodiphenyl ether or hexabromocyclododecane despite environmental concerns (though their use in the near future may be curtailed [44]; see **Chapter 4** and **Chapter 6**). Upon heating, the bromine-containing flame retardant releases HBr and Br• radicals. These interfere with the flame chemistry by removing the R•, CH_2•, H• and OH• species essential for propagation of the flame oxidative chain reaction which consumes fuel (R-CH_3) and oxygen [39, 45]. This reaction is schematised in **Figure 2.6**.

$$\mathrm{R{-}Br} \longrightarrow \mathrm{R}\bullet + \mathrm{Br}\bullet$$

$$\mathrm{Br}\bullet + \mathrm{R{-}CH_3} \longrightarrow \mathrm{R{-}CH_2}\bullet + \mathrm{HBr}$$

$$\mathrm{HBr} + \mathrm{OH}\bullet \longrightarrow \mathrm{H_2O} + \mathrm{Br}\bullet$$

$$\mathrm{HBr} + \mathrm{H}\bullet \longrightarrow \mathrm{H_2} + \mathrm{Br}\bullet$$

Figure 2.6 Decomposition mechanism of a bromine-containing flame retardant under heating

The role of antimony in the effectiveness of the flame retardation of bromine and chlorine has been considered to involve the formation of flame-active species such as antimony trihalides (e.g., $SbBr_3$) and oxyhalides (e.g., SbOCl [39]). Based on these studies, most textile back-coating formulations are based on a antimony:bromine molar ratio of 1:3.

2.7.3 Quantification of Synergism

A brief digression on the term 'synergism' seems to be necessary in a comprehensive text focused on the flame retardancy of materials. Hence, examples of synergism in the true chemical sense are provided.

As mentioned above, the most well-known synergistic combination is phosphorus-nitrogen flame retardants for cellulosics [3, 46].

The consensus of opinion suggests that nitrogen in P-N synergistic retardants acts by a nucleophilic attack on the phosphate group, creating polymeric species having P-N bonds. The latter are more polar than the already present P-O bonds, and the enhanced electrophilicity of the P atom increases its ability to phosphorylate the C(6) primary hydroxyl group of cellulose [2]. In this way, the intramolecular C(6)-C(1) rearrangement reaction forming levoglucosan is blocked. Meanwhile, the auto-crosslinking of cellulose promotes and consolidates the char formation derived by the action of the same flame retardants.

Numerous studies referring to the P-N synergism for cotton have been cited in reviews [2, 3] but few qualitative determinations of this phenomenon have been established. However, Lewin [47] demonstrated that it is possible to identify real synergism between two species (i.e., P and N) only through calculation of *synergism effectiveness (SE)*. Indeed, in some cases, the effect of the two species can be merely additive (or even antagonist).

SE can be defined according to **Equation 2.1**:

$$SE = \frac{(Fp)_{fr+s} - (Fp)_P}{((Fp)_{fr} - (Fp)_p)) + ((Fp)_{\mathrm{s}} - ((Fp)_p))} \tag{2.1}$$

where (Fp) is a given flammability parameter (from flammability or combustion tests), $(Fp)_{\mathrm{p}}$ is the flame-retardant property of the polymer alone, $(Fp)_{\mathrm{fr}}$ is that of the polymer plus flame retardant, $(Fp)_{\mathrm{s}}$ is that of the polymer treated with the synergist, and $(Fp)_{\mathrm{fr+s}}$ is that of the full formulation comprising the flame retardant and synergist. This parameter allows direct quantitative comparison of the synergistic properties between different flame retardants. SE>1 means that synergy is occurring; 0<SE≤1 indicates a simple additive or cumulative effect, and SE<0 implies antagonism.

The LOI is a numerical measure of flammability, so this parameter provides a means of testing the SE concept. Horrocks and coworkers applied the concept to several polymers containing halogen-containing systems to compare the relative synergistic effectiveness of antimony III oxide and possible replacements such as zinc stannate and zinc hydroxystannate [48]. Previously, this research team compared various nanoparticle/flame-retardant combinations in PA6 and PA6.6 to distinguish between possible synergistic, additive and even antagonistic combinations [49, 50] using the SE concept.

As an example of this concept in a fibre-forming polymer, **Table 2.2** shows the LOI values for cast films of PA6.6 with and without a nanoclay and in the presence of ammonium polyphosphate (APP), Proban® polymer (see **Figure 4.2, Chapter 4**), a proprietary intumescent MPC1000 supplied by Rhodia (now Solvay) (comprising APP, pentaerythritol (PER) and melamine (MEL)) as well as a mixture of PER and MEL, with each formulation present at various concentrations [49]. PA6.6 was supplied by a commercial supplier with and without a dispersed nanoclay of undisclosed type, but presumed to be of montmorillonite origin. SE values were calculated according to **Equation 2.2**

$$SE = \{(LOI_{(nano + FR)} - LOI_{(PA66)})/((LOI_{(PA66\ nano)} - LOI_{(PA66)}) + (LOI_{(FR)} - LOI_{(PA66)})\} \tag{2.2}$$

and the results listed in **Table 2.2**. Synergy is observed particularly when nanoclay and APP are present (SE>1), marginally when nanoclay and Proban® polymer are present (SE≥1) and absent if either MEL/PER formulations are present (SE<1).

2.7.4 Char Formation

As stated above, the most effective flame retardants are those that promote char formation by converting the organic fibre structure to a carbonaceous residue or char (mode (**c**) in **Figure 2.1**). Indirectly, these flame retardants, which require absorption of heat before becoming active, will offer additional mode (**a**) and, by releasing non-flammable molecules such as CO_2, NH_3 and water during char formation, mode (**c**). In addition, the char behaves as a carbonised replica of the original fabric, which continues to act as a thermal barrier, unlike flame-retarded thermoplastic fibres.

Char-forming flame retardants, therefore, offer resistance to flame and heat to a textile fibre and therefore can compete with many of the ‘high performance’ flame- and heat-resistant fibres such as aramids and similar fibres (see **Chapter 5**).

Table 2.2 LOI values and SE values for PA6.6 films, with and without nanoclay, in the presence of selected flame retardants [49]

Additive/level, wt%	%P	PA6.6 film	PA6.6 nanofilm	SE
		$LOI_{(PA66)}$, %	$LOI_{(PA66nano)}$, %	
No additive	–	21	21.8	–
13% APP	3.2	21.4	22.2	1.0
15% APP	4.8	21.4	23	1.7
20% APP	6.4	21.4	23.8	2.3
23% APP	7	23.4	25	1.3
27% APP	8.2	24.6	25.8	1.1
11% clay	1.8	21.6	22.2	0.9
15% clay	2.4	22.4	23.4	1.1
20% clay	3.2	22.8	24.2	1.2
23% clay	3.7	23.6	24.6	1.1
27% clay	4.3	24.4	24.6	0.9
11% MPC1000	2	21.8	21.8	0.5
15% MPC1000	2.7	21.8	22.6	1.0
20% MPC1000	3.6	23.8	24.2	0.9
23% MPC1000	4.1	24.2	24.6	0.9
27% MPC1000	4.9	25.4	24.6	0.7
11% APP/PER	2.2	21.8	22.2	0.7
15% APP/PER	3	22.6	22.6	0.7
20% APP/PER	4	23	23	0.7
23% APP/PER	4.6	24.2	23.4	0.6

For char formation to be most effective, the polymer backbone must comprise side-groups which, upon removal, lead to the formation of unsaturated carbon bonds and eventually of a carbonaceous char after the elimination of most of the non-carbon atoms. Most P- and N-containing retardants, if present in cellulose, reduce volatile formation and catalyse char formation. This finding can be ascribed to their Lewis-acid properties which, upon heating, release polyphosphoric acid which then phosphorylates the C(6) hydroxyl group in the anhydroglucopyranose moiety, and simultaneously acts as an acidic catalyst for dehydration of these same repeat units (**Figures 2.3** and **2.4**). However, vapour-phase active bromine-containing species may also influence pyrolysis to the extent that they favour volatile reactions by enhancing the decomposition of levoglucosan to flammable furans, aldehydes and similar species. Here, release of the acidic hydrogen bromide has an obvious dehydrating catalytic role.

Clearly, char formation is not a simple process but is essential if flame-retardant textiles are to resist ignition as well as maintain heat and fire barrier characteristics. Elements such as N and sulfur are known to synergistically enhance the performance of P-containing retardants by further increasing char-forming tendencies. Such reactions also occur in wool fibres as a consequence of their complex protein (keratin) structure and in non-thermoplastic aromatic fibres (which have whole aromatic chains and behave as char-precursor structures).

A major problem is encountered, however, with the commonly available synthetic polymers polyester, PA, and PP which, because of their tendencies to pyrolyse by chain scission or unzipping reactions as well as their general lack of reactive side groups, do not tend to be form char. An ideal char-promoting flame retardant would have to promote crosslinking reactions before thermoplastic effects physically destroy the coherent character of the textile. This creates a conflict between being thermally stable during processing above the respective melting point and yet forming char at or close to the respective processing temperature. As **Table 2.1** shows, T_m values for these fibres are 160–260 °C with melt processing temperatures 25–50 °C higher. Typically, many P- and N-containing flame retardants start to decompose at ≈250 °C, hence the conflict.

The effect of water on the thermal degradation of cellulose is another important aspect that should be taken into account. Thermohydrolysis is considered to be the key reaction that determines the rates and outcomes of the char-forming and volatilisation pathways [51]. This important effect is sometimes neglected despite the interest provided by Camino and co-workers [51, 52].

2.7.5 Smoke, Fumes and Combustion Gases

Smoke has a vague definition, as stated by Price and co-workers [53]. Indeed, smoke is considered to denote a cloud of particles (individually invisible because of their reduced size) that can scatter and/or absorb visible light. Smoke differs from fumes because the latter can be considered to be a less opaque form of smoke. During polymer combustion, production of 'combustible gases' (e.g., CO) and 'visible smokes' are crucial factors to consider because the loss of visibility due to heavy smoke can hinder escape pathways, whereas the concentration of toxic gases (especially at high temperatures) can be very critical and, as mentioned in **Chapter 1**, most fire deaths are associated with the inhalation of CO. Escape time during a fire can benefit from a reduction of the rate and intensity of development of visible smoke, so investigation of effective smoke suppressants for polymers becomes a key parameter in the combustion processes of the latter. Visible smoke from burning polymers is usually a consequence of incomplete combustion. Upon heating, at certain temperatures, polymers undergo pyrolysis, thereby giving rise to low-molecular-weight species. These species diffuse from the solid into the gas phase, where they form smoke and other reactive species that further fuel polymer combustion. Aliphatic species are cracked to small alkyl radicals and grow to form conjugated polyenes or polybenzenoids that react and condense with other unsaturated species to give soot. Conversely, fibre-forming polymers which already contain aromatic groups can act as smoke precursors. Meanwhile, oxidation of carbon to oxides (CO and CO_2) occurs through a competitive pathway to soot formation. Several approaches that involve certain chemical reactions occurring in gas, solid or liquid phases have been developed for reducing smoke production. The chemical reactions taking place in the solid phase seem to be one of the most promising and encouraging routes because they allow dilution of the content of combustible polymers, dissipation of heat, insulation and protection of the surface of the combustible substrate, promotion of char formation, and modification of pyrolysis reactions.

The general consensus is that use of the most effective flame retardants containing P- and in particular antimony/bromine-based compounds may result in significant effects on toxic potency by modifying combustion efficiency and increasing the yields of smoke and asphyxiant gases. For example, cotton treated with a bromine/antimony back-coating can produce a greater amount of CO (by a factor of 10) with respect to the untreated fabric in non-flaming conditions at 700 °C [54].

The use of fillers, classified as 'inert' or 'active', on the basis of their apparent smoke-suppressant functions, for bulk polymers has been documented, and these are largely irrelevant for flame-retardant textiles except if coatings are present. This is because fillers are present at very high levels, which would otherwise negatively influence the desirable textile properties required. However, notwithstanding this *caveat*, inert fillers such as silica, clays and calcium carbonate can lower the amount of smoke generated from a given mass or volume of polymer by diluting or decreasing the amount of combustible substrate, and also by absorbing heat (so that the burning rate slows down). Conversely, aluminium hydroxide and magnesium hydroxide behave as active fillers with considerable smoke-reducing properties, and may be used in textile coatings. This is because, as stated above, they give rise to the endothermic release of water, which cools the flame and reduces smoke-forming reaction rates. However, among these species, only tin-based compounds can be classified as smoke suppressants from the true chemical point of view [47, 55–57], even though they are also synergists and effective replacements for antimony III oxide.

Finally, the chemical character of smoke and fire gases and their general toxicity are very complex subjects and beyond the scope of this chapter. However, Hull [27] and Purser [54] have reviewed these topics.

2.8 Effect of Fabric and Yarn Structures

The burning behaviour of fabrics comprising a given fibre type or blend is influenced by several factors in addition to the burning behaviour of the fibres present. These include the nature of the ignition source and time of its impingement, fabric orientation and point of ignition (e.g., at the edge or face of the fabric, or top or bottom), ambient temperature and relative humidity, velocity of the air, and variables of the fabric structure. Fabric orientation, point of ignition source, time variables and atmospheric variables are controlled in any standard test (*see* **Chapter 3**). Thus, the degree of burning intensity measured as burning rate, for example, for the same fabric ignited at the bottom will increase with the angle of inclination to the horizontal in the order:

$$0^{\circ} < 45° < 60° < 90° \text{ (i.e., vertical)}$$

In addition, as shown by Backer and co-workers [58], low values for fabric area density and open structures aggravate burning rate and so increase the hazards of burn severity more than heavier and multilayered constructions. Hendrix and co-workers [59] related the LOI linearly with respect to area density and logarithmically with air permeability for a series of cotton fabrics, but the correlations were weak. They showed that, for the same fibre type, LOI values increased with area density but decreased with increasing air permeability. This is one reason why the LOI test is not the standard method for textiles because there is no 'standard' value for a given fabric comprising a specified fibre. Thus, fabric flammability is determined not only by fibre behaviour but the physical geometry of fibrous arrays in fabrics. This dependence of the LOI on variables in the fabric structure was reviewed by our research team in 1989 [41].

The effect of the geometry and structure of yarn on burning behaviour has not been studied in depth, but the referenced works stated above on fabric structure infer that coarser yarns have greater resistance to ignition. This assumes that fibre type and area density remain constant (for coarser yarns, the cover factor will reduce and air permeability will increase, which will have the converse effect). Recent work by Garvey and co-workers [60] examined the burning behaviour of blended yarns comprising modacrylic/flame-retardant viscose. In this yarn, the flame-retardant viscose is Visil® (Sateri Fibres, Finland), which is produced by ring-spinning and rotor-spinning methods, having the same nominal linear densities, and is knitted into panels. This work is also discussed in **Chapter 5** with regard to the behaviour of fibres blends generally (**Figure 5.1** shows char lengths for modacrylic/Visil blends tested according to BS 5438:1989: Test 2). For a given blend, the tighter ring-spun yarns tend to yield higher char lengths than the more open rotor-spun yarn-containing fabrics. This effect is mirrored in **Figure 2.7**, in which the LOI is plotted against blend content for the same series of fabrics. The more flammable rotor-spun yarns are believed to be a consequence of the improved randomisation of fibre components that occurs using this spinning method; in ring-spun yarns, aggregation of component fibres is known to be a feature. That same research has shown that combining two 100% yarns each of different fibre content and half the previous linear densities during knitting to give a plaited yarn having a 50:50 composition can give improved flame retardancy relative to blended yarns of the same linear density. It is evident, therefore, that yarn structure can influence the burning behaviour of fabrics but in a complex manner.

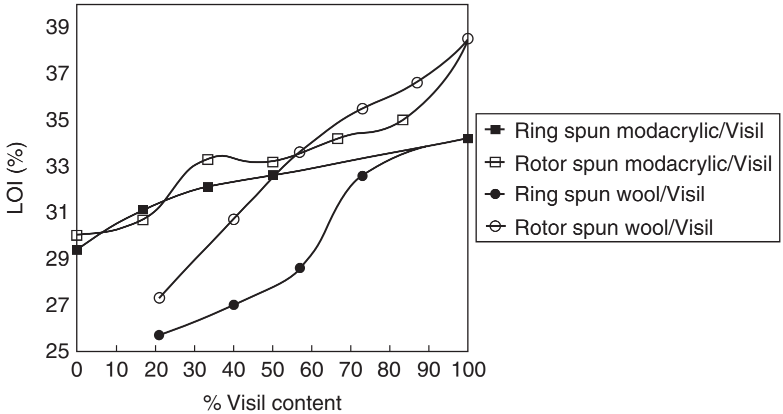

Figure 2.7 LOI values of knitted fabrics from blended yarns of Visil® and modacrylic staple fibres. Reproduced with permission from S.J. Garvey, S.C. Anand, T. Rowe and A.R. Horrocks in *Fire Retardancy of Polymers – The Use of Intumescence*, Eds., M.J. Le Bras, G. Camino, S. Bourbigot and R. Delobel, Royal Society of Chemistry, London, UK, 1998, p.376. ©1998, Royal Society of Chemistry [60]

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3 Regulatory and Testing Requirements for Flame-retardant Textile Applications

A. Richard Horrocks

3.1 Introduction

Chapter 1 has presented statistical data that have demonstrated that certain types of textiles are more hazardous than others in terms of their ability to ignite and lead to fire injuries and fatalities. However, these alone rarely drive the drafting of legislation and regulation. Within the UK, the first textiles requiring levels of defined flame retardancy were children's nightwear. In general, this requirement arose not from statistical data but from the work of Bull and co-workers published in 1964 [1] in which they studied the severities of burn casualties from the Birmingham Burns Unit in the UK. During that period, most British homes had open-coal fires, and the incidence and severity of burns to young girls wearing cotton nightdresses was of particular concern. The result was the UK nightdress regulations of 1967 [2], which required all young girls' nightdresses to have a minimum burn rate requirement (see below). These regulations effectively removed cotton flannelette nightdresses from the market. These were amended in 1985 to cover the testing of all nightwear (including pyjamas and dressing gowns) and required adult and children's nightwear to carry a permanent label showing whether or not each item meets the requirements of the British Standards (BS)

5722:1984 (revised in 1991 and which uses Test 3 of BS 5438: 1976, amended 1989- see **Section 3.3.1** below). Before testing, garments must be washed once in accordance with BS 5651, and adult garments failing the standard have to be labelled ‘keep away from fire’.

In the USA, very similar observations were being made. The 1976 study of Tovey and Vickers [3], which analysed 3087 case histories of textile ignition-caused fire deaths, showed that loose-fitting clothes such as shirts, blouses, trousers and underwear ranked higher as potential hazards than bedding and upholstered furniture; pyjamas, nightgowns, dresses and housecoats presented very similar hazards to these two latter items. The hazard of fast-burning textiles in clothing had, of course, been recognised in the USA in the 1950s with publication of the US Flammable Fabrics Act 1953, which covers clothing, children’s nightwear, carpet, rugs, and mattresses [4], and which is mentioned in **Chapter 1**.

However, in most other examples of UK fire legislation and regulations, these usually follow only if large loss of life or property occurs. Within the UK over the last 30 years, several significantly well-publicised fires involving textiles as major fuel and ignition elements have driven the need to create new or review current fire precautionary and preventative regulations and procedures. **Table 3.1** lists these major incidents, all of which were associated with textiles being the first ignited material or being responsible for major loss of life or damage.

Table 3.1 Major textile-related fires in the UK and Ireland, 1979–present

Fire	Cause	Consequences
Rail sleeper fire, Taunton, 6th July 1978	Sacks of soiled and clean laundry adjacent to electric heater.	12 fatalities/15 non-fatal casualties
Woolworths Store Fire, Manchester, 8th May 1979	Ignition by smoker's material of a stack of polypropylene fabric-covered, polyurethane-filled furniture in restaurant area.	10 fatalities/53 non-fatal casualties
Stardust Disco Fire, Dublin, 14th February 1981	Ignition of PVC-covered, foam-filled furnishings leading to flashover of multi-seating array.	48 fatalities/128 non-fatalities
Boeing 737 Fire, Manchester Airport, 22nd August 1985	Punctured fuel tank causing external pool fire which broke through the fuselage into the cabin. Cabin engulfed in toxic fumes and smoke from burning seating materials.	55 fatalities/15 serious non-fatalities
Windsor Castle, 1992	Flood lighting ignition of upper region of large curtain funnelling growing fire into the wooden ceiling and structure.	No casualties/£40 million damage and loss of heritage

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Notable among these is the fire at a Woolworths store in 1979 from which the first UK cigarette-ignition requirement for upholstered furnishings was derived. More comprehensive legislation followed in 1988 [5] with a demand for match ignition and mandatory combustion modification of foam filling. Similarly, the Manchester Boeing 737 fire brought forward the planned UK Civil and US Federal Aviation Authorities' requirement for fire-resistant seating materials in all passenger aircraft designed to carry >30 passengers [6].

All the fires listed in **Table 3.1** have a common feature that the textiles present at each scene functioned as the material first ignited by the relevant igniting source. Secondly and subsequently, the speed with which this caused the fire to grow and spread to adjacent materials was a significant feature in the inability of victims to escape or the firefighters to bring the fires under control. Therefore, these catastrophic fires serve to demonstrate more obviously initially the ignitability of textiles followed by the associated speed with which the resulting fire can grow.

With this last factor in mind, most fire regulations relating to textiles are designed to:

- Prevent facile ignition of common textiles in the first instance.
- Offer potential victims more time to escape.
- Provide protection of the body or parts of the body from fire.

Those responsible for issuing fire regulations fall into several categories:

- National governments: typically all national governments within the European Union (EU) issue their own fire regulations which can now fall (if relevant) within an overarching EU directive and its requirements. Related standards may be issued also by national standards organisations such as the American Society for Testing and Materials (ASTM), BS and Deutsche Industrial Norms (DIN), as well as international organisations such as European Standards

(CEN) and International Organization for Standardization (ISO). In the USA, standards are also issued by the Consumer Product Safety Commission (CPSC) and the National Fire Protection Association (NFPA) and federal regulations may specify them to be appropriate.

- State or provinces: in the USA, states such as California issue their own fire regulations, which may differ from national or federal regulations. An example is the Californian regulation for the flame retardance of upholstered furniture defined in Technical Bulletin 116: 1980 (**Section 3.2.2**).

- International organisations responsible for transport systems such as civilian air and marine transport (**Section 3.2.3**).

Examples of all these issues will become apparent in the foregoing sections of this chapter.

3.2 Textile-related Fire Regulations

Textile-related fire regulations between different nations may offer an overall confusing picture in terms of the items regulated and the applications covered by them but, in general, regulations fall into one of several categories depending on whether they apply: to a normal consumer living in a domestic environment; a member of the public in a public environment (e.g., hotel, airport, public building (including hospitals and prisons)); in the workplace for worker protection; for personal protection in the emergency and defence services; in transport where escape by passengers and personal is restricted. Thus, regulations cover:

- Nightwear (domestic environment).

- Upholstered furnishings (domestic and contract or public).

- Bedding (domestic and contract or public).

- Protective clothing (workplace, civil emergency and defence).
- Transport (land, marine and air).

If textiles become a part of a building such as a wall- or floor-covering, they may be covered by the normal building fire regulations for that particular country or region.

3.2.1 Nightwear Regulations

Table 3.2 lists a selection of nightwear regulations and **Table 3.3** lists nightwear- related fire regulatory tests from different parts of the world [7, 8].

Table 3.2 Selected national and international nightwear fire regulations

Country	Regulation	Mandatory/ voluntary
UK	The Nightdress (Safety) Regulation, Statutory Instrument S.I. 839:1967 and The Nightwear (Safety) Regulations S.I. 2043:1985, HMSO, London, UK.	Mandatory
Ireland	I.S. 148 Flammability and Labelling Requirements of Fabrics and Fabric Assemblies Used in Children's Nightwear. Covered by S.I. 215/1979 Industrial Research and Standards (Section 44) (Children's Nightdresses) (Amendment) Order, 1979.	Mandatory
Netherlands	The Nightwear (Safety) Regulations 1985; from 2008 all clothing must meet minimum burning requirements.	Mandatory
EU	General Product Safety Directive (2001/95/EC); European Standard (EN) 14878:2007. Textiles – Burning Behaviour of Children's Nightwear – Specification, 2007.	Mandatory

Norway, Sweden and Switzerland	No specific nightwear regulations but have general clothing flammability regulations.	
USA	Standard for the Flammability of Children's Sleepwear, Title 16, Code of Federal Regulations (CFR), 16 CFR Parts 1615 and 1616 (recodified from Department of Commerce to Consumer Product Safety Commission at 40 FR 59917, 30th December 1975). Standard for the Flammability of Clothing Textiles, 16 CFR 1610, February 2007.	Mandatory
Australia (AS)/New Zealand (NZS)	Australian Government: Trade Practices (Consumer Product Safety Standards) (Children's Nightwear and Paper Patterns for Children's Nightwear) Regulations 2007. Product Safety Standards (Children's Nightwear and Limited Daywear Having Reduced Fire Hazard) Regulations, 2008 (declares AS/NZS 1249:2003 as the standard with variations stated in Amendment A 2008).	Mandatory

Table 3.3 Selected test standards for nightwear (safety) regulations before 2000 [7]

Country	Test standard	Face/edge	Flame height, mm	Testing – type of test	Ignition time (s)	Frame	Label
Germany/ France	EN ISO 6940	F-E	40	Ignitability	0–20	ISO V	–
	EN ISO 6941	F-E	40	Flame spread	10	ISO V	–
	EN 1103	F	40	Flame spread	10	ISO V	–
				Flash			
				Flaming debris			
Netherlands	Normen Europäischer Modellbahnen 1722 (based on EN/ISO 6941	F-E	40	Flame spread		ISO V	Yes
Ireland	IS 148	F	45	Flame spread	10	BS V	Yes
UK	BS 5722 (using BS 5438:1976 Test 3 or BS 5438:1989:Test 3A)	F	45/40*	Flame spread	10	BS V	Yes
AS/NZS	AS 2755/2 Now replaced by AS/NZS 1249:2003	F-E	40	Flame spread	5–15	ISO V	Yes

Denmark, Finland, Norway and Sweden	Nordtest FIRE 029	F	16	Flame spread	1–20	45°	–
	ASTM 1230		40	Flame spread	1	45°	
	Konsumentverkets författningssamling 1985:8/ASTM 1320		40	Flame spread	1	45°	
Germany	DUTCH CONVENANT	F	40	Flame spread	5 Spread 1 Flash	ISO	Yes
				Flash			
				Flaming debris			
USA, Norway and Sweden	ASTM D1230	F	16	Flame spread	1	45°	-

E: Edge
F: Face
V: Vertical
Adapted from Anon, *Mandate/263 to CEN in the Field of Standardisation Relative to the Safety of Consumers for a Feasibility Study on Possible Standardisation on Fire Resistance of Nightwear*, Directorate General XXIV, Brussels, 8th December 1997 [7]

Even though they have been reviewed comprehensively by the author [8], a summary of the main features of the regulations will be presented here together with more recent and relevant information. Not all of the test methods in **Table 3.2** are covered by regulations and may not be mandatory. Apart from the UK whose regulations [2] have been discussed above, mandatory regulations exist in Ireland (which are similar to the UK regulations [2, 9]) and the USA [10]. Here the US CPSC flammability standards 16 CFR Parts 1615 and 1616 for children's sleepwear are based on flame spread. If the mean char length of burning for five specimens exceeds 178 mm (7 inches), the fabric is deemed not to comply with the flammability regulations, and garments must pass this test after withstanding 50 launderings. In 1996, the US CPSC voted to amend the children's sleepwear standard under the Flammable Fabrics Act. The amendments permitted the sale of tightfitting children's sleepwear for infants aged ≤9 months, even if the garments did not meet the flammability standards ordinarily applicable to such sleepwear. The amendments were based on the fact that there were virtually no reported injuries associated with single-point ignition incidents of tightfitting sleepwear, or from sleepwear worn by infants aged <1 year [8, 11].

Australia and New Zealand have regulations that require labelling of all the children's night-clothes to display an appropriate hazard classification [12]. The Australian philosophy regarding consumer protection is to inform consumers of the hazard and hence permit them to make their own judgement as to whether the risk is acceptable. The standard AS/NZS 1249:2003 [13] enables nightwear to be classified as 1, 2, 3 or 4. Categories 1, 2 and 3 carry a label signifying a low danger of fire, and category 4 a label signifying a high danger of fire.

Within the European Community, several countries had regulations which were usually voluntary (**Table 3.2**) but in 1997 a mandate from the EU [7] required the CEN 248 to investigate the feasibility of introducing nightwear flammability regulations. Two task groups reported respectively on the nightwear standards then currently available (**Table 3.3**) and the possible toxicological hazards associated with flame-retardant treatments available for nightwear [14]. For instance, the Dutch and French standards in **Table 3.3** were derived from an ISO-standard (ISO 6941) on the measurement of flame-spread properties and ISO 6940 on determination of the ease of ignition. The Swedish and Norwegian regulations were based on the ASTM 1230 standard test method for the flammability of clothing textiles. Most of the national test methods listed in **Table 3.3** were and remain based on existing national standards which, outside of the respective country of origin, do not have acceptance. The second task group of committee for CEN 248 considered the possible toxicological consequences of using several of the most appropriate flame-retarded textiles in nightwear. Because of the nature of the end-use involved, antimony-bromine-based flame retardants were excluded from the study [14]. For the established durable phosphorus-containing finishes for cotton-based fibres and inherently flame-retardant viscose as well as synthetic (e.g., polyester, modacrylic) fibre-containing fabrics, respective toxicological hazards were considered to be low and hence the toxicological risk negligible. As a consequence of the submitted report [14] this same CEN 248 Committee were asked to draft an appropriate test method and standard by September 2003 [15]. In 2007, a new EN 14878:2007 [16] was issued although a voluntary one is currently under review for publication in the Official Journal of the EU (*OJEU*) under the General Product Safety Directive (2001/95/EC (European Commission)). The standard covers all types of nightwear, including nightdresses, nightshirts, pyjamas, dressing gowns, and bath robes. It provides requirements for an absence of surface flash and the maximum burn rate acceptable for different categories of nightwear garments. It also places responsibility on the manufacturer to ensure that any flame-retardant chemicals used are effective throughout the life of the garment and do not present a health hazard.

The test methods required by EN 14878 are based upon BS EN 1103:2005 [17] but without any prior washing requirement. This standard defines the following classes:

- *Class A – All Nightwear (except pyjamas)*: There shall be no surface flash and the third marker thread (520 mm) must not be severed in <15 s.
- *Class B – Pyjamas*: There shall be no surface flash and either the third marker thread (529 mm) must not be severed in <10 s, plus certain design criteria must be met (including hem circumference, sleeve cuff, and bottom trouser width dimension) or the burn rate from Class A is applicable without the design criteria.
- *Class C – Babies' Nightwear (up to 6 months)*: No criteria.

This standard does not override existing legislation in any EU country, which must still be complied with (e.g., UK, Ireland) and which are more stringent with regards to burn rate. For example, in the UK BS 5722:1984 (revised 1991) requires a minimum burn time of 25 s before reaching the second marker thread and 50 s before reaching the second marker thread using BS 5438:1976: Test 3 (or 30 s and 42 s, respectively, using BS 5438:1989:Test 3A) (**Section 3.3.1** below) and, in the case of flame retardant-treated clothing, washing before testing and labelling. However, additional aspects covered by this standard, include no surface flash and requirements for terry towelling bathrobes and pyjamas and children's nightwear from ages 13–14 years.

3.2.2 Upholstered Furniture, Furnishing and Bedding Regulations

Table 3.4 lists the current regulations relating to furnishings and furniture in Europe and the USA [18]. This area has been reviewed in detail by Nazaré and Davis very recently [19] and the following discussion will focus only on the main aspects of soft-furnishing regulation and testing methods.

Table 3.4 Selected national and international furniture and furnishing fire regulations [18]

Country	Regulation	Test method	Domestic/contract or public
UK/Ireland	*Consumer Protection Act (1987), the Furniture and Furnishings (Fire) (Safety) Regulations*, *1988*, SI1324 (1988), London, HMSO, 1988; revised 1993.	BS 5852:1979: Part 1	Domestic
	Regulatory Reform (Fire Safety Order) 2005 (Fire safety of furniture and furnishings in non-domestic environments).	BS 5852:1979: Part 2 and BS 7176:1995 revised 2007 (seating) and BS 7177:2008 (bedding) using EN 1021-1 and EN 1021-2.	Contract/public
France	No.200-164 - Bedding	EN ISO 12952-1 and 12952-2	Domestic
	U 23 (Health) – Bedding Mattress	EN ISO 12952-1 and 12952-2 EN 597	Contract/public
	AM 18 (Public) – Seat	NF D 60013N, NF P 92501 and NF P 92507	Contract/public
	GPEM D1-90 (Prison) – Mattress	EN 597-1, EN 597-2 and GPEM D1-90	Contract

Italy	DM26/06/1984; seat and mattress fillings	CSE RF 4/83	Public
Finland	No.743/1990 and No.479/96.	EN 1021-1	Domestic
	Finnish fire safety guidelines for furnishings; A-56, 1988.	EN 1202-1 and EN1202-2	Public
Sweden	No regulations only recommendations from the consumer agency: seating and mattresses.	EN 1021-1 EN 1202-1 and EN 597-1	Domestic and public
Norway	Crown Prince Regent's Decree 07/09/1990: seating and mattresses.	EN 1021-1 EN 1202-1 and EN 597-1	Domestic and public
Spain and Portugal	Same as French regulations.	-	-
Germany	Requirements for seating in cinemas.	DIN 4102 (classification B2 required)	-
USA California	Technical Bulletin 116: 1980 - Requirements, test procedures and apparatus for testing the flame retardance of upholstered furniture.	Tech Bull 116:1980	Domestic
	Technical Bulletin 117: 2002 - Requirements, test procedures and apparatus for testing the flame retardance of resilient filling materials in upholstered furniture.	Tech Bull 117:2002: test method No. 191	

	Technical Bulletin 603: 2005 - California open flame standard for mattresses.	Method 5903.2 or FF 3-71	
USA Federal	CPSC 16 CFR Part 1634. Proposed standard for the flammability of residential upholstered furniture; proposed rule, US CPSC, 4th March 2008.	CPSC 16 CFR Part 1634	Domestic
	CPSC 16 CFR Part 1632: Standard for the flammability (cigarette ignition) of mattresses and mattress pads (FF 4-72, Amended 2013), US CPSC.	CPSC 16 CFR Part 1632	
	CPSC 16 CFR Part 1633: Standard for the flammability (open flame) of mattress sets, US CPSC, 15th March 2006.	CPSC 16 CFR Part 1633	

In **Chapter 1**, the UK furnishing regulations have been briefly discussed as well as their known effect on UK Fire Statistics since their implementation in 1988 [5]. These are the only mandatory regulations that exist for domestic furnishings, and they cover all forms of upholstered furniture, including: children's furniture; mattresses; bedheads; sofabeds; futons and similar convertible furnishings; garden furniture suitable for use in the home; furniture in caravans; scatter cushions and pads; and loose and stretch covers. Excluded items are bedding, duvets, pillowcases and curtains. The amendment in 1993 introduced secondhand furniture and also included furnishings in rented dwellings and furnishings manufactured since 1950 into the regulations. The amendment in 2010 enabled the polyester-cover fabrics used in the testing of filling materials to be updated given that the one defined in the 1988 regulations is no longer available commercially. The UK regulations cover the testing requirements for fillings (e.g., polyurethane foam) and furnishing fabrics tested over a commercial filling and standard polyurethane foam. Thus, fabrics are tested as a fabric/filling composite (**Section 3.3.2** below). A guide to these regulations has been published by the UK Fire Industries Research Association (FIRA) International [20].

In the USA, while the proposed US standard CPSC 16 CFR Part 1634 covers furniture, CPSC 16 CFR Part 1632 and Part 1633 cover mattresses for cigarette and open-flame hazards, respectively. The US standard CPSC 16 CFR Part 1634 for furniture was proposed in 2008 and is currently a source of much debate regarding current (February 2013) concerns in the USA about introducing flame retardants into the home environment. The proposal seeks to establish performance requirements as well as certification and labelling requirements for upholstered furniture and manufacturers who would choose one of two possible methods of compliance. Either they could use cover materials that are sufficiently smoulder-resistant to meet a cigarette-ignition performance test or they could place fire barriers that meet smouldering and open-flame resistance tests between the cover fabric and interior filling materials. The CPSC still intend to finalise these proposed regulations but it is probable that these may be modified so that they may be met by non-use of flame-retardant chemicals [21]. A similar debate is being undertaken in California, where the current 30-year-old Technical Bulletin 117: 2002 (requirements, test procedures and apparatus for testing the flame retardance of resilient filling materials in upholstered furniture (**Table 3.4**) is proposed to be replaced by one that removes the open-flame or simulated match test. This requires flame-retardant chemicals in the foam and fabric components of furniture [22]. The proposed regulation will require only cigarette ignition resistance of cover or barrier fabric using the procedure outlined in ASTM E1353-08a [23].

All other national regulations for domestic furnishings are not mandatory, only in the public and/or contract sector are respective regulations mandatory because of the need to protect public safety. For instance, in the UK, the Regulatory Reform (Fire Safety Order) 2005 (**Table 3.4**), which became law in 2006, replaced >70 former pieces of UK fire safety regulations, such as the Fire Precautions Act of 1971, the Fire Precautions (Factories, Offices, Shops and Railway Premises) Regulations 1976 and the Fire Precautions (Workplace) Regulations 1977. While such regulations relate to buildings and their fire safety, textiles are covered if they are a part of that building such as walls, floor-coverings, curtains and blinds. To ensure that textiles comply with the necessary regulations, premises are inspected by the local Fire and Rescue Authority. With regard to furnishings in non-domestic buildings, the advisory standard BS 7176:2007 [24] is used by fire authorities. **Table 3.5** summarises the essential features of this standard, which identifies the ignition sources to be used for buildings of low to very high hazard.

Table 3.5 Ignition source/hazard combinations – BS 7176: 1995 revised in 2007 (for full details, see the actual standard)

Requirements	Low hazard	Resistance to ignition source: smouldering cigarette of BS EN 1021-1:2006 and the match flame of BS EN 1021-2:2006.
	Medium hazard	Resistance to ignition source: smouldering cigarette of BS EN 1021-1:2006 and the match flame of BS EN 1021-2:2006. Resistance to ignition Source 5 in BS5852: 2006.
	High hazard	Resistance to ignition source: smouldering cigarette of BS EN 1021-1:2006 and the match flame of BS EN 1021-2:2006. Resistance to ignition Source 7 in BS5852: 1990.
	Very high hazard	Resistance to ignition source: smouldering cigarette of BS EN 1021-1:2006 and the match flame of BS EN 1021-2:2006. At discretion of the specifier but at least high hazard requirements.
Typical examples	Low hazard	Offices, schools, colleges, universities, museums, exhibitions and day centres.
	Medium hazard	Hotel bedrooms, public buildings, public (boarding) schools, restaurants, places of public entertainment, public baths, public houses and bars, casinos, hospitals and hostels.
	High hazard	Sleeping accommodation in certain hospital wards and hostels. Offshore installations.
	Very high hazard	Prison cells.

For instance, 'low hazard' relates to schools and colleges, where only cigarette (Source 0) and simulated match (Source 1) ignition resistance are required. This is similar to UK domestic furnishings except that tests BS EN 1021-1 and -2 are used instead of BS 5852:2006 Sources 0 and 1. Buildings in which the public are generally admitted or sleep, such as hotels, restaurants and places of entertainment, are in the 'medium' hazard category and these require Crib 5 (BS 5852:2006: Source 5) ignition resistance. The 'high' hazard rating relates to hospital wards (UK National Health Service and private) and offshore accommodation, where Crib 7 (BS 5852:2006: Source 7) ignition resistance is required. The 'very high' hazard rating is required in prison cells and here the criteria required are at least those required in the previous high hazard category plus other safety factors at the specifiers' discretion. BS 7176 also defines the labelling requirements for items, as does the similar standard for bedding, BS 7177 [25], which also falls under UK Furnishing and Furniture and regulatory Reform requirements (**Table 3.4**). FIRA International has produced a guide to the UK contracts furnishing regulations in which these standards are explained more fully [26]. BS 7177:2006 mirrors BS 7176 exactly in determining low, medium, high and very high hazard environments, each of which requires a specific test regimen. There are three cited test methods: BS EN 597-1:1995 (Furniture: Assessment of the Ignitability of Mattresses and Upholstered Bed Bases. Ignition Source: Smouldering Cigarette); BS EN 597-2:1995 (Furniture: Assessment of the Ignitability of Mattresses and Upholstered Bed Bases. Ignition Source: Match Flame Equivalent); and BS 6807:2006 (Methods of Test for the Assessment of Ignitability of Mattresses, Divans and Upholstered Bed Bases with Flaming Types of Primary and Secondary Sources of Ignition) (**Section 3.3.2**). For all hazard levels, bedding items should conform to BS EN 597-1 and BS EN 597-2. Medium-hazard areas require a pass to ignition Source 5 (BS 6807), high hazard areas a pass to ignition Source 7 (BS 6807) and, for very high hazard areas, there may be additional requirements in tandem with the latter.

Other countries such as France and Germany (**Table 3.4**) specify the public places where different (but specific) regulations apply.

3.2.3 Protective Clothing (Workplace, Civil Emergency and Defence)

In the UK, the need for protective clothing is regulated by the Health and Safety at Work Act of 1974. In the main, protective clothing falls into one of two groups [27]:

- Protective clothing for workwear, hazardous industrial occupations, firefighters and defence personnel.

- Extreme hazard protection, e.g., furnace operators' aprons to protect against hot metal splash, fire entry suits, and racing car drivers' suits.

Within the EU, the Directive on Personal Protective Equipment (PPE) 89/686/EEC (European Economic Community) of 1989 belongs to the family of directives under Article 114 of the Treaty on the functioning of the EU. In the case of protective clothing, these directives harmonise products to ensure a high level of protection for citizens throughout Europe. National regulations incorporate the requirements of the relevant directive for the various types of protective clothing.

Underpinning the directive are several CEN testing methods for heat- and fire-protective clothing, which include:

- BS EN 469:2005 - Protective Clothing for Fire-fighters - Performance requirements for protective clothing for fire-fighting [28].

- ISO 11613:2000 - Protective Clothing for Fire-fighters - Laboratory test methods and performance requirements [29]. This is a combination in one document of EN 469:1995 (revised 2006) and NFPA 1971 from a similar date. It is intended to be revised as the basis for all of the PPE items which are required for 'conventional' fire-fighting and hence issued as an ISO test.

- BS EN IS0 11611:2007 (replacing former BS EN 470-1:1999) - Protective Clothing for Welders [30]. These are the performance requirements for a weld droplet test and flammability behaviour, and also have detailed design criteria (to prevent weld spatter being trapped in turn-ups). A unique aspect is that it contains a note as to the dangers of ultraviolet radiation from welding processes in the context of potential skin cancer.

- BS EN ISO 11612:2008 (replaces BS EN 531:1995) - Protective Clothing - Clothing to protect against heat and flame [31]. This is a complex performance specification providing a choice of several main performance levels to various heat sources, including molten metal splash protection (as distinct from welding spatter) plus one extreme level of heat protection. It also sets design criteria for garments and seams.

- BS EN ISO 14116:2008 (replacement for BS EN 533:1997- Protective Clothing - Protection against heat and flame - Limited flame spread materials, material assemblies and clothing. This is a means of classifying clothing materials subjected to ISO 15025:2000, which is a test to determine the extent of damage to a fabric sample subjected to a small flame. The final index gives a measure of flame resistance and durability (**Section 3.3.4**).

While some of these standards refer to a specific application or hazard (e.g., BS EN ISO 11612 for welders protective clothing), others such as those for fire-fighters define a set of performance requirements for protective properties such as flame resistance and heat protection as well as for setting design criteria. An objective of the 2005 revision of EN 469 is to offer two levels of heat protection so as to take account of various ambient conditions and fire-fighting methods (**Section 3.3.4**).

In the USA, there is no federal standard for protective clothing. However, various USA regulatory agencies, such as the Occupational

Safety and Health Administration (OSHA), under several of its regulations, and the US Departments of Defence and of Transportation, in their regulations (where appropriate) incorporate by ‘reference’ a standard vertical flame test such as ASTM D6413 or similar [32]. This requirement is essentially regulated as a mandatory standard because most regulatory agencies’ legislative requirements include a ‘general duty clause’. For example, under OSHA, an employer is required to maintain ‘a safe and healthful workplace’.

The methodologies underlying some of these regulatory test methods have been reviewed in detail by Haase very recently [33] and will be discussed concisely in **Section 3.3**.

3.2.4 Regulations and Tests Relating to Transport

Textiles in transport are, in general, associated with seating, floor-coverings and other furnishings within the vehicle or vessel interior. Within the defence, civil emergency and industrial sectors, similar associations may be made, although protective clothing and other safety/protection-related equipment will comprise textile components. Textiles are also present in fibre-reinforced composites, which form major structural components in vehicles as well as in functional components such as tyres, beltings, wiring harnesses, and filters. In most of these transport applications in which safety is an issue, there are national or international regulations that govern their fire-performance requirements. Automobiles may be included here because of their many textile components but only those in internal passenger compartments such as seating, carpet as well as internal side and roof-lining fabrics require a defined level of flame resistance.

In aircraft, all internal textiles such as seatings, internal decor and blankets require defined levels of flame or fire resistance to internationally recognised standard levels. However, higher levels of fire- and heat-resistant textiles are required in engine insulation (e.g., ceramic fabric structures around combustion chambers), reinforcements for composites (e.g., carbon-fibre reinforcements for major structural elements), and aramid honeycomb reinforcement for wall and floor structures as well as fuselage acoustic and fire/heat insulation.

In surface marine vessels, whether for commercial, pleasure or naval purposes, similar textile solutions to those seen in aircraft include interior textiles as well as those present in metal-replacing composites used in fibre-reinforced composite hulls, bulkheads and superstructures, for example.

3.2.4.1 General Testing and Performance Requirements

National and international operating transport systems such as air and marine are subject to international fire regulations and standards.

Marine regulations fall within the remit of the International Maritime Organisation (IMO) whereas commercial air regulations are affected by national organisations such as the Civil Aviation Authority in the UK, the European Aviation Safety Agency across Europe, and the US Federal Aviation Administration (FAA) in the USA. These and national authorities belong to the International Civil Aviation Authority and together define the various fire standards relating to commercial aircraft across the world. However, the US FAA and its associated regulations and test methods largely determine the world's commercial regulations and associated test methods [34, 35].

While most national railways recognise the fire hazard posed by rail travel, outside of the EU national standards exist and these differ from country to country [34]. The same mix of fire standard requirements also existed across the EU member states until 2008, when the European Directive 2008/57/EC was published covering high-speed and conventional rail vehicles as a means of coordinating fire requirements across Europe. The standards to be implemented across the EU with regard to assessing the performance of materials and components within rail vehicles were published in BS EN 45545 in 2010, with Part 2 being especially relevant to the materials within rail vehicles [34]. This standard will take time to be implemented and, in the meantime, respective EU national standards will prevail, such as BS 6583 (UK), Normalisation Francais (NF), NF-F 16-101/ NF-F-102 (France), Ente Nazionale Italiano di Unificazione Comitato Elettrotecnico Italiano 11170:2005 Part 3 (Italy) and Polskie Normy, PN-K-02511 March 2000 (Poland), in which textile items such as seating materials feature.

A more detailed discussion of these international regulations and standards are beyond the scope of this chapter, but examples of test methods and performance requirements can be found from various sources [34–39]. Below is presented an outline of those most significant textile-related fire regulations and test methods for the various transport sectors.

3.2.4.2 Land Transport

Regulations extend mainly to public transport such as buses, coaches and trains although, as shown below, automobiles with global markets accept the need for some level of textile flame resistance.

Automobiles: Referring to fire risk in the USA, 70% of vehicle fire losses occur in road vehicles, over 90% of which involve private cars [40] **Figure 3.1** shows that the total number of fires in automobiles has reduced by more than fourfold, of which deliberate fires form the major part (which in 2010/11 was ≈ 65%) [41].

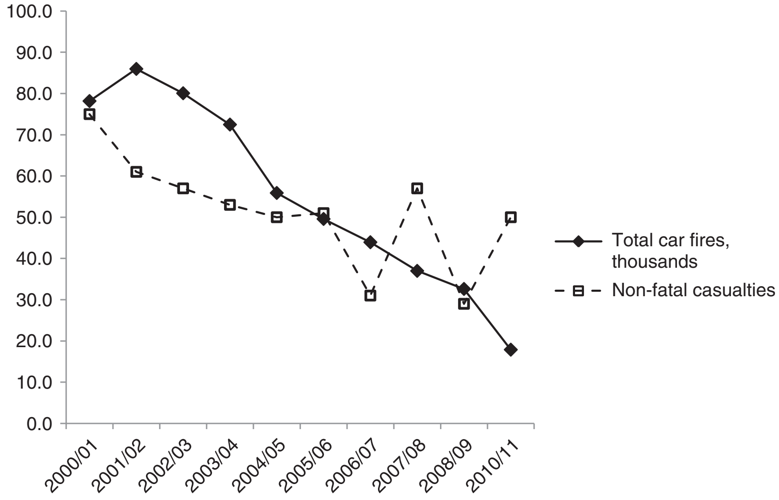

Figure 3.1 Incidence of car fires and non-fatal casualties in the UK, 2000–2011 [7]

The decrease in the incidence of deliberate fires has been attributed to several factors, including an improved UK licensing regimen (and related success of vehicle-removal schemes) and the increase in metal prices (which makes car abandonment less attractive). While fatal casualties are very few and often zero in any one year, the number of non-fatalities has, in general, reduced in a fluctuating manner. These figures would suggest that the internal contents of cars are, in general, safe even with the increasing wiring hazard content (although what fraction of these fires relates to the interior textile content is not known). These statistics might suggest that automobiles do not require international fire regulations. However, while there are no official international regulations for establishing a minimal level of fire safety in cars worldwide, its global character has forced adoption of the US Federal National Highway Traffic Safety Administration (Federal Motor Vehicle Safety Standards, (FMVSS)) 302 standard [42] test developed in 1969 and implemented in 1972. This standard was designed to prevent ignition in the passenger compartment of textile materials to a lighted cigarette by defining a minimum burning rate of 100 mm/min of the sample held in a horizontal geometry. This standard has now been re-designated in many countries by their respective test organisations, e.g., ISO 3795, BS AU 169 (UK), Union Technique de l'automobile, cycle and motorcycle standard, UTAC ST 18-502 (France), DIN 75200 (Germany), Japanese International Standard (JIS) D 1201 (Japan) and ASTM D-5132 (US). Typical fabric types occurring in automobiles and which pass these criteria have been described by Fung and Hardcastle [43].

Buses and coaches are often determined by national regulations depending on previous fire experiences. Troizsch [34] has summarised the position in the EU following its issuing of a directive in 1995 (EU Council Directive 95/28 EC (10.95)) which defines requirements for the fire behaviour of interior materials in vehicles carrying ≥22 passengers. Textile materials include decorative fabrics used to line the ceilings and walls, those with an acoustic function, curtain and blind materials, and those used in seating. A test similar to FMVSS 302 is described to test fabrics for a minimum burning rate of 101 mm/min in the horizontal geometry. The ISO 6941 vertical strip test is used to assess blind and curtain flammability and testing for potential flaming drip formation is also required for roof linings.

Trains and rapid transit systems: As stated above, national railways are traditionally required to conform to national fire standards, which are typically often quite different from one another [34]. Within the EU standard BS EN 45545 discussed above, the main concerns for materials in a fire are heat release, spread of flame and toxicity, and smoke density, which reflect the similar stringent material requirements which have been applied within the aviation sector for many years (see below). Hazard levels (HL) are designated to the type of railway vehicle. For instance, a standard carriage is given the lowest level, HL1, and a couchette/sleeper carriage, HL3, the highest. Within all carriage vehicles, a significant hazard is posed by furnishings and bedding (listed in **Table 3.6**) which must be tested to protocols described in BS EN 45545-2 [36].

Table 3.6 Furnishing items identified in BS EN 45545-2 together with their test protocol requirements [36]

Item	Description
Complete passenger seat	Complete passenger seat including arm and head rests, separate pillows, tip up seats and driver seat accessible to the passenger.
Upholstery for passenger seats and head rest	Upholstery for seats and head rest.
Armrest passenger seats – upwards facing surface	Armrest – surface on which the arm rests.
Armrest passenger seats vertical surface	Armrest – inside surface (or outside surface on transverse seating) which is against the body of the seat occupant.
Armrest passenger seats – downwards facing surface	Armrest – underside surface of the arm rest.
Back shell; base shell of passenger seats	Back shell; base shell of passenger seats.
Seats in staff areas	Tested as an assembled product from upholstery, back and base shell side.
Mattresses	Mattresses
Bed clothes for couchettes and beds (blanket, duvets, pillows, sleeping bags and sheets).	Bed clothes for couchettes and beds (blanket, duvets, pillows).
Underside surface of couchettes and beds.	Underside surface of couchettes and beds.

Other potential textile materials may also be present in curtains, blinds, decorative panels and floor-coverings, each of which is covered by a set of defined requirements and hazard-related performance criteria. Readers are advised to consult the actual standard to fully understand the complexity of the test protocol defined for each material type.

Not surprisingly, textile materials that achieve the desired fire performance criteria will be similar to those in aircraft, and include flame-retardant wool and blends for seatings, flame-retardant polyester for curtains, and polyamide for floor-coverings with flame retardant back-coatings.

Metropolitan railways, especially those underground, are particularly high-fire-risk transport systems and, within the textile field, only seats are of significance. Again, flame-retardant wool and blends feature significantly.

3.2.4.3 Marine Transport

Maritime shipping falls into two groups: commercial passenger and cargo vessels, and naval surface vessels and submarines. The entire area of the factors determining choice of flame-retardant materials for use in this sector has been reviewed recently by Sorathia [44].

Naval vessels: Naval-vessel regulations will be defined by each country with respect to its own surface and submarine craft. For example, the primary regulatory body for the fire performance of materials in US Navy ships and submarines is the Naval Sea Systems Command, also referred to as the Naval Technical Authority [44]. However, textile materials rarely feature in regulations from such a body and where they are used, they are subject to separate governmental military specifications. For instance, in the US military, standard 1623 [45] provides the fire performance requirements and approved specifications for various categories of interior finish materials and furnishings for use on naval surface ships and submarines. This standard identifies the Federal Standard 191 (Tests for Textiles) in which, for instance, Method 5903 defines a 45° strip method for determining the flame resistance of clothing and Method 5905 as the method for assessing material behaviour if subjected to a high heat flux contact. This latter test involves a larger (Fisher) gas burner as opposed to the simple Bunsen burner defined in 191A Method 5903, and the fabric is suspended vertically. Clearly, different textiles having varying levels of flame retardancy may be assessed using either of these standards and so enable them to be used for naval applications.

Similar methods are used by other navies and, in the UK, the Ministry of Defence will determine the standards for protective clothing, general uniforms and interior textiles. Outer garments, in particular, must protect against high heat fluxes, and these will be based on protective textiles used in non-defence and other defence applications [27, 46]

Commercial passenger and cargo ships have to comply with the fire performance requirements contained in the International Convention for the Safety of Life at Sea as Codes Safety for High Speed Craft of the IMO [47]. In the main, these codes are concerned with fire prevention, detection, containment and control of flame, as well as smoke spread and suppression, and escape. The selection of potentially flame-resistant textiles, including textile-reinforced composites and the associated standard testing methods, will be defined within the fire-prevention arena defined in Part B (Prevention of Fire and Explosion) [47,48]. The fire tests to be carried out and the acceptance criteria are defined in the International Code for Application of Fire Test Procedures (IMO/FTP), which have been mandatory since 1998 [49].

Textile materials are covered (often indirectly) if they are part of a structure. For example, wall décor and floor-coverings are covered by FTP Code Part 1 - Non combustibility test using the standard ISO 1182; 1990, by Part 2 - Smoke and toxicity test (using ISO 5659) and by Part 5 - Test for surface flammability procedures, which applies also to floor-coverings and which are tested in accordance with resolution A.653(16) [50].

Textile materials not part of another structure are more specifically covered in IMO FTP Parts 7-9 which are:

- Part 7: Test for vertically supported textiles and films: draperies, curtains and other textile materials are required to have qualities of resistance to the propagation of flame not inferior to those of wool of mass 0.8 kgm^{-2}; they shall comply with this part and be tested in accordance with resolution A.563(14) [51].

- Part 8: Test for upholstered furniture: this requires that eligible upholstered furniture shall be tested in accordance with resolution A.652(16) [52]. The test method used is based on the BS for upholstered furnishings, BS 5852 for cigarette and simulated match ignition sources, and so fabrics conforming to the current UK furnishing regulations [5] will be satisfactory in marine applications.

- Part 9: Test for bedding components: bedding components must be tested in accordance with resolution A.688(17) [53]. The test method used is similar to that in Part 8 except that a mock-up of a mattress or pillow of the same size (450 × 450 mm) is subjected to the cigarette and simulated match source.

Fabrics should be tested after a defined wash or durability test and in the case of Part 7 for fabrics treated with a flame retardant; this is a single specified wash cycle which only durable flame-retardant finishes will pass. However, furnished cabins comprising several different fabrics (e.g., cotton and cellulosic blends, silk- and wool-containing fabrics) are often after-treated by spray or roller application of solutions of soluble flame retardants comprising typically ammonium or organic base phosphates sometimes in the presence of ammonium bromide to confer an element of vapour-phase activity. These treatments are often semi-durable at best but at the present time are accepted and certified to FTP Code standards if they are durable to dry-cleaning [54]. However, fabrics containing inherently flame-retardant fibres such as flame-retardant-modified polyester (e.g., Trevira CS®), polyacrylics (e.g., modacrylics such as Kanecaron®) and flame-retardant polypropylene do not require a prewash treatment before testing.

Not surprisingly, all textiles conforming to Parts 7–9 must also comply with Part 2, which relates to smoke and toxicity. **Table 3.7** lists the maximum permissible toxic gas emissions from curtains tested under the Part 2 regulation.

Table 3.7 Maximum concentrations of toxic gas emissions allowed for curtains for use in commercial shipping and tested to IMO FTP Part 2 method, ISO 5659:1994 Part 2

Carbon monoxide	1450 ppm
Hydrochloric acid	600 ppm
Hydrofluoric acid	600 ppm
Nitrogen-containing oxides	350 ppm
Hydrobromic acid	600 ppm
Cyanuric acid	140 ppm
Sulfur dioxide	120 ppm

Regulations for high-speed craft >40 knots require certain additions or modifications to the regulations stated above. These require that structural materials (including textiles) do not create a flashover in a fire, have average heat release rates (HRR) ≤100 kW, maximum HRR values over 30 s period ≤500 kW, minimal smoke emissions and flame spread rates, an absence of flaming drops and all seatings conforming to FTP Code Part 8 above.

As cruise ships become ever larger, so fire risk increases. The need to reduce this has been addressed largely in the carpet and upholstered furnishings areas, where in the former, for instance, IMO/FTP approval is given if the carpet has minimal flame spread under method A.563 (FTP Part 7) and low smoke and toxic gas generation under IMO Resolution, Maritime Safety Committee 61(67) (FTP Part 2). Carpets, in addition to the resolution A.653(16) method (FTP Part 5) are also often required to pass the reaction-to -fire test BS EN ISO 9239-1:2010 (**Table 3.8**), which specifies a method for assessing the burning behaviour and spread of flame of horizontally mounted floorings exposed to a heat flux radiant gradient in a test chamber if ignited with pilot flames.

Table 3.8 Selected test methods for textiles

Test type	Nature of test	Textile type	Standard	Ignition source
Simple fabric strip tests	BS based vertical strip method BS 5438:1989.	Curtains and drapes	BS 5867: Part 2:1980 (1990).	Small flame
		Nightwear	BS 5722:1991	Small flame
	ISO vertical strip similar to Tests 1 and 2 in BS 5438.	Vertical fabrics	BS EN ISO 6940/1:1995 revised 2003. ISO 15025:2002	Small flame
	US strip tests	Vertical fabrics	ASTM D6413. US Federal Test Method Standard 191, Method 5136(3).	Small flame Sample size 305 × 70 mm, Small flame impinging for 20 s.
		Horizontal 0, 45, 60, 90° 45°	FMVSS 302 US Federal Aviation Regulation (FAR) 25. 853(b) CFR-2012-16-2.	Small flame Small flame, 12 s ignition Small flame
Textile composite and product tests	Apparel not for protective clothing.	Vertical clothing fabrics	BS EN 1103:2005	Uses BS EN ISO 6941:2003, 10 s ignition.

	UK small-scale composite test for furnishing fabric/fillings. See also Table 3.4 for non-UK countries.	Furnishing fabrics	BS 5852: Parts 1 and 2:1979	Cigarette and simulated match flame (20 s ignition).
			BS 5852:1990 (revisions 1998, 2006) replaces BS 5852: Part 2	Small flames and wooden cribs applied to small and full scale tests.
			ISO 8191: Parts 1 and 2 (same as BS 5852:1990)	–
			BS EN 1021-1:2006	Cigarette
			BS EN 1021-2:2006	Simulated match flame (15 s ignition).
			BS 7176:2007	Advises on test selection (BS 5852 *versus* BS EN 1021/2) *versus* hazard (see Table 3.5).
		Bedding (mattresses)	BS 6807:2006	Specifies sources from BS 5852:2006.
			BS EN 597-1 and -2:1995	Cigarette and match ignition tests.
			BS 7177:2008	Advises on which test method/ source to use for specified hazard levels.
			BS EN ISO 12952-1 and 12952-2:2010	International standard for cigarette and match ignition testing.

		Carpets	BS 6307:1982/ISO 6925-1982	Methenamine pill ignition source.
			BS EN ISO 9239-1:2010	Reaction to fire test using a radiant source at 30° (≈10 kWm^{-2}).
		Curtains	BS EN 13772:2003	Uses EN ISO 6941 fitted with an additional radiator source.
			BS 5867-2:2008	Uses BS EN ISO 6941 for domestic and ISO 15025 for contract fabrics.
			BS EN 1102:1996	Uses EN ISO 6941with 10 s ignition time
Tests undertaken with the addition of radiant heat including reaction to fire tests.	Use of radiant flux plus specified ignition.	Carpets: All fabrics/composites often for use in seatings.	EN ISO 9239-1:2010 NF 92503, French 'M test'	Irradiate with 30° gas heated panel (≈10 kWm^{-2}). Irradiate with small burner.
		Aircraft seat assemblies, so-called 'Boeing' test.	ASTM E906: 1983 and FAR 25.853 Part 4, App F uses Ohio State University heat release calorimeter.	Irradiate under 35 kWm^{-2} with small flame ignite.

Thermal protection (including protective clothing and manikin tests).	Protective clothing: General requirements.		BS EN 340:2003	Design, comfort, durability and labelling requirements.
	Resistance to radiant heat.	–	BS EN ISO 6942:2002 (formerly BS EN 366:1993 which replaced BS 3791:1970)	Exposure to radiant source.
	Resistance to convective heat (flame).	–	BS EN 367:1992	Determine heat transfer index.
	Resistance to molten metal splash.	–	BS EN ISO 9185:2007 (replaces BS EN 373:1993)	Molten metal.
	Gloves against thermal risks.	–	BS EN 407:2004	Composite standard (including firefighters' and welders' gloves).
	Fire-fighters' clothing.	–	BS EN 469: 2005	Composite standard.
	Welders' and allied industrial clothing.	–	ISO 11611:2008 (replaces BS EN 470-1:1999)	Composite standard.
	Protective clothing-against heat and flame.	–	BS EN ISO 11612:2008 (replaces BS EN 531:1995)	Composite standard.

	Protection against limited heat and flame.	–	BS EN ISO 15025:2000 (formerly BS EN 532:1995)	Small flame.
	Protective clothing – protection from limited flame spread.	–	BS EN ISO 14116:2008 (uses BS EN ISO 15025 method and replaces BS EN 533:1997)	Damage definition enables fabric classification.
	Contact heat transmission.	–	BS EN 702:1995	Contact temperatures 100–500 °C.
	Fire-fighters' hoods.	–	EN 131911:2004	–
	Instrumented manikin testing of whole garments.	–	BS ISO 13506:2008	Prediction of burn injury in terms of first-, second- and third-degree burn propensity.
Durability tests	Cleansing and wetting procedures for use in flammability tests.	All fabrics	BS 5651:1989	Used on fabrics before submitting for standard ignition tests.
		Commercial laundering	BS EN ISO 10528: 1995	–
		Domestic laundering and dry-cleaning	BS EN ISO 12138: 1997 BS EN ISO 6330:2012	–

It is probably generally true to say that pure wool and wool-rich blends can conform easily to the standards required for carpets, although sometimes flame-retardant wool (e.g., Zirpro® wool) may be used depending on the carpet structure and weight.

3.2.4.4 Aviation

As stated above, the FAA is the principal regulation-defining body in the world because it influences all other national and international regulators. The FAA materials test procedures are covered comprehensively in their online handbook [55]. Lyon [56] has described those test methods in detail as they relate to aerospace and aviation. According to Troitzsch [57], within a modern, high-capacity jet such as the Boeing 747, there are ≈4000 kg of plastics materials, of which about half comprise glass- and carbon-fibre-reinforced composites. Within the other half are the textiles that are part of the aircraft itself, including decorative features. In addition there will be carpets, blankets and other textile-based equipment.

All textiles such as seating fabrics, carpets, curtains/drapes, and blankets used anywhere in a commercial aircraft flying on national and international flights must pass a simple ignition test defined in the requirements given in FAR 25.853(b) (and its other national/international equivalents) using the test procedures defined in FAR Part 25. This latter test defines a series of 'Bunsen burner ignition in vertical, 60°, 45° or horizontal strip tests' which assess whether or not a given material is self-extinguishing. For instance, vertical strip samples (75 × 305 mm) of textile materials used in blankets and seatings are subjected to a flame at the bottom edge of the specimen for 12 s and after its removal must experience a burn or damaged length ≤152 mm, an after-flame time ≤15 s and a flame time of any drippings ≤3 s. Typical textiles used in these areas include [55, 57] modacrylics and flame-retarded viscose and wool. For textiles used in liners for cargo and baggage compartments, the 45° test is used with similar requirements except that flame penetration through the fabric should not occur.

However, many textiles are used as part of assemblies which pose greater fire risks (e.g., seating and wall panels) and so require to be tested additionally as part of such an assembly. For instance, textiles which form a decorative or reinforcing element of structures within the passenger cabin must be tested as a composite or assembly according to the requirements of FAA specification FAR 25.853 Part IV Appendix F [56] for their ability not to spread fire using the Ohio State University (OSU) calorimeter. In this test, textiles for use as decorative coverings for wall panels are mounted on an appropriate wallboard material and are subjected to a heat flux of 35 kWm^{-2} yield. To pass, the burning composite must emit a maximum heat flux output <65 kWm^{-2} and generate an average flux over 2 min of <65 kWm^{-2}.

In seatings, the external fabrics must be able to prevent ignition of internal filling materials, hence the use of fire-blocking fabrics between the outer fabric and the inner seat filling. In specification FAR 25.853(c), a seat assembly mock-up is subjected to a kerosene burner having a heat flux of ≈ 115 kWm^{-2} for 2 min. After extinction of the burner, the assembly must extinguish within 5 min, not burn beyond the seat dimensions, and the overall mass loss must be ≤10%. To enable seating assemblies to pass this test, it is usual to have an outer fabric (e.g., flame-retardant wool or flame-retardant wool/polyamide 6.6) that passes FAR 25.853(b) and an underlying fire blocking or barrier layer typically based on high-performance fibres such as aramid, oxidised acrylic, glass or blends of these with other each other or with fibres such as flame-retardant wool.

Apart from the normally accepted textile products, heat- and fire-resistant textiles find use in engine insulation (e.g., ceramic structures around combustion chambers), fuselage acoustic insulation (e.g., glass fibre-based battings in flame-retardant polymeric film containers), reinforcements for composites (e.g., carbon fibre reinforcements for major structural elements), aramid honeycomb reinforcement for wall and floor structures, and fuselage acoustic and fire/heat insulation, each of which requires its own fire performance requirements [56, 58]. Associated with all these tests and materials or composites are toxic fire gas and smoke requirements similar to those required by IMO regulations in **Table 3.7**. Hence, the choice of fibre and textile structures will be influenced by the need to pass the minimum emission standards for gases, including carbon monoxide, nitrogen oxides, sulfur dioxide, hydrogen chloride and hydrogen cyanide.

3.3 Flammability Testing of Textiles

It is probably true to state that nearly every 'developed' country has its own set of textile fire testing standard methods which, together with those defined by other national and international bodies (such as air, land, and sea transport authorities, insurance organisations and governmental departments relating to industry, defence and health), in particular pose a very complex picture. A brief overview of the various and many test methods available up to 1989 is given in [59] and a more recent and detailed review of textile fabric flammability tests 2008 [60]. **Table 3.8**, however, attempts to give an oversight of the complexity of the range of tests available for textile products at the present time.

The complexity of the burning process for any material such as a textile which, because not only is it a 'thermally thin' material, but also has a high specific volume and oxygen accessibility relative to other polymeric materials, proves difficult to quantify and hence rank in terms of its ignition and post-ignition behaviour. Most common textile flammability tests are currently based on ease of ignition and/or burning rate behaviour which can be easily quantified for fabrics and composites in varying geometries. Few, however, yield quantitative and fire science-related data unlike the often maligned oxygen index method: the limiting oxygen index (LOI) [59]. The LOI, while it proves to be a very effective indicator of ease of ignition, has not achieved the status of an 'official' test within the textile arena. For instance, it is well known that to achieve a degree of fabric flame retardancy sufficient to pass a typical vertical strip test (**Section 3.3.1** below), an LOI value ≥26–27% is required, which must be measurable in a reproducible fashion. However, because the sample ignition occurs at the top to give a vertically downward burning geometry, this is considered not to be representative of the most typical ignition geometries. Furthermore, the exact LOI value is influenced by fabric structural variables (see **Section 2.8**) for the same fibre type and is not single-valued for a given fibre type or blend. However, it finds significant use in developing new flame retardants and optimising levels of application to fibres and textiles.

Based on the apparent complexity of the many tests available (some of which have been alluded to in **Section 3.2** as well as **Table 3.8**), they may discussed in this chapter in terms of a typography where the many types of test may be more simply categorised as below:

- Simple fabric strip tests.
- Textile composite tests.
- Tests undertaken with the addition of radiant heat (including reaction to fire tests).
- Thermal protection (including protective clothing and manikin tests).

Each will be discussed with respect to the sample character, and the flammability properties will be measured using the previously mentioned (**Section 3.2**) and **Table 3.8** examples. Many of these tests require samples to have undergone some form of durability test [54] especially if flame retardant-treated textiles are present (examples of these tests are also included in **Table 3.8**).

3.3.1 Simple Fabric Strip Tests

Fabric strip testing constitutes the oldest form of reproducibly assessing the burning behaviour of fabrics in terms of such parameters as time to ignite, burning rate, char length, damaged length, nature of debris (including melt dripping) and extinction time for a fabric having specified dimensions, held at a specified angle to the horizontal

(0, 45, 60 or 90°) and subjected to a small flame of standard dimensions. These must be undertaken in an atmosphere having a specified range of temperature and relative humidity. Ideally, all practical tests should be based on quite straightforward principles which transform into practically simple and convenient-to-use test methods. **Figure 3.2** is a schematic representation of a typical vertical strip test such as BS 5438: 1989 test method 2 (and ISO 15025) in which a simple vertically orientated fabric may be subjected to a standard igniting flame source at the edge or on the face of the fabric for a specified time such as 10 s.

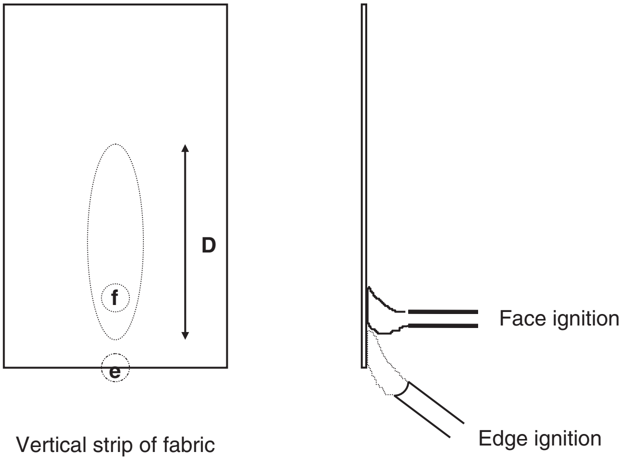

Figure 3.2 The vertical strip test in BS 5438:1989 test method 2A (face) and (2B edge) (schematic)

For flame-retarded fabrics, the properties measured after extinction of the ignition source are the damaged (or char) length, size of hole (if present), times of after-flame and afterglow and nature of debris (e.g., molten drips). For slow-burning fabrics, such as those required in nightwear, a longer fabric strip is used, across which cotton trip wires connected to timers are placed so that times of burning a specified distance and/or burning rates may be assessed. Examples here are BS 5438 test method 2 and BS EN ISO 6941: 2003 (**Sections 3.2.1** and **3.3.1** and below) for use in assessing nightwear.

In the USA, a 45° test was and is still used today to assess whether all clothing fabrics for sale are safe within the General Apparel regulations [4] using the test defined in CFR-2012-16-2 in terms of a maximum burn rate requirement. The previously mentioned automotive standard FMVSS 302 is a horizontal test shown schematically in **Figure 3.3**. Again, a maximum burn rate of 101 mm/min (4 inch/min) is the defined pass requirement.

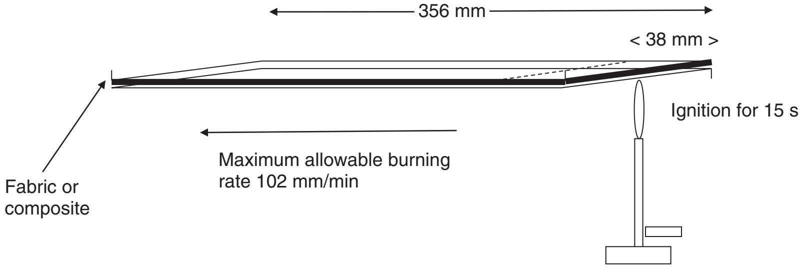

Figure 3.3 Automobile interior textile test FMVSS 302 (also ISO 3795, BS AU 169 (UK), ST 18-502 (France), DIN 75200 (Germany), JIS D 1201 (Japan) and ASTM D-5132 (US) (schematic). Reproduced with permission from *Handbook of Fire Resistant Textiles*, Ed., F Selcen Kilinc, Woodhead Publishing, Cambridge, UK, 2003, p.603. ©2003, Woodhead Publishing [39]

For flame-retardant fabrics, the more stringent vertical (90°) test geometries are required and several are listed in **Table 3.8**. Of these, in the USA, the often termed '12 inch vertical strip test' is formalised in the standards ASTM D6413 and US Federal Test Method Standard 191, Method 5136(3). FAR 25 853(b) demands that most textiles in use in passenger compartments must pass the vertical test version of this requirement after ignition for 12 s by a standard gas burner. The damaged length must be <152 mm (6 inches) for a pass to be achieved.

In the UK, the principles of vertical flame spread on fabrics were discussed >50 years ago by Lawson and co-workers [61], which led to the development of the now obsolete British Standard of 1950–60 [59]. Subsequently, these were replaced by BS 5438:1976 (revised in 1989) which, during subsequent normalisation, influenced the development of the EU standards BS EN ISO 6940 and 6941:1995 (current revision is 2003) and international standard ISO 15025:2002. Analyses of these respective test standards suggest that BS EN ISO 6940 is comparable with BS 5438 test method 1, BS EN ISO 6941 is similar to BS 5438 test method 3, and ISO 15025, used to assess protective clothing (see below), is similar to BS 5438 test method 2. These tests are then used within performance standards relating to given applications such as nightwear, curtains and drapes. For instance, BS 5722:1991 uses BS 5438:1976 or 1989 test method 3/3A to test and define performance levels for nightwear fabrics [2], which demands that fabrics having a maximum average burn rate of 12 mm/s to pass the requirement for children's nightwear. As stated above, using BS 5438:1976 test method 3, on introducing the burner to the lower face of the fabric for 10 s, the time for the flame advancing up the fabric to reach the 300-mm marker should be ≥25 s, and to reach the upper 600-mm thread should be 50 s, if the nightwear is to receive a label that it meets the requirements of BS 5722:1991.

Similarly, in the UK, curtains and drapes use the same BS 5438:1989 test method 3 within the standard BS 5867: Part 2:1980. In the latest revised version, BS 5867-2:2008, the test methods BS EN ISO 6941:2003 for Type A fabrics and ISO 15025:2002 for Types B and C fabrics are used. ISO 15025:2002 is really a test method for protective clothing (**Table 3.8**) that assumes fabrics are flame retardant or are of limited flame spread. The method is not dissimilar to BS EN ISO 6941 except that a frame size of 150 × 170 mm is used, unlike the longer frame (150 × 560 mm) used in BS EN ISO 6941:2003. Part 1 of this standard, BS 5867-1:2004, describes the general requirements, including labelling for the fabrics to be tested. Using this test method for curtains and drapes used for domestic usage (Type A), the flame application time is typically 10 s whereas for curtains used in contract furnishing (Type B), the test is more severe with a longer flame application time of 15 s. The flammability test is even more stringent for the curtains and drapes used in more hazardous applications such as hospitals and prisons (Type C). For these applications, the fabric has to be tested with four flame application times of, 5, 15, 20 and 30 s.

Within the EU, a simpler test BS EN1102:1996 is defined for curtain and drapes, which again uses the test method BS EN ISO 6941 but only with a 10-s ignition time. However, the standard BS EN 13772:2003, also for curtains and drapes, is a more stringent standard that uses EN ISO 6941, to which a small radiator is attached to increase the intensity of the ignition source to represent a larger burning source, such as a wastepaper basket.

For apparel not used for protective clothing, BS EN 1103:2005 defines how flammability may be assessed using the method BS EN ISO 6941: 2003 with a 10-s ignition time.

A variant of these fabric strip test methods are required if testing for surface flash, which is important not only for high pile toys [62] but also children's nightwear (as mentioned in **Section 3.2.1** (EN 14878:2007 [16, 17]). In such test methods, a flame is passed for a short time, typically ≈ 2 s, about 50 mm over the surface of the fabric held at 45° or 90° and, if ignition occurs, the duration of flaming is measured and the length of specimen damaged by flames noted. For certain types of toys, the rate of flame spread is also measured through severing of marker threads but, for nightwear, any surface flash should not be sufficient to ignite the fabric itself.

3.3.2 Textile Composite Tests

With recognition of the hazards posed by upholstered fabrics that comprise outer fabrics and inner fillings, development of the small-scale composite test BS 5852 (**Table 3.8**) represented a milestone in the development of realistic model tests which cheaply and accurately indicate the ignition behaviour of full-scale products of complex structure. BS 5852 Parts 1 and 2:1979 and BS EN 1021 Parts 1 and 2 are employed for testing upholstered furnishing fabric/filling composites to simulated cigarette and match ignition sources. These sets of BS and BS EN standards are similar with regard to Source 0, the cigarette ignition source, but differ in the time of application of Source 1 in that BS 5852: Part 1: Source 1 has a flame ignition time of 20 s and that for BS EN 1021-2, an application time of 15 s. Both standards have been reviewed and the latest versions are cited in BS 7176:2007, which advises on test method selection for a given hazard level, as shown in **Table 3.5**. However, for UK domestic furnishings BS 5852 Parts 1 and 2:1979 is still valid because it is contained within the current legislation (**Table 3.4**) [5]. **Figure 3.4** is a schematic diagram of this and the related EN and ISO tests (**Table 3.8**) for undertaking tests with Sources 0 (cigarette) and 1 (simulated match). Again, the test has proved to be a simple to use, cost-effective and reproducible test that may be located in the manufacturing environment as well as formal test laboratory environments. A similar testing methodology is described in the proposed US standard for furnishing fabrics CPSC 16 CFR Part 1634 discussed in **Section 3.2.2** (**Table 3.4**).

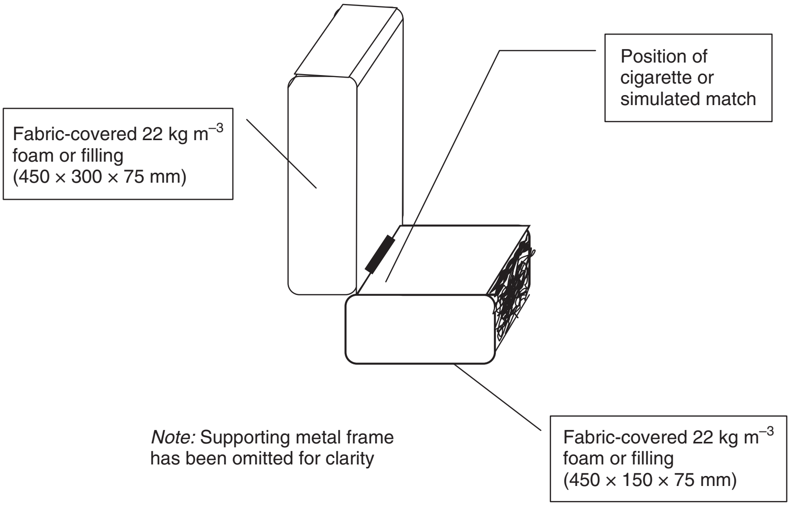

Figure 3.4 Filling and fabric geometry in BS5852: Part 1:1979 and subsequent revisions (schematic). Reproduced with permission from A.R. Horrocks in *Flame Retardant Materials*, Eds., A.R. Horrocks and D. Price, Woodhead Publishing, Cambridge, UK, 2001, p.128. ©2001, Woodhead Publishing [63]

The original BS 5852:1979 Parts 1 and 2 (which were amalgamated into a single test standard in subsequent revisions), describe seven ignition sources of increasing intensity, and these are more fully described in **Table 3.9**.

Table 3.9 Ignition sources described in BS 5852

Source	Ignition source	Gas flow rate or mass	Energy output, kWh	Time of application
0	Cigarette	–	–	Throughout the test
1	Burner	45 ml min^{-1}	0.001	20 s
2	Burner	160 ml min^{-1}	0.004	40 s
3	Burner	350 ml min^{-1}	0.016	70 s
4	Crib	8.5 g	0.04	Throughout the test
5	Crib	17 g	0.08	Throughout the test
6	Crib	60 g	0.28	Throughout the test
7	Crib	126 g	0.59	Throughout the test

BS 7176:2007 defines how they may be used in public and contract environments, as shown in **Table 3.5** for upholstered furnishings. This range of sources covers that of a simple smouldering cigarette to a simulation of four sheets of newspaper (Source 7).

With regard to bedding in the UK, the standard BS 6807:2006 is used to assess the ignitability of mattresses and uses ignition sources specified in BS 5852, whereas BS 7177:2008 specifies various combinations of ignition sources for four hazard classifications (low, medium, high and very high) based on the standards BS 6807 and BS EN 597-1 and 597-2. The 0/NS (cigarette plus non-smouldering insulation) ignition source is also described in Annex B of BS 7177:2008 to provide guidance for users on the ignitability behaviour of mattresses if covered with bedding. These test methods are mandatory in contract furnishings.

The US equivalents for bedding with regard to cigarette (CPSC 16 CFR Part 1632) and match (CPSC 16 CFR Part 1633) ignition have been discussed in **Section 3.2.2** and are listed in **Table 3.4**.

Finally, for bedding, the latest versions of the international standard for bedding BS EN ISO 12952-1:2010 have been established for smouldering cigarette ignition and BS EN ISO 12952-2:2010 for match flame. Both standards are quite similar to the UK standard BS 6807.

Other furnishing materials such as carpets have appropriate tests such as BS 6307:1982, which determines the flame spread of a carpet sample in a horizontal orientation in the presence of a simulated match, namely a methenamine pill of diameter 6 mm and weight 150 ± 5 mg. The standard test methods for contract curtains described in BS 5867-2:2008 have been discussed in **Section 3.2.2**.

3.3.3 Tests Undertaken with the Addition of Radiant Heat (Including Reaction to Fire Tests)

It is well known that, if textiles are subjected to elevated temperatures, they become more easily flammable, and even flame-retardant textiles may become flammable at heat fluxes >25 kWm^{-2}. Consequently if textiles are required to perform well at elevated temperatures, test methods that reflect this must be devised.

To simulate this scenario, a radiant panel is usually mounted at an angle to the textile sample, which may be vertically or horizontally oriented. The specimen is typically exposed to radiant heat from an air-/gas-fuelled radiant panel and the textile fabric specimen is at an angle (typically 30°) to the panel face. The mounted specimen is thus exposed to a gradient of heat flux ranging from a maximum of 10 kWm^{-2} immediately under the radiant panel to a minimum of 1 kWm^{-2} at the far end of the test specimen, remote from the panel. The specimen closest to the panel is usually subjected to a small flame and the distance burned until flame extinguishes is converted into an equivalent critical radiant flux (in Wm^{-2}) related to the panel intensity at that point. Such a test method has been included by the EU for fire test approval of floorings such as BS EN ISO 9239-1:2010.

For textile materials used as interior wall-coverings in UK buildings (including railway carriages) in which the fabric could be in a vertical orientation attached to the wall panel, measurement of rate of flame spread under external heat flux is one of the requirements. For such applications, the test method BS 476-7:1997 (Fire tests on building materials and structures. Method of test to determine the classification of the surface spread of flame of products) essentially requires a vertically oriented specimen exposed to a gas-fired radiant panel with an incident heat flux of 32.5 kWm^{-2} for 10 min. In addition, a pilot flame is applied at the bottom corner of the specimen for 90 s and rate of flame spread measured. The same principle is used in the French test for carpets, NF P 92-506.

In the French suite of test methods, NF P 92-501-507, for testing building materials, the presence of a radiant panel is a significant test feature. In the main, only the method NF P 92-503 is relevant to textiles. NF P 92-503 is often known as the Breuleur Electrique, 'epiradiateur' or 'M' test, and is used for flexible textile materials (e.g., it is often used in contract seatings). The schematic of the test apparatus is shown in **Figure 3.5**.

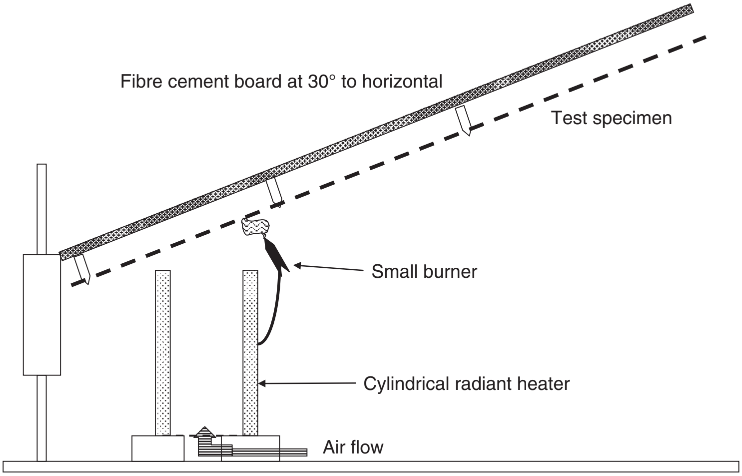

Figure 3.5 The French 'Epiradiateur' or 'M' test NF P 92-503 (schematic)

The fabric sample is inclined at 30° to the horizontal and is subjected to a radiant heat flux for 5 min and a flaming ignition source applied to the heated fabric. Time to ignition or time to hole formation, presence of burning droplets, and length of damaged specimen are recorded to classify materials from M1 to M4 (M1 textiles can be classed as 'non-flammable', M2 as 'low flammable', M3 as 'moderately flammable' and M4 as 'highly flammable'). While this test is used mainly in France, Belgium, Spain and Portugal to certify the use of flexible materials in buildings for public use, it affects many UK and other EU manufactures supplying into EU markets.

Sometimes a textile is required to be tested under simulated fire conditions (which usually means heat fluxes >25 kWm^{-2}) and this is especially the case for testing textile composites such as textile-covered structural items in transport such as aircraft. The best and most original example of such a reaction-to-fire test is the Ohio State University Calorimeter designed to test such textile composite samples in FAR 25.853 Part 4 Appendix F and ASTM 906:1983. The apparatus is shown schematically in **Figure 3.6** and all decorative panels in commercial aircraft throughout the developed world must pass this standard.

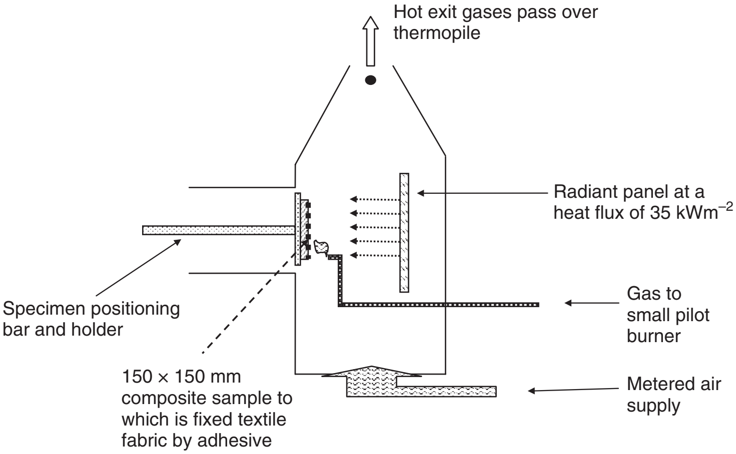

Figure 3.6 OSU Calorimeter designed to test textile composite samples in FAR 25.853 Part 4 Appendix F (schematic)

The test applies an incident heat flux of 35 kWm^{-2} to a vertically oriented sample which, on ignition by a small flame burner, must not generate a peak heat release rate of 65 kWm^{-2} and a mean heat release rate of 65 kWm^{-2} over 2 min. This test measures the ease of ignition under a high heat flux, and the associated heat release may be used to define the ignition and fire propagating of textiles in composite structures used in commercial aircraft. The more recently available cone calorimeter [64] has yet to make a significant impact on the assessment of textile fire behaviour apart from in the defence and extreme protective clothing-related sectors. However, the author has attempted to correlate the two methods, and has met with some success [65].

In **Section 3.2.4.4**, another of the aviation fire tests mentioned which could be included in this discussion as examples of extreme heat flux fire performance tests is FAR 25.853(c), which subjects a seat assembly unit to a 'kerosene burner' test in which an assembly is subjected to an incident heat flux of 115 kWm^{-2} for 2 min. There is also a not dissimilar second FAR test for assessing the burn-through resistance of fuselage thermal/acoustic insulation, usually based on glass or ceramic fibre nonwoven structures – FAR 25.856(a) Appendix F Part VI. This describes a test in which a burner having a flame temperature of »1050 °C and a heat flux of 160 kWm^{-2} impinges on the back of a 810 × 910 mm sample. To pass, none of the specimens must allow the flame to penetrate through the thickness for 4 min or register a heat flux >23 kWm^{-2} at 31 cm behind the sample face. The full details of these and other related FAR tests are given in [56].

3.3.4 Thermal Protection (Including Protective Clothing and Manikin Tests)

As textile materials are used in more complex and demanding environments, so the associated test procedures become more complex. This is especially the case for protective clothing, where the garment and its components have to function not only as a typical textile material but be resistant to several agencies, including heat and flame. However, before the mid-1990s, most protective clothing tests were simply based on vertical strip burning tests and are still today in the USA, as discussed in **Section 3.2.3** [27, 32]. However, during 1970–80, the realisation for and development of measures of thermal protection from radiant and convective (i.e., flame) heat sources were recognised. Resistance to heat transfer by convective flame, radiant energy or plasma energy sources may be quantified in terms of a thermal protective index (TPI) that is often related to the time taken for an underlying skin sample with or without an insulating air gap to achieve a minimum temperature or energy condition sufficient to generate a second-degree burn [66]. One early authoritative study of the thermal insulative properties of fabrics was that by Perkins [67], who studied a large number of fabrics with an area density range of 85–740 gsm as single layers. He selected an incident radiant source intensity of ≤16.8 kWm^{-2} and a convective flame source of 84 kWm^{-2}, which are considered to be reflect the exposure typically experienced by fire-fighters. Behind each fabric was a heat flux meter which enabled time *versus* heat flux to be determined. Using a standard burn-injury curve that relates delivered heat to incipient second-degree burn threshold level, fabric performance could be measured in terms of time to reach the latter. Their results may be summarised as follows:

- For radiant heat fluxes of 8.4 kWm^{-2}, fabric area density determines protection efficiency, with air permeability also influencing performance.
- At heat fluxes of 12.6 and 16.8 kWm^{-2}, the fibre properties become important and char-forming fibres such as flame-retardant cotton and flame-retardant wool become superior.
- Exposures to the convective flame at 84 kWm^{-2} show that flame-retardant wool fabrics yield significantly higher times than flame-retardant cotton and aramid fabrics of similar weight.

An alternative method is to determine the thermal protective performance index (TPP), as described in the ASTM D4108-82 (revised 1987) [68], where TPP for a fabric assembly is the burn threshold time multiplied by the incident heat flux.

A similar bench-scale experimental setup is used for test methods described in BS EN ISO 6942:2002 (Protective Clothing - Protection

Against Heat and Fire. Method of test: Evaluation of Materials and material assemblies when exposed to a source of radiant heat) and EN 367:1992 (Protective clothing. Protection against heat and fire. Method for determining heat transmission on exposure to flame) (**Table 3.8**) for measuring radiant heat transfer index (RHTI) and convective heat transfer index (HTI), respectively. RHTI and HTI are the mean times taken, t_{12} and t_{24}, for the calorimeter at the rear of the assembly away from the flame to rise respectively by 12 ± 0.2 °C and then by 24 ± 0.2 °C.

Based on such developments, as **Table 3.8** shows, several tests have been developed across the EU since 1990 to accommodate the different demands of varying types of protective clothing and the hazards, whether open flame, hot surface, molten metal splash or indeed a combination are catered for as defined in both standards for fire-fighters' (BS EN 469:1995 revised 2005) and general workers' (BS EN ISO 11612:2008) clothing, referred to in **Section 3.2.3** and which will be more fully discussed below. Furthermore, the entire aspect of design, comfort and durability in addition to performance requirements are defined within BS EN 340:2003 together with the specified labelling requirements of protective clothing sold within the EU under the Directive on PPE 89/686/EEC discussed in **Section 3.2.3**. A current list of all CEN standards relating to protective clothing valid at 2009 has been published by the UK Health and Safety Executive [69].

Metal splash protection, reviewed recently elsewhere [70], requires further comment with respect to the current argument in that BS EN ISO 9185:2007 (Protective clothing. Assessment of resistance of materials to molten metal splash) is now the established test method. This replaces the earlier BS EN 373:1993 and the test defines a means of enabling molten drops of metal (e.g., steel, copper, aluminium) to impinge up on upper-fabric surfaces oriented at 45^o to the horizontal so that droplets during impact have time to thermally degrade the fabric surface and glance off or stick to and burrow into the fabric. An underlying embossed poly(vinyl chloride) (PVC) film (with an area density of 160 gsm) is present as a skin simulant and when heated first loses its embossing and then generates small holes. In this test, shown in **Figure 3.7**, 50 g molten metal (≈ 50 °C higher than its respective melting point) is dropped onto a supported fabric. If

PVC damage is not apparent, the test is repeated with fresh fabric and PVC samples but with an increasing incremental mass of molten metal (10 g) until damage is apparent. Conversely, if 50 g molten metal damages the PVC, incrementally decreasing masses are used until no damage is apparent. The molten mass index for a given fabric is the mean value of the four highest masses that do not give rise to PVC damage.

Figure 3.7 The hot metal splash test, BS EN ISO 9185:2007 (replaces BS EN 373:1993). Reproduced with permission from BTTG Fire Testing Laboratory, Altrincham, UK

With regard to skin damage, one test not yet standardised is that based on the simulation of a human torso and its reaction to a given fire environment when clothed. The original Du Pont 'Thermoman' [71] or instrumented manikin provided the means of recording the temperature profile and simulated burn damage sustained by the torso if clothed in defined garments (usually prototype protective garments) during exposure to an intense fire source. This latter is typically a series of gas burners yielding a heat flux of 84 kWm^{-2}. This method has been made an official standard in the USA since ≈ 2000 as ASTM F 1930 [72]. However, its adoption as a CEN or ISO standard has occurred only recently, although Sorensen [73] reviewed attempts to establish this and related manikin methods as a standard method during 1990 which, at that time, were impeded by the claimed poor reproducibility of the test and its sensitivity to garment fit. Subsequently, the ISO standard test specification was published as BS ISO 13506:2008 [74] and its final development to achieve this is reviewed by Camenzind and co-workers [75]. **Figure 3.8** is a schematic representation as defined in BS ISO 13506:2008 of a manikin under test in which a clothed manikin is subjected to the heat from six burners (two at each side and two behind) which focus on the jacket and trouser areas.

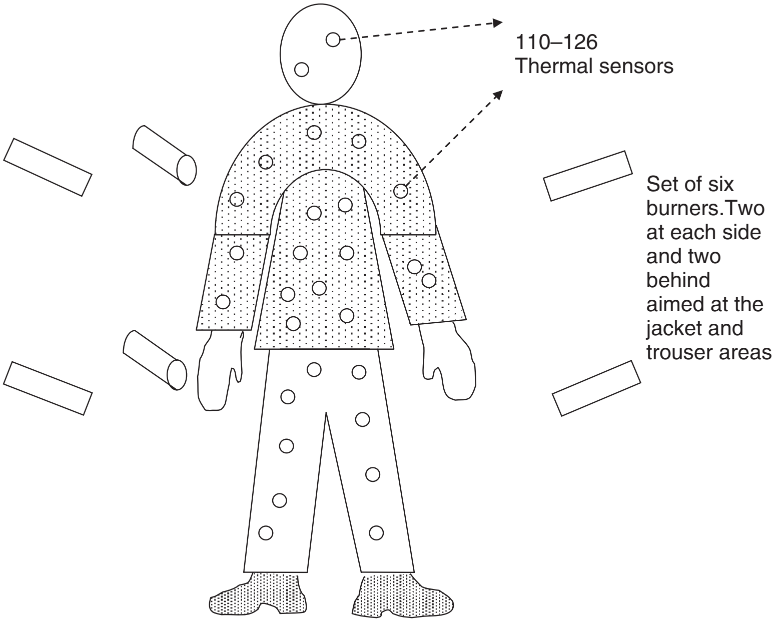

Figure 3.8 A manikin under test according to BS ISO 13506:2008 showing the position of six gas burners and sensors (schematic)


(a) (b)

Figure 3.9 Images of the BTTG Ltd., manikin RALPH [68] as (a) the undressed torso and (b) as a manikin under test. Reproduced with permission from BTTG Fire Testing Laboratory, Altrincham, UK

Figures 3.9a and **3.9b** show images of the BTTG Ltd., RALPH manikin [73] as the undressed torso and a manikin under test, respectively. The number of sensors in the torso ranges from 110 to 126 divided across the torso, including the head region, as recommended by the standard to produce an effective body map of potential damage by first-, second- and third-degree burns. This test is listed as a possible additional test as BS EN 469:2005 (E) within the standard for fire-fighters' clothing, BS EN 469: 2005 [28] and in Annex C of BS EN ISO 11612:2008 [31] (see below). Recommended flame application times at a heat flux of 84 kWm^{-2} are 4 s or 8 s depending on the level of protection requirement. Within the USA, however, to assess the flash-fire resistance of textile materials for industrial and military applications [76], the ASTM F 1930 requires exposure of a fully dressed manikin to a heat flux of 84 kWm^{-2} for 3s and to pass the related performance standard US NFPA 2112 [77]; materials used in the tested flame-resistant garments should yield a body burn rating ≤50%.

The standard BS EN 469:2005 is a composite standard that attempts to determine all the significant factors that determine the overall protective character of a fire-fighter's garment for two levels of performance. **Table 3.10** shows the number of tests and required minimum performance requirements at each level within this standard. This standard may be applied to any part of the full garment assembly from the outer shell jacket and over trousers (or a single outer coverall) to the underlying outer and underwear garments. Gloves and hoods are covered by the other standards listed in **Table 3.8**.

Table 3.10 Test methods within the composite standard for firefighters' clothing, BS EN 469: 2005 [28]

Property tested	**Standard**	**Principal performance specifications**	
		Level 1	**Level 2**
Flame spread (material and seams)	BS EN ISO 15025:2002 (replaces BS EN 532:1995)	No flame extending to top or edge, no hole formation and after flaming and afterglow times ≤2 s; flame spread index 3.	
Heat transfer (flame)	BS EN 367:1992 (ISO 9151)	$HTI_{24} \geq 9.0$s $RHTI_{24} - RHTI_{12} \geq 3.0$	$HTI_{24} \geq 13.0$s $RHTI_{24} - RHTI_{12} \geq 4.0$
Heat transfer (radiant)	BS EN ISO 6942:2002 at 40 kWm^{-2}	$RHTI_{24} \geq 10.0$s $RHTI_{24} - RHTI_{12} \geq 3.0$	$RHTI_{24} \geq 18.0$ s $RHTI_{24} - RHTI_{12} \geq 4.0$
Residual strength when exposed to heat	EN ISO 13934-1 or EN ISO 1421:1998, method 1 after pre-treatment to EN ISO 6942:2002, method A at 10 kWm^{-2}.	Tensile strength ≥450 N	
Heat resistance	ISO 17493 at 180 ± 5 °C for 5 min	No shrinking (≤5%), melting, dripping or ignition	
Tensile strength	EN ISO 13934-1 or EN ISO 1421:1998	Tensile strength ≥450 N	
Tear strength	ISO 4674-1:2003, method B (coated); EN ISO 13937-2:2000 (uncoated).	Tear strength ≥25 N	

Surface wetting (after washing and drying)	BS EN 24920:1992 (ISO 4920:1981)	Spray rating ≥4	
Dimensional change	ISO 5077	≤3%	
Penetration by liquid chemicals	EN ISO 6530 (for 40% NaOH, 36% HCl, 36% H_2SO_4 and o-xylene at 20 °C).	≥80% run off	
Water resistance (pressure for water entry)	BS EN 20811:1992 (ISO 811:1981)	<20 kPa (without moisture barrier)	≥20 kPa (with moisture barrier)
Breathability	BS EN 31092:1994 (ISO 11092:1993)	$>30\ m^2PaW^{-1}$	$\leq 30\ m^2PaW^{-1}$
Ergonomic performance	BS EN ISO 469:2005 Annex D	Defined by manufacturer/customer	
Visibility (optional)	EN 471:2003	Defined by manufacturer/customer	
Manikin (optional)	BS EN ISO 469:2005 Annex E (method BS ISO 13506:2008)	Defined by manufacturer/customer	

The performance specifications relating to thermal protection include ignition and flame spread (BS EN ISO 15025:2002) as well as heat transfer to radiant (BS EN ISO 6942:2002) and convective (BS EN 367:1992) heat. For instance, the RTHI values for the rear of a multilayer assembly (to BS EN ISO 6942 Method B at 40 kWm^{-2}) to rise by 24 °C ($RHTI_{24}$) should be ≥10.0 s and ≥18.0 s for level-1 and -2 performance, respectively, and the differences ($RHTI_{24} - RHTI_{12}$), ≥3.0 s and ≥4.0 s indicate that the initial rise by 12 °C usually occurs in a longer period than the time taken to rise another 12 °C to a total of 24 °C. However, the time limits prescribed ensure that this second stage of the temperature rise is not unduly rapid. A similar set of HTI values for flame exposure (80 kWm^{-2}), are defined for level-1 and -2 performances. In addition are tests relevant to the overall performance of fire-fighters' clothing, including tensile and tear strength, and surface wettability. Again, the reader is referred to the main standard and its component parts for the full details of each test.

BS EN ISO 11612:2008 [31] is also a composite standard which, as stated in **Section 3.2.3**, defines several performance levels for various industrial protective clothing subjected to convective (flame), radiant, molten metal splash (iron and aluminium) and contact heat sources. All fabric samples (including those used in garment parts such as pockets and seams) are subjected to a prescribed cleansing process before testing and, like BS EN 469:2005 above, has an option for full garment testing for burn injury protection to BS ISO 13506:2008 as defined in Annex C of the Standard. The full specifications for each level are complex and the standard relates to textile and leather garments, but an outline of those for textile garments is presented in **Table 3.11**, which shows the number of tests and required minimum performance requirements at each level within this standard. Once tested, a garment may be labelled according to the provisions in ISO 13688 with the appropriate level of performance (e.g., B1/C2/D1).

Table 3.11 Test methods within the composite standard for industrial heat protective textile clothing, BS EN ISO 11612:2008 [31]

Property tested	Standard		Principal performance specifications			
			Level 1	Level 2	Level 3	Level 4
Heat resistance	ISO 17493:2000 180 ± 5 °C 260 ± 5 °C		 No ignition, melting or shrinking (≤5%) No ignition, melting or shrinking (≤10%)			
Flame spread (material and seams)	BS EN ISO 15025:2002		No flame extending to top or edge, no hole formation and after flaming and afterglow times ≤2 s			
Heat transmission	*Convective heat* (Code B)	ISO 9151:1995	B1/4.0 min ≥ HTI_{24} ≤10 min	B2/10.0 min ≥ HTI_{24} ≤20 min	B3/B1/20.0 min ≥ HTI_{24}	–
	Radiant heat (Code C)	BS EN ISO 6942:2002 at 20 kWm^{-2}	C1/7 min ≥ HTI_{24} ≤20 min	C2/20 min ≥ HTI_{24} ≤50 min	C3/50 min ≥ HTI_{24} ≤95 min	C4/HTI_{24} ≥13.0 s
	Molten metal splash Aluminium (Code D) Iron (Code E)	ISO 9185:2007	D1/100 g ≥ Al mass ≤200 g E1/60 g ≥ Fe mass ≤120 g	D2/200 g ≥ Al mass ≤350 g E2120 g ≥ Fe mass ≤200 g	D3/350 g ≥ Al mass E1/200 g ≥ Fe mass	–
	Contact heat (Code F)	ISO 12127-2:2007 at 250 °C	F1/5 s ≥ threshold time ≤10 s	F2/10 s ≥ threshold time ≤15 s	F2/15 s ≥ threshold time	–

Tensile strength	EN ISO 13934-1	Tensile strength ≥300 N
Tear strength	EN ISO 13937-2	Tear strength ≥15 N
Burst strength	ISO 13938-1	Burst strength ≥200 kPa
Seam strength	ISO 13925-2	Seam strength ≥225 N
Resistance to water penetration (optional)	EN 343	Requirements within EN 343
Resistance to water vapour penetration (optional)	EN 343	Requirements within EN 343
Ergonomic performance	BS EN ISO 11612:2008 Annex D	Defined by manufacturer/customer
Innocuousness/pH	ISO 3071	3.5 ≥ pH ≤ 9.5
Manikin (optional)	BS EN ISO 11612:2008 Annex C (method ISO BS 13506:2007)	Defined by manufacturer/customer

Finally, a standard that enables a clothing fabric to be indexed in terms of flame retardancy and durability is BS EN ISO 14116:2008 (a replacement for BS EN 533:1997), mentioned in **Section 3.2.3**. The standard entitles 'Protective Clothing - Protection against heat and flame - Limited flame spread materials, material assemblies and clothing' uses ISO 15025:2000, Procedure A, face ignition (**Table 3.8** and **Figure 3.2**). BS EN ISO 14116 defines a method of classifying the extent of damage to a fabric sample subjected to a small flame using test method BS EN ISO 15025:2000. Fabrics are tested before and after a specified cleansing process for several cycles according to ISO 11611:2007 (which is similar to BS 5651:1989). Fabrics are classified in terms of thermal performance as 1 (no flame or damage (e.g., hole or char) to reach the upper or vertical specimen edge, no flaming debris, no after-flame spreading beyond char edge); 2 (as for 1 except no hole formation); or 3 (as for 2 but after-flame should not exceed 2 s). A final index is stated as 'x/y/z' where x is the flame spread index, y is the number and type of cleansing process, and z is the temperature of that process. For example, 3/5I/75 indicates material that meets the flammability index 3, five-times industrially washed at 75 °C; 2/5H/60 indicates a material that meets flammability index 2, five-times home-washed at 60 °C; and 3/5C/P indicates a material that meets flammability index 3, five-times dry-cleaned with perchlorethylene, Thus, the final index gives a measure of flame resistance and durability, and single-layer fabrics, assemblies of fabrics and garments may be labelled as described in the BS EN ISO 14116:2008 standard.

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4 Overview of Traditional Flame-retardant Solutions (including Coating and Back-coating Technologies)

A. Richard Horrocks

4.1 Introduction

Within recent years, there have been several comprehensive reviews that have not only critically reviewed research to about 1980 (during which period most of the presently used commercial flame retardants for fibres and textiles were developed, excluding back-coatings [1, 2]) and references within these publications direct the reader to more contemporary reviews of particular fibre types. Further reviews have considered developments since that time [3–5]. Up to about 1960–80, the established durable and flame-retardant treatments for cotton and wool fibres as well as those additives and comonomers introduced into regenerated (e.g., viscose) and synthetic (notably polyester, polypropylene and modacrylics) fibres during manufacture were synthesised and developed into commercially acceptable products, many of which are available today (see **Chapter 5**). The years 1975–1980 were when back-coatings were first developed and have become extremely commonly used in certain applications, particularly furnishing fabrics, where their use prevents the aesthetics of the front fabric face being influenced by their presence [6]. In fact, it is probably true to say that most of the currently available flame retardants for textiles and fibres reviewed by Weil and Levchik in 2008 [5] are derived from chemical developments made before 1980.

A major reason for the significant drop in research into novel flame retardants after this period was the report in 1977 stating that the very efficient flame retardant *tris*(2,3-dibromo propyl) phosphate failed clinical tests resulting in carcinogenic behaviour; in the following years, many other products were also withdrawn on grounds of health and safety [7, 8]. The history of their development during this period has been reviewed by Horrocks in 2011 [9].

In this chapter, I will focus on semi- and fully durable flame-retardant methods and application technologies for textile fabrics having little (if any) inherent flame-resistant properties. I will concentrate on those flame-retardant technologies that are well-established and in current use worldwide, and will include textile-coating technologies that have technical textile applications. I will not consider more recent potentially commercial processes that have yet to be fully accepted and proven – these have been reviewed by Weil and Levchik [5] and myself [9] previously. Examples of such exclusions are the recently developed phosphorus-based Fyroltex® HP (Akzo) and Noflan® (Firestop Ltd) products which, while claiming to be commercially viable, have yet to be fully accepted into the marketplace as fully durable flame retardants for cotton (although the former claims to withstand up to 25 home launderings [5]).

Non-durable flame retardants have changed little over recent years, and have been reviewed in [2, 3]. They comprise primarily soluble salts of ammonia and organic bases (e.g., urea, guanidine) and phosphorus oxyacids (sometimes augmented by ammonium bromide) and may be applied by simple pad-dry methods and spraying. Typical methods for applying most flame retardants in which open-width cloth may be processed commercially are presented schematically in **Figure 4.1** and referred to in more detail in the text below.

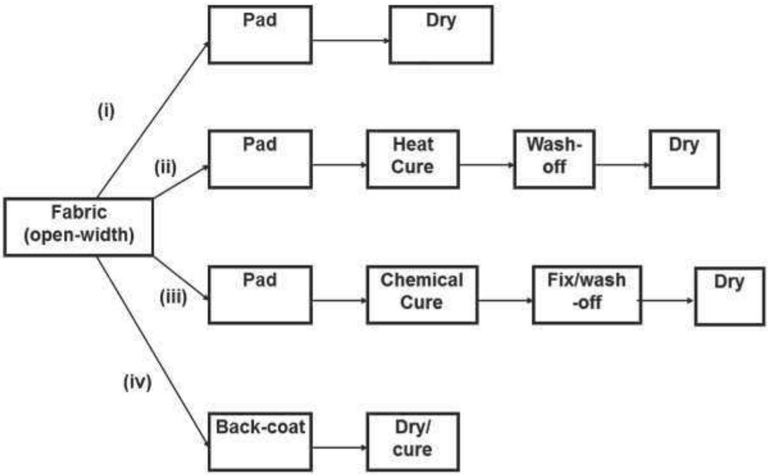

Figure 4.1 Common application technologies for flame retardants in open-width fabric processing (schematic). Reproduced with permission from A.R. Horrocks in *Flame Retardant Materials*, Eds., A.R. Horrocks and D. Price, Woodhead Publishing, Cambridge, UK, 2001, p.128. ©2001 [10]

Durable flame retardants can be applied only if the retardant species interacts with the chemical structure of the fibres. It then forms strong chemical bonds, and creates an interpenetrating polymeric network within a fibre structure, thereby 'locking in' the flame-retardant species or is contained within a surface coating or back-coating. Synthetic fibres, in general, have little chemical reactivity and are very polycrystalline, impenetrable structures. Hence, unless they contain a comonomer with inherent flame retardancy or an additive introduced during their production, they may be effectively flame-retarded only by surface treatment or by transfer of flame-retardant activity from a co-blended natural fibre already containing a flame retardant.

This chapter will comprise, therefore, the following main textile types:

- Durable flame-retarding of cellulose-containing (usually cotton) textiles and cellulose blends.
- Durable flame-retarding of wool and wool blends.
- Durable flame-retarding of man-made fibre-containing fabrics.
- Coating and back-coating natural fibre-containing and synthetic fibre-containing fabrics.

4.2 Durable Flame-retardant Treatments for Cellulose-containing Textiles

Textile finishes having semi-wash durability or ≥50 domestic wash durability applied to cotton and their blends, unless applied as a coating or back-coating (see **Section 4.5.2**), comprise phosphorus-containing species. In general, these are thought to release phosphorus acids upon heating, which act as Lewis acids and promote char formation [1, 2, 11]. This release of Lewis-acid properties should not occur significantly at <150 °C if the treated textile is to resist normal drying and curing temperatures. Often, the simple non-durable salt finishes start to decompose at <150 °C, so drying treatments should be ≤130 °C. However, in the case of soluble ammonium phosphates (explained more fully in [3]), careful heating at <150 °C enables some phosphorylation of cellulose to occur and hence some level of durability. Simultaneous acid degradation of the cellulosic chains can be reduced by an organic base such as urea, which increases penetration of cotton fibre and buffers the overall acidity during this curing process. Urea-ammonium phosphate flame-retardant treatments for cotton have a considerable history, with the earliest reviews appearing in the late 1940s [12, 13]; several commercial versions appeared in 1950–60 but these have been superseded by organophosphorus compounds (see below). The main drawback of these relatively simple chemical treatments was the ion exchange with calcium ions during laundering in hard water. Formation of calcium cellulose phosphate stabilises the phosphate and prevents the formation and release of phosphoric acid, thereby inhibiting char formation and flame retardancy. However, if wash durability is not a problem, an acceptable level of water-soak durability is achieved. This system applied to cotton interliners is claimed to be able to pass the 30-min, 40 °C water soak test according to British Standard (BS) 5651 as required by UK Furnishing and Furniture (1988) regulations [14] when testing to BS 5852:1979: Part 1, Sources 0 (cigarette) and 1 (simulated match).

Higher durability requires use of functional finishes based on organophosphorus compounds typified by the alkylphosphonamide derivatives pioneered by Ciba and now manufactured and marketed by Huntsman under the Pyrovatex® brand, or tetrakis(hydroxymethyl) phosphonium salt (THPX) condensates, principally Proban®, invented by the former Albright & Wilson and now produced by Solvay (formerly Rhodia).

Most of these treatments have become well-established during the last 40+ years, and few changes have been made to the basic chemistries since that time [1, 2]. Those that have been made often involve minor changes which influence properties such as handle [15] or decreased levels of formaldehyde release during application as seen, for example, in Pyrovatex® LF [16]. However, during the same period, many other flame retardants based on phosphorus chemistry and reviewed extensively elsewhere [2] have ceased to have commercial acceptability because of toxicological properties during application or during end-use, antagonistic interactions with other acceptable textile properties, and cost. These examples continue to satisfy technical performance and enable flammability regulatory requirements to be met, while having acceptable costs and meeting current demands for health, safety and the environment.

The chemistry of functional organophosphorus finishes is quite complex [1, 2, 5]. Hence, it is important to consider the important chemical features that influence the application process and the overall flame-retarded textile performance.

4.2.1 THPX Condensates

THPX condensates were developed in the 1950s by Albright and Wilson (now Solvay and formerly Rhodia) in the UK and Hooker Chemicals in the USA. The essential chemistry was undertaken by the Southern Regional Research Laboratory of the US Department of Agriculture. Vail and co-workers published several articles regarding the chemistry of THPX where X may be OH^-, Cl^- or SO_4^- [17, 18]. Tetrakis(hydroxymethyl) phosphonium chloride (THPC) is the most important of these and, although described first in 1921 by Hoffman [19], its commercial potential was realised by Reeves and Guthrie in 1953 [20]. THPC is prepared as follows [21]:

$$PH_3 + 4HCHO + HCl \rightarrow [(CH_2OH)_4.P{=}O]^+Cl^-$$

However, by itself THPC cannot confer flame retardancy unless a nitrogen-containing species, and hence phosphorus/nitrogen synergy, are present. Sources of nitrogen include urea, thiourea, trimethylol melamine, and cyanamide, which have been reviewed by Horrocks [2]. These bases form THPX complexes, which are the precursors for the formation of flame retardants. The chemistry of the application and finishing of THPX complexes have also been reviewed in detail by Vail and co-workers [22, 23].

Heating THPX with cotton causes some crosslinking to the cellulose molecules in the presence of an amine-ended species, and polymerisation of the THPC-base complex is the favoured reaction. However, control of pH is essential if excessive degradation is to be avoided [24]. This property of THPX-based polycondensation and subsequent development of ammonia as a crosslinker by Albright and

Wilson led to the currently successful Proban® process [25]. The result of such polycondensation is a polyphosphine in which the unstable phosphorus(III) must be oxidised to the stable phosphorus(V) state, giving rise to the final poly(phosphine oxide), which has a combination of flame retardancy and durability [26].

The former Hooker Chemical process used tetrakis(hydroxymethyl) phosphonium hydroxide (THPOH) whereas the Proban® process has always involved formation of a THPC condensate. Proban® nomenclature can be quite confusing because it has changed with time. The current position is that Perform is the generic name for THPC-urea monomers or precondensates of which Solvay (formerly Rhodia) market two variants:

- Perform CC®, which is the standard finish monomer, precondensate of urea and THPC (formerly Proban® CC)
- Perform STi®, which is a soft handle finish based on a modified monomer precondensate of urea and THPC (formerly Proban® STi).

The generic brand Proban® refers to the polymer, related processing technology, and downstream finished fabrics.

Figure 4.2 outlines the essential chemical and processing stages (shown schematically also as process (iii) in **Figure 4.1**) for the Perform® CC THPC-urea complex in which the THPC and urea are probably in a 2:1 molar ratio with a molar phosphorus:nitrogen ratio of 1:1.

The chloride is, in general, preferred relative to other salts (e.g., sulfate derivative) because, as a univalent anion, the salt-urea complex achieves a higher degree of penetration into the fibre microstructure. Experience has shown that the divalent sulfate complex, which is considerably larger, leads to lower levels of penetration with consequent reduction in durability.

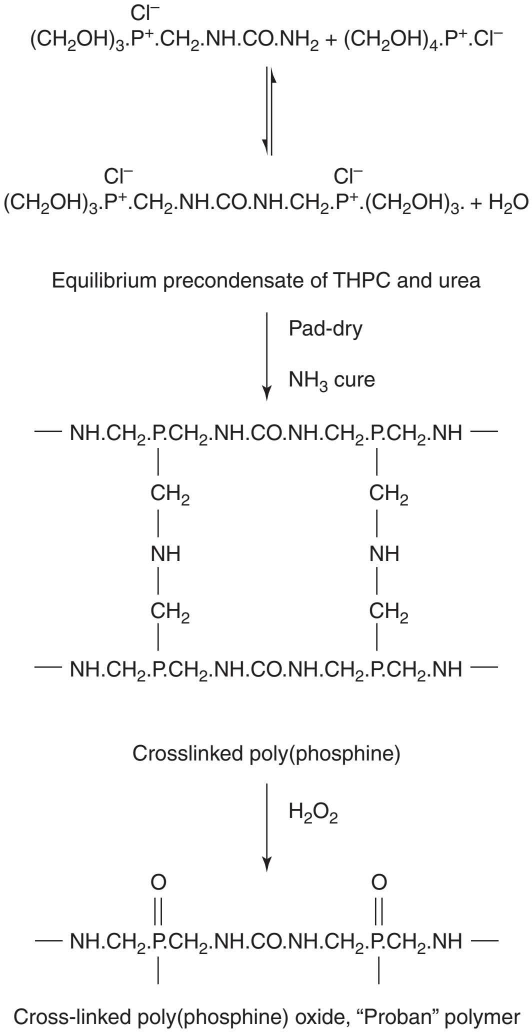

Figure 4.2 Chemistry of the Proban® process

The THPC-urea complex solution is applied by a pad or foam application method (see **Figure 4.1**, process (iii)) in the presence of wetting and softening agents. To ensure a high degree of penetration, the cotton fabric must have been scoured and bleached to a high degree of absorbency. After application (at a level commensurate with 2.0–3.0 wt% phosphorus on the final cloth), the fabric is dried to a moisture level of ≈8–10%. This dried fabric is passed in open-width form to an ammonia-cure reactor into which ammonia gas is fed at a controlled rate. An exothermic crosslinking reaction occurs, preferably within the component fibre microstructure, yielding an insoluble polymeric phosphine having a molar phosphorus:nitrogen ratio of 1:2. This ratio yields a high degree of synergy which, if phosphorus >2 wt% with respect to fabric, gives an acceptable level of flame retardancy for most applications. The final polymeric structure is not grafted onto the supporting cellulose molecular structure but more of an interpenetrating network of crosslinked Proban® polymer within a microfibrillar cotton cellulose structure. Its extreme durability derives from the intimacy of this interpenetrating network character.

As stated above, to stabilise the highly reducing phosphine polymer, after ammonia curing, the fabric is passed through a bath of dilute hydrogen peroxide to oxidise the polymer to a poly(phosphine oxide) [27, 28]. After this, the fabric is washed and dried. If the fabric has been prepared correctly and impregnated, and the ammonia cure controlled, then the final fabric will have a durable finish with little surface deposits and good handle. Finished softness is improved by inclusion of softeners such as long-chain fatty amines [29] but increases after laundering because the surface polymer is removed [30]. The final properties (both good and bad) are summarised in **Table 4.1.**

Table 4.1 Comparison of the strengths and weaknesses of THPX condensate- and *N*-methylol *N,N*' dimethylpropionamide derivative-based flame retardants for cotton

Flame retardant	Advantages	Disadvantages
THPX condensates	• Durable to >100 hospital washes (75 °C) • Minimal losses in fabric tensile and tear properties • No reported significant emissions of formaldehyde in use	• Require specialist ammonia gas cure unit • Can react adversely with some dyes e.g., sulfur • May require softeners to improve fabric handle
N-methylol dimethylpropionamide derivatives	• Durable to >100 hospital washes (75 °C) in the absence of bleach only • Applied by normal pad-cure methods • Compatible with all dyes, hence ideal for prints • May be applied and co-cured together with other finishes such as soil-release agents	• Significant losses in tensile (typically ≤20%) and tear (≤50%) strengths • Often forms tarry deposits in curing plant • Poor abrasion resistance • Formaldehyde release is a problem during application and end-use • Autocatalytic hydrolysis during storage releases formaldehyde • Cannot be used in sensitive applications such as children's nightwear

The main advantages are its exceptional durability to laundering: it can withstand >100 hospital washes (75 °C) [30]. After application, there are minimal losses in the tensile and tear properties of the fabric, and there are no reported significant emissions of formaldehyde in use (see below). In fact, emission of formaldehyde is a consequence of poor final oxidation of polyphosphine oxide because there is no known chemistry that would release this gas form the poly(phosphine oxide) polymer. At best, the emissions are <20 ppm.

The major disadvantages of this treatment are that the application process cannot be carried out on normal textile heat-curing equipment. A specialist ammonia gas cure unit is essential and is a part of the Proban® licensed process. The former Hooker THPOH-ammonia process suffers from the same problem, and this treatment is believed to be undertaken by several US finishers. The extreme reducing character of the ammonia cure process ensures that there can be adverse reactions with some dyes (e.g., sulfur dyes) and, as stated above, there is often a requirement for softeners to improve fabric handle. Attempts have been made to reduce or remove the need for ammonia gas curing [2, 3, 5], but none have been effective replacements at the commercial level.

4.2.2 Phosphonamide Finishes

The basic chemistry of phosphonamide finishes are based on the *N*-methylol dimethyl phosphonopropionamide $(CH_3O)_2.PO.CH_2.CH_2.CO.NH.CH_2OH$ as well as the associated chemistry described by Aenishaenslin and co-workers in 1969 [31] on behalf of the then Ciba-Geigy company. This molecule (synthesised by methylolating the adduct from dimethyl phosphate and acrylamide) does not have the reactivity with cellulose required for achieving an effective and durable flame-retardant finish. It may bond only to cellulose molecules *via* a methylolated resin bridge molecule (see **Figure 4.3**). Typically, this is a methylolated melamine derivative or dihydroxydimethylol ethylene urea in the presence of an acidic catalyst. Orthophosphoric acid has been shown to be the most effective catalyst in that it is sufficiently acidic to promote crosslinking reactions and yet it is not too acidic to create excessive hydrolytic degradation of cellulose chains (and hence undesirable decreases in the tear and tensile strengths of the fabric). However, if an effective finish with minimum stiffness and surface deposits is to be achieved, as for the Proban® finishes described above, a well-prepared fibre is essential, and careful padding or foam application of the formulation is essential to maximise penetration (see **Figure 4.1**, process (ii)). A typical formulation for application to a 150–200 gm^{-2} cotton fabric at 80% expression or wet pickup is shown in **Table 4.2** [32, 33]. The advantage of this overall process compared with the THPC-urea/ammonia cure process stated above is that it may be undertaken on a conventional open-width, pad-dry-cure-wash-off (see **Figure 4.1**, process (ii)) range. A more detailed schematic is shown in **Figure 4.4**.

Table 4.2 Pyrovatex CP standard and optimised application recipes and pilot-scale results [30, 31]

	Standard recipe	Optimised recipe
Recipe component, g/l		
Pyrovatex CP	280	260
Melamine resin	35	32
Softener	25	27
Acid catalyst	20	15
Wetting agent	1.25	1.25
Fabric response, %		
Limiting oxygen index (LOI)	28	30
Phosphorus on fabric	1.9	2.0
Emission level after curing stage, ppm		
Formaldehyde	20	5

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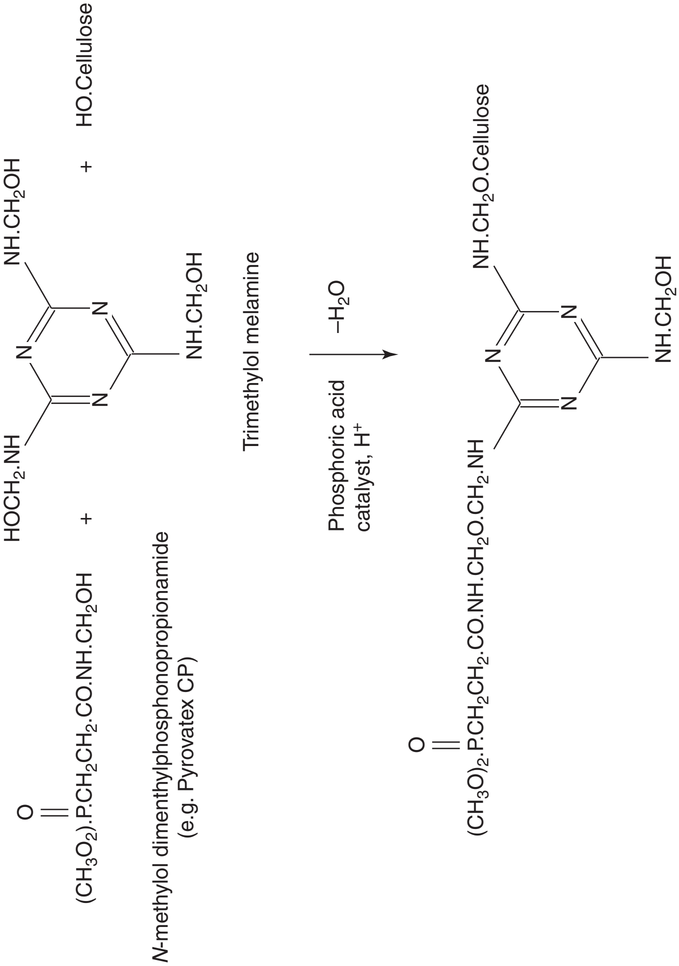


Figure 4.3 Chemistry of the Pyrovatex® (and similar phosphonamide) finishes

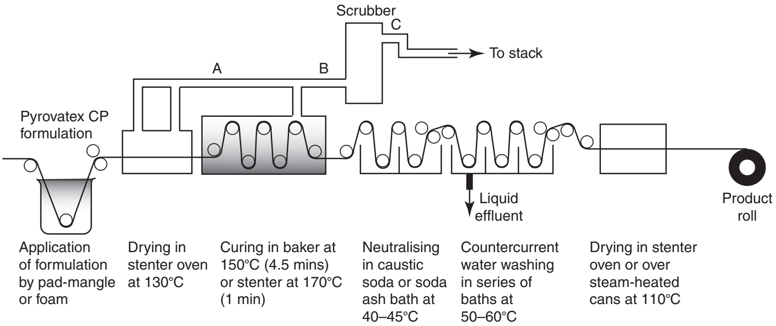


Figure 4.4 Detailed scheme of the overall Pyrovatex® CP application process. Adapted from A. Edmunds and A.R. Horrocks in *Environmental Technology Best Practice Programme*, FP 70, ETSU, Harwell, Oxford, UK, 1997 [34]

After application, the padded fabric is dried at 130 °C and then passed to a curing oven or baker at 150 °C for 4.5 min or 170 °C for 1 min. Generation of gaseous formaldehyde is a serious problem. It must be contained, extracted and removed by water scrubbing along with other emitted volatile organic compounds (VOC). Work by the author and his colleagues [32, 33] has indicated that formaldehyde emission can be decreased by optimising the bath formulation (see below, **Section 4.2.3** and **Table 4.2**). A secondary effect of the possible high levels of formaldehyde release during curing is the formation of highly intractable tarry deposits on the inside of the curing chamber, which necessitates removal unless volatiles are removed from the air in the curing oven. Lower-temperature curing and higher concentrations of the catalyst (phosphoric acid) also reduce tar levels, but this may reduce levels of fixation and promote greater loss in tensile properties, respectively.

Curing must be followed by an immediate alkaline (caustic soda (NaOH) or soda ash (Na_2CO_3)) neutralisation at 40–45 °C, if acid tendering is to be minimised. This neutralisation removes all residual catalyst (phosphoric acid), uncrosslinked phosphonamide, and some surface-crosslinked polymer. Subsequent washing-off with water and drying completes the process.

If controlled, the finishing process will yield high levels of durable flame retardancy at phosphorus levels of 1.5–2.0 wt% (see **Table 4.2**), as well as a fabric which has some degree of crease resistance, minimal losses in tensile and tear strengths (≈20–25%) and acceptable handle. Disadvantages are the need to minimise formaldehyde emissions and loss of tensile property, plus high losses of active flame retardant from poor fixation and reagent purity. Because of the influence of two of these factors upon effluent discharges, they will be explored in greater detail in **Section 4.2.4.**

Compared with THPC-ammonia cure systems, the cured phosphonopropionamide flame retardant has better dye compatibility (hence its preferred use on printed upholstery fabrics) and better flame retardancy per unit level of phosphorus, but yields inferior tensile properties and poor resistance to bleaches during laundering. Furthermore, during storage, there may be slow release of formaldehyde to the environment as well as loss in tear and tensile strength through acid hydrolysis. This is because the condensation reactions involved (see **Figure 4.3**) are equilibria, catalysed by acids and formaldehyde present during application and regenerated during service life. The presence of atmospheric moisture and acidic residues (which increase in concentration with the degree of hydrolysis) present in cotton favour the reverse reaction, hence generation of formaldehyde during storage and service [35]. This hydrolysis may be minimised by careful neutralisation during the washing stage after curing. Periodic washing of treated fabrics such as flame-retardant curtains removes acidic residues and so reduces (or even eliminates) fabric tendering during service life. However, it is because of this ubiquitous presence of formaldehyde (even though Pyrovatex®-treated fabrics can achieve formaldehyde levels <75 ppm and hence pass stringent tests such as Japanese Law 100 and Oeko-Tex requirements for skin contact [36]) that manufacturers such as Huntsman recommend that their Pyrovatex® products should not be used to treat children's nightwear.

Table 4.1 summarises the overall advantages of the cured phosphonoproprionamide group of treatments, and allows comparison with those respectively of the THPC finishes applied to cotton. One particular and noteworthy additional advantage of the former over THPC-based finishes is the ability to apply concurrently other finishes (e.g., soil-releasing agents) which can be co-cured during the normal oven-curing process [37].

The Pyrovatex® brand was developed by Ciba-Geigy, but it is currently owned by Huntsman. Two products are currently available: Pyrovatex® CP New and Pyrovatex® CP-LF (where LF stands for low formaldehyde (see below)) [37]. Other commercial examples of *N*-methylol dimethyl phosphonamide include Aflammit® KWB and Clariant's Pekoflam DPM (both made by Thor Chemicals).

4.2.3 Minimisation of Effluent and Water

As a consequence of current environmental legislation across the European Union (EU) (e.g., UK Environmental Protection Act, 1990), demands for stricter controls over effluent discharge have identified several problems associated with textile flame-retardant applications during the last 20 years. These relate to the following:

- Effects of discharge to effluent of unused flame-retardant liquors.
- Effects of emissions of formaldehyde to the atmosphere, especially during curing (currently required to be ≤ 20 ppm).
- Emissions of VOC (currently ≤ 50 ppm).
- Use and emission of ammonia in THPX-based treatments.
- Discharge of unfixed flame retardants from washing-off effluent.

The Proban® process comprises a conventional padding process followed by a specialised ammonia cure process followed by oxidation and washing off. Excessive release of phosphorus- and nitrogen-containing species into effluents and the atmosphere has not generally been seen to be a problem, perhaps because of the closed nature of the patented ammonia cure process [27, 28] and the effectiveness of the crosslinking process. However, this was a significant problem during the early 1990s, in particular for the *N*-methylol dimethyl phosphonopropionamide finishes, which stem from the impurity of the reagent itself and the difficulty of optimising the chemistry to minimise formaldehyde release. Research by Kapura [38, 39] showed that the percentage solids active species in commercial Pyrovatex® CP during this period was as little as 27 wt% with the methyl ether derivative of *N*-methylol dimethyl phosphonopropionamide ($(CH_3O)_2.PO.CH_2.CH_2.CO.NH.CH_2OCH_3$) present at 28 wt%. If these agents are considered to be similarly effective in their ability to react chemically, this is equivalent to a total effective solids content of only 55 wt%. Remaining components include the non-methylolated form, $(CH_3O)_2.PO.CH_2.CH_2.CO.NH_2$, (8 wt%) and the dimer, $[(CH_3O)_2.PO.CH_2.CH_2.CO.NH.CH_2]_2O$, (37 wt%). In 1990, Ciba introduced a purer version, Pyrovatex® CP New which, according to Kapura, comprises 61 wt% main reagent $R.CO.NH.CH_2OH$, 10 wt% of the methylated derivative, 21 wt% of the non-methylolated form, and a much decreased dimer content of 8 wt%. This product has given higher levels of fixation after curing and decreased levels of resin deposits in the curing/baking zones. Ciba introduced Pyrovatex® 757 during the 1990s, possibly the dimethylolated derivative $(CH_3O)_2.PO.CH_2.CH_2.CO.N(CH_2OH)_2$, to increase fixation further, although current Huntsman literature suggests that this does not form the basic chemistry of the current Pyrovatex® New product [37]. An alternative product, Pyrovatex® 7620, was also developed with decreased formaldehyde emissions, and it is possible that this is the forerunner of the current Pyrovatex® CP-LF finish.

Research by the author under a UK Environmental Technology Best Practice Programme [32–34] has shown that, during the application of Pyrovatex® CP, decreases in formaldehyde emissions by ≤75% are achievable together with reductions of effluent phosphorus levels by improved finish fixation. This work showed that application of a chemometrics software package to the five variable component liquor (see **Table 4.2**) could be analysed in terms of identifying component concentrations which significantly affected flame resistance (measured as the LOI), formaldehyde emission levels, and degree of fixation. From these analyses, an optimised recipe could be predicted and tested. The standard and optimised recipe with associated fabric properties and formaldehyde levels measured at the curing stage for laboratory-based experiments are presented in **Table 4.2**. The optimised recipe was little different from the standard formulation, but the analytical software predicted and demonstrated that the latter was on a 'knife edge' with regard to the sensitivity of the concentration of formaldehyde emission. Scaling up to full plant scale at three UK installations reduced the fourfold decrease in formaldehyde from the 20 ppm to 5 ppm obtained previously under the laboratory conditions shown in **Table 4.2** to between 36% and 59% reductions when measured at point B in the production line in **Figure 4.4**.

4.2.4 Durable Flame Retarding of Cotton/Synthetic Fibre Blends

Experience has shown that flame retardants which are effective on one fibre, when in contact with a second differently flame-retarded fibre, may prove to be antagonistic and render the blend flammable [2]. Consequently, the current rules for the simple flame retarding of blends are to apply flame retardant only to the majority fibre present or apply halogen-based back-coatings (which are effective on all fibres because of their common flame chemistries in the vapour phase).

The widespread use of polyester-cotton blends coupled with the apparent flammability-enhancing interaction in which both fibre components participate ('*scaffolding effect*', reviewed in [2]) has promoted greater attention than any other blend. However, because of the observed interaction, only halogen-containing coatings and back-coatings find commercial application to blends which span the whole range of blend composition. The earlier (1975) Caliban F/R P-44 decabromodiphenyl oxide and antimony III oxide (ATO) in a 2:1 mass ratio (equivalent to a molar ratio of bromine:antimony = 3:1) in a latex binder [40] has been the model for current coating and back-coating formulations for polyester-cotton blends as well as for coatings and back-coatings in general [6] (see **Section 4.5**). The presence of a binder may adversely affect fabric handle, and the usually off-white particles of the organobromine flame retardant and ATO yield a surface chalkiness with consequent effects on the depth of shade of any dye present. However, such fabrics in work-wear applications have been found to be advantageous in some off-shore applications, where they possess an oil-shedding property.

In the case of durable, phosphorus-containing cellulose flame-retardants, they are generally effective only on cellulose-rich blends with polyester because, even though they may have some positive effects on the polyester component, they are substantive only on the cellulose component. THPC-based systems such as Proban® are effective on blends containing ≥55% cotton if a combination of flame retardation and acceptable handle is required. This is because the THPC condensate is substantive only on the cellulose content, which would require >5 wt% phosphorus to be present on this component to confer acceptable flame retardancy to the whole blend. However, high phosphorus and hence finish levels lead to excessive surface deposits on fibres, decreased durability to laundering, and create unacceptable harshness of handle. Furthermore, such applications work well only on medium-to-heavy weight fabrics (>200 gm^{-2}) and so are effective particularly for protective clothing applications. The use of a cotton-rich blend here is particularly advantageous because the lower polyester content confers a generally lower thermoplastic character to the fabric, with less tendency to produce an adhesive molten surface layer if exposed to a flame.

To achieve the high finish levels necessary, often a double pass pad (or foam)-dry stage is required before the THPC-urea-impregnated fabric is ammonia-cured in the normal way. If a lower degree of durability is required, then cheaper semi-durable flame-retardant combinations are feasible. For example, combination of an oligomeric ammonium polyphosphate/urea formulation (e.g., Antiblaze® LR2, Solvay (formerly Rhodia)) at phosphorus levels of ≈6 wt% with respect to the cotton component together with 5–6 wt% of the monomeric cyclic phosphonate as exemplified by Antiblaze® CU/CT (Solvay (formerly Rhodia)) or Aflammit® PE (Thor) with respect to the polyester component applied to cotton and polyester components, respectively, in the blend will give a 40 °C, 30-min water soak-resistant finish as required for UK domestic upholstery fabrics [14].

Application of methylolated phosphonamide finishes (e.g., Pyrovatex® CP) is effective on blends containing ≥70% cellulose content. This is because the phosphorus present is less effective on the polyester component than in THPX-based finishes [2]. The reasons for this are not clear, but are thought to be associated with some vapour-phase activity of phosphorus in the latter finish on the polyester component [41].

Blends of cotton with polyester comprise the majority of cotton/synthetic fibre mixtures but, in the USA especially, majority cotton blends with nylon are quite common for work-wear, where the latter is present to increase abrasion resistance. In this respect, Weil and Levchik [5] cite blends of 88% Proban®-treated cotton with 12% high-tenacity nylon sold by Westex as Indura® Ultra Soft fabric for high-comfort work clothing. Within the UK, Carrington work-wear market a range of 88% Proban® cotton/12% nylon fabrics under its Flamgard range, with specific examples being Flamtuff® 200, Flamtuff® 250 and Flamtuff® 330 (where the number relates to the area density in g/m^2). They also market antistatic versions comprising 88% Proban®/12% nylon/1% antistatic nylon. The nylon component may be increased, and the US Alexium International Group claims to have a durable flame-retardant treatment that will be effective on 50/50 blends with applications in military fatigue fabrics [42]. Information regarding the flame-retardant system used is not available. However, one Burlington Industries patent [43], for instance, claims that for nylon contents between 10% and 65%, THPX finishing of cotton combined with a monomeric cyclic phosphonate (e.g., Antiblaze® CU/CT, Solvay (formerly Rhodia)) or hexabromocyclododecane are required to achieve acceptable levels of flame retardancy. The process must be carried out in two stages: the first is application of the THPX/ammonia finish, followed by padding on and heat curing of the second agent. Burlington Industries patents of a similar type for cotton/nylon blends have been reviewed by Weil and Levchik [5].

4.3 Durable Flame-retardant Finishes for Wool

Of all conventional fibres, wool has the lowest inherent flammability and for some end-uses, where high density of structure and horizontal orientation (e.g., carpets) are required in the product, wool fabrics will pass the required flame retardancy tests untreated. Its relatively high LOI value (≈25%), high ignition temperature (570–600 °C) and low flame temperature (≈680 °C) are a consequence of its higher moisture regain (8–16% depending upon relative humidity), high nitrogen (15–16%) and sulfur (3–4%) contents and low hydrogen (6–7%) content by weight. Organo-sulfur compounds are generally flame retardant to some degree, but the disulfide cystine links are easily oxidisable, so this can offset some of the anticipated natural flame retardancy. Pre-oxidation of wool and hence cystine to cysteic acid residues restores this expected activity, and oxidised wools can have greater inherent low flammability.

Notwithstanding the above, if wool is to be effective in applications such as curtains, upholstery, protective clothing and barrier fabrics, flame-retardant finishing is essential (although durability often needs to extend only to dry-cleaning in most instances). If heated, wool (like cellulose) tends to form a char, and this reaction is highly favoured in untreated wool. Furthermore, because wool chars *via* a semi-liquid state, char formation is accompanied by intumescence to give an expanded (though brittle) char that is often thicker than the original fabric. Thus, the charred structure provides an equivalent (if not superior) thermal barrier, provided that the char remains coherent relative to the original fabric. This makes wool an ideal fibre for use in protective clothing, especially if the hazard of molten metal splash is present. This is because the intumescent char provides a thermal barrier to the solidifying metal splash (and its associated emission of latent heat of fusion), and the mass of the metal enables it to fall away as the weak encapsulating char fractures. An added advantage of the char is that, after its formation by a point ignition source of short duration (e.g., brief cigarette or match contact), it can be brushed away to leave little (if any) sign of damage assuming that only the fabric surface has been exposed. Finally, the absence of significant inorganic salt concentration in natural wool gives few (if any) afterglow problems, which can be a feature of cellulosic textiles.

The review by Horrocks [2, 44] comprehensively discusses developments in non-durable and durable flame retardants for wool up to 1986, and very little has changed since that time as the very recent review [44] shows. Readers should consult these reviews and their many cited references for a more detailed understanding of flame-retardant treatments for wool.

It is significant that the nominally non-durable ammonium phosphates and derivatives (which function as Lewis acids) release phosphorus acids and promote the deamination of wool protein and so encourage char promotion, when dried and cured at ≤130 °C, give dry-clean durability up to 10 cycles. Even the highly water-soluble ammonium bromide can give some degree of dry-clean durability on wool.

As detailed in [2, 44], despite considerable research into the use of functional phosphorus-based finishes (including THPX and methylolated phosphonamide derivatives), polymeric treatments, and substantive halogenated species such as chlorendic, tetrabromophthalic and dibromo-maleic anhydrides as well as brominated salicylic-acid derivatives, the most commonly used durable flame retardants are based on Benisek's Zirpro® system [2], which were initially developed and marketed by the International Wool Secretariat. The major advantages of this treatment are the absence of discoloration or other effects on wool aesthetics, coupled with its application *via* a simple exhaust process usually during the normal acid-dyeing process.

The Zirpro® process is based upon the exhaustion of negatively charged complexes of zirconium or titanium on to positively charged wool fibres under acidic conditions (pH ≤3) at 60 °C. Zirpro®

treatments can be applied to wool at any processing stage from loose fibre to fabric using exhaustion methods during or after dyeing. The relatively low treatment temperature is an advantage because this limits the felting of wool.

The processor has the choice of potassium hexafluorozirconate (K_2ZrF_6) or a mixture of this and potassium hexafluorotitanate (K_2TiF_6). Both components are stable metal fluoride complexes which are substantive to wool. Exhaustion is rapid, achieving 80% after 30 min. The simple chemistry of application is:

$$\text{Wool - NH}_2 + \text{H}^+ \longrightarrow \text{Wool-NH}_3^+$$

$$[\text{ZrF}_6]^{2-} + 2\,[\text{Wool-NH}_3^+] \longrightarrow [\text{Wool.NH}_3^+]_2\,[\text{ZrF}_6]^{2-}$$

Some hydrolysis of the complex occurs. However, Benisek demonstrated that acceptable flame retardancy results if the molar ratio F:Zr ≥ 5 if maximum exhaustion occurs [45] and the zirconium concentration on the fabric is 2.3 wt%. Use of a titanium complex (because of the smaller ionic size and hence the greater penetrative character of titanium) enables an equivalent or higher level of flammability to be achieved at similar bath concentrations. K_2TiF_6, however, causes discoloration, so is used as a mixture with K_2ZrF_6 to minimise this effect and decrease concentrations and cost [2].

It is important to maintain a low pH (≤ 3) to maximise fibre penetration and wash-fastness to ≤ 50 washes at 40 °C or 50 dry-cleaning cycles in perchloroethylene. Acids such as hydrochloric acid and formic acid are preferred because, unlike sulfuric acid, for example, they do not have anions which compete with the metal fluoride ions for the protonated amino groups in wool. However, the general simplicity of the entire process enables it to be used concurrently with 1:1 premetallised and acid-levelling dyes, or after dyeing if applying acid milling-reactive 1:2 premetallised and chrome dyes. Furthermore, treatments are compatible with shrink-resistant, insect-resistant and easy-care finishes.

Should smoke emission be a problem then, because the Zirpro® treatments detailed above can increase smoke generation with respect to untreated wool, a low-smoke variant that comprises a fluorocitratozirconate complex may be used. This is applied from formic acid to achieve a molar ratio F:Zr = 2 and a zirconium concentration of ≥2–3 wt%.

The effectiveness of Zirpro® treatment is not fully understood from a mechanistic viewpoint and, while Benisek [46] attributes it to enhanced formation of intumescent char, Beck and co-workers contest this view [47]. They state that the treatment promotes scission of peptide bonds with increased loss of mass. Clearly, however, its ability to create extremely effective flame- and heat-barrier properties at high heat fluxes is associated with the char structure generated.

Zirconium hexafluoride as the fluorozirconate salt was in the recent past supplied by MEL Chemicals (UK), although its website now suggests otherwise. However, Thor have a product, Aflammit® ZR, that comprises potassium hexafluorozirconate as a suitable flame retardant to achieve a Zirpro®-type finish. They also have a product, Aflammit® ZAL, comprising zirconium acetate solution which, if used with Aflammit® ZR, claims to give a reduced smoke flame-retardant finish to wool fabrics. The Avocet Dye and Chemical Company (UK) produce similar flame-retardant formulations, Cetaflam® PHFZ and Cetaflam® ZAS, for normal and low-smoke Zirpro®-type finishes, respectively. They also supply Cetaflam® DTB to reduce after-flaming times in conjunction with the previous formulations: this is probably tetrabromophthalic acid (TBPA) or a similar chemical (see below).

Recently, the Zirpro® process has come under the critical eye of environmentalists as a consequence of the release of heavy metal ions into effluent discharges. In attempts to decrease effluent problems, replacement of the exhaust method by padding methods has not been successful because both potassium metal fluoride complexes are not very soluble (≈10 g/l) at room temperature.

In some applications, such as fabrics for transport seating, where excess after-flame is seen to be a problem, Zirpro® treatment may be combined with a bromine-containing agent such as TBPA, which has a substantive for wool under acid conditions [48]. This enables slightly lower concentrations of zirconium to be used but this is offset, from an environmental viewpoint, by addition of the bromine present.

In spite of these concerns, research during the last ≈15 years has been limited. For instance, Lewin and Mark [49] demonstrated that sulfation with ammonium sulfamate followed by curing at 180–200 °C in the presence of urea can give a 50 hard-water, wash-durable finish for wool fabrics with little change in handle. Research by the author into the possibility of using treatments based on intumescents has shown that enhanced barrier properties are possible, and that this occurs for the flame-retarded (Zirpro®) and unretarded wool fibres present [50, 51].

Several finishes must be imparted to wool fabrics if they are to achieve the many performance requirements demanded by protective clothing and aircraft (and other transport) upholstery applications, for instance, coupled with the need for easy-care properties. Developments in this area have been reviewed [2] and certain factors are worthy of note:

- Oxidative shrink-resist treatments should be applied before Zirpro® treatment.
- Insect-resistant treatments should be added to a Zirpro® bath first.
- Resin-based shrink-resistant treatments can promote flammability unless, like the Hercosett (Hercules) resin, they contain elements such as chlorine and nitrogen; such resins should be applied after Zirpro® treatment.
- Co-application of water-repellent (e.g., resin-wax dispersions) and oil-repellent (e.g., fluorocarbon) finishes should follow Zirpro® treatment, for example, by a pad-dry-cure-rinse-dry process.

If processing wool blends, given the position of the Zirpro® process as the currently major durable flame-retardant treatment, its specificity ensures that little (if any) transferability of the zirconium complex or its flame-retardant activity occurs to the other fibres present.

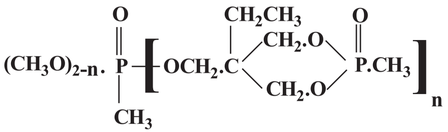
Furthermore, Benisek reported antagonisms between Zirpro® and other flame-retardant fibres, principally Trevira® CS, in 1981 [52]. In the absence of a back-coating treatment, acceptable flame retardancy of Zirpro®-treated blends are obtainable in 85/15 wool/polyester or polyamide combinations (although synthetic fibre content may be increased to ≈25% if the zirconium tungsten-modified treatment is used). For lower wool contents in blends and without the possibility of using alternative flame-retardant treatments, flame retardance can be maintained only if some of the Zirpro®-treated wool is replaced by certain inherently flame-retardant fibres, except for Trevira® CS polyester [52]. Chlorine-containing fibres such as poly(vinyl chloride) (PVC) and modacrylics are particularly effective in this respect.

4.4 Flame-retardant Finishes for Man-made Fibres

Man-made (including regenerated and often-called 'chemical' or 'synthetic') fibres may be rendered flame retardant during their production, thereby creating a degree of inherent flame retardancy. Apart from viscose and, more recently, lyocell fibres, the conventional synthetic fibres are hydrophobic with physical structures inaccessible to the salt-like materials used for semi-durable flame retardants and even the most reactive precursor organophosphorus agents. Consequently, only regenerated cellulose fabrics and blends are amenable to durable flame-retardant finishing with the treatments used for cotton. Viscose, in particular, is more delicate than cotton and lyocell fibres, and so must be finished with care to avoid undue strength losses during drying and curing. Very rarely, to the author's knowledge, are viscose fibres durably flame retardant-treated because inherently flame-retardant alternatives such as Lenzing's flame-retardant viscose are available and are more commercially attractive (see **Chapter 5**).

The remaining common synthetic fibres, i.e., polyamide, polyester, polyacrylic and polypropylene, may be semi-durably and durably flame retarded. **Table 4.3** lists examples of those currently available for polyester and polyamide (and blends).

Table 4.3 Durable finishes for synthetic fibre-containing textiles [3]

Company	Chemical constitution/comments
Solvay (formerly Rhodia)	
Antiblaze® CU/CT	 n=1; cyclic oligomeric phosphonate; and pad-dry (110–135 °C) – cure (185–200 °C). Primary use: polyester. Secondary uses: polyamide and polypropylene.
Thor	
Aflammit® PE	As above for Antiblaze® CU, polyester.
Aflammit® NY	Organic nitrogen and sulfur compound (probably a thiourea derivative) and a reactive crosslinking compound; polyamide. Cure at 150–170 °C for 45–60 s.
Schill & Seilacher	
Flacavon AM	Nitrogen- and sulfur-containing compound (thiourea derivative); polyamide; 100–110 °C dry only; and durable to dry cleaning.
Flacavon AZ	Organic phosphorus compound (as for Antiblaze® CU) and polyester.

Flacavon H14/94	Antimony oxide + bromine compound (+ binder) and all fibres, especially polyester-cotton blends.
Clariant	
Pekoflam PES new liq.	Cyclic organic phosphorus compound (as for Antiblaze® CU) and polyester.
Apexical (US)	
Apex Flameproof 1506	Organohalogen compounds: polyester.
Apex Flameproof 1528	Non-toxic, durable non-halogen flame-retardant: polyester and polyamide.
Apex Flameproof 2952	Durable FR for 100% polyamide.
Avocet (UK)	
Cetaflam® DB 9 and DBeXL	Non-halogen, phosphorus-containing, dye-bath applicable durable flame retardants for polyester.
Adapted from A.R. Horrocks in *Textile Finishing*, Ed., D. Heywood, Society of Dyers and Colourists, Bradford, UK, 2003, p.214 [3]	

In the case of acrylics, because of the difficulty of finding an effective flame-retardant finish, modacrylic fibres are preferred.

The low melting point, non-functionality and high hydrocarbon fuel content (see **Table 4.3**) of polypropylene have created problems in finding an effective durable flame-retardant finish and also pose difficulties in the design of effective back-coatings (see **Section 4.5**).

This leaves only polyamides and polyesters as possible candidates for durable flame-retardant treatments. The literature contains several possible solutions [2], but few have entered the commercial arena, as examples in **Table 4.3** show [3].

The Antiblaze® CU product (formerly Antiblaze® 19 [2]) based on the cyclic phosphate formula in **Table 4.3** is claimed to be effective on polyamides and polypropylene as well as polyester (for which it was initially developed). It is essentially monomeric although it has been available as the high boiling point dimer, Antiblaze® P45, for use as a melt additive. Antiblaze® CU has high phosphorus content (21.5 wt%). It is a clear, viscous liquid that is applied to polyester at 3–6 wt% add-on buffered at pH 6.5 with disodium phosphate and a small amount of wetting agent. After padding at ≈40–60% expression or wet pickup, the fabric is dried at 110–135 °C followed by thermofixation at 185–205 °C for 1–2 min. Thermofixation usually results only at ≈80% retention of the original finish because of its volatility at high temperature. After rinsing and drying, the finish should resist 50 washes at 60 °C or 10 dry-cleaning cycles with 90% retention.

This same finish may be incorporated in a resin for coating for polyester and its blends. Durability is not as great, but loss does not occur during processing as in thermofixation treatment. Inclusion of melamine increases the finish effectiveness on 100% polyester. A typical binder mass ratio of Antiblaze® CU:melamine:binder would be 8:13:34 with the residual weight made up of water and a viscosity modifier. Aflammit PE (Thor) and Flacavon AZ (Schill & Seilacher) are believed to have a similar chemical composition (if not the same) as Antiblaze CU.

The other durable flame-retardant finishes for polyester listed in **Table 4.3** are those that may be applied directly from the dyebath. These include Cetaflam® DB 9 and DBeXL (Avocet, UK) and the very recently introduced TexFRon® 3000 (ICL-IP), both of which have undisclosed chemistries.

Few treatments are satisfactory for the flame-retardant treatment of nylon fabrics. Application of 10 wt% ammonium bromide or 18 wt% ammonium dihydrogen phosphate by a pad-dry route is effective but non-durable. Hence, urea-formaldehyde resins or aminotriazine-aldehyde condensates can be used with ammonium bromide using a pad-dry-cure process to improve the durability of the finish. Durable but fabric-stiffening flame-retardant finishes based upon methylated urea-formaldehyde with thiourea-formaldehyde have been applied to nylon nets for evening wear and underskirts. For example, Thor's Aflammit® NY comprises two components, Aflammit® NY 1 based on an organic nitrogen/sulfur compound (probably a thiourea derivative) and Aflammit® NY 2, the crosslinking methylolated urea component. Typically for such formulations, ≈15–20 wt% thiourea-formaldehyde precondensate is padded with ammonium chloride (1 wt% on the weight of the resin) as a latent catalyst followed by low-temperature drying and then curing at 170 °C for 1 min. Examples of these finishes are included in **Table 4.3** (although the exact chemical constitutions of polyamide–specified retardants are not available).

4.5 Flame-retardant Coatings and Back-coatings

Coating technologies have been around for many years, and the review by Woodruff [53] shows that the main uses are for technical and industrial textile applications that may involve the need for flame retardancy. Back-coatings are more usually applied to the reverse faces of furnishing fabrics, and so have applications in consumer and contract markets. The entire area of flame-retardant textile coatings and back-coatings has been reviewed recently by the author [54]. Readers are invited to peruse this reference for greater detail, especially into recent research and innovations in these areas.

4.5.1 Flame-retardant Coatings

Given the detailed reviews cited above [53, 54], this section will focus only on currently used flame-retardant coatings with certain service applications. Flame-retardant coated textiles include a wide range of materials in which flame retardancy is only one property (e.g., tarpaulins, awnings and outdoor textiles which also require waterproof and weather-resistant properties). This area also overlaps the area of laminated textile materials (e.g., airbags and seating composites for automotive and other transport applications, and decorative textile laminates). Coating technologies are quite numerous and varied [53] and, from the viewpoint of applied polymeric formulations, include:

- Solvent-based systems
- Chemically-cured systems
- Hot melt processes.

With the need for reduced volatile organic species produced in the workplace and rising costs of solvents, chemically cured and hot-melt formulations have become more popular in recent years. Furthermore, the former are often applied as polymer dispersions in aqueous media. In the main, flame-retardant coating formulations are applied to conventional fibre-containing fabrics such as cotton, polyester, and polyamide, unless very high levels of fire resistance are required, in which case glass fabrics are often the textile substrate. **Table 4.4** lists a selection of the coating polymers used alongside their respective limiting oxygen index (LOI) values. Those with a LOI ≥25% have some degree of inherent flame resistance [54].

Table 4.4 Typical coating resins and their limiting oxygen index (LOI) values

Polymer or resin		**Acronym or trivial name**	**LOI, vol% oxygen**
Natural rubber		–	19–21
Synthetic rubbers	Polyisobutylene	Butyl rubber	20–21
	Styrene butadiene	SBR	19–21
	Poly(butadiene-acrylonitrile)	Nitrile rubber	20–22
	Poly(chloroprene)	Neoprene	38–41
	Chlorosulfonated polyethylene	–	26–30
	Poly(fluorocarbon)	–	>60
	Silicone elastomers	–	26–39
Poly(vinyl chloride)		PVC unplasticised	45–47 23–25
		PVC plasticised	23–25
Poly(vinyl alcohols) and poly(vinyl acetate)		PVA	19–22
Formaldehyde resins:	Phenolic	-	21–22
	Urea	-	≈30
	Melamine	-	≈30

Acrylic copolymers		Acrylics	17–18
Polyurethanes		PUR	17–18
Silicones		-	≥26
Ethylene-vinyl acetate and related copolymers (emulsions); vinyl chloride presence will increase the LOI.		EVA; and EVA-VC	≥19–20
Poly(fluorocarbons)	Poly(tetra fluoroethylene)	PTFE	98
	Fluorinated ethylene polymer	FEP	≈48
	Poly(vinyl fluoride)	PVF	23
	Poly(vinylidene fluoride)	PVDF	44
Fusible/powders	Low-density poly(ethylene)	LDPE	17–18
	High-density poly(ethylene)	HDPE	17–18
	Polyamides	PA6, PA66	24–26
	Polyesters	PES	20–21
	Ethylene-vinyl copolymers	EVA	19

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Flame retardancy or enhanced flame resistance is usually introduced by means of additives, which fall into one or more of the following groups:

- Phosphorus-containing agents
- Halogen-containing agents
- Intumescents
- Synergists only in the case of halogen-containing coating polymers
- Inorganic agents.

Ideally those selected should be liquids so that polymer coatings remain flexible (and indeed may be plasticised) and retain desirable surface properties. This is not possible if intumescents or synergists like ATO are used because of their usually white (or off-white) particulate characteristics.

Table 4.5 Selected phosphorus-containing flame retardants for use in coatings

Chemical formula/name	Commercial examples	Comments
Triaryl phosphates	Reofos 35-95; Chemtura Phosflex 71B; Supresta	Proprietary formulations with 7.6–8.0% P
Cresyl diphenyl phosphate	Kronitex CDP; Chemtura	9.1% P
Tricresyl phosphate	Kronitex TCP; Chemtura	8.4% P
Trixylyl phosphate	Kronitex TXP; Chemtura Phosflex 179; Supresta	7.8% P
Triethyl phosphate	Fyrol TPE; ICL	17% P
Isodecyl diphenyl phosphate	Phosflex 390; Supresta	Functions as plasticiser in PVC; 7.9% P
Oligomeric phosphate-phosphonate	Fyrol 51; Supresta	Textile back-coatings; 20.5% P
Cyclic organophospates and phosphonates	Antiblaze® CU; Rhodia Pekoflam PES; Clariant Aflammit PE ; Thor	Substantive to PES fibres but may be incorporated in most coating resins; 17% P
Nitrogen-containing polyol phosphate	Exolit OP 920; Clariant	Non-halogen flame retardant for lattices with plasticising effects; 16% P, 9% N

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Table 4.6 Halogen-containing flame retardants for coatings

Chemical formula/name	Commercial examples	Comments
Dibromostryene	Great Lakes DBS; Chemtura	59% Br
Decabromodiphenyl ether (DecaBDE)	Great Lakes DE-83R; Chemtura FR-1210; ICL Saytex 102E; Albemarle Myflam and Performax; Noveon	Principal flame retardant for textile back-coatings; 83% Br
Hexabromocyclododecane (HBCD)	Great Lakes CD-75; Chemtura Flacavon H14; Schill & Seilacher FR-1206; ICL Saytex HP-900; Albemarle	Competes with DecaBDE in textile back-coatings; 73% Br
Tetrabromophthalic anhydride and diol	Great Lakes PHT4 and PHT4-DIOL; Chemtura Saytex RB-49; Albemarle	68% Br 46% Br 68% Br
Tetrabromobisphenol A	Great Lakes BA-59; Chemtura FR-720; ICL	59% Br
Dedecachloropenta-cyclooctadecadiene	Dechlorane; Occidental	Used in elastomeric coatings (synthetic and silicone); 65% Cl

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4.5.1.1 Phosphorus-containing Agents

Table 4.5 lists typical examples of acceptable flame retardants, including, for example, the long-chain alkyl/aryl-substituted phosphates, in which plasticisation is also required. **Table 4.5** concentrates on single chemical entities, but many commercial proprietary flame retardants are formulated mixtures or blends which are especially easily achievable if the components are liquids. Such blends enable balances of flame retardancy to be achieved while offering acceptable processing and end-product performance.

4.5.1.2 Halogen-containing Flame Retardants

Within halogen-containing flame retardants (see **Table 4.6**), bromine-containing agents predominate because not only are they more efficient than similar chlorine-containing species, but also the high atomic weight of bromine ensures that it is present in a high mass fraction within most organo-bromine compounds. Typically, for many polymers, acceptable levels of flame retardancy are achieved if ≥5 wt% bromine is present in the final formulation. For example, the very commonly used DecaBDE (see **Table 4.6**), in which the bromine content is 83 wt%, its presence is often <10 wt%, which is quite low compared with most flame-retardant polymers containing other additive flame retardants. However, the synergist ATO is usually present [55] and assuming a molar ratio of bromine:antimony of 3:1 (reflecting the possible formation of $SbBr_3$ as an intermediate), this equates to a mass ratio of ATO:DecaBDE of 1:2, thereby ensuring that the total concentration of the flame retardant present in the polymer may be ≤15 wt%. Similarly high total formulation levels are seen for other brominated flame retardants, although still often less than the >20 wt% levels required by phosphorus-containing flame retardants and >50 wt% levels for some inorganic agents (see below). Recently, several tin compounds, including zinc stannate (ZS) and zinc hydoxystannate (ZHS), have been shown to be synergistic with halogen-containing flame retardants but, unlike ATO, bromine-containing FR/ZS or ZHS combinations have to be selected for maximum efficiency [56, 57]. These are also discussed briefly in the following sections on synergists and inorganic flame retardants.

4.5.1.3 Intumescent Systems

Intumescent flame retardants are those that form highly expanded, insulative chars upon heating, and so offer high levels of flame barrier properties [58, 59] within the polymer. These are especially beneficial in polymers such as the polyolefins and polyesters, which lack char-forming ability and where the intumescent char provides a supportive network, thereby preventing melt dripping and restricting the overall burning process. Such formulations may be intumescent in their own right and generate carbonaceous chars independently of the surrounding polymer matrix or they may interact with the matrix so that the flame retardant-polymer together give rise to an expanded, intumescent char if exposed to heat and flame. Most of these are based on ammonium polyphosphate (APP) and melamine chemistries, and selected examples are presented in **Table 4.7** [54].

Table 4.7 Selected intumescent and intumescent component flame retardants

Chemical formula/ name	Commercial examples	Comments
APP	*Phase I types**: Antiblaze® MC; Albemarle	Water solubility ≈4 g/100 cm^3
	Exolit AP 412; Clariant	–
	FR CROS 480-485; Budenheim	–
	Phase II types*: Exolit AP 422; Clariant	Water solubility ≈4 g/100 cm^3
	FR CR0S 484; Budenheim	–
	Coated Phase II types: Exolit AP 462 and 463	Microencapsulated version of AP 422; water solubility <0.5 g/100 cm^3
	FR CROS 486; Budenheim	Silane-coated: melamine-formaldehyde (MF)
	FR CROS 487; Budenheim	MF coated: water solubility ≈ 0.1 g/100 cm^3
	FR CROS C30/C40/C60/C70/ 489; Budenheim	Surface-reacted MF, varying particle sizes D^{50} = 7–18 μm; water solubility ≤0.1 g/100 cm^3
Melamine phosphates	BUDIT 310; Budenheim	Dimelamine orthophosphate
	Antiblaze® ND; Albemarle	Dimelamine orthophosphate
	BUDIT 311; Budenheim	Dimelamine pyrophosphate
	BUDIT 312; Budenheim	Melamine phosphate

	Antiblaze$^{®}$ NH; Albemarle	Melamine phosphate
	Melapur MP; Ciba	Melamine phosphate
	Antiblaze$^{®}$ NJ; Albemarle	Melamine pyrophospahte
	Melapur 200; Ciba	Melamine polyphosphate
	BUDIT 3141; Budenheim	Melamine polyphosphate
Other melamine salts	BUDIT 313; Budenheim	Melamine borate
	BUDIT 314/315	Melamine cyanurate
	Melapur MC; Ciba	Melamine cyanurate
Other pentaerythritol derivatives	Great Lakes NH 1197; Chemtura	Phosphorylated pentaerythritol
	Great Lakes NH 1511; Chemtura	Phosphorylated pentaerythritol/melamine salt
Intumescent blends	BUDIT 3077 and related products; Budenheim	-
	Antiblaze$^{®}$ NW; Albemarle	Melamine phosphate and dipentaerythritol

[*] Phases I and II refer to different levels of molecular weight, crosslinking and hence crystalline characteristics. Phase I APP variants have much lower degrees of polymerisation and crosslinking and greater water solubility.

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All are particulate solids, of which one or more components may be soluble in water. Hence, for water soak or wash durability they may be used only in hydrophobic polymeric coating matrices, which may create dispersion problems during processing. Hence, many commercial particulates are coated or microencapsulated to reduce water solubility and/or to improve compatibility with the polymer matrix. Furthermore, as seen in **Table 4.7**, manufacturers such as Budenheim offer variations with reduced particle sizes, as shown for APP and melamine phosphates in particular.

APP is not an intumescent in its own right, but it is a powerful char-former in the presence of oxygen-containing polymers and copolymers. Hence, it is particularly effective on cellulosic and polyamide textiles. To ensure intumescent action, it is used in combination with other agents, such as pentaerythritol and melamine [58]. The melamine phosphates shown in **Table 4.7** have a greater degree of inherent intumescent activity because the acid-forming component phosphate is combined chemically with the gas-forming melamine. They also have superior water insolubilities (often <1 g/100 cm^3) before subsequent coating or microencapsulation. Particle sizes are often less than normal APP samples, and may have a median particle diameter (D_{50}) ≤8 µm.

Of all flame-retardant coating innovations of the last few years, those incorporating intumescent flame-retardant agents have been the most commonly reported [58–60]. Indeed, the recent demand for halogen-free, flame-resistant barrier fabrics in US markets driven by Californian regulations for furnishings (TB 133) and mattresses (TB 129 and 630) as well as federally by the US Consumer Product Safety Commission 16 Code of CFR 1633) for mattresses [61] has encouraged the development of intumescent coatings applied to inherently fire-resistant fibre-containing fabrics, including glass. These are exemplified by established products from Springs Industries [62] and fabrics from Sandel International Inc., USA.

4.5.1.4 Synergistic Additives

Pure PVC has an LOI of ≈45–47% but, in the presence of a typical plasticiser such as di-isononyl phthalate, the LOI falls to 23–25%. If the plasticised polymer is to achieve acceptable levels of flame retardancy then the plasticiser is replaced by a similar flame retardant with plasticising properties such as a phosphate ester (e.g., isodecyl diphenyl phosphate (e.g., Phosflex® 390, (Supresta); see **Table 4.5**) or a synergist such as ATO is added to act together with the chlorine present and so raise the LOI to >30%. In practice, addition of ATO is the cheaper option, and so more often used for various flame-resistant PVC-coated textiles such as awnings, carpet backings and tarpaulins. The ATO can be replaced by zinc hydroxystannate which, although slightly more expensive, does not have associated toxicological risk factors [57].

4.5.1.5 Inorganic Flame Retardants

Inorganic flame retardants are typified by hydrated aluminium oxides and magnesium oxides. The former are often referred to as alumina trihydrate (ATH) or aluminium hydroxide, and the latter as magnesium hydroxide (MDH) [63]. Both release water if heated; this action increases the overall endothermicity of the flame-retardant polymer and generates water vapour, which then dilutes the flame, thereby promoting flame extinction. However, both hydroxides must be used at high mass concentrations (typically >50 wt%) and then may promote stiffness and chalkiness if used in coatings. They have different sensitivities to heat, with aluminium hydroxide releasing water (≤34.6 wt% of initial mass) if heated >200 °C, so may be used only in low melting fusible polymers such as polyethylene and ethylene vinyl acetate. Magnesium hydroxide, which is more expensive, is stable up to 300 °C and so may be used in many higher-temperature processed polymers such as polypropylene, polyamides and fluorinated copolymers. Neither hydroxide may be used in thermoplastic polyesters because they can catalyse decomposition. If used in textile coatings, control of particle size is essential and, whereas the coarser grades produced by grinding may have mean diameters of ≈35 µm, the finer grades (in particular of ATH) are preferred. These are produced by precipitation and can have diameters <5 µm. The finest grades of ATH at ≈1 mm are preferred for coating fabrics whereas the coarser grades (3–12 mm) find application in polyethylene carpet-backing formulations [64]. To improve dispersion and rheology, surface-coated variants are commercially available.

Other well-established inorganic flame retardants such as zinc borate (e.g., Firebrake® ZB, Rio Tinto) while being used primarily in bulk polymeric applications, may be used as ATO synergist replacements in flexible PVC in waterproof coatings (e.g., tentage, awnings) and carpet backings. The presence of zinc borate also has a smoke-reducing effect, as do ATH and MDH if present in coating formulations. Other inorganic salts used as ATO-replacement synergists include zinc stannate (Flamtard S, William Blythe, UK) and zinc hydroxystannate (Flamtard H, William Blythe), both of which have the advantage of very low particle size (1–2 µm) as well as the ability to suppress smoke.

In conclusion, whereas most major manufacturers of flame retardants offer non-halogen coating formulations, they do not disclose which of the non-halogen methodologies detailed above are used. For example, ICL Industrial Products market their TexFRon 9020 and 9025 low melting coating formulations as being alternatives to DecaBDE and HBCD with better efficiency in terms of percentage bromine requirement. This suggests that bromine is still present and that it is a bromo-containing polymer because this company developed a range of such products and stated they were ‘ecotoxicologically superior'. These are typified by their portfolio of brominated polystyrene (FR803), brominated epoxy (FR 2400) and brominated benzyl acrylate (FR1025) products [65]. Of these, it is likely that poly(pentabromobenzyl acrylate) forms the basis of their latest TexFRon P and P+ coating and back-coating formulations (see **Section 4.5.2**) [66]. TexFRon P+ also contains a phosphorus-containing agent as well as the bromine-containing polymeric binder which enables less ATO be required in comparison with DecaBDE/HBCD-based formulations.

4.5.2 Flame Retardant Back-coatings

'Back-coating' describes a family of application methods that has grown in importance since the 1980s in which the flame-retardant formulation is applied in a bonding resin to the reverse surface of an otherwise flammable fabric (see **Figure 4.1**, process (iv), and **Figures 4.5** and **4.6**). During the last 30 years, back-coating has come to dominate the UK furnishing fabric market as a consequence of the UK furnishing regulations first of 1979 (amended in 1983 [67]) and then 1988 [14]. The success of back-coating has been due to its relative cheapness and because it can be applied to the reverse of any fabric structure comprising any fibre type(s) without affecting the aesthetics of the front face of these fabrics. Careful use of viscosity modifiers and general variables of back-coating applications ensures that 'grin-through' is minimised and low second-order transition resins (glass transition temperature (T_g) <10 °C) are recommended if fabric handle effects are to be minimised. Application methods include doctor blade or knife-coating methods [53] and the formulation is as a paste or foam. These processes and finishes are used on fabrics in which the aesthetics of the front face are of paramount importance, such as furnishing fabrics and drapes. **Figure 4.5a** and **Figure 4.5b** show (schematically) blade-in-air and blade-over-roll methods, respectively. **Figure 4.6** shows a schematic diagram of the entire back-coating process from application, oven curing and final fabric wind-up.

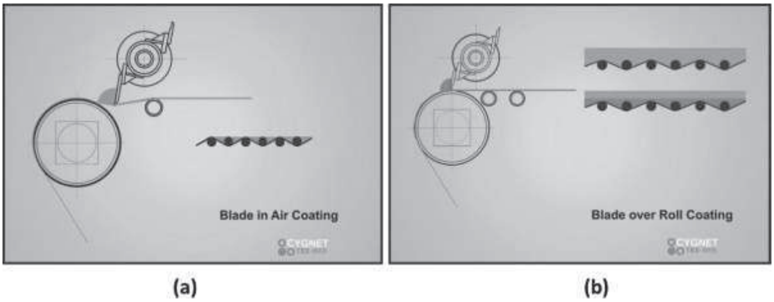

Figure 4.5 (a) Blade-air-air and (b) blade-over-roll methods (single or double layer coating) (schematic). Reproduced with permission from of Cygnet Tex-Web, UK

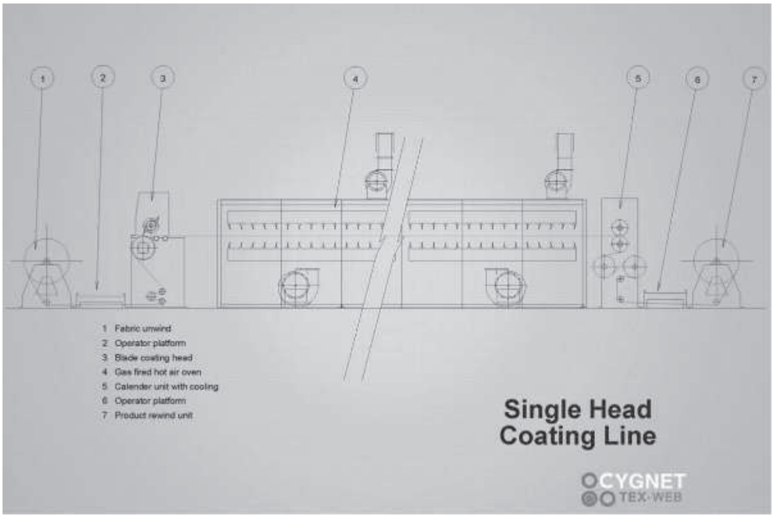

Figure 4.6 Typical complete back-coating line (schematic). Reproduced with permission from of Cygnet Tex-Web, UK

The underlying scientific principles of back-coating have not been studied in detail. In 1999, the author's research team attempted to analyse the important variables involved [68]. In that study, the effect of coating parameters of a typical DecaBDE/ATO formulation (see below) on the levels of penetration within a cellulosic upholstery fabric was investigated with the overall aim of improving the effectiveness of the antimony/bromine-free flame retardants present. Three variables were studied using a blade-over-air coating method: blade angle, blade height, and viscosity of the coat formulation. It was seen that low viscosity (as might be expected) allowed best penetration, as did a low blade height (which increases the force exerted on the coating and so helps to push it through the fabric). An optimum blade angle of 10° was observed, suggesting that, in any back-coating process, selection of blade variables is crucial if optimal coating and penetration are to be achieved.

The vapour-phase activity of the typical halogen-containing/ATO oxide synergised flame-retardant formulations discussed above [55] ensures their effectiveness. This is because their activity may transfer readily from the coating on the rear face of the fabric to the front face, where an igniting source such as a match or cigarette will impinge. Within the furnishing textile back-coatings market in the UK, the standard formulations based on ATO and brominated hydrocarbons (notably DecaDBE) dominate in spite of environmental concerns, although these are becoming increasingly active with the likelihood of it being withdrawn during 2016 (see below). A typical back-coating formulation is based on the recipe:

- DecaDBA or oxide: 33 wt%
- Antimony III oxide: 17 wt%
- Acrylic binding resin: 50 wt%

This recipe is applied to the back of the fabric at 20–30 wt% total solids add-on. With respect to the coating formulations discussed above, a mass ratio for ATO:DecaBDE of 1:2 relates to an elemental molar ratio for antimony:bromine of 1:3, and a bromine concentration of ≈5–10 wt% on fabric. Such a back-coating application equates with dry coating weights of 70–80 gm^{-2} for velour pile fabrics, 30–40

gm^{-2} for cotton woven fabrics, and 40–50 gm^{-2} for other flat woven furnishing fabrics in which the solids content of DecaBDE equates with 30–40 wt% of the dry coating weight, as shown above [69]. For all synthetic fibre-containing fabrics, back-coating levels are much greater because the char-forming character of the resin needs to offset the shrinking back and melting of the face fabrics which would otherwise reveal the underlying filling to the igniting source. Back-coating levels here may be ≈50–100 wt%.

When DecaBDE came under environmental scrutiny some years ago [3], HBCD was considered to be a viable alternative, and was used during the late 1990s and early 2000s. However, even though DecaBDE and HBCD were considered to have low toxicological risk in risk analyses carried out by the US National Academy of Sciences in 2000 [70], subsequent EU risk analyses [69, 71] while finding no significant risk for DecaBDE, did so with HBCD. This latter risk assessment [69] concluded that HBCD is persistent, bioaccumulative and toxic and, even though there is no risk to consumers by exposure to products containing HBCD or *via* the environment, there are possible risks to the workforce during processing. As a consequence, HBCD will be phased out from use in Europe by October 2015. During this same period and especially in the USA, DecaBDE has continued to be subjected to environmental pressures to the extent that the two US manufacturers ceased production by 31 December 2012 and the three major US suppliers have agreed to cease supply by 31 December 2013. In the EU, similar pressures have increased to the extent that on 19 December 2012 [72], DecaBDE was included on the European Chemicals Agency list of Substances of Very High Concern under Article 57 of the EU Reach regulation [73] as persistent, bioaccumulative and toxic (Article 57d:PBT) and very persistent and very bioaccumulative (Article 57 e:vPvB). Thus, it is under increasing pressure to be withdrawn from use in Europe and this will probably occur sometime after 2016. Consequently, several companies are marketing bromine-containing alternatives such as decabromodiphenyl ethane (or ethane 1,2-*bis*(pentabromophenyl), marketed as Great Lakes Emerald 1000, and by Albemarle as Saytex 8010. Even though it has a similarly high bromine content (82.3 wt%)

as DecaBDE, it is claimed to have no adverse toxicological and ecotoxicological effects. Similarly, DecaBDE alternatives are being marketed by ICL-IP under TexFRon 9000 as an immediate DecaBDE replacement in back-coating formulations as well as TexFRon 9020 and 9025 (see **Section 4.5.1**).

In general, coating methods (unlike those requiring impregnation (see **Figure 4.1**, processes (i–iii)) lead to little or no waste of application chemical formulation and hence effluent problems. However, there remain increasing pressures to replace antimony-bromine formulations by less environmentally questionable retardants based on phosphorus. In this respect, the use of halogen-containing resins such as PVC-vinyl acetate as well as PVC-ethylene-vinyl acetate copolymers and poly(pentabromobenzyl acrylate) [65, 66] may be used to decrease the amount of the less effective, alternative phosphorus-containing replacement retardants required, and hence maintain acceptable levels of coating applications.

Currently, even though several commercial halogen-free back-coating formulations are available, they tend to be fabric-specific and less effective than the antimony-bromine ones they replace. Of these 'halogen-free alternatives', most will probably contain APP. APP is not only effective on most cellulose, wool and even acrylic-containing fabrics, but also its solubility is less than the simple phosphates which would pass the UK regulatory 40 °C soak test before testing to BS 5852:Part 1:1979 [14]. However, the solubility of the simpler APP types is often not sufficient to withstand this durability requirement, and it depends on the degree of polymerisation of the linear $-[P(O).(ONH_4).O]_n-$ chains and the type of crystalline structure. **Table 4.7** lists a range of commercial currently and formerly available APP types and associated data on solubility, mean particle size and several commercial examples are listed in **Table 4.7**. In addition, APP has a phosphorus content of ≈32 wt%, and so add-ons of 5–15 wt% are required to achieve phosphorus levels of ≈1.5–4.5 wt%.

Of the commercial variants available not marketed under an APP umbrella, the Eco-flam series of products (Devan Chemicals, Belgium) were pioneers in this area. For example, Devan Chemicals recently claimed that its products Ecoflam® PU 222, PU254 and PU, if applied to upholstery, comply with European Norm Standard (EN) 597-1 cigarette and EN 597-2 match tests as well as achieving M1 of the French NF P 92504 test after water soaking [74]. Thor also have two non-halogen-based products, Aflammit® UCR and Aflammit® FMB, which are based on phosphorus and nitrogen compounds and, after pad-cure application, are claimed to yield 40 °C water soak durability and to pass BS 5852:Part 1:1979 furnishing regulatory requirements. Whereas the bromine-antimony formulations function on all fabric/fibre types, the non-halogen alternatives are fibre/fabric-specific, with Thor products, for example, being recommended only for fabrics containing high percentages of cellulosic fibres.

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5 Inherently Flame-resistant Fibres

A. Richard Horrocks

5.1 Introduction

Inherently flame-retardant fibres are those which have no need of any external finish or treatment to impart some desired level of flame retardancy. There are principally three types of such fibre:

- Fibres which are based on conventional or the more common man-made or synthetic fibre structures to which flame retardancy has been conferred during modification of the manufacturing process.

- Fibres that have a structure that is inherently flame retardant without additional treatment during processing.

- Inorganic and ceramic fibres.

This chapter will review examples of the fibres that are currently available commercially. Most were developed >20–50 years ago and have stood the test of time despite possible toxicological and commercial concerns that have affected their ability to maintain an acceptable fraction of the total market for such fibres in various applications having differing demands in terms of level of flame retardancy coupled with their associated physical and general textile fibre properties. Development of these fibres and many others which have not seen successful commercial development have been reviewed [1–6].

5.2 Inherently Flame-retardant Fibres based on Modified Versions of Conventional Synthetic and Regenerated Fibres

Table 5.1 summarises those major fibres falling into this group, which include synthetic and regenerated fibres.

Table 5.1 Inherently flame-retardant conventional fibres in common use

Fibre	**Structural components of flame retardant**	**Mode of introduction**
Regenerated: viscose	Organophosphorus and nitrogen/ sulfur-containing species e.g., Exolit® 5060 (2,2-oxybis(5,5-dimethyl-1,3,2-dioxaphosphorinane)2,2-disulfide), 10–15 wt%] in Lenzing FR® (Lenzing AG); 30 wt% polysilicic acid and complexes e.g., Visil AP (Sateri).	A
Inherent synthetic: Polyester	Organophosphorus species: Phosphinic acidic comonomer e.g., Trevira CS®, (Trevira GmbH); phosphorus-containing additive, Avora CS (KoSa); sulphonyl *bis* phenol phenylphosphinate oligomer, Heim/Toyobo GH (Toyobo, Japan); phosphorus-containing additive, Fidion FR® (Montefibre), Brilén FR (Brilén, Spain).	C/A
Polyamide	Unknown modification, Nexylon FR (polyamide 6.6 (PA6.6) (EMS-GRILTECH).	-
Acrylic (as modacrylic)	Halogenated comonomer (35–50% *w/w*) plus antimony compounds e.g., Velicren FR® (Montefibre); Kanecaron® (Kaneka Corp.); Sevel®FRSC (Fushun Huifu Fire Resistant Fibre Co., Japan).	C

Polypropylene (PP)	Halo-organic compounds usually as brominated derivatives, e.g., *tris*(tribromneopentyl) phosphate (FR-370, ICL); hindered amine stabiliser, e.g., Ciba Flamstab® NOR 116, plus bromo-organic species.	A
Polyhaloalkenes	Poly(vinyl chloride) or chlorofibre, e.g., Clevyl (Rhovyl SA); Rhovyl (Rhovyl SA) Polyvinylidene chloride, e.g., Saran™ (Asahi Kasei).	H C
A: Additive introduced during fibre production C: Homopolymer H: Copolymeric modifications		

Conventional synthetic fibres may be rendered inherently flame retardant during production by incorporation of a flame-retardant additive in the polymer melt or solution before extrusion, or by copolymeric modification before, during or immediately after processing into filaments or staple fibres. However, problems of compatibility, especially at the high temperatures used to extrude melt-extruded fibres such as polyamide (PA), polyester and polypropylene (PP), and in reactive polymer solutions such as viscose dope and acrylic solutions, have ensured that only a few fibres are available commercially. A major problem in developing inherently flame-retardant fibres based on the chemistries of conventional fibres is that modification, if present at >10wt% (whether as additive or comonomer) can severely reduce tensile properties and the other desirable textile properties of dyeability, lustre and appearance and handle. **Table 5.2** [2, 7–9] lists the flame-retardant fibre properties of the limiting oxygen index (LOI) and selected tensile properties of selected flame-retardant fibres listed in **Table 5.1** compared with their typical non-flame-retardant analogues. Thus, the increases in flame-retardant properties measured as increases in the LOI are not matched by significant changes in tensile properties. That is, the mechanical properties of the fibres will, in general, be comparable with the respective unmodified analogues. Other properties, such as dyeability, are also little affected by the respective flame-retardant modifications present.

Table 5.2 Properties of inherently flame-retardant conventional (medium tenacity) staple fibres [2, 7–9]

Fibre	LOI, %	Tenacity, cN/dtex	Breaking strain, %
Viscose	18–19	2.1–2.5	15–20
Lenzing FR*	28	1.6–2.4	14–22
Visil AP	28–30	1.4–1.6	20–25
Polyester	20	3.5–4.5	30–50
Trevira CS	28–30	N/A	–
Toyobo GH/Heim	30	N/A	–
Nylon 6.6	21–22	3.5–4.0	30–40
Nylon 6.6 FR (Nexylon FR)	28	4.5–5.0	>50
Acrylic	18	2.0–3.6	20–55
Modacrylic (generic)	29–32	1.8–2.5	20–40
PP	18	3.0–7.0	15.25
FR PP**	Est. >23	Est. ≈3.0	N/A
Polyethylene	18–19	2–3	≈40
Poly(vinyl chloride)	37	1.6–2.0	≈40
Poly(vinylidene chloride)	60	2.0	15–30

*Taken from Lenzing web-site: *http://www.lenzing.com/en/fibers/lenzing-fr/specifications.html*

**No commercial branded form currently is produced but use of additive systems should give the estimated values.

5.2.1 Flame-retardant Regenerated Cellulose Fibres

At the present time, only two significant contenders, both based on the traditional viscose process, are available commercially: Lenzing FR® from Lenzing AG comprises an organophosphorus and nitrogen/sulfur-containing species; Clariant's Exolit® 5060 (2,2-oxybis(5,5-dimethyl-1,3,2-dioxaphosphorinane)2,2-disulfide) at 10–15 wt% loading and Visil AP (Sateri) contains ≈ 30 wt% polysilicic acid. The former was developed by Sandoz and Lenzing >30 years ago [10] and remains today the most significant flame-retardant viscose variant although now manufactured by Clariant. A successful flame-retardant additive for viscose fibre must be very finely divided if a solid (e.g., Exolit® 5060) and not show any tendency to aggregate in the viscose dope and so enable extrusion through the very fine nozzles used in viscose spinnerets. Typically, dispersible solid additives such as Exolit® 5060 should have particle diameters <2 microns. No such problem lies in the production of the Visil fibre dope because polysilicic acid is dissolved in the dope as the sodium salt. The Visil fibre was produced originally by Kemira Oy (Finland) [11] and later by Sateri. However, when that company ceased to exist, production was transferred back to Kemira Oy [12].

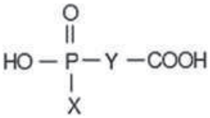
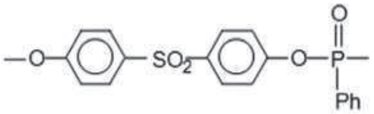
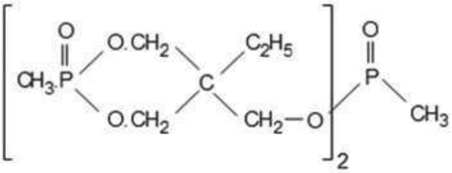
The Exolit® 5060 additive confers condensed phase, char-promoting activity in a similar manner seen for the phosphorus- and nitrogen-containing finishes applied to cotton described in **Chapter 4**. The polysilicic acid present in Visil viscose fibre is particularly interesting in that not only is it largely phosphorus-free but, upon heating, a carbonaceous and siliceous char is formed. The aluminium salt after-treatment (probably aluminium phosphate, hence the 'AP' in Visil AP) raises the LOI from 26–27 to ≈30%, decreases sensitivity to alkalis in the pH range 7–9, and increases wash durability to acceptable commercial levels. The presence of silica in the residue ensures that thermally exposed fabrics revert to a ceramic char, thus affording high levels of protection to temperatures (≤1000 °C). Both flame-retardant viscose types have acceptable tensile properties (see **Table 5.2**) as well as general textile properties.

Weil and Levchik [4] cite similar silicic acid-containing viscose fibres such as Daiwado's Corona® and others made in China. The entire area of flame-retardant regenerated cellulose fibres has been reviewed extensively recently by Burrow [12].

5.2.2 Polyester

Several have been developed to semi-commercial scales, but one group of flame-retardant poly(ethylene terephthalate) fibres that continues to be successful is the well-established Trevira CS® range of products originally developed by Hoechst [13], which contains the phosphinic acid comonomer shown in **Table 5.3**. Phenyl-P substituted variants of this structure are believed to be produced in Korea and China [5].

Table 5.3 Flame-retardant modifications for polyester fibres

Generic type	Nature	Structure
Phosphinic acid derivative (Trevira CS)	Comonomer	 $HO-\overset{\overset{O}{\parallel}}{\underset{\underset{X}{\vert}}{P}}-Y-COOH$ X = H or alkyl Y = alkylene
Bisphenol-S oligomer (Toyobo GH)	Additive	
Cyclic phosphonate (Amgard/ Antiblaze 1045)	Dimeric additive	

Adapted from A.R. Horrocks, H. Eichhorn, H. Schwaenke, N. Saville and C. Thomas in *High Performance Fibres*, Ed., J.W.S. Hearle, Cambridge, Woodhead Publishing, UK, 2001, p.289 [23]

Other flame-retardant systems, both based on phosphorus-containing additives, are also known. Only Toyobo GH (and variants) introduced in the 1970s have been available commercially, but their availability today is not known. The additive is sulfonyl *bis* phenol phenylphosphinate oligomer and is present at ≈7–9 wt% [14]. The Rhodia Antiblaze® 1045 additive is the former Mobil Chemical Antiblaze® 19 compound which is available in dimeric form as a melt additive and in monomeric form as a polyester textile finish (Antiblaze® CU) as described in **Chapter 4**. All three of these flame-retardant polyester variants do not promote char but function mainly by reducing the flaming propensity of molten drips normally associated with unmodified polyester. As yet, no char-promoting flame retardants exist for any of the conventional synthetic fibres. This fact constitutes the real challenge for the next generation of acceptable inherently flame-retardant synthetic fibres.

5.2.3 Polyamide

Inspection of **Table 5.1** shows the presence of only one flame retardant, PA6.6 (Nexylon FR, EMS-GRILTECH) of unknown composition (although some properties are given in **Table 5.2**) and which was announced commercially in September 2012 [9]. This paucity of flame-retardant PAs reflects their high melt reactivities and hence poor potential flame-retardant additive compatibilities. This problem has been discussed further by Weil and Levchik [5]. Flame retardants that are acceptable commercially for bulk and engineering aliphatic nylons such as PA6 and PA6.6 include the poly(bromostyrene)/antimony and melamine cyanurate-based systems which are unsuitable for fibres because of the high concentrations (>10 wt%) required and the associated reduction in fibre tensile properties [5]. However, the recent interest in metal salts (notably aluminium) dialkyl phosphinates by Clariant suggest that acceptable flame-retardant fibres might be possible because they manufacture a special low particle diameter (D_{50} ≈2–3 µm) fibre grade: Exolit OP930/935. This phosphinate may be used alone or can be combined with melamine polyphosphate although, in bulk, total levels of polymers of 15 wt% are required for acceptable levels of flame retardancy. It is not known whether commercially successful PA6 and PA6.6 fibres based on this agent are available.

5.2.4 Acrylics and Modacrylics

Flame-retardant acrylics are usually so highly modified in terms of comonomer content that they are termed 'modacrylics'. This latter group has been available commercially for ≈50 years [2] but, at present, few manufacturers continue to produce them. The principal preferred comonomer is vinylidene choride and, to enhance the flame-retardant activity of the chlorine present, antimony III oxide (ATO) is included (although this may reduce the lustre of the fibres and resulting fabrics). Furthermore, the presence of chlorine and ATO is causing questions regarding environmental sustainability to be asked. The lack of real success of modacrylics in the furnishing sector is largely because of the superiority of back-coatings (see **Chapter 4**) applied to normal acrylic fabrics which create high levels of flame retardancy more cost-effectively and without affecting fabric aesthetics. Currently there are no acrylic fibres containing simple additive systems.

5.2.5 Polypropylene

PP fibre poses a particular challenge because of its low melting point (≈165 °C), its tendency to undergo random scission to highly flammable smaller hydrocarbons, and complete absence of any tendency to form char [15]. However, because of the relative ease of producing PP fibres, manufacturers are more likely to produce their own flame-retardant versions without use of specific brands and based on additive formulations which are traditionally based on bromo-organic species in the presence of a synergist. Examples of the former include *tris*(tribromoneopentyl) phosphate (FR-370, ICL) and pentabromoacrylate (FR-1025, ICL), both of which may be used without the need for an ATO synergist. A review by Weil and Levchik [4] cites alternative synergists to include free-radical generators such as 2,3-dimethyl-2,3-diphenylbutane (Perkadox® 30, Akzo) or the hindered amine radical stabiliser Flamstab® NOR 116, which is an *N*-alkoxy-2,2,6,6-tetramethyl-4-substituted morpholine, as reviewed by Zhang and Horrocks [15]. This latter agent enables lower-than-expected levels of bromo-organic species to be used [16].

5.2.6 Blends of Conventional Inherently Flame-retardant Fibres

Often an inherently flame-retardant fibre is blended with a flammable or less flame-retardant fibre to create a yarn and hence a textile having intermediate flammability results. As Tesoro and Rivlin showed >40 years ago [17] and as reviewed by ourselves >25 years ago [8], the final blend or composite (if the yarn contains doubled component yarns of each fibre type) rarely has a final flammability that is linearly dependent upon blend composition. For example, the blends flame-retardant viscose/poly(vinyl chloride) (PVC) and PVC/polyester gave LOI values much less than expected from a weighted mean of their individual component values. Also, blends of aromatic high-performance fibres such as polyaramid (see **Section 5.3**) for example, aramid/cotton, aramid/polyester and aramid/wool show similar behaviour. For aramid/polyester and aramid/wool and flame-retardant viscose/PVC, the lowest blend LOI value is lower than that of the flammable component alone usually when this is present in the 25–50% mass range. This phenomenon is a result of the 'scaffolding effect' first seen for polyester/cotton blends [8, 18]. Positive deviations from the calculated linear trends have been reported for aramid/modacrylic, flame-retardant viscose/aramid, flame-retardant viscose/wool and flame-retardant viscose/cotton blends [17]. Carroll-Porczynski [19] and Ishibashi and co-workers [20] carried out similar investigations on a large series of 50/50 blends of flame-retardant, chlorine-containing fibres such as PVC, modacrylic and polychal (copolymer of PVC and poly(vinyl alcohol) blended with most conventional natural and man-made fibres to show that the expected transfer of flame-retardant activity from the chlorine presence in the former to the latter fibres is not always predictable. Thus, blends containing PVC or modacrylic showed little (if any) expected transfer of activity until the chlorofibre content was >50%, with flame-retardant viscose/modacylic blends showing modest positive effects in a 50/50 composition. More recently, we studied the more normal negative 'S-shaped' trend as shown in **Figure 5.1** for blends of modacrylic/Visil viscose when char length determined by BS 5438:1989, Test 2 (face ignition) was plotted against blend composition [21].

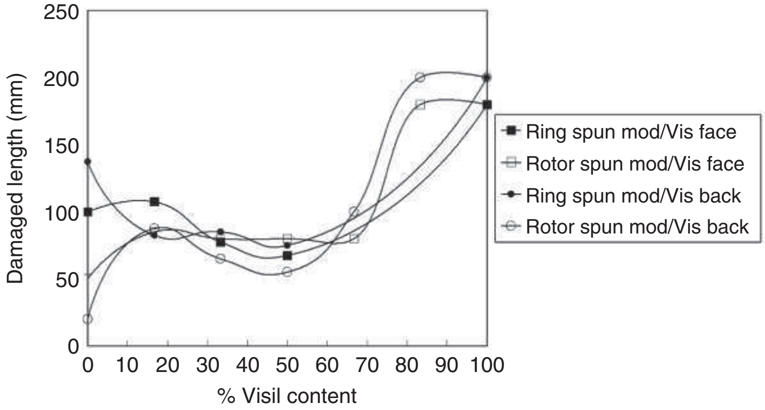


Figure 5.1 Effect of blend composition on the maximum damaged or char length of knitted modacrylic/Visil viscose samples tested on back and face (BS 5438:1989, Test 2, face ignition) [21]; Reproduced with permission from S.J. Garvey, S.C. Anand, T. Rowe and A.R. Horrocks in *Fire Retardancy of Polymers – The Use of Intumescence*, Eds., M.J. Le Bras, G. Camino, S. Bourbigot and R. Delobel, Royal Society of Chemistry, London, UK, 1998, p.376. ©1998, Royal Society of Chemistry [21]

This trend actually shows a positive flame-retarding effect because char lengths are minimal in the 50/50 blend region which corroborates the work cited above [8, 17–20] in that the inherently flame-retardant modacrylic component with expected vapour-phase activity is transferred to the greater char-forming Visil component only if present in the 30–70% range with a minimum char length of

≈50 mm. **Figure 5.1** also shows results after ignition application to the face and back of single jersey fabrics and indicates that, whereas they are little influenced by the mode of ignition, there is an effect of yarn structure. At lowest Visil contents, the rotor-spun blends show lower char lengths and hence superior flame retardance; the converse is seen at the highest Visil blends. This is also certainly the case in blends of cotton and PVC. The Protex M (Waxman Fibres and Kanecaron) range of fabrics feature blends of the modacrylic Kanecaron Protex fibre with cotton in almost equivalent fractions (55% modacylic/45% cotton). The fabrics are suitable for furnishings, bedding and protective clothing (including welding and similar hazard protection). Similar inherently flame-retardant/wool blends also find commercial acceptance in several similar applications.

Blends may also be designed to replace part of a more expensive, high-performance flame-retardant fibre in a fabric. This feature is exemplified by several flame-retardant viscose/aramid blends developed over the years. Polyaramid and other high-performance fibres are discussed in **Section 5.3** below, but 50/50 polyaramid/Lenzing FR® (Lenzing AG) [22] blends are used for protective clothing items. Furthermore, blending conventional flame-retardant fibres such as Lenzing FR® with high-tenacity polyaramids increases wear and tensile characteristics. Other blend examples exist and will be discussed in the next section.

5.3 High Heat- and Flame-resistant Fibres and Textiles based on Aromatic and Crosslinked Structures

In the UK, Europe and USA, most (≈80% by weight) flame- and heat-resistant fibres and textiles are chemically after-treated. Inherently flame- and heat-resistant fibres and textiles, including the inherently flame-retardant viscose and synthetic fibres mentioned above, comprise the remaining percentage. **Table 5.4** lists the main members of the group of high heat- and flame-resistant fibres available with transition temperatures, maximum service-use temperatures and LOI values [23, 24].

Table 5.4 Maximum service lifetimes for heat-resistant fibres in thermally protective textiles [23, 24]

Fibre genus	Second order temperature, °C	Melting temperature, °C	Onset of decomposition, °C	Maximum, continuous use temperature, °C	LOI, vol %
Melamine - formaldehyde	N/A	N/A	370	190	32
Novoloid	N/A	N/A	>150	150/air; 250/inert	30–34
m-Aramid	275	375–430 (decomp)	425	150–200	28–31
p-Aramid	340	560 (decomp)	>590	180–300	29–31
Copolymeric *p*-aramid	–	–	500	200–250	25
Arimid (P84)	315	–	450	260	36-38
Aramid-arimid	<315	–	380	NA	32
Semicarbon	N/A	N/A	N/A	≈200/air	55
PBI	>400	N/A	450/air; 1,000/inert	≈300 (est)	>41
PBO	–	–	650; >700/inert	200–250 (est)	68

decomp: with decomposition
est: value estimated value
env: depends on chemical inertness of the environment

It is evident that in the case of those having highly aromatic structures which have associated high second-order transition temperatures, glass transition temperature (T_g) of ≥275 °C and ill-defined melting temperatures even higher, these fibres may be used at service temperatures of ≥150 °C because they show neither significant thermoplastic properties nor tendencies to thermally degrade at ≈350 °C. Consequently, and unlike the inherently flame-retardant fibres based on conventional fibre chemistries described in the previous section, these fibres may be used in textile structures having heat and fire resistance. Included in this table are the melamine-formaldehyde fibres which, although not aromatic in structure, are highly crosslinked and extremely char-forming in character. They also may resist temperatures of ≥150 °C during service life because they start to crosslink and then form char at temperatures above this level. All fibres in **Table 5.4** have high char-forming potentials which are responsible for their low flammabilities and, as established by van Krevelen [25], their high LOI values (usually ≥30%).

Bourbigot and co-workers have produced one of the few recent comparisons of the fire performance of several of these high temperature- and fire-resistant polymer-based fibres based on cone calorimetric data [26]. **Figure 5.2** shows a comparison of the rate of heat release (RHR) *versus* time curves after exposure to fabric samples at 75 kW/m^2 flux. The peak values in each curve are a measure of the maximum energy released during a simulated combustion.

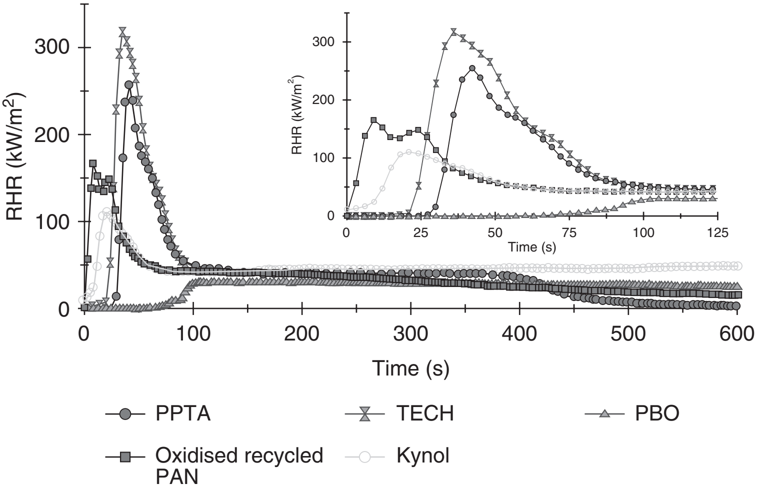


Figure 5.2 Rate of heat release curves (external heat flux = 75 kW/m²) of selected knitted high-performance fibres in spun yarn. (PPTA: poly(*p*-phenylene terephthalamide) (Kevlar), TECH: Technora, PBO: poly(benzoxazole) (Zylon), oxidised recycled polyacrylonitrile (PAN) is a semicarbon and Kynol is a novoloid. Reproduced with permission from S. Bourbigot and X. Flambard, *Fire and Materials*, 2002, **26**, 4-5, 155. ©2002, John Wiley & Sons [26]

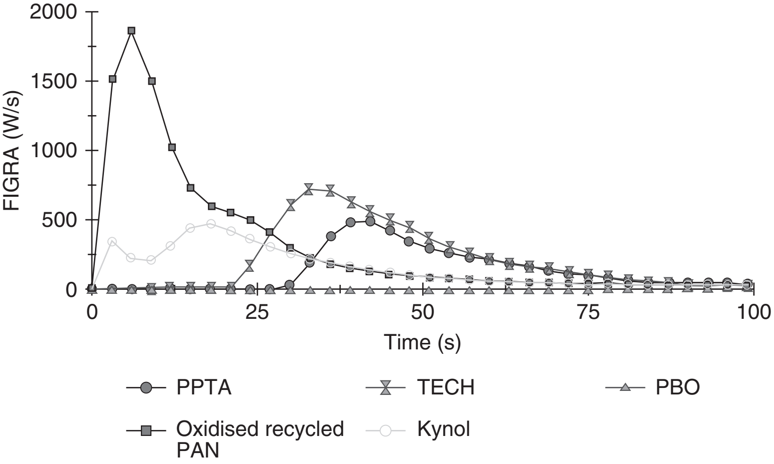


Figure 5.3 Fire growth index curves (external heat flux = 75 kW/m²) of selected knitted high-performance fibres in spun yarn. Key as in **Figure 5.2**. Reproduced with permission from S. Bourbigot and X. Flambard, *Fire and Materials*, 2002, **26**, 4-5, 155. ©2002, John Wiley & Sons [26]

If each of the datasets in **Figure 5.2** is expressed as RHR per second, then the parameter fire growth index (FIGRA) results. FIGRA may be plotted against time to give a better measure of relative fire-propagating behaviour. **Figure 5.3** presents these results, from which it is seen that the increasing fire growth property is in the order:

PBO < Kynol ≈ PPTA < Technora < Oxidised acrylic

The decreasing order in terms of the LOI as a fire measure is:

PBO > Oxidised acrylic > PPTA ≈ Kynol > Technora

Both these measures used to order these fibre types indicate that PBO is the least flammable and hence most protective fibre whereas the respective orders for the other fibres differ. However, given that cone calorimetry is recognised to be a reasonable simulation of a fire, then the FIGRA order is probably closer to defining the relative fire-protective behaviour of these fibres.

Each of these major fibre groups has been described elsewhere [23, 24] so their major features only are presented below. The main groupings of these inherently heat- and fire-resistant fibres may be divided into thermosets, aramids, arimids, polybenzazoles, semicarbons and inorganics. Not only are the generic chemistries similar within each grouping, but their properties and potential application suitabilities are similar.

5.3.1 Thermoset Polymeric Fibres

Typified by the melamine-formaldehyde fibre Basofil® (BASF) and the phenol-formaldehyde (or novoloid) fibre Kynol® (Kynol GmbH), thermoset polymeric fibres have a common feature that, if heated, they continue to polymerise, crosslink and thermally degrade to coherent char replicas. Derived chars have especially high flame and heat resistance as a consequence of their high carbon contents, although their relatively low strengths prevent them being processed readily into yarns, so they are more often incorporated into nonwoven fabric structures. In addition, their inherent colour (pink for Basofil® and gold for Kynol®) ensures that they are usually employed as a barrier fabric and not in face fabrics (although the melamine-formaldehyde structure in Basofil® allows the fibre to be dyed with small molecular disperse dyes). Respective thermal properties are listed in **Table 5.4**, which indicates very similar high levels of heat and flame resistance. Typical end-use applications of Basofil ®and Kynol® in thermal protection include fire-blocking and heat-insulating barriers as well as heat- and flame-protective apparel. Typically, fibres may be blended with *meta*- and *para*-aramid fibres to improve tensile properties, including strength and abrasion resistance in nonwoven felts and fleeces for fire-blocking aircraft seat fabrics and fire-fighter clothing. Such fabrics can be aluminised to improve heat reflection and hence fire performance.

5.3.2 Aramid and Aramid Family

The aramid family is perhaps the most well-known and exploited of all the inherently heat- and flame-resistant fibres developed since 1960. All members of this group are typified by having thermal resistances of >300 °C for short-term exposures and high levels of inherent flame resistance (see **Table 5.4**).

The most commonly used thermally resistant aramids are based on a *meta*-chain structure as typified by the original Nomex® (Du Pont) fibre and more recent commercially available fibres, e.g., Conex® (Teijin), Apyeil® (Unitika) and Fenilon® (Russia), in addition to modifications having modified tensile properties (e.g., Inconex, Teijin) and antistatic properties (Apyeil-a, Unitika). Nowadays, these fibres have improved dyeing properties and are available in full colour ranges. They have the advantage of acceptable 'nylon-like' tensile and physical properties, minimal thermoplastic characteristics with second-order transition temperatures, T_g, of ≈275 °C, and an ill-defined melting point accompanied by thermal degradation starting at 375 °C (see **Table 5.4**). They are ideal for use in protective clothing. Improvements in thermal performance in terms of increased char strength have been achieved by blending with small amounts of *para*-aramid fibres (e.g., Nomex III contains 5% Kevlar) and so are more suitable for applications in which direct exposure to heat is possible, e.g., firefighter uniforms, coveralls, jackets, trousers, gloves, flight suits or tank-crew coveralls. Other variants include antistatic and moisture-management properties (Nomex Comfort) and one specifically designed for firefighter clothing (Nomex Outershell).

The *para*-aramids are typified by Kevlar® (DuPont) and Twaron® (Teijin) and are based on poly(*para*-phenylene terephthalamide) or PPTA. While having enhanced tensile strengths and moduli as a consequence of the extreme symmetry of their polymer chains (and hence order or crystallinity), they also have improved thermal performance with a second-order transition temperature of ≈340 °C and decompose at >590 °C (see **Table 5.4**). However, thermal degradation is similar to that occurring in the *meta*-aramids, so the LOI values are also similar (30–31%). Their higher cost, inferior textile-processing properties and higher modulus ensure that use in applications such as protective textiles are limited to 100% contents only if performance demands are exceptional. Hence, more often than not they are used as minor blend components (e.g., 5% in Nomex III®).

A copolymeric derivative of the *para*-aramid fibres was introduced by Teijin in 1985 under the tradename Technora®. This fibre is based on the 1:1 copoly(terephthalamide) of 3,4'-diaminodiphenyl ether and *para*-phenylenediamine [23] and is claimed to have a much higher chemical resistance than PPTA as well as increased abrasion and steam resistance, which are useful properties in many protective applications. Technora® has a decomposition temperature of ≈500 °C and its other properties are comparable with PPTA, although its LOI value is slightly lower (25%).

Of several reported aramid fibres, only P84® introduced by Lenzing AG during the mid-1980s and now produced by Inspec Fibres (USA) has been exploited commercially. As **Table 5.4** indicates, these fibres have superior thermal properties to aramid, and so find use in applications such as protective outerwear, underwear and gloves, either as 100% or blended with lower-cost fibres such as flame-retardant viscose. For instance, a 50/50 P84/Lenzing FR® (Lenzing AG) blend is available for knitted underwear with high moisture absorbency. Spun-dyeing of P84 fibres enables their natural gold colour to be replaced by those often demanded by customers, who may require more appropriate and bright safety colours.

The final member of this grouping is the poly(aramid-arimid) fibre, Kermel®, which was produced initially by Rhone-Poulenc of France in 1971 and is now produced by Rhodia Performance Fibres. Its overall properties are very similar to those of the *meta*-aramids. In 1993, a 'third generation' Kermel was announced claiming to have superior colouration properties. Typical of this group is its poor ultraviolet stability, and so it must be protected from intense radiation sources. It competes in protective-clothing markets where again it is used as 100% or as blends with other fibres, including flame-retardant viscose and wool. Composite yarns with high-modulus aromatic fibres such as the poly(*para*-aramids) have yielded the modification Kermel HTA®, a yarn with a *para*-aramid core (35%) and a Kermel fibre wrapping (65%) to give improved abrasion resistance.

5.3.3 Polybenzazole Group: Polybenzimidazole and Polybenzoxazole Fibres

The polybenzazole group are fibre-formimg polymers ('ladder polymers') and are essentially wholly aromatic polymer chains. The two common examples available commercially are polybenzimidazole (PBI®) (Celanese) with the full chemical name poly(2,2'-(*meta*-phenylene)-5,5'-bibenzimidazole) and polybenzoxazole, Zylon® (Toyobo) with the full chemical name poly(*para*-phenylene benzobisoxazole) (PBO). Their similarity in polymer chain structures and high degree of chain rigidities gives both of these fibres superior thermal properties, as shown in **Table 5.4**, with thermal degradation temperatures (>400 °C) and superior LOI values (>40%).

PBI was introduced to commercial markets only during the last 20 years even though it was developed during the early 1960s. The current PBI fibre is a sulfonated version of the polymer described above, and this feature improves shrinkage resistance at high temperature. Like many highly aromatic polymers it has an inherent colour – bronze – and cannot be dyed. The fibre is more often than not used as a blend. One well-known blend is PBI Gold®, in which a yarn is spun with PBI and Kevlar in a 40/60 blend. This gives rise to gold-coloured fabrics with fire-protective properties claimed to be superior even to those made from Nomex III®. This blend is now well-established in firefighter clothing in the USA and UK for outer-shells as well as underwear, hoods, socks and gloves. Other uses include industrial workwear, aluminised proximity clothing, military protective clothing and fire barrier/blocker applications and, because PBI is several times as expensive as *meta*-aramids, this superior performance comes at a price.

Zylon® or PBO is a more recently developed fibre than PBI®. It has outstanding tensile properties as well as thermal and fire properties superior to any of the polymer-based fibres mentioned in this chapter (see **Table 5.4**). There are at least two variants of fibres, Zylon-AS and Zylon-HM, of which the latter has the higher modulus. Both have the same thermal and burning parameter values. Principal examples of thermally protective textiles include heat-protective clothing and aircraft fragment/heat barriers where its price, similar to that of PBI, restricts its use to applications where strength, modulus and fire resistance are at a premium.

5.3.4 Semi-carbon

The semi-carbon fibres include any in which the structure is essentially carbon while retaining acceptable textile properties, unlike ‘true’ carbon fibres [27]. Within the group, the oxidised acrylics represent the sole commercial group and are produced after controlled, high-temperature oxidation of acrylic fibres during the first stages of production of carbon fibres. Since the early 1980s, several commercial versions were announced, including Celiox (Celanese), Grafil O (Courtaulds), Pyron (Stackpole), Sigrafil O (Sigri Elektrographit, now SGL) and Panox (SGL UK Ltd., formerly R K Textiles), many of which are now obsolete. Current examples include Panox® (SGL Carbon Group), Pyromex® (Toho Rayon) and Lastan® (Asahi). Their low tenacity creates the problem of ease of processability for these weak fibres, although they can be spun into yarns by the woollen system. Thus, they are produced as a continuous tow that is stretch-broken by conventional means for eventual conversion into coarse woollen-type yarns. The LOI is typically ≈55% and so fabrics are extremely thermally resistant, giving off negligible smoke and toxic gases if subjected to the even the most intense of flames. Unfortunately, the fibres are black and so are rarely used alone except in military and police coverall clothing, where the colour is a bonus. Therefore, oxidised acrylic fibres are usually blended with other fibres, typically wool and aramid, to dilute the colour and introduce other desirable textile properties. Because of their extreme fire resistance and lower cost than PBI and PBO, they find applications as blends in anti-riot suits, tank suits, flame-retardant underwear, fire blockers for aircraft seats and heat-resistant felts (insulation), hoods and gloves. If aluminised, they are very effective in fire entry/fire proximity suits.

5.3.5 Blends of High-performance Organic Fibres

Blends of high-performance organic fibres have been exploited commercially for several years, with aramid-flame-retardant viscose being perhaps one of the first attempts to reduce the cost of the final fabric while maintaining a high level of fire protection. As also mentioned in the foregoing sections, blends of *meta*-aramids with *para*-aramid or PPTA (e.g., Nomex III®, Du Pont; Kermel HTA®, Rhodia) and PBI and *para*-aramid (PBI Gold®, Celanese) have been developed to give a balance between the fire properties of both, with the higher modulus and strength of the *para*-aramid. Very few (if any) blends have been produced to generate synergies of fire resistance and other properties while, perhaps, improving other desirable features (including cost). Bourbigot and co-workers [28] reported recently on several, possibly synergistic, blends made by mixing yarn-by-yarn of wool with PPTA to give improved flame retardancy and generally improved thermal stability of the whole fabric. The suggested mechanism of action was that the molten char of wool coats adjacent *para*-aramid fibres, hindering the diffusion of oxygen to them and so negating their sensitivity to oxygen from the air and consequent thermal oxidative degradation. Subsequent research [29] has indicated that intimate blends of wool/PPTA show synergy if only ≥30% PPTA is present as opposed to ≥70% in the previously blended yarn results. Furthermore, synergy was noted in wool/Technora® blends, which can show reduced peaks of heat release rates with respect to 100% Technora®. Some wool/PBO blends show similar encouraging results, suggesting that enhanced fire performance at reduced cost and improved aesthetics using these interesting blends is feasible commercially.

5.4 Inorganic and Ceramic Fibres

Inorganic and ceramic fibres do not tend to burn and so may be used in applications in which high temperature and chemical reactivity of the environment combine to determine respective durabilities. These fibres include the various forms of glass, silica and alumina available, although more exotic ones like stainless steel, boron nitride and silicone carbide are available for specialist end-uses. Such extreme thermal protection, as shown in **Table 5.5** [30], is a desirable feature in applications such as furnace linings or hot component insulation in car exhaust catalysts or around combustion chambers in jet engines, where working temperatures and occasional flash temperatures are >500 °C and even 1,000 °C in extreme circumstances. However, even though fire resistance is an intrinsic feature of these inorganic fibres and textiles, their poor aesthetics limit their use to these extreme technical applications, although glass or ceramic-cored, organic fibre-wrapped yarns may be used to improve this feature.

Table 5.5 Maximum service lifetimes for inorganic heat-resistant fibres [30]

Fibre genus	Second order temperature, °C	Melting temperature, °C	Onset of decomposition, °C	Maximum, continuous use temperature, °C	LOI, vol %
Glass	650–970	NA	850	>300	N/A
Silica-based (e.g., Quartzel®)	–	>1,700	–	1,200	N/A
Alumina-based (e.g., Saffil®	–	>2,000	N/A	1,600	N/A
Alumina-silica-based (e.g., Nextel®)	–	>1,800	N/A	1,260–1,370	N/A
Silicone carbide (e.g., Nicalon, Nippon Carbon)		2,650–2,950	N/Aww	<1,800	N/A
Basalt (e.g., Basaltex)	–	1,300–1,700	N/A	650–850	N/A

The most well-established are the family of glass fibres, which has been reviewed exhaustively recently [31] and which continues to service many protective needs in which heat and fire resistance are essential. The prime use has usually focussed on their reinforcing quality. Hence, the fibres, because of inherent brittleness and poor general characteristics of the textile, are used as reinforcing elements in flexible-textile and rigid-composite structures. Where glass fibre assemblies are used in non-reinforcing applications, they are usually contained to prevent fibre damage and loss of product coherence. Their use as filter media for high-temperature gas and liquid filtration, as battery separators, and as fire and acoustic insulation in aircraft and other transport systems are examples. To respond to these different application needs, a wide range of glass compositions is available to suit many textile applications, and fibres made from various compositions have softening points in the range 650–970 °C. If heated >850 °C, devitrification and partial formation of polycrystalline material occurs because the former glass fibres become more similar in character to ceramic materials. This devitrified form melts at 1,225–1,360 °C, which is high enough to contain most fires for several hours. Recent examples of their use in high-performance applications include flexible roofings for sports and similar constructions. The recently developed and installed roof of the Olympic Stadium in Berlin with a surface area of 42,000 m^2 is a recent example in which the upper roof is made up of a highly tear-resistant fibreglass fabric of coated with polytetrafluoroethylene. This gives it a lifespan of ≥30 years, excellent fire resistance, and a self-cleaning surface [32].

Ceramic fibres have even poorer textile properties, are often more expensive, and are mostly used as refractory fibres as insulating and fire barrier materials for applications requiring resistance to temperatures of ≥1,000 °C for prolonged periods. They tend to have polycrystalline structures, hence their exceptional high-temperature characteristics. These often very specialist fibres, reviewed recently [30, 33], are not often produced in appropriate fibrous dimensions for normal textile processing, and are more usually available as nonwoven or wet-laid webs. This group may be classified into four major groups: alumina-based, silica-based, alumina-silica and silicone carbide fibres.

Alumina-based fibres reflect those of monocrystalline α-alumina fibres which, while resisting temperatures ≤1,400 °C in oxidising atmospheres with little or no creep <1,600 °C, cannot be produced as fine, staple or continuous filaments. However, polycrystalline fibres such as Saffil® (Saffil Ltd., UK) are available as a lofty, nonwoven, wet-laid web or 'blanket' with a density of ≈100 kg/m^2 and may be used in refractory and fire-barrier applications at ≤1,600 °C (see **Table 5.5**).

Silica-based fibres such as Quartzel® (Saint-Gobain, France), while having slightly inferior fire and heat performance, are available as continuous filament yarns, filament-based nonwovens and wet-laid papers. Thus, they may be knitted and woven to yield fabrics with applications in furnace insulation, combustion-chamber insulation in aircraft, ablative composites for military and other markets, and hot corrosive gas and liquid filtration.

Falling between these two extremes are the alumina-silica fibres as exemplified by the Nextel® range of products (3M, USA), which are determined by the alumina:silica ratio and rarely contain <60% alumina. Even small amounts of silica (≈3.0 wt%) permit sintering of the transitional forms of alumina. This delays nucleation and growth of α-alumina at ≤1,300 °C. Thus, varying the amount of silica leads to various forms of alumina-silica fibres with a range of high-temperature behaviours. For example, Nextel 610® comprises 99% (being similar to Saffil®), Nextel 720 comprises 85% and Nextel 312 comprises 62% Al_2O_3 to give a maximum user temperature range of 1,260–1,370 °C. These are available in yarn, fabric and nonwoven forms for similar applications. Variations to the properties of these mixed oxide fibres, principally fibre physical characteristics such as flexibility or strength retention at high temperature with time, may be made by introducing other oxides such as boric oxide (B_2O_3; Nextel 312 and 440) or zirconia (ZrO_2; Nextel 650), although these do not enhance the maximum thermal working conditions.

Silicone carbide fibres are obtained by pyrolysing precursor fibres spun from an organosilicone polymer at >1,200 °C. As **Table 5.5** shows, these have some of the highest service use temperatures of all ceramic fibres, reflecting their extremely high melting points. Polycarbosilane or a derivative thereof is a typical precursor polymer, and such polymers consist of six atom rings of silicone and carbon. One commercial example of silicone carbide is Nicalon®, (Nippon Carbon), which is available as continuous filament (cf) tow for use in high-temperature rigid composites with polymer-based resin or metal matrices such as tungsten.

There are a range of other inorganic fibres such as basalt fibres (e.g., Basaltex®, Marureel, Belgium) from a naturally occurring complex silica/alumina/other oxide basalt rock that is similar to glass in composition. They are used as asbestos replacements and available in filament and nonwoven forms with claimed superiority to glass fibres in terms of temperature performance (see **Table 5.5**). Fibres such as Basaltex® are bronze and available as continuous filaments with nominal diameters in the range 9–24 μm. Derived woven fabrics are used as fire barriers, thermal insulation and composite reinforcements.

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6

Flame-retardant and Environmental Issues

A. Richard Horrocks

6.1 Introduction

Apart from the inevitable pressure to reduce costs throughout the textile industry and use the most cost-effective finishes and application processes available, a major issue of the last ≈25 years has been the influence of environmental factors and the related current concerns levelled at the use of flame retardants in general.

Environmental concerns became significant issues during the late 1980s with regard to the following:

- Minimisation of effluent and water.
- Reduction and/or removal of formaldehyde as an agent during the manufacture and processing of flame retardants.
- The potential environmental risks associated with halogen-containing flame retardants.

6.2 Minimisation of Effluent and Water

The European Union (EU) directives Environmental Impact Assessment 85/337/EC (European Commission), 1985 (amended by the directive 97/11/EC, 1997) and Integrated Pollution Prevention and Control Directive 96/61/EC, 1996, demanded strict controls over effluent discharge. Their embodiment in national legislation occurred across the community during 1990–2000. Within the UK, as stated briefly in **Chapter 4**, the consequence of this was the Environmental

Protection Act, 1990, which identified the need for the following controls associated especially with flame-retardant applications involving formaldehyde:

- Emissions of formaldehyde to the atmosphere, especially during curing (currently required to be ≤20 ppm).
- Emissions of volatile organic compounds (VOCs) (currently ≤50 ppm).
- Discharge of unfixed flame retardants from washing-off effluent.

How these regulations have impacted on commercial finishers applying tetrakis(hydroxymethyl) phosphonium (THPX) salt- or phosphonamide-type flame-retardant treatments has been discussed in **Chapter 4**. In addition to optimising the chemistry so that byproduct formation is minimised [1, 2], for most commercial textile finishers to achieve acceptable formaldehyde and VOC emissions when applying formaldehyde-based finishes such as Pyrovatex® CP and its analogues, gaseous exhausts from the drying and curing stages must pass through scrubbers before release into the environment. Liquid effluents require neutralisation and dilution before release. Not surprisingly, use of methods such as controlled-impregnation technologies, low-formaldehyde finishes and recycling of wash waters were found to not only reduce effluents but save money, and so became economically attractive to finishers. It has been a requirement since this time that all UK textile finishing plants account for all effluents, seek agreed permissions for chemical discharges, and are charged accordingly for their disposal. This has encouraged them to adopt minimum and even zero waste strategies.

In a not-unrelated similar manner, flame-retardant users of decabromodiphenyl ether (DecaBDE) and similar bromine-containing flame retardants have adopted the Voluntary Emissions Control Action Programme, VECAP™, system now operated under the auspices of the European Flame retardants Association (EFRA) to ensure that none of these chemicals are released into the environment (see **Section 6.4** below) [3].

6.3 Attempts to Reduce/Remove Formaldehyde from Textile Flame Retardants

As evident from **Chapter 4**, the main targets for replacement are the two major and commercially dominant generic types of durable flame retardants for cotton and cotton-rich blends, i.e., those based on: (i) THPX condensates and (ii) *N*-methylol dimethylpropionamide derivatives. Surprisingly, while THPX-ammonia-cured treatments are one of the targets here, there is no published evidence that formaldehyde release is a problem during application of the flame retardant or during service life. However, there is commercial evidence that some formaldehyde may be released during use but at levels much less than in cured *N*-methylol dimethylpropionamide derivatives. This would be possible only if, after ammonia-curing, the subsequent oxidation of the polyphosphine structure to the stable poly(phosphine oxide) form with an idealised generic structure -CO-NH-CH_2-P(=O).(CH_2-NH-$)_2$- were not 100% efficient. Otherwise, it is difficult to visualise how significant quantities of formaldehyde could be released from this structure during normal use.

However, this is not the case with *N*-methylol dimethylpropionamide. As explained in **Chapter 4**, the condensation reactions involved are equilibria in which formaldehyde is a product and hence always present in a finished fabric (albeit at very low levels if applied correctly).

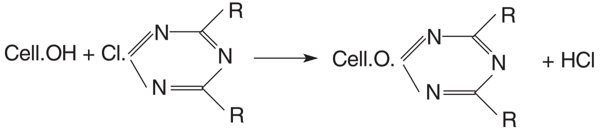
Notwithstanding this formaldehyde issue, to replace either of these products and their derivatives, it is most likely that any flame retardant must be cellulose-reactive, which usually means, in the first instance, a reaction *via* the anhydroglucopyranose C(6) hydroxyl group. Possible alternatives to phosphonamide- and THPX-based finishes (which are discussed in detail below) must be cognisant of their respective previously discussed strengths and weaknesses (which are summarised in **Chapter 4**, **Table 4.1**). Several recent research articles assume only the worst properties of both of these finishes as being reasons for their replacement and, in doing so, ignore their respective strengths, not least their exceptional durabilities, which can exceed 100 domestic and even commercial wash cycles [4]. Therefore, for any new durable flame retardant for cotton to become accepted and to compete with these two market leaders requires that they have most (if not all) of the following properties:

- Equivalent or superior ease of application.
- Zero formaldehyde-releasing properties.
- Comparable textile service-life properties in terms of durability, effect on handle and tensile properties.
- Overall comparable cost-effectiveness (and preferably cheaper).
- Equivalent or superior toxicological and environmental impacts.

Because of the formaldehyde issue and in spite of its apparent absence from ammonia-cured-THPX treatments, considerable literature has appeared in attempts to develop formaldehyde-free flame-retardant replacements. This chapter is not intended to be a comprehensive review of all research undertaken in this area [4, 5] but some of the more salient alternatives will be discussed briefly with a focus on those research areas that might have some reasonable chance of commercialisation. Furthermore, **Table 6.1** summarises the chemical character of each of the examples discussed below if there is the greatest promise of effective levels of flame retardancy coupled with durability (which implies a chemical interaction between cellulose and the flame retardant). For a recent review that includes the more recent speculative research attempts to develop novel flame retardants, the reader is directed to the work of Yang [7].

Table 6.1 Cellulose-reactive and potentially reactive flame-retardant bonding types discussed in Section 6.3

Bond	Structure	Comments	References
N-methylol species	Cell.O.CH_2.NH-	Resists hydrolysis but releases formaldehyde during storage.	[4] and see **Chapter 4**
Cellulose ester with Fyroltex HP	Cell.O. CH_2.CH_2 .(O.CH_2.CH_2 .O.P(O)(OCH_3))$_{2x}$. (O. CH_2.CH_2 .P(O)(CH_3))$_x$. CH_2.CH_2.OH	Poor wash stability.	[7–13]
Cellulose ester with butyl tetracarboxylic acid (BCTA) (and/or Fyroltex HP)	Cell.O.CO.CH_2.CH(COOH).CH(COOH). CH_2.CO.R where R=O.Cell or .FR (e.g., Fyroltex HP)	Poor hydrolysis and wash resistance.	[14, 15]
Cellulose/BCTA link stabilisation: effect of triethanolamine (TEA)	Cell.O.CO.CH.CH(CO_2)–.CH(COOH). CH.CO.R (CH_2.CH_2.O)$_3$.NH^+ Cell.O.CO.CH.CH(CO_2)–.CH(COOH). CH.CO.R (CH_2.CH_2.O)$_3$.NH^+	Claimed 30 wash durability for Fyroltex/TEA/BCTA on 35/65 cotton/ Nomex® blend.	[15, 17]
Cellulose-diacid-hypophosphite link; where diacid is maleic, succinic, malic or tartaric acids.	Cell-O-CO-CH_2-CH(COOH)-P(O). (O^-M^+)-CH(COOH)-CH_2-CO-O-Cell Note that with ≥3 –CO.OH groups in a polycarboxylic acid, evidence of increased cellulose chain crosslinking is observed. M^+ are Na^+ or K^+ cations.	20 home wash cycles.	[19–24]

Cellulose-phosphoramidate systems	$(C_2H_5.O)_2$-P(O)-NH-R, where R = -H, $-C_2H_5$, $-C_2H_4.OH$ and $-C_2H_4.O.CH_3$	No reactivity with cellulose.	[26–28]
Cellulose-phosphoramidate ester interchange	Cell.O. $P(O)(C_2H_5.O)-C_4H_8N_2.CH_3$; linkage to cellulose after heat curing at 160 °C in slight alkaline conditions.	Some water soak (40 °C) durability.	[30]
Cellulose-chloro triazinyl condensation.	 where $R = –O.CH_2.PO(OCH_3)_2$	Durability as yet unknown.	[32]
Cellulose phosphonate and derivatives	$Cell.OH + HO.PH(O).O^-M^+ \rightarrow Cell.O.PH(O).O^-M^+ + H_2O$ $Cell.O.P(O)H.O^-M^+ + HO.Cell \rightarrow Cell.O.PH(O).O.Cell + M^+OH^-$ where $M^+ = Na^+$ or K^+, plus MOCN, $CN.NH_2$ and derivatives	Durable to ≥30 washes.	[33–35]
Cellulose-polymer systems	Cellulose microfibrillar network interspersed with a copolymer based on branched poly(ethylene diamine) reacted with a phosphonitrilic chloride (N3P3Cl6)/ acrylamide condensate $(N_3P_3(NH.CO.CH{=}CH_2)_6)$ Phosphorylated cellulose – chitosan-SnO2, pad-dry-cure process Cellulose-DNA pad-dry process	Durable to 30 49 °C AATCC washes Durable to 30 launderings Durability unknown	[39] [41] [42]

6.3.1 Oligomeric Phosphate-phosphonate

In 2002, Akzo Nobel re-introduced their former Fyrol 51 product (an oligomeric phosphate-phosphonate, $H\text{-}(O.CH_2.CH_2.O.P(O)(OCH_3))_{2x}.(O.\ CH_2.CH_2.P(O)(CH_3))_x.O.CH_2.CH_2.OH$), as Fyroltex HP [5, 6], which could be a durable flame retardant for cellulosic textiles. However, in spite of a considerable amount of research on this compound by Yang and co-workers (discussed in greater detail below), this product was withdrawn in 2005, although the same molecular product is available as DM 3070 (Dymatic Chemicals, China) and ALC HP51 (Allison Associates, USA) [7]. This research [8–13] has been undertaken to achieve acceptable levels of multiple laundering durability if applied in the presence of an aminoplast or principally a methylolated resin species such as dimethylol dihydroxyethylene urea (DMDHEU) or methylated formaldehyde-urea. These publications show that ≤12 launderings are feasible if the correct crosslinker is chosen (though the problem of formaldehyde release remains). Subsequent publications claimed ≤40 wt% retention and 50 laundering durability for a Fyroltex/trimethylol melamine/DMDHEU combined finish applied to 50%/50% nylon (6 or 6.6)/cotton blends [13] and this entire area has been reviewed recently by Yang [7].

6.3.2 Butyl Tetracarboxylic Acid

In the USA, interest in char-forming polycarboxylated species such as BTCA along with other functional species has shown that they may interact with cellulose in particular to generate levels of flame retardancy acceptable for certain textile applications such as carpets with moderate levels of durability to washing [14]. Unfortunately, because of the ease of hydrolysis of the BTCA-cellulose ester links formed, durability to domestic laundering is limited, so flame treatments based on this chemistry may lead only to semi-durability. Subsequent work by Yang and colleagues has combined BTCA as the cellulose bridging species with phosphorylated species such as the hydroxyalkyl organophosphorus oligomer, Fyroltex HP, to enhance flame retardancy and durability [6, 7, 15]. BTCA forms a bridge between the oligomer and cellulose molecules, and durability is improved, but the ease of ion exchange between the hydrogen ions of the free carboxylic acid group with calcium ions during washing in hard water is accompanied by a loss in flame retardancy as a consequence of formation of calcium salts [10]. Addition of TEA reduces the calcium ion pick-up as a consequence of esterification of free carboxylic acid groups and, using a Fyroltex/BCTA/TEA combination applied to a 35%/65% cotton/Nomex® blend, acceptable levels of durability were achieved with vertical strip test (American Society for Testing and Materials (ASTM) D6413-99) passes after 30 home launderings [15]. A subsequent publication extended this work to show that the mixed Fyroltex/BCTA system may be applied to silk to yield a 15 hand-wash level of durability [16], whereas more recent work re-examined the possible role of Fyroltex and BCTA in 100% cotton fleece which, if TEA is present, also achieves class I after multiple home launderings [17].

It is in the cotton fleece fabric area that the use of polycarboxylic acid species such as BCTA can find application where the conventional THPX- and *N*-methyl phosphonamide-based durable finishes cannot be used because of associated stiffness and/or processing difficulties, and if limited durability is required [18]. Yang's research team developed this idea further and reported that treatment of cotton fleece with maleic acid (MA) and sodium hypophosphite enables class-1 passes to 16 CFR 1610 (US Federal Standard for the Flammability of Clothing Textiles) to be achieved if exposed to the 45° ASTM D1230-94A apparel test after 20 home launderings [19]. These authors propose that the hypophosphite anion interacts with the MA entity to form a crosslink of the type:

$\text{Cell-O-CO-CH}_2\text{-CH(COOH)-P(O).(O}^-\text{.M}^+\text{)-CH(COOH)-CH}_2\text{-CO-O-Cell}$

where M^+ are Na^+ or K^+ cations. Subsequent work extended this to include the dicarboxylic acids (succinic, malic and tartaric acids [20]) and polycarboxylic acids (BCTA and citric acid (CA)) to yield similar flame-retardant performance [21]. This latter work showed that acids with ≥3 carboxylic acid groups (CA, BCTA) increase the level of cellulose crosslinking, which increases the dimensional stability and stiffness of the fabric.

Their work with MA has been extended to include phosphorus-containing MA oligomers (PMAO) synthesised by aqueous free radical polymerisation of MA in the presence of potassium hypophosphite. PMAO is considered to be a mixture of species having the general formulae:

$H\text{-}P(O)(O^-.M^+).[MA]_x\text{-}H$, $H\text{-}[MA]_x\text{-}P(O)(OMA).[MA]_y\text{-}H$ and $HO\text{-}P(O)(O^{-M+}).[MA]_x\text{-}H$

where x and y are between 3 and 5 and M^+ are Na^+ or K^+ cations. This mixture is applied to cotton fleece fabrics in the presence of sodium hypophosphite with no significant changes in fabric MA/sodium hypophosphite system can form ester crosslinks between cellulose chains to confer wrinkle resistance [23] and improved fire performance [24] as described above [19].

6.3.3 Alkyl Phoshoramidate Adduct

Quite different from the approaches described above is the recently introduced Firestop product Noflan, a phosphorus-, and nitrogen-containing molecule reported to have the structure $[CH_3\text{-}P(O).(ONH_4)\text{-}NH_2]\ NH_4Cl$ in which an alkyl phoshoramidate is stabilised as a salt adduct with ammonium chloride [25]. This is obviously a formaldehyde-free molecule, but it may react only with cellulosic substrates *via* the phosphoramidate-NH_2 group, which is not very reactive. It is most likely that for this to be effective in cellulosic-based textiles it must be applied in a resin binder or crosslinked using a methylolated resin. It is claimed to be effective on cotton and cotton-polyester blends with reasonable levels of durability. If applied to wool, it can survive dry cleaning and finds application in technical end-uses such as aerospace interior fabrics.

6.3.4 Organophosphoramidates

In a not-unrelated article, work by a Swiss research team [26] investigated the particular value of organophosphoramidates as flame retardants for cellulose. They are claimed to be not only easily synthesised from chlorophosphates, but also to exert high levels of flame retardancy because of nitrogen-phosphorus synergy which can be varied depending on the level of substitution of the nitrogen-containing moiety. The research focussed on the behaviour of secondary organophosphoramidates because a study by Pandya and co-workers >30 years previously [27] suggested that they were superior to tertiary analogues. These specially synthesised structures have the general formula $(C_2H_{5.}O)_2$-P(O)-NH-R, where R = -H, $-C_2H_5$, $-C_2H_4.OH$ and $–C_2H_4.O.CH_3$. They demonstrated high levels of condensed-phase activity [28] although no attempt was made to assess or improve their poor durability. The study therefore remains academic but poses the question of whether or not suitable cellulose reactivity can be introduced to confer the necessary levels of durability for commercial exploitation.

6.3.5 Phosphonyl Cyanurates

An interesting and novel approach has been published by Chang and co-workers [29] from the USDA Southern Regional Research Centre in New Orleans, where much of the pioneering research into durable flame-retardant finishes for cotton was undertaken during 1950–70 [4]. This group has synthesised two new monomers (2-methyl-oxiranylmethyl)-phosphonic acid dimethyl ester and 2-(dimethoxy-phosphorylmethyl)-oxyranylmethyl]-phosphonic acid dimethyl ester which, together with dicyandiamide ($NH_2.C{=}NH.NH.CN$) and citric acid, impart flame resistance to woven 100% cotton and 80/20 cotton/polyester fleece fabrics. The resulting mono- and *bis*-(dimethoxy-hydroxymethyl phosphonyl) cyanurate derivatives may be padded onto fabrics and, whereas the former can give rise to limiting oxygen index (LOI) values of ≤25.5% at ≈21 wt% add-on, higher LOI values of >28% were obtained when the latter was applied at add-ons <20 wt%. Fabrics passed the standard 45° and vertical strip tests ASTM D1230-94 and D6413-99 before laundering. Durability is not, however, very good, with only ≈5 wash cycles being achievable while maintaining acceptable levels of flame retardancy in spite of the claimed cellulose reactivity of cyanurate derivatives.

6.3.6 Cellulose-phosphoramidate Ester Interchange

This same group of researchers [30] has recently extended their work to include further work on phosphoramidates, specifically diethyl 4-methylpiperazin-1-ylphosphoramidate. This molecule, similar to those synthesised by Gaan and co-workers [26] and where R= $-C_4H_8N_2.CH_3$, was applied to cotton and cured at 160 °C for 5 min. They propose that bonding to cellulose may occur by the transesterification shown in **Scheme 6.1**:

$$\text{Cell.OH} + (C_2H_5.O)_2\text{-P(O)-NH-}C_4H_8N_2.CH_3 \rightarrow \text{Cell.O. P(O)}(C_2H_5.O)\text{-}C_4H_8N_2.CH_3 \quad (6.1)$$

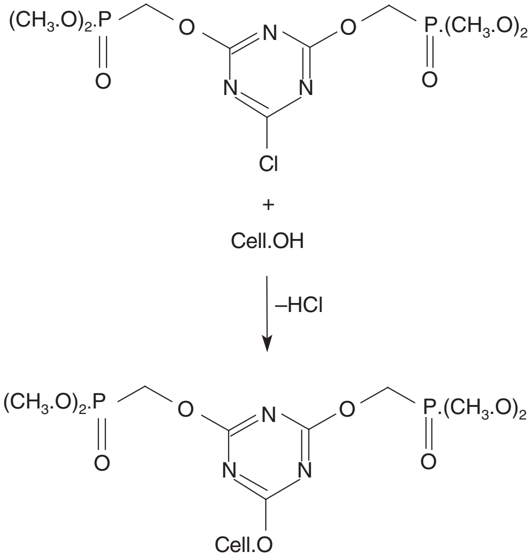
The reaction is sensitised in slightly alkaline conditions similar to those within the mercerised cotton fibres present in the fabrics studied. They claim LOI values >27% and, in some cases, 31% at phosphorus levels of 2.1% and 2.7%, respectively, with significant char formation and absence of after-flame and afterglow. Although formal durability trials were not undertaken, after washing in water at 40 °C for 10 min, original add-ons reduced to ≈83–84% of the original values, which remained identical after a third wash. Clearly, durability has improved with regard to the earlier work on phosphoramidates, but these authors claim that it is the focus of future research.

6.3.7 Cellulose-chloro Triazinyl Derivative Condensation

One means of achieving strong bonding to cellulose (and hence high levels of durability) is to exploit reactive dye chemistry where strong covalent Cell.O.Dye bonds having extremely good wash fastness are achieved [31]. The more common reactive species within a reactive dye is the 6-chloro-1,3,5-triazine group, in which the chlorine replaces the anhydroglucopyranose repeat group C(6) primary -OH group hydrogen under alkaline conditions to create a strong Cell.O.N bond which is resistant to hydrolysis under normal laundering conditions. To the author's knowledge there has been no academic study, until recently [32], of this possibility. However, there were some attempts by the former ICI Dyestuffs Division during the 1980s, the inventors of reactive dyes and the famous Procion® range of dyes (now produced by Dystar Colours GmbH), to develop a flame retardant based on this chemistry. To the author's knowledge no patents arose from these studies, and no commercialised products were developed.

This is perhaps because the major challenge is the limited accessibility of the potentially reactive primary C(6) CH_2OH groups in the polycrystalline cotton fibre and the fact that even the highest dye uptakes were rarely >5 wt% for the deepest shades. This, coupled with the fact that most phosphorus-containing flame retardant species rarely contain >20 wt% phosphorus, means that obtaining >1 wt% phosphorus bonded would require (at the very least) ≥5 wt% bonding of the reactive species to the accessible cellulose within cotton fibres; this poses a significant challenge.

This challenge has been addressed recently, however, by Chang and coworkers, again at the USDA Southern Regional Research Centre [32]. They reported in 2012 the synthesis and reaction with cotton of tetramethyl(6-chloro-1,3,5-triazine-2,4,diyl)*bis*(oxy)*bis*(methylene) diphosphonate, as shown below in **Scheme 6.2**:



(6.2)

This reagent was padded onto cotton in 50% aqueous isopropanol, dried at 100 °C for 5 min and cured at 140 °C for 5 min at add-ons at 5–19 wt%. Treated fabrics were white and only the highest add-ons (17% do not require) and 19 wt%) were self-extinguishing with a LOI>35%. Analyses of phosphorus and nitrogen showed great variability across the 19 wt% add-on sample, with mean values of ≈2.4 and ≈6.4%, respectively. Scanning electron microscopy (SEM) photographs indicated the significant presence of surface deposits, and no attempts were made to assess the durability of the treatment, but the authors stated that this was their immediate priority. Thus, at the present stage, there is no indication of what level the flame retardant is firmly covalently bonded to the cellulose within the microfibrillar, polycrystalline interiors of the cotton fibres.

6.3.8 Phosphorus Acid Derivatives of Cellulose

As yet unpublished research undertaken at the University of Leeds over the last decade has given rise to several significant patent applications through its company Perachem Ltd. that describe the basis of a durable flame-retardant treatment for cotton involving phosphorous acid [33–35]. The 2009 application [34] discloses the interaction between cellulose, urea and phosphorous acid as the potassium or sodium salt at pH 8–10 to yield cellulose phosphonate (Cell-HPO_3^-) and/or the dimer Cell-O-PH(O)-O-Cell, which gives rise to a wash-durable flame-retardant treatment. The earlier 2007 application describes the application to cotton of H_3PO_3 or the phosphate followed by potassium cyanate, cyanamide or derivatives, and then curing at 200 °C to yield a wash-durable, flame-retardant finish. In 2010, a third application extended the claims to include a first component selected from a phosphorous-containing acid or a salt of a phosphorous-containing acid, and a second compound selected from an isocyanic acid, a cyanate salt, a thiocyanate salt or isothiocyanate precursor, dicyandiamide, cyanamide or carbodiimide precursor. The exact chemistry has not been published, but there is an obvious reaction between the cellulose phosphonate moiety and the cyanate (or other disclosed nitrogen-containing derivative), which then introduces the necessary synergistic nitrogen into the structure. However, it has been recorded previously that replacement of hydrogen in the phosphonic residue by 2-cyanoethyl and 2-carboxyethyl groups retarded the subsequent dehydration of cellulose, and so it is likely in the chemical mechanism that substitution of the P-H group by an electron-withdrawing group does not occur [36]. If the resulting treatment is to have the claimed wash fastness and resistance to calcium ion exchange, then removal of the acidic P-OH moiety is essential, and possible products of the P-OH interaction with the CNO^- ion, for example, should offer P-N synergy and hydrolysis resistance providing that a strong P-N, P-O or P-C bond is formed as a result. The processes described have provoked sufficient commercial interest for its licensing to Clariant, who have announced a commercial version called Pekoflam®ECO/SYN claimed to be applicable to 100% cotton and cotton/synthetic blends and offering high durability. The number and type of wash cycles has not been disclosed, but treatments prove to be resilient to wash-fastness tests in 5 g/l Na_2CO_3 at 60 °C for 12 min repeated up to 12 times, after which they continue to pass standard vertical strip tests by demonstrating self-extinction and char lengths <15 cm in length [33, 35]. They also claim the product to be free of any Oeko-Tex®-restricted chemicals such as formaldehyde.

6.3.9 Phosphorus-nitrogen-silicone Developments

Recent interest has also been shown in the potential for combining phosphorus, nitrogen and silicone onto cellulose substrates to create the potential for carbonaceous and silicaceous char-forming characteristics. Lecoeur and co-workers [37, 38] have combined monoguanidine diphosphate (MGDP) and 3-aminopropyltriethoxysilane, $NH_2(CH_2)_3Si(OC_2H_5)$, applied in the presence of phosphoric acid, which is a required catalyst if water soak durability (20 min in hard water at room temperature) is to be achieved. Treated cottons behave typically for those containing char-promoting flame retardants in that flame retardancy is improved (M1 rating to NF P 92-503), the peak of the heat release rate reduces, and residual char increases. The level of durability achieved is a consequence of MGDP phosphorylating cellulose during the 180 °C cure, and polymerisation of the silane and its partial reactivity with cellulose. Again, the challenge remains of developing a reactive flame-retardant species that effectively bonds to cellulose through hydroxyl groups, is hydrolysis-resistant and withstands normal textile-processing conditions.

6.3.10 Cellulose-polymer Interactive Treatments

In contrast to the methods mentioned above that attempt to bond reactive agents directly to cellulose, Yang and co-workers [39] created a polymer network within the cotton microfibillar structure not unlike that observed in the THPX condensate-ammonia-cured finishes. However, here cotton is first treated with a solution of a branched poly(ethylene diamine) followed by a condensate of phosphonitrilic chloride ($N_3P_3Cl_6$) and acrylamide to yield the hexasubstituted product $N_3P_3(NH.CO.CH{=}CH_2)_6$ and then dried at 80 °C. The resulting treatment appears to yield fibres with little or no surface deposits observable by SEM, and fabrics that show self-extinguishing properties even after 30 49 °C standard American Association of Textile Chemists and Colorists washes. This recent research appears to be novel, but the use of (and possible release in use of) acrylamide needs to be questioned, as does the presence of a phosphonitrilic or phosphazene component on potentially commercial [40] as well as health and safety grounds given that some earlier flame retardants like the now-obsolete Fyrol 76 [4], which comprised acrylonitrile, were withdrawn for similar reasons.

Recent interest in the interaction of cellulose with some biopolymers has shown that wash-durable flame retardancy is achievable. For example, in 2008 El-Tahlawy et al., [41] published a triple pad-dry-cure process in which the biopolymer chitosan is added to a phosphorylation bath to act as a nitrogen source and to facilitate phosphorylation. Firstly, cotton fabric is treated with sodium stannate (Na_2SnO_3) dried, then treated with $(NH_4)_2SO_4$ and dried, padded with a solution of diammonium phosphate, chitosan, citric acid and sodium hypophosphite, dried and cured. Reaction of the Na_2SnO_3 with $(NH_4)_2SO_4$ is claimed to form tin II oxide (SnO_2) which, together with any phosphorylation derivatives produced during the final cure, subsequently function as a condensed-phase retardant and dehydrate cellulose to char. During the third pad-dry-cure stage, citric acid phosphorylates and bonds chitosan to cellulose *via* a bridge of the form:

$\text{Cell.CO.O.CH}_2\text{.C(OH)COOH.CH}_2\text{.CO.NH.Chit}$

where –NH.Chit represents the chitosan biopolymer having reacted *via* a pendant $–NH_2$ group present on each β 1-4-linked D-glucosamine monomeric repeat unit. The treatment is claimed to be durable to 30 launderings.

Very recently, Alongi and co-workers [42] demonstrated that deoxyribonucleic acid (DNA) can be applied to cotton to yield flame-retardant fabrics, indicating that the DNA phosphate groups can generate phosphoric acid upon heating, and so catalyse the dehydration of cellulose. This research has only just been published and shows great promise as a novel and potentially eco-sustainable method of achieving acceptable levels of flame retardancy. The work to date is discussed more fully in **Chapter 8, Section 8.3.5.**

6.4 The Halogen (Bromine) – Antimony Question

Concerns regarding halogens in flame retardants started some years ago with an initial focus regarding the possible formation of polybrominated dioxins associated with incineration of organobromine compounds, especially those based on polybrominated diphenyls and diphenyl oxides [43].

Without wishing to enter into extreme detail, after the initial concern in Germany in 1986, the EU published a draft amendment to EC Directive 76/769/EEC (European Economic Community) in 1991 which would essentially ban use of all polybrominated diphenyl oxides (PBDPO) or ethers within 5 years. In 1994, this Directive was withdrawn because subsequent studies cast doubt on the earlier concerns. Simultaneously, other organisations (e.g., US Environmental Protection Agency (OECD)) initiated risk analyses of these compounds. At the same time, the World Health Organisation initiated an evaluation of the risk to health of PBDPO which, in 1994, indicated that they did not pose a significant hazard. The full details of the OECD programme are complex [44], but one outcome was an industrial commitment to address the environmental exposure and purity of these agents as well as minimisation of the presence of non-commercial congeners.

During this same period, the role of antimony III oxide in ‘cot deaths’ or sudden infant death syndrome was raised on UK Television in 1994 and, although refuted [45] and subsequently shown to be without foundation [46], the image of antimony/bromine flame-retardant formulations (and especially back-coatings in general) became increasingly questioned within the media and environmental circles.

In 1997, Stevens and co-workers published work funded by the then UK government Department of Trade and Industry [47] which reviewed the fire-safety value and effectiveness of flame retardants in consumer products and assessed the risk benefits of the latter. A major conclusion was that, based on the information available at the time, any risks to health and the environment were more than offset by their benefits in terms of lives saved and reduced fire injuries. This study was followed by an analysis of the effects of the UK furnishings regulations of 1988 in terms of their ability to reduce domestic dwelling fire casualties [48, 49]. These authors estimated that implementation of these domestic fire regulations saved, on average, 140 lives *per annum* and the decrease in UK fire casualties since 1990 discussed in **Chapter 1** are reflected in the overall reduced figures for fire deaths (see **1.3, Chapter 1**). A subsequent and more recent study commissioned by the UK Government [50] concluded that between 2003 and 2007, implementation of these regulations continued to save 54 lives, with 780 fewer casualties, each year. It is likely that the lower casualty numbers compared with those in the previous report [48] are in part due to the reductions in fire casualties in UK dwelling fires and hence increased safety of furniture and furnishings in the home as a consequence of the regulations during the period 1990–2003. The wider area of the risks and benefits of flame retardants has been reviewed more fully recently by Emsley and Stevens and extend their previous studies [51].

Meanwhile, in the USA during the late 1990s, as a result of pressures primarily from the US National Association of Fire Marshalls regarding concerns about domestic fire deaths of children as a result of playing with matches, the US Consumer Product Safety Council (CPSC) planned to introduce a small ignition source test for furnishing fabrics similar to the British Standard 5852: Part 1:1979. However, it was realised that the use of flame-retardant furnishing fabrics across the US would become mandatory if any resulting US Federal regulations were implemented in which such a test was defined. Because of concerns raised with regard to health and safety and the environment as a consequence of introducing flame retardants into the home, in 1999 the US Congress directed CPSC to arrange an independent study by the National Research Council (NRC) to assess the risks of flame retardants in furnishings. In turn the NRC passed this request onto its Committee on Toxicology which set up a Sub-committee to undertake this work. The report from this Sub-committee was published in 2000 and though this may be considered to be out of date, it remains the most authoritative risk analysis of the 16 selected flame-retardant chemicals to date [52]. **Table 6.2** lists these flame-retardant chemicals and whether or not they are useful for flame-retarding furnishing fabrics based on the UK experience. Those in the upper half of the table were deemed to be toxicologically safe whereas those in the lower half were deemed to have unacceptable risks and required further research.

Table 6.2 Risk analyses of 16 selected flame retardants [52]

Risk	**Chemical**	**Use in furnishings**
Acceptable	Hexabromocylcododecane (HBCD)	Yes
	Decabromodiphenyl oxide	Yes
	Alumina trihydrate	Yes
	Magnesium hydroxide	Yes
	Zinc borate	No
	Ammonium polyphosphates	Yes
	Phosphonamide (‘Pyrovatex’ type)	Yes
	Tetrakis(hydroxymethylol) phosphonium derivatives (‘Proban’ type)	Yes
Unacceptable	Antimony III oxide	Yes
	Antimony pentoxide and antimonates	Yes
	Calcium and zinc molybdates	No
	Organic phosphonates	Yes
	Tris(1,3-dichloropropyl 1-2) phosphate	No
	Tris(monochloropropyl) phosphates	No
	Aromatic phosphate plasticisers	No
	Chlorinated paraffins	No

Of special significance at this time was that, contrary to many contemporary EU member-state and pressure-group viewpoints, this study exonerated the bromine-containing retardants DecaBDE and HBCD and yet signalled a risk to the use of antimony III oxide and other antimony-containing synergists used in these same finishes. One major issue that caused concern within this study was that even though they had been instructed specifically to undertake risk analyses of the designated 16 chemicals, if present within a textile finish or back-coating, some of these flame retardants were precursors which become chemically very different if present in a flame-retarded fabric (e.g., THPX-condensates are present as polyphosphine derivatives and phosphonamide derivatives are crosslinked to cellulose molecules, see **Chapter 4**). Furthermore, even the free chemicals would be embedded in a resin which would severely reduce their mobility possible release into the environment.

This risk assessment promoted further research which is continuing today. In particular, there has been increasing activity in the USA and Europe to define more effectively the environmental risks posed by the use of brominated flame retardants in particular. Wakelyn has reviewed US and EU positions up to 2008 [53], including concerns over the use of polybrominated diphenyls as well as penta- and octabromodiphenyl ether and their subsequent bans since August 2004 on health and bioaccumulation grounds. These flame retardants had little (if any) application to textiles, but their ban increased the focus of attention on DecaBDE and HBCD (as outlined in **Chapter 4**) and which, as described in **Section 4.5.2**, has led to their phasing out in Europe by 2016 and 2015, respectively.

However, to more fully understand the background of the processes leading to these withdrawals from use, it is worth discussing the various parallel activities during 2000–2010, which contributed to the environmental debate and subsequent actions. The focus was on these two major retardants, but it continued with regard to all other brominated flame retardants in general use as well as those being applied specifically to textiles.

The EU risk assessments undertaken on DecaBDE [54] found no real cause for this flame retardant to be controlled because of any toxic factor, whereas that for HBCD [55] found possible health risks to workers during its processing. As stated in **Chapter 4**, the major cause for banning DecBDE is because of its claimed persistence and bioaccumulation in the environment. Any claimed toxicity is associated with possible debromination during ultraviolet degradation to yield products that include the known toxic congeners penta- and octabromodiphenyl ether (although this is disputed and appears to depend on whether or not an oxidative or anaerobic environment is present). This chapter is not intended to present a review of this entire contentious area, but a few recent and pertinent references may be cited regarding this debate [56–62].

The expected ban on DecaBDE, rather than being based on firm scientific evidence, appears to be based on a precautionary principle that future science may conclude more definitely in favour of a ban. What is rarely considered is that even though analytical methods become increasingly sensitive, leading to the discovery of many chemicals in the environment at very low levels (often at ng/g), the levels found must be related to known toxicological dose data. This entire area has been discussed by Stevens and co-workers [63] together with service-life simulation data regarding the possible release of HBCD and DecaBDE from back-coated textile furnishing fabrics. In this work, particulate debris from fabrics abraded in a modified Martindale Abrasion Tester was analysed for size distribution and morphology using SEM and energy-dispersive X-ray spectroscopy. Results showed that much of the debris produced is in the form of short fibres arising from the target cotton fabric and the wool wear abradant material. Only after 30,000 rubs, after which the top fabric surface had started to fail and to reveal the underlying fibres and back-coating, were particles produced which were associated with the back-coating, and these were released as agglomerates having sizes of 2–5 µm up to 50–100 µm. Even then, the observed particles containing flame retardant were surrounded by the back-coating resin, and no evidence was found of free bromine or antimony particles (and hence free flame retardant).

In an attempt to reduce possible release of bromine-containing flame retardants after publication of the EC risk assessment of DecaBDE completed in 2004 [54], the Bromine Science and Environment Forum launched VECAP™ [3] (later adopted by EFRA (see **Section 6.2**) in 2004, to reduce levels of DecaBDE in the environment. Under this programme, manufacturers and users of DecaBDE for textiles and plastics formed a voluntary action group that agreed to limit releases of the flame retardant into the environment by providing data on the use of the chemical, and establishing and demonstrating control over processing waste. VECAP™ advises manufacturers, processors and users of brominated flame retardants by stating the following actions [3]:

- Increasing understanding of chemicals management in the value chain beyond existing legislation.
- Promoting and facilitating open and constructive dialogue with all interested parties, such as industry, regulators and other stakeholders.
- Raising awareness among all those involved in the process, from the shop floor to the boardroom.
- Implementing best practices identified through progressive development of the programme.

In so doing, all interested parties may work together to establish and implement best practices on managing brominated flame retardants to reduce and prevent emissions to the environment. The VECAP™ process is shown schematically in **Figure 6.1**, in which the user procedures and self-audit processes are present followed by mass balance calculation and emission reporting [3].

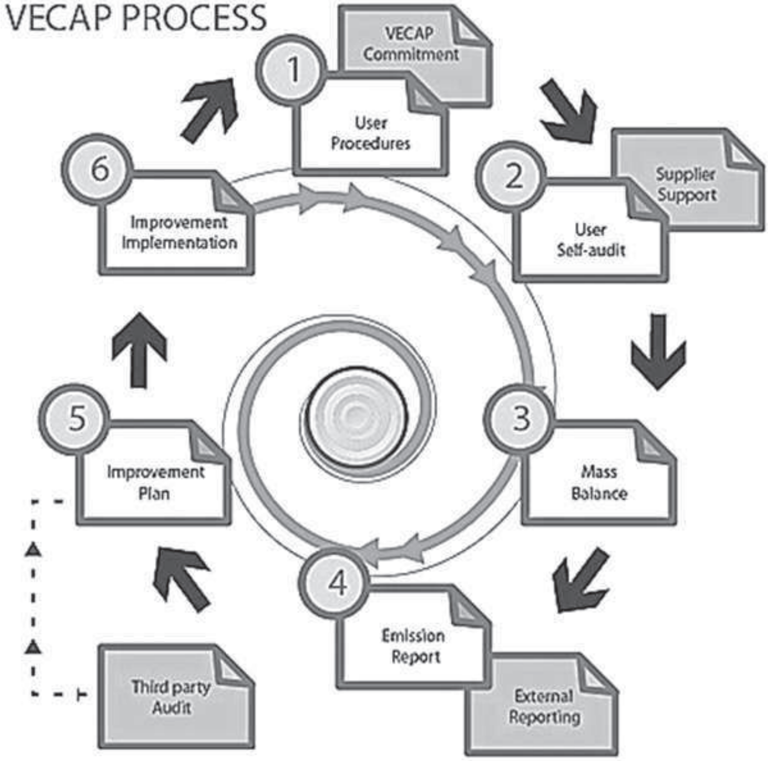


Figure 6.1 VECAP™ process. Reproduced with permission from *The Voluntary Emissions Control Action Programme*, VECAP™, European Flame Retardants Association (EFRA), Brussels, Belgium [3] and VECAP, *Maintaining the Momentum, European Annual Progress Report 2012*, EFRA and BSEF Secretariat, Belgium [64]. ©EFRA

External auditing of the process overseen by EFRA is undertaken, after which an improvement plan is developed and implemented. A VECAP™ initiative specific to DecaBDE was introduced in the UK in 2004, extended to other EU countries in 2005, and then launched in the USA and Canada in 2006. During the early years of the programme, there was an exclusive focus on emissions to air and water, mainly following a request from EU regulators to the producers of brominated flame retardants to monitor and report progress in this area of handling of chemicals. Subsequently the programme was extended to cover all bromine-containing flame retardants. VECAP™ issues annual reports to indicate the progress of this initiative [64]. **Table 6.3** presents the data from 84% of DecaBDE sold by EFRA members for 2008–2012 in terms of the consumption *versus* emissions and based on audit data undertaken in 2011. In spite of the reductions of DecaBDE emissions and other flame retardants into the environment which VECAP™ has caused, there still remain concerns over DecaBDE in particular, and hence an expected ban towards the end of this decade.

Table 6.3 Usage *versus* emission data for DecaBDE published by EFRA under VECAPTM [64]

Tonnes/year	**2008**	**2009**	**2010**	**2011**	**2012**
Total 2011 volume sold, tonnes	5,000–7,500	5,000–7,500	5,000–7,500	7,500–10,000	2,500–5,000
Total emissions, tonnes	<4	<1.5	<1.5	<0.5	<0.3

Adapted from VECAP, Maintaining the Momentum, European Annual Progress Report 2012, EFRA and BSEF Secretariat, Belgium [64]

Last but not least of the environmental influences on flame retardants for textiles are the EU's Registration, Evaluation, and Authorization of Chemicals (REACH) legislation which came into force in 2007 [65]. REACH requires that manufacturers of chemicals that are made in or imported into the EU in large volumes, such as brominated flame retardants, register those chemicals and provide information about how they can be used safely. REACH is a complex piece of legislation that is having an impact on a vast spectrum of substances contained within materials, which are made, sold, used, and disposed of across the EU. Registration of chemicals must be made by manufacturers or importers of >1 metric ton of a chemical substance per year with the European Chemicals Agency. For each qualifying chemical they must provide all information regarding the properties, uses and safe handling of the substance. REACH provisions, phased in over 11 years from 1st June 2007, should be complete by June 2018. However, the regulations cover only molecular substances having a diameter <100 nm and which are deemed as being small enough to penetrate a human cell wall. This criterion excludes polymers, and this is why most manufacturers of bromine flame retardants are now focussing on the development of polymeric bromine-containing flame retardants, as discussed in **Chapter 4** with regard to alternatives to HBCD and DecaBDE.

In conclusion, it is evident that the pressures from health and safety as well as environmental sectors are not going to reduce in future years, and that the flame-retardant industry must continue to react constructively to these pressures. However, in the continuing debates, the current safety advantages in terms of reduced fire casualties that the application of flame retardants to fibres and textiles confers are often lost, and the concept of the risk–benefit equation ignored. In the USA (and as discussed in **Chapter 3**, **Section 3.3.2**), the proposed US standard CPSC 16 CFR Part 1634 for the resistance of residential furniture to a smouldering and open flame ignition source is currently under scrutiny so that compliance may be achieved without the need for flame-retardant chemicals. Whether or not this can be achieved without eliminating the open-flame requirement remains to be seen.

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7 Nanostructuring of Synthetic Fibres

Jenny Alongi and A. Richard Horrocks

7.1 Introduction

In the last 20 years, nanotechnology has attracted great interest from industrial and academic researchers. Indeed, encouraging and surprising results have been achieved in many fields by using nanosized objects. **Chapters** 7 and 8 focus on the new perspectives as well as innovatory solutions achieved recently in the textile field from the flammability and combustion point of view which result from the introduction of nanoparticles either into the component fibres themselves or on to their surfaces, including those of derived yarns and fabrics.

It has been established that during combustion, these nano-objects can migrate to the fibre surface, acting as a 'thermal shield' that has a protective role on the polymer [1]. More specifically, two main strategies have been highlighted by the results collected by the academic and scientific community [2, 3].

The first is based on the possibility of introducing finely dispersed nanoparticles of various types within thermoplastic fibres during melt spinning. This aspect can be referred to as the 'nanostructuring' of synthetic fibres, which is the focus of this chapter. Alternatively, it is possible to directly deposit novel and smart coatings conferring flame-retardant features to the fabric surfaces, including those of the component yarns and fibres (i.e., ceramic protective layers or flame-retardant species alone or coupled to ceramic protective layers). To this aim, novel approaches such as nanoparticle adsorption, layer-by-layer assembly, sol-gel processes, dual-cure processes, and plasma deposition will be described thoroughly in **Chapter 8**. **Figure 7.1** illustrates both strategies schematically.

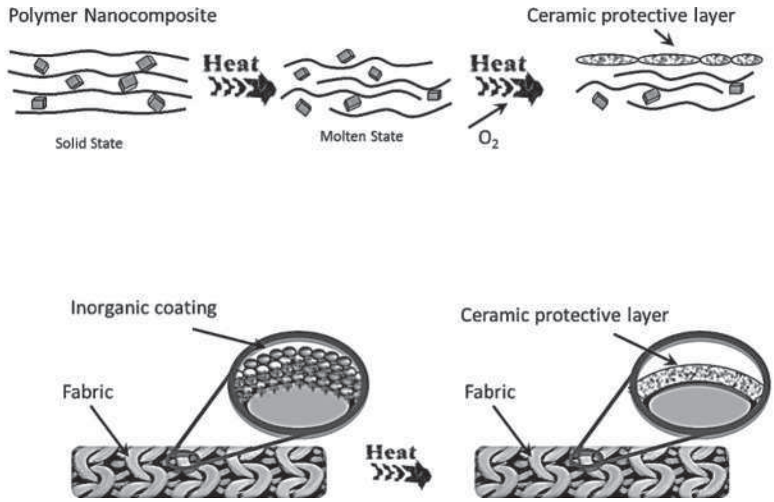

Figure 7.1 Strategies adopted to confer flame-retardancy properties to fibres and fabrics (schematic)

Given the concerns raised about environmental issues mentioned in **Chapter 4** and expanded in **Chapter 6** regarding halogen-containing flame retardants and those involving formaldehyde in their manufacture and application, nanotechnology seems to offer new perspectives as well as innovatory solutions. Because of their recorded tendency to increase char even in non-char-forming polymers such as polyester and polypropylene (PP), possible solutions to improving char-forming in derived fibres from these fusible polymers also exist. Not surprisingly, the nanostructuring of synthetic fibres and novel nanocoatings suitable for any type of flame-retardant fibre and textile (natural and synthetic) has been investigated very recently.

7.2 Nanostructuring of Synthetic Fibres

Nowadays, the application of nanotechnology to flame retardancy has become a consolidated research field that leads to many novel articles and reviews each year.

The term *nanotechnology* associated to flame retardancy is related to the use of additives (mostly inorganic or hybrid organic-inorganic) having different morphologies but with the restriction of possessing at least one dimension <100 nm, which enables them to be classified 'nanoparticles'. Nanoparticles are then introduced into a polymer matrix at ≤5 wt%, which is very low if compared with the standard concentration used for conventional flame retardants (20–30 wt%). These very low concentrations are related to the particle dimensions used that should be able to effectively disperse within the polymer without the formation of aggregates, thus resulting in a nanostructured material.

The potential applications of nanotechnology in terms of improving the flame retardancy and fire performance of fibres and textiles have been reviewed recently by Bourbigot [4] and Horrocks [5]. In particular, the application of nanotechnology to textiles must address the following issues:

- Compatibility between polymer and nanoparticle: this is crucial because the best performances can be achieved only if an acceptable degree of nanodispersion is obtained during processing. To this aim, a compatibiliser is often used for reducing the differences of surface tension between matrix and nanofiller, although it can also degrade at processing conditions and hence lose its effectiveness [6].

- Effect on rheology during extrusion or coating: the addition of nanoparticles usually increases the viscosity and shear stress sensitivity during melt extrusion and other polymer-blending processes, thereby increasing thermal degradation because of the high shear rate in the former case [7].

- Level of flame retardancy achieved: nanostructured materials show a great reduction of the heat release rate (HRR) measured by cone calorimetry. However, they more than often reduce the time to ignition and extend the burning time without affecting the total heat release [8].

Thus, nanotechnology can add improved fire performances directly to the fabric or to an already present flame-retardant system (e.g., a synergistic effect with a conventional flame retardant may occur [8]).

During the last decade, nanoparticles such as sodium montmorillonite, silica (or other metal oxides), magnesium hydrate phyllosilicates, carbon nanotubes or carbon nanofibres have been introduced within fibres showing high efficiency in reducing HRR but simultaneously presenting big drawbacks such as a reduced ignition resistance and a thickness-dependent performance, as described by Kashiwagi and co-workers [9, 10]. Indeed, thin samples show lower reductions in HRR because of the competition between formation of a carbonaceous-inorganic shield on the surface and volatilisation of the underlying polymer. In thick samples, shield formation is favoured whereas volatilisation dominates the phenomena occurring in thin nanocomposites [9–11]. As a result, in thin-fabric nanocomposites, the shield-forming effect (which is well known for bulk nanocomposites) may be too slow to ensure effective improvement of fire behaviour. Thus, a nanoparticle alone within fibres, films and textiles would be significant only if samples are tested at low heat fluxes.

However, as observed for bulk polymers, the next step is the combination of nanoparticles with conventional flame retardants to search for a possible synergistic or simple additive effect [11]. Most of the research articles published recently will be described below as a function of the type of thermoplastic fibre.

7.2.1 Polyamide 6 and Polyamide 6.6

Bourbigot and co-workers [12, 13] showed that nanocomposite polyamide 6 (PA6) fibres converted into fabrics having an area density of 1020 gm^{-2} and thickness 2.5 mm if exposed to 35 kWm^{-2} heat flux in a cone calorimeter had reduced peak heat release rate (PHRR) values (35%) with respect to pure PA6 fabrics. However, ignition resistance was reduced significantly and total heat release was little (if any) affected. Although there appeared to be higher char formation, it was clear that the fibres were not flame retardant in the more accepted sense in that ignition resistance would normally be increased.

Shanmuganathan and co-workers [14] showed that nanocomposite monofilaments with 10 wt% organo-modified montmorillonite (OMMT) burned slowly and steadily in a bunsen flame without dripping. In a cone calorimeter under a heat flux of 35 kWm^{-2}, nanocomposite fabrics with 8 wt% OMMT exhibited reduced HRR and mass loss rate compared with pure PA6 with increase in fabric tightness (≈40–60% less). In addition, the residue structure remained intact after burning.

In contrast to melt spinning, PA6/organo-modified Fe-OMMT nanocomposite fibres can be prepared by electrospinning [15]. Cai and co-workers have carried out studies about the carbonisation effect catalysed by Fe-OMMT on the thermal stability of PA6 electrospun fibres. Thermogravimetric analyses revealed that the presence of Fe-OMMT led to crosslinking of PA6, promoting formation of a charred residue and catalysing graphitisation. The presence of graphite sheets in the residue has been confirmed by X-ray diffraction, high-resolution transmission electron microscopy, selected-area electron diffraction and laser raman spectroscopy. The authors ascribe the possible carbonisation mechanism to: (i) the catalytic effect of Fe^{3+} species being able to promote PA6 crosslinking; (ii) Hofmann degradation of Fe-OMMT, whose degradation products can further promote PA6 crosslinking; and (iii) gas barrier properties of clay nanoplatelets capable of inhibiting or reducing the release of volatile pyrolytic products.

However, as observed for bulk polymers, combination of nanoparticles with conventional flame retardants can promote overall additive (and even synergistic) activity [11]. Work from our research teams has shown that this is possible in PA6 and polyamide 6.6 (PA6.6) films used as models for the respective fibres [16]. Normally, minimally flame-retardant additive contents of ≈15–20 wt% are required to render these polyamides (PA) flame retardant, levels which are too high for inclusion in conventional synthetic fibres. Additive and/or synergistic effects were observed for selected phosphorus-containing flame retardants in PA6 and PA6.6 polymer films (thickness, ≈80 µm) in the presence of commercial or experimental nanoclays. Of these, ammonium polyphosphate (APP) is not only the most synergistic but also has a decomposition temperature of 250–300 °C [17] and this overlaps with the melting point of PA6.6 (≈260 °C), which encourages flame-retardant mechanisms to start alongside polymer fusion. The effectiveness of adding nanoclay is shown by the ability to reduce by 25–33 wt% the concentration of APP necessary to create a defined level of flame retardancy. For example, to achieve limiting oxygen index (LOI) values ≤24% in PA6.6, addition of 2 wt% nanoclay reduced the normally required level of APP from 28.5 wt% to 20.1 wt%.

7.2.2 Polypropylene

Similar studies of nanoclays in the presence of flame retardants in PP have also been undertaken by our research team [16–20]. Initial work noted that addition of a nanoclay to a flame-retardant formulation based on a hindered amine stabiliser and a char-promoting APP at ≈5 wt% enhances char formation but cannot increase the LOI to >22% [18].

Later work considered the effects of nanoclays alone [19] as well as in the presence of more conventional flame retardants [20] in PP fibres and fabrics. **Table 7.1** presents data on composition and flammability for PP fibres and fabrics containing Cloisite® 20A clay and a maleate-grafted PP (Polybond® 3200, Crompton Corporation) at different concentrations [19].

Table 7.1 PP fibre compositions and fabric PHRR values [19]

Sample	Nanoclay (wt%)	Polybond (wt%)	Fabric area density (gm^{-2})	PHRR ± σ (kWm^{-2})
1	0	0	430	525 ± 40
2	2.5	0	400	477 ± 105
3	2.5	1	390	531*
4	2.5	3	430	420 ± 90

*Only one sample tested

All polymer samples were twice compounded to maximise dispersion before fibre extrusion. The presence of nanoclay alone (sample 2) promotes a decrease in PHRR determined by cone calorimetry under a heat flux of 35 kWm^{-2}. Addition of the compatibilising maleate-grafted PP suggests that, apart from sample 3, it causes further reductions in PHRR values. This is associated with improved dispersion, as shown by transmission electron microscopy micrographs reported in [19]. While there was insufficient fibre sample to enable LOI values to be obtained, values for cast films indicated that all samples had values within the range 19.6–20.0%, thereby confirming the absence of any flame-retarding property.

Subsequent work [20] investigated the effect of introducing the phosphorus-containing flame retardants APP, melamine phosphate and pentaerythritol phosphate, the hindered amine stabiliser NOR 116 (Ciba) [21], and the bromine-containing *tris*(tribromopentyl) phosphate and *tris*(tribromophenyl) cyanurate. These were compounded with the selected clays (Cloisite®20A and 30B, Southern Clays Inc.), Bentone 107 (a bentonite clay; Elementis), and a montomorillonite modified with vinyltriphenyl phosphonium bromide and compatibilisers (Polybond) as well as polypropylene grafted with diethyl-*p*-vinylbenzyl phosphonate. Extrusion into filaments proved to be challenging because of problems with optimising clay and flame-retardant dispersion, and this was especially the case if APP was present because of its very poor dispersion and relatively large particle size (25–30 µm). As a consequence, extrusion of these formulations often resulted in broken filaments and reduced tenacities and moduli.

LOI values were within the range 17.2–20.6% and so were largely unaffected by the presence of clays and/or flame retardant, but then the low concentrations of flame retardants present (5 wt% except for NOR 116 at 1 wt%) would not be expected to raise LOI values significantly if present alone [21]. However, the burning behaviours of knitted fabrics which were recorded as time-to-burn for successive 60-mm distances if subjected to the standard vertical strip test British Standard 5438:1989: Part 3, showed some dependence on the respective flame-retardant formulation. The collected results, however, suggested that the there is no synergism between Cloisite® 20A and APP (although the poor dispersion of the latter could have influenced the results).

Analogous results were achieved by our research team replacing montmorillonite with an organo-modified sepiolite (Tolsa). Indeed, under a heat flux of 35 kWm^{-2} PP compounds containing various concentrations of APP (15, 18 and 20 wt%) and sepiolite (2 and 5 wt%) a remarkable reduction of PHRR, total heat release (THR) and total smoke release (TSR) was observed, as shown in **Table 7.2** and **Figure 7.2**.

Table 7.2 Combustion data of PP compounds

Sample	TTI (s)	Δ (%)	PHRR (kW/m²)	Δ (%)	THR (MJ/m²)	Δ (%)	TSR (m²/m²)	Δ (%)	Residue (%)
PP	82 ± 8	-	827 ± 83	-	222 ± 22	-	3298 ± 330	-	3
PP + 20% APP	39 ± 4	-52	74 ± 7	-91	31 ± 3	-86	266 ± 27	-92	80
PP + 18% APP + 2%sepiolite	37 ± 4	-55	150 ± 15	-82	69 ± 7	-69	608 ± 61	-82	67
PP+ 15% APP + 5% sepiolite	36 ± 4	-56	278 ± 28	-66	198 ± 20	-11	643 ± 164	-80	21
TTI: Time to ignition									

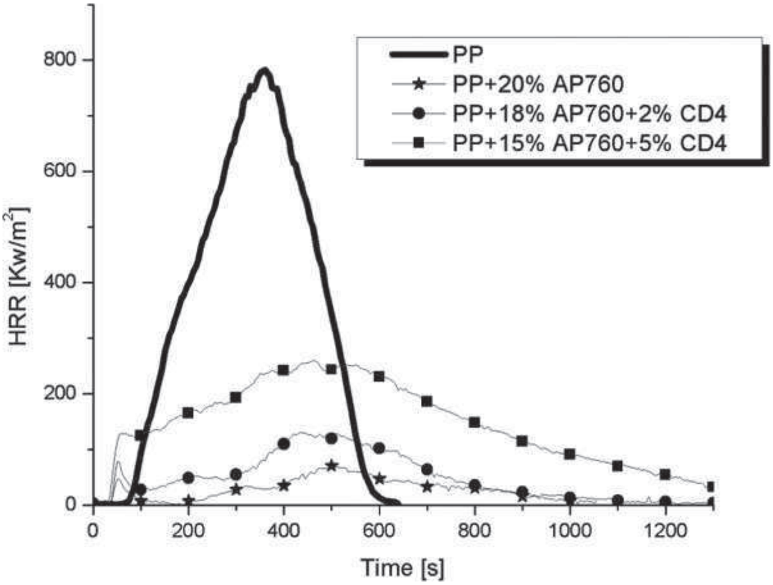

Figure 7.2 Heat release rate (HRR) curve of PP compounds

However, no significant enhancement was achieved by partially replacing APP with sepiolite. Obviously, if the compounds were melt spun, diluting PP + 18% APP + 2% sepiolite to 1 wt% in resulting fibres led to the same trend being observed. A possible synergism between APP and sepiolite does not occur.

Bourbigot and co-workers [22] also introduced poly(vinylsilsesquioxane) (POSS) nanoparticles at 10 wt% loadings in PP from which multifilament yarns and knitted fabrics were produced. Despite the promising results achieved by the same research team for PA6 nanocomposite fabrics [12, 13], no reduction in PHRR values occurred relative to the pure fibre-containing samples. However, under a heat flux of 35 kW/m^{-2}, the time to ignition increased from 21 s to 76 s for POSS-PP fabrics. Related work reported that introduction of 1 wt% multiwalled carbon nanotubes into PP filaments and fabrics [23] showed a 50% reduction in PHRR values if examined by cone calorimetry (at 35 kW/m^{-2} heat flux). However, as seen for the earlier

PA6 fabrics, the presence of nanoparticles reduced the time to ignition considerably from 60 s to 30 s.

7.2.3 Polyacrylics

Other recent work from our research team [24] has shown that fibre-grade poly(acrylonitrile) copolymer, if polymerised in the presence of a functionalised nanoclay, can absorb APP during filament extrusion and yield fibres having a LOI >40%. In these fibres, a clear synergy between nanoclay and flame retardant was observed, and filament properties were little changed from those acceptable for normal textile applications. Unfortunately, APP is not durable to water soaking or washing, so introduction of a crosslinkable or insoluble flame retardant would be required to achieve the required levels of launderability. Notwithstanding this observation, it is clear that clays in the presence of a suitable flame retardant benefit the overall fire performance of polyacrylic filaments in a manner similar to that observed in PA films [16].

7.2.4 Polyesters

More recent work by Bourbigot and co-workers [25] has extended their PA research to include nanoclays into melt-spun poly(lactic acid) (PLA) filaments where again loadings of ≤4 wt% reduce PHRR values by ≤38% and increase char yields at a heat flux of 35 kW/m^{-2}, but time to ignition (TTI) was still reduced. Fibres of PLA loaded with an OMMT or a natural sepiolite were produced *via* electrospinning by our research team [26]. The collected results showed a remarkable increase of thermal stability in nitrogen and air, strong reduction in oxygen permeability and, as a consequence, an increase in the fire resistance for the sample consisting of PLA and 10 wt% Cloisite®30B. Indeed, a 50 × 150 mm specimen did not drip when a 3 s methane flame was applied.

A reduction of TTI was also observed if poly(ethylene terephthalate) (PET) filaments containing 0.5 wt% carbon nanofilaments were tested as fabrics. Once again, nanoparticles on their own could not confer flame retardancy in terms of increasing ignition times (–20%), but they could strongly decrease PHRR (–45%) and TSR (–40%) [27].

In PET-based polymers, the char-enhancing effects of added functionalised montmorillonite clay were observed by Wang and co-workers [28] in a copolymer of PET and a phosphorus-containing comonomer (5 wt% 2-carboxyethyl(phenylphosphinic) acid), in which higher char residues >450 °C were recorded. Subsequent work showed that introduction of montmorillonite clay at 1, 2 and 3 wt% raised the LOI from 31.5 for the pure copolymer to ≈34% [29]. However, the Underwriter's Laboratories 94 test results increased from a V-2 rating at 0 and 1 wt% clay levels to V-0 at 2 and 3 wt%.

Very recently, our research team reported the compounding of several formulations comprising an expandable graphite (EG) intumescent with unmodified (Cloisite® Na, coded as CloNa) and organo-modified (Cloisite® 10A and 30B, coded as Clo10A and Clo30B) montmorillonite clays in PET [30]. All formulations appeared to have melting and thermal degradation behaviours similar to 100% PET at ≤450 °C in nitrogen and air. X-ray diffraction analyses suggested that the organo-modified clays generated intercalated nanocomposite structures whereas the native clay (CloNa) developed an exfoliated structure in PET. Cone calorimetric analyses at 35 kWm^{-2} heat flux confirmed the latter in that addition of 2.5 wt% EG and 2 wt% CloNa to PET reduced PHRR from 523 to 231 kWm^{-2} (the greatest reduction of all the formulations studied). Furthermore, this clay gave the highest increases in the LOI. The CloNa-containing formulations were diluted with PET and then spun into filaments (173.5 dtex/f48) containing very low clay levels of 0.25 wt% and converted to fabrics (area density, 152 gm^{-2}). Cone data from the fabrics showed that PHRR values were significantly reduced, as shown in **Figure 7.3**.

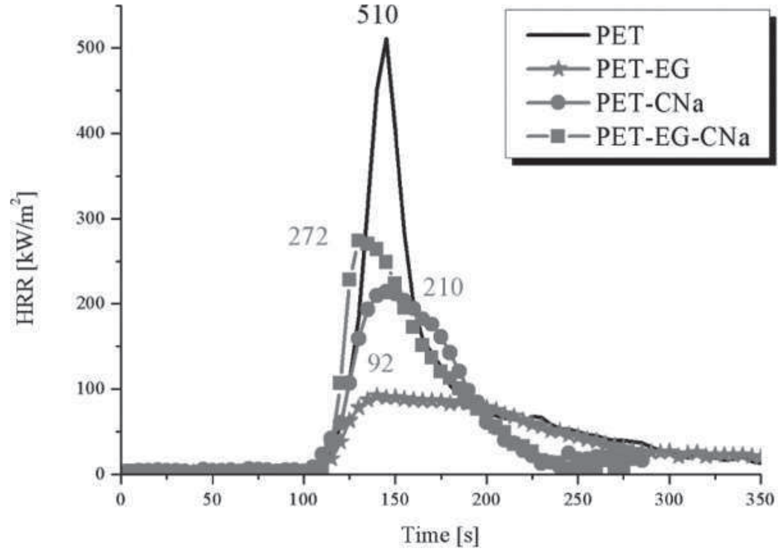

Figure 7.3 HRR curve of PET_EG_CloNa fibres [30]

A ranking of the filler type and content (from the most to the less efficient) as function of the PHRR variation could be established:

PET_EG (0.25 wt%) >> PET_CloNa (0.25 wt%) > PET_EG (0.25 wt%) CloNa (0.25 wt%) > 100%PET

This showed that, even though significant reductions were observed even at such low additive levels, the previously observed EG_CloNa synergy appeared to be absent.

In a parallel publication, our research team [31] studied the effect of adding zinc phosphinate (ZnP) and an organo-modified sepiolite to PET. In the bulk polymer formulations, evidence of ZnP-sepiolite synergy was presented with LOI values increasing from 22% for 100% PET to 30% and 33% for PET_ZnP and PET_ZnP_sepiolite formulations, respectively. Filaments produced containing 0.5 wt% inorganic content (173.5 dtex/f48) and derived fabrics (152 gm^{-2}) under scanning electron microscopy showed aggregates of submicron size. **Table 7.3** shows the collated flammability results from these fabrics, which demonstrate the potential retarding effectiveness of the PET_ZnP_sepiolite formulation. Interestingly, the ZnP_sepiolite combination can strongly reduce PHRR (as clearly seen in **Figure 7.4**) and does not have a negative effect on time-to-ignition values (114 *versus* 110 s for PET_ZnP_sepiolite and PET, respectively).

Table 7.3 Formulations and cone calorimetric data for PET fabrics containing ZnP and an organo-modified sepiolite [31]

Sample	Additive content (wt%)	Cone data (heat flux = 35 kW/m²)		LOI (%)
		TTI ± σ (s)	PHRR ± σ (kW/m²)	
PET	-	110 ± 5	510 ± 25	22
PET_ZnP	0.5	70 ± 3	361 ± 18	29
PET_ZnP_sepiolite	0.25 (ZnP); 0.25 (sepiolite)	114 ± 6	292 ± 15	31

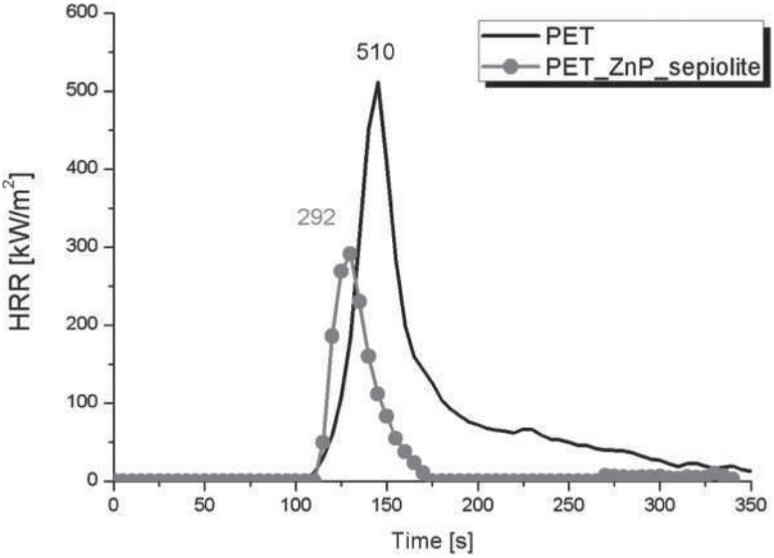

Figure 7.4 HRR curve of PET_ZnP fibres [31]

In conclusion, even though the research findings are mixed, there are some positive indications that introducing nanoparticles into fibre-forming polymers together with appropriate, more conventional flame retardants, can give rise to novel flame-retardant systems present at sufficiently low concentrations to have minimal effects on the other desirable textile properties required. Clearly, further research needs to be undertaken together with the very necessary scaling up to semi-scale plant extrusion before full commercial exploitation follows, but we consider that such work will be successful in the future.

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8

Smart (Nano) Coatings

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8.1 Introduction

As described in **Chapter 7**, nanotechnology has attracted great interest recently from industrial and academic research viewpoints. This chapter focuses on new perspectives as well as innovatory solutions achieved recently in the textile field based on the deposition of novel and potentially smart coatings able to confer flame-retardant features to fabric surfaces (including those of the component yarns and fibres). Principally, these relate to ceramic protective layers or flame-retardant species alone or coupled to ceramic protective layers. To this aim, novel approaches such as nanoparticle adsorption, layer-by-Layer (LbL) assembly, sol-gel and dual-cure processes, as well as plasma deposition will be described thoroughly. The advantages of such approaches in terms of flame-retardant properties achieved are highlighted together with the possibility of conferring multifunctionality to fabrics such as hydrophobicity, soil release, self-cleaning and bioactivity. **Figure 7.1**, as reported in the previous chapter, shows a scheme of the coating deposition.

One of the major goals in the research and development of new flame-retardant systems is the possibility of increasing char formation even in non-char-forming polymers such as polyesters and polyolefins. Thus, not surprisingly, novel nanocoatings as potential char enhancers and applicable to any type of fibre and textile (natural and synthetic) have been investigated very recently.

A major issue when considering surface flame-retardant treatments for fibres and textiles compared with other treatments is the high concentrations required to match those achieved using conventional methods. Indeed, if the level of flame retardancy to be conferred is to be acceptably high because the underlying substrate is highly flammable (as in the case of cotton), then the level of flame-retardant formulation applied may have to be in the range 20–100 wt% with respect to the underlying fabric, and the surface treatment will be quite thick (tens and possibly hundreds of microns). Thus, any novel or smart way of applying flame-retardant coatings must achieve such high levels of application, unless they have unexpectably high levels of effectiveness, which is a severe challenge unless the underlying fibres have a defined level of flame retardancy. Recent reviews [1–4] highlight the possibilities of conferring films and coatings at nano dimensions onto fibre and textile surfaces to achieve high levels of multifunctionality such as hydrophobicity, soil release, self-cleaning, and bioactivity.

Even assuming that the deposited nanofilms possess the required flame-retarding functions and efficiencies of conventional coatings, it is likely that none of these will be relevant to the present argument because of the need to use high loadings for achieving acceptable flame retardancy. However, the possibility of reducing the coating thickness while maintaining an overall acceptable level of flame retardancy can be fulfilled if the coating, instead of being coated on the textile surface, is applied to the fibre surfaces only. Taking into account the microfibre dimensions (diameter, 10 μm), the thickness of the surface layer on the increased surface area of the fibre reduces to ≈10 nm and at sub-microfibre dimensions (although, theoretically, thinner films can be obtained) [1].

Notwithstanding the discussion above, some level of heat and fire protection can be obtained using coatings or films applied at the nano level if they are not considered as simple replacements for conventional flame-retardant coatings. In usual flame-retardant textiles and coated fabrics, which can be classified as thermally thin materials [5] unless they are quite thick (>3–5 mm), the ability to form a thick, surface insulating char is limited and the underlying fibres, during their degradation, reach temperatures approaching that of the igniting source (>500 °C) and may ignite. However, a thermally thin textile can be converted into one showing 'thermally thick behaviour' and its overall fire-protective character will increase. Several conventional surface treatments and coatings, especially those comprising intumescent additives, attempt to do this. It is highly unlikely that nanocoatings could promote a similar effect unless they could offer a heat-shield effect of unusual efficiency.

8.2 Nanotechnology in Coatings and Back-coatings

Nanotechonology has also been applied in fire-retardant polymeric coatings and back-coatings.

Bourbigot and co-workers investigated the use of polyurethane coatings containing nanoclays and poly(silsesquioxanes) for conferring flame retardancy to cotton and polyester fabrics. Experimental data showed a reduced peak heat release rate (HRR) but, at the same time, shortened time to ignition (TTI) values and prolonged burning times, which is opposite to what is expected from a flame-retarded coating [6–8]. For example, under a heat flux of 35 kWm^{-2}, the TTI of polyamide 6 (PA6) fabric occurs at 70 s and HRR values increase to 400 kWm^{-2}. A *plateau* is observed between 125 s and 160 s and then HRR values fall to zero. For the PA6 nanofabric, however, the TTI occurs at 20 s and the *plateau* is observed at 250 kWm^{-2} between 50 s and 150 s (a reduction of 40% with a respect to pure PA6). In this last case, HHR values decrease slowly after the *plateau* to zero [7].

In a parallel publication, Dubois and co-workers [9] showed that Closite® 30B can be used to increase the mechanical and thermal properties of polyurethane coatings.

As demonstrated by Horrocks and co-workers [10], the effectiveness of a back-coating is related to its ability to transfer flame retardancy activity to the fabric; this is essential, especially if the flame is applied to the front face of the fabric. In general, the use of char-forming back-coatings (including those containing nanoparticles) does not allow the above-mentioned transfer to occur. Indeed, the flame-retardant species should be able to move through the fabric to the front face, where the flame is applied. Furthermore, it has been shown that the addition of nanoclay alone to back-coatings has no beneficial effects. It was also noted that if fumed (nano) silica was added with ammonium polyphosphate to the back-coating formulation, not only was there an adverse effect with respect to formulation rheology, but also the flame-retardant character (as determined by the limiting oxygen index (LOI)) was reduced with increasing silica content [11].

8.3 Smart (Nano) Coatings

Nowadays, much scientific effort is focused on surface modifications as after-treatments capable of changing or adding different properties to the selected textile. Such after-treatments should have minimal effects on the underlying fabric properties. Therefore, they must rely on surface modifications and coatings ranging between micro- and nano-levels. This also implies the interesting possibility of producing smart coatings that may theoretically be applied to any kind of fibre.

These smart coatings have a complete inorganic or hybrid organic-inorganic composition. They can be generated by using different approaches, i.e., exploiting the following top-down and bottom-up strategies [12]:

- Nanoparticle adsorption
- LbL deposition
- Sol-gel treatments
- Cold plasma deposition
- Biomacromolecular engineering

8.3.1 Nanoparticle Adsorption

Nanoparticle adsorption represents the easiest way of pursuing a surface modification using nanoparticles. It involves immersion of the fabric into an aqueous suspension of nanoparticles to promote their adsorption on the fibre surface, similar to normal finishing treatment (e.g., impregnation/exhaustion). Our research team recently demonstrated that it is possible to achieve enhanced flame-retardancy properties for polyester, cotton and their blends using this simple method to create a nanocoating and so mimic the impregnation/exhaustion steps currently employed as finishing treatments for industrial applications. In doing so, an inorganic shield may be deposited on the fibre surface that can protect the surrounding polymer from heat and flame. To evaluate the flame-retardancy properties of such treated fabrics, an optimised procedure has been created using cone calorimetry for fabrics [13] and fibres [14]. As is well known, this instrumentation was designed for plastic substrates having a mass of ≥80 g and a thickness of 6 mm, and not for testing thin materials such as fabrics. However, several methods have been established that attempt to overcome this problem [13–15]. Indeed, to describe a realistic fire scenario, it is important to test the ignitability of a sample and subsequent flame spread as well as the combustion behaviour of the same sample under irradiative heat flow developed as a consequence of flame exposure (i.e., within a scenario similar to that created in a cone calorimeter).

As far as poly(ethylene terephthalate) (PET) is concerned, hydrotalcite, titania, silica [16] and Cloisite® Na (CloNa) [17] have been investigated. Several experimental conditions such as immersion time, pH of the nanoparticle dispersions, and surface pre-treatment (by cold oxygen plasma) have been studied. On the basis of the results collected by cone calorimetry, it is possible to conclude that hydrotalcite is the most promising nanoparticle under study [16] due to the increase of TTI values in comparison with silica and titania at a fixed immersion time of 60 min. Further experimentation with (i) pH variation of the nanoparticle suspension and (ii) surface pre-treatment of the PET fabrics using cold oxygen plasma allowed even better flame-retardant properties, as compared with the standard procedure. Furthermore, the TTI values obtained suggest that the flame-retardant properties of PET can be improved further by combining different nanoparticles such as hydrotalcite and silica.

For unfunctionalised sodium montmorillonite clay, PET fabrics (twill 2/1, 167/330 dtex, warp 47 and weft 22, density of 171gm^{-2}) were plasma-treated to encourage nanoparticle adsorption and to create a functional coating with thermal stability and flame-retardant properties [17]. Thus, plasma surface activation using different process parameters (power and etching time) was combined with nanoparticle adsorption by simple dipping. Cone calorimetry results showed that plasma pre-treatment can enhance the effect of adsorbed nanoparticles during combustion, increasing clay surface density and making stronger the interaction between the inorganic nanoparticles and PET fabric surface. The best sample, sample 6 in **Table 8.1**, which was obtained by previous plasma pre-treatment of 180 s at 80 W of power gives TTI = 322 s *versus* 158 s for untreated PET, equivalent to an increase of 104% and accompanied by a 10% reduction of the peak heat release rate (PHRR).

Table 8.1 Etching conditions and combustion data by cone calorimetry of PET fabrics previously plasma-treated and subsequently dipped in an aqueous suspension of CloNa [17]

Sample	Power (W)	Etching time (s)	TTI ± σ (s)	PHRR ± σ (kWm^{-2})	THR ± σ (MJ/m^{-2})
Reference	–	–	158 ± 4	90 ± 9	2.5 ± 0.4
Sample 1*	–	–	198 ± 8	105 ± 2	2.8 ± 0.4
Sample 2	120	15	244 ± 21	85 ± 7	2.4 ± 0.4
Sample 3	120	60	261 ± 10	89 ± 2	2.6 ± 0.1
Sample 4	120	180	192 ± 34	94 ± 12	2.3 ± 0.4
Sample 5	50	180	241 ± 10	92 ± 9	2.2 ± 0.8
Sample 6	80	180	322 ± 29	81 ± 18	1.8 ± 0.4

*Sample 1 was dipped only in an aqueous suspension of Cloisite® Na
THR: Total heat release

Referring to natural fibres, it has been demonstrated that the same nanoparticles employed for PET can also impart good flame-retardancy properties to the cotton fabrics [18]. Surface pre-treatment with cold oxygen plasma has been also combined with the immersion process to increase nanoparticle uptake onto the textile fibres. A homogeneous distribution of nanoparticles onto textiles has been assessed by electron microscopy coupled with elemental analysis on the samples with and without pre-treatment. The immersion time was found to be a function of the nanoparticle type. Indeed, the highest loading was achieved at 30 min for silica, whereas for hydrotalcite no significant differences between 30 min and 60 min were noticeable. For samples pre-treated with plasma, a general increase in the uptake of both types of nanoparticle was observed. Both types of nanoparticle increased the TTI and decreased the PHRR. When the nanoparticles were mixed together, a further improvement in flame retardancy was achieved.

These results agree with those published by Horrocks and coworkers [19], who demonstrated that formation of an inorganic coating is responsible for changes in the ignition behaviour of cotton under high heat flux. If the cotton is pre-treated with plasma and subsequently treated with functionalised clays or a polysiloxane, an inorganic coating that confers reduced flammability is formed. In an alternative experiment in our research team, cotton was linked using different binders to boehmite modified by sulfonate salts (BOE) or a poly(vinylsilsesquioxane) (POSS) carrying eight n-propylammonium chloride groups [20]. Scanning electron microscopy (SEM) and elemental analysis showed that these nanoparticles were distributed homogeneously on the surface of cotton fibres and finely dispersed at a nanometric level. Furthermore, the nanoparticles were found to have a protective role in the thermo-oxidation of the cotton, modifying its degradation profile. They also enhanced the thermal stability of cotton in air, favouring carbonisation and thus increasing the final residue at high temperatures, slowing down the overall thermo-oxidation kinetics. Cone calorimetry data demonstrated that the kinetics of the cotton combustion process was modified by nanoparticle treatment, compared with that of neat cotton. TTI increased and PHRR decreased up to 40% if POSS is used (**Table 8.2**).

Table 8.2 Sample formulations, cone calorimetry data and LOI values of untreated and treated cotton fabrics [20]

Sample	Binder type	TTI (s)	PHRR ($kWm^{-2}g^{-1}$) (reduction %)	LOI
Cotton		14	57	19
NP=BOE (1% (on weight fabric))				
Cotton + BOE	–	22	50 (–12)	19
Cotton + A	A = blocked bifunctional isocyanates	18	38 (–33)	19
Cotton + A + BOE		22	41 (–28)	20
Cotton + B	B = blocked bifunctional isocyanates	20	37 (–35)	19
Cotton + B + BOE		20	45 (–18)	19
Cotton + C	C = dicyanamide-formaldehyde polymer	17	42 (–26)	19
Cotton + C + BOE		20	36 (–37)	20
Cotton + D	D = melamine formaldehyde (MF)	20	39 (–32)	20
Cotton + D + BOE		21	35 (–39)	20
Cotton + E	E = dimethylol dihydroxyethylene urea (DMDHEU)	16	43 (–25)	19
Cotton + E + BOE		20	46 (–19)	19
NP = POSS				
Cotton + POSS	-	18	35 (–39)	20
Cotton + E + 1% POSS	E = DMDHEU	22	34 (–40)	20
Cotton + E + 2% POSS		34	30 (–30)	21
Cotton + E + 5% POSS		26	30 (–30)	21

NP: Nanoparticle

Unfortunately, the investigated nanoparticles cannot increase the LOI value of cotton. Simple nanoparticle adsorption has been exploited also by Liu and co-workers [21], who have carried out the functionalisation of common cotton fibres with carbon nanotubes (CNT). It was demonstrated that the cotton fabrics treated by CNT exhibit enhanced mechanical properties, extraordinary flame retardancy, improved ultraviolet (UV)-blocking and super water-repellent properties.

8.3.2 Layer-by-Layer Assembly

Nanoparticle adsorption can be repeated multiple times (using different reagents at each adsorption step), leading to a multistep process known as 'LbL assembly' [22].

This step-by-step film build-up based on electrostatic interactions was introduced in 1991 for polyanion/polycation architectures to obtain 'polyelectrolyte multilayers' [23] and was subsequently extended to inorganic nanoparticles [24]. The procedure for obtaining such multilayer films requires alternate immersion of the substrate into an oppositely charged polyelectrolyte solution (or nanoparticle dispersion). This process, which leads to a total surface-charge reversal after each immersion step [25], creates a structure of positively and negatively charged layers 'piled up' on the substrate surface (**Figure 8.1**).

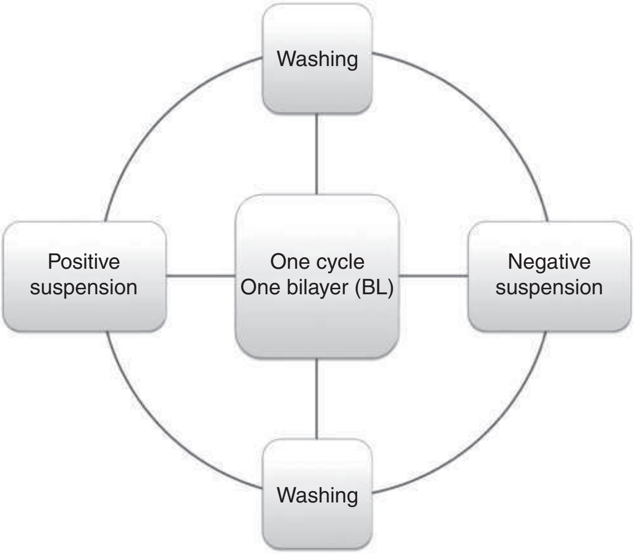

Figure 8.1 LbL assembly (schematic)

LbL was first described in 1966 [26] and was rediscovered and optimised decades later [22, 27–29]. More specifically, this self-assembly method has been used to impart barrier properties toward oxygen [30], anti-reflectivity [31], electrical conductivity [32–34], and antibacterial features [36–38].

Very recently, such an approach proved to be extremely advantageous if exploited for the flame retardancy of foams [39, 40] plastics [41, 42], thin films [43, 44] fibres and fabrics.

8.3.2.1 Inorganic Layer-by-Layer Coatings Deposited by Dipping

The first attempt in the textile field was carried out by Grunlan and co-workers on cotton fabrics, who built architectures consisting of a lamellar clay (i.e., laponite, negative counterpart) coupled with a branched polyethylenimine (positive counterpart). Vertical flame testing (American Society for Testing and Materials (ASTM) D6413 standard) showed that 10 BL do not significantly improve the flame-retardancy properties of cotton because similar ignition and afterflame times were observed (although the afterglow times for coated fabrics were 8–10-s less than those of the uncoated fabrics). However, at the end of the test, the final residue of the treated fabrics appeared incoherent and fragile [45]. This problem has been partially solved by replacing laponite with sodium montmorillonite [46]. Better results were achieved if a completely inorganic coating was deposited on cotton fabrics [47–51].

Indeed, thin films of colloidal silica (silica(+)/silica(–)) [50] and of polyhedral oligomeric silsesquioxanes, POSS® (octa-3-ammoniumpropyl POSS(+)/octakis (tetramethylammonium) pentacyclo [9.5.1.$1^{3.9}$,$1^{5,15}$.$1^{7,13}$] octasiloxane 1,3,5,7,9,11,13,15-octa kis(cyloxide)hydrate POSS(–) [51] could enhance the thermal stability of cotton, favouring char formation in air, hence leaving a residue after the vertical flame test. In addition, these coatings exhibited a significant reduction of the PHRR (approximately –20%), as assessed by a micro cone calorimeter.

At the same time, our research team has exploited the same approach to solve the problem of flammability and dripping of PET. More specifically, nanoarchitectures consisting of silica nanoparticles [52] or α-zirconium phosphate nanoplatelets with different counterparts (i.e., polydiallyldimethylammonium chloride, polyhedral oligomeric silsesquioxanes, or alumina-coated silica nanoparticles) have been investigated [53]. LbL assemblies of colloidal alumina coated silica (+) and silica (–) were deposited on PET with the aim of reducing its flammability [52]. Two systems were investigated using large (30 nm) and small (10 nm) negative colloidal silica alternated with positively charged alumina-coated silica (10 nm). The flammability and combustion properties of the fabrics were found to be greatly influenced by the morphology of the coating and its physical stability during testing. The coatings were found to improve the fire properties of the fabric as long as an effective inorganic barrier was maintained through continuous coverage of the fibres. Cone calorimetry results showed that the best system for PET contained the smallest nanoparticles (i.e., 10 nm), which increased TTI by 99 s (≈45%) and reduced PHRR by 20% with 5 BL. The same system tested with a vertical flame test (ASTM D6413 standard) could reduce the burning time by 95% and eliminate melt dripping, which is one of the most significant issues for PET.

This ability to dramatically reduce the flammability of PET fabric using an environmentally sustainable process and relatively few BL (5–10) makes LbL a promising alternative to current textile treatments. Indeed, the great advantage of this novel method is represented by the use of water as solvent, relatively low nanoparticle amounts (0.2 wt%) and the possibility of recycling the suspension bath after use. Recently, novel LbL coatings have been prepared by alternatively assembling α-zirconium phosphate nanoplatelets with a cationic polyelectrolyte (polydiallyldimethylammonium chloride), a polyhedral oligomeric silsesquioxane or with alumina-coated silica nanoparticles [53]. The nanostructured assemblies obtained were applied to PET fabrics to enhance their thermal and fire stability, with particular attention to the reduction of smoke and toxic gases (and especially carbon monoxide produced during combustion). The thermal and thermo-oxidative stability of the treated fabrics was improved significantly. Other improvements included an increased TTI (+86%), a lowered HRR (–26%) and a significant decrease in smoke release rate (–25%) and production of carbon monoxide (–35%).

8.3.2.2 Hybrid Organic-inorganic or Intumescent Layer-by-Layer Coatings Deposited by Dipping

Although the collected results in the section described above appear extremely advantageous, flame suppression has not been achieved by employing a completely inorganic coating. Hence, fire protection through intumescent systems has been considered to be an effective alternative to fire protection by inorganic barriers because intumescent systems act as flame retardants in the condensed phase during combustion. For this reason, the attention of several researchers has been focused recently on the possibility of creating different architectures having intumescent or intumescent-like behaviour. As mentioned above, if an intumescent material is subjected to heat flow, it develops a carbonaceous shield (char) on its surface. This protection acts as a physical barrier that can limit the transfer of heat, fuel and oxygen between the flame and polymer. Usually, the intumescent material consists of an acid source, a carbon source and a blowing agent that releases considerable amounts of expandable or non-combustible gases upon heating [6–8].

Pursuing this research, our research team has deposited architectures with intumescent-like features on cotton-rich polyester blends (70% and 30%, repsectively). These coatings consist of 5 BL and 10 BL of ammonium polyphosphate (APP) and chitosan and 5 BL and 10 BL of APP and silica [54]. In particular, the chitosan-APP pair represents an intumescent-like system in which chitosan can act as a carbon source and foaming agent, whereas APP produces phosphoric acid *in situ* at high temperatures, thereby favouring char formation. Conversely, the silica-APP pair exploits the joint effect between the phosphoric acid generated by APP that induces the carbonisation of the polymer, and the thermally insulating behaviour of a ceramic precursor such as silica. The two systems under study turned out were found to be responsible for overall enhancement of flame retardancy. Indeed, both coatings could suppress the afterglow phenomenon and leave a residue of 7 wt% after the flammability test. In the case of chitosan-based assemblies, the residue appeared more coherent than that left by silica. Furthermore, the silica/APP system showed a significant increase in TTI and a strong decrease in the total heat release during cone calorimeter tests.

With the same components, more complex architectures consisting of BL+BL or QL (namely chitosan/ammonium polyphosphate BL alternated with silica/silica BL or silica/silica/chitosan/ammonium polyphosphate quadlayers (QL)) have been investigated as well [55]. Thus, it was possible to evaluate the effect of the architecture complexity derived from the quadlayer structure with respect to the BL plus BL counterpart. The most interesting result refers to the formation of a more coherent and homogeneous coating present at the end of vertical flame and cone tests when the quadlayer architecture has been deposited on the fabrics. This phenomenon is considered to be responsible for slowing down the thermal decomposition of the blends.

Also in the case of cotton, the intumescent systems were found to be the most promising flame-retardant strategy, as demonstrated by Grunlan and coworkers [56, 57], although the macroscopic blowing effect typical of an intumescent system in the true chemical sense was not observed. However, worthwhile results have been achieved when poly(sodium phosphate) (PSP) and poly(allylamine) (PAAm) were coupled in architectures having a different number of BL (5, 10 and 20 BL). In such systems, PSP (negative counterpart) and PAAm (positive counterpart) act as the acid source and blowing agent, respectively. The intumescent formulation is completed by the presence of the cellulose fibre itself, which acts as the carbon source. Vertical flame tests have shown that the coating protects the fibres by forming a swollen layer, which preserves the fabric from burning further while maintaining the texture, structure and integrity of the fibre. The same authors also claim that the nature of the investigated coating is not properly intumescent because of the absence of voids and of an expanded structure in the final residue after combustion. However, this coating feature can be considered 'intumescent-like'. In addition, the micro cone calorimeter registered a significant decrease of the total heat release and PHRR if 10 BL are deposited (approximately –76 and –62%, respectively) [56].

Pursuing this research further, the possibility of depositing intumescent multilayer nanocoatings made with renewable polyelectrolytes has been investigated recently [57]. In particular, the possibilities of having a phosphorus-nitrogen-based flame retardant from renewable sources have been assessed. As is well known, the history of flame retardants for cellulosic substrates has demonstrated that the only way for blocking the combustion of cotton (and other cellulosic fibres) while avoiding the presence of halogens and their derivatives is the use of phosphorus-nitrogen-based flame-retardant systems in which the P/N molar ratio is ≈1:2. This system also favours char formation (and thus the dehydration route, see **Figure 2.4**, **Chapter 2**) and inhibits the production of volatiles (and thus chain depolymerisation). However, Grunlan and coworkers have made the first attempt of using LbL components originating from renewable sources [57]. More specifically, they have coupled phytic acid (which is the major storage form of phosphorus in cereal grains, beans and oil seeds) with chitosan (obtained from the shells of crustaceans) and applied the resultant adduct to cotton. By assessing the final properties by vertical flame tests and micro cone calorimetry, it was demonstrated that the thinnest coating (30 BL; thickness, 10 nm) can completely stop flame propagation on cotton fabrics and so reduce the PHRR (approximately –50%).

All the results achieved in the last 3 years exploiting the LbL approach have shown that the key for imparting flame retardancy to natural and synthetic fibres focuses on the production of char, including blends in which each componet may have differeing thermal degradation mechanisms.

Based on these principles, our research team has applied complex architectures (i.e., QL) having a char-forming character on cotton, polyester and their blends [58]. Here, different numbers of QL (1, 5 and 10) consisting of poly(diallydimethylammonium chloride)/poly(acrylic acid) (PAA)/poly(diallydimethylammonium chloride)/APP have been deposited on the chosen fabrics and investigated. Thermogravimetric analysis (TGA) coupled with isothermal tests undertaken in a gravity convection oven at fixed temperatures have shown that such architectures can strongly enhance char formation in a remarkable way, as reported in **Table 8.3**.

Table 8.3 TGA data for cotton, polyester, their blends and LbL-treated fabrics in nitrogen and air [58]

Sample	**Residue at 700 °C (%) by TG in nitrogen**	**Residue at 700 °C (%) by TG in air**
COT	8	–
COT 1 QL	25	–
COT 5 QL	30	–
COT 10 QL	29	–
COT	–	0
COT 1 QL	–	3
COT 5 QL	–	8
COT 10 QL	–	11
PET	10	–
PET 1 QL	16	–
PET 5 QL	28	–
PET 10 QL	32	–
PET	–	0
PET 1 QL	–	9
PET 5 QL	–	14
PET 10 QL	–	22
COT-PET	14	–
COT-PET 1 QL	24	–
COT-PET 5 QL	29	–
COT-PET 10 QL	29	–
COT-PET	–	0
COT-PET 1 QL	–	2
COT-PET 5 QL	–	8
COT-PET 10 QL	–	9

COT: Cotton
TG: Thermogravimetric

Furthermore, infrared spectroscopy has shown that these coatings can promote formation of a char having an aromatic nature, regardless of the QL number and fabric type. This finding is very important because chars normally derived from polymer combustion usually show a lower stability with respect to pure graphite, which is highly stable to heat and oxygen as a consequence of the efficient van der Waals interactions between the closely packed polynuclear carbon layers. Thus, these coatings seem to be able to induce formation of a thermally stable aromatic char that protects the textile substrates (regardless of type) from the application of a flame (as assessed by vertical and horizontal flame tests) or to different external heat fluxes (as assessed by cone calorimetry). Indeed, the coatings could enhance remarkably the char formation of each substrate after just 1 QL deposition. Furthermore, 5 and 10 QL assemblies favoured the formation of intumescent structures with further improvement of the final residue. As a consequence, the treated fabrics have shown a strong reduction in flammability in terms of afterglow, suppression of flaming melt drips, and reduced heat release. Infrared spectroscopy has confirmed the aromatic nature of the residues left after combustion, in agreement with the data from TGA [59].

The use of PAA as component in a LbL assembly has been also investigated by Huang and co-workers [60]. More specifically, they have synthesised a new type of flame-retardant system acting in the gas-phase exploiting the LbL approach (unlike the previously discussed studies in which the coating is effective only in the condensed phase). A flame-retardant poly(acrylic acid) copolymer produced by free-radical polymerisation of acrylic acid with **N**-2-(5,5-dimethyl-1,3,2-dioxaphosphinyl-2-*g*-amino)-ethylacetamide-2-propenyl acid, coupled further with sodium montmorillonite platelets, was prepared. Application of 20 BL produced a significant increase in TTI (approximately +40%) and of a strong reduction of total heat release and PHRR (approximately –50 and –18%, respectively).

Analogous results have been achieved by the same authors on cotton, assembling thin films of intumescent flame retardant-polyacrylamide and exfoliated graphene oxide *via* LbL [61].

8.3.2.3 Inorganic Layer-by-Layer Coatings Deposited by Spray

All of the articles mentioned above refer to LbL assemblies obtained through the dipping method. However, spraying could represent an appealing alternative to dipping due to its efficiency and feasibility at an industrial scale, as reviewed recently and thoroughly by Schaaf and coworkers [62]. They described the basics and application fields of LbL deposition by vertical spray. The first attempt of spray-assisted LbL was carried out by Schlenoff and co-workers [63]: LbL films consisting of poly(styrene sulfonate) (PSS) and poly(diallyldimethyl ammonium chloride) layers were deposited by dipping or spraying. Results have shown that both methods allow the same high level of uniformity of deposited coatings.

Similar results have been found by Izquierdo and co-workers [64], who coupled poly(allylamine hydrochloride) with PSS and investigated the efficiency of dipping *versus* spraying. Once again, the uniformity and homogeneity of the LbL coatings obtained by vertical spraying were comparable with those from dipping, with the additional advantage of the very short deposition time (3 s) during the former.

Although the spray method can also be exploited for covering larger surfaces with respect to dipping, the number of applications of spraying is extremely poor and limited to bioactive materials, surface protection, and coatings with enhanced optical properties [62]. To the best of the authors' knowledge, the first attempt to use spraying to impart flame retardancy was carried out by our research team [65]. More specifically, silica-based architectures by dipping and vertical/horizontal spraying have been deposited on the cotton surfaces to form LbL assemblies. The fire performances of the coated cotton fabrics, evaluated through flammability and fire tests, have been related to the resultant morphologies as assessed by SEM, thereby allowing a comparison of efficiency among the three approaches mentioned above. In particular, SEM observations have shown that the most homogeneous and consistent depositions were achieved using the horizontal spray, which has been shown to confer the best flame-retardancy properties. A significant increase in TTI (approximately +40%) and decrease in PHRR and total smoke release values (–30 and –20%, respectively) as well as an appreciable decrease in the burning rate, were assessed by cone calorimetry and flammability tests, respectively. With respect to vertical spraying, this configuration can be extremely effective in avoiding drip patterns in the mobile film, thereby leading to formation of a homogeneous and compact silica coating. These conclusions agree with those reported in the literature [66].

8.3.3 Sol-gel Treatments

The sol-gel method has already shown its potential with regard to the synthesis of new materials with a high degree of homogeneity at the molecular level and with extraordinary physical and chemical properties [67]. The process is a versatile synthetic route based on a two-step reaction (hydrolysis and condensation) starting from semi-metal alkoxides (e.g., tetraethoxysilane, tetramethoxysilane, titanium tetraisopropoxide, aluminiumisopropoxide), that leads to formation of completely inorganic or hybrid organic-inorganic coatings at or near room temperature. Several process parameters must be considered, including the nature of the semi-metal atom and alkyl/alkoxide groups, the structure of the semi-metal alkoxide, water/alkoxide ratio, pH (acidic or basic conditions), temperature, reaction time and presence of co-solvents. These parameters determine the structure/morphology of the resulting ‘oxidic networks’ [67]. A schematic representation of the process is reported in **Figure 8.2**.

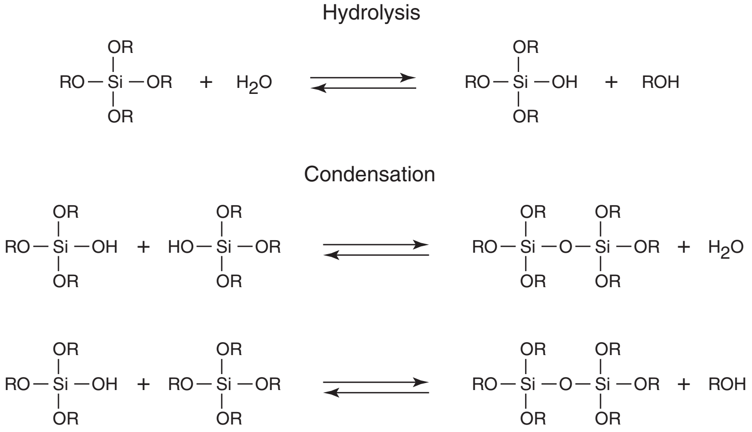

Figure 8.2 Sol-gel process (schematic)

The use of sol-gel processes for obtaining silica nanoparticles to melt blend with bulk polymers is very well documented and several authors have investigated the possibility of reducing the flammability of epoxy resins [68–72], phenolic resins [73, 74], polymethylmethacrylates [75] and polyesters [76] by employing silica phases derived from sol-gel processes. However, fumed or fused silica has shown less efficiency than that of sol-gel-derived silica in the flame retardancy of polypropylene and polyethylene oxide, as reported by Kashiwagi and co-workers [77].

With respect to textiles, usually the sol-gel approach has been proposed for introducing new functional features such as antimicrobial or UV-radiation protection [78–83], dye fastness [84, 85], anti-wrinkle finishing [86], super-hydrophobicity [87–89], biomolecule immobilisation [90], photocatalytic properties [91, 92] and sensor applications [93, 94]. Sol-gel processes have been known from the 1950s, but their application in the flame retardancy of textiles is very recent, and has been documented only in the last few years. For thermally thick polymers (thickness >3–5 mm), it has been clearly demonstrated that sol-gel-derived hybrid architectures can protect the polymer surface by acting as a thermal insulator, thus improving the flame retardancy of the treated substrates by a thermal shield effect. Indeed, by absorbing heat from the surrounding area, these architectures can protect the polymer substrate by creating a physical barrier to the transfer of oxygen and heat, hindering the formation of volatile species that fuel further degradation and, simultaneously, favouring char formation [95]. Thus, such systems operate only in the condensed phase during the combustion of a polymeric material and not in the vapour phase (**Figure 2.7** in **Chapter 2**). However, textiles are thermally thin materials [5] (see **Chapter 2**) upon which surface coatings exert less of a protective shield to the underlying polymer, so sol-gel-derived architectures cannot considered to be fully effective flame-retardant systems unless functioning in synergistic or joint effects achieved by combining the sol-gel oxidic phases with other flame-retardant active species such as phosphorus and/or nitrogen-containing agencies. In parallel, evolution of the sol-gel strategy as a dual-cure process has occurred in terms of a photopolymerisation reaction followed by thermal treatment for promoting the formation of silica phases. This novel approach has also been exploited for preparing hybrid organic-inorganic protective coatings.

These developments will be described in the following sections on the basis of the type of synthesised architecture.

8.3.3.1 Inorganic Architectures

Sol-gel processes can be undertaken to deposit pure oxidic phases on fabrics. Hribernik and co-workers [96] have exploited such a synthetic strategy as an alternative route for reducing the flammability of regenerated cellulose fibres (i.e., viscose). To this aim, viscose fibres pre-treated with sodium hydroxide were impregnated with a mixture of tetraethylorthosilicate (TEOS), ethanol, water and ammonia (as a condensation catalyst). The silica coating obtained (thickness, 350 nm) improved thermal stability and, as a consequence, the flame resistance of the viscose fibres. Indeed, the temperature of their first degradation increased by 20 °C, the temperature of flame combustion of volatile products by ≈20 °C, and the temperature of glowing combustion of the residual char by >40 °C, with respect to untreated fibres. Even the application of SiO_2-TiO_2 and SiO_2-Al_2O_3 mixed nanosols to textile filters was shown to improve the heat resistance of cellulose [97].

Similar results have been achieved by our research team in the case of cotton, polyester and their blends [98]. Indeed, formation of a continuous silica film deposited on the fibres has been found to exert a protective role with regard to their degradation in nitrogen and air. In addition, such films can reduce heat release rate during combustion, as assessed by cone calorimetry. For example, under a 35 kWm^{-2} heat flow, the sol-gel-treated 35/65 cotton/polyester blend showed a remarkable TTI increase (≤98%) and a strong decrease in PHRR (≤34%) with respect to the untreated counterpart.

Alternatively to TEOS, tetramethylorthosilicate (TMOS) has been employed as a silica precursor because of its complete solubility in water [99]. The various process parameters outlined above (e.g., nature of semi-metal atom and alkyl/alkoxide groups, structure of the semi-metal alkoxide, water/alkoxide ratio, pH, temperature, reaction time and presence of co-solvents) that influence formation of a homogeneous and continuous film of the resulting oxidic networks on a substrate surface must be considered.

To this end, the conditions of the sol-gel process (i.e., molar ratio of precursor:water; temperature; time of thermal treatment; the fabrics subjected to treatment after impregnation with the sol solution) have been optimised, including achievement of high durability to washing [99]. Cone calorimetry tests showed that the best fire performances of cotton fabrics are achieved if the sol-gel process is carried out at 80 °C for 15 h using a molar ratio of TMOS:H_2O of 1:1 to yield increases in TTI of 56% and of PHRR of 15%) These improvements were attained even though solid-state ^{29}Si-nuclear magnetic resonance (NMR) analyses showed that the degree of condensation was always <80%. Despite this fact, the level of silica distribution as well as dispersion on and within the fabrics can be strictly related to the precursor type and reactivity. In fact, the more homogeneous the morphology of the coating, the better is the flame retardancy [98].

Further research was undertaken in which several silica precursors characterised by a different number and type of hydrolysable groups were selected and their effect on the flammability and combustion behaviour of cotton assessed [100]. More specifically, the flame-retardant properties of cotton treated with TMOS were compared with those of the fabric treated with TEOS and tetrabuthylorthosilicate (TBOS) to study the effect of the chain length of the precursor on final properties. Furthermore, TEOS was compared with analogous precursors having a different number of hydrolysable groups. That is: diethoxy(methyl)phenylsilane (DEMPhS), 3-aminopropyl triethoxysilane (APTES), triethoxy(ethyl) silane (TEES), 1,4-*bis*(triethoxysilyl)benzene (bTESB) and 1,2-*bis*(triethoxysilyl)ethane (bTESE) (see **Table 8.4**).

Table 8.4 Silica precursors employed in the study [100]

Name	Number and type of alkoxy functionalities
TMOS	4 methoxy
TEOS	4 ethoxy
TBOS	4 buthoxy
DEMPhS	2 ethoxy
TEES	3 ethoxy
APTES	3 ethoxy
bTESB	6 ethoxy
bTESE	6 ethoxy

Vertical flame tests showed that, if a propane flame was applied directly to the cotton fabrics for 5 s, even a small amount of silica slowed down the burning rate. Indeed, two flame applications were necessary to ignite sol-gel-treated specimens, and the total burning time increased from 40 s (untreated fabric) to 70 s for TMOS-treated cotton and 57 s for TEOS- and TBOS-treated fabrics. Furthermore, the final residue increased significantly from 10 wt% to 48 wt% for untreated cotton and TMOS-treated fabrics, respectively, with residues of 48, 35 and 33 wt% for TMOS, TEOS and TBOS treatments, respectively. These tests have shown that, the shorter is precursor chain length, the lower is the cotton flammability. The same trend has been registered for resistance to an irradiating heat flow, as assessed by cone calorimetry. The ranking of precursors (from the most to the least efficient in terms of TTI increase) as a function of the role that they have on cotton can be summarised as:

TMOS> TEOS ≈TBOS

By comparing TEOS with the analogous precursors bearing a different number of hydrolysable groups, it was concluded that:

- Precursors having a lower number of hydrolysable groups (2 and 3) show flammability behaviour similar to that of TEOS, with the only exception being their large smoke release and nature of their final residues (which were shrunken, not dense/compact and very thin).

- The presence of an alkyl chain instead of an amino group (APTES *versus* TEES) generates a more compact and thicker residue.

- By increasing the number of hydrolysable groups (bTESB and bTESE), the flammability behaviour changes completely. Indeed, the fabric treated with bTESB precursor performs the best because even 10 flame applications of 5 s are not enough to burn the specimen.

Thus, it is possible to establish a ranking of the precursors (from the most to the least efficient) as a function of flame protection on cotton:

bTESB > > TMOS> TEOS ≈TBOS≈ TEES≈ DEMPhS> bTESE> APTES

Sol-gel processes have been devised for obtaining oxidic phases other than silica. Very recently, our research team reported that the flame-retardant properties of cotton could be enhanced by depositing alumina, titania or zirconia, starting from tetraethylortho-silicate, -titanate, -zirconate and aluminium isopropylate, respectively [101]. In this case, the best flame retardancy, as assessed by cone calorimetry, has been achieved by depositing a silica coating on cotton fibres, However, the most significant improvements in terms of abrasion resistance have been observed if alumina and titania coatings have been used. For this reason, new silica coatings containing alumina micro- or nano-particles have been tested to reach an optimal formulation for conferring both these features to fabrics by exploiting the characteristics of two ceramics (i.e., silica and alumina). It was found that very small amounts of alumina particles (irrespective of their size) within the silica network can:

- Increase the total burning time.
- Decrease the total burning rate.
- Increase the final residue.
- Increase the abrasion resistance of both fabrics [102].

These results are in accordance with those of Brzezinski and co-workers [103]. Indeed, they have deposited SiO_2-Al_2O_3 xerogel coatings on cotton fabrics to provide very good and durable protection against abrasion under use and care conditions so that significant enhancement of service durability has been achieved. The abrasion resistance exceeded 100,000 cycles in the Martindale abrasion tester, which indicates a fivefold improvement to that of untreated fabrics, determined also after prolonged laundering (under standard conditions).

The oxidic phases derived from sol-gel processes can thermally protect cotton not only because of the thermal insulating effect of a ceramic layer, but also because of the metal ions present in the precursor. Moreover, it is well described in the literature that metal ions can influence the thermal oxidative degradation of cotton cellulose because these species can catalyse the reaction of cellulose dehydration, favouring formation of high amounts of char [104]. In general, this effect is observed if the metal ions are used alone or in combination with phosphorus-based flame retardants [105, 106]. For example, Camino and co-workers [104] found that organometallic additives as zinc ethylhexanoate, potassium ethylhexanoate and cobalt ethylhexanoate strongly modified the decomposition of cellulose, enhancing char formation and reducing tar formation. Furthermore, it was observed that Zn^{2+} and Co^{2+} ions can increase the formation of aromatic char, whereas K^{+} ions promote aliphatic char. The mechanism of action of metal ions changes if they combine with phosphorus-based species because they can increase their thermal stability. Indeed, the volatility of the phosphorus oxides formed during pyrolysis is reduced, so these species are still available to phosphorylate the cellulose and so induce char formation.

In particular, Horrocks and coworkers [107] have demonstrated that Mn^{2+} and Zn^{2+} shift the thermal degradation of ammonium polyphosphate toward lower temperatures so that flame retardancy is induced at lower temperatures. Similar results were observed also employing other transition metal ions, such as Cu(II), Zn(II), Fe(II), Co(II), Cr(III), Ce(IV), La(III), Y(III) and Ho(III), or Mn(II), Pb(II) and Bi(III) in combination with cellulose ammonium phosphate [105, 106, 108].

In all of the previously mentioned articles, the coating acts as a physical barrier and thus as a thermal insulator that can shift the temperature at which degradation starts toward higher values. Furthermore, the dehydration of cellulose as well as char formation is favoured with respect to volatile production due to chain depolymerisation (**Figures 2.3** and **2.4** in **Chapter 2**). In this context, a key factor is the role of moisture and heat transfer coupled with moisture transfer in cotton fabrics under a simulated fire. Few studies have been carried out [109, 110], but one example in the investigation of the efficiency of thermal insulation to the radiant heat of sol-gel-derived silica coatings on cotton fabrics that follows exposure to the International Organization for Standardization (ISO) 6942 standard and an optimised method using a cone calorimeter as a heating source [111]. The inorganic coating was found to significantly influence the transfer of heat and moisture within cotton fibres. Indeed, the thermal conductivity of the sol-gel-treated samples was found to be strongly affected by the method of conditioning of the samples and consequently by moisture uptake [111].

8.3.3.2 Phosphorus-doped Silica Architectures

To enhance the flame-retardant properties of pure oxidic phases, a joint or synergistic effect with phosphorus and/or nitrogen can be exploited. For example, Cireli and co-workers [112] have prepared phosphorus-doped silica thin films mixing TEOS and phosphoric acid or ethyldichlorophosphate. Flammability tests showed that cotton does not burn if phosphoric acid acts synergistically with the silica coating. In addition, the surface treatment is stable for ≤10 washing cycles according to EN (European Standard) ISO 105-C06-A1S if a polyurethane film is applied on the film.

Recently, the coexistence of phosphorus and silicon elements in the same molecule to synthesise a hybrid organic-inorganic coating turned out to be a promising route that exploits the cumulative effect between the char due to the phosphoric-acid source and the thermal shield of an inorganic ceramic as a silica phase. Indeed, Cassagneau and co-workers [113-114] have shown that employing diethylphosphatoethyltriethoxysilane (DPTES) as a monomer to synthesise a hybrid phosphorus-silicone organic-inorganic material results in the enhanced flame retardancy of ethylene-vinyl-acetate (EVA) copolymers. Results showed a synergistic effect between silicone and phosphorus for low add-ons (1.3 wt% of silicone and 1.4 wt% of phosphorus). The PHRR measured with a cone calorimeter decreased by 35% for EVA hybrid materials compared with pure EVA due to the formation of a compact charred layer. The charred residues analysed by NMR spectroscopy showed that silicophosphorated complexes were present.

The same approach has been carried out in the textile field as well. Indeed, Brancatelli and co-workers [115] have used DPTES sols coupled to APTES or to a melamine-based resin (M) for impregnating cotton fabrics by padding/squeezing to achieve flame-retardant features. Flammability tests (according to ASTM D1230) showed significant enhancement of char-forming properties and thus of flame retardancy of cotton as a consequence of the synergistic effects between phosphorus and nitrogen with the silica phase. Indeed, char yields of 9, 42 and 38 wt% for APTES-, APTES/DPTES- and APTES/DPTES/M-treated samples, respectively, in air have been found by TGA.

Synergistic effects have also been observed in sol-gel-derived architectures doped with different phosphorus-based compounds (i.e., aluminium phosphinate, a mixture of aluminium phosphinate, melamine polyphosphate and zinc and boron oxide, and α-zirconium dihydrogen phosphate (ZrP) [116]). Indeed, the presence of ≥5 wt% phosphorus compounds with respect to the sol-gel precursor strongly improved the flame retardancy of cotton: TTI increases from 14 s (untreated cotton) to 40 s were recorded.

This approach turned out to be efficient also if samples had been washed for 1 h at 60 °C in distilled water. The thermo-oxidative stability in air of cotton was strongly modified because the carbonisation step is favoured by the synergistic effect between silica and phosphorus species, as evidenced by the significantly high final residues obtained at 750 °C. Indeed, in the presence of 5 wt% phosphorus compound, the cotton residue increased from 3 wt% to 26 wt%. Furthermore, LOI values increase from 18% to 30% if a ZrP-silica film is applied to cotton.

Among the flame retardants investigated was 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) because of the synergism with silica phases and the possible application as a flame retardant for cotton. Moreover, Hu and coworkers [117] synthesised organic-inorganic coatings *via* a sol-gel method employing a complex strategy of DOPO modification for cotton fabrics. These materials turned out to be responsible for a significant increase in char formation during the thermal degradation of cotton. Synergism was observed as the phosphorus released by DOPO promoted char formation in addition to the silica phase having a shield effect on the surrounding polymer. Measurements by micro cone calorimetry showed a strong decrease in the HRR and corresponding PHRR that increases with increasing add-on of the deposited flame retardant coatings. A significant decrease in the ignition temperature was observed at the highest coating add-ons. This finding suggested that phosphorus flame-retardant species present in the coating do not act only in the condensed phase (as claimed by the authors) but also in the vapour phase, as shown by the decrease of flammable degradation products (carbonyl compounds, hydrocarbons, and methanol) found by TGA coupled with infrared spectroscopy.

Very recently, our research team have exploited sol-gel processes to assess the effects derived from the concurrent presence of silica, phosphorus and nitrogen on cotton thermal and fire stability [118]. To this aim, a specific combination of a silica precursor with P and N donors (APTES, DPTES, and MF, *N*,*N*,*N*',*N*',*N*",*N*"-hexakis-methoxymethyl-[1,3,5]triazine-2,4,6-triamine) was chosen and exploited for obtaining hybrid phosphorus-doped silica films on the surface of the fabric. Such sol-gel treatments showed significant enhancements of the thermal and thermo-oxidative stability (as assessed by TGA) as well as flammability resistance of the fabric. In particular, the char-forming character of such coatings protects cotton and promotes high residues (≈50 and ≈70 wt% for APTES-DPTES and MF-DPTES, respectively).

Subsequently, a novel multistep process consisting of 1–6 consecutive depositions was formulated to obtain architectures with a different number of layers [119]. Formation of the hybrid phosphorus-doped silica phase was assessed by infrared spectroscopy. In addition, as clearly shown by SEM analyses, all the treated fabrics were covered homogeneously by the oxidic phase formed, irrespective of the number of layers deposited or the use of a condensation catalyst. The presence of the coating turned out to be responsible for strong sensitisation of the cellulose decomposition but, simultaneously, promoted a significant increase in the residues obtained at high temperatures. With respect to flammability, the architectures prepared without the condensation catalyst could enhance the total burning time in a very efficient way and so form the highest residues after the test. Despite the strong reduction of TTI, the hybrid coatings protected the cotton fabrics by decreasing the duration of the combustion, as shown by the flame out (FO) values found during cone calorimetry tests by hindering the formation of volatile species. Finally, smoke production was significantly lowered in the presence of the hybrid architectures. Better results were achieved after an optimisation process consisting of the pre-hydrolysis of the precursor (DPTES) [120]. Indeed, upon optimisation, it was demonstrated that just one phosphorus-doped silica layer can strongly reduce the HRR (–52%), and total smoke release (–56%) and its rate (–62%) with respect to the untreated fabric. These coatings also showed good durability if subjected to ≤5 washing cycles according to ISO 6330 standard.

As mentioned in **Chapter 2**, an important aspect to take into consideration if ≥2 flame-retardant systems are used is quantification of their synergistic effects. For this reason, the concurrent presence of phosphorus- and/or nitrogen-based compounds on the flame retardancy of sol-gel-treated cotton fabrics has been investigated by using the concept of ‘synergistic effectiveness’ [121]. It was demonstrated that only hybrid phosphorus-doped silica coatings can synergistically act with 1-hydroxyethane 1,1-diphosphonic acid, whereas a simple additive effect occurs if the hybrid phosphorus-doped silica coatings are doped further with **N**-containing molecules such as melamine or urea. Indeed, silica and bisphosphonate can cooperate in char formation, as shown by TGA as well as flammability and cone calorimetry tests. This finding can probably be ascribed to decomposition of the bisphosphonate (at ≈260 °C), which gives rise to acidic species that catalyse cellulose dehydration. Meanwhile, the hybrid-phosphorus silica coating (acting as a thermal insulator) helps further in the formation of an aromatic char resistant to flame propagation. From an overall viewpoint, the sol-gel-derived coatings doped with melamine or urea seem to show lower flammability performances with respect to conventional P-N-containing flame retardants. This could be ascribed to the limited diffusion of P and N species from the outside to the inside of the fibres because of the silica coating. As a consequence, the presence of melamine or urea does not substantially contribute to the formation of char, indicating that levoglucosan formation is favoured.

The synergistic effect between phosphoric acid and silica has been also applied to polyacrylonitrile (PAN) synthetic fibres. P-doped silica films were shown to make PAN fibres non-ignitable to a small flame source (as reported in the ISO 6941 standard) if a 15-s flame was applied. Furthermore, such sol-gel treatment turned out to be resistant to ≤10 washing cycles according to TS EN ISO 105-C06-A1S [122].

8.3.3.3 Smoke-suppressant Architectures

The quest for safe, eco-friendly systems acting as smoke suppressants or flame retardants or for those having both of these features is growing continuously. The latter solution seems to be the most promising and appreciable from an economical viewpoint. The use of fillers, classified as ‘inert’ or ‘active’ on the basis of their apparent smoke-suppressant functions, is already documented in the literature for bulk polymers. Also, inert fillers such as silica, clays and calcium carbonate can lower the amount of smoke generated from a given mass or volume of a polymer simply by diluting or decreasing the amount of combustible substrate present and also by absorbing heat (so that the burning rate slows down) [123, 124]. Conversely, aluminium and magnesium hydroxides behave as active fillers and give rise to endothermic processes, which can absorb more heat per unit weight as well as being diluents.

Inert fillers, silica nanoparticles or silica-based coatings can be synthesised easily through sol-gel processes. For example, cotton fabrics have been subjected to sol-gel treatments in the presence of different smoke suppressants (i.e., zinc oxide, zinc acetate dihydrate and zinc borate) or flame retardants (i.e., ammonium pentaborate octahydrate, boron phosphate, ammonium polyphosphate and DOPO), or in the presence of barium sulfate (which possesses both of these properties). In the presence of zinc-based smoke suppressants, the release of carbon monoxide (CO) and carbon dioxide (CO_2) as assessed by cone calorimetry has been reduced significantly with respect to the fabric treated with the silica coating alone. In particular, the joint effect of ZnO and silica has promoted the most significant decrease in yields of CO and CO_2, whereas the combination of silica with phosphorus- or boron-based flame retardants did not achieve any remarkable decreases in their production [125].

8.3.3.4 Hybrid Organic-inorganic Architectures

Very recently, we have demonstrated that dual-cure processes involving a photopolymerisation reaction and a subsequent sol-gel process can be exploited for the preparation of hybrid organic-inorganic coatings able to enhance the flame retardancy of cotton [126]. To this end, different amounts of TMOS (30–80 wt%) have been added to an acrylic UV-curable formulation (*bis*-phenol A ethoxydiacrylate, added with 4 wt% 2-hydroxy-2-methyl-1-phenylpropan-1-one as an photoinitiator) in the presence of a suitable coupling agent (methacryloyloxypropyltrimethoxysilane). The hybrid organic-inorganic coating turned out to be an efficient thermal insulator for inhibiting cotton combustion. Indeed, the formulation containing 60 wt% silica was found to: (i) extend the total burning time (40 s *versus* 150 s for untreated and dual-cure-treated fabrics, respectively); (ii) increase residue formation during the flammability tests in a horizontal configuration (from 8 wt% to 29 wt%); and (iii) postpone ignition during the combustion tests under an irradiating heat flow (from 18 s to 34 s).

Another attempt was carried out by Xing and co-workers [127], who prepared UV-cured flame-retardant coatings using *tri*(acryloyloxyethyl)phosphate and trigycidyl isocyanurate acrylate. Once again, the coating turned out to be responsible for a decrease in the ignition temperature as well as in the total heat release and corresponding rate, as assessed by micro cone calorimetry. The flame-retardant mechanism of such coatings has been attributed to their char-forming feature, as observed by TGA and by evaluating the properties of the final residue after flammability tests.

8.3.4 Plasma Surface Treatments

Among the different types of surface treatments, the cold plasma method is one of the few processes that allows covalent grafting to underlying substrates of small functional groups as well as macromolecular compounds. One of the most important features of this method is the lack of alteration or modification of the bulk properties of a material, as documented thoroughly by Yasuda [128].

Different strategies can be employed using cold plasma:

- Simple modification of the surface structure of the material and/or functionalisation using non-polymerisable gases (etching), such as N_2, H_2, O_2, Ar, NH_3, and CO_2.
- Deposition of a thin film on the surface of the material by generating the plasma from a volatile organic, organosilicone or organometallic compound.
- Two-step plasma polymerisation: plasma is used initially just for activating the material surface (etching) before grafting a preformed polymer. The polymer is preformed in a separate step in a solution containing the monomer that polymerises by heating or using UV or γ radiation.
- Plasma-induced graft-polymerisation (PIGP): the surface activation and simultaneous grafting and polymerisation of a non-volatile monomer can be done in a single step [129–132].

However, as stated by Horrocks [133], although plasma technology can be applied to fibres and/or fabrics, it has been in use for over 40 years, and is currently employed in a significant capacity only within industrial sectors such as microelectronics, paints and coatings. The uses of this technology are limited in the textile field because of the necessity of using atmospheric-pressure plasma, which has only recently become available commercially. It is not very versatile because for plasma quenching but has been utilised for:

- Simple modification of the surface structure of the material and/or functionalisation by using non-polymerisable gases (etching), such as N_2, H_2, O_2, Ar, NH_3, and CO_2.
- Grafting of phosphorus non-volatile compounds in cold plasma [134].
- Deposition of organosilicone compounds by plasma polymerisation [135, 136].
- Exploitation of the cold remote nitrogen plasma method recently developed by Bourbigot and coworkers [137, 138].
- CF_4/CH_4 deposition.
- Plasma grafting using acrylic monomers [139, 140].

The use of atmospheric pressure plasma is one of the easiest and most efficient ways for improving finishing process on cotton fabrics. This treatment is usually employed to prepare the fabrics by etching, as reviewed critically by Bourbigot & Duquesne [141] and Weil [142]. Some attempts have also been carried out by Rajpreet & Gita [143] and Wang [144]. Recently, Lam and co-workers [145] have shown that atmospheric-pressure plasma can be used as an etching pre-treatment to enhance the flame retardancy of cotton if combined with further treatments with an organic phosphorus compound in combination with melamine resin (as a crosslinking agent), phosphoric acid (as the catalyst) and zinc oxide (as the co-catalyst). However, the same authors have claimed that the treated fabrics are characterised by poor mechanical properties if compared with the reference. Conversely, the plasma pre-treatment and zinc oxide co-catalyst may compensate for the reduction in tensile and tearing strength caused by the presence of the flame retardant. The collected data have underlined that the specimens do not ignite and that the flame extinguishes immediately after removal of the ignition source without spreading.

Very recently, Horrocks and coworkers [19] have demonstrated the effectiveness of atmospheric-plasma treatments in which a functionalised clay, a polysiloxane (poly(hexamethyldisiloxane)) or both are deposited onto plasma-activated fibre surfaces. It was found that the generated surface layer has a measurable effect on fabric ignition and burning characteristics if exposed in a cone calorimeter to heat flux levels up to 70 kWm^{-2}. PHRR values decreased for all substrates, especially for argon/clay- and argon/clay/polysiloxane plasma-treated samples, with reductions of >50% being observed for Proban® cotton and smaller reductions (<20%) for Nomex® fabrics. The results have provided evidence that atmospheric-plasma treatment of fabric surfaces in the presence of a functionalised clay produces an inorganic coating that confers reduced flammability at high heat fluxes, suggesting an increased resistance to flash-fire ignition.

We have also carried out pre-treatment with cold oxygen plasma coupled with nanoparticle adsorption. These studies have been done on PET [16, 17] and cotton [18] fabrics, as described thoroughly in **Section 8.3.1**.

The most interesting results in this field have been achieved if a thin-film deposition occurs on the surface of the material by generating plasma. More specifically, the plasma-induced fire retardancy of textiles has been demonstrated to be feasible using several approaches.

Of the bulleted examples detailed above, PIGP seems to be the most promising and versatile route for industrial exploitation. Tsafack & Levalois-Grützamcher [130, 131] have investigated the argon PGIP of some acrylic monomers containing phosphorus, and demonstrated their efficiency in terms of LOI improvements. Application of this method to PAN fibres [130, 132] shows a significant increase in the LOI by 4, 5 and 8 units with respect to untreated material

(18.5%) depending on the monomer grafted. For example, use of the phosphonate monomer dimethyl(acryloyloxymethyl)phosphonate (DMAMP) give rise to a self-extinguished fabric with a high LOI (26.5%). An increase in the LOI by 4 units is also achieved if cotton is treated with diethyl(acryloyloxymethyl)phosphonate, up to 7 units with diethyl-2-(methacryloyloxyethyl)phosphate (DEAEP), diethyl(acryloyloxyethyl)phosphate and DMAMP and up to 9 and 10 units with diethyl(acryloyloxyethyl)phosphoramidate (DEAEPN) and acryloyloxy-1,3-*bis*(diethylphosphoramidate)propan, respectively. Furthermore, as the monomer concentration increases, the amount of grafted polymers also increases significantly, whereas the LOI increases only slightly. The acrylate phosphoramidate monomers are the most efficient types of flame retardants probably because of the synergism between nitrogen and phosphorus elements. These species applied by PIGP have turned out to be extremely efficient in improving the flame-retardant properties of silk [129]. Indeed, the LOI of silk increases from 25% up to 31% if the fabrics are treated with phosphate and phosphoramidate (DEAEPN, DEAEP). For equal concentrations of grafted phosphorus atom on the fabrics, the LOI values measured for poly(DEAEPN)-finished fabrics were higher than those of poly(DEAEP) (30.5% *versus* 29.0%). The same coatings were also responsible for significant decreases in the total heat release of silk (6.2 and 6.5 *versus* 7.7 kJg^{-1} for DEAEPN, DEAEP and cotton, respectively), PHRR (90 and 95 *versus* 147 Wg^{-1}) and heat release capacity (91 and 97 *versus* 149 kJg^{-1}) as assessed by pyrolysis combustion flow calorimetry.

8.3.5 Biomacromolecule-based Coatings

As far as plastics and textiles are concerned, the possibility of using green flame-retardant systems for replacing traditional additives is also a driving force that continues to stimulate industrial and academic research toward novel and innovative solutions. In particular, the availability of formaldehyde-free flame-retardant systems based on natural macromolecules such as proteins could be extremely interesting for possible industrial applications.

Our research team has recently demonstrated that it is possible to enhance the flame retardancy of cotton fabrics by using whey protein isolate (WPI) products [146]. Unfolded and folded WPI have been deposited on cotton fabrics by dipping to achieve a homogeneous coverage on cotton fabrics and a final 20 wt% add-on. The presence of the protein coating, irrespective of its structure (folded or unfolded) has significantly sensitised cotton degradation but, simultaneously, assured very high final residues. The flame resistance of the WPI-treated fabrics, which have shown an increased total burning time together with a reduced burning rate (**Table 8.5**), has been ascribed to the good oxygen-barrier properties and adsorption of water vapour by the protein coatings. Therefore, these systems may represent a novel and quite promising 'green' finishing treatment for cellulosic substrates, also taking into account their origin from natural sources.

Table 8.5 Flammability data of untreated and WPI-treated cotton fabrics

Sample	**Total burning time (s)**	**Burning rate (mm/s)**	**Residue (%)**
COT	78	1.5	–
COT_WPI	126	1.0	30

Alternatively, proteins that bear groups with potential flame-retardant features can be considered extremely interesting and advantageous. In particular, caseins and hydrophobins, which contain phosphorus and sulfur elements, respectively, have exhibited potential as flame-retardant systems for cellulosic substrates [147]. Furthermore, the phosphate groups of caseins as well the disulfide bonds of hydrophobins have been shown to influence cellulose pyrolysis toward char formation. As a consequence, an increased total burning time, as well as a decreased total burning rate, have been observed. In addition, the presence of the protein coating has also modified the resistance of cotton to a heat flux of 35 kWm^{-2}, with a significant reduction of PHRR, i.e., –27% and –45% for caseins and hydrophobins, respectively.

In this same scenario, the complex double-helix of deoxyribonucleic acid (DNA) represents a potential and intrinsic intumescent flame-retardant system because it contains the three typical components of an intumescent formulation. That is, phosphate groups (able to produce phosphoric acid), deoxyribose units (acting as a carbon source and blowing agents (upon heating a (poly)saccharide dehydrates to form char and release water)) and nitrogen-containing bases (guanine, adenine, thymine, and cytosine that can release ammonia [148–150]). The first results have clearly shown that, after two applications of a methane flame for 3 s (in a horizontal configuration), DNA-treated cotton fabrics do not burn [151]. This study has also shown that the DNA phosphate groups can generate phosphoric acid, which catalyses the dehydration of cellulose, favouring its auto-crosslinking to an aromatic char and inhibiting the production of volatile species. Pursuing this research, we have also elucidated the: (i) effect of different DNA add-ons on the thermal stability (in air) and flammability of the cotton; (ii) resistance of the treated cotton fabrics to an irradiating heat flux; (iii) correlation between the morphology of the coatings with the resulting flame-retardant properties of the treated fabrics. In doing so, three add-ons (5, 10 and 19 wt%, respectively) have been deposited on cotton by impregnation/exhaustion. Collected results have shown that the thermal stability of cotton is strongly affected by DNA regardless of the coating add-on. In particular, TGA from 50 °C to 800 °C (heating rate of 10 °C/min) in air showed that DNA-based coatings can favour the formation of a coherent and thermally stable residue at the temperature at which the first weight loss is registered (T_{max1}), as shown in **Table 8.6**, despite a slight reduction of the same temperature.

Table 8.6 Thermogravimetric data of pure cotton and DNA-treated cotton fabrics in air [152]

Sample	T_{max1*} (°C)	T_{max2*} (°C)	Residue at T_{max1*} (%)	Residue at T_{max2*} (%)	Residue at 600 °C (%)	Residue at 350 °C** (%)
COT	347	492	45.0	4.0	0	13.0
COT_DNA_5%	313	506	65.0	19.0	8.0	30.0
COT_DNA_10%	302	511	69.0	24.0	13.0	35.0
COT_DNA_19%	299	515	68.0	29.0	19.0	42.0

*From derivative TG curves

**From isothermal tests

T_{max2}: Temperature at which the second degradation step occurs

For each add-on, comparing the residue at T_{max1} shows a significant increase regardless of the coating add-on level. This residue is thermally stable at ≤600 °C. The char-forming effect of DNA on cotton has been confirmed further by isothermal testing at 350 °C (the temperature at which the main weight loss of cotton in air occurs). As is clearly evident in **Table 8.6**, DNA affects the first step of cotton thermo-oxidation by favouring the dehydration process toward the formation of a thermally stable residue. The DNA flame-retardant mechanism could involve the deoxyribose units that produce further aromatic char, thereby thermally protecting the cotton fibres, therefore acting as a physical barrier, and hence limiting the transfer of heat, fuel and oxygen between the flame and polymer. Simultaneously, decomposition of purine and pyrimidine bases could give rise to the formation of azo-compounds that can further induce char development and production of non-combustible gases (i.e., N_2, CO_2 and CO).

Furthermore, analyses of all the data have clearly shown that 10 wt% represents the minimum add-on necessary to reach the self-extinction condition of cotton if a methane flame is applied. However, under cone calorimetric exposure, 19 wt% is the minimum level required to confer ignition resistance to an irradiating heat flux of 35 kWm^{-2} (see **Table 8.7**). Indeed, all COT_DNA_19% specimens tested in these conditions do not burn under exposure in the cone calorimeter, as well as only 2 of 5 samples treated at the lower add-on of 10 wt%. However, if the add-on is <19 wt%, the combustion time is short. Indeed, from a qualitative observation, the FO is reached very quickly and only very small amounts of volatile product are released during combustion.

Table 8.7 Combustion data of pure cotton and DNA-treated cotton fabrics (heat flux=35 kWm^{-2}) [152]

Sample	TTI (s)	FO (s)	Combustion time (s)	PHRR (KW/m^2)	Residue (%)
COT	45	75	30	125	<3
COT_DNA_5%	24	39	15	68	15
COT_DNA_10%	19	29	10	62	15*
COT_DNA_19%	No ignition				24

*2 specimens of 5 do not ignite

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Abbreviations

APP	Ammonium polyphosphate
APTES	3-Aminopropyl triethoxysilane
AS	Australia
ASTM	American Society for Testing and Materials
ATH	Alumina trihydrate
ATO	Antimony III oxide
BCTA	Butyl tetracarboxylic acid
BL	Bilayer
BOE	Boehmite modified by sulfonate salts
BS	British Standard
bTESB	1,4-*Bis*(triethoxysilyl)benzene
bTESE	1,2-*Bis*(triethoxysilyl)ethane
CA	Citric acid
CEN/EN	European Standards
CFR	Code of Federal Regulations
CloNa	Cloisite® sodium
CNT	Carbon nanotube(s)
COT	Cotton
CPSC	Consumer Product Safety Commission
DEAEP	Diethyl-2-(methacryloyloxyethyl)phosphate
DEAEPN	Diethyl(acryloyloxyethyl)phosphoramidate
DecaBDE	Decabromodiphenyl ether

DEMPhS	Diethoxy(methyl)phenylsilane
DIN	Deutsche Institüt für Norms
DMAMP	Dimethyl(acryloyloxymethyl)phosphonate
DMDHEU	Dimethylol dihydroxyethylene urea
DNA	Deoxyribonucleic acid
DOPO	9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DPTES	Diethylphosphatoethyltriethoxysilane
EC	European Commission
EEC	European Economic Community
EFRA	European Flame Retardants Association
EG	Expandable graphite
EN	European Norm
EU	European Union
EVA	Ethylene-vinyl acetate
EVA-VC	Ethylene-vinyl acetate vinyl chloride
FAA	US Federal Aviation Administration
FAR	US Federal Aviation Regulation
FEP	Fluorinated ethylene polymer
FIGRA	Fire growth index
FIRA	UK Fire Industries Research Association
FMVSS	Federal National Highway Traffic Safety Administration
FO	Flame out
FTP	Fire Test Procedures
HASS	Home Accident Surveillance Scheme
HBCD	Hexabromocyclododecane
HDPE	High-density poly(ethylene)
HL	Hazard levels
HRR	Heat release rate

HTI	Heat transfer index
IMO	International Maritime Organisation
ISO	International Organization for Standardization
JIS	Japanese International Standard
LbL	Layer-by-Layer
LDPE	Low-density poly(ethylene)
LF	Low formaldehyde
LOI	Limiting oxygen index
MA	Maleic acid
MDH	Magnesium hydroxide
MEL	Melamine
MF	Melamine-formaldehyde
MGDP	Monoguanidine diphosphate
NF	Normalisation Francais
NFPA	National Fire Protection Association
NMR	Nuclear magnetic resonance
NP	Nanoparticle
NRC	National Research Council
NZ	New Zealand
OECD	US Environmental Protection Agency
OMMT	Organo-modified montmorillonite
OSU	Ohio State University
PA	Polyamide(s)
PA6	Polyamide 6
PA6.6	Polyamide 6.6
PAA	Poly(acrylic acid)
PAAm	Poly(allylamine)
PAN	Polyacrylonitrile
PBDPO	Polybrominated diphenyl oxides

PBI	Polybenzimidazole
PBO	Poly(para-phenylene benzobisoxazole)
PCL	Poly(ε-caprolactone)
PE	Polyester
PER	Pentaerythritol
PES	Polyesters
PET	Poly(ethylene terephthalate)
PHB	Poly(3-hydroxy butyrate)
PHRR	Peak heat release rate
PIGP	Plasma-induced graft-polymerisation
PLA	Poly(lactic acid)
PMAO	Phosphorus-containing maleic acid
POSS	Poly(vinylsilsesquioxane)
PP	Polypropylene
PPE	Personal protective equipment
PPTA	Poly(*para*-phenylene terephthalamide)
PSP	Poly(sodium phosphate)
PSS	Poly(styrene sulfonate)
PTFE	Poly(tetra fluoroethylene)
PUR	Polyurethanes
PVA	Poly(vinyl alcohol) and poly(vinyl acetate)
PVC	Poly(vinyl chloride)
PVDF	Poly(vinylidene fluoride)
PVF	Poly(vinyl fluoride)
QL	Quadlayers
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RHR	Rate of heat release
RHTI	Radiant heat transfer index
SBR	Styrene butadiene

SE	Synergism effectiveness parameter
SEM	Scanning electron microscopy
TBOS	Tetrabuthylorthosilicate
TBPA	Tetrabromophthalic acid
T_c	Ignition flaming combustion temperature
T_d	Degradation temperature
TEA	Triethanolamine
TECH	Technora
TEES	Triethoxy(ethyl)silane
TEOS	Tetraethylorthosilicate
T_g	Glass transition temperature
TG	Thermogravimetric
TGA	Thermogravimetric analysis
THPC	Tetrakis(hydroxymethyl) phosphonium chloride
THPOH	Tetrakis(hydroxymethyl) phosphonium hydroxide
THPX	Tetrakis(hydroxymethyl) phosphonium salt
THR	Total heat release
T_m	Melting temperature
T_{max1}	Temperature at which the first weight loss is registered
T_{max2}	Temperature at which the second weight loss is registered
TMOS	Tetramethylorthosilicate
T_p	Pyrolysis temperature
TPP	Thermal protective performance
TSR	Total smoke release
TTI	Time to ignition
UV	Ultraviolet
VECAP	Voluntary Emissions Control Action Programme

VOC	Volatile organic compound
WPI	Whey protein isolate
ZHS	Zinc hydroxystannate
ZnP	Zinc phosphinate
ZrP	α-Zirconium dihydrogen phosphate
ZS	Zinc stannate
ΔH_c	Heat of combustion

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This publication describes progress in the flame retardancy of natural and synthetic fibres/fabrics. Such progress evolves from traditional approaches (back-coating methods), current chemical solutions (P-, N-, S-, B-based flame retardants) to novel contemporary strategies (deposition and/or assembly of architectures, plasma treatments, sol-gel processes, and so on).

More specifically, the fundamental aspects and chemistry of flame-retardant textile technologies (including back-coating process) and the obtained improvements are reviewed thoroughly, taking into account the detrimental environmental effects due to the use of halogen-based additives such as bromine derivatives.

Then, an overview of the chemical development of flame retardant strategies based on halogen-free compounds is summarised.

The third part of this book is devoted to the description of contemporary innovatory solutions based on nanotechnology. In detail, the surface deposition of coatings having a different chemical structure is highlighted. To this aim, the effect of (nano)architectures derived from (nano)particle adsorption, plasma deposition/grafting, layer-by-layer assembly, and sol-gel treatments on fibres/fabrics are discussed thoroughly.

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