

## **3 Fire-retardant textiles**

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### **3.1 The problem**

Fire takes a steady toll of both human life and property. The results are often tragic and in many cases (at least potentially) avoidable. The problem has many components which can be summarized as follows.

1. A wide range of commonly used materials is flammable.
2. A range of situations, in theatres, restaurants, clubs and aircraft, can cause heavy loss of life in the event of fire.
3. Use of particular materials, garments and upholstery structures can lead to sharply increased personal hazard.

Use of reduced flammability materials, testing of both materials and complete products, regulations and legislation have been applied to the problem. Each has contributed to reducing the risk of accidental injury, death or loss.

Progress in reducing the hazard has been made, but is constrained by a series of factors.

1. The risk is not widely appreciated by the general public, except when a major disaster occurs.
2. Any solution which restricts personal freedom is likely to be avoided by a significant number of people.
3. Any product with reduced aesthetic qualities will be less successful even if it has fire-retardant properties.
4. Any solution which adds significantly to product cost will tend to be resisted.

#### *3.1.1 The risk*

About 16 000 fires a year result from ignition of textile materials in the UK, most of them domestic fires.

In the UK, fires in dwellings produce about 6000 casualties per year, 650 of them fatal (Home Office, 1985). A major proportion of deaths (at least 50%) are attributable to toxic fumes and smoke, but in clothing fires the major hazard is burns.

In the USA one person is burned to death every 44 minutes in clothing and other fires.

If fire happens in public places horrific loss of life has occurred, as the following examples illustrate.

At Boston, Massachusetts, USA, 750 customers were present at a nightclub in 1942. The fashion at the time included stiffened lace party dresses. A common finishing stiffener was, unbelievably, nitrocellulose. In the flash fire which engulfed the customers, 432 died and 214 were injured. The notorious 'Ring Theatre Disaster' in Vienna, Austria, caused 450 deaths when a back-stage fire spread rapidly to the auditorium. A relatively minor fire at a store in Manchester, UK, killed ten people. It is however important in that it highlighted the danger of inflammable upholstery foam.

A whole range of aircraft, train and auditorium fires have been influential in both highlighting dangers and generating legislation to control risks.

### 3.2 The combustion process

In order to understand how flammability hazards can be reduced, it is necessary to study the nature of the combustion process. Combustion can very easily develop into a runaway self-feeding event producing enormous heat, suffocating and toxic fumes, and total destruction. Figure 3.1 shows the essential components: fuel, an oxidant (usually air) and an ignition source.

Heat and fumes feed back readily burned gases and give increased ignition. The rate of combustion increases, and can reach explosive violence in so called 'flashover' events. Such an event caused major loss of life in the Kings Cross Underground station disaster in London, UK, in 1989.

A major contribution to saving life is to 'retard' the combustion process. By slowing down the developing situation, crowds can escape, fires can be extinguished, and garments removed. Time is available to formulate and execute the necessary measures.

### 3.3 Developing a fire-retarding solution

Over many years a fourfold attack has been mounted on loss of life and injury by fire.

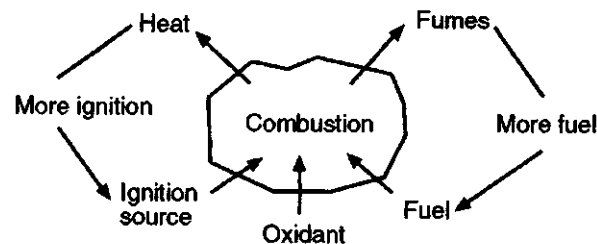


Figure 3.1 The combustion process.

- (a) *Design for fire retardancy and escape.* This covers every aspect of garment, furniture, architectural, and transport design. It has resulted in fire fighters' uniforms capable of protecting against 2000°C exposure for 30s. Buildings are designed to prevent spread of fire and smoke, and theatres have a safety curtain between stage and auditorium.
- (b) *Legislate to eliminate known risks.* The UK Children's Nightwear (Safety) Regulations, SI 616 (HMSO, 1959), prohibit the sale of nightwear which does not pass appropriate flammability tests. The UK 1980 Upholstered Furniture (Safety) Regulations were the result of much detailed assessment of fires in the home. The Manchester store fire, long predicted by those aware of hazards, gave the final impetus to legislation in the UK on foam-filled upholstery.
- (c) *Develop adequate test methods.* It is often not clear precisely what the nature of the hazard is, until similar events can be reproduced in a laboratory. Flammability testing has been continuously improved in recent years. It has also been realized that testing materials and components on their own is inadequate. Modern testing often involves complete structures, furniture, windows, drapes, etc., tested in carefully designed settings (Horrocks, 1986).
- (d) *Develop fire-retardant materials.* It is probably true to say that fire-retardant materials have been developed to meet every conceivable hazard. In theory nobody should be injured if the best available fire-retardant material were always used, and an optimum garment or furnishing structure were chosen. It is, however, also equally true that only space programmes and the like can afford the really exotic materials. Many cheaper solutions give reduced comfort, colour, or aesthetic properties. There are no solutions at all which do not add significantly to the cost of products.

In the following sections we will concentrate on the chemistry of fire retardancy, fire-retardant fibres, and fire-retardant finishes for flammable materials.

### 3.3.1 Terminology and standards

It is important, when discussing fire retardancy, and when selling fire-retardant products, to use precise terminology. If you make an assertion that a product 'has low flammability' or 'is flame-resistant' or 'does not burn', you may have to defend the statement in a court of law. Terminology, testing and labelling must be clear and unambiguous.

1. Use approved and defined terminology.
2. Refer to the BS or ISO tests by which the terminology is established (e.g. BS 6336: 1982)
3. Ensure that the products and materials pass the appropriate tests.

The terms 'flameproof' and 'fire-proof' should be avoided. 'Fire-retardant' is a useful general term. 'Does not sustain flame' is the approved term (BS 6336: 1982). 'Self-extinguishing' is widely used to describe materials which only burn in contact with an ignition source. 'Reduced fire hazard' or 'resists ignition' are also acceptable terms but should only be used in connection with a specified test. A variety of carefully designed tests is available by which the property can be measured.

Test methods and their execution and interpretation are a highly specialized area. Individual testing houses set up appropriate apparatus, train staff and receive validation and certification. It is common practice to use such certified testing procedures to ensure product integrity.

Relevant British and international standards include ISO 9000, BS 5750 and 7750, and NAMAS certification. These cover validation and accreditation. All British standards in this field make a clear distinction between methods of test and performance in testing. BS 5438, 6807, 5852 for example, describe test methods. Performance in these tests is classified in standards such as BS 5722, 7177, 6249. Both the test and the performance criteria met need to be quoted when describing a product; for example, 'Flame-retardant finish durable to repeated washing BS 5438: 1976 Test 2a to BS 5722 performance for sleep wear'. Table 3.1 lists some important British Standards. Some equivalent US standards include:

DOC FF 3-71 & 5-74 CS191-53	Children's sleepwear
ASTMD 1230-1983 NFPA 702-1975	Tests for flammable fabrics
CPSC NBBIR 76-1072 (1976) US FAR 25.85b	Burn simulation (mannequin) test Fire resistance of aircraft seating

**Table 3.1** Some important British Standard tests for flammability

British Standard	Purpose
BS 2963: 1958	Test for flammability of fabrics
BS 3119: 1959	Tests for flameproof materials
BS 3120: 1959	Performance requirements for flameproof clothing
BS 3121: 1959	Performance requirements for fabrics of low flammability
BS 5438: 1976	Test methods for vertically orientated fabrics and assemblies (small flame ignition)
BS 5722: 1974	Performance of fabrics and assemblies for sleepwear and dressing gowns
BS 5852: 1979	Fire tests for furniture, textile and foam interior combinations: pt 1 ignition by smokers' materials; pt 2 ignition by flaming sources
BS 5867: 1980 (pt 2)	Flammability requirements for curtains and drapes
BS 6307: 1982	Ignition of textile floor coverings (small ignition source)
BS 6357: 1983	Tests for resistance to molten metal splash for protective clothing

### 3.4 Flammability of materials

Materials can be classified quite clearly into those which will burn in air once ignited, and those which are self-extinguishing if not in direct contact with an ignition source. Amongst those materials which will burn freely, two other properties may add significantly to the hazard:

- (1) *The heat of combustion.* Any material with a high heat of combustion provides increased ignition for surrounding material. Heats of combustion can vary from 11.6 kcal/g for polypropylene down to 3.4 kcal/g for viscose rayon.
- (2) *Thermal properties.* A series of thermal transition temperatures cover important events when a material is exposed to an ignition source.

- $T_g$  The glass transition or softening temperature, particularly in clear rigid plastics
- $T_m$  The melting point (thermoplastics only)
- $T_p$  Pyrolysis temperature: rapid thermal degradation of the polymer
- $T_c$  Combustion temperature: spontaneous ignition occurs

Some materials such as wool and modacrylic have a  $T_c$  as high as 600–700°C and are difficult to ignite.

#### 3.4.1 Limiting oxygen index

The atmosphere contains about 21% oxygen. The rest (nitrogen, CO<sub>2</sub>, water, etc.) does not support combustion. It has been found by experiment that increasing the ratio of oxygen to nitrogen makes some materials burn that are self-extinguishing in air. Conversely, materials which burn readily in the air are self-extinguishing in nitrogen-rich atmospheres.

This leads to a useful and general test for classifying flammability. The limiting oxygen index (LOI) test seeks to establish the minimum oxygen content atmosphere in which a material will continue to burn.

Those materials with a LOI greater than 25 are generally self-extinguishing in air. Those with the lowest LOI values burn most readily. Very few materials indeed refuse to burn in atmospheres approaching 100% oxygen.

A full description and discussion of the LOI test is given elsewhere (Lewin and Sello, 1984), and Table 3.2 lists a range of materials and their LOI values.

#### 3.4.2 Insulation and retardancy

An important feature of fire retardancy is heat insulation. Any structure or material which prevents heat reaching further combustible material, or the

**Table 3.2** Limiting oxygen indices (LOI): minimum percentage oxygen contents for sustained combustion

Substance	LOI
Polyethylene oxide	15.0
Poly(methyl methacrylate) (Perspex)	17.0
Polyacrylonitrile	18.0
Polyethylene	18.0
Polystyrene	18.5
Polypropylene	18.6
Cellulose	19.0
Poly(ethylene terephthalate)	21.0
Poly(vinyl alcohol)	22.0
Nylon 6.6	23.0
Wool	25.2
Modacrylic	26.8
Polycarbonate	27.0
Nomex (Aramid)	28.5
Phenol-formaldehyde resin	35.0
Neoprene	40.0
Poly(vinyl chloride)	60.0
Carbon	60.0
Polytetrafluoroethylene	95.0

human body, is valuable. Several types of material achieve this:

1. Non-thermoplastic materials (wool, carbon fibre)
2. Carbonaceous char
3. Silica and silicon-based polymers

A further by-product of insulating properties is the limitation of access of oxygen to the combustion centre.

### 3.5 Which materials are best?

This is a typically ill-defined question. We must distinguish between end uses. We must solve the often contradictory demands of performance, cost, and aesthetic effects, and we must assess the effects of combining materials into products. For example, a very different solution is called for in hazardous environments such as those a firefighter may encounter or a racing driver may suffer in a crash.

We will leave a fuller discussion until we have reviewed what can be done to enhance the flame-retardant properties of popular cellulosic fibres, polyester and wool.

#### 3.5.1 Wool as a low-flammability material

Wool has many of the required properties. Its LOI at 25.2 is, however, marginally above the atmospheric oxygen content. It will thus burn in air

under favourable conditions. It is non-thermoplastic and has a very high  $T_c$  (600°C). Furthermore, its heat of combustion is low at 4.9 kcal/g. In dense tightly woven structures wool is an excellent insulator, and produces dense black char when burnt.

From the above it is possible to predict that wool drapes, furnishings, and carpets will not be a major hazard. Any fire will burn, if at all, only slowly. In a carpet, heat generated rises away from the fuel and the ignition source is lost. In a curtain, heat rises towards fresh fuel, so burning behaviour is quite different.

### 3.5.2 *Flammability of polypropylene*

With an LOI of 18.6 and a heat combustion of 11.6 kcal/g, polypropylene burns readily and fiercely in air. As a thermoplastic with  $T_m$  165°C it shrinks and melts away, exposing more material or skin to heat. Molten flaming polymer readily starts fires elsewhere. Its  $T_c$  at 550°C indicates some resistance to casual ignition, e.g. by a smouldering cigarette.

### 3.5.3 *Flammability of cellulosic materials*

Cellulosics have a similar LOI to polypropylene but lower heat of combustion (4.3 kcal/g). A  $T_c$  value of 350–420°C indicates relatively easy ignition. As a result, cotton and viscose textiles burn freely if ignited. A small flame is enough to ignite the hem of a nightdress. Combustion spreads rapidly, and can cause fatal burns within 15 s of ignition. By contrast, flame-retardant treated cotton is self-extinguishing and completely safe for use in nightwear.

### 3.5.4 *Thermoplastic fibres as low-flammability materials*

Both polyamide (LOI 23.0) and poly(ethylene terephthalate) (LOI 21.0) support combustion in air. Thermoplasticity, however, has an important effect on burning behaviour. Synthetic fibres shrink considerably just below their melting point,  $T_m$ . This causes materials to shrink away from ignition sources making established combustion less likely. Further, molten flaming polymer falls away and removes the heat likely to spread combustion. Thus, in free-hanging garments such as nightdresses, brushed nylon provides an acceptable risk and good aesthetic properties.

### 3.5.5 *Testing flammability*

The tests established in BS 5438 and ASTM D1230 provide controlled reproducible ignition systems, and measurement of following combustion. This may be either as flame or as glowing char. Each test has been carefully compared with the burning behaviour of garments, furnishings, and carpets.

In addition, appropriate test methods lay down standardized washing and solubility tests. These are used to assess durability of flame-retardant finishes.

Several special hazards have been identified and allowed for in testing. Both soap and fabric softeners are flammable materials. In hard-water conditions, significant deposits can build up, masking the flame-retardant effect.

Bleaching of garments with sodium hypochlorite, which is widely used in the USA, particularly for children's clothes, can modify the finish, or produce oxycellulose. This renders an otherwise durable finish ineffective.

### 3.5.6 Durability

A dilemma faces a garment maker who wishes to describe a finish as 'durable'. How long must the protection last? Detailed research suggests that if the protection is still intact after 200 domestic wash-dry cycles, it is likely to outlast the garment. Both extended testing and accelerated testing have been used and compared in establishing suitable standards, e.g. BS 3121, BS 5722, and the American DOC FF 3.71.

### 3.5.7 Tests for furniture

The dramatic and powerful combustion resulting from ignition of foam-filled upholstery has caused serious loss of life. House fires can become uncontrollable in under 3 min. Tests (e.g. BS 5852) have been established for such composite structures. The tests use a series of ignition sources of increasing intensity. They simulate ignition sources from a smouldering cigarette, through a lighted match, to burning debris. The latter simulates situations such as train and aircraft fires, or a domestic fire which is already in progress.

In each case, a controlled reproducible ignition source is used. Time, temperature, duration and size of ignition event are the critical factors.

The outcome of the attempted ignition will depend mainly on the materials involved. However, 'barrier layer' structures are important. Figure 3.2 shows such a structure.

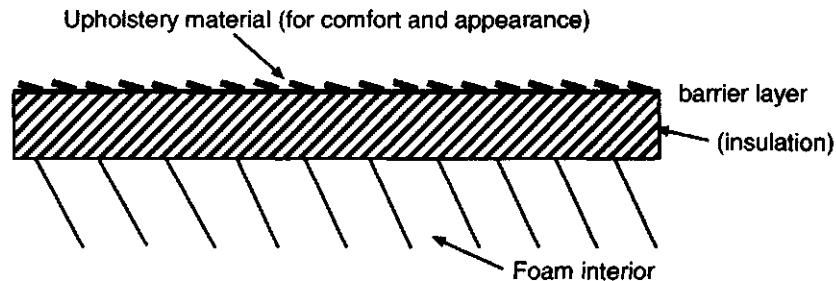


Figure 3.2 A barrier-layer fire-retardant structure.



### 3.5.8 *Barrier-layer fire-retardant structures*

The barrier layer must:

- (a) Stay substantially intact even after pyrolysis
- (b) Minimize heat transfer to the interior
- (c) Limit the supply of oxygen to any combustion occurring underneath.

A variety of materials have been used successfully as barrier-layer materials. Carbon fibre is widely used, so is treated cotton.

Back coating of upholstery with polymer-bound fire-retardant chemicals is widely used for less demanding domestic applications.

## 3.6 **The chemistry of fire-retardant finishing**

A range of strategies can be used to modify the combustion characteristics of textile materials.

### 3.6.1 *Exclusion of oxygen*

If it is possible to separate the fuel (fibres and flammable combustion gases) from the oxidant the combustion will collapse and be extinguished.

*Vapour phase* flame retardants achieve this by generating large volumes of nonflammable gases on pyrolysis, usually HBr and HCl. This is the mechanism which gives PVC its high LOI. It is also the basis of several back-coating formulations.

*Fibre coating* flame retardants use a different strategy. A medium-high melting-point glass-forming material such as borax-boric acid is used. This has the added advantage of not producing toxic fumes on pyrolysis.

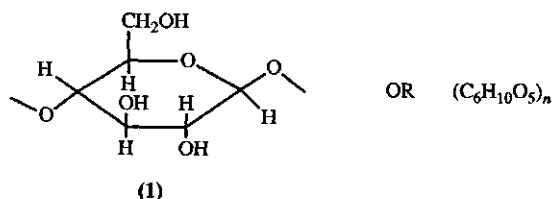
*Chlorinated hydrocarbon* fire extinguishing systems and to some extent water-based fire extinguishers also work in part by excluding oxygen. However, removal of heat (ignition source removal) is also an important strategy.

### 3.6.2 *Modification of the pyrolysis route*

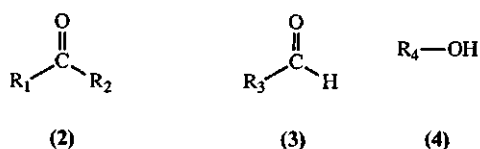
Given that combustion is maintained mainly by heat generation, any system that reduces heat of combustion is likely to be helpful. The two major natural fibre classes, cellulosic and protein, can be made self extinguishing (LOI up to 30) by this strategy.

The detailed chemistry of pyrolysis is highly complex. Several texts, and indeed multivolume publications, are devoted to it (Fenimore, 1970; Kuryla, 1979; Lewin and Sello, 1984; Horrocks, 1986).

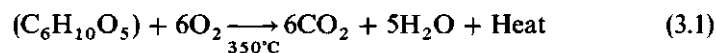
*Pyrolysis of cellulose.* Fortunately the overall process can be expressed more simply. Cellulose (1) can be considered for this purpose as a polymeric carbohydrate.



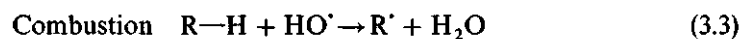
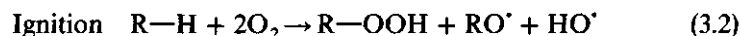
On pyrolysis the chains break up, giving a wide range of low molecular weight aldehydes (3), ketones (2) and alcohols (4), which are highly volatile and flammable. In addition, less volatile but equally flammable higher molecular weight tars are produced. Some material is also turned into solid carbonaceous char.



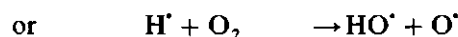
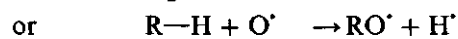
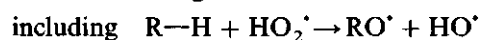
Given a free supply of oxygen and an ignition source cellulose oxidizes completely with a substantial evolution of heat.



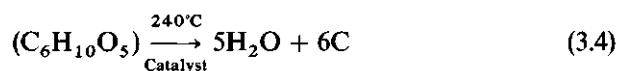
The mechanism of oxidation is largely a free-radical one:



Chain branching:



Cellulose may also decompose by dehydration:



The result is a mass of carbonaceous char, little if any flammable volatiles, and much less heat.

Under normal combustion conditions a mixture of equations (3.1) and (3.4) occurs. Reaction (3.1) is favoured by lightweight, open, free-hanging materials, which burn fiercely. Heavily folded tight-woven materials will often smoulder and char, mainly by equation (3.4).

It is also possible to influence pyrolysis by using suitable chemicals in favour of equation (3.4). By favouring dehydration:

- (a) Pyrolysis starts at a lower temperature
- (b) Less heat is evolved
- (c) Much less volatile flammable gas and tar is produced

The combustion of cellulose will then be inhibited successfully:

- (a) By reducing the heat and flame which spread the fire
- (b) By promoting char formation which may limit access to air

The result is a self-extinguishing material with an LOI of 28 or above.

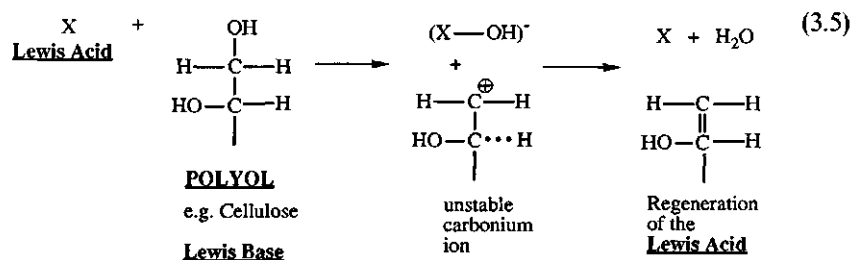
Wool can be raised to a fire-retardant standard suitable for any environment by appropriate finishing. The strategy is similar to that of cellulose, but the chemistry is more complex due to the proteins involved.

Many of the commercial finishes available promote dehydration and char formation rather than oxidation.

### 3.6.3 The role of Lewis acids in promoting dehydration

The action of Lewis acids is central to the fire-retardant finishing of cellulose, by favouring dehydration.

A Lewis acid is a chemical which, under appropriate conditions, is strongly electron-absorbing. It is paired in the reaction with a Lewis base, which donates electrons (equation 3.5).



Thermogravimetric analysis of cotton treated with monoammonium phosphate (MAP; a good Lewis acid) confirms a fundamental change in the pyrolysis route (Table 3.3).

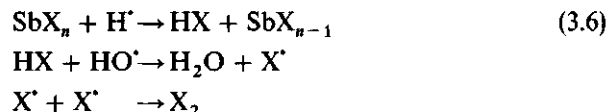
A wide range of water-soluble phosphorus-containing chemicals are active Lewis acids and give good temporary flame retardancy to cotton. The problem



### 3.6.5 *Metal oxides and salts as flame retardants*

Good flame retardancy can be achieved on both cellulose and wool by incorporating metal oxides and/or salts in an appropriate finish.

The literature does not give many references to mode of action, but one author suggests they might act as free radical chain terminators, e.g.:



Titanium and zirconium are used successfully on wool as their citrates and fluorides. Antimony oxide and chloride find use on cellulose.

### 3.6.6 *Synergistic flame-retardant effects*

Synergism is the term used when the sum of the effects is greater than the individual effects of the components. It seems mysterious and almost magical, but can be understood if the complex nature of combustion and retardant action are understood.

Many of the mechanisms of combustion are interdependent. Generation of volatiles precedes the spread of flame. Oxidation produces volatiles. Dehydration reduces material for volatile generation. It thus follows that simultaneous attack on more than one mechanism can produce a collapse of the combustion process.

In practice, metal oxides are often combined with vapour-phase retardants. Nitrogen-containing materials are combined with phosphorus. This results in some remarkable 'witches' brews' which are sold as commercial flame retardants. The picture is further complicated by the need to bind the chemicals to the fibre to make them durable.

The above account of combustion and pyrolysis mechanisms is necessarily over-simplified. In practice, the pyrolysis of cellulose and protein follow a wide range of routes between the two extremes of equations (3.1) and (3.4). Hundreds of intermediate chemicals, short-lived free radicals, tars and volatile products have been identified.

It follows that no clear equations or specific routes for fire retardant action can be stated with certainty. The mechanisms and reactions given above illustrate some of the possible routes.

## 3.7 **Commercial solutions for fire retardancy**

### 3.7.1 *Design*

Substantial progress has been made in the design of buildings, aircraft, trains, upholstery and garments to avoid flammability and larger-scale fire risks.

Alongside this, progress has been made in testing. The emphasis in testing is on complete structures rather than individual materials, which are adequately characterized by existing tests.

The key to designing low-risk structures is spread of combustion and combustion products (toxic fumes, smoke, etc.). If a fire remains small, it can be dealt with easily, and does not cause panic.

For a given material, e.g. cellulose, the rate of combustion varies enormously. This is illustrated (with suitable precautions) by igniting two sheets of newspaper. The first is held open and ignited at the bottom edge. (Be prepared to extinguish substantial flames within seconds.) The second sheet is rolled tightly. This burns very much more slowly, and controllably.

It is clear from this and similar observations that fabric and garment structure can play a substantial role in fire retardancy. Fine nets, free hanging edges, streamers, and open structures with free access to air all present maximum combustion rates, and likely points for casual ignition. By contrast, heavy close-woven materials, multilayer structures, and freedom from easily ignitable features reduce the risk.

In many design briefs it is not possible to avoid the risks described above for aesthetic or comfort reasons. In such cases designers return to flame-retardant materials to minimize the risk. In structures for particularly hazardous environments such as firefighters' uniforms, aircraft interiors, and protective overalls, both flame-retardant materials and fire-resistant structures are used.

### 3.7.2 *Intrinsically fire-retardant materials*

Few natural materials, with the exception of mineral fibres, are intrinsically self-extinguishing. Most synthetic polymers are flammable, unless specifically modified to make them self-extinguishing, by physically or chemically including fire-retardant chemicals.

Substantial research effort has been invested in the manufacture of intrinsically fire-retardant textile fibres. All the major polymer types with the exception of polyolefins have fire-retardant versions. The chemical nature of the modifications is not generally revealed. It is however reasonable to assume that the fire-retardant properties are obtained by addition of one or more fire-retardant chemicals to the polymer mass prior to spinning the fibre.

Examples chosen at random from the many commercial offerings include:

Viscose F.R. made by Lenzing of Austria. This has normal textile properties associated with viscose and is promoted for upholstery, domestic and industrial protective markets.

FIDION F.R. is a flame retardant polyester produced by Enichem Fibre Spa of Italy, who also produce SIRONIL F.R. and PANOX described below.

Trevira C.S. (comfort and safety) is another fire-retardant polyester by Hoechst of Germany. It is widely used and promoted for domestic and public auditorium upholstery and curtain applications. It is described as a phosphorus-containing copolymer.

Acrylic co-polymers: a wide range of flame retardant acrylic fibres is on the market including SIRONIL F.R. The comonomers used, up to 30% in some cases, include vinyl chloride, vinyl alcohol, and vinylidene chloride.

All the above are very similar in both appearance and properties to their generic fibre types.

Poly(vinyl chloride) fibres, such as Rhovyl and Clevyl, have a share of the fire-retardant market.

Oxidized acrylics such as PANOX (Enichem) and PANOTEX Universal. Carbon fibres are highly fire-resistant and widely used as barrier-layer materials.

The oxidized acrylics are essentially carbon fibres and are naturally black. They are non-thermoplastic, and resist even an intense blow torch flame for a significant time.

Aramid fibres, such as Nomex and Kevlar, have high enough LOI values to be self-extinguishing. In addition, they are strong and have high melting points. They find use in applications such as racing drivers' overalls.

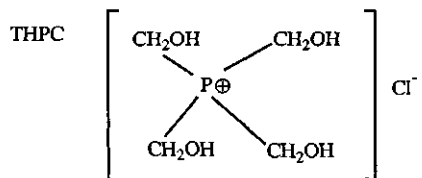
Silicon-based polymers, unlike carbon-based materials, are generally incombustible. The Kemira company of Finland have recently announced their new fibre VISIL 33 A.P. (The Textile Institute, 1993). It is a viscose fibre with a silicic acid backbone. Smoke emission is low and it is free from toxic fumes.

The potential hazards from the use of phosphorus-containing and chlorine-based products add to the cost of fire retardant solutions containing them. In an environmentally conscious era it is vital to test the chemicals used, the effluents produced (both air and water), and the products themselves. No responsible company can ignore the safety of its workers or its customers.

Tests of both chemicals and products for toxicity, carcinogenic activity, teratogenic (damage to unborn foetuses) activity, and dermatitis are used. Concern is growing over the hazards from combustion products as well as from materials themselves. It will no doubt be an interesting problem for future chemists to isolate hazards, devise tests and invent new fire-retardant solutions avoiding the hazards.

### 3.7.3 *Commercial fire-retardant treatments for cotton*

Good commercial fire-retardant treatments successfully combine durability with low flammability. It is necessary to deliver the appropriate active chemical in a washfast form. The resulting material should not lose strength, abrasion resistance, lightfastness or general durability, so the finish needs to be chemically inert and neutral in pH.



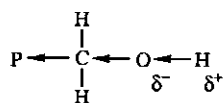
Tetrakis-hydroxymethylphosphonium chloride (6)

For upholstery fabrics, back coating with a polymeric binder containing metal oxide and chlorinated hydrocarbon flame retardants is commercially successful. Water-based rather than solvent-based application systems are preferred for environmental reasons.

Two different approaches are used to obtain durable phosphorus-containing finishes on cotton.

- (1) *Use of highly cross-linked polymeric resins.* These are applied as low molecular weight chemicals and polymerized inside the fibre. This locks the resin permanently into the interior structure of the fibre.
- (2) *Use of reactive chemicals which bond covalently with cellulose.* A chemical bond with cellulose ensures high durability, provided the chemical bond is not easily attacked by conditions in use or washing. Domestic and industrial washing can involve both bleaches and alkali so the choice of chemical link must be made carefully.

3.7.3.1 *Systems based on THPC (tetrakis-hydroxymethylphosphonium chloride (6)).* THPC has several important properties. The *P*-methylol groups are quite reactive due to the electron withdrawing effect of the phosphorus atom:



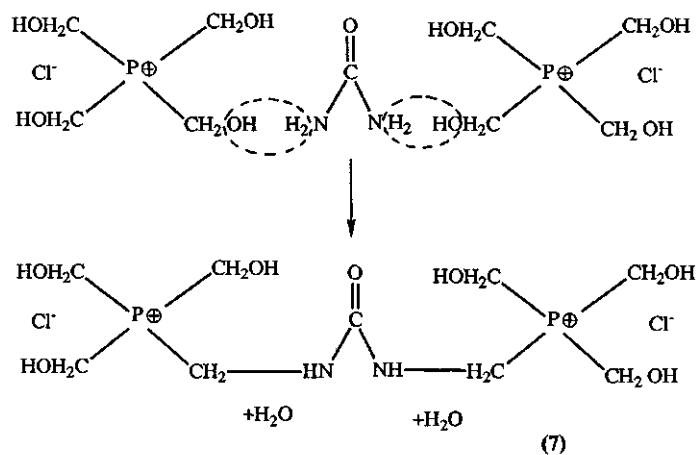
They thus readily undergo condensation reactions, e.g. with other *P*-methylol groups or with amine groups such as urea or ammonia (Scheme 3.1).

Compound (7) is a widely used resin precondensate. It has six reactive *P*-methylol groups, which react to produce highly cross-linked insoluble resins. Proban 210 from Albright & Wilson is based on this precondensate.

Resin formation based on condensation reactions of both *P*-methylol and *N*-methylol are widely used in textile finishing. In almost all cases the condensation polymerization is carried out at elevated temperatures with an acid catalyst in a pad-dry-bake sequence.

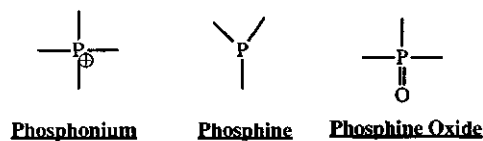
The Proban process is unique in using a room temperature ammonia



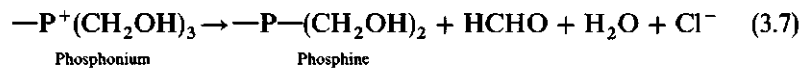


Scheme 3.1

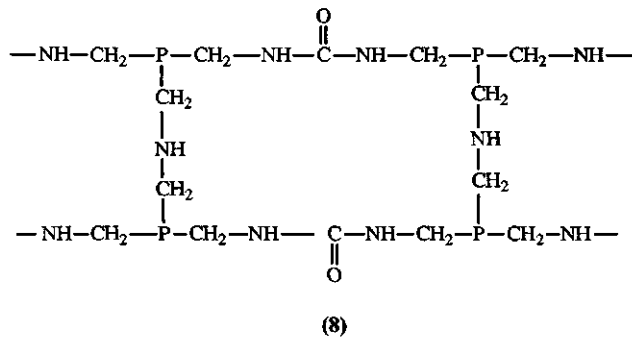
gas-based polymerization. The central phosphorus atom can be in one of three states:



The phosphonium salt precondensate is buffered to pH 6 in a pad-dry application using sodium acetate; at pH 6 most of the salt has been converted to the phosphine form. At this pH, reaction rate with ammonia is at a maximum.



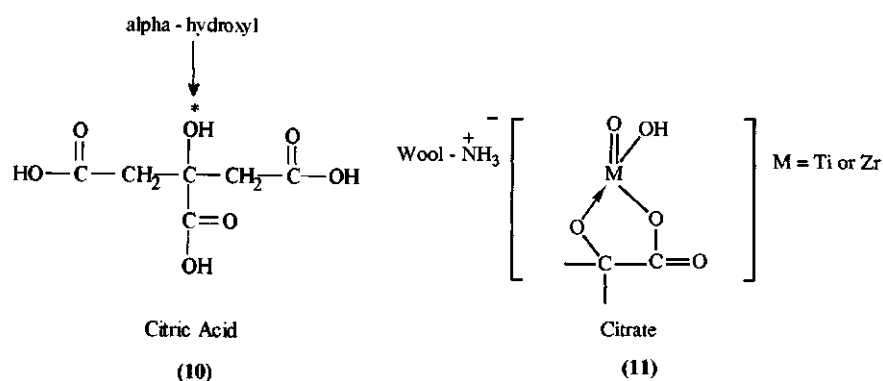
Full polymerization is very rapid and exothermic, giving a three-dimensional cross-linking polymer (8). It should be noted that stoichiometrically the atomic ratio N:P has risen to 2:1 in the polymer from 1:1 in the precondensate.







zirconium complexes; 0.5% Ti and 1.9% Zr add-on are required to raise the LOI to 27. Citric (10) acid is a useful addition to the formulation. The alpha hydroxyl (\* in compound 10) stabilizes the complexes (11). Titanium hexafluoride  $[\text{TiF}_6]^{2-}$ , zirconium hexafluoride  $[\text{ZrF}_6]^{2-}$  and zirconium difluorocitrate  $[\text{ZrF}_2(\text{citrate})]^{2-}$  are also used in various versions of Zirpro wool finishing (International Wool Secretariat). Flame-retardant finishes can be applied to wool simultaneously with shrink-resist finishes in some instances.



### 3.7.5 Finishes for polyester/cotton

Finishes for 100% polyester have been largely unsuccessful, mainly for durability. Polyester is too hydrophobic for penetration by precondensates, and has too few sites for covalent bonding. The necessary phosphorus-containing chemicals can, however, be incorporated during fibre manufacture, as in Trevira CS and DuPont's Dacron 900F.

Polyester/cotton with up to 50% polyester can be successfully finished by using either THPC or phosphonate-type flame retardants. Rohringer *et al.* (1975) give a graph relating LOI to percentage blend composition at various phosphorus add-on levels. They report LOI greater than 30 for all blends above 50% cotton using a phosphonopropionamide finishing (Pyrovatex) with 3% phosphorus content.

Several attempts have been made to include bromide, either in the precondensate or by post-treatment, when using phosphorus-based retardants.

Caliban F.R. P.44 (White Chemical Co.) has been shown to be a safe and effective coating retardant. It is bound with a latex to give durability and combines aromatic bromide and antimony oxide. Further improvement is given by using a brominated latex.

Both these approaches use vapour-phase as well as condensed-phase mechanisms to increase the retardant effect synergistically.

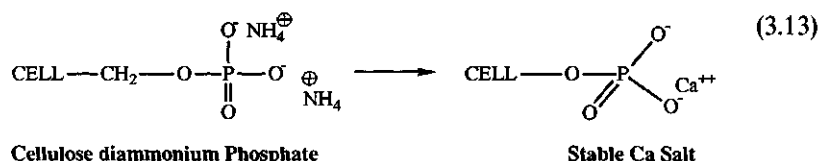
### 3.8 Premature failure of flame retardancy

The possibility that an otherwise durable finish might suddenly lose its effect is a serious matter. Several cases of this have been identified. In most cases specific causes have been revealed, and can be avoided.

#### 3.8.1 Ion-exchange effects in hard water

Phosphate, phosphonate and/or phosphoric acid groups perform well as Lewis acids, providing condensed-phase flame retardancy. Unfortunately, the calcium and magnesium salts are too stable and have much reduced effect.

Free phosphate groups can pick up  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  by ion exchange from hard water (equation 3.13), causing failure of appropriate tests after as few as 20 domestic laundering cycles. This compares with the 50-plus of normal durability.



Phosphonates, as used in Pyrovatex C.P., are less susceptible to this problem; however, some ion-exchange activity has been demonstrated.

#### 3.8.2 Sensitivity to chlorine-containing bleaches

All the phosphorus-containing flame retardants suffer premature loss of durability if laundered with hypochlorite-type bleaching agents. In laboratory tests THPOH-amide and THPC-urea finishes failed after only ten launderings (Horrocks, 1986). Failure appears to be due to direct loss of phosphorus by attack on the resin. As a result of the above findings, such fire-retardant finishes are sold with the explicit warning 'use no bleach' clearly labelled on the garment.

#### 3.8.3 Detergent and softener effects

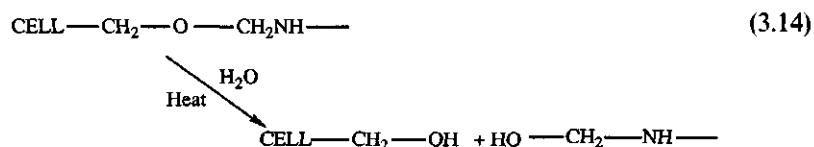
Laundering with soap in hard-water areas can lead to a build-up of insoluble lime soaps on the fabric. These are flammable and can cause premature failure of flammability tests.

Hospitals often use soap/bleach laundering which combines two possible causes of failure.

The recent popularity of domestic fabric softeners gives rise to concern. Many of the cheaper and most effective softeners are either poly(ethylene oxide)- or hydrocarbon-based. Both materials are highly flammable, and if present in significant quantities, can mask flame retardancy.

#### 3.8.4 Steam sterilization

The practice of steam sterilizing hospital laundry has an unexpectedly strong effect on finishes which depend on covalent linking to cellulose. THPC-based finishes are reasonably resistant, but some phosphonate-based finishes have been shown to lose up to 60% of added phosphorus after only five steam sterilizations with complete loss of flame retardancy. The probable cause is hydrolysis of the ether link to cellulose (equation 3.14).



### 3.9 The cost of fire-retardant solutions

Even before the extra cost of fire-retardant materials is taken into account, some additional costs are incurred when offering flame-retardant products. These include testing, certification, labelling and promotional costs. It is also likely that product liability insurance will cost more.

The extra cost of materials with reduced fire hazard is also significant. In the upholstery field, back-coating finishes are available which give durable fire retardant action. They add about 10–20% to material costs. At the other end of the scale, specialist fire-retardant fibres can cost three to five times as much as equivalent general textile fibres.

In barrier-layer applications, the choice of barrier fabric is between oxidized acrylic (e.g. Panotex by Universal Carbon Fibres) and fire-retardant treated cotton. Oxidized acrylic has reduced fume generation, and costs up to four times the price of an equivalent cotton fabric.

Fire-retardant treated cotton and wool costs 20–50% more than equivalent untreated fabric. There is also some loss of aesthetic properties.

In view of the above, it is not perhaps surprising that fire-retardant solutions tend to be confined to products that meet specific hazards. Good examples are children's nightwear, aircraft and train interiors, public auditoriums, and protective clothing. Some progress has also been made in domestic upholstery. Here, elimination of highly flammable interior foam has also been a major contributor to reducing the risk.

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