



# Fire Retardant Textiles

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Dr. Oulha

Fire Retardant Materials

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## 1.0 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 are flammable.
2. In theatres, restaurants, clubs and aircraft there can be heavy loss of life in the event of fire.
3. Use of particular materials, garment 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.

### 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, 650 of them fatal (Home Office fire statistics 1985.) A major cause of death (at least 50% of fatalities) 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.

A Swiss survey shows that mortality is 43% in severe burn accidents and 27% from all cases where burns needing hospital treatment are involved.

If fire happens in public places horrific loss of life has occurred.

At Boston, Massachusetts, USA 750 customers were present at the Coconut Grove Club, on November 28<sup>th</sup> 1942. The fashion at the time included stiffened lace party dresses. A common finishing stiffener was unbelievably, nitro cellulose. In the flash fire which engulfed the customers:-

432 died and 214 were injured.

The notorious 'Ring Theatre Disaster' in Vienna caused 450 deaths when a back stage fire spread rapidly to the auditorium.

A relatively minor fire at Woolworth's store in Manchester 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.

## 2.0 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 run-away self feeding event producing enormous heat, suffocating and toxic fumes, and total destruction.

Fig. 1 shows the essential components. FUEL, an OXIDANT, (usually air), and an IGNITION SOURCE.

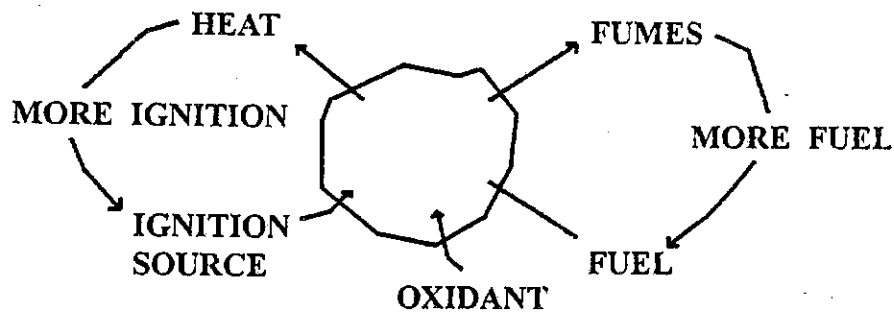


Fig. 1 The Combustion Process

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 'flash-over' events. Such an event caused major loss of life in the Kings Cross Underground disaster, London 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, garments removed. Time is available to formulate and execute the necessary measures.

### 3.0 Developing a Fire Retarding Solution

Over many years a four-fold attack has been mounted on loss of life, and injury by fire.

#### a) Design for fire retardancy and escape

This covers every aspect of garment, furniture, architectural, and transport design. It has resulted in firemen's uniforms capable of protecting against 2000°C exposure for 30 seconds. 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) prohibits the sale of nightwear which does not pass appropriate flammability tests. The 1980 upholstered furniture (safety) regulations were the result of much detailed assessment of fires in the home. The Woolworth's 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, window, 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.

### 3.1 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 (eg. BS 6336: 1982)
3. Ensure that the products and materials pass the appropriate tests.

The terms 'flame proof' 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 are available by which the property can be measured.

Test methods, 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, BS5750 & 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 1. lists some important British Standards

Table 1. British Standard Tests for Flammability

<u>British Standard</u>	<u>Purpose</u>
BS2963: 1958	Test for flammability of fabrics.
BS3119: 1959	Tests for flame proof materials.
BS3120: 1959	Performance requirements for flameproof clothing.
BS3121: 1959	Performance requirements for fabrics of low flammability.
BS5438: 1976	Test methods for vertically orientated fabrics and assemblies (small flame ignition.)
BS5722: 1974	Performance of fabrics and assemblies for sleepwear and dressing gowns.
BS5852: 1979	Fire tests for furniture, textile and foam interior combinations pt1 ignition by smokers' materials pt2 ignition by flaming sources
BS5867:1980 (pt2)	Flammability requirements for curtains and drapes.
BS6307: 1982	Ignition of textile floor coverings (small ignition source.)
BS6357: 1983	Tests for resistance to molten metal splash for protective clothing.

Some Important British Standards

Some equivalent US standards include

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

4.0 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.

## 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.

Heats of combustion can vary from 11.6 kilo calories/gram for polypropylene down to 3.4 kcal/g for viscose rayon.

### 4.1 Limiting Oxygen Index

The atmosphere contains about 21% oxygen. The rest (nitrogen, CO<sub>2</sub>, water etc.) do not support combustion. It has been found by experiment that increasing the ratio of oxygen to nitrogen makes some materials burn, which are self extinguishing in air. Conversely materials which burn readily in 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 1984.) and Table 2. lists a range of materials and their LOI values.

Table 2. Limiting Oxygen Indices

Polyethylene oxide	15.0
Polymethyl methacrylate (perspex)	17.0
Polyacrylo nitrate	18.0
Polyethylene	18.0
Polystyrene	18.5
Polypropylene	18.6
Cellulose	19.0
Polyethylene terephthalate	21.0
Polyvinyl alcohol	22.0
Nylon 66	23.0
Wool	25.2
Modacrylic	26.8
Polycarbonate	27.0
Nomex (aramid)	28.5
Phenolformaldehyde (resin)	35.0
Neoprene (butadiene/styrene)	40.0
Polyvinyl chloride	60.0
Carbon	60.0
Polytetrafluoroethylene	95.0
Minimum % oxygen values for sustained combustion	

## 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 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.

## 5.0 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 fireman 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.

### 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  $T_c$  ( $600^\circ$ .) 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.

### 5.2 Flammability of Polypropylene

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

### 5.3 Flammability of Cellulosic Materials

Cellulosics have a similar LOI to polypropylene but lower heat of combustion (4.3 kcal/g.) A  $T_c$  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 seconds of ignition. By contrast flame-retardant treated cotton is self extinguishing and completely safe for use in nightwear.

### 5.4 Thermoplastic Fibres as Low Flammability Materials

Both polyamide (LOI 23.0) and polyethylene terephthalate (LOI 21.0) support combustion in air. Thermo-plasticity however has an important effect on burning behaviour. Synthetic fibres shrink considerably just below 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.

### 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 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.

#### 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. eg. BS 3121, BS 5722 and the American DOC FF 3.71.

#### 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 three minutes. Tests (eg. 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 2 shows such a structure.

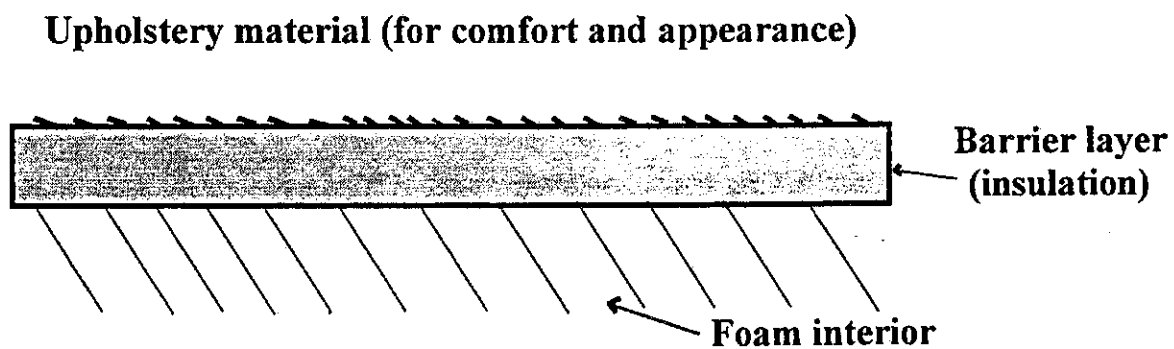


Fig. 2 A Barrier layer fire retardant structure

## 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 material. 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.

## 6.0 The Chemistry of Fire Retardant Finishing

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

### 6.1 Exclusion 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 non-flammable 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.

## 6.2 Modification of the Pyrolysis Route

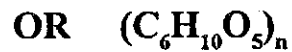
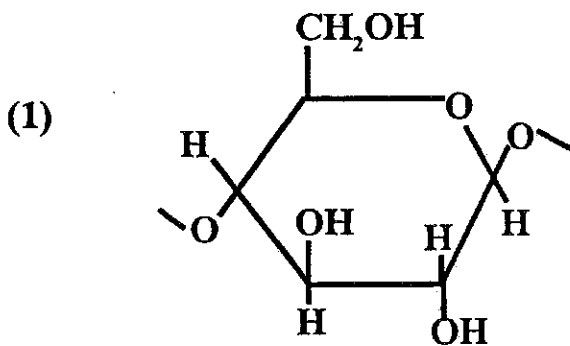
Given that combustion is maintained mainly by heat generation, any system that reduces heat of combustion is likely to be helpful. The two major natural fibre classes, cellulosic and protein can be made self extinguishing (LOI up to 30) by this strategy.

The detailed chemistry of pyrolysis is highly complex. Several texts, and indeed multi-volume publications are devoted to it, (Kuryla et al 1979, Lewin, 1984, Fenimore, 1970, Horrocks, 1986).

### Pyrolysis of Cellulose

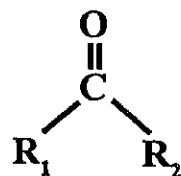
Fortunately the overall process can be expressed more simply. Cellulose can be considered for this purpose as a polymeric carbohydrate.



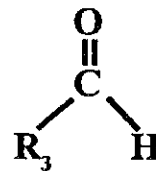


On pyrolysis the chains break up giving a wide range of low molecular weight aldehydes, ketones and alcohols, which are highly volatile and flammable.

(2)



KETONE



ALDEHYDE

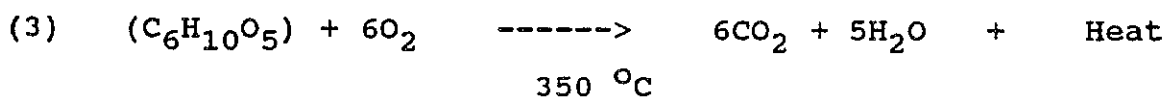


ALCOHOL

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.



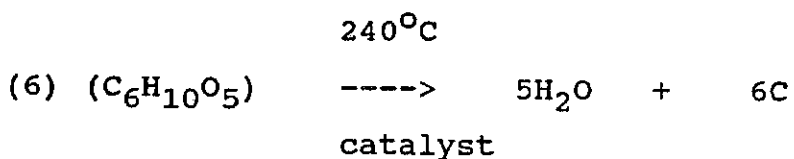
The mechanism of oxidation is largely free radical:-



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 (3) and (6) occurs. Reaction (3) is favoured by lightweight open, free hanging materials which burn fiercely. Heavily folded tight woven

materials will often smoulder and char, mainly by route (6)

It is also possible to influence pyrolysis by using suitable chemicals in favour of route (6) - dehydration.

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 for cellulose, but the chemistry is more complex due to the proteins involved.

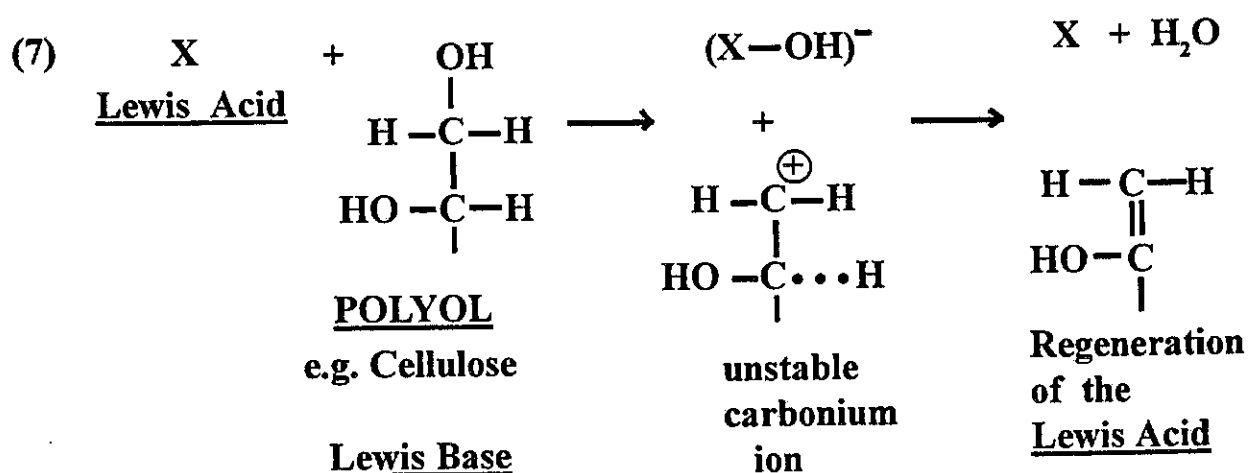
Many of the commercial finishes available promote dehydration and char formation rather than oxidation.

### 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.



Thermo gravimetric analysis of cotton treated with MAP, mono ammonium phosphate (a good Lewis acid) confirms a fundamental change in the pyrolysis route (Table 3)

Table 3.

Loss in weight % after 10 min

Temp	250°C	280°C	300°C
Untreated	3%	5%	7% - (of dry wt.)
MAP (1.7% P add-on)	50%*	70%	80%

\*carbonization virtually complete

A wide range of water soluble phosphorus containing chemicals are active Lewis acids and give good temporary flame retardacy to cotton. The problem is to combine this with:

- a) Durability lasting the life of the garment;
- b) Minimal effect on the softness and drape;
- c) Minimal effect on dyes;
- d) Low cost;
- e) Low emission of toxic fumes;
- f) Environmentally friendly application;
- g) No health hazard to wearer or finisher.

A large number of commercial finishes have met most of these criteria but none have met all of them.

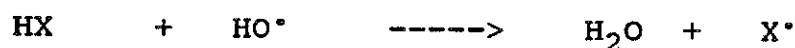
#### 6.4 Vapour Phase Fire Retardant Action

The majority of chemicals active by the vapour phase mechanism are chlorinated hydrocarbons. On pyrolysis these release large quantities of non flammable gases such as HBr and HCl and Cl<sub>2</sub>.

A good example is the now notorious 'tris' - tris (2,3



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



Titanium and Zirconium are used successfully on wool as citrates and fluorides.

Antimony oxide and chloride find use on cellulosics.

#### 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 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 (2) and (6). 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.

## 7.0 Commercial Solutions for Fire Retardancy

### 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 doesn't cause panic.

For a given material eg. 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 slower, 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, multi layer 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 turn to flame retardant materials to minimize the risk. In structures for particularly hazardous environments such as firemen's uniforms, aircraft interiors, and protective overalls, both flame retardant materials and fire resistant structures are used.

## 7.2 Intrinsically Fire Retardant Materials

Few natural materials, with the exception of mineral fibres

are intrinsically self extinguishing. Most man made 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 poly-olefins have F.R. versions. The chemical nature of the modifications is not generally revealed. It is however reasonable to assume that F.R. 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 F.R. 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 co-polymer.

Acrylic co-polymers. A wide range of flame retardant acrylic fibres is on the market including SIRONIL F.R. The co-monomers 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.

Polyvinyl 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 thermo plastic, 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. (Flammability 93 Textile Inst. Conference.) 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 F.R. 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 fetuses) 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 F.R. solutions avoiding the hazards.

### 7.3 Commercial F.R. Treatments for Cotton

Good commercial F.R. 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, light fastness or general durability, so the finish needs to be chemically inert and neutral in pH.

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.

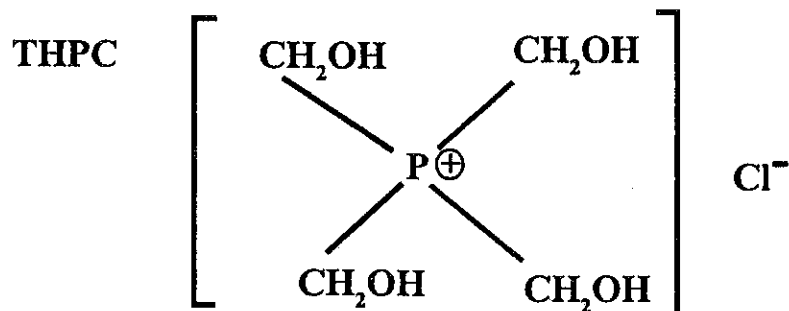
1. Use of highly cross-linked polymeric resins.

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.

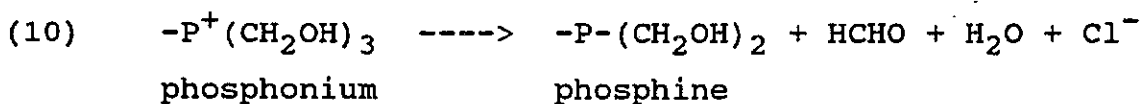
2. Use of reactive chemicals which bond covalently with cellulose.

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.

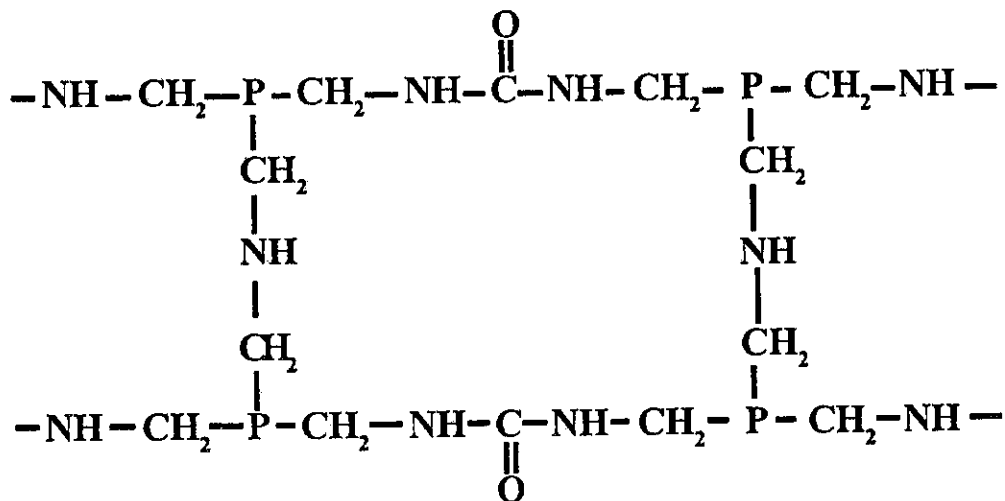
7.3.1 Systems Based on THPC (Tetrakis Hydroxymethyl Phosphonium Chloride)



Tetrakis hydroxymethyl Phosphonium Chloride

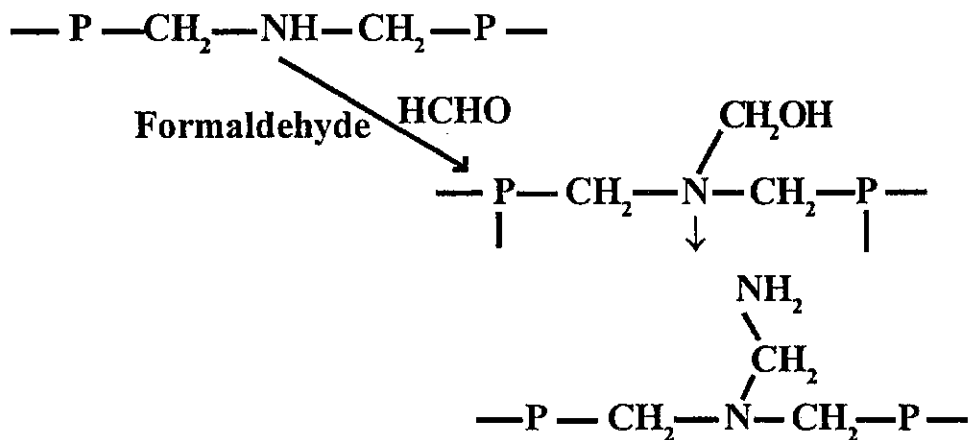


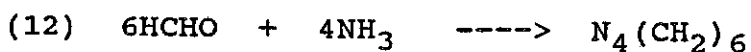
Full polymerization is very rapid and exothermic giving three dimensional cross linking polymer.



It should be noted that stoichiometrically the ratio N:P (atomic) has risen to 2:1 in the polymer from 1:1 in the precondensate. This ratio can be monitored to ensure efficient curing. Side reactions of secondary amine groups may increase the ratio

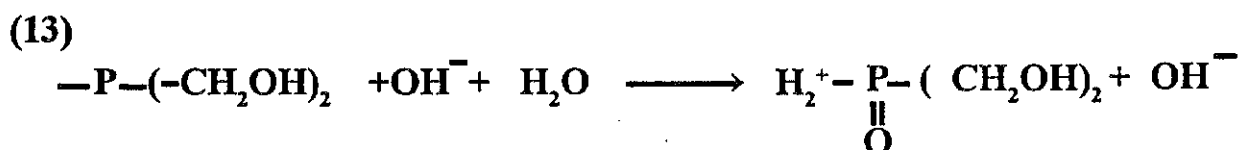
(11)





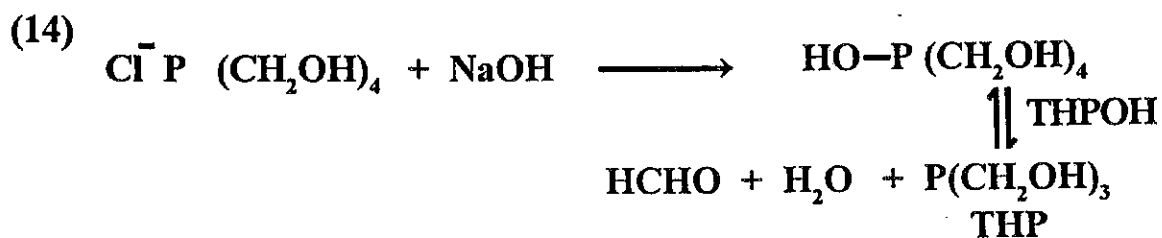
hexamethylene tetramine

If the pH rises significantly above 6 the reactivity of the precondensate falls due to phosphine oxide formation.



#### The THPOH Process

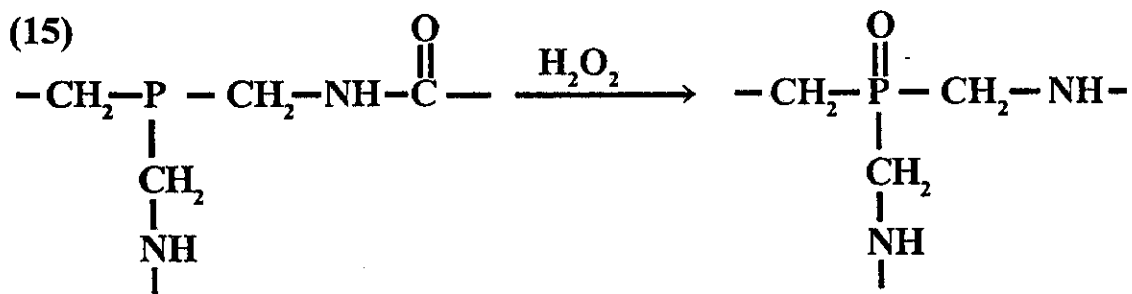
In a similar finishing process known as the THPOH process, THPC (the phosphonium salt) is converted to the phosphonium hydroxide form.



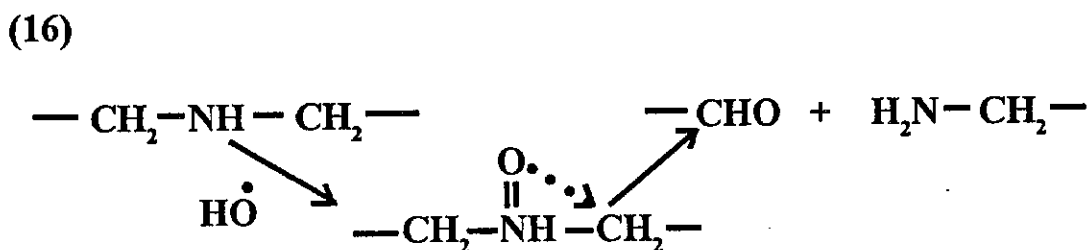
THPOH/THP show high reactivity with ammonia. The reaction rate peaks very sharply at pH6

The phosphine form of the resin smells quite strongly. It also has a tendency to reduce light fastness of dyes. It is thus

necessary to follow polymerization by an oxidative wash-off with hydrogen peroxide, which converts the phosphine form to the phosphine oxide.

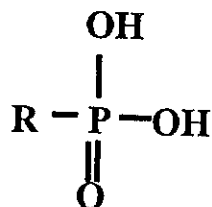


Over oxidization can lead to loss of durability due to the formation of amine oxides and subsequent rupture of  $\text{CH}_2\text{-NH}_2$  bonds.



### 7.3.2 Flame Retardancy by Phosphonylation of Cellulose

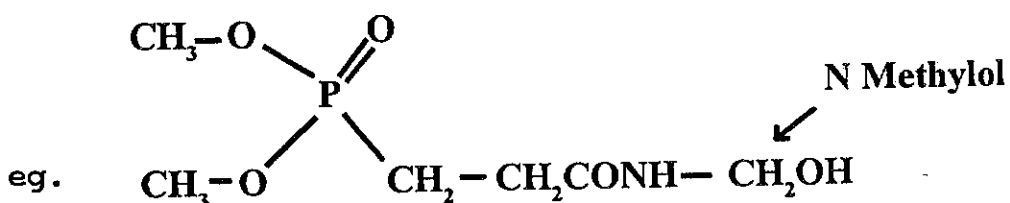
The general formula for phosphonic acid is



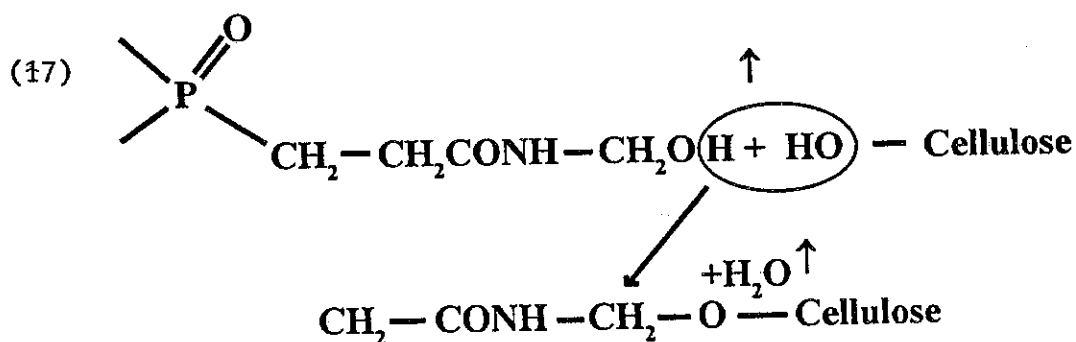
where R is an organic group.



The N-methylol-dialkyl phosphonopropionamides:-



form stable covalent bonds with cellulose and give good wash fastness in a typical N-methylol condensation reaction.



The commercially successful Pyrovatex CP (Geigy) finish is based on this method.

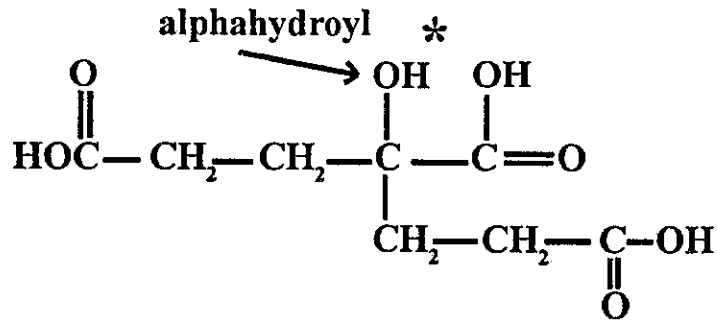
#### 7.4 Finishes for Wool

Wool is only weakly flammable (LOI 25), has a high ignition temperature, and low heat of combustion. Considerable effort has been invested, however, into making it thoroughly flame retardant, for use in high risk environments.

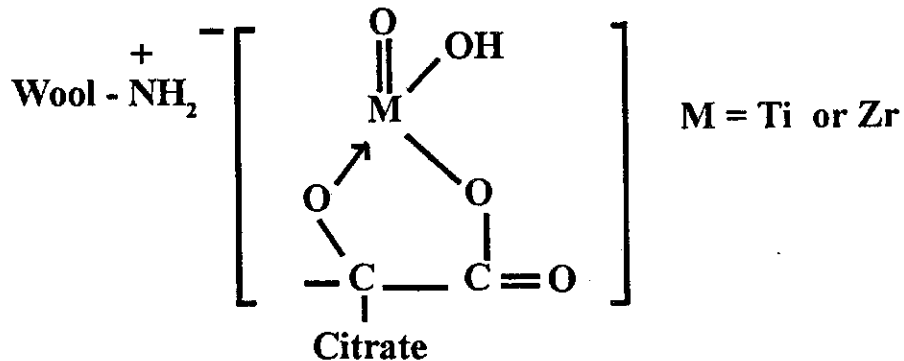
THPC and halogenated hydrocarbons have been used effectively, but cheap effective durable finishes are now widely used based on titanium and zirconium complexes.

0.5% Ti and 1.9% Zr add on are required to raise the LOI to 27.

Citric acid is a useful addition to the formulation.



The alpha hydroxyl (\* above) stabilizes the complexes



Titanium Hexafluoride  $[\text{TiF}_6]^{2-}$  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.

## 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 up to 50% polyester can be successfully finished using either THPC or phosphonate type flame retardants. (Rohringer et al 1975) give a graph relating LOI to % 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) giving 3% phosphorus content.

Several attempts have been made to include bromine 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.

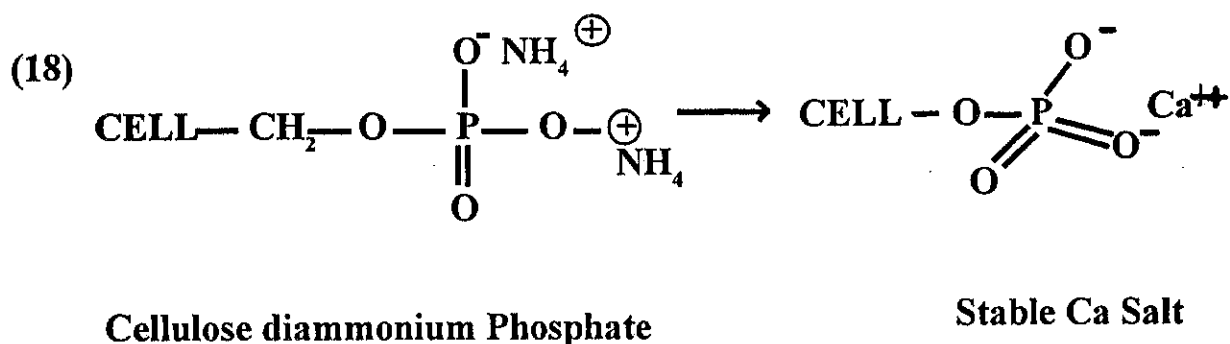
## 8.0 Premature Failure of Flame Retardancy

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

### 8.1 Ion Exchange Effects in Hard Water

Phosphate phosphorylate 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 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.

## 8.2 Sensitivity to Chlorine Containing Bleaches

All the phosphorus containing flame retardants suffer premature loss of durability if laundered with hydrochlorite type bleaching agents. In laboratory tests THPOH - amide and THPC urea finishes failed after only ten launderings (Rev. Prog. Col. V16 1966 p.90). Failure appears to be due to direct loss of phosphorus by attack on the resin. As a result of the above findings such F.R. finishes are sold with the explicit warning 'use no bleach' clearly labelled on the garment.

## 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. You may wish to work out what they are.

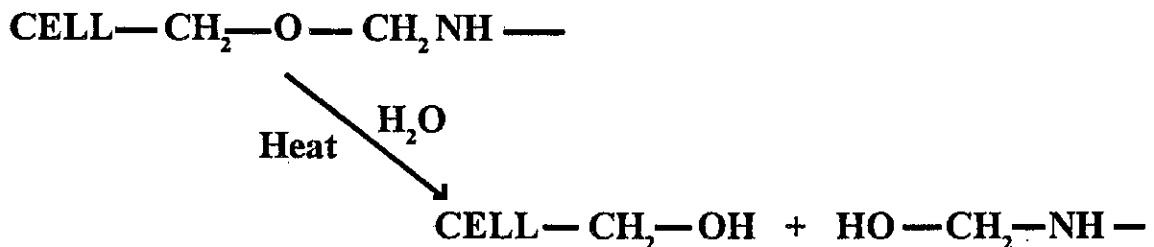
The recent popularity of domestic fabric softeners gives rise to concern. Many of the cheaper and most effective softeners are either polyethylene oxide or hydrocarbon based. Both materials are highly flammable, and if present in significant quantities, can mask flame retardancy.

#### 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 ester link to cellulose

①9



#### 9.0 The Cost of Fire Retardant Solutions

Even before the extra cost of F.R. 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 (eg. Panotex by Universal Carbon Fibres) and F.R. treated cotton. Oxidized acrylic has reduced fume generation, and costs up to four times the price of an equivalent cotton fabric.

F.R. treated cotton and wool costs between 20 and 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 F.R. solutions tend to be confined to products which 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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