CHAPTER 11

FLAME RETARDANT FINISHES

The desire for textiles having a reduced tendency to ignite and burn has been recognized for considerable time during man's recorded history. The use of asbestos as a flame resistant material was recorded in Roman times. Wyld (6) was issued a patent in 1735 describing a finishing treatment for cellulosic textiles based on alum, ferrous sulfate and borax. In 1882, Gay-Lussac (3) published the first systematic study of the use of flame retardants. Before delving into the chemistry of flame retardant finishes, it is necessary to first understand that there is no single test that determines whether a fabric is flame retardant or not. The test conditions used to make this determination will reflect on the specific fabric and its intended end-use. For example, all apparel fabrics are expected to pass a 45 degree flame test; however, those destined to be used as children sleep-wear are expected to pass a vertical ignition test. Drapery, upholstery and carpets all have their own ignition tests designed to evaluate how the article performs in its environment. Flame retardant tests and fabric performance specifications are discussed in detail in other references (1,2,3), and the reader is urged to consult these for a more in-depth understanding. The important point here is that the following discussions must be viewed in context with the test used to make the observations. The terms associated with flame-retardant finishing and fabric flammability in general are often confusing, for example flammable versus inflammable, fire resistant versus flame resistant. If clarification is needed, the reader is referred to Tesoro's (5) compilation of definitions associated with flammability.

Generally speaking, a fabric is deemed to be flame retardant if it does not ignite and create a self-sustaining flame when subjected to a heat source. Therefore a pile fabric made from rayon fibers is considered to be highly flammable while a tightly woven fabric made from high twist yarns easily passes the 45 degree ignition test. Neither however pass the vertical ignition test. Thermoplastic fibers present another anomaly - certain fabrics do not ignite when tested by the vertical test, the fabric melts and shrinks away from the heat source. Other fabrics made from the same fiber ignite and fail the test because the fabric construction prevents the rapid withdrawal of the melt from the flame. And finally, there are some fibers which will not ignite at all, they will however char.

I. THEORY OF COMBUSTION

When solid materials are heated, physical and chemical changes occur at specific temperatures depending on the chemical make-up of the solid. Thermoplastic polymers soften at the glass transition temperature (Tg), and subsequently melt at Tm. At some higher temperature (Tp), both thermoplastic and non-thermoplastic solids will chemically decompose (pyrolyze) into lower molecular weight fragments. Chemical changes begin at Tp and continue through the temperature at which combustion occurs (Tc). These four temperatures are very important when considering the flame resistance of fibers. Another important factor in combustion is the Limiting Oxygen Index (LOI). This is the amount of oxygen in the fuel mix needed to support combustion. The higher the number, the more difficult it is for combustion to occur. Values for these parameters for various fibers are given in Table 22.

Table 22

Flammability Parameters for Fibers

Fiber	°C				%	Thermo-plastic
	Tg soften	Tm melts	Tp pyrolysis	Tc combustion	LOI	
Wool			245	600	25	no
Cotton			350	350	18.4	no
Viscose rayon			350	420	18.9	no
Nylon 6	50	215	431	450	20-21.5	yes
Nylon 6,6	50	265	403	530	20-20.1	yes
Polyester	85	255	420-427	480	20-21	yes
Acrylic	100	220	290	250	18.2	yes
Polypropylene	-20	165	469	550	18.6	yes
Modacrylic	80	240	273	690	29-30	yes
PTFE	126	327	400	560	95	yes
Nomex	275	375	410	500	28.5-30	yes
Kevlar	340		590	550	29	no
PBI	400		500	500	40-42	no

For non-thermoplastic fibers, Tp and/or Tc is less than Tg and/or Tm, however for thermoplastic fibers Tp and/or Tc is greater than Tg and/or Tm. Natural fibers are not thermoplastic, therefore when they are subjected to a heat source, pyrolysis and combustion temperatures are encountered before softening or melting temperatures are reached and eventually ignite. On the other hand, low melting

thermoplastic fibers will melt and drip away from the flame before pyrolysis and combustion temperatures are reached. However if the melt doesn't shrink away from the flame front, pyrolysis and combustion temperatures are eventually reached and ignition will occur.

Natural fibers can be made flame retardant and like some synthetic fibers, e.g., Nomex, Kevlar and PBI, offer protection to a wearer because they do not shrink away from a flame. Thermoplastic fibers may appear to offer protection because they pass the ignition test by shrinking away from the flame; however, in reality this exposes to wearer to direct heat and to burns caused by contact of the molten mass with the body.

II. COMBUSTION OF CELLULOSE

When cellulose fibers are heated, three classes of volatile chemicals are generated at pyrolysis temperature, 350° C,   1. flammable volatiles, e.g., alcohols, aldehydes and alkanes, 2. flammable gases, e.g., carbon monoxide, ethylene and methane and 3. non-flammable gases, e.g., carbon dioxide and water vapor. If oxygen is present when the pyrolysis products reach or exceed the combustion temperature, oxidation takes place (burning) and the volatiles are converted to carbon dioxide and water as shown in figure 64.

Figure 64. Combustion Cycle
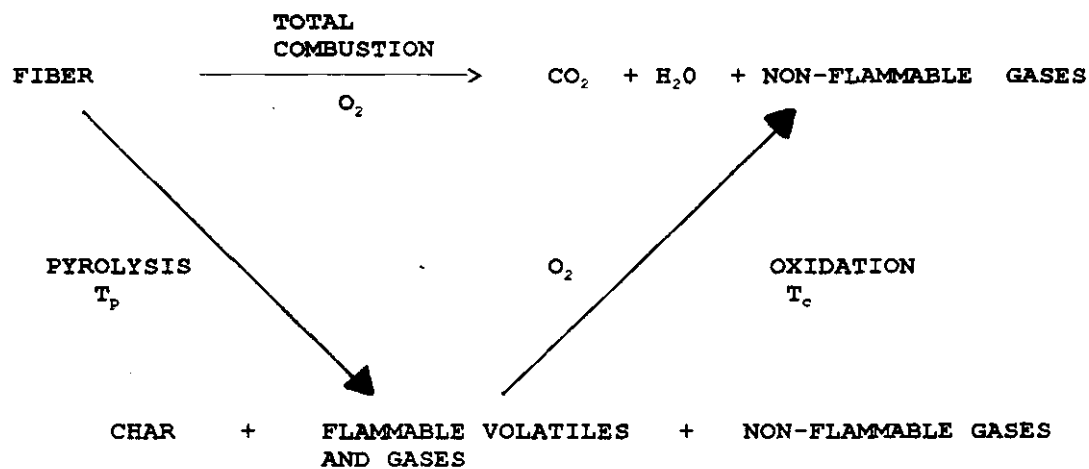
Levoglucosan, shown in figure 6. is the major product formed by the pyrolysis of cellulose. It is the cyclic acetal created when the alpha-1,4-glucosidic linkage is split, and a molecule of water is lost between the C(1) and C(6) hydroxyls of the anhydroglucose unit.
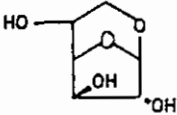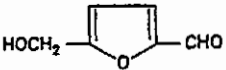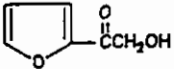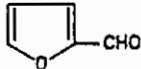
Figure 65. Cellulose Pyrolysis Products
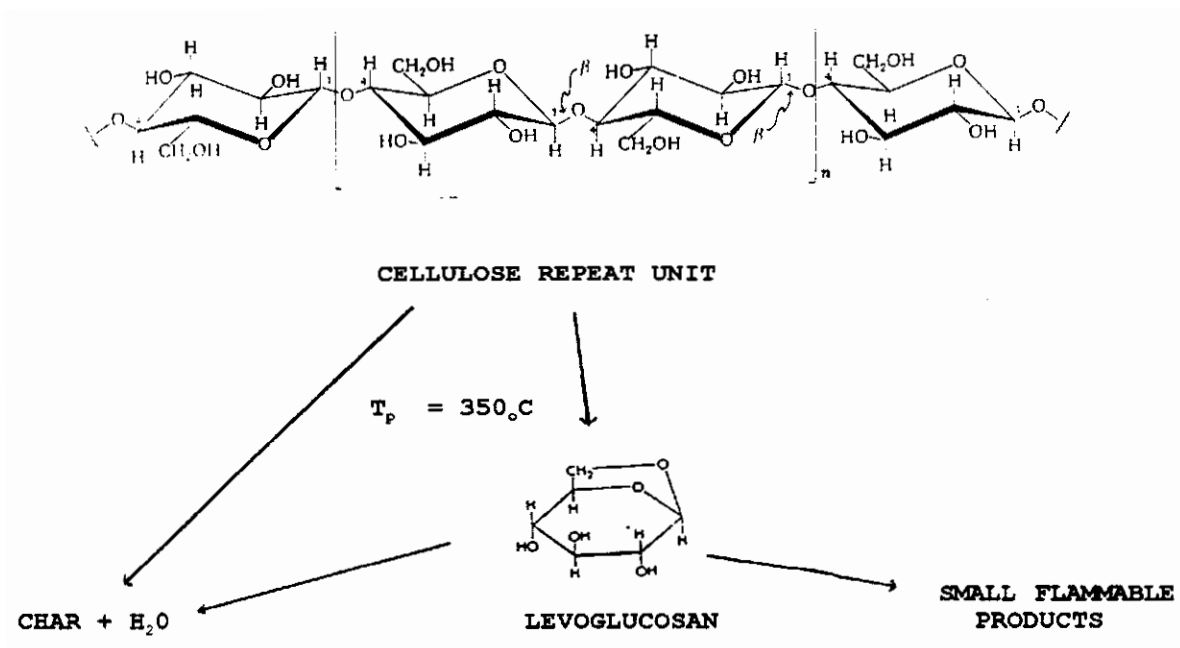
Other products created by pyrolysis are listed in table 23. These volatile products and levoglucosan can be considered the "fuel" that when mixed with oxygen propagates the combustion process. Should these products not be present, ignition would not occur or be sustained.

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Table 23

Other Pryolysis Products

1,6-Anhydro-beta-glucofuranose	
5-Hydroxymethyl-2-furfural	
2-Furylhydroxymethyl ketone	
Furfural	

III. FLAME RETARDANCY

A. Feedback Mechanism

Figure 66 shows the combustion process as a feedback system which may be interrupted at various points to create flame retardancy. Thus to be effective, a flame retardant must interfere with the feedback mechanism in one or more of the following ways:

(a). Removal of heat.
(b). Increase decomposition temperature T_p at which significant volatiles form.
(c). Decrease the amount of combustible gases and promote char formation. This should happen at reduced temperatures so ignition will not occur.
(d). Prevent the access of oxygen to the flame or dilute the fuel gases in the flame to concentration below which they will not support combustion.
(e). Increase the combustion temperature, T_c, of the fuels and/or interfere with their flame chemistry.

Rarely do flame retardants function by a single mode. Today it is more common to refer to their retardant activity as either functioning in the *condensed phase* (modes (a), (b) and (c)), the *vapor phase* (modes (d) and (e), or both. Water, either from a fire hose or water from a hydrated salt will extinguish a flame by mode

(a). Nomex and Kevlar function by mode (b). The structures of these polymers are such that T_p has been significantly increased. Most flame retardants for cellulose fibers function by mode (c), promoting the formation of char and reducing the amount of levoglucosan produced by pyrolysis. Some phosphorous and borate flame retardant are thought to form glassy polymers on the surface of the fibers, insulating the polymer from heat (modes (a) and (d)).

Figure 36. Combustion Feedback Mechanism
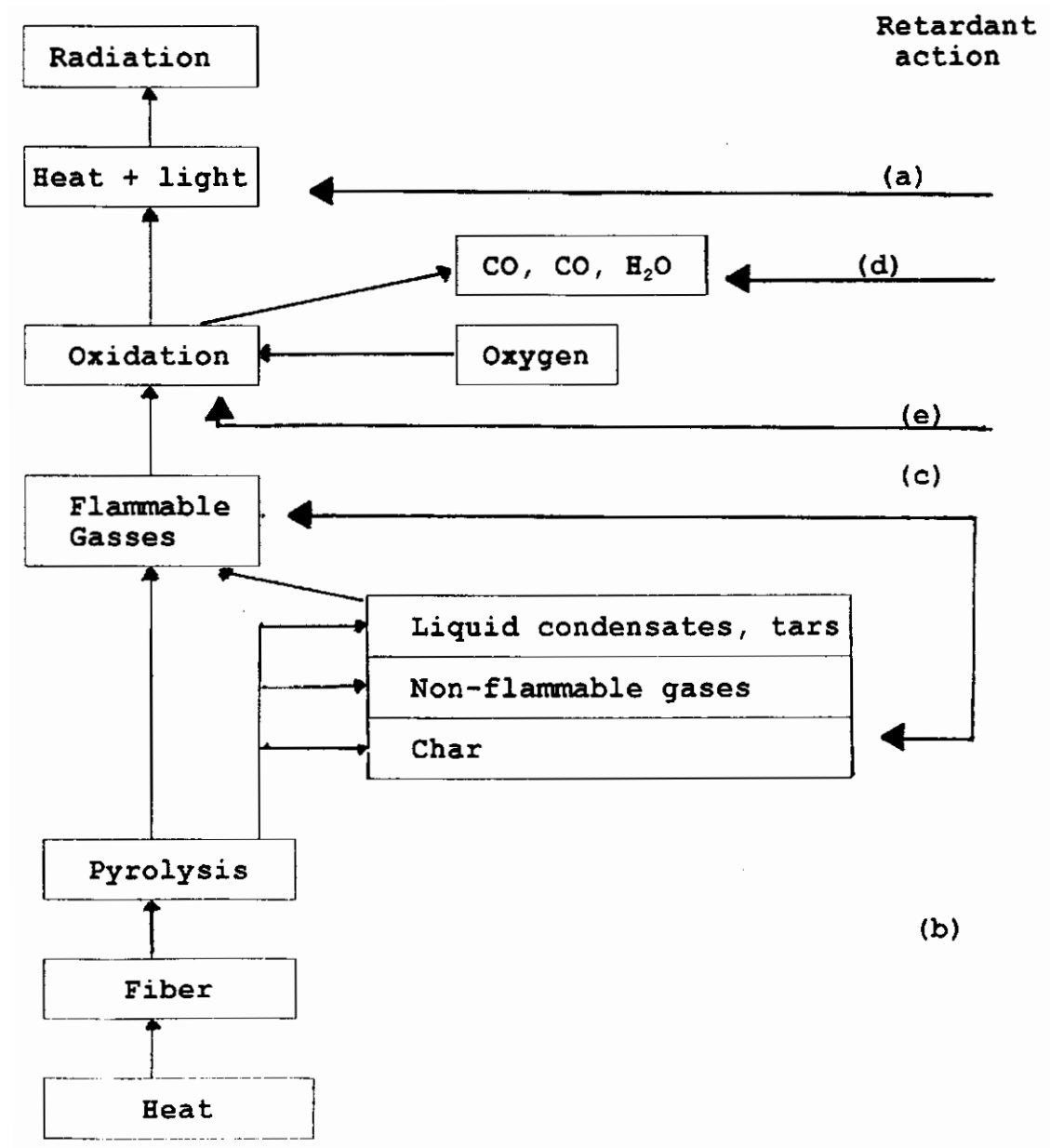
Some of the variables that must be identified in order to characterize the burning behavior of a textile material are listed in table 24. These factors are influenced by the nature of the fiber, yarn and fabric structure, density and dimensions, presence of moisture, dyes, finishes and impurities, environmental factors, e.g., temperature, humidity, oxygen availability and air velocity. Test procedures usually standardize environmental factors so the other factors may be evaluated.

Table 24
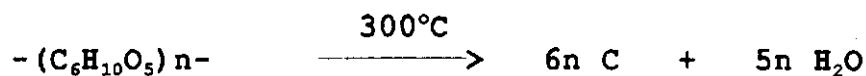
Parameters that Characterize Burning Textiles

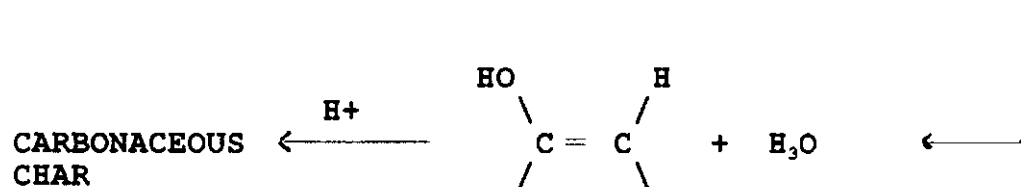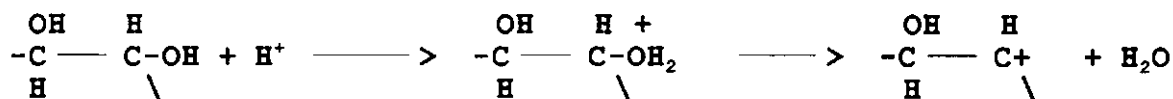| Parameter	Detail
Ignition	Nature of ignition source, ease of ignition.
Flame propagation	Propagation velocity in all directions, and direction influence of mode of ignition, extent of burning, rate of sample consumption, rate of flame extinction, character of afterglow.
Energy	Total energy output, rate of energy evolution, rate of mass loss, rate of energy transfer to skin, rate of energy transfer across specimen.
Combustion	Gaseous products and concentrations, particulates (smoke) products and densities, toxicity of products, nature of flaming debris, nature of char.

B. Char Formation

Since char is a major factor in retarding the burning of cellulosic fibers, it is beneficial for the reader to briefly look at the mechanism of its formation in order to appreciate and understand the significance of the materials that work well as flame retardants. Overall, the formation proceeds by the total dehydration of cellulose into carbon and water.

1. Reactions Leading to Char Formation

a. Overall Reaction

$$- (C_6H_{10}O_5) n- \xrightarrow{\quad 300°C \quad} 6n\ C\ +\ 5n\ H_2O$$

b. Mechanism

OH   H
-C —— C-OH + H$^+$ ————>
H   \

OH   H +
-C —— C-OH$_2$ ————>
H   \

OH   H
-C —— C+   + H$_2$O
H   \

CARBONACEOUS CHAR <————$^{H+}$
HO   H
\   /
C = C   + H$_3$O
/   \   <——

C. How Certain Elements Work

There are many compounds reported in the literature that function as flame retardant finishes for specific fibers. Most all of these compounds have a few elements in common that provide the necessary protection - namely boron, phosphorous, nitrogen and halogens. Before delving into the specific flame retardant compounds, it would be instructive to discuss how these elements work.
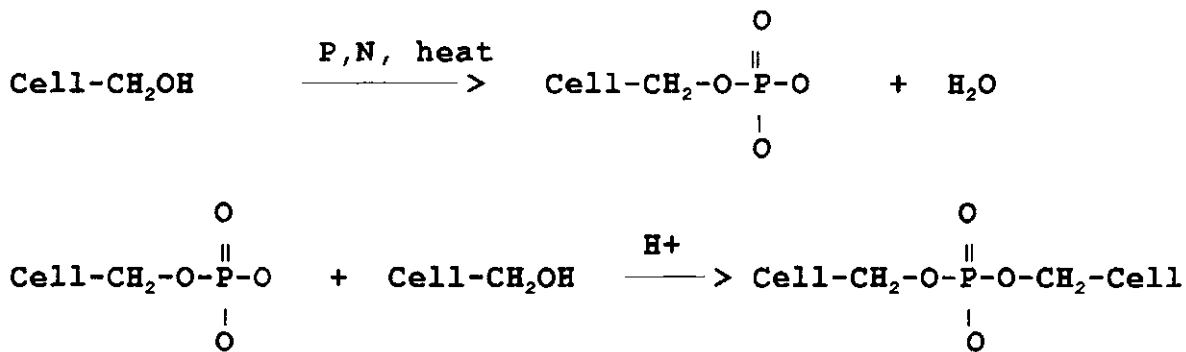
1. Boron

Boric acid (H_3BO_3) and borax ($Na_2B_4O_7$) are often used as non-durable flame retardants in applications such as cellulose batting and shredded newspaper for insulation. Boron functions in the *condensed phase* as a lewis acid and as mentioned earlier, coats the fiber with a glassy polymer to insulate the polymer.

2. Phosphorus and Nitrogen

Phosphorus and nitrogen also work in the *condensed phase*. Phosphorus compounds react with the $C_{(6)}$ hydroxyl of the anhydroglucose unit blocking the formation of levoglucosan. This reduces the amount of fuel to the flame. Additionally, phosphorous promotes char formation. The acidity associated with certain phosphorous analogues and its electrophilic nature lowers the activation energy for dehydrating cellulose. Additionally there is the possibility of crosslinking cellulose chains which further enhances char formation.

Nitrogen alone is not an effective flame retardant, however it acts synergistically with phosphorous. It is thought that nitrogen reacts with phosphorous to form polymeric species containing P-N bonds. Nitrogen enhances the electrophilicity of phosphorous thereby making it a stronger Lewis acid and also promoting the phosphorylation reaction with the $C_{(6)}$ hydroxyl of the anhydroglucose ring. This mechanism may be written as follows:

$$Cell-CH_2OH \xrightarrow[\text{P,N, heat}]{} Cell-CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O \quad + \quad H_2O$$

$$Cell-CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O \quad + \quad Cell-CH_2OH \xrightarrow[]{\text{H+}} Cell-CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O-CH_2-Cell$$
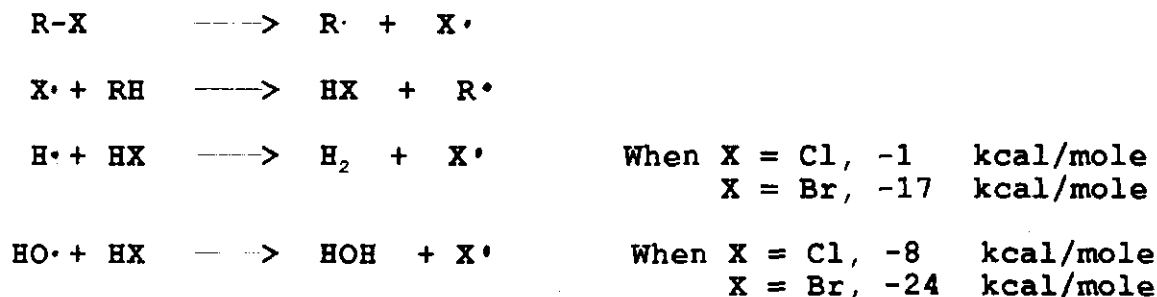
3. Halogens

Chlorine and bromine operate in the *vapor phase* by forming free radicals that scavenge hydrogen and hydroxyl free radicals. Combustion occurs by a free radical, chain reaction mechanism of which hydrogen and hydroxyl radicals are major reaction species. The halogen radicals deactivate them, causing the chain reaction to break down. Antimony and phosphorus enhances the efficiency of the halogen radicals. Phosphorus effect is additive while antimony is synergistic. The optimum ratio of Sb:X is 1:3. This suggests that SbX_3 is an important intermediate in this process. The important gas phase reactions in combustion are:

$$H\cdot + O_2 \longrightarrow HO\cdot + O\cdot \qquad\qquad +8 \text{ kcal/mole}$$

$$O\cdot + H_2 \longrightarrow HO\cdot + H\cdot \qquad\qquad -7 \text{ kcal/mole}$$

$$HO\cdot + CO \longrightarrow CO_2^- + H\cdot \qquad\qquad -81 \text{ kcal/mole}$$
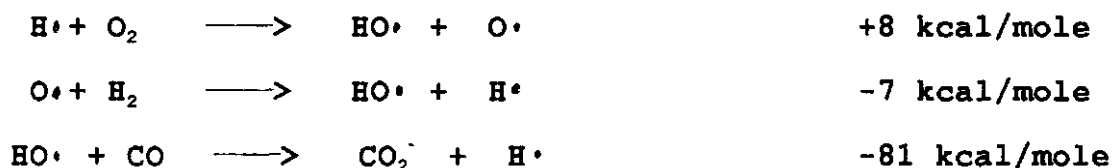
Species that remove H and or HO will slow the combustion reaction. Halogen do this in the following manner:

$$R-X \longrightarrow R\cdot + X\cdot$$

$$X\cdot + RH \longrightarrow HX + R\cdot$$

$$H\cdot + HX \longrightarrow H_2 + X\cdot \qquad \text{When } X = Cl, -1 \quad \text{kcal/mole}$$
$$X = Br, -17 \quad \text{kcal/mole}$$

$$HO\cdot + HX \longrightarrow HOH + X\cdot \qquad \text{When } X = Cl, -8 \quad \text{kcal/mole}$$
$$X = Br, -24 \quad \text{kcal/mole}$$

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The X radical is much less reactive than H and HO and cannot effectively propagate chain reaction. Antimony reacts with X radicals to form SbOX and SbX_3 both of which will thermally decompose to yield halogen radicals.

IV. FLAME RETARDANT CHEMICALS AND PROCESSES FOR CELLULOSE

Durable and non-durable finishes may be used to render cotton, rayon or other cellulosic fibers flame retardant. There are many applications where non-durable flame retardants are adequate, for example, on drapery and upholstery fabrics that will not be laundered. Should the products need cleaning, the finish can be reapplied afterwards. However, there are applications where durability is important, e.g. firefighter suits, foundry worker clothing, children sleepwear.

A. Non-Durable

1. Boric Acid/Borax

A mixture of boric acid/borax (sodium borate) is a commonly used non-durable flame retardant finish for cellulosic fibers. It is the safest with regard to carbon monoxide and smoke production during burning.

2. Diammonium Phosphate and Phosphoric Acid

Phosphorus based flame retardants function in the *condensed phase*. Non-durable, semi durable and durable treatments can be obtained with phosphorus based compounds. The presence of calcium ions negates the activity of phosphorous compounds. Whereas the ammonium salts decompose thermally into phosphoric acid by the loss of ammonia, the calcium salts do not. Presumably the calcium salts are not volatile and buffer the acidity of phosphoric acid so the generation of char is diminished.

3. Sulfamic Acid and Ammonium Sulfamate

Combinations of these compounds also function as non-durable flame retardants.

B. Durable

1. Tetrakis(hydroxymethyl)Phosphonium Derivatives

The bulk of today's durable flame retardant for cellulose centers around the use of derivatives of tetrakis(hydroxymethyl)- phosphonium salts (THP). These

derivatives can be applied by padding, drying, curing and oxidizing to yield serviceable flame retardant fabrics. Add-ons are high and the handle of the fabric is stiffer so the finish is normally used for protective clothing applications.

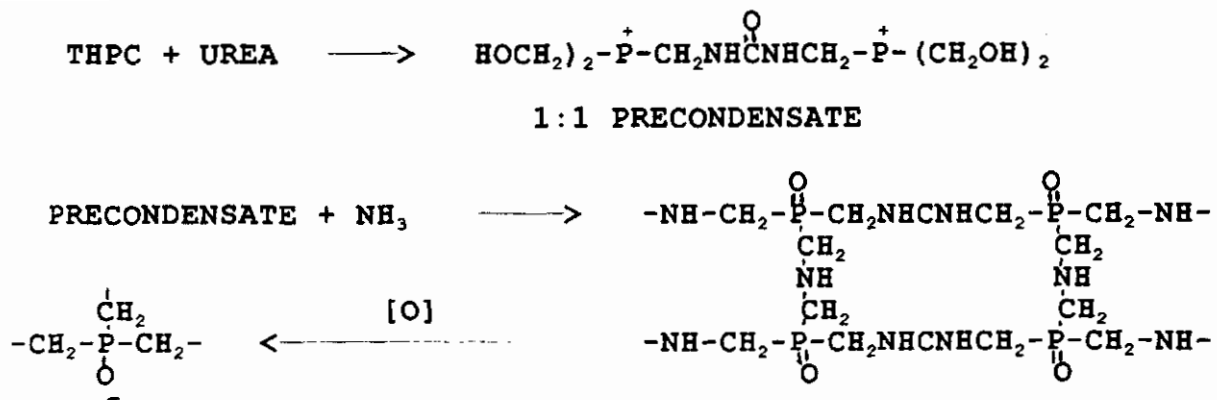## a. Tetrakis(hydroxymethyl)phosphonium Chloride (THPC)

THPC is the most important commercial derivative and is prepared from phosphine, formaldehyde and hydrochloric acid at room temperature. It contains 11.5 % phosphorous and is applied by a pad-dry-cure -> oxidize -> scour process.

$$PH_3 + 4\ CH_2O + HCl \longrightarrow (HOCH_2)_4\ P^+Cl^-$$
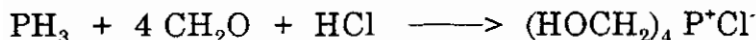
The compound is highly reducing in character and the methylol groups condense with amines to form insoluble polymers. It is applied with urea, dried and cured. Control of pH and the oxidation state of the phosphorus is important in determining the flame retardant properties and the durability of the finish. The release of HCl may cause the fabric to tender during curing unless pH is controlled. The final step in finishing requires oxidation of P^{+3} to P^{+5} with hydrogen peroxide. This step too must be controlled to prevent excessive tendering of the fabric. An alternative to the THPC is THPS. Sulfuric acid is used instead of HCl and the corresponding phosphine sulfate is formed in place of the phosphine chloride.

b. THPC-Urea Precondensate

The Proban process (Albright and Wilson) replaces heat curing with an ammonia gas curing at ambient temperature. This minimizes fabric tendering associated with heat and acids. A Precondensate of THPC with urea (1: 1 mole ratio) is applied, dried and the fabric passed through an ammonia gas reactor. An exothermic reaction creates a polymeric structure within the voids of the cotton fiber. The ammonia cure gives a P:N ratio of 12. Weight percentages of the respective elements should be P,N > 2%. To enhance durability and lightfastness of dyes, P^{+3} is oxidized to P^{+5} with hydrogen peroxide.

## C. Tetrakis(hydroxymethyl)phosphonium Hydroxide (THPOH)

From the forgoing discussion, THPC is usually partly neutralized with amines, amides and/or alkali. Complete neutralization of THPC with sodium hydroxide yields a compound referred to as THPOH. The distinction between THPC used in a partially neutralized condition and THPOH is difficult to define. If the curing agent is basic as is ammonia, the distinction become meaningless.

$$(HOCH_2)_4P^+Cl^- \quad + \quad NaOH \quad \xrightarrow{\text{pH 7}} \quad (HOCH_2)_4P^+OH^-$$

$$(HOCH_2)_4P^+OH^- \quad \longrightarrow \quad (HOCH_2)_3P \quad + \quad CH_2O \quad + \quad OH^-$$

THPOH-ammonia has received a great deal of commercial attention. The major advantage over THPC is reduced fabric tendering and reduced stiffness. Fabrics padded with THPOH give off formaldehyde during drying.

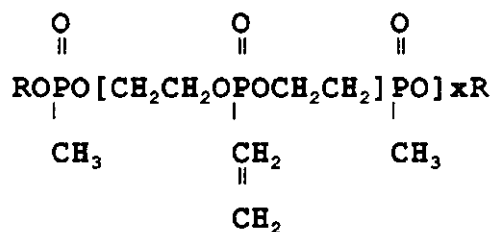## 2. N-Methyloldimethyl Phosphonopropioamide (PYROVATEX CP)

Pyrovatex CP provides a method of attaching phosphorus to cellulose making use of N-methylol reactivity with cellulose. It is applied with a methylolated melamine resin using a phosphoric acid catalyst by a pad-dry-cure process. The high nitrogen content of melamine provides synergistic activity to the phosphorus of the flame retardant.

$$(CH_2O)_2PCH_2CH_2CNHCH_2OH \quad + \quad Cell\text{-}OH \quad \xrightarrow{H^+} \quad CellOCH_2NHCCH_2CH_2P(OCH_2)_2$$
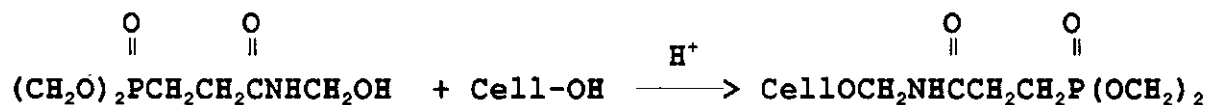
Fabric stiffening occurs when sufficient chemical is applied to give 2-3% phosphorus on weight of fabric. Also the acid may cause high strength loss if left in the fabric after curing; therefore, it is desirable to wash the fabric following the curing step. The finish tends to produce smoke in the curing oven. The smoke is composed of volatile fragments of the finish which condense in the cooler reaches of the oven. The condensate may drip back onto the fabric causing unsightly spots.
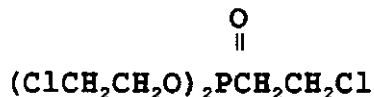
3. Fyrol 76

Fyrol 76 is an oligermeric phosphonate containing vinyl groups. The finish is applied with N-methylol acrylamide with a free radical initiator (potassium persulfate), dried and cured.

$$\underset{\substack{O\\\parallel}}{R} PO[\underset{\substack{O\\\parallel}}{CH_2CH_2OPOCH_2CH_2}]\underset{\substack{O\\\parallel}}{PO]xR}$$

$$\underset{CH_3}{} \quad \underset{\substack{CH_2\\\parallel\\CH_2}}{} \quad \underset{CH_3}{}$$

CH₃ (ROPO structure with subscripts)

$$R = alkyl, \quad CH_2CH_2OH$$

Antiblaze 77

$$(ClCH_2CH_2O)_2\underset{\substack{O\\\parallel}}{P}CH_2CH_2Cl$$

This product exhibits better abrasion resistance than THPOH-NH$_3$.

5. Phosphonic and Phosphoric Acid Derivatives

The literature is rich with references showing many imaginative ways of introducing phosphorus and nitrogen into cellulose fibers. Many products have been offered by chemical companies which have not succeeded as commercial ventures. It is beyond the scope of this book to completely review the full range of flame retardants, the reader is urged to consult other literature readings for a more thorough understanding (1,2,4).
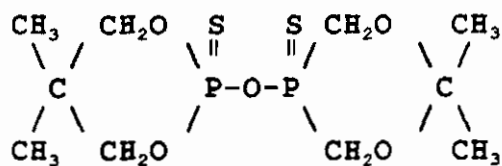
Cellulose phosphorylates with phosphoric and phosphonic acids. Urea, dicyandiamide and cyanamide are used to buffer the tendering action of the acids. Whenever levels of phosphorus attached are high enough, flame retardancy protection is good. Cellulose phosphate esters are hydrolytically unstable so durability to laundering is poor. The phosphonate esters are more durable however. The phosphates tend to chelate calcium ions when laundered in hard water. This reduces the flame retardancy of the finish as discussed earlier in the chapter. The phosphonates are less prone to do this.
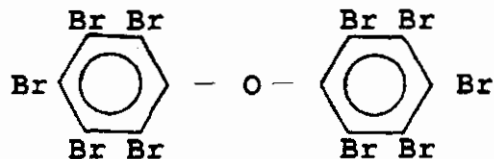
V. RETARDANT SYSTEMS FOR SPECIFIC FIBERS

A. Rayon Additives

Flame retardant agents have been incorporated into rayon fibers during the fiber extrusion process. Listed below are several that have been used.
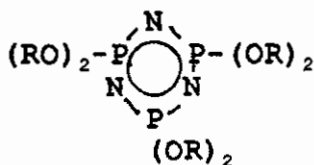
1. Thiophosphate (SANDOFLAM 5060)

$$CH_3 \quad CH_2O \quad S \quad S \quad CH_2O \quad CH_3$$

(structural diagram of thiophosphate with two C centers bearing CH$_3$ and CH$_2$O groups connected to a P–O–P backbone with S double bonds)

2. Decabromodiphenyl Oxide (DBDPO) and Antimony Oxide

(structural diagram of two brominated phenyl rings linked by an oxygen atom, with Br substituents; labeled DBDPO)

DBDPO

3. Phosphazines

$$(RO)_2-P \overset{N}{\underset{N}{\bigcirc}} P-(OR)_2$$

(structural diagram of a phosphazine ring with N and P atoms; third P bearing (OR)$_2$)

$$(OR)_2$$

B. Polyester

Polyester fabrics, being thermoplastic, will melt and shrink away from the heat source allowing some fabrics to pass particular tests without any treatment. Certain tests however, have a melt drip specification to meet so finishes will be needed. The flame retardants that work best for polyester are halogenated compounds that function in the *vapor phase*. One of the best products to serve this purpose was tris-(2,3 dibromopropyl) phosphonate. (TRIS). The product offered good flame retardancy, acceptable fabric hand and good durability to repeated laundering. It passed the children sleepwear requirements. It could be exhausted from a dye bath or applied via the pad-dry-thermosol method. However TRIS is banned from commercial use because it failed the Ames mutagenicity test. It is on the regulated suspect carcinogen list. This finding came after the product had been on the market several years causing several million yards of treated fabric to be recalled by the Consumer Protection Agency (CPSC). The fabric producer was stuck with this inventory.

There are many halogenated compounds that improve polyester's flame retardancy. The trick is to apply the finish so that it doesn't affect the fabric hand

and still be durable to repeated launderings. Basically there are two methods of applying finishes. One method will bind insoluble compounds to the surface of the fiber. Finely ground particles are dispersed in water and glued to the surface with a binder. The second method is to find materials that are soluble in the polyester fiber and apply them as if they are disperse dyes. They can either be exhausted out of a dye bath or padded, dried and thermosoled. Listed below are several which have found some commercial success.

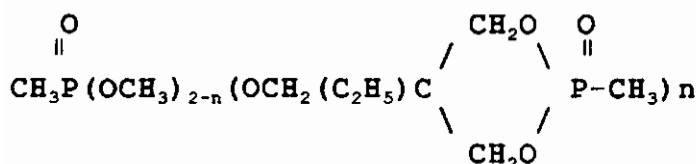## 1. Decabromodiphenyl Oxide (DBDPO)
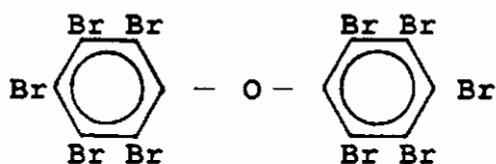
DBDPO

DBDPO is a solid material melting at 300-350 °C. which contains 83% bromine. It is sold as a water dispersion and is applied with a suitable binder to impart effective and durable flame retardancy to 100% polyester fabrics. There are many commercial formulations on the market differing in the blend of antimony oxide. One formulation, a 2:1 mixture of DBDPO and Sb_2O_3, is effective on polyester. Disadvantages of DBDPO are high add-ons needed for optimum retardancy and the stiff, boardy hand imparted due to the level of binder needed for durability. Additionally, the product is a white finely divided pigment which causes a loss in color yield.

2. Tris-(2,3-Dibromopropyl) Phosphate (TRIS)

$$P(OCH_2CHBrCH_2Br)_3$$

with a carbonyl (O) double-bonded to P.

TRIS can be either be exhausted out of a dye bath or applied via the thermosol process. Hydrolysis products were found to be potentially carcinogenic and the product has been banned from use. All fabrics treated with TRIS have been recalled by CPSC.

3. Antiblaze 19T

$$CH_3P(OCH_3)_{2-n}(OCH_2(C_2H_5)C \begin{smallmatrix} CH_2O \\ / \quad \backslash \\ \quad \quad P-CH_3)_n \\ \backslash \quad / \\ CH_2O \end{smallmatrix}$$

This product is a cyclic phosphonate containing 20% phosphorous. It is a clear, water soluble, oily liquid. It can be applied by the pad-dry-thermos01 process. Because of its high water solubility, it does not exhaust from a dye bath. Heat treatment causes the hand to stiffen. The finish is durable to repeated launderings.

C. Nylon

Most nylon fabrics pass flammability standards because the polymer burns at a very slow rate. However several finishes will enhance the fiber's response to flammability tests.

a. Thiourea-Urea-Melamine

This finish is applied by pad-dry-cure. It functions by lowering the melting point of nylon 40 ^{0}C.

b. Halogenated Systems

Halogenated compounds such as DBDPO and chlorinated paraffins combined with Sb_2O_3 are effective. These finishes are often used in industrial applications such as tents, tarpaulin etc.

D. Polyester /Cotton Blends

It is very difficult to impart flame resistance to polyester/cotton blends because the fibers have such different burning characteristics. One would think that blending flame retardant polyester fibers and applying THPC or THPOH technology would accomplish the job. However even this doesn't do it. Polyester normally melts and shrinks away from the flame, but in cotton blends, the melt is held in place by the charred backbone. Horrocks (2) reviews the major works on these blends.

## 1. Decabromodiphenyl Oxide - Antimony Oxide

Commercially, the antimony-bromine system is one most often used. Aqueous dispersions of 2:1 DBDPO and Sb_2O_3 and acrylic latex binders are preferred to give the desired durability and a safe effective finish. The finish is normally applied by the pad-dry-cure process. The level of flame retardancy is related to the add-on, more being better. However the fabric hand becomes stiff and boardy as the add-on increases. This narrows the range of acceptable fabric to those where flame retardancy is more important than aesthetics.

E. Wool

Wool is inherently a flame retardant fiber. Clean wool will pass most horizontal burning test although open pile structures fail carpet tests. Wool is blessed with a high Tc (680^0 C) and LOI index (25). However flame retardants can improve the burning characteristics of wool fabrics. Nondurable treatments which are effective on cellulose are also effective on wool, e.g. boric acid/borax, phosphates and sulfamic/sulfuric acid. Durable systems based on THPC are also applicable to wool. An inexpensive, durable system based on titanium and zirconium complexes have recently been introduced which is unique to wool.

1. Dyebath Exhaustible Finishes

a. Chlorendic Acid and Tetrabromophthalic Anhydride

Chlorendic
Acid

Tetrabromophthalic
Anhydride
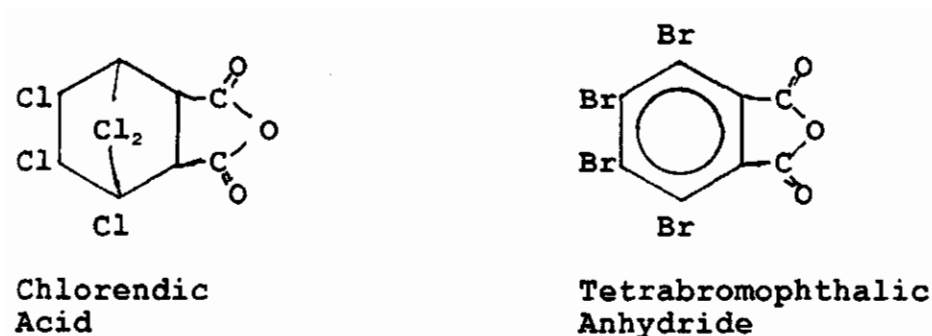
Chlorendic acid and tetrabromophthalic anhydrides will exhaust into wool fibers. Add-ons of 6-18% give good flame retardancy, dye compatibility and are reasonably durable to dry cleaning.

b. Titanium Complexes.

Titanium chloride is an effective flame retardant agent for wool. In the presence of an alpha hydroxy carboxylic acid (citric acid), a stable complex is formed which almost completely exhausts when applied at a pH < 3.5 at the boil. It is important to not allow the titanium to hydrolyse to TiO_2 because as TiO_2, titanium is ineffective. The process is good for wool used in protective clothing, carpets and upholstery. Titanium complexes yellows wool.

c. Hexafluoro-Zirconates

The need to boil wool to exhaust titanium and zirconium chelates leads to felting. low dye fastness and is energy intensive. To overcome these deficiencies, the

IWS developed a process based on titanium and zirconium hexafluoride know as the *Zirpro Process.* Hexafluorotitanates and hexafluorozirconates are extremely stable in acid solutions and exhaust onto wool well below the boil. The titanates yellow wool so the zirconates are preferred commercially. K_2ZrF_6 at a pH < 3 gives 77% exhaustion at 50^0 C, 30 minutes at 70^0 C gives good levelling. A bath containing 3 % K_2ZrF_6, 10% (37%) HCl for 30 minutes at 75^0 C, gives rise to a washfast, lightfast and improved heat and flame resistant fabric. Pad-batch and pad-dry application process may also be used. It is accepted that the hexafluorozirconate ion is bound to the cationic wool in the same manner as acid dyes.

$$ZrF_6^= + {}^+NH_3\text{-Wool} \longrightarrow ZrF_6^{=+}NH_3\text{-Wool}$$
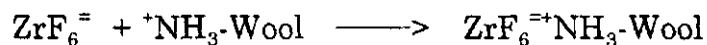
VII. FLAMMABILITY TESTS

Determining the fammability potential of a fabric requires an understanding of a number of different tests because flammability test and specifications vary with the end-use of the textile article. Some tests have been developed as research tools to quantify the retardancy value of finishes and fibers, LOI is one that is used often. Other tests have been developed to assess the flammability hazard of fabrics. These emulate actual in-service conditions that the textile is liable to encounter. Some of the variables are: 1. the way the heat source is presented as it is being ignited, i.e., vertical, horizontal or 45 degree angle, 2. temperature of the heat source, 3. Char length, after flame and after glow and melt drip are some of the specifications of the specific test. Horrocks (1,2) presents a thorough review of the tests.

A sampling of the more important fabric flammability tests are listed in table 16. The reader is urged to consult the cited references for more in-depth information.

Table 16

Some Important Fabric Flammability Tests

FABRIC TYPE	TEST	COMMENTS
CHILDREN'S SLEEPWEAR	DCO-FF-3 DOC-FF-5	VERTICAL TEST
UPHOLSTERY FABRICS WALL COVERINGS	NFPA-701	VERTICAL TEST
MILITARY FABRICS	FED. STDS. 191-5903 191-5904	VERTICAL TEST
FABRICS	LOI TEST ASTM D-2863	TOP VERTICAL
FLOOR COVERINGS	RADIANT PANEL NFPA 253	HORIZONTAL
	PILL TEST ASTM D-2859	HORIZONTAL
PROTECTIVE CLOTHING	TPP NFPA-1971	HORIZONTAL
CLOTHING	S-191	45 DEGREE

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