Kirk-Othmer Encyclopedia of Chemical Technology.

FLAME RETARDANTS FOR TEXTILES

As early as the first century BC, Virgil wrote of the treatment of wood with vinegar to impart fire resistance (1). In the early 1700s a patent was granted for flame retarding cellulose using a mixture containing alum [7784-24-9] (aluminum potassium sulfate dodecahydrate), iron(II) sulfate [7782-63-0], and borax [1303-96-4] (sodium tetraborate decahydrate) (2). In 1821 Gay-Lussac carried out a systematic study of flame proofing (3) using water solutions of ammonium chloride [12125-02-9] and ammonium phosphate, or of boric acid and ammonium chloride, to treat cellulosic material such as linen or jute. He concluded that the most effective salts either had low melting points and gave off nonflammable vapors, or they covered the fabric surface with a glassy layer of the salt.

The first known fire-retardant process found durable to laundering was developed in 1912 (4). A modification of an earlier process (5), this finish was based on the formation of a tin(IV) oxide [18282-10-5] deposit. Although the fabric resulting from treatment was flame resistant, afterglow was reputed to be a serious problem, resulting in the complete combustion of the treated material through smoldering.

A significant advance in flame retardancy was the introduction of binary systems based on the use of halogenated organics and metal salts (6, 7). In particular, a 1942 patent (7) described a finish for utilizing chlorinated paraffins and antimony(III) oxide [1309-64-4]. This type of finish was invaluable in World War II, and saw considerable use on outdoor cotton fabrics in both uniforms and tents.

Work began in the 1930s on the development of flame-retardant cottons based on chemical systems that either reacted directly with the cellulosic substrate, or polymerized on or in the cotton fiber. A serious effort in this direction, mounted from the 1950s through the 1970s, resulted in most of the state-of-the-art flame-retardant finishes for cotton available.

1. Terminology

Flame resistance and fire resistance are often used in the same context as the terms flameproof and fireproof. A textile that is flame or fire resistant does not continue to burn or glow once the source of ignition has been removed, although there is some change in the physical and chemical characteristics. Although the terms resistant and retardant have similar meanings, flame resistant is normally used when referring to that property of a material which prevents it from burning when an external source of flame is removed; flame retardant is used when referring to the chemicals or chemical treatment applied to a material to impart flame resistance. Flameproof or fireproof, on the other hand, refer to materials totally resistant to flame or fire. No appreciable change in the physical or chemical properties is noted. Asbestos (qv) is an example of a fireproof material.

Most organic fibers undergo a glowing action after the flame has been extinguished. From a practical standpoint, flame-resistant fabrics should also be glow resistant because the afterglow may cause as much damage as the flaming itself, in that it can completely consume the fabric.

Another related term is smolder resistance. Smolder resistance implies resistance to ignition by a smoldering source, such as a lit cigarette, placed on the surface of a fabric or in the crevice formed between two butting fabrics. Smolder resistance does not necessarily imply flame resistance, although the material in question may well be flame resistant. A fabric can be smolder resistant and not flame resistant, or vice versa.

2. Flame Resistance

2.1. Factors Affecting Performance

The flame resistance of a textile fiber is affected by the chemical nature of the fiber, its ease of combustion, the fabric weight and construction, the efficiency of the flame retardant, the environment, and laundering conditions. Fibers are classified into natural fibers, eg, cotton, flax, silk, or wool; regenerated fibers, eg, rayon; synthetic fibers, eg, nylons, vinyls, polyesters, and acrylics; and inorganic fibers, eg, glass or asbestos. Combustibility depends on chemical makeup and whether the fiber is inorganic, organic, or a mixture of both (see Fibers, survey).

The weight and construction of the fabric affect its burning rate and ease of ignition. Lightweight, loose-weave fabrics burn much faster than heavier weight fabrics; therefore, a higher weight add-on of fire retardant is needed to impart adequate flame resistance.

2.2. Mechanism of Flame Retardants

The burning process of cellulose depends on both a source of ignition and the presence of oxygen. A low temperature degradation of cellulose proceeds by the formation of levoglucosan, which in turn undergoes dehydration and polymerization, leading to tars, flammable gases, liquids, and other solids (8, 9). The flammable gases thus produced ignite, causing the liquids and tars to volatize to some extent. This produces additional volatile fractions which ignite and produce a carbonized residue that does not burn readily. The process continues until only carbonaceous material remains. After the flame has subsided, the carbonized residue slowly oxidizes and glowing continues until the carbonaceous char is consumed.

In general, cotton treated with an effective flame retardant provides the same decomposition products upon burning as does untreated cotton; however, the amount of tar is greatly reduced, with a corresponding increase in the solid char. Consequently, as decomposition takes place, smaller amounts of flammable gases are available from the tar, and greater amounts of nonflammable gases from the decomposition of the char fraction. Char is essentially carbon. Its oxidation causes afterglow. Phosphorus-containing compounds, in some cases polymers, are particularly effective in inhibiting char oxidation. Numerous studies have been made on burning of untreated and flame-retardant-treated cellulose (8, 10–14).

Several theories have been postulated to explain the various types of flame retardants for cotton. These theories include coating, gas, thermal, and dehydration or chemical.

2.2.1. Coating Theory

This theory includes fire retardants which form an impervious skin on the fiber surface. This coating may be formed during normal chemical finishing, or subsequently when the fire retardant and substrate are heated. It excludes the air necessary for flame propagation and traps any tarry volatiles produced during pyrolysis of the substrate. Examples of this type of agent include the easily fusible salts such as carbonates or borates.

2.2.2. Gas Theory

The gas theory utilizes two approaches in explaining flame retardancy. In one approach, the flame retardant decomposes to give gases which do not burn. These gases diffuse and mix with the oxygen present around the combustible cellulosic, thereby protecting it from further combustion. Examples of these gases include water vapor, carbon dioxide [124-38-9], sulfur dioxide [7446-09-5], and hydrogen chloride [7647-01-0]. In the second approach, flame retardants function in the gas phase by producing free-radical terminators when the retardant is heated to flaming temperatures. The gas-phase oxidation of cellulose derivatives is a free-radical process utilizing such free radicals as $^\bullet$H, $^\bullet$OH, $^\bullet$OOH. The function of the flame retardant is to form other free radicals, which trap the active radicals, leading to chain cessation or substitution with less active radicals. The end result is termination of the free-radical chain propagation and hence, flame retardation.

2.2.3. Thermal Theory

The thermal approach to flame retardancy can function in two ways. First, the heat input from a source may be dissipated by an endothermic change in the retardant such as by fusion or sublimation. Alternatively, the heat supplied from the source may be conducted away from the fibers so rapidly that the fabric never reaches combustion temperature.

2.2.4. Dehydration or Chemical Theory

In the dehydration or chemical theory, catalytic dehydration of cellulose occurs. The decomposition path of cellulose is altered so that flammable tars and gases are reduced and the amount of char is increased; ie, upon combustion, cellulose produces mainly carbon and water, rather than carbon dioxide and water. Because of catalytic dehydration, most fire-resistant cottons decompose at lower temperatures than do untreated cottons, eg, flame-resistant cottons decompose at 275–325°C compared with about 375°C for untreated cotton. Phosphoric acid and sulfuric acid [8014-95-7] are good examples of dehydrating agents that can act as efficient flame retardants (15–17).

Another aspect of the dehydration theory is that the dehydration process proceeds through either an acid (Lewis acid) or basic mechanism, altering the path of cellulose decomposition to eliminate levoglucosan formation and thus leading to more char and less tar (11). However, it should be pointed out that whereas relatively low levels of applied flame retardant, ie, 2.0%, do inhibit levoglucosan formation, much higher levels, ie, 10.0% or more, are normally required to produce flame resistance. These higher add-ons of flame retardant appear necessary to maximize char formation, thereby imparting flame resistance. In the base-catalyzed dehydration it is postulated that dehydration proceeds with the formation of dehydrocellulose. This is followed by formation of char (15, 16).

3. Durability of Retardant Finishes

Fire resistance of a treated cellulosic fabric is reduced when the retardant contains acid groups and the treated fabric is soaked or laundered in water containing calcium, magnesium, or alkali metal ions. Phosphate- and carbonate-based detergents affect durability of fire retardants (18). Soap-based detergents can result in a substantial loss of fire resistance because of the deposit of fatty acid salts (19). Phosphorus-based flame retardants are adversely affected by water hardness and laundry bleach, sodium hypochlorite [7681-52-9]. Exposure to sunlight and weathering can lead to sufficient loss of flame retardant so that the fabric is no longer flame resistant (20). Similarly, a combination of sunlight followed by laundering or autoclaving can also lead to loss of flame resistance in a cellulosic fabric (8, 21, 22).

3.1. Nondurable Finishes

Flame-retardant finishes that are not durable to laundering and bleaching are, in general, relatively inexpensive and efficient (23). In some cases, a mixture of two or more salts is more effective than either of the components alone. For example, an add-on of 60% borax (sodium tetraborate) is required to prevent fabric from burning, and boric acid is ineffective as a flame retardant even at levels equal to the weight of the fabric.

Table 1. Water-Soluble Flame-Retardant Formulations,[a] % Composition

Formulation	Borax	Boric acid	Diammonium phosphate	Sodium phosphate dodecahydrate	Other
	[1303-96-4] $Na_2B_4O_7 \cdot 10H_2O$	[10043-35-3] H_3BO_3	[7783-28-0] $(NH_4)_2HPO_4$	[10101-89-0] $Na_3PO_4 \cdot 12H_2O$	
1	70	30			
2	47	20	33		
3		50		50	
4		50	50		
5	50	35		15	
6			25		75[b]
7	15	47			38[c]

[a] 100% ammonium bromide [12124-97-7], NH_4Br, is also used.

[b] Ammonium sulfamate [7773-06-0], $NH_4OSO_2NH_2$.

[c] 18% sodium phosphate [7601-54-9], Na_3PO_4, and 20% sodium tungstate dihydrate [10213-10-2], $Na_2WO_4 \cdot 2H_2O$.

However, a mixture of seven parts borax and three parts boric acid imparts flame resistance to a fabric with as little as 6.5% add-on.

The water-soluble flame retardants are most easily applied by impregnating the fabric with a water solution of the retardant, followed by drying. Adjustment of the concentration and regulation of the fabric wet pickup controls the amount of retardant deposited in the fabric. Fabric can be processed on a finishing range which consists of any convenient means of wetting the fabric with the solution, such as a padder or dip tank. This is followed by drying on steam cans, in an oven, on a tenter frame, or merely by tumbling in a mechanical dryer. Water-soluble flame retardants also may be applied by spraying, brushing, or dipping fabrics, as well as a final rinse in a commercial or home laundry (24). The water-soluble flame retardants used most widely for textiles are listed in Table 1. Less commonly used retardants include sulfamates of urea or other amides and amines; aliphatic amine phosphates, such as triethanolamine phosphate [10017-56-8], phosphamic acid [2817-45-0] (amido phosphoric acid, $H_2PO_3NH_2$), and its salts; and alkylamine bromides, phosphates, and borates. For a blend of polyester and cellulosic, it is advisable to include a bromine-containing salt such as ammonium bromide in the finish.

3.2. Semidurable Finishes

Semidurable fire retardants resist removal from 1 to approximately 15 launderings. Such retardants are adequate for applications such as drapes, upholstery, and mattress ticking. If they are sufficiently resistant to sunlight or can be easily protected from actinic degradation, they can also be applied to outdoor textile products. The principal disadvantage of water-soluble flame retardants is their lack of durability. This undesirable property can be overcome by precipitating their inorganic oxides on the fabric, eg, $WO_3 \cdot xH_2O$ and $SnO_2 \cdot yH_2O$:

$$2\ Na_2WO_4 + SnCl_4 + (2x + y)\ H_2O \longrightarrow 4\ NaCl + 2WO_3 \cdot xH_2O + SnO_2 \cdot yH_2O$$

These codeposits add flame- and glow-resistance properties to textile fabrics. However, some insoluble deposits may also degrade the fabrics. Codeposits frequently improve glow resistance, but are usually more soluble than the deposit responsible for flame resistance and more easily removed during the laundering process.

There are several methods for introducing the insoluble deposits into the fabric structure. The multiple bath method, in which the fabric is first impregnated with a water-soluble salt or salts in one bath and is then passed into a second bath which contains the precipitant, is used most often. Most semidurable retardants used on cotton are based on a combination of phosphorus and nitrogen compounds (25).

A research area that has seen considerable activity in nondurable and semi-durable smolder-resistant applications is the development of finishes for cotton batting products. Materials such as monoammonium phosphate [7722-76-1], sodium borate [1330-43-4], urea phosphate [4861-19-2], and borated amido polyphosphate have been investigated (26). Subsequent work has focused on the means of depositing boric acid (27). In some cases this was accomplished via vapor-phase deposition. The unstable ester, methyl borate [121-43-7], has seen considerable use in batting applications. It is first sprayed onto the batting, and the treated batting is then passed through a steam chamber. The water quickly reacts with the methyl borate, producing boric acid in and on the cotton fibers of the batting (28, 29).

3.3. Early Durable Finishes

Early studies to produce durable flame retardants for cellulose were based on treatment with inorganic compounds containing antimony and titanium (30–35). Numerous patents have been issued based on these types of treatments, eg, the Erifon process (Du Pont) (36–38) and the Titanox flame-retardant process (Titanium Pigment Corp.) (39). In the Erifon process, titanium and antimony oxychlorides are applied from acid solution (pH 4) to fabric, which is then neutralized by passing through a solution of sodium carbonate [497-19-8], followed by rinsing and drying. Fabrics thus finished exhibit good flame resistance but also considerable afterglow. A large amount of tent fabric has been treated by this type of process for the military service. The basic chemicals used in the Titanox flame-retardant process are titanium acetate chloride and antimony oxychloride. In both the Titanox and the Erifon processes, it is difficult to process the fabric without dulling its appearance.

3.4. Outdoor Finishes

Excellent fire-resistant fabric has been obtained by treating fabric with a suspension or emulsion of insoluble fire-retardant salts or oxides, eg, antimony(III) oxide [1309-64-4], along with a chlorinated organic vehicle such as chlorinated paraffin (7). Antimony(III) oxide alone is a poor flame retardant. However, when used in conjunction with a halogenated compound a very good flame retardant is produced. The active agent is the antimony halide formed *in situ* from Sb_2O_3 and the acid halide under flaming conditions.

In the 1990s, two types of flame retardants are preferred for outdoor fabrics, ie, a system based on phosphorus and nitrogen such as the precondensate–NH_3 finish and an antimony–bromine system based on decabromodiphenyl oxide [1163-19-5] and antimony(III) oxide (20, 40–42).

3.4.1. FWWMR Finish

The abbreviation for fire, water, weather, and mildew resistance, FWWMR, has been used to describe treatment with a chlorinated organic metal oxide. Plasticizers, coloring pigments, fillers, stabilizers, or fungicides usually are added. However, hand, drape, flexibility, and color of the fabric are more affected by this type of finish than by other flame retardants. Add-ons of up to 60% are required in many cases to obtain adequate flame resistance. Durability of this finish is good and fabric processed properly retains its flame resistance after four to five years of outdoor exposure. This type of finish is suited for very heavy fabrics, eg, tents, tarpaulins, or awnings, but not for clothing or interior decorating fabrics. The metal oxides can be fixed to cotton by use of resins, eg, vinyl acetate–vinyl chloride copolymers (vinylite VYHH) or poly(vinyl chloride) [9002-86-2] (PVC) (43–45). A flame retardant has been developed based on an oil–water emulsion containing a plasticizer (PVC latex) and antimony(III) oxide (46, 47). High add-ons are necessary to impart adequate flame resistance but the strength of the fabric is little affected.

Table 2. Oxygen Indexes of Fabrics

Fabric	Oxygen index[a]
acrylic	0.182
acetate	0.186
polypropylene	0.186
rayon	0.197
cotton	0.201
nylon	0.201
polyester	0.206
wool	0.252
flame-resistant cotton	0.270
aramid	0.282

[a] A higher OI indicates a less flammable material.

4. Test Methods

Numerous tests covering flame retardancy and related matters are available. The requirements most often specified for fire resistance of a textile materials are that it must pass either Federal Specification Method 5903 or NFPA 701.

The most extensive body of tests are provided under the auspices of ASTM Standard methods. Specific ASTM test designations and descriptions are available (48). The other compendium of fire-retardant tests are contained in Federal Test Method Standards 191A (49).

The Fire Tests for Flame Resistant Textiles and Films, issued by the National Fire Protection Association (NFPA) in 1989, is the method most used by industrial fire-retardant finishers (ca 1993) (50). It has been approved by the American National Standards Institute.

4.1. Oxygen Index Test

The oxygen index test (OI) is based on the minimum oxygen concentration that supports combustion of various textile materials (51–53). A fabric which would not burn in pure oxygen would have an OI of 1.0. One which would just barely burn in an atmosphere of 20% oxygen and 80% nitrogen would have an OI of 0.20. The higher the OI of a given fabric, the less flammable it is and vice versa. The OI values of various untreated fabrics are listed in Table 2.

A modified method of estimating the OI for fibrous or finely divided cellulosic materials has been developed (53). The fibers or powdered materials are first pressed into disks, then the OI is measured in the usual way.

5. Types of Retardants

5.1. Overview, Fire Retardants for Cellulosics

Phosphorus-containing materials are by far the most important class of compounds used to impart durable flame resistance to cellulose (see Flame retardants, phosphorus flame retardants). Flame-retardant finishes containing phosphorus compounds usually also contain nitrogen or bromine or sometimes both. A combination of urea [57-13-6] and phosphoric acid [7664-38-2] imparts flame resistance to cotton fabrics at a lower add-on than when the acid or urea is used alone (8). Other nitrogenous compounds, such as guanidine [133-00-8] or guanylurea, could be used instead of urea. Amide and amine nitrogen generally increase flame resistance, whereas nitrile nitrogen can detract from the flame resistance contributed by phosphorus. The most efficient flame-retardant systems contain two retardants, one acting in the solid and the other in the vapor phase. Nitrogen, when used in conjunction with phosphorus compounds, has a synergistic effect on fire retardancy (54–56). In some cases, the phosphorus content can be reduced without changing the efficiency of the flame retardant (57). Bromine in flame-resistant fabric escapes from the tar to the vapor phase during pyrolysis of the textile in air. It appears to have little or no effect on the amount of phosphorus remaining in the char. Bromine contributes flame resistance almost completely in the vapor phase. Another system for making cellulosic fabrics flame-resistant is based on the use of halogens in conjunction with nitrogen or antimony. In the case of systems employing halogen moieties, bromine is more effective than chlorine.

5.2. Mesylated and Tosylated Celluloses

It has been established that the flame resistance of cellulose (qv) is improved by oxidation of $\text{—CH}_2\text{OH}$ groups to —COOH (58–60). To correct some of the shortcomings of this treatment, mesyl or tosyl cellulose was prepared and then the mesyl (CH_3SO_2) or tosyl ($CH_3C_6H_4SO_2$) group was replaced with bromine or iodine (58–60):

$$\text{cell—OSO}_2\text{CH}_3 + \text{NaBr} \longrightarrow \text{cell—Br} + \text{CH}_3\text{SO}_3\text{Na}$$

This treatment produced a fabric with durable flame resistance and good strength retention, but an undesirable afterglow; this was eliminated by phosphorylation with diethyl chlorophosphate [814-49-3].

5.3. Urea–Phosphate Type

Phosphoric acid imparts flame resistance to cellulose (16, 17), but acid degradation accompanies this process. This degradation can be minimized by incorporation of urea [57-13-6]. Phosphorylating agents for cellulose include ammonium phosphate [7783-28-0], urea–phosphoric acid, phosphorus trichloride [7719-12-2] and oxychloride [10025-87-3], monophenyl phosphate [701-64-4], phosphorus pentoxide [1314-56-3], and the chlorides of partially esterified phosphoric acids (see Cellulose esters, inorganic).

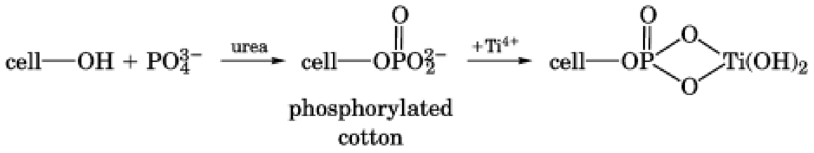
Cellulose phosphate esters are also produced by treatment with sodium hexametaphosphate [14550-21-1] by the pad-dry-cure technique. These treated fabrics have high retention of breaking and tearing strength (61). The reaction products contain more than 1.6% phosphorus and are insoluble in cupriethylenediamine [15243-01-3], indicating that some cellulose cross-linking occurs. However, since durable-press (DP) levels and wrinkle recovery values are low, it seems reasonable that only limited cross-linking takes place.

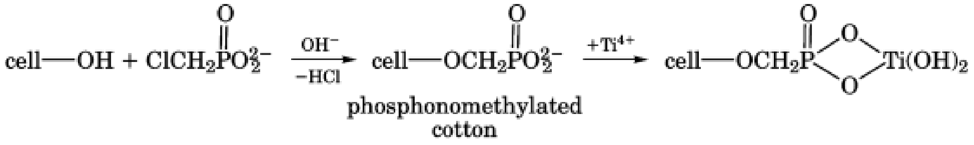
Phosphorylated cottons are flame resistant in the form of the free acid or the ammonium salt. Since these fabrics have ion-exchange properties, conversion to the sodium salt takes place readily during laundering if basic tap water is used. However, flame resistance can be restored if the fabric is treated with either acetic acid [1563-80-8] or ammonium hydroxide [1336-21-6] after washing.

5.4. Phosphonomethylated Ethers

A phosphorus-containing ether of cellulose can be prepared by the reaction of cotton cellulose with chloromethylphosphonic acid [2565-58-4] in the presence of sodium hydroxide [1310-73-2] by the pad-dry-cure technique (62). Phosphorus contents of between 0.2 and 4.0% are obtained. This finish is durable but has high ion-exchange properties and is flame resistant only as the ammonium salt. Durability on medium weight fabrics is obtained with chloromethylphosphonic diamide. This finish has never penetrated the flame retardant market (63).

A durable flame-retardant cellulosic fabric with good hand is obtained by treating phosphorylated or phosphonomethylated cotton with titanium(IV) sulfate [13825-74-6] (64):



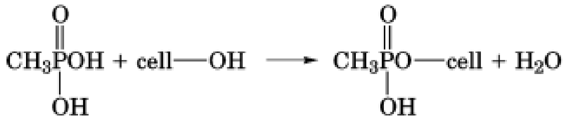


5.5. Amide-Based Systems, Cyanamide

Pyroset CP, originally the trade name for a 50% solution of cyanamide, produces a semidurable fire-retardant finish on cotton fabric when used in conjunction with phosphoric acid (65). Treated fabrics have an excellent hand as well as an increase in wrinkle recovery. Drying and curing is accomplished in a single step, preferably at 150°C for 2–5 minutes. The finish is subject to ion exchange and therefore the hardness of the washwater has a decisive effect on durability of the flame-retardant finish. Fabric flammability fails after seven washings at a water hardness of 70 ppm, whereas in soft water (0 ppm hardness) flame retardancy can withstand 50 wash cycles. Tensile strength losses of Pyroset CP-treated fabric are 40–45%. The treated fabrics are dimensionally stable and have improved rot resistance.

5.5.1. Methylphosphoric Acid–Cyanamide System

In another system (65), based on methylphosphoric acid [993-13-5] (MPA) and cyanamide [420-04-2], one or more of the hydroxyls in MPA or in its dimer react with cellulose and the water is taken up by the cyanamide, forming urea:



$$CH_3\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}OH + \text{cell}{-}OH \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}O{-}\text{cell} + H_2O$$

$$H_2NCN + H_2O \longrightarrow H_2N\overset{\overset{\displaystyle O}{\|}}{C}NH_2$$

Fabrics are treated by a pad-dry-cure technique; however, smoke is evolved in the curing step. At an add-on of 10%, this flame-retardant finish is durable to 40–50 laundry cycles, has dry wrinkle recovery angles of 200–200°, and wet wrinkle recovery angles of 220–270°. The wrinkle recovery angle reported is the sum of the recoveries in the warp and fill directions $(W + F)$; thus the maximum possible wrinkle recovery is 360°. The same finish gives tensile strength retention of 60–80%, tear strength retention of about 50%, and raises the moisture regain of the fabric about 3%. The system shows a high tolerance for calcium.

5.6. Dialkyl Phosphite and Related Retardants

Pyrovatex CP is based on the reaction product of a dialkyl phosphite and acrylamide [79-06-1]; the adduct is methylolated with formaldehyde [50-00-0] (66–68):

$$(CH_3O)_2\overset{O}{\overset{\|}{P}}H + CH_2{=}CH\overset{O}{\overset{\|}{C}}NH_2 \longrightarrow (CH_3O)_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{HCHO} (CH_3O)_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{C}}NHCH_2OH$$

Excess formaldehyde reacts with cotton in the presence of an acid catalyst. A cross-linking agent that induces polymerization and contributes to flame resistance, such as trimethylolmelamine [1017-56-7] (TMM), improves the efficacy and durability of this finish. TMM does not greatly affect the hand of the treated fabric. The finish is durable to dry cleaning but not necessarily to washing. Tensile strength losses are between 20 and 30% and tear strength losses are about 30%. Cotton textiles require add-ons of about 20–35%. Because of TMM's questionable safety when used in applications involving contact with the skin, most flame-retardant applications involving it have been discontinued.

5.6.1. Pyrovatex CP "New"

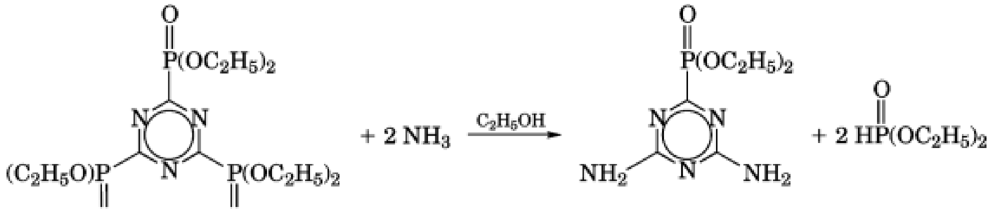
A modification of Pyrovatex CP has replaced the original formulation. It is believed that this new product has had TMM removed from the formulation and replaced by a more ecologically friendly cross-linking agent. This finish is much like that achieved with Pyrovatex CP, except that it is more subject to hydrolysis over an extended period of time. Of the heat-cured fire-retardant finishes available (ca 1993), Pyrovatex CP "New" is the most commercially significant (69). It should be noted, however, that NH_3-cured finishes command a much larger share of the domestic market in the 1990s, and that heat-cured finishes are used more in Europe than in the United States (70).

5.6.2. Dialkylphosphonopropionamides

Cellulosic derivatives that closely resemble those based on the dialkylphosphonopropionamides have been prepared (71). The fabric was treated with *N*-hydroxymethylhaloacetamides (chloro, bromo, or iodo) in DMF solution by a pad-dry-cure technique with a zinc nitrate [10196-18-6] catalyst. It was then allowed to react in solution with trimethyl phosphite [121-45-9] at about 140–150°C; the reaction rates decreased in the order $\text{iodo} > \text{bromo} > \text{chloro}$. With phosphorus contents above 1.5%, good flame resistance, durable to laundering, was obtained without noticeable loss in fabric strength.

5.6.3. Triazines

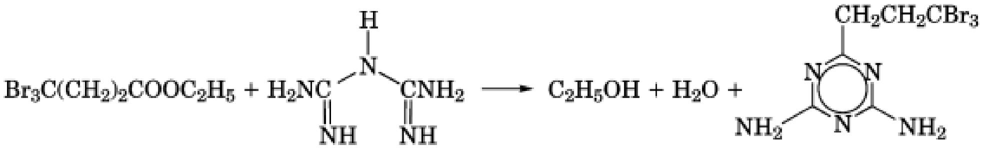
When the dialkoxyphosphinyl group is attached to the triazine ring rather than to an alkyl group, 2,4-diamino-6-diethoxyphosphinyl-1,3,5-triazine [4230-55-1] (DAPT) is obtained:



DAPT

Formaldehyde and DAPT form a derivative that readily gives an insoluble cross-linked polymer. The fabric is padded with a DAPT solution having an optimum pH of 6.6 (no catalyst), dried, and cured. Fabrics containing from 17.5–20% resin add-on passed the standard vertical flame tests after 35 laundry cycles. Tear strength losses are about 35% and tensile strength losses about 18%. Although the treated fabrics do not yellow on chlorine bleaching and scorching, some strength loss results, indicating chlorine retention (72–74).

An effective, but not very practical, flame retardant for cotton based on 2,4-diamino-6-(3,3,3-tribromopropyl)-1,3,5-triazine [62160-38-7] (DABT) was prepared from ethyl γ-tribromobutyrate and biguanide [56-03-1]:



DABT

The tetramethylol derivative of DABT, prepared by reaction of DABT with alkaline aqueous formaldehyde, polymerized readily on cotton. It imparted excellent flame retardancy, very durable to laundering with carbonate- or phosphate-based detergents as well as to hypochlorite bleach. This was accomplished at low add-on without use of phosphorus compounds or antimony(III) oxide (75–77).

5.7. THPC-Based Retardants

One flame-retardant finish for cotton (78) is based on tetrakis(hydroxymethyl)phosphonium chloride [124-64-1] (THPC), $(HCOCH_2)_4P^+Cl^-$ [124-64-1]. It is water-soluble and is prepared by the reaction of phosphine with formaldehyde and HCl. THPC reacts with aminized cotton to impart flame resistance; this has led to further studies with materials such as melamine [108-78-1] and urea in an effort to eliminate the costly aminization step. THPC reacts and polymerizes with methylolmelamine [937-35-9], as well as with many other materials containing active hydrogens, eg, amines, phenols, and polybasic acids (79), to form insoluble polymers. When these polymers are deposited in the cotton fiber they produce good flame- and glow-resistant finishes (see also Amino resins and plastics). The methylol groups in THPC react with amines or amides in the following manner:

$$(HOCH_2)_4PCl + RNH_2 \longrightarrow RNHCH_2PCl(CH_2OH)_3 + H_2O$$

5.7.1. THPC–Amide Process

The THPC–amide process is the first practical process based on THPC. It consists of a combination of THPC, TMM, and urea. In this process, there is the potential of polymer formation by THPC, melamine, and urea. There may also be some limited cross-linking between cellulose and the TMM system. The formulation also includes triethanolamine [102-71-6], an acid scavenger, which slows polymerization at room temperature. Urea and triethanolamine react with the hydrochloric acid produced in the polymerization reaction, thus preventing acid damage to the fabric. This finish with suitable add-on passes the standard vertical flame test after repeated laundering (80).

An improved version of the THPC–amide process, developed in 1972, is based on a finish containing THPC, cyanamide, and disodium phosphate [13708-85-5], Na_2HPO_4. It has the advantage of removing the mutagenically suspect TMM from the finish while retaining many of its attributes (81).

5.7.2. THPC–Urea–Disodium Phosphate

A further improved variation uses a combination of THPC, urea, and disodium phosphate (82, 83). In this case, the components are mixed, the pH adjusted to about 6.0 with sodium hydroxide, and the solution applied to the textile via a pad-dry-cure treatment. The combination of urea and formaldehyde given off from the THPC further strengthens the polymer and causes a limited amount of cross-linking to the fabric. The Na_2HPO_4 not only acts as a catalyst, but also as an additional buffer for the system. Other weak bases also have been found to be effective. The presence of urea in any flame-retardant finish tends to reduce the amount of formaldehyde released during finishing.

Another modification of this process was reported in 1988 (84). In this process, a precondensate of THPC and urea, plus excess urea, are neutralized to a pH of about 5.7, and the buffer salt is added. The fabric is then given a standard pad-dry-cure process followed by oxidation and laundering. The principal advantage of this modification is a reduction in both formaldehyde vapors and phosphine-like odors released during processing (84).

Finally, a modification has been carried out in which a polyacrylate emulsion is added to a normal tetrakis(hydroxymethyl)phosphonium sulfate [55566-30-8] (THPS), urea, and TMM fire-retardant treatment in an attempt to completely alleviate the strength loss during the finishing. Indeed, better retention of tensile properties is achieved with no loss in fire resistance (85).

5.7.3. THPOH–Amide Process

In the THPOH–amide process, the THPC is neutralized to pH 7.2–7.5 with aqueous sodium hydroxide. The specific active species present in solution at this point is not precisely known, but is thought to be a mixture of tris(hydroxymethyl)phosphine [2767-80-8] (THP) and formaldehyde, or the hemiacetal adduct of these components (86–89). A disadvantage to this system is that an inactive by-product, tris(hydroxymethyl)phosphine oxide [1067-12-5] (THPO), is frequently formed. A further by-product of this reaction is hydrogen gas. In order to avoid formation of THPO, neutralization of THPC is frequently discontinued at $\simeq$pH 7.2. Fabrics given this treatment (THPOH, TMM, and urea) show less stiffness and better tearing strength than are observed for the same fabrics treated with the THPC–amide process. Good retention of breaking strength and less tendency to yellow when exposed to hypochlorite bleach are also observed for this finish (90–92).

5.7.4. THP–Amide Process

THP has also been made directly from phosphine [7803-5-27] and formaldehyde. The THP so generated contains one less mole of formaldehyde than either THPC or THPOH. It can be used in a THP–amide flame-retardant finish. The pad formulation contains THP, TMM, methylol urea, and a mixed acid catalyst (93–95).

5.8. Ammonia–Gas-Cured Flame Retardants

The first flame-retardant process based on curing with ammonia gas, ie, THPC–amide–NH_3, consisted of padding cotton with a solution containing THPC, TMM, and urea. The fabric was dried and then cured with either gaseous ammonia or ammonium hydroxide (96). There was little or no reaction with cellulose. A very stable polymer was deposited *in situ* in the cellulose matrix. Because the fire-retardant finish did not actually react with the cellulose matrix, there was generally little loss in fabric strength. However, the finish was very effective and quite durable to laundering.

Two ammoniation processes, ie, the THPOH–NH_3 and the precondensate–NH_3 processes, have seen considerable commercial use.

5.8.1. THPOH–NH_3 Process

In the THPOH–NH_3 process, the fabric is padded with a formulation containing 25–40% THPOH, plus wetting agent and auxiliaries. It is dried to approximately 12–15% moisture, exposed to ammonia gas, and passed through a bath containing H_2O_2 (91). The hydrogen peroxide treatment stabilizes the phosphorus components of the THPOH in the higher oxidation or phosphorous(V) oxide [1314-56-3] form. The process can be modified by the addition of copper salts to produce a system stable in the presence of ammonium hydroxide (97). Variations of the ammonia cure have also been reported based on the use of ammonium hydroxide applied by low wet add-on techniques (98, 99).

The THPOH–NH_3 process was used extensively for children's sleepwear in the early 1970s. However, the advent of the Tris problem on polyester led to a sharp decline in commercial production of chemically finished children's flame-resistant cotton sleepwear.

5.8.2. Precondensate–NH_3 Process

From a historical point of view, the precondensate–ammonia process is a simplification of the THPC–amide–NH_3 process. In this case, the chemical manufacturer forms a precondensate of THPC and urea by refluxing these components for about 30 minutes. This mixture is padded on the fabric, sometimes with a sodium acetate buffer, dried, and then ammoniated (100–102). Polymer formation is very rapid in the ammoniation step. Subsequent to ammoniation, the polymer is stabilized by oxidation, usually with hydrogen peroxide [7722-84-1]. This product has been marketed under the Proban trademark. Somewhat analogous products are available from other producers using the same or similar chemistry. These producers have made further improvements in this type of finish, but published data describing them are proprietary and not available.

In 1992, the precondensate–NH_3 finish was the dominant flame retardant for cotton. Although THPOH–NH_3 is reputed to give a softer hand to finished fabric than precondensate–NH_3, commercial finishers have achieved an excellent hand on fabrics and garments using softening techniques, such as Sanforization or chemical softeners. Apart from hand, two other advantages are possessed by the precondensate–NH_3 finish. First, the odors of phosphorus chemicals and formaldehyde released during padding and drying fabric are greatly reduced when compared to similar treatments with THPOH. Second, the partial replacement of the ammonia moiety with a urea linkage increases the nitrogen content of the P–N polymer. This results in a somewhat more economical finish because cheaper nitrogen is partially used to replace more expensive phosphorus. Westex Corp. (Chicago, Ill.) claims that its version of the THP–precondesate–NH_3 process, Indura, is comparable if not superior to Nomex, the standard for synthetic inherently fire-resistant textiles (103).

A series of articles takes a comprehensive look at the chemistry of hydroxy-methyl phosphorus compounds (86–89).

5.9. APO

Research on ethylenimine [151-56-4] led to the development of tris(aziridinyl) phosphine oxide [545-55-1] (APO) as a flame retardant for cotton. The aziridinyl groups are very reactive, particularly under acidic conditions (see Imines, cyclic). Polymer formation can occur through self-polymerization, but occurs readily with compounds containing active hydrogen atoms such as acids, amines, phenols, and glycols. In addition to conferring flame retardance, these systems confer durable-press performance as well. Although a considerable amount of research and accompanying literature were produced from 1960 to 1990 (104–107), the health problems linked with the aziridinyl system preclude its use in commercial finishing. Similar comments apply to the flame-retardant system based on the reaction of THPC and APO (108, 109).

5.10. Miscellaneous Consumer Finishes

5.10.1. Fyrol 76

This flame retardant from Stauffer is a reactive vinyl phosphorus ester containing 22.5% phosphorus. It can be used alone or with methylolacrylamide (NMA) and a free-radical catalyst, eg, potassium persulfate [7727-21-1]. Fabric is treated with the conventional pad-dry-cure technique, rapid steam curing, or radiation curing. Sleepwear fabric requires approximately 25–30% add-on to pass flammability requirements. The fabric has an excellent hand and some permanent press properties. Approximately 80–100% tensile strength and about 65% tearing strength are retained. Chlorine bleach and some carbonate detergents reduce the durability of this finish, whereas perborate bleaches do not affect it. As with the THPC-type finishes, an oxidation step generally is used. Stauffer has withdrawn Fyrol 76 from the market.

5.10.2. Pentamethylphosphorotriamide

Of the phosphoramide derivatives, pentamethylphosphorotriamide [10159-46-3] is the most effective finish when applied to fabric in conjunction with dimethylolmelamine and an amine hydrochloride catalyst. The finished fabric passes the FF3-71 flammability test. Its main application is for use on heavyweight clothes since the finish imparts a harsh hand to lightweight fabrics (99).

5.11. Application Techniques

5.11.1. Radiation

Use of radiation to affect fixation of some flame retardants is being investigated (110). Electron-beam fixation requires the selection of compounds that can be insolubilized inside or outside of the fiber with high yield in a short time. Polyunsaturated compounds, eg, Fyrol 76, have shown promise (see Radiation curing).

5.11.2. Incorporation of Flame Retardants in Fiber

Flame retardants suitable for cotton are also suitable for rayon. A much better product is obtained by incorporating flame retardants in the viscose dope before fiber formation. The principal classes of flame retardants used in viscose dope are tabulated annually (111).

6. Textile-Specific Uses of Flame Retardants

6.1. Smolder-Resistant Upholstery Fabric

Chemical finishing to improve the smolder resistance of cotton fabric received some attention during the late 1970s. It was thought that regulatory activity would impact the market position of cotton upholstery fabric; research on semidurable and durable finishes capable of withstanding occasional scrubbing was initiated for cotton upholstery fabric. Two chemical treatments are of particular interest. In one system, a formulation comprised of borax, an acidic compound, and TMM was applied by conventional padding as well as by low wet add-on techniques (112, 113). Another successful approach consisted of the application of various polymers as backcoatings to upholstery fabric (114). The most effective polymers for this purpose were copolymers in which one of the monomers contained halogen. One particularly effective copolymer contained butadiene, styrene, and vinylidene chloride. Although the use of synthetic barrier fabrics have largely supplanted the need for this type of finishing, these finishes did provide an effective means for making cotton smolder resistant.

6.2. Combination Flame Retardant–Durable Press Performance

Systems using THPC, urea, and TMM can be formulated to give fabrics which combine both flame-retardant performance and increased wrinkle recovery values (80). Another system employs dimethylol cyanoguanidine with THPC under acidic conditions (115). Both of these systems lead to substantial losses in fabric tensile and tearing strength.

The combination of THPOH, urea, and TMM in a ratio of 2:4:1 gives fabrics with flame-retardant performance and high wrinkle recovery values (90). Similarly, trimethylol methylglycoluril [5001-82-1] has been used to replace TMM (116). Although this overcomes problems associated with yellowing and bath instability, as well as removing the suspect mutagenic agent, TMM, wrinkle recovery values are not as high as observed when TMM is included.

As previously noted, the APO system leads to fabrics which combine flame resistance and durable press properties; however, the toxicity of the aziridinyl system precludes its use in modern textile finishing.

There has been some effort since 1980 to achieve combined durable press–flame-retardant properties in finished fabrics involving the precondensate–NH_3 system (117–119). In general, adequate durable press performance together with flame resistance can be achieved if one applies the flame-retardant finish (precondensate–NH_3) first, followed by application of a cross-linking agent such as dimethyloldihydroxyethyleneurea [1854-26-8]. However, adjustments in finish concentration, acid catalyst, acidity of fabric substrate, and curing conditions are necessary to achieve the desired level of durable press performance. Because a certain amount of the cross-linking agent is diverted to the polymer substrate, losses in strength are much less than they would be if the cross-linking treatment were applied to unmodified cotton.

Another approach to producing durable press–flame-resistant fabric is to utilize an antimony–halogen system. Such a system seems particularly suited for polyester–cotton blends. The Caliban P-44 (White) system, developed in 1972, uses a combination of decabromodiphenyl oxide for the halogen component and antimony(III) oxide for the antimony component (40–42). These materials are usually bound to the fabric by means of a polymeric latex, such as a polyacrylate. If a cross-linking system is included in the finish, it is possible to achieve both durable press and flame-retardant performance on blend fabrics. It should be noted, however, that the basic finish can be applied to a variety of fabrics, especially tenting material and other bottom-weight goods. Care must be taken with polymer binders because pad–roll contamination and whitening of dark fabrics are potential hazards. Caliban P-44 is used extensively on 100% cotton fabric of 10.0 oz. and above as well as many polyester–cotton blends. It is perhaps the best finish available for the flame-retardant treatment of blends (70). Several companies produce commercial finishes similar to Caliban P-44.

Another approach to durable press–flame retardancy uses a combination of a cross-linking system, antimony(III) oxide, and a bromine-containing reactive additive, namely dibromoneopentyl glycol, to achieve dual properties (122, 123).

6.3. Flame-Retardant Treatments For Wool

Although wool is regarded as a naturally flame-resistant fiber, for certain applications, such as use in aircraft, it is necessary to meet more stringent requirements. The Zirpro process, developed for this purpose (122, 123), is based on the exhaustion of negatively charged zirconium and titanium complexes on wool fiber under acidic conditions. Specific agents used for this purpose are potassium hexafluoro zirconate [16923-95-8] [16923-95-8], K_2ZrF_6, and potassium hexafluoro titanate [16919-27-0], K_2TiF_6. Various modifications of this process have been made to improve durability and compatibility with wool shrinkproof finishes (124–126).

6.4. Thermoplastic Fibers

The thermoplastic fibers, eg, polyester and nylon, are considered less flammable than natural fibers. They possess a relatively low melting point; furthermore, the melt drips rather than remaining to propagate the flame when the source of ignition is removed. Most common synthetic fibers have low melting points. Reported values for polyester and nylon are 255–290°C and 210–260°C, respectively.

6.4.1. Tris

Flame retardancy of the synthetic fibers is obtained by either mechanically building the retardant with the polymer before it is drawn into a fiber, or chemically modifying the polymer itself. Incorporation of chemicals in the dope before spinning the fiber has not been very successful. The most widely used technique for flame-retarding polyester acetate and triacetate is the application of Tris [126-72-7] (tris(2,3-dibromopropyl)phosphate, TDBP), by a Thermosol diffusion or an exhaustion technique (127–130). Polyester fiber can only retain about 4–5% TDBP calculated on the weight of the fiber. The use of Tris was banned in 1977 by the Consumer Product Safety Commission (CPSC) as a potential carcinogen (see also Flame retardants, halogenated flame retardants; Flame retardants, phosphorus flame retardants). Tris is not effective on cotton fabrics and has only been used as a flame retardant for polyester–cotton blends.

6.4.2. Decabromodiphenyl Oxide–Polyacrylate Finishes

An alternative to the diffusion technique is the application of decabromodiphenyl oxide on the surface of fabrics in conjunction with binders (131). Experimental finishes using graft polymerization, *in situ* polymerization of phosphorus-containing vinyl monomers, or surface halogenation of the fibers also have been reported (129, 130, 132, 133).

6.4.3. Antiblaze 19

Antiblaze 19 (Mobil), a flame retardant for polyester fibers (134), is a nontoxic mixture of cyclic phosphonate esters. Antiblaze 19 is 100% active, whereas Antiblaze 19T is a 93% active, low viscosity formulation for textile use. Both are miscible with water and are compatible with wetting agents, thickeners, buffers, and most disperse dye formulations. Antiblaze 19 or 19T can be diffused into 100% polyester fabrics by the Thermosol process for disperse dyeing and printing. This requires heating at 170–220°C for 30–60 s.

6.4.4. Nylon Finishes

Halogens are less effective flame retardants on nylon than on polyester. Most of the flame retardants effective on cellulosics or on polyester substrates are not effective on nylon. Thiourea [62-56-6] and thiourea formaldehyde appear to be the most effective treatments for imparting flame resistance to nylon (135, 136).

6.5. Polyester–Cotton Fiber Blends

The burning characteristics of synthetic and natural fibers are very different. Synthetic fibers tend to melt, drip, and shrink away when in contact with a flame; cotton does not distort when subjected to a heat source. When synthetic and natural fibers are combined, the cotton serves as a grid for the polyester, preventing it from dripping, and the polyester, which has a higher heat of combustion, accelerates the pyrolysis of cotton. Thus when natural and synthetic fibers are combined, many of the resulting fabrics are more hazardous than fabrics made from the individual components. Table 2 lists the oxygen indexes of a number of commercially available inherently flame-resistant fibers. The flammability behavior of thermoplastic and nonmelting polyester–cellulosic fiber blends cannot be predicted from the flammability of the single-fiber structures (137–140). The treatment of one of the fiber components with a flame-retarding agent specifically effective for that component does not necessarily render the two-component blend flame resistant. The exception to this statement is the situation in which the treated component comprises at least 85% of the blend (137, 139, 141). In general, an effective flame-retardant treatment must reduce the flammability of each component. Some exceptions do exist, however (142), eg, situations in which the fire-retardant finish is effective on both blend components, but is only present on one.

Considerable effort is being made (ca 1993) to develop satisfactory flame retardants for blended fabrics. It has been feasible for a number of years to produce flame-resistant blended fabrics provided that they contain about 65% or more cellulosic fibers. It appears probable that blends of even greater synthetic fiber content can be effectively made flame resistant. An alternative approach may be to first produce flame-resistant thermoplastic fibers by altering the chemical structure of the polymers. These flame-resistant fibers could then be blended with cotton or rayon and the blend treated with an appropriate flame retardant for the cellulose, thereby producing a flame-resistant fabric. Several noteworthy finishes have been reported since the early 1970s.

6.5.1. THPOH–Ammonia–Tris Finish

By far the most effective finish for polyester–cotton textiles was a system based on the THPOH–NH_3 treatment of the cotton component either followed or preceded by the application of Tris finish to the polyester component.

This combined treatment appeared to be effective on almost any polyester–cotton blend. A large amount of fabric treated in this way was sold throughout the United States and much of the rest of the world. Shortly after the introduction of Tris finishing, Tris was found to be a carcinogen. Most of the Tris treated production was in children's sleepwear, and this created a situation in which almost all chemical fire-retardant-treated textiles were unfairly condemned as dangerous. Manufacturers rushed to replace chemically treated textiles with products produced from inherently flame-resistant fibers. Nowhere was the impact more severe than in the children's sleepwear market. New, safer materials have been introduced to replace Tris. Thus far none has been as completely effective.

6.5.2. Decabromododiphenyl Oxide–Polyacrylate Finish

This finish, effective on both polyester and nylon fabrics, is one of the most effective finishes available (ca 1993) for cotton–polyester blends (131). Relatively high cost and difficulty in application may have prevented more widespread use.

6.5.3. THPC–Amide–Poly(vinyl bromide) Finish

A flame retardant based on THPC–amide plus poly(vinyl bromide) [25951-54-6] (143) has been reported suitable for use on 35/65, and perhaps on 50/50, polyester–cotton blends. It is applied by the pad-dry-cure process, with curing at 150°C for about 3 min. A typical formulation contains 20% THPC, 3% disodium hydrogen phosphate, 6% urea, 3% trimethylolglycouril [496-46-8], and 12% poly(vinyl bromide) solids. Approximately 20% add-on is required to impart flame retardancy to a 168 g/m^2 35/65 polyester–cotton fabric. Treated fabrics passed the FF 3-71 test. However, as far as can be determined, poly(vinyl bromide) is no longer commercially available.

6.5.4. THPOH–NH_3 and Fyrol 76

The THPOH–NH_3 finish and the Fyrol 76 finish also impart flame retardancy to certain polyester–cotton blends if the blends contain at least 65% cotton.

6.5.5. LRC-100 Finish

The use of LRC-100 flame retardant for 50/50 polyester cotton blends has been reported (144). It is a condensation product of tetrakis(hydroxymethyl)-phosphonium salt (THP salt) and *N,N′,N″*-trimethylphosphoramide [6326-72-3] (TMPA). The precondensate is prepared by heating the THP salt and TMPA in a 2.3-to-1.0-mole ratio for one hour at 60–65°C. It is applied in conjunction with urea and trimethylolmelamine in a pad-dry-cure oxidation wash procedure. Phosphorus contents of 3.5–4.0% are needed to enable blends to pass the FF 3-71 Test.

6.5.6. Phosphonium Salt–Urea Precondensate

A combination approach for producing flame-retardant cotton-synthetic blends has been developed based on the use of a phosphonium salt–urea precondensate (145). The precondensate is applied to the blend fabric from aqueous solution. The fabric is dried, cured with ammonia gas, and then oxidized. This forms a flame-resistant polymer on and in the cotton fibers of the component. The synthetic component is then treated with either a cyclic phosphonate ester such as Antiblaze 19/19T, or hexabromocyclododecane. The result is a blended textile with good flame resistance. Another patent has appeared in which various modifications of the original process have been claimed (146). Although a few finishers have begun to use this process on blended textiles, it is too early to judge its impact on the industry.

6.6. Cotton–Wool Blends

Although they command only a very small fraction of the cotton blend market, cotton–wool blends are easier to make fire resistant than cotton itself. As might be expected, twill fabrics containing both cotton and wool had decreased burning rates and increased OI values both before and after fire-retardant treatment (147).

6.7. Core-Yarn Fabric

Core yarns are structures consisting of two component substructures, one of which forms the central axis or core of the yarn, and the other the covering. Generally, the core is a continuous monofilament yarn, while the outer covering is composed of staple fibers, usually cotton. Core yarns were popularized because their strong synthetic core made them stronger than conventional blend yarns and because their 100% cotton staple covering provided enhanced comfort in the fabric form. Although good coverage of the core has always been a problem, new techniques have greatly reduced core grin-through. It has been reported that fabrics made from such core yarns, and constructed to limit their polyester core content to no more than 40% of the total yarn weight, can be made flame resistant. It is only necessary to treat the cotton component with an appropriate flame retardant. No treatment is necessary for the polyester core. It appears that higher level treatments than normally required for pure cotton fabric are necessary for good flame resistance (148–150). Similar results have been reported using glass fiber cores (151) and nylon cores (152).

7. Economic Aspects

The identification of Tris as a potential carcinogen dealt a resounding blow to the flame-retardant finishing industry. From 1977 to 1984, several principal suppliers of flame-retardant chemicals either reduced the size of their operations or abandoned the market completely. However, Albright and Wilson Corp. (UK) continues to produce THPC–urea precondensate and market it worldwide, and Westex Corp. (Chicago) continues to apply precondensate–NH_3 finish to millions of yards of goods for various end uses. American Cyanamid reentered the market with a precondensate-type flame retardant based on THPS.

American Cyanamid and Albright and Wilson were the primary manufacturers of fire-retardant precondensates in the world in 1993. These agents are distributed in the United States by Albright and Wilson and by Freedom Textile Chemicals (Charlotte, North Carolina). Thor Chemicals, Ltd. markets both precondensate-type and heat-cure-type flame retardants in Europe. The heat-cure finish, marketed as Aflammit KWB, is an acrylamide–dialkyl phosphite agent and has been sold to finishers in the United States. The largest commission finishers of fire-resistant textiles in the United States (ca 1993) are Westex and MF&H Textiles, Inc. (Butler, Georgia). Specialized flame-retardant applications to cotton-wrapped polyester, Kevlar, nylon, and glass core yarns are beginning to attract the interest of the industry for special-purpose fabrics (70).

8. Health and Safety

Because Tris polyester flame-retardant chemical has been demonstrated to be a potential carcinogen (153–155), workers in this field have tested a number of commonly used chemicals for potential mutagenicity. Neither the THPOH–NH_3 finish nor its extracts caused a significant systematic increase in mutations when tested by the Ames mutagenicity test (156–161). The Hooker Chemical Co. has reported results of tests conducted by an independent laboratory which indicate no significant mutagenic potential from any of the company's proprietary textile flame retardants. Although Fyrol 76 was reported to be nontoxic, results from its mutagenic screening are not known. Stauffer's substitute for Tris, Fyrol FR2, was accused of mutagenic activity by the

Environmental Defense Fund, and has been withdrawn from the market by the company. A study has been made by the National Toxicology Program Study on the carcinogenicity of THPC and THPS which concluded that there is no evidence of carcinogenic activity for either compound in rats or mice (162).

8.0.1. Regulatory Legislation

In February 1978, the Consumer Products Safety Commission approved changes in the FF-3 and FF-5 standards for children's sleepwear. It eliminated the melt–drip time limit and coverage for sizes below 1 and revised the method of testing the trim. This permits the use of untreated 100% nylon and 100% polyester for children's sleepwear (157–162).

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