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**Developments in the Flame
Retardant Treatment of
Cotton/Polyester Blends
(1973 TO 1983)**

by

Wendy A. Black and A.P.B. Maasdorp

SOUTH AFRICAN
WOOL AND TEXTILE RESEARCH
INSTITUTE OF THE CSIR

P.O. BOX 1124
PORT ELIZABETH
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ERRATA

p.5: Table 1. Title to read: FLAME RETARDING AGENTS WHICH IMPART FLAME
RESISTANCE TO POLYESTER THROUGH POLYMERISATION.

p.5: The first compound in table 1 to read:
2,5 Dibromo-terephthalic acid

p.5: The fourth compound in table 1 to read:
Tetra halo phthalic acid

DEVELOPMENTS IN THE FLAME RETARDANT TREATMENT OF COTTON/POLYESTER BLENDS (1973 TO 1983)

by *WENDY A BLACK and A P B MAASDORP*

1. INTRODUCTION

Since ancient times, man has attempted to reduce the flammability of combustible materials. For example, the Egyptians soaked wood in a solution of alum in an attempt to reduce its flammability, while the Romans dipped the material of their houses and war vessels into a bath of vinegar and clay. Louis XVII was also interested in the development of an effective flame retardant finish. He commissioned Gay-Lussac to develop such a treatment, and he subsequently achieved a small amount of success with ammonium salts of sulphuric, hydrochloric and phosphoric acid on hemp and linen fabric. The incident was noteworthy in that it was the earliest report of a government authority taking an interest in flame retardancy¹.

Significant progress in the field of flame retardancy of textiles, was first observed during the second World War, which saw an increase in the commercial use of durable flame retardants. Another boost for the development of more effective and more acceptable flame retardants was the revision, in 1967, of the United States Act of 1953 for flame retardant textiles. This act was extended to include all household textiles and clothing, and provision was made for new, stricter test methods. The importance of this legislation is obvious considering a report that in the USA, it is estimated that about 500 lives are lost annually due to clothing fires¹. Records of incidents of this nature are difficult to come by in South Africa, however about 400 lives are lost every year in fires and fire related accidents².

The problem of flame retarding cotton and polyester textiles, is that it is a large complex field of chemistry which has grown enormously over the years. This has resulted in the publication of numerous books and reviews on the flame retardancy of cotton and polyester materials. This overview will therefore deal briefly with some of the more common and effective flame retardant treatments for cotton and polyester, whereupon the treatments for cotton/polyester blends, the subject of this review, will be discussed in greater detail.

Factors affecting the flammability of a textile fabric are the chemical composition, degree of polymerization of its constituent fibres and to a lesser extent weight per unit area, construction and surface smoothness¹. There are three main approaches which have been employed to impart flame retardancy to textiles, namely; (1) deposition of the flame retardant on and in the fabric,

(2) chemical modification of the polymer fibre constituting the fabric, (3) copolymerization with a flame retardant monomer during manufacture. Method (3) is useful only for synthetic and regenerated fibres¹.

1.1 Cotton flame retardant treatments

The cotton flame retardant treatments have been divided into two groups, namely, durable flame retardant finishes which can withstand at least 50 laundering cycles under specific washing conditions, and non-durable flame retardant treatments mainly based on inorganic salts.

One of the most common flame retardant compounds used to impart durable flame resistance to cotton is THPC (tetrakis hydroxymethyl phosphonium chloride), a phosphorus-containing reagent. Examples of some of these formulations will be given briefly. Firstly, a THPC-cyanamide formulation has imparted durable flame retardant properties to cotton fabrics⁵. Addition of dibasic sodium phosphate to the THPC-cyanamide formulation resulted in the improvement of the flame retardant durability, fabric handle and wrinkle recovery⁶. Secondly, THPOH (tetrakis hydroxymethyl phosphonium hydroxide), the neutralization product of THPC, reacts with amines and amides and durable flame retardant properties can be imparted to cotton fabrics when treated with this THPC-amide combination. Limitations of this treatment include stiffening of tightly constructed fabrics and reduction in tensile and tear strengths of treated fabrics⁷. Thirdly, a solution of THPC, urea and trimethylolmelamine applied to cotton fabrics imparts flame resistance to these fabrics⁸. However, it has been claimed that the treatment is not very successful, since HCl is liberated through a decomposition reaction of the THPC solution when applied to cotton⁹. An advantage of THPOH in the above formulation, is that it does not liberate HCl when reacted with urea and trimethylolmelamine at an elevated temperature. The fabrics treated with this process possess wash-wear, permanent press and durable flame resistant properties¹⁰. Lastly, aminized cotton, prepared by treating cotton cellulose with an aqueous solution containing 2-aminoethylsulphuric acid and sodium hydroxide, followed by heating, washing and then drying the material¹¹, can be made permanently flame resistant by reacting it with THPC¹². Alternatively, the combustibility of aminized cotton can also be reduced by applying acid reacting azo dyes which contain phosphate or sulfo radicals¹.

The effectiveness of phosphorus-containing reagents to impart durable flame resistance can be increased by simultaneous fixation of nitrogen-containing compounds³. This is due to the synergistic enhancement of the flame retarding efficiency of phosphorus by nitrogen¹. The most important compounds of this class are trisaziridinyl phosphoramidate (APO), bisaziridinyl chloromethyl phosphonate (BACPO) and N,N',N'', trimethyl phosphotriamide¹. The catalyst Zn (BF₄) is a prerequisite for the APO treatment and should be present in the aqueous solution when the cotton is treated

with this compound. The APO-treated cotton fabrics are flame resistant, wrinkle, rot, mildew and glow resistant. Disadvantages, however, can include a loss in tear strength, toxicity of treated fabrics and high cost of manufacture⁴.

An APO-tetrakis hydroxymethyl phosphonium chloride (APO-THPC) formulation can also be used for imparting flame resistance to cotton. When treating cotton with an APO-THPC formulation, certain chemical compounds may be added which are capable of attacking the nitrogen of APO, thereby initiating polymerization. Examples of these chemical compounds are alkylating agents capable of forming quarternary nitrogen compounds, acids, oxidizing agents, amines, Lewis acids and diammonium phosphate (DAP). The advantages of DAP over other APO combinations include a reduction in cost materials, an ease of handling and a greater bath stability³.

The nitrogenous compound trimethylolmelamine, together with urea and triethanolamine imparts durable flame resistance to cotton by forming insoluble cross-linked condensation-type polymers with the melamine component^{3,8,10}. Urea combines with the HCl which is formed during the reaction and thus prevents acid tendering while the triethanolamine is used to stabilize the resin forming solution at room temperature. Thiourea, when used in place of urea, gives a more durable finish to laundering³, while the addition of a softener improves the tear strength⁸.

Flame retardant transfer effects between treated and untreated cottons in close proximity have also been investigated. The ignition of an untreated fabric in close contact with a treated fabric results in the burning of the untreated fabric which causes a charring of the treated fabric. This can create a potential fire hazard^{14,15}. When using certain flame retardant treatments, smoke acts as the transfer vehicle, i.e. it transfers the flame retardancy of the treated fabric to the untreated fabric¹⁶. Hobart and Mack¹⁶ showed that flame retardant transfer occurs for the following treatments of cotton: Pyrovatex[®] (a N-methylol dimethyl phosphonopropionamide), Fyrol 76[®] (a dioligomeric vinyl phosphate), THPC-amide, THPOH-amide, ammonium dihydrogen phosphate and diammonium hydrogen phosphate.

Chemical combinations of borax, boric acid and diammonium phosphate are examples of non-durable flame retardants for cotton fabrics^{1,17}. These finishes are used as flame retardants for tentage and upholstery fabric, which do not require frequent washing¹. It was found that cotton batting, used for mattresses, which were treated with chemical systems which contain boric oxide donors passed the U.S. Mattress Flammability Standard FF 4-72¹⁸. The non-durability of the abovementioned chemical combinations results from an initial loss of the treating compound¹⁹. This loss depends on the boric oxide donor used, method of application, solvent used, storage temperature and the humidity of the storage conditions¹⁹. The resistance of mattresses constructed with urea phosphate treated cotton batting to cigarette ignition can be increas-

ed by adding diammonium phosphate, alumina with or without clay and cresyl phenyl phosphate to a vinylidene chloride acrylic polymer²⁰.

Certain inorganic salts picked up by flame retardant cotton fabrics through ion exchange and precipitation during laundering can cause a leaching out of the flame retardant. This results in a decrease in the flame resistance of the fabric^{1,21}. Examples of these salts are calcium and magnesium^{21,22} which are deposited by hard water²³. Carbonate-based detergents apparently also cause deposits which make some flame retardants ineffective on cotton^{23,24}. Furthermore, it has been reported that non-phosphate detergents and soaps cause destruction of commercially available flame retardant finishes on garments, while phosphate based detergents do not affect the finish^{20,22,24}.

1.2 Polyester flame retardant treatments

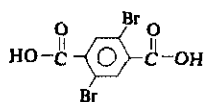
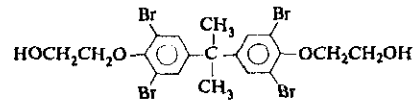
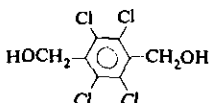
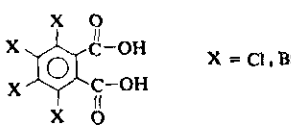
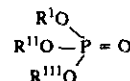

Polyesters have high strength and chemical resistance and are therefore used extensively in carpets, furnishing and apparel²⁵. However, they have average flammability performance and, therefore, various flame retardant treatments are required. There are two methods for making polyester materials non-flammable, namely, the "melt-blending" method and the "after-finishing" method.

Permanent flame retardant properties for polyester can be achieved by making use of the "melt-blend" method of flame retarding polyester. The inclusion of suitable flame retardant compounds at the manufacturing stage of the polyester fibre, e.g. the addition of phosphorous-containing compounds together with halogenated compounds to the polymerization bath, results in partial or complete substitution of terephthalic acid or ethylene glycol²⁶. Table I gives examples of flame retarding agents which impart permanent flame retardant properties to the fibre through polymerization²⁷. While the aesthetic properties are good, the addition of a third monomeric species to the bath is not recommended since this results in problems in fibre spinning and polymerization.

Another "melt-blending" flame retardant method is photo-induced fixation of flame retardant finishes onto the polyester. The photo-induced fixation of acrylic and methacrylic acid has met with limited success and had little effect on the properties of the polyester. However, the photo-induced fixation of Fyrol 76[®] onto the polyester was shown to be a far better proposition, although, in some respects, it increased the flammability of the polyester by altering its melt-drip characteristics^{28,29}.

The incorporation of certain anhydrous stannates into glass reinforced polyester results in a reduction in smoke emission. These tin compounds have an advantage since they are non-toxic smoke-suppressant additives. The anhydrous stannates which decrease the smoke emission of polyester are the methastannates, $MSnO_3$ (where M = Mg, Ca, Sr, Ba, Co, Ni, Cu or Zr). Since

TABLE I
FLAME RETARDING AGENTS WHICH IMPART FLAME RESISTANCE TO POLYESTER
THROUGH POLYMERISATION

COMPOUND	STRUCTURE	COMMENTS
2,5 Dibromo-terephthalic acid ²⁸		When condensed with 2 hydroxyethyl terephthalic acid gives a PE fibre with OI value of 25. 4% Sb ₂ O ₃ added to the spinning melt increases the OI values to 28
Bis (2-hydroxyethyl) ether of tetrabromobisphenol A		
1,4 Bis (hydroxymethyl) 2,3,5,6 tetrachlorobenzene ²⁸		Gives flame retardant properties. 12–37% Cl present Condensed with dimethylterephthalate and ethylene glycol
Tetra halo phthalic acid ²⁸		Polyethyleneglycolterephthalate when modified with tetrachloro or tetrabromo phthalic acid and about 15% halogen shows flame retardant properties
Phosphates ²⁸ , where:		Copolymerize with polyester in the presence of catalysts e.g. zinc acetate and antimony oxide to form linear phosphorous containing polyester fibres.
(a) R ^I , R ^{II} , R ^{III} = alkyl or hydroxyl alkyl groups		
(b) R = ethoxy or phenoxy groups Q = aziridinyl group		Form ring structures with terephthalic acid and ethylene glycol and the resultant fibres exhibit flame retardant properties.

they require high temperatures for volatilization to occur, it is therefore likely that they do act as smoke suppressants in these systems³⁰.

Addition of additives into the polyester before it is melt spun²⁷, or the incorporation of additives into the fibrous polymer backbone, is another method of imparting flame retardant properties to the polyester. There are certain drawbacks in that this method can cause a lowering of the melting point and a decrease in the mechanical properties of the polyester. One advantage, however, is that these polyesters are easier to dye. Table II gives some more examples of the abovementioned flame retardants²⁷.

TABLE II
FLAME RETARDANT COMPOUNDS ADDED TO THE POLYESTER FIBRE DURING MANUFACTURE

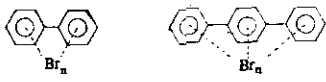
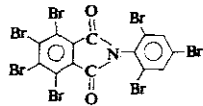
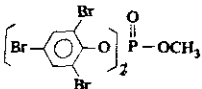
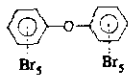
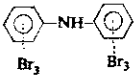
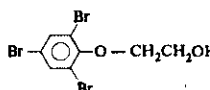
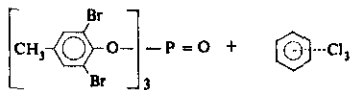
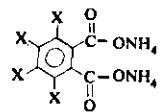
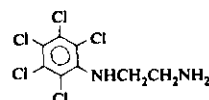
COMPOUND	STRUCTURE	COMMENTS
Poly (tribromoneopentylacrylate) ²⁸	$\left[-\text{CH}_2\text{CH}- \right]$ $\text{COCH}_2\text{C}(\text{CH}_2\text{Br})_3$	Oxygen index = 23,1 Passes the vertical flammability test
Brominated diphenyl or terphenyl ²⁸	 $n = 2 - 10$ $n = 9 - 11.5$	When combined with Sb_2O_3 good results are obtained
Tris (3-chloro-2,2-bis (chloromethyl) propyl phosphate) ²⁸	$[(\text{CH}_2\text{Cl})_3\text{CCH}_2\text{O}]_3\text{P} = \text{O}$	Effective flame retardant
N-(2,4,6-tribromophenyl) 3,4,5,6-tetrabromophthalimide ²⁸		Imparts good fire retardant properties
Bis (tribromophenyl) methyl phosphonate ²⁸		Effective flame retardant
Decabromodiphenyl oxide		
Hexabromodiphenyl amine ²⁸		15% add-on results in flame retardant properties
Tris (2-hydroxyethyl) phosphate ²⁸	$(\text{HOCH}_2\text{CH}_2\text{O})_3\text{P} = \text{O}$	Employed with polyethylene glycol. Good fire retardant properties with fibre containing about 5% phosphorus.

TABLE III
CHEMICAL AFTERFINISHES FOR FLAME RETARDING POLYESTER

FLAME RETARDANT	STRUCTURE	COMMENTS
2-(2,4,5-tribromophenoxy) ethanol ²⁸		At 121 °C flame retardant fabrics produced. Fabric handle and laundering adversely affected.
Tris (2,6 dibromocresyl) phosphate mixed with trichlorobenzene applied from an aqueous emulsion ²⁴		Passes the DOC FF3-71 test
Allyl bis (2,3-dibromopropyl)-phosphate or diallyl-2,3 dibromopropyl phosphate ²⁴	$(CH_2BrCHBrCH_2O)_2 - \overset{O}{\parallel} P - CH_2 - CH = CH_2$ $(CH_2 = CH - CH_2 - O)_2 - \overset{O}{\parallel} P - OCH_2CHBrCH_2Br$	Applied by using benzoyl peroxide or UV-irradiation Gives permanent flame retardant properties
2 (acryloyloxy)-ethyl-1,2-dibromoethyl phosphate ²⁴	$CH_2 = CH - C - OCH_2CH_2O - \overset{O}{\parallel} P - CHBrCH_2Br$	Catalyst used in benzoyl peroxide
Ammonium-tetra halogeno phthalamide ²⁴	 X = Cl, Br	Permanent flame retardant properties when applied with a latex binder
N-(Penta chlorophenyl) ethylenediamine ²⁴		Flame retardant properties and improved dyeability imparted to polyester
N,N-Methylene bis (diallyl)-2-carbamoyl ethyl phosphate	$(CH_2 = CH - CH_2 - O)_2 - \overset{O}{\parallel} P - CH_2CH_2O - \overset{O}{\parallel} C - N = CH_2$	Ammonium persulphate acts as catalyst to impart permanent flame retardant properties
Trimethyl phosphite with siloxane ²⁴	$(CH_3O)_3P$	Good flame retardant properties

The "after-finishing" of a fabric or fibre is a more popular method of flame retarding polyester than the "melt-blending" method, since excellent flame retardant properties have been imparted to the polyester by this method. Table III gives a few examples of these flame retardants.

Recently, Mischutin³¹ has developed a new "after finishing" treatment for imparting flame retardant properties to polyester. It is based on the use of a solid, water-insoluble, brominated organic component, e.g. a polybrominated biphenyl oxide, polybrominated biphenyl, polybrominated cyclodecane, polybrominated cyclohexane and polybrominated bisphenol, or mixtures thereof.

It is interesting to note that in multilayer polyester fabrics, the flame retardant treatment of one layer of polyester fabric was found to be essentially as effective as treating both layers, while the desirable characteristics of the multilayer polyester are maintained³².

The flame retardant treatment of cotton and polyester materials is a vast field encompassing many thousands of publications and many excellent book reviews. In this introductory section, the reader has been shown some examples of the more common flame retardant treatments for these materials while advantages and disadvantages, if any, have also been mentioned briefly.

2. FLAME RETARDANT TREATMENTS FOR POLYESTER/COTTON BLENDS

Polyester/cotton blend textiles have rapidly gained in popularity because the polyester component gives easy care and durability properties, while the cotton component has moisture absorbancy and softness qualities. Therefore, it was logical to blend the two fibres to take advantage of the desirable properties of both. The use of polyester/cotton blend fabrics in the apparel world extends to the manufacture of childrens' sleepwear, blankets, mattresses and upholstery material. With the increase in the use of polyester/cotton blend fabrics in the apparel world, the US government introduced flammability regulations with respect to these blend fabrics. This resulted in a considerable increase in research into the development of effective flame retardants for these blend fabrics.

Some of the more important parameters which determine the flammability of these blended textile fabrics are: ease of ignition, rate of flame propagation, ease of extinguishment and rate of heat production³³. The flammability behaviour of the component fibres of polyester/cotton blend fabrics cannot be used to predict accurately the flammability behaviour of the blend fabric³⁴. It is believed that cotton, which chars when exposed to a flame maintains its structural rigidity, thereby forming a support for the polyester, which melts and drips. This is known as the "scaffolding effect"³⁴. However, since

polyester has a high heat of combustion, when it drips onto the cotton component, this results in the enhancement of the pyrolysis of the cotton. The burning characteristics of the blend depend on its composition, mass, structure, thermo-physical properties, pre-drawing conditions of the polyester and heating intensity.

The chemical natures of cotton and polyester are vastly different, since cotton is reactive and highly hydrophilic, whereas polyester is inert and highly hydrophobic. Although the ideal would be to find a single flame retardant which would be effective on both fibres, at this stage, the only possibility to render a satisfactory level of flame retardancy to polyester/cotton blend fabrics³⁴ is by means of a dual flame retardant system, where each flame retardant must react effectively and separately with the polyester or cotton portion of the blend.

The methods of approach for flame retarding polyester/cotton blends are:

- (i) construction of the fabric from flame retardant polyester and cotton fibres³⁴, or blending the cotton with inherently flame retardant polyester fibres³⁵,
- (ii) treatment of a non-retardant portion e.g. cotton with an appropriate flame retardant when the polyester portion is an inherently flame retardant fibre³⁴,
- (iii) chemical after-treatment of polyester/cotton blends³⁵ by application of two different flame retardants in a one or two step process.

Some of the abovementioned techniques are incorporated in the discussion which follows.

2.1 Modification of the surface of blend fabrics

Modification of the surface of blend fabrics is not a flame retardant treatment as such, rather a preparatory step to ultimately flame retard the blend fabric. However, since durable flame retardancy is imparted to the blend fabric by making use of this preparatory step, it will be discussed in this section.

The techniques considered for the modification of the surface of blend fabrics include surface modification by oxygenplasma, corona discharge or irradiation, grafting of reactive compounds with functional groups onto the fibre surface and saponification of the fibre surface with alkali^{36,37}. The treatment of the fibre with alkali appears to be the most viable method, since cotton is chemically stable under the conditions needed for altering the polyester surface of the blend. It was found that an alkali pretreatment resulted in a reduction of the amount of flame retardant required to produce the same results as the fabric not treated with alkali. The increase in the durability of the flame retardancy is due to enhanced fixation, distribution, wetting and adhe-

sion of the finish. Further advantages are improved fabric aesthetics and cost savings³⁷.

2.2 Synergism antagonism and the additive effect of flame retardant compounds

The concept of synergism, which is pertinent to this report can be explained in terms of antagonism and the additive effect. The additive effect is one where the combined effect of two compounds leads to the same result as the effect of two individual compounds where the results were added separately. Antagonism results when the combined effect is less than the additive effect, while synergism results when the combined effect is greater than the additive effect³⁸.

Phosphorus-nitrogen synergism is claimed to be very effective in improving flame retardancy of fabric blends but it only takes place between specific combinations of phosphorus-based flame retardants and nitrogenous compounds³⁸. Urea formaldehyde-diammonium hydrogen phosphate (UF-DAP) treatments decompose at low advantageous temperatures, since crosslinking is not probable. The low decomposition temperatures promote volatilization of the phosphorus-based flame-inhibiting species. The flame-retardant species, which may contain P-N bonding, promote the flame-inhibition processes of polyester fibres by adding to the vapour phase contribution of the process. The magnitude of the N-P synergism decreases as the concentration of phosphorus in the blend decreases.

The dimethyloldihydroxy ethylene urea/diammonium hydrogen orthophosphate (DMDHEU-DAP) and the pentamethylol melamine-diammonium hydrogenorthophosphate (PMM-DAP) treatments appear to lead to antagonism. However, when the DAP is removed from the system, some flame retardancy is observed³⁸.

2.3 Addition of flame retardants to the spinning melt

The addition of flame retardants to the polyester spinning melt results in inherently flame retardant polyester fibres. The addition is made prior to spinning, thereby allowing for modifications which would maximise the durability of the flame retardant and minimise the undesirable effects on the physical properties of the fibre. However, the addition of foreign compounds into the spinning melt causes fibre rigidity and brittleness. There are only a few inherently flame retardant finishes known (see introduction) and therefore a commercial chemical after-treatment of blend fabrics seems more feasible.

2.4 One- or two-step application of flame retardants

The cost of flame-retarding polyester/cotton blend fabrics, and the aesthetic properties of the treated fabric are important to the textile industry. Therefore, an intensive search is in progress in order to find a new single-bath system which contains compatible cellulose-active and polyester-active

components³⁹. There is however a disadvantage in this process, namely, severe thermal conditions are needed for the fixation of the polyester components, which could damage the cellulosic finishes. The alternative approach to the problem is a commercially available two-stage process, which consists of first treating the cotton with a suitable flame retardant finish followed by a thermosol application of the polyester flame retardant finish.

2.5 Chemical after-treatment of the fabric

A number of halogen-containing compounds as well as organophosphorus compounds have been applied to polyester/cotton blend fabrics in an attempt to render these fabrics flame retardant by means of a chemical after treatment. Organophosphorus compounds, of which tetrakis (hydroxymethyl) phosphonium chloride is an example, render durable flame retardant properties to cellulosic materials^{40,41}, by forming an insoluble resin film on the fibre⁴¹. Polyester materials can be rendered flame retardant by applying halogenated compounds containing, e.g. bromine, which act as free radical terminators⁴²⁻⁴⁴. When flame retarding polyester/cotton blend fabrics, a binary system is effective since the combined effect of the system is the sum of the individual effects of the retardants in the system⁴⁵.

An effective binary flame retardant for 50/50 polyester/cotton blend fabrics is a system based on tetrakis (hydroxymethyl) phosphonium chloride, urea and polyvinylbromide, (THPC-urea-PVB)^{42,44,45}. Urea is essential in the system as a source of nitrogen, although ammonia or amine resins such as methylolmelamines can also be used⁴¹. There are disadvantages in this THPC—urea—PVB system, namely, poor thermal stability of the PVB because of the premature release of the active bromine species⁴⁵, and yellowing of the material, which can only be removed by a hypochlorite bleach. The yellowing of the fabric can be eliminated by adding a vinyl chloride/vinyl bromide copolymer to the THPC-urea formulation, with which it is compatible. The handle of the fabric is good and it passed the DOC FF 3—71 test⁴².

An advantage of using a binary mixture of phosphorus and bromine-containing reagents is that it allows variation of the individual components of the system, so that optimization of characteristics such as handle, cost, and ease of application can be obtained. The wrinkle recovery of the fabric can be improved by adding trimethylolmethyl-glycoluril (TMMGU) and trimethylolacetylenediurea to the treating bath^{44,46}. An electron microscopic study⁴⁶ of the THPC-urea-TMMGU-PVB flame retardant formulation for cotton/polyester blends has shown that the PVB flame retardant component completely penetrates the cotton fibres while a certain amount of PVB also penetrates the polyester fibres.

Another binary system for the finish of 50/50 polyester/cotton blend

fabrics is one which is based on tetrakis (hydroxymethyl) phosphonium chloride and tris(2,3-dibromopropyl) phosphate⁴⁷. This finish imparts excellent flame retardant properties to polyester/cotton blend fabrics. The finish is durable to washing and dry cleaning and it does not significantly affect the light and wash fastness, nor change the shade of the disperse and vat dyes which are commonly used in thermosol dyeing. Unfortunately, it was found to be carcinogenic and therefore tris (2,3-dibromopropyl) phosphate (T23P) was banned by the US Consumer Product Safety Commission.

The durability of a flame retardant finish is important and in order to achieve a certain standard, one must use chemicals which react with the hydroxy groups of the cellulose. Two chemicals which have achieved this objective are the insoluble film-forming type, namely, THPC, which has been mentioned before and Pyrovatex CP[®], which is also a cellulose-reactive type^{40,41}. Pyrovatex CP[®] (N-methylol phosphonopropionamide) reacts with the hydroxy groups in cellulose, but no network formation occurs, since the reagent contains only one methylol group. The finish with phosphonopropionamide therefore imparts a soft hand to the fabric. Phosphonopropionamide only reacts with the cellulose portion of the blends, which can be a disadvantage.

Experiments performed by Hofmann *et al*⁴¹, showed that phosphonopropionamide is more effective when the cotton content is high, (polyester content no greater than 12,5%), whereas a phosphonium salt type is more effective when the ratio of polyester is greater.

As has been mentioned, THPC successfully flame retards cellulosic fabrics. Le Blanc and Gray⁴⁰ showed that THPC can flame retard polyester/cotton blend fabrics as well. However, successful flame retardance was only obtained when the polyester portion did not exceed 50% of the blend. In spite of this finding, the polyester/cotton blends treated with THPC had a stiff hand.

The flame retarding performance of phosphates and phosphonates, when reacted with polyethylenimine (PEI), was studied by Bertoniere and Rowland^{48,49}. They found that the reaction of tris (2,3-dichloro-2-propyl) phosphate (DCPP) with PEI imparted flame resistance to cotton-containing fabrics. The reaction yielded phosphorus-, nitrogen-, and halogen-containing prepolymers, which were responsible for imparting the flame retardance properties. Disadvantages of the treatment include water insolubility of the prepolymers, which must therefore be applied from a dimethylformamide solution, discoloration of the fabric when cured and the durability of the treatment which only lasts for 5 laundering cycles⁴⁸.

The reaction of the phosphonates Antiblaze 78[®] and Antiblaze 77[®], which were used in the experiment with PEI, gave better results than the phosphate-PEI treatment. The phosphonates form water soluble prepolymers

TABLE IV
COMPARISON OF TEXTILE PROPERTIES OF COTTON/POLYESTER
SHEETING FLAME-RETARDANT TREATED WITH
FINISHES BASED ON ALKYL PHOSPHATE-PEI PREPOLYMERS AND
THPOH-NH₃

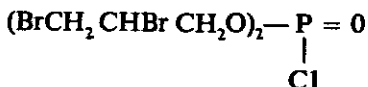
FABRIC PROPERTY	A78-PEI	A77-PEI	FYROL76-PEI ^a	THPOH-NH ₃ ^b
Durable-press rating (1—5)	1,1	1,6	—	0,9—1,3
Wrinkle recovery angle				
Conditioned (degrees, W + F)	217	216	171—192	178—183
Wet (degrees, W + F)	245	249	243—258	185—214
Breaking strength (% of original)	111	106	103—112	66—72
Elongation (% of original)	98	94	86—91	56—68
Tearing strength (% of original)	58	63	72—75	60—68
Stoll Flex Abrasion resistance (% of original)	91	110	75—108	65—77
Accelerator abrasion resistance (% actual mass retained)	96	97	98—99	94—98
Bending modulus (N.mx10 ⁻⁵)	14,1	13,8	17,1—23,9	5,7—17,1

^aData from ref.⁵⁰

^bData from ref.⁵¹

which impart flame resistant finishes to the cotton component of the blend, with less discoloration and greater durability to laundering than the corresponding phosphate prepolymers. These treatments cause a harsh handle and they bear a similarity to the finish from oligomeric vinyl phosphonate (Fyrol 76) plus PEI^{48,50}. The results, summarized in Table IV, illustrate the similarity in the textile properties of fabrics treated with Antiblaze-® PEI and oligomeric phosphonate-PEI, and the differences between the fabrics treated with these reagents and those treated with THPOH-NH₃⁴⁸.

A compound related to T23P, namely, bis(2,3-dibromopropyl) phosphoryl chloride readily reacts with compounds such as diethanolamine, ammonia, ethylene glycol, etc., thereby forming structures similar to that of T23P, but forming reactive groups which could be co-reacted with resins. However these compounds which were formed showed insufficient stability to heat to be suitable for a textile finishing operation⁵². The structure of bis(2,3-dibromopropyl) phosphoryl chloride is given below:



The Southern Regional Research Centre in the USA has shown that tetrakis (hydroxymethyl) phosphonium hydroxide (THPOH), which is the neutralisation product of THPC, successfully flame retards 35/65 polyester/cotton blend fabrics⁵³. They found, in fact, that organic bromine compounds, when used in combination with THPOH-NH₃, flame retard 50/50 polyester/cotton blends. Although a two-step process can be used for the application of the TPOH-NH₃ and organic bromine compounds, a single bath emulsion is preferred⁴³. Another flame retardant system based on THPOH which imparts flame retardancy to 50/50 polyester/cotton blend fabrics is THPOH-urea-PVB/PVC. Researchers have been studying various durable press finishes for this system, since the consumer expects outerwear apparel to have durable press properties. The finishes which were studied are dimethylol dihydroxy-ethyleneurea (DMDHEU), trimethylol melamine (TMM), tetramethylol glycouril (TMGU), glyoxal, N-methylolacrylamide (NMA) and formaldehyde. It was found that a blend of 35/65 polyester/cotton provided the best balance of durable press and flame retardant properties.

The polyester/cotton THPOH-NH₃ flame retardant system is capable of transferring its flame retardant properties to an untreated polyester/cotton blend fabric lying adjacent to it when subjected to thermal heating. The percentage of polyester in the blend fabric is a significant factor when flame retardant transfer occurs. The transfer is substantial only when the percentage of polyester in the blend fabric is between 0% and 35%. One can therefore

but it cannot impart durable washing properties. NMDEPPA does not impart durable retardancy to polyester/cotton blend fabrics. Similarly, DBDPO-Sb₂O₃ cannot durably flame retard polyester/cotton blend fabrics. However, when NMDEPPA and DBDPO-Sb₂O₃ are applied in two steps, they impart durable flame retardancy to blend fabrics and the treated samples withstand the vertical flammability test.

A non-phosphorous flame retardant which has been applied to 50/50 polyester/cotton flannelettes is tetramethylol-2,4-diamino-6(3,3,3-tribromo-1-propyl)-1,3,5 triazine (TM-DABT)⁵⁴. It is applied in combination with colloidal antimony oxide in DMF/water with no latex binder. This treatment does have a few disadvantages, namely, afterglow and yellowing with laundering.

3. SUMMARY

A review of the literature has revealed the complexity of the problem of flame retarding cotton, polyester and in particular polyester/cotton blend fabrics. Research into the development of flame retardants for polyester and cotton fabrics has produced some successful results. However, the flame retarding of polyester/cotton blend fabrics has proven to be an extremely difficult problem, since flame retardant treatments which are effective for the one part of the blend, are not necessarily effective for the other part of the blend. Some of the more successful flame retardant treatments which have recently been developed for polyester/cotton blend materials can be examined in tabulated form below

TREATMENT	COMMENT
(i) THPC	Flame retards 50/50 polyester/cotton blend fabrics.
(ii) THPC-urea-PVB	Flame retards 50/50 polyester/cotton blend fabrics. TMMGU affords improved wrinkle recovery. Problem, poor thermal stability and fabric yellowing.
(iii) Pyrovatex CP®	Flame retards polyester/cotton blends where polyester content not to exceed 12.5%.
(iv) Antiblaze 77® Antiblaze 78®	Flame retards polyester/cotton blend.
(v) Fyrol 76® -PET	Flame retards polyester/cotton blend.

- | | |
|--|---|
| (vi) Fyrol 76® -NMA | Imparts durable flame retardance to polyester/cotton blend materials. |
| (vii) THPOH | Flame retards 35/65 polyester/cotton blend fabrics. Organic bromine compounds with THPOH flame retard 50/50 polyester/cotton blend fabrics. |
| (viii) THPOH-NH₃ | Flame retards polyester/cotton blends. Can transfer its flame retardancy to untreated polyester/cotton fabrics. |
| (ix) THPOH-urea-PVB-PVC | Flame retards 50/50 polyester/cotton blend fabrics. |
| (x) DAP-DMDHEU
DAP-PMM | Flame retards polyester/cotton blend materials. Antagonism a detracting feature. |
| (xi) Caliban FR- 44® | Flame retardant for polyester-rich blends. |
| (xii) NMDEPPA-DBDPO-Sb₂O₃ | Effective flame retardant treatment for polyester/cotton blends. Durable when applied in two-step manner. |
| (xiii) TM-DABT.SB₂O₃ | In DMF/H ₂ O imparts flame resistance to cotton/polyester blend fabrics. Afterglow and yellowing of the fabrics a problem. |

THE USE OF PROPRIETARY NAMES

The names of proprietary products, where they appear in this publication, are mentioned for information only. This does not imply that SAWTRI recommends them to the exclusion of other similar products.

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