

COMPARISON OF DIFFERENT FLAME RETARDANT FINISHES

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Abstract

Flame retarding in textiles can be obtained either with high performance fibers like aramid fibers or with chemical modifications. These chemical modifications can be used in the different stages of the production: polymerization, extrusion or finishing stages. Flame retardants can work according to four mechanisms, namely chemical, thermal, gaseous and coating mechanisms. Fiber and flame retardant material types and end use of the material are important to choose the suitable mechanism. Flame retarding with phosphorus is used in cotton, polyester and viscose fabrics. Flame retarding with halogens can work with wool and viscose . Boric acids and its hydrated salts used in flame retardants work via coating mechanism. In this study, flame retarding with phosphorus, halogen and borates are compared. Their application methods and handling problems are also discussed.

1. Combustion and approaches for stopping combustion:

Flame retardation is vital for people who have a risk of heat damages like fire fighters, emergency personnel, spacemen and workers in glass and metal industries. Recently it becomes important for the curtains, upholstery and floor covers in public areas and apparel for baby and child. The flame retarding investigation gets important in 1940ies after the recognition of the flammability hazard posed by textiles and the need to produce effective and durable finishes and treatments, which have minimal effects on the desirable features such as handle, comfort and general aesthetics [1].

There are some requirements for commercially successful flame retardant finishes. These are as follows:

- It should not change the physical properties of textiles
- It should not affect the aesthetics of textiles
- After the treatment, textile's physiological properties should be retained same.
- It can be produced by simple process with conventional equipments and cheap chemicals
- It should be durable against the repeated laundering and dry cleaning.

To understand the mechanism of flame retarding, the mechanism of combustion should be known. The combustion is an exothermic spontaneous process where flame, oxygen and

carbon containing fuel are needed to start it. To stop the combustion, either oxygen or fuel should end in the environment [2]. Figure 1 shows the combustion cycle for fibers.

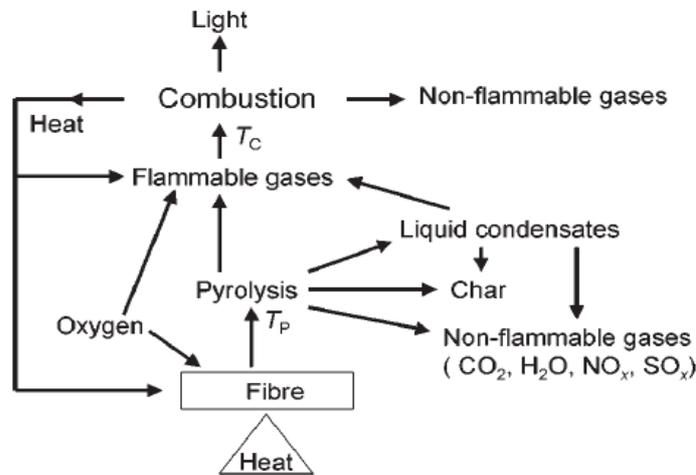


Figure 1: Combustion cycle for fibers [2].

If we disrupt the combustion cycle, the combustion of textiles can not continue. There are four different approaches for stopping the combustion:

- Using a chemical which influences the steps of pyrolysis reaction to produce less flammable volatiles and more residual char. This method is suitable for phosphorous containing flame retarding known as chemical mechanism.
- Using a chemical which interferes with the free radical reactions that provide the heat needed for process to continue. This can be defined as gaseous mechanism.
- Using a chemical which thermally decomposes through strongly endothermic reactions to provide a heat sink on/in the fiber. This is called a thermal mechanism.
- Applying a chemical on the fibers that forms an insulation layer around the fiber at the temperature below the fiber pyrolysis temperature. Boric acid and its hydrated salts work according to this mechanism called coating [2].

2. Limiting Oxygen Index and Thermal properties of some conventional textile fibers:

Since air comprises about 21% oxygen by volume, any material with a limiting oxygen index (LOI) less than this will burn easily in air. Conversely, the burning behavior and tendency to propagate flame for a polymer with a limiting oxygen index greater than 21 will be reduced or even zero after removal of the igniting source. Self-sustaining combustion is not possible if $LOI > 100$, such values are not physically meaningful [6].

Thermal properties of some conventional textile fibers are shown in Table 1. As seen from the table, wool has the best LOI percentage among the natural fibers. Also it has better value than Nylon, Polyester, Acrylic and Polypropylene. Wool has a very high T_c (600°C) and its heat of combustion is low. When wool is used in tightly woven structures, it will be a good insulator.

Table 1: Thermal properties of some fibers [3].

Fibre	T_g °C	T_m °C	T_p °C	Heat of combustion		LOI %
				(kJg ⁻¹)	T_c °C	
Wool	-	-	245	20.5	600	25.2
Cotton	-	-	350	19	350	18.4
Viscose	-	-	350	19	420	18.9
Nylon6	50	215	431	39	450	20-21.5
Nylon 6.6	50	265	403	33	530	20-21.5
Polyester	80-90	255	420-447	24	480	20-21
Acrylic	100	>220	290	32	>250	18.2
Polypropylene(PP)	-20	165	470	45	550	18.6
Nomex	275	375	410		>500	29-30
Kevlar	340	560	>590		>550	29

LOI: Limiting Oxygen Index

T_g : Glass transition temperature where the material softens

T_m : Melting temperature where the solid liquid transition occurs

T_p : Pyrolysis temperature where the irreversible chemical changes occur

T_c : Temperature of combustion

Cotton and viscose have both low LOI and low heat of combustion. Their T_c is about 350-420°C, they can burn readily and freely. The thermoplastic property of sythetic fibers has an important affect on their burning behaviors. For example PP has low melting temperature (T_m) and glass transition temperature (T_g). Then it can melt and shrink at 165 °C. Polyamid and Polyester support combustion in the air. They both shrink below the melting point. They can show shrinkage and melt down before combustion that causes risks [4].

3. Production parameters of fibers affecting the burning behavior

Ease of ignition, rate of burning and heat release rate, melting and shrinkage behaviors, emission of smoke and gases or adsorption of liquids affect the burning behaviors of textiles and determine the extent of fire hazard [5]. Some production parameters that have an affect on the burning behaviors of textiles are shown in Figure 2.

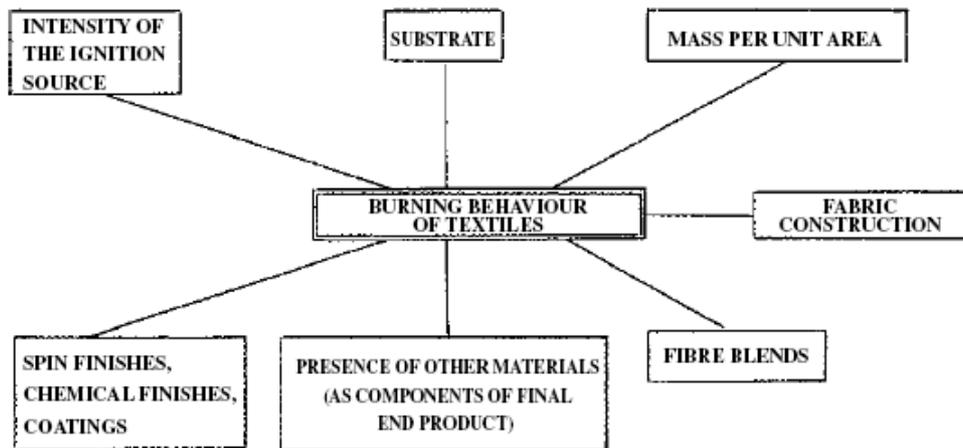


Figure 2: Factors influencing the burning behavior of textiles [6].

4. Types of flame retardant finishes for textiles

The flame retardant finishes for textiles can be classified as non-durable and durable according to given conditions. There are some factors affect the durability of finishes such as [1]:

- Functionality and reactivity of finishes.
- Hydrophilic property of fibers.
- Internal voids within the fibers.
- Resistance of the applied finish to hydrolysis and oxidative bleaching conditions.

The use of sodium tetraborate decahydrate, namely borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), for cellulose as a flame retardant goes back about two centuries. Water soluble sodium borates as well as boric acid and the mixtures thereof still can be used for cellulose materials and other hydroxyl group containing polymers. Action mechanism of borates and boric acid is seen in a combination of the effect of the formation of a glassy inorganic layer, which is often intumescing (swelling as a result of heat exposure, thus increasing in volume, and decreasing in density), and an increase in char formation perhaps through the formation of borate esters as well as through the blocking off of volatile fuel release. Borates and boric acid can also give off water during the reaction. Water acts as a heat sink with its high specific heat capacity ($4.18 \text{ J}^\circ\text{C}^{-1}\text{g}^{-1}$), a propellant for the fuel out of the flame zone with its organophobe property, and a blowing agent for the glassy intumescent. Other important and new flame retardant borates are zinc borates, both flame and smoke retardant, hydrated barium borate and hydrated calcium borate with low water solubility [3]. In textile applications, a mixture of boric acid and borax salts is effective flame retardant for cotton, but this retardant is not durable in apparel use like laundering or dry cleaning.

Organic phosphates such as tri-alkyl or tri-aryl phosphates, tri-chloroalkyl phosphates, dialkyl phosphites, tetrakis-(hydroxymethyl)phosphonium chloride and related structures have been used for flame inhibition. Heat loss due to melt flow, surface obstruction by phosphorus-containing acids, acid-catalyzed char accumulation, char enhancement and protection of char from oxidation have all been noted in particular polymer systems containing phosphorus-based flame retardants [3]. In textile applications, the most successful durable flame retardants for cellulose are based on phosphorous- and nitrogen-containing chemical systems that can be react with the fiber or from crosslinked structures on fiber. The most important ingredient of one of these finishes is Tetra(hydroxymethyl)phosphonium chloride (THPC). THPC is produced as a result of the reaction between phosphine, formaldehyde and hydrochloric acid(See Figures 3). THPC reacts with urea to form an insoluble structure on cellulose in pad-dry-cure process [2].

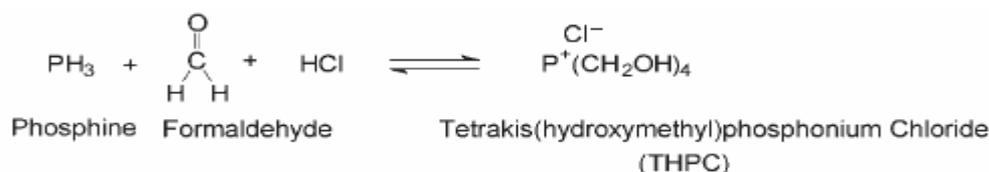


Figure 3. Synthesis of THPC [2]

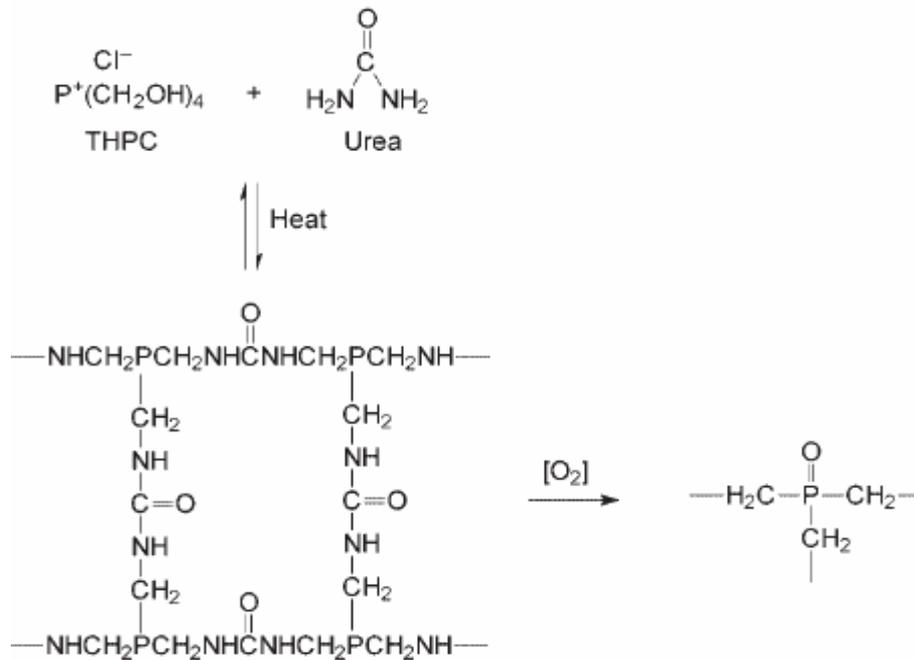


Figure 4. Reaction of THPC with urea [2]

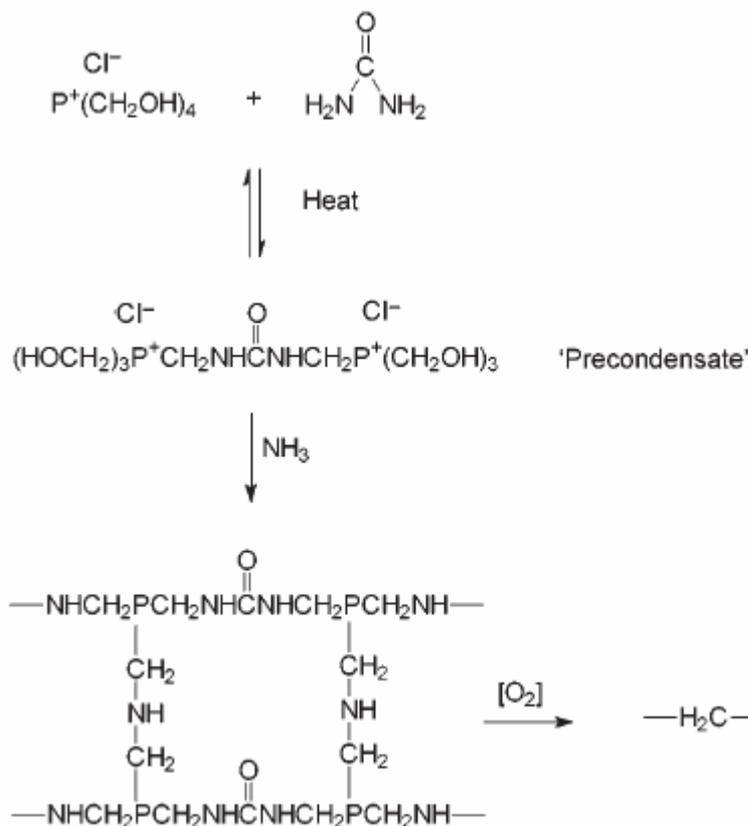


Figure 5. THPC-Urea-ammonia reaction [2]

To convert the phosphorous atoms to their highest oxidation state, the cured finish is treated with hydrogen peroxide. As a result of that, very durable flame retarding is obtained in cellulose containing materials. Figure4 and Figure 5 show the reaction of THPC with urea/ urea-ammonia resulting in a fire retardant layer on the textile.

Another application of durable phosphorous-containing finishes for cellulose containing materials is the use of *N*-methylol dimethyl phosphonamide in the combination with trimethylol melamine and phosphoric acid as a catalyst in a pad dry cure process [1]. One commercial flame retardant for polyester is a mixture of cyclic phosphate/phosphonates (Figure 6). It can be used in a pad-dry- heat set process.

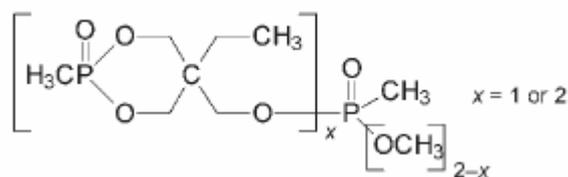


Figure 6. Cyclic phosphate/phosphonate flame retardant [2].

A major factor in the combustion of plastics is the presence of highly active OH and H free radicals. The hydrogen halides released by decomposition of halogenated flame retardants react with these radicals and convert them to less active radicals. The activation of halogenated flame retardants occurs mainly in the gas phase. The activity of halogenated flame retardants occurs in the gas phase but they are thought to inhibit further burning in the solid or liquid. Halogenated flame retardants are generally used with antimony trioxide, which is not itself a flame retardant [3]. As shown in Figure 7, materials that act in this 'gas phase' mechanism include halogen containing compounds which, during combustion, yield hydrogen halides that form relatively long lived, less reactive free radicals, effectively reducing the heat available for perpetuating the combustion cycle, and which decrease the oxygen content by flame gas dilution [2].

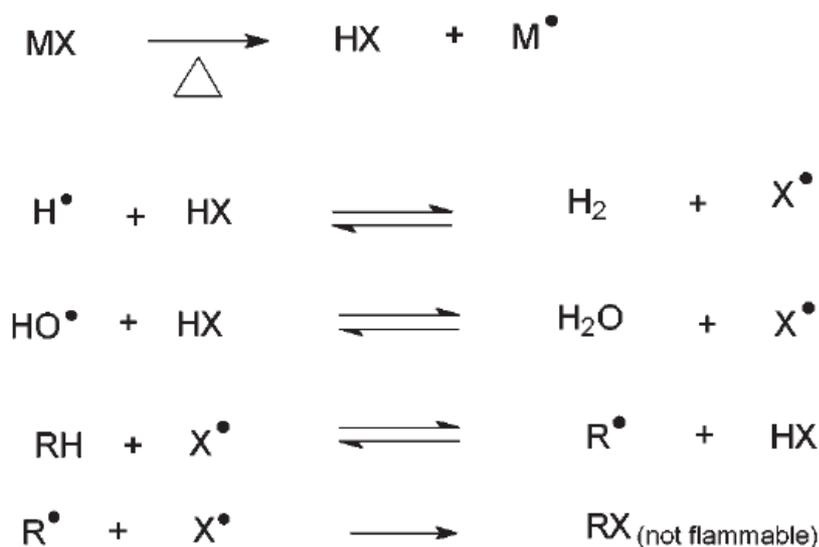


Figure 7. Competing free radical reactions during combustion of halogen (X) containing material (M). R is the organic residue [2].

In textile applications, antimony-halogen retardants are the most successful within both the bulk polymers and back-coated textiles because of their effectiveness and cost [1]. Common halogenated flame retardants are shown in the Table 2.

Table 2. Synergistic combination of flame retardant [2].

Synergistic combination	Suitable for	Generated primary active compounds
P/N Halogen (X)/Sb ₂ O ₃	Cellulose Synthetic fibres, especially PAN, PP, PA	H ₃ PO ₄ , P-amides SbOX → SbX ₃
P/halogen (X) Halogen/radical generator	PP, (PET, PAN, PA) Synthetic fibres, especially PET, CT, CA	POX ₃ , PX ₃ Halogenated polymers

PP = polypropylene, PET = polyethylene tetrachloride, PAN = polyacrylonitrile, PA = polyamide, CT = cellulose triacetate, CA = cellulose acetate.

In conclusion, flame retardant textiles are developed to reduce the ease of ignition and reduce the flame propagation rates. There are some text methods to evaluate the flame retarding of textiles. These methods are available in ASTM and BS. These standards contain a vertical specimen test for fabrics and tests to determine LOI or critical oxygen content of textiles. To choose suitable flame retardant, toxicity and cost factors are as important as durability, efficiency of flame retardants [5].

The toxicity of the flame retardants is very important for textiles. Toxicity of some flame retardant components and of their combustion gases are particular concerns for flame retardant based on halogens and several heavy metals. The cost of flame retarding is important. While application of fire retardants in normal textile finishing procedures, minimum application systems such as foam application can be chosen to decrease the usage of water and energy [1]. Also material type on which flame retardant will be applied is important.

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