FLAME RETARDANTS FOR TEXTILES

Hazards associated with the ready combustibility of cellulosic materials were recognized as early as the 4th century BC, when Aeneas is said to have recommended treatment of wood with vinegar to impart fire resistance (1). The annals of Claudius record that wooden storming towers used in the siege of Piraeus in 83 BC were treated with a solution of alum to protect them against fire.

The technique of imparting flame resistance to textile fabrics is relatively new. Among the earliest references is an article by Sabattini published in 1638. Recognizing a need to prevent fire, he suggested that clay or gypsum pigments be added to the paint used for theater scenery to impart some flame resistance. Perhaps the first noteworthy recorded attempt to impart flame resistance to cellulose was made in England in 1735 (2) when Obadiah Wyld was granted a patent for a flame-retardant mixture containing alum, ferrous sulfate, and borax.

In France in 1821, Gay-Lussac (3) developed a flame-resistant finish by treating linen and jute fabrics with a mixture of ammonium phosphate, ammonium chloride, and borax.

The first successful, launder-resistant, flame-retardant finish for fabric was based on the work of Perkin (4) who precipitated stannic oxide within the fiber. This fabric was flame resistant but afterglow was severe and persistent enough to completely consume the fabric.

Flame retardants are mainly used on cottons and rayons. Fabrics made from wool (qv), silk (qv), and protein-like synthetic polymers are not considered sufficiently combustible, for the most part, to warrant the need for flame-retardant finishes (see Biopolymers; Textiles).

Since World War II the flammability of textiles of all types has received greatly increased attention, spurred by the Conference on Burns and Flame Retardant Fabric in 1966 (5), and by the 1967 amendment to the Flammable Fabrics Act of 1953 (6). Flammability standards were established by the Department of Commerce and enforced by the Federal Trade Commission. This responsibility was taken over by the Consumer Product Safety Commission when it was created in 1973.

The terms used in connection with flame-resistant fabrics are sometimes confusing. Fire resistance and flame resistance are often used in the same context as the terms fireproof or flameproof. A textile that is flame resistant 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. Fireproof or flameproof, on the other hand, refer to material that is totally resistant to fire or flame. No appreciable change in the physical or chemical properties is noted. Asbestos is an example of a fireproof material.

Most organic fibers undergo a glowing action after the flame has been extinguished, and flame-resistant fabrics should also be glow resistant. Afterglow may cause as much damage as the flaming itself since it can completely consume the fabric. The burning (decomposition) temperature of cellulose is about 230°C, whereas afterglow temperature is approximately 345°C.

Chemical modification of cellulose with fire retardants gives products whose resistance to laundering and weathering is superior to that of finishes based on the physical deposition of the flame retardant within the fabric, yarn, or fiber. The reactions involved are either esterification or etherification. The latter is preferred because ether linkages are more stable to hydrolysis.

Flame Resistance

The flame resistance of a textile fiber is affected by the chemical nature of the fiber; ease of combustion; fabric weight and construction; efficiency of the flame retardant; environment; and laundering conditions.

Fire-resistant characteristics can change significantly when treated fabric is exposed to sunlight, followed by laundering, even though repeated washing and tumble drying of samples of the same specimen did not indicate any significant changes, especially in the durability of the finish (7). Dry heat alone, followed by laundering or autoclaving can also have a deleterious effect (8).

Fibers are classified into natural fibers, eg, cotton, flax, silk, or wool; regenerated fibers, eg, rayon; synthetic fibers, eg, nylons, vinyls, polyester, 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, chemical).

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

Phosphorus-containing materials are by far the most important class of compounds used to impart durable flame resistance to cellulose (see also Flame retardants, phosphorus compounds). They usually contain either nitrogen or bromine and sometimes both. A combination of urea and phosphoric acid imparts flame resistance to cotton fabrics at a lower add-on than when the acid or urea is used alone (9). Other nitrogenous compounds, such as guanidine, 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.

Bromine in flame-resistant fabric escapes from the tar to the vapor phase during pyrolysis 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.

Nitrogen when used in conjunction with phosphorus compounds has synergistic effects (10–12). Phosphorus content can be reduced without changing the efficiency of the flame retardant (13).

The temperature of the environment influences the burning characteristics of fabric as measured by the oxygen index (OI). This is true for untreated as well as flame-retardant fabrics. For example, the OI value of untreated fabric is 0.18 when burned at 25°C and 0.14 when burned at 150°C. For flame-retardant fabric, an OI value of 0.35 at 25°C may be reduced to 0.27 when burned at 150°C. Sunlight and heat can also destroy some flame retardancy (13–15), especially when followed by laundering or autoclaving (7–8). The moisture content of fabric can also affect flame retardancy (16).

Fire retardancy 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 (17). Soap-based detergents can result in a substantial loss of fire resistance because of deposit of fatty acid salts (18). Phosphorus-based flame retardants are adversely affected by water hardness and sodium hypochlorite (see Drycleaning and laundering).

Mechanisms. Cellulose, as such, has no appreciable vapor pressure and does not burn. However, on exposure to high temperatures it decomposes exothermically into flammable compounds causing further degradation and decomposition until complete disintegration has taken place. Numerous studies have been made on burning of untreated and flame-retardant-treated cellulose (19–24). Decomposition takes place in two stages. First, thermal decomposition causes cellulose to decompose heterogeneously into gaseous, liquid, tarry, and solid products (25,26). The flammable gases thus produced ignite, causing the liquids and tars to volatilize to some extent. This produces additional volatile fractions which ignite and produce a carbonized residue which does not burn readily. This process continues until only carbonaceous material remains. After the flame has subsided, the second stage begins: the residual carbonized residue slowly oxidizes and glowing continues until carbonaceous char is consumed.

Cotton (qv) treated with an effective flame retardant forms, in general, the same decomposition products upon burning as 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 the flammable gases are available from the tar, and greater amounts of nonflammable gases from the decomposition of the char fraction.

Char is essentially carbon and its oxidation causes afterglow. Phosphorus-containing compounds (in some cases, polymers) are particularly effective in inhibiting char oxidation. The oxidation of carbon takes place through either of the following reactions:

$$C + \tfrac{1}{2}\,O_2 \rightarrow CO \qquad \Delta H = 110.45\ \text{kJ}\ (26.4\ \text{kcal})$$

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = 394.96\ \text{kJ}\ (94.4\ \text{kcal})$$

Effective glow-retardant chemicals, such as compounds containing phosphorus, cause the first reaction to be prevalent. Oxidation of carbon monoxide is not sufficiently exothermic to maintain afterglow of the char.

Imparting flame resistance to cellulose has been explained by the following theories:

Coating theory. As early as 1821, Gay-Lussac (3) suggested that fire resistance was due to formation of a layer of fusible material which melted and formed a coating thereby excluding the air necessary for the propagation of a flame. This was based on the efficiency of some easily fusible salts as flame retardants. Carbonates, borates, and ammonium salts are good examples of coating materials that produce a foam on the fiber by liberation of gases such as carbon dioxide, water vapor, ammonia, etc.

Gas theory. The flame retardant produces noncombustible gases at burning temperature which dilute the flammable gases produced by decomposition of the cellulose to a concentration below the flaming limit.

Thermal theory. Heat input from a source is dissipated by an endothermic change in the retardant and the heat supplied from the source is conducted away from the fibers so rapidly that the fabric never reaches temperature of combustion.

Chemical theory. Strong acids, bases, metal oxides, and oxidants that tend to degrade cellulose, especially under the influence of heat, usually impart some degree of flame resistance to cellulose (27). This is also true of the more efficient flame retardants, such as phosphoric and sulfuric acid, which are good dehydrating agents. When this happens, cellulose on combustion produces mainly carbon and water rather than carbon dioxide and water.

Flame retardants for cotton may possibly act through a dehydration process by Lewis acid or base formation through a carbonium ion or carbanion mechanism (21). This theory is being further investigated.

Earlier theories suggested that flame-retarded cellulose decomposed at high temperatures to *l*-glucosan which in turn broke down to form other volatile products which were highly flammable. However, if bases are present in the fabric during burning, dehydrocellulose is formed by a base-catalyzed dehydration followed by char formation (28). Base-catalyzed dehydration prevents formation of *l*-glucosan by propagating structural changes at an energy level below that required to convert the coformers of the glucopyranose ring (29).

Durability

Nondurable Finishes. Flame-retardant finishes that are not durable to laundering and leaching are, in general, relatively inexpensive and efficient (30). In some cases, mixtures of two or more salts are much more effective than any one of the components alone. For example, an add-on of 60% of borax $Na_2B_4O_7.10H_2O$ is required to prevent fabric from burning. Boric acid, H_3BO_3, by itself, is ineffective as a flame retardant even in amounts that equal the weight of the fabric. However, a mixture of seven parts borax and three parts boric acid imparts flame resistance to a fabric with as little as 6½% 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 consisting of any convenient means of wetting the fabric with the solution, such as a padder or dip tank, followed by a drying on 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 or brushing, or dipping fabrics, or as a final rinse in a commercial or home laundry (31). The water-soluble flame retardants most widely used for textiles are listed in Table 1. Less commonly used are sulfamates of urea or other amides and amines; aliphatic amine phosphates, such as triethanolamine phosphate [*10017-56-8*], phosphamic acid [*2817-45-0*] (monoimido phosphoric acid), $H_2PO_3NH_2$, and its salts; and alkylamine bromides, phosphates, and borates.

Semidurable Finishes. Semidurable fire retardants are those that resist removal for one to about 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 the water-soluble flame retardants is their lack of durability. It can be overcome by precipitating inorganic oxides on the fabric; for example, $WO_3.xH_2O$ and $SnO_2.yH_2O$:

$$2\,Na_2WO_4 + SnCl_4 + (2x + y)H_2O \rightarrow 4\,NaCl + 2\,WO_3.xH_2O + SnO_2.yH_2O$$

Table 1. Water-Soluble Flame Retardants for Textiles

Component	CAS Registry Number	Formula	Composition
borax–	*[1330-43-4]*	$Na_2B_4O_7.10H_2O$	70
boric acid	*[10043-35-3]*	H_3BO_3	30
borax–			47
boric acid–			20
diammonium phosphate	*[7783-28-0]*	$(NH_4)_2HPO_4$	33
sodium phosphate dodecahydrate–	*[10101-89-0]*	$Na_3PO_4.12H_2O$	50
boric acid			50
boric acid–			50
diammonium phosphate			50
borax–			50
boric acid–			35
sodium phosphate dodecahydrate			15
ammonium sulfamate–	*[7773-06-0]*	$NH_4OSO_2NH_2$	75
diammonium phosphate			25
ammonium bromide	*[12124-97-9]*	NH_4Br	100
borax–			15
boric acid–			47
sodium phosphate–	*[7601-54-9]*	Na_3PO_4	18
sodium tungstate dihydrate	*[10213-10-2]*	$Na_2WO_4.2H_2O$	20

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

There are several methods for introducing the insoluble deposits into the fabric structure. Most generally used is 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.

Most semidurable retardants are used on cotton and are based on a combination of phosphorus and nitrogen compounds (32).

Durable Finishes. Earlier studies to produce durable flame retardants for cellulose were based on treatment with inorganic compounds containing antimony and titanium (33). Numerous patents were issued based on these types of treatments, eg, DuPont's Erifon process (34) and the Titanox FR process of the Titanium Pigment Corporation (35).

In the Erifon process titanium and antimony oxychlorides were applied from acid solution (pH 4) to fabric, which was then neutralized by passing through a solution of sodium carbonate, followed by rinsing and drying. Fabrics thus finished exhibited good flame resistance but also considerable afterglow. Some fabric characteristics were changed by this treatment. A large amount of tent fabric was treated by this type of process for the military service. However, it has now been replaced by flame retardants based on phosphorus.

The basic chemicals used in the Titanox FR process were titanium acetate chloride and antimony oxychloride. As with the Erifon process, it was difficult to process the fabric without dulling its appearance.

Excellent fire-resistant fabric was obtained by treating fabric with a suspension or emulsion of insoluble fire-retardant salts or oxides, eg, antimony oxide, with a chlorinated organic vehicle, such as chlorinated paraffin (36). Antimony oxide alone is only a poor flame retardant. When used, however, in conjunction with a chlorinated compound, which can form hydrochloric acid on heating, a very good flame retardant is produced.

The abbreviation, FWWMR, for fire, water, weather, and mildew resistance has frequently been used to describe treatment with a chlorinated organic metal oxide. A plasticizer, coloring pigments, fillers, stabilizers, or fungicides are usually 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 finish is well 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–chloride copolymers (vinylite VYHH) or PVC (37).

A flame retardant has been developed based on an oil–water emulsion containing a plasticizer (PVC latex) and antimony oxide (38). High add-ons are necessary to impart adequate flame resistance but the strength of the fabric is little affected.

Test Methods

The important test methods are listed in Table 2.

Fire Resistance. The most widely used test is the standard vertical flame test, although it is only one of the many tests in which the fabric to be tested is suspended vertically. A strip of fabric (30 cm × 6.3 cm) is suspended vertically with its lower edge hanging just 1.9 cm above the top of a bunsen or tirrell burner. The burner is adjusted to give a 3.8-cm luminous flame, extending 1.9 cm over the fabric. After an ignition time of 12 s the flame is removed and the duration of the afterglow and the length of the charred area are measured. Most of the specifications allow an afterflaming of 2 s and an average char length (10 strips) of 8.9 cm, with a maximum of 11 cm for any one strip. These values are, of course, based on weights of the fabric. This method has been incorporated into a great many specifications, including CCCT 191a and CCCD 746 (Federal), 6-345 (Army), 24-C-20 (Navy), DOC FF 3-71, DOC FF 5-74, and others.

Refinements of this method include standard draft-free cabinets, conditioning the specimens, special fabric clamps and holders, manometers to control flow of gas to the burner, and techniques for measuring char length.

Flammability. The position of a fabric usually influences its burning rate. A fabric suspended vertically and ignited on the bottom burns considerably more rapidly than one held in a horizontal position. The speed with which vertically suspended fabrics burn makes distinctions among fabrics difficult and for that reason many flammability testers mount the fabric specimen at some angle from the vertical position.

The AATCC (American Association of Textile Chemists and Colorists) or inclined flammability tester was developed after World War II and has been more widely used than any other rate-of-burning device: A strip of fabric (15.2 cm × 5 cm) is clamped in a rack inclined at 45°, and the surface of the fabric near the bottom is exposed to the flame of a microjet burner for 1 s. If the sample is ignited by this flame, the time