9

Coloration of technical textiles

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9.1 Introduction

Technical textiles are used in a very wide variety of end-uses in which the functional performance requirements are paramount. Thus, technical textiles must possess the requisite physical and mechanical properties to maintain the structural integrity throughout all the manufacturing and fabrication processes and during the service life of the material. For some end-uses, therefore, coloration is not strictly necessary because the aesthetic properties of the technical textile, for example colour and pattern, and also lustre, texture, handle and drape, may not always be required to appeal to the visual and tactile senses of the customer.

Coloration of technical textiles by dyeing or printing is primarily intended for aesthetic reasons but also provides a ready means of identifying different qualities or fineness of the materials. For example, the fineness of a surgical suture and its visibility at the implant site are easily identified by colour. High visibility clothing and camouflage printing clearly provide the extreme ends of the coloration spectrum for technical textiles.

Coloration also introduces other functional properties distinct from the aesthetic appeal of colour. Colorants can hide fibre yellowing and aid fibre protection against weathering, both factors of importance where the physical properties of the technical textile must be maintained over a long service life under adverse end-use conditions.[1] Heat absorption is also increased where black materials are exposed to sunlight, an important factor for baling materials for agriculture.

9.2 Objectives of coloration

The objectives of coloration treatments are first to produce the desired colour in dyeing and colours in the coloured design image in printing on the technical textile.[2] Second, coloration treatments are to ensure that the necessary colour fastness requirements for the end-use are achieved. Third, the whole operation should be

carried out at the lowest cost commensurate with obtaining the desired technical performance. After dyeing, the levelness and uniformity of colour across the width and along the length of a technical textile fabric must be within the defined colour tolerances agreed between the dyer and the customer prior to coloration. Preservation of the original appearance and quality of the technical textile prior to coloration is also essential in order to ensure that the technical textile is of marketable quality.

9.3   Coloration of technical textiles

Coloration involves the application of colorants to the technical textile and is a complex field because of the variety of fibres, filaments, yarns, fabrics and other materials requiring coloration and the diverse nature of the end-use and performance requirements. Coloration may be carried out by dyeing the materials to a uniform colour, or by printing to impart a design or motif to the technical textile. Fibres, yarns and fabrics may also be multicoloured by specialised dyeing techniques, for example space dyeing, or by weaving or knitting different coloured yarns.[3]

The colorants used may be either water-soluble (or sparingly water-soluble) dyes, or alternatively water-insoluble pigments.[4] Most dyes are applied to technical textiles in an aqueous medium in dyeing and in printing, although selected disperse dyes may also be dyed in supercritical fluid carbon dioxide (above the critical point under very high pressure) for a few specialised end-uses, for example polyester sewing threads.[5] By contrast, pigments are either physically entrapped within the filaments during synthetic fibre extrusion, for example by mass pigmentation, to give a spun-dyed fibre,[6] or alternatively adhered to technical textiles in pigment printing through the use of an adhesive binder.[7]

Dyeing is normally carried out on textile materials from which surface impurities, for example fibre lubricants, spin finishes, sizes, particulate dirt or natural colouring matters and so on, have been removed by appropriate pretreatments (e.g. by desizing and scouring), and to which a stable whiteness has been imparted by chemical bleaching.[8] However, many synthetic fibres do not normally require chemical bleaching prior to coloration because the fibres may be whitened by incorporation of a fluorescent brightening agent during fibre manufacture.

Printing may be carried out mainly on technical fabrics that may be in their natural state, or chemically bleached, or whitened with a fluorescent brightening agent, or after tinting or dyeing. Conventional dyeing and particularly printing are most conveniently and economically carried out on fabrics, which also allow greater flexibility through the selection of colours late in the technical textile production sequence to meet the varying market requirements.

9.3.1   Dyes
The dyes used commercially to dye technical textiles may be selected from the very wide range of synthetic organic colorants, based upon aromatic compounds derived from petroleum.[4] Dyes are conjugated organic structures containing an alternating system of single and double bonds within the molecule which impart the ability to absorb certain wavelengths of visible light, so that the remaining light scattered by the dyed technical textile is perceived as coloured.[4,9]

The dye structure must contain a chromophore, a chemical group that confers upon a substance the potential to becoming coloured, for example nitro, nitroso, azo and carbonyl groups. To become a useful dye, however, the molecule should contain other chemical groups such as amino, substituted amino, hydroxyl, sulphonic or carboxyl groups which are called auxochromes. These generally modify or intensify the colour, render the dye soluble in water and assist in conferring substantivity of the dye for the fibre.[4,9] High substantivity aids a high degree of dye exhaustion on to the fibres during exhaust dyeing when dyes are progressively and preferentially adsorbed by the fibres from the dyebath to give coloured technical textile materials. High dye-fibre substantivity also generally confers high colour fastness during end-use, for example high colour fastness when exposed to washing and light.

Manufactured dyestuffs are formulated colorants typically containing only 30–40% active colorant. The rest of the dyestuff formulation consists of diluents to dilute the colour strength, electrolytes to improve the dye exhaustion on the fibre, and dispersing agents to facilitate dispersing of the dye in the dyebath.[10] To avoid dusting dyestuffs into the air during weighing and dispensing, granular, grain or pearl forms of dyestuffs are used. Antidusting agents are added to powdered dyestuffs for the same reason. Water-soluble dyes can be produced as true liquid dyestuffs (e.g. basic dyes), but liquid dispersions of disperse and vat dyestuffs are also produced. The latter may contain a viscosity modifier to minimise sedimentation/settling of the dye particles during storage and must be stirred prior to use. Liquid dyestuffs are preferred for continuous dyeing and for printing because of their convenience for use on automated weighing, metering and dispensing systems.

Commercial dyestuffs are subjected to stringent quality control procedures for hue and colour strength, average particle size and particle size distribution, and are dried to a uniform moisture content and packaged in drums or plastic containers suitable for transportation, storage and dispensing.[10,11] Resealable packaging may be used to prevent the ingress of moisture from the atmosphere, and in many colour kitchens the ambient temperature and relative humidity are controlled in order to maintain reproducibility in weighing. Some dyestuffs are mixtures formulated for specific shades such as black, or contain dyes from different application classes suitable for dyeing specific fibre blends, for example 65/35 polyester/cellulosic fibre blends.[12]

9.3.2   Pigments

Pigments are synthetic organic or inorganic compounds that are insoluble in water, although some are soluble in organic solvents.[4,9] The pigment particles are ground down to a fine state of subdivision (0.5–2 μm) and stabilised for use by the addition of dispersing agents and stabilisers. Both powder and liquid (i.e. dispersions of) pigments are used for the coloration of technical textiles, and the pigment finish must be compatible with the application conditions used in mass pigmentation of manufactured fibres or in pigment printing of technical textile fabrics.[13,14]

9.3.3   Fluorescent brightening agents

These are organic compounds that absorb some of the ultraviolet radiation in sunlight or other sources of illumination and re-emit in the longer wavelength

Table 9.1   Percentage distribution of each chemical class between major application ranges

Chemical class	Distribution between application ranges (%)								
	Acid	Basic	Direct	Disperse	Mordant	Pigment	Reactive	Solvent	Vat
Unmetallised azo	20	5	30	12	12	6	10	5	
Metal complex azo	65		10				12	13	
Thiazole		5	95						
Stilbene			98					2	
Anthraquinone	15	2		25	3	4	6	9	36
Indigoid	2					17			81
Quinophthalone	30	20		40				10	
Aminoketone	11			40	8		3	8	30
Phthalocyanine	14	4	8		4	9	43	15	3
Formazan	70						30		
Methine		71		23		1		5	
Nitro, nitroso	31	2		48	2	5		12	
Triarylmethane	35	22	1	1	24	5		12	
Xanthene	33	16			9	2	2	38	
Acridine		92		4				4	
Azine	39	39				3		19	
Oxazine		22	17	2	40	9	10		
Thiazine		55			10			10	25

Source: see ref 4.

blue–violet region of the visible spectrum.[15–17] Such compounds can be applied to technical textiles either by mass pigmentation (in manufactured fibres) or via machinery used for conventional dyeing of all types of materials, and add brightness to the whiteness obtained from chemical bleaching of the textile.

9.3.4   Range of colorants available

The Colour Index International is the primary source of information on colorants and lists the majority of commercial dyestuffs and pigments (both past and present) although the situation continually changes as the manufacture of some colorants ceases, to be replaced by new products.[18] The wide variety of colorants available is based upon many chemical types that make up the major application groups of colorants. The percentage distribution of each chemical class between major application ranges is illustrated in Table 9.1, based upon all the dyes listed where the chemical class is known, but also including products which are no longer used commercially.[4] Azo colorants make up almost two-thirds of the organic colorants listed in the Colour Index International. Anthraquinones (15%), triarylmethanes (3%) and phthalocyanines (2%) are also of major importance. Where the structure of the colorant is known, it is assigned a specific CI (Colour Index) chemical constitution number, although for many new commercial products the structure is undisclosed.

In the Colour Index International dyes are classified by application class, by colour and by number, for example CI Acid Blue 45. The commercial name of the dyestuff will, however, vary according to the dye maker, and dyestuffs, being formulated products, although nominally the same CI number, may vary in active colorant content and in the nature of the additives incorporated within the formulation.[19] Metamerism may also be observed on the dyed textile, that is a difference in colour is observed when two colours are viewed under different illumination conditions, even when using dyestuffs that nominally possess the same colour index number. The Colour Index International is available in book form and on CD–ROM.

Table 9.2   Major classes of dyes and the fibres to which they are applied

Dye class	Major fibre type
Acid (including 1:1 and 1:2 metal complex dyes)	Wool, silk, polyamides (nylon 6, nylon 6.6)
Mordant (chrome)	Wool
Azoic	Cellulosic fibres (cotton)
Direct	Cellulosic fibres (cotton, viscose, polynosic, HWM, modal, cuprammonium, lyocell fibres), linen, ramie, jute and other lignocellulosic fibres
Reactive	Cellulosic fibres (cotton, viscose, polynosic, HWM, modal, cuprammonium, lyocell, linen, ramie, jute), protein (wool, silk)
Sulphur	Cellulosic (cotton)
Vat	Cellulosic fibres (cotton, linen)
Basic	Acrylic, modacrylic, aramid
Disperse	Polyester, cellulose triacetate, secondary cellulose acetate, polyamide, acrylic, modacrylic, polypropylene, aramid

HWM = high wet modulus.

The major classes of dyes and the fibres to which they are applied are illustrated in Table 9.2. The type of dyestuff used for dyeing technical textiles depends upon the fibre(s) present in the material, the required colour and the depth of colour, the ease of dyeing by the intended application method and the colour fastness performance required for the end-use. Some dyestuff classes will dye a number of different fibres, but in practice one fibre will predominate. For example, disperse dyes are mainly used to dye polyester fibres, although they can also be applied to nylon 6, nylon 6.6, acrylic, modacrylic, secondary cellulose acetate, cellulose triacetate and polypropylene fibres, but with limitations upon the depth of colour and the colour fastness that can be attained.[20]

There are, however, many types of manufactured fibres, particularly synthetic fibres, which are currently virtually impossible to dye with conventional dyestuffs using normal dye application methods. This is because filaments which are designed for high strength end-uses are often composed of polymer repeat units that do not contain functional groups that could act as dyesites (e.g. polyethylene, polypropylene, polytetrafluoroethylene), and/or may be highly drawn to produce a highly oriented fibre with a high crystallinity.[21]

Because dyes are considered to diffuse in monomolecular form into the fibre only through non-crystalline regions, or regions of low order (i.e. high disorder), it follows that highly oriented fibres such as meta-aramid, para-aramid, and high strength polyethylene fibres, are extremely difficult to dye. In some cases, specialised dyeing techniques utilising fibre plasticising agents ('carriers') to lower the glass transition temperature (T_g) of the fibre (i.e. the temperature at which increased polymer segmental motion opens up the fibre structure) together with selected dyes may be employed to speed up the diffusion of dyes into the fibres, but the colour depth may be restricted to pale-medium depths.[21–23] In addition, or alternatively, resort may be made to high temperature dyeing in pressurised dyeing machinery at temperatures in the range 130–140 °C for the same purpose.

However, for many high strength fibres, mass pigmentation offers a more satisfactory production route to coloured fibres, provided that the introduction of the pigments does not significantly impair the high strength properties.[6] Some fibres such as carbon fibres and partially oxidised polyacrylonitrile fibres cannot be dyed, simply because they are already black as a result of the fibre manufacturing process. However, contrasting colours may be printed on such fibres using pigment printing methods, or by blending with other dyed fibres.

Microfibres are generally defined as fibres or filaments of linear density less than 1 dtex.[24] Such silk-like fibres pose considerable difficulties for level dyeing of medium to heavy depths of colour. The high surface area per unit volume of microfibres increases the light scattering, necessitating the use of greater amounts of dye to achieve the same colour depth as on coarser fibres. The use of bright trilobal filaments, or the incorporation of titanium dioxide delustring agents within the microfibres increases the light scattering, making the difference even more noticeable.[25]

9.4   Dye classes and pigments

9.4.1   Acid dyes

Acid dyes are anionic dyes characterised by possessing substantivity for protein fibres such as wool and silk, and also polyamide (e.g. nylon 6 and nylon 6.6) fibres, or any other fibres that contain basic groups. Acid dyes are normally applied from an acid or neutral dyebath.[24]

As the size of the acid dye molecule generally increases from level dyeing (or equalising) acid dyes to fast acid, half-milling or perspiration-fast dyes to acid milling dyes and thence to supermilling acid dyes, the colour fastness to washing increases because of the increasing strength of the non-polar forces of attraction for the fibre.[26] 1:1 Metal complex and 1:2 metal complex dyes also behave like acid dyes from the viewpoint of application to the fibre, and possess good colour fastness to washing and light. Level dyeing acid dyes yield bright colours, while the larger sized milling acid and supermilling acid dyes are progressively duller. 1:1 and 1:2 metal complex dyes also lack brightness, but can provide good colour fastness performance.[27]

Acid dyes contain acidic groups, usually sulphonate groups, either as $—SO_3Na$ or $—SO_3H$ groups, although carboxyl groups ($—COOH$) can sometimes be incorporated. Wool, silk and polyamide fibres contain amino groups ($—NH_2$) which in an acid dyebath are protonated to yield basic dyesites ($—NH_3^+$). The acid dye anion $D.SO_3^-$, where D is the dye molecule, is thus substantive to the fibre and is adsorbed, forming an ionic linkage, a salt link, with the fibre dyesite. Monosulphonated acid dyes can be adsorbed to a greater extent than di-, tri-, and tetrasulphonated acid dyes because the number of basic dyesites in the fibres is limited by the fibre structure. Thus, the colour build-up is generally greatest with monosulphonated dyes on wool. However, the dyestuff solubility in water increases with the degree of dye sulphonation.

Dyed wool fibre quality is improved by pretreatment before dyeing with Valsol LTA-N(TM), an auxiliary which extracts lipids from the cell membrane complex of wool, thereby speeding up the intercellular diffusion of dyes.[28] In this Sirolan (TM)

LTD (low temperature dyeing) process, wool may be dyed for the conventional time at a lower temperature, or for a shorter time at the boil, decreasing fibre degradation in the dyebath.

Levelling agents may be used to promote level dyeing of acid dyes on wool and other fibres.[29] Anionic levelling agents enter the fibre first and interact with basic dyesites, restricting dye uptake. Amphoteric levelling agents, which contain both a positive and a negative charge, block the basic dyesites in the fibre but also complex with the acid dyes in the dyebath, slowing down the rate at which the dyes exhaust on to the fibres. As the dyebath temperature is increased, the anionic (or amphoteric) levelling agent desorbs from the fibres, allowing the dye anions to diffuse and fix within the fibre. In addition, as the dyebath temperature is raised, the dye/amphoteric levelling agent complex breaks down, releasing dye anions for diffusion inside the fibre. The dyes are thus gradually adsorbed by the wool as the dyebath temperature is increased.

In the iso-ionic region (pH 4–5), the cystine (disulphide) crosslinks in the wool are reinforced by salt links formed between charged carboxyl and amino groups in opposing amino acid residues in adjacent protein chain molecules within the wool fibre. This temporarily strengthens the wool and the abrasion resistance of the dyed fabric is improved. Fibre yellowing is decreased and brighter colours may be dyed.[30]

The build-up of acid dyes on silk and polyamide fibres is limited by the fewer number of fibre dyesites compared with wool. Acid dyes are attracted to the amine end groups (AEG) in polyamide fibres such as nylon 6 and nylon 6.6. Nylon 6 has a more open physicochemical structure and a lower glass transition temperature (T_g) compared with nylon 6.6. Thus, acid dyes diffuse more readily into nylon 6 but the colour fastness to washing of a similar dye on nylon 6.6 will generally be superior because of the more compact fibre structure.[31] False twist texturing processes, which use contact heating of the yarns, open up the fibre structure and may modify some of the fibre cross-sections which were in contact with the heater, resulting in a slightly lower colour fastness to washing.

Chemical variations due to changes in the AEG of nylon fibres, can give rise to dyeability variations with acid dyes, a problem often referred to as barré or barriness.[31] Physical variations caused by temperature and/or tension differences in nylon fibres can similarly lead to differences in the uptake of disperse or 1:2 disperse premetallised dyes. Physical variations can be minimised by dyeing at higher temperatures (e.g. up to 120 °C) with nylon 6.6, or prolonging the dyeing time. High temperature dyeing is used with the larger 1:2 metal complex acid dyes in order to achieve better fibre levelling and also fibre penetration, which leads to improved colour fastness to washing. Acid dyes can also be printed on to wool (which has been pretreated by chlorination), degummed silk, polyamide and other fibres using conventional print thickeners in a print-dry-steam fixation-wash off and dry process.[32]

Colour fastness to washing with acid dyes on nylon fibres, especially nylon microfibres, is improved by after-treatments such as syntanning, that is, the adsorption of a sulphonated synthetic tanning agent that provides a physical barrier to desorption by blocking the fibre pore structure in the fibre surface regions and by providing electrostatic (ionic) repulsion to dye desorption.[31] Combining an appropriate syntan with a fluorochemical treatment can provide, in addition, stainblocking properties.[33] However, syntan treatments degrade during high temperature or steaming treatments and tend to yellow the dyed fabric, dulling the colour.

9.4.2   Mordant dyes

Chrome dyes are the only type of mordant dye of any commercial significance.[26] These are used in exhaust dyeing to dye wool or occasionally polyamide fibres to deep dull colours of high colour fastness to wet treatments and light. The fibres are usually dyed by the afterchrome method in which a chrome dye (similar to an acid dye) is dyed on to the fibre and then the dyed fibre is given a treatment at pH 3.5 in a second bath containing sodium or potassium dichromate.[34] The absorption of dichromate ions leads to the formation of a 1:1 and/or 1:2 chromium metal complex dye inside the fibre, which can lead to some problems in batch-to-batch reproducibility of shade, particularly if the pH control in chroming is variable. Low chrome dyeing procedures can promote exhaustion of the chromium on to the fibres, decreasing environmental pollution from the waste water from dyeing.[26,34] A major disadvantage of the afterchrome method is that the final colour is not developed until the chroming stage which can give difficulties in shade matching. Ammonia aftertreatment can improve the colour fastness to washing.

9.4.3   Basic dyes

Basic dyes are cationic dyes characterised by their substantivity for standard acrylic, modacrylic, basic-dyeable polyester and basic-dyeable nylon fibres.[24] Basic dyes can be applied to protein and other fibres, for example secondary cellulose acetate, but the light fastness of basic dyes on hydrophilic fibres is poor.[35] The major outlets for basic dyes are acrylic and modacrylic fibres, on which basic dyes can impart bright colours with considerable brilliance and fluorescence. The ionic attraction between the basic dye and the sulphonic acid dyesites in acrylic fibres is strong, which yields high colour fastness to washing. The close-packed physicochemical nature of acrylic fibres and the strong dye-fibre bonding can result in poor migration and levelling properties during dye application, but impart very high colour fastness to light.[21,35]

Acrylic fibres vary widely in their dyeability because of the different amounts of different co-monomers used with poly(acrylonitrile) that modify the fibre glass transition temperature. This may range from 70–95 °C according to the source of the acrylic fibre manufacturer.[36] Cationic retarders are widely used on acrylic and modacrylic fibres to promote level dyeing and the basic dyes used should preferably be selected with the same compatibility value. The compatibility value may range from 5 (slow diffusing) down to 1 (rapid diffusing). A compatibility value of 3 has been recommended for package dyeing, but for printing, compatibility values are of much less importance. Print fixation is by the print-dry-steam-wash off and dry process, although wet transfer printing techniques are also possible using selected dyes.[35]

The acidic dyesites in acrylic fibres become much more accessible over a narrow band of temperatures in the glass transition temperature range. Therefore, even when using cationic retarders, which initially adsorb on to the fibre blocking the dyesites, the dyebath temperature must be raised slowly through this temperature range to allow the cationic retarder to desorb slowly and allow the basic dye to be adsorbed uniformly.[35,36] Alternatively, constant temperature dyeing methods may be used in exhaust dyeing. Continuous pad-steam-wash off and dry methods can also be used for dyeing acrylic fabrics.

The basic dye uptake is limited by the number of acidic dyesites in the fibre, but approximately 95% of all colours on acrylic fibres are dyed using basic dyes.

However, where very pale colours are to be dyed it is common to use disperse dyes, which have superior migration and levelling properties, in order to attain a level dyeing, because the strong dye-fibre bonding renders this very difficult to achieve using basic dyes.[35] The build-up of disperse dyes on acrylic fibres is limited and the colour fastness to washing and light are generally lower than for basic dyes. The colour fastness of basic dyes on acrylic fibres is superior to similar dyeings on modacrylic fibres. Some modacrylic fibres are prone to delustring during dyeing and may require relustring by boiling for 30 min in a high concentration of electrolyte (e.g. 50–200 g l^{-1} sodium chloride) or by dry-heat or treatment in saturated steam.[36]

9.4.4   Azoic colouring matters

Azoic colouring matters are formed inside the fibre (usually cellulosic fibres) generally by adsorption of an aromatic hydroxyl-containing compound, such as a naphthol or naphtholate (azoic coupling component) followed by coupling with a stabilised aromatic diazonium compound (the azoic diazo component also termed fast base or salt) to form a coloured insoluble azo compound.[2,37] The application method has to be carried out with care and the final colour is only obtained after soaping off to remove any traces of the azoic dye on the fibre surface that would give inferior colour fastness to washing and rubbing (crocking). Although they are economical for the production of red and black, the colour range is now more limited as some diazo components based upon certain aromatic amines have been withdrawn because of their possible carcinogenic nature. Precise colour matching with such a complex two-bath procedure can also give problems in practice.

9.4.5   Direct dyes

Direct dyes were the first class of synthetic dyes to dye cotton directly without the use of a mordant. Direct dyes are sulphonated bisazo, trisazo or polyazo dyes and are anionic dyes which are substantive to cellulosic fibres when applied from an aqueous bath containing an electrolyte.[2,38] Direct dyes based on stilbene, copper-complex azo, oxazine, thiazole and phthalocyanine structures are also used. Less bright in colour than acid or basic dyes, the brightness diminishes with the molecular complexity of the dye. Phthalocyanine dyes are used for very bright blue and turquoise-blue colours of good colour fastness to light, and copper-complex azo dyes also exhibit good fastness to light, although these dyes yield relatively dull colours.

   Electrolyte, in the form of sodium sulphate, is usually added into the dyebath to overcome the negative charge on the cellulosic fibre surface which otherwise would repel the approach of the direct dye anions. The sodium cations from the electrolyte neutralise the negative charge at the fibre surface, allowing the dye anions to be adsorbed and retained within the fibre.[38]

   Coulombic attraction, hydrogen bonding and non-polar van der Waals forces may operate depending upon the specific direct dye and the fibre structure. Direct dyes are normally linear and planar molecules allowing multipoint attachment to cellulose chain molecules, but the forces of attraction between dye and fibre are relatively weak when the dyed fibre is immersed in water.[38,39] Thus, the colour fastness to washing is moderate to poor, but the colour fastness to light may vary from excellent to poor depending on the molecular structure.

   The colour fastness to washing can be improved by aftertreatment of the dyed

fibre, originally by the use of after-coppering (i.e. treatment with copper sulphate to form a metal-complex direct dye) or by diazotisation and development. Both approaches lead to a pronounced shade change and copper in the waste water from dyeing is environmentally undesirable. Modern aftertreatments make use of cationic fixatives that may simply complex with the anionic dye, and/or form a metal complex and/or react with the cellulose fibre hydroxyl groups to form strong covalent bonds. Improvement in colour fastness to washing may be accompanied by some diminution in colour fastness to light.[38,40]

Direct dyes may be used on all cellulosic fibres and selected dyes may also be used to dye wool, silk and nylon fibres in the manner of acid dyes. Addition of electrolyte into the dyebath increases dye aggregation in the dyebath. As the dyeing temperature is increased, the dye aggregation decreases, releasing individual direct dye anions for diffusion and adsorption inside the fibre. Direct dyes have been separated into three classes, Class A – salt-controllable, Class B – temperature-controllable, and Class C – both salt- and temperature-controllable. It is normal to select compatible dyes from within the same class, but selected dyes from Class A and B, and Class B and C may be dyed together in the same dyebath in exhaust dyeing. Direct dyes may also be applied to cellulosic fabrics by continuous pad-steam-wash off and dry methods.[2,38]

The depth of colour obtained using direct dyes is deeper on viscose, lyocell and high wet modulus fibres and on mercerised cotton compared with bleached cotton, and careful dye selection is required to produce level, solid colours when dyeing blends of these fibres.

9.4.6   Reactive dyes

Reactive dyes, sometimes termed fibre-reactive dyes, are a very important class of dyes for dyeing cellulosic fibres[41] and are also used to dye protein fibres such as wool[42] or silk.[43] Although relatively expensive they provide a wide colour gamut of bright colours with very good colour fastness to washing. This is because during dye fixation, usually conducted under alkaline conditions, strong covalent bonds are formed between the dye and the fibre.[2,44] Reactive dyes may react by substitution (e.g. monochlorotriazinyl and dichlorotriazinyl dyes) or by addition (e.g. vinylsulphone dyes).

Typical ranges of reactive dyes and their respective reactive groups are illustrated in Table 9.3. Recent developments have led to the introduction of homobifunctional reactive dyes (e.g. two monochlorotriazine groups) and heterobifunctional reactive dyes (e.g. using monochlorotriazine plus vinyl sulphone) in an attempt to increase the dye fixation on the fibre under alkaline conditions from 50–70% with one reactive group, to 80–95% with two reactive groups. Dye application methods on fabrics include exhaust dyeing, cold pad-batch-wash off or continuous pad-steam-wash off and dry methods. Fixation by dry heat, saturated steam or superheated steam may also be used according to the type of reactive dye employed.[41]

Reactive dyes hydrolyse in contact with water and alkali, and during dyeing some hydrolysed reactive dye is adsorbed by the fibre because it behaves like a substantive direct dye, but with lower colour fastness to washing than the reactive dye that is covalently bonded. Thus, the dyeing stage must always be followed by an extended washing-off treatment to remove hydrolysed reactive dye.[41,45] Provided that the residual hydrolysed reactive dye left within the cellulosic fibre after dyeing or print-

Table 9.3 Important reactive dye systems

System	Typical brand name
Monofunctional	
Dichlorotriazine	Procion MX (BASF)
Aminochlorotriazine	Procion H (BASF)
Aminofluorotriazine	Cibacron F (Ciba)
Trichloropyrimidine	Drimarene X (Clariant)
Chlorodifluoropyrimidine	Drimarene K (Clariant)
Dichloroquinoxaline	Levafix E (DyStar)
Sulphatoethylsulphone	Remazol (DyStar)
Sulphatoethylsulphonamide	Remazol D (DyStar)
Bifunctional	
Bis(aminochlorotriazine)	Procion H-E (BASF)
Bis(aminonicotinotriazine)	Kayacelon React (Nippon Kayaku)
Aminochlorotriazine–sulphatoethylsulphone	Sumifix Supra (Sumitomo)
Aminofluorotriazine–sulphatoethylsulphone	Cibacron C (Ciba)

Source: see ref 41.

ing is at a concentration $<0.1\,g\,m^{-2}$, the best colour fastness to washing will be obtained.[46] If the concentration of hydrolysed reactive dye in the final hot wash bath is $<0.003\,g\,l^{-1}$, staining of white grounds in the fabric will be prevented.[46]

Generally reactive dyes are produced in granular form, but vinyl sulphone dyes are also available as liquids, which are more convenient for use in continuous dyeing and printing. Reactive dyes are sulphonated and highly water soluble and are exhausted on to the fibre using electrolyte (e.g. in the manner of direct dyes) and fixed using an appropriate alkali. The high water solubility creates an environmental problem in waste water treatment plants because generally only 0–30% of the hydrolysed reactive dye is removed by such treatment.[47] Low salt reactive dyes have also been introduced to decrease dyeing costs and to avoid corrosion problems in concrete waste water pipework networks caused by high concentrations of sulphate anions.

9.4.7 Sulphur dyes

Sulphur dyes are chemically complex and are prepared by heating various aromatic diamines, nitrophenols, and so on with sulphur and sodium sulphide. Sulphur dyes are produced in pigment form without substantivity for cellulose.[2] Treatment with a reducing agent (e.g. sodium sulphide or sodium hydrosulphide) in an alkaline dyebath converts the sulphur dye into an alkali-soluble reduced (leuco) form with substantivity for cellulosic fibres. Once absorbed within the fibre, the dye is then oxidised, usually with hydrogen peroxide, back to the insoluble pigment form. Soaping off after dyeing is important to ensure the maximum colour fastness to washing and rubbing is obtained.[2,48]

Sulphur black and navy are the major dyestuffs used and the colour gamut is limited to dull colours of moderate colour fastness to washing and light. The colour fastness to chlorine and to bleach fading is poor when using multiple wash cycles with detergents containing low temperature bleach activators such as TAED (tetraacetylethylenediamine, UK) or SNOBS (sodium nonanoyloxyben-zenesulphonate, USA).[49] Sulphur dyes cost less than many other dyes but the waste

water from dyeing may require specialised treatment before release to a conventional waste water treatment plant.

9.4.8 Vat dyes

Vat dyes are water-insoluble, but contain two or more keto groups ($>C=O$) separated by a conjugated system of double bonds that are converted into alkali-soluble enolate leuco compounds ($>C—O^-$) by alkaline reduction, a process called vatting.[2,50] The dye application method involves three stages, namely, alkaline reduction and dissolution of the vat dye (normally using sodium hydroxide and sodium dithionite (hydrosulphite)), absorption of the substantive leuco compound by the fibre, aided by electrolyte (e.g. sodium sulphate and wetting, dispersing and levelling agent), followed by regeneration of the vat dye inside the fibre by oxidation in air or hydrogen peroxide. The dyed fibre is then thoroughly soaped off (washed with soap or special detergent at a high temperature) to remove any surface dye and to complete any dye aggregation inside the fibre in order to obtain the final colour.
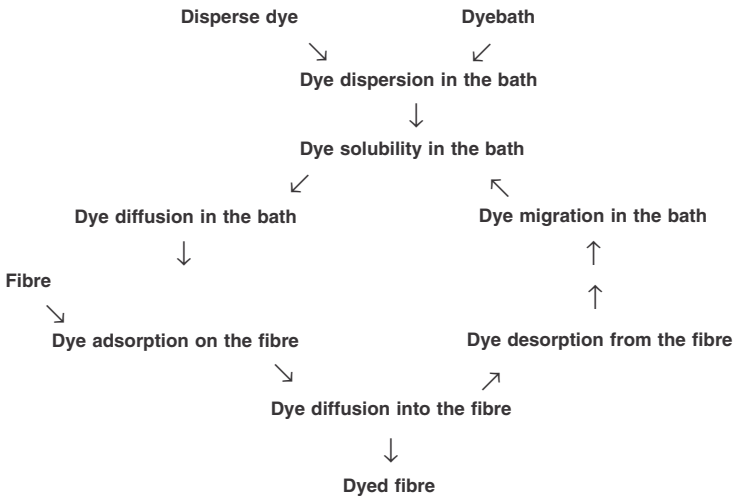
Vat dyes are based upon indanthrone, flavanthrone, pyranthrone, dibenzanthrone, acylaminoanthraquinone, carbazole, azoanthraquininone, indigoid and thioindigoid structures.[2,50] Application methods include both batch exhaust dyeing and continuous pad-steam-wash off and dry methods, and apart from sodium dithionite, formaldehydesulphoxylate or hydroxyacetone may be used for the reduction stage.[50]

Vat dyes are relatively expensive but do offer outstanding colour fastness to light and washing on cellulosic fibres. In the unreduced form some vat dyes behave like disperse dyes and can therefore be applied to polyester and polyester/cellulosic blends to achieve pale-medium colour depths. For polyester/cellulosic fabrics a pad-dry-bake-chemical pad-steam-oxidise-wash off and dry production sequence is used. For exhaust dyeing, the novel technique of electrochemical reduction dyeing has been claimed to provide a redox potential of up to –960 mV suitable for the reduction of vat dyes and also sulphur dyes. Cathodic reduction of vat dyes with the addition of a mediator (a soluble reversible redox system, e.g. an iron [II/III]–amino complex) could potentially decrease the chemical costs for reduction and lower the chemical load in the waste water by 50–75%.[51]

9.4.9 Disperse dyes

Disperse dyes are substantially water-insoluble dyes which have substantivity for one or more hydrophobic fibres (e.g. secondary cellulose acetate) and are usually applied as a fine aqueous dispersion.[2,52,53] The major chemical classes used are aminoazobenzene, anthraquinone, nitrodiphenylamine, styryl (methine), quinophthalone and benzodifuranone-based dyes. Disperse dyes are milled (ground) with a dispersing agent (e.g. polymeric forms of sodium dinaphthylmethane sulphonates) to a fine dispersion (0.5–2 µm) and may be supplied as grains, powders or liquid dispersions.

Disperse dyes are essentially nonionic dyes that are attracted to hydrophobic fibres such as conventional polyester, cellulose triacetate, secondary cellulose acetate and nylon through non-polar forces of attraction.[33,52,53] In the dyebath, some of the disperse dye particles dissolve to provide individual dye molecules that are

Disperse dye   Dyebath

         ↘   ↙

Dye dispersion in the bath

↓

Dye solubility in the bath

    ↙   ↖

Dye diffusion in the bath   Dye migration in the bath

↓   ↑

Fibre

   ↘   ↑

Dye adsorption on the fibre   Dye desorption from the fibre

       ↘   ↗

Dye diffusion into the fibre

↓

Dyed fibre

9.1 General dyeing mechanism for disperse dyes (source: see ref 35, p. 126).

small enough to diffuse into the hydrophobic fibres. The aqueous solubility of dis-
perse dyes is low, for example $0.2–100\,mg\,l^{-1}$ at 80 °C, but increases with increase in
dyebath temperature, in turn increasing the concentration of soluble dye available
for diffusion so that the dyeing rate increases.

Dispersing agents are essential because they assist in the process of decreasing
the dye particle size and enable the dye to be prepared in powder and liquid forms.[52]
In addition, the dispersing agent facilitates the reverse change from powder to
dispersion during dyebath preparation and maintains the dye particles in fine dis-
persion during dyeing. This prevents agglomeration of the dye particles in powder
form and aggregation in the dyebath. The dye solubility in the dyebath can be
increased by the use of levelling agents and carriers.

The general mechanism of dyeing with disperse dyes under exhaust dyeing con-
ditions is illustrated in Fig. 9.1. The diffusion and adsorption of dye molecules is
accompanied by desorption of some of the dye molecules from the dyed fibre back
into the dyebath, to facilitate dye migration from fibre to fibre to achieve level
dyeing.[35] The disperse dyes are considered to dye fibres via a solid solution mecha-
nism that involves no chemical change.[23] Each disperse dye dissolves in the fibre
more or less independently of any other disperse dye present. Under constant
dyebath conditions the ratio of the amount of dye on the fibre to the amount of dye
in the bath is a constant at equilibrium, which varies according to the particular dye,
but ultimately a separate different saturation level (or solubility limit) is achieved
for each dye above which no more of that dye can be taken up by the fibre. However,
most commercial dyeings are never carried out to equilibrium.

Apart from high temperature (high pressure) exhaust dyeing at 110–140 °C, dis-
perse dyes may also be exhaust dyed using carriers (e.g. fibre plasticising agents that
decrease the fibre T_g) at 100 °C.[22,52,53] This method is not very popular except where
blend dyeing is practised and where high temperature dyeing, if used, would degrade
one of the fibres. Odourless carriers are preferred, but there are problems with
carrier spotting, and carrier retention by the fibres leads to fuming of the carrier
as it is volatilized off during post-heat setting treatments, while some carriers may

potentally pose environmental pollution problems.[22] Some 50% of disperse dye consumption is used for navy and black shades, and some 70% of disperse dyes are applied to polyester and polyester/cellulose blends by exhaust dyeing.[54]

Disperse dyes may also be applied by a pad-dry-thermofix-wash-dry process in a continuous open width fabric treatment. This utilises the sublimation properties of disperse dyes, which vaporise directly from the solid state without prior melting. Polyester can be dyed at 190–220 °C by such a process, originally called the Thermosol process by DuPont.[23] Sublimation of disperse dyes is also utilised in dry-heat transfer printing,[55] but conventional print application by printing and fixing in saturated or superheated steam is also practised, followed by washing off and drying.[32]

To minimise potential problems linked to the presence of disperse dyes on the fibre surface after dyeing (e.g. poor colour fastness to washing, rubbing and thermomigration), reduction clearing after dyeing with sodium hydroxide, sodium dithionite (hydrosulphite) and a surfactant followed by hot washing is normally practised, particularly with medium-heavy depths of colour.[52] However, some classes of disperse dyes (e.g. di-ester and thiophene azo dyes) are clearable by alkali alone.[56]

9.4.10   Pigment formulations

The range of chemical compounds used as pigments varies widely and includes both inorganic pigments such as titanium dioxide, and the oxides of antimony, iron and zinc, as well as carbon.[57] Organic pigments may be based upon a very wide variety of chemical structures, for example azo, anthraquinone, dioxazine, indanthrone, isoindolinone, perylene, quinacridone, copper phthalocyanine, heterocyclic nickel complexes and many others (see, for example, Table 9.4).[58] The general considerations relating to the manufacture of pigments and their application to technical textiles are separately discussed in Section 9.3.2 (manufacture), Sections 9.5.1–9.5.3 (mass pigmentation), Section 9.5.5 (coating) and Section 9.9.1 (printing). The finishing of pigment formulations is technically complex and strict quality control is required to ensure satisfactory application and performance of the pigment in practice.

9.5   Mass coloration of manufactured fibres

9.5.1   Dyes and pigments for mass coloration

In mass coloration, dyes or pigments are incorporated into the polymer melt (in the case of polyamide, polyester and polypropylene) or into the polymer solution (in the case of viscose, secondary cellulose acetate, cellulose triacetate and acrylic or modacrylic fibres) during fibre manufacture.[6,13] The dyes that are being used pass into a dissolved phase on incorporation into the polymer melt or solution, but pigments remain as finely dispersed particles. In the main, mass pigmentation is much more widely used for colouring manufactured fibres (both synthetic and regenerated fibres)[6,13] except on wet-spun acrylic fibres, where gel dyeing is used (see Section 9.5.4).[35,59] However, mass pigmentation can be used for dry-spun acrylic polymers which are dissolved in a solvent (e.g. dimethyl formamide) and spun into hot air.

Technical criteria that are important for mass coloration include:[13]

Table 9.4 High performance pigments for polypropylene fibres

CI generic name	CI number	Chemical class
CI Pigment Yellow 93	20710	Azo condensation
Yellow 95	20034	Azo condensation
Yellow 109	56284	Isoindolinone
Yellow 110	56280	Isoindolinone
Yellow 155	Not known	Azo condensation
Yellow 181	11777	Monoazo
Yellow 182	Not known	Heterocyclic monoazo
Orange 61	11265	Isoindolinone
Red 122	73915	Quinacridone
Red 144	20735	Azo condensation
Red 149	71137	Perylene
Red 166	20730	Azo condensation
Red 177	65300	Anthraquinone
Red 202	Not known	Quinacridone
Red 214	Not known	Azo condensation
Red 242	20067	Azo condensation
Red 257	Not known	Heterocyclic nickel complex
Violet 19	73900	Quinacridone
Violet 23	51319	Dioxazine
Violet 37	51345	Dioxazine
Blue 15:3	74160	Copper phthalocyanine
Blue 60	69800	Indanthrone
Green 7	74260	Copper phthalocyanine

CI denotes Colour Index. Source: see ref 58.

- pigment particle size and particle size distribution, both in the spinning mass and in the filament
- pigment preparations
- solubility of the colorant in the spinning mass
- colour fastness properties
- ability to remain stable under the mass processing conditions of the polymer.

Fine pigment particles ($<1\,\mu m$) are required because coarse particles would interfere with the filterability of polymer solutions or melts and could impair the tensile strength of fibres, the diameter of which normally lies in the range $16–45\,\mu m$. The pigments used must have good resistance to organic solvents and good heat stability for use in fibre manufacture.

Products suitable for the bath dyeing and mass coloration of manufactured fibres are illustrated in Table 9.5.[13]

9.5.2   Mass coloration methods

There are four main methods of incorporating colorants into manufactured fibres, which depend upon the specific fibre production process.[6,13] These are:

- batch process
- injection process
- chip blending
- chip dyeing.

Table 9.5   Products for the bath dyeing and mass coloration of manufactured fibres

Fibre	Bath dyes	Solvent dyes and pigments for mass coloration
Viscose	Direct	Aqueous pigment pastes
	Vat	
	Reactive	
Acetate	Disperse	Acetone-soluble dyes
		Pigment dispersions in acetate
Acrylic	Disperse	Pigment dispersions in polyacrylonitrile
	Basic	
Polyamide	Disperse	Aqueous dyes
	Acid	Polymer-soluble dyes
	Metal complex	
Polyester	Disperse	Polymer-soluble dyes
		Pigment dispersions in polyester
Polypropylene	Acid chelatable	Pigment dispersions in various carriers

Source: see ref 13.

Pigment preparations or solvent dyes may be used in the batch method in which the whole of the spinning mass is coloured, the colorant concentration being equal to that in the coloured filament after extrusion. In the injection process, a coloured concentrate is continuously metered into the spinning mass which is then extruded. Chip blending is suitable only for melt coloration, for example for polyamide, polyester and polypropylene. Polymer chips are homogeneously mixed with the colour concentrate prior to extrusion. Chip dyeing is a more specialised technique used with nylon 6. The polymer chips are precoloured with polymer-soluble dyes and then melt spun.[13]

Mass pigmentation is widely used as the major coloration route for polypropylene fibres.[1,6,13] The flexibility of the smaller scale nature of polypropylene fibre manufacture compared with the large continuous polymerization/extrusion processes for polyamide and polyester fibres, the lower polymer melt temperature of polypropylene and the difficulties in dyeing this hydrophobic, low linear density fibre in conventional dyeing equipment, ensure that mass pigmentation is the major coloration route. Mass coloration of many other melt-spun fibres is not economic unless large fibre weights per colour may be spun for a known end-use, because of the high costs of cleaning out the production machinery to avoid subsequent colour contamination problems. However, attempts continue to find a satisfactory conventional dyeing method for modified polypropylene fibres using exhaust dyeing or continuous dyeing techniques.[1,60]

9.5.3   Mass coloration and colour fastness properties
The colour fastness properties of manufactured fibres produced by mass dyeing, and particularly by mass pigmentation, are generally superior to those obtained on technical textiles by conventional dyeing and printing. Mass pigmentation is used where high colour fastness to light and weathering is required, for example in tenting fabrics, awnings, sun blinds, carpets, synthetic sports surfaces and so on, and where the colour can be economically produced.

The organic pigments and a few inorganic pigments used for mass pigmentation of polyester and polypropylene fibres must exhibit:[58]

- sufficient thermal stability
- colour fastness to light, adequate for the intended end-use
- no migration (no blooming or contact bleed)
- compatibility with other additives, e.g. the UV stabilisers widely used in polyolefins, with no photodegradation effects on the polymer
- no adverse effect on the mechanical properties of the fibres.

High performance organic pigments are used for brilliant colours and good overall colour fastness performance on polypropylene fibres (see Table 9.4).

Inorganic pigments such as titanium dioxide (rutile), zinc oxide, and antimony oxide are used for white, and carbon (small particle size channel black) is used for black, while some iron oxide browns are used for cost reasons. The tensile strength of mass-pigmented polypropylene fibres after 300 hours exposure in an Atlas 600 WRC accelerated light fastness testing equipment is markedly higher than the uncoloured fibre, demonstrating the protective effect of the presence of the pigments against the deleterious effects of ultraviolet radiation on the fibres.[58]

Colour retention in awning fabrics in outdoor applications is critical, and two types of climatic conditions are most critical where pigments are incorporated within acrylic and modacrylic technical textiles:[61]

- hot and dry (typically 38–49 °C, relative humidity <20%) with high average sunshine
- warm and humid (32–38 °C, relative humidity >70%) with average sunshine.

In hot and dry conditions, both the polymer and the pigment may degrade, whereas in warm and humid conditions pigment degradation is more likely. However, pigments that are degraded and fade under warm and humid conditions may often be quite stable under hot dry conditions.

9.5.4   Gel dyeing of acrylic fibres

For wet-spun acrylic fibres, the manufacture of producer-dyed fibres involves the passage of acrylic tow in the gel state (i.e. never-dried state) through a bath containing basic dyes.[35,59] This is utilised in the Courtelle Neochrome process (formerly Courtaulds, now Acordis) to produce dyed acrylic fibres from a continuous fibre production line typically at a speed of 50 m min^{-1} with economic batch weights per colour of 250–500 kg.

The liquid basic dyes are metered in at a rate appropriate to the acrylic tow mass and speed, the recipe being based on a computerised colour match prediction system allowing the selection of a very wide range of colours using a choice of the technically best dyes (i.e. easiest to apply and highest colour fastness), or lowest cost dyes, or least metameric dyes.[62] As the freshly coagulated acrylic tow passes through the dyebath, the basic dyes diffuse inside the gel-state acrylic tow in a matter of seconds. The dyed tow is then drawn and steamed, crimped and cut to the appropriate staple length for use in technical textiles, or may be used alternatively in filament form.[59]

9.5.5   Pigments for technical coated fabrics

Many technical textiles are coated in order to provide the high performance specification demanded by the end-use. The many considerations governing the use of

coloured organic pigments in coatings, and the range of pigments available, have been reviewed by Lewis.[63]

9.6   Conventional dyeing and printing of technical textiles

9.6.1   Pretreatments prior to conventional coloration

Before fibres, yarns or fabrics are to be dyed via batch exhaust or continuous pad-fixation methods, or printed by print-dry-steam-wash off-dry or pigment print-dry-cure methods, it is important to remove any natural, added, or acquired impurities from the fibres in order that these impurities do not interfere with coloration. Natural fibres such as cotton, wool, silk and flax (linen) fibres contain appreciable quantities of impurities naturally associated with the fibres, which are removed by scouring and by other treatments, for example degumming of silk to remove sericin (gum) and carbonizing of wool to remove vegetable matter (e.g. burrs, seeds etc.).[64] Particularly important for cotton and flax (linen) fibres is the efficient removal of the natural waxes present mainly on the fibre surface, in order to impart hydrophilicity to the fibres, thereby ensuring satisfactory wetting out, with high levels of uniformity and reproducibility in subsequent dyeing or printing treatments.[65]

Manufactured fibres and filaments, that is, artificial fibres from synthetic or regenerated fibres, are produced under carefully controlled conditions so that water-soluble/emulsifiable spin finishes or fibre lubricants are the main impurities, and these are simply removed by scouring.[64]

9.6.2   Singeing

For many woven or knitted technical fabrics, it may be necessary to singe the fabric surface, by passage through a gas flame or an infrared zone at open width, to remove protruding surface fibres. This gives a clear fabric surface and more uniform coloration, because a hairy fabric surface can impart a lighter coloured surface appearance (termed frostiness) after dyeing or printing. Singeing may be integrated with subsequent wet processes such as desizing.[66]

9.6.3   Desizing

The warp yarns of most woven fabrics are generally sized with a film-forming polymer that adheres fibres together with a more cohesive structure.[67] Sizes are used to increase yarn strength, decrease yarn hairiness and impart lubrication to staple fibre warp yarns in order to minimise the number of warp breaks during weaving. In the weaving of synthetic continuous filament yarns, the size provides good inter-filament binding to prevent filament snagging as well as providing yarn lubrication and antistatic performance to decrease the build-up of electrostatic charges on the yarns during high speed weaving. Yarns for knitting are not sized and a desizing treatment is not therefore required.

All sizes, together with any other sizing components, for example waxes, softeners and lubricants that may be hydrophobic, must be removed by appropriate desiz-

ing treatments.[68] Synthetic water-soluble sizes, (e.g. acrylates, polyvinyl alcohol) may be simply removed by washing, whereas natural sizes, (e.g. starch, modified starch) may require chemical degradation treatments, like oxidation, hydrolysis and so on. If considered appropriate, desizing may be integrated with scouring, or with scouring and bleaching to provide a shorter integrated treatment, while in large, vertically integrated plants, undegraded sizes that are removed in desizing may be recycled using ultrafiltration and reused.

After every desizing treatment, all traces of size or degraded size are removed by thorough washing followed by efficient mechanical removal of liquid water (e.g. hot mangling or vacuum extraction). This is followed by thermal drying on steam heated cylinders (called cylinder or can drying) or by hot air drying on a stenter (also known as a tenter, or frame (USA)).

9.6.4   Scouring
Scouring is a critical treatment for natural cellulosic fibres, for example cotton and flax (linen) and their blends with other fibres, because all traces of hydrophobic waxes (whether naturally occurring or applied during the manufacturing sequence) must be effectively removed in order to achieve satisfactory wetting in all subsequent dyeing, printing, finishing, coating, lamination and bonding operations.[65] Scouring is normally accomplished by hot alkaline treatment (e.g. sodium hydroxide) followed by a thorough hot wash off. It is also important for the removal of fatty materials from wool and any manufactured fibres using hot detergent solutions.

9.6.5   Bleaching
Fibres must be uniformly white if pale colours or bright colours are required, and hence natural fibres such as cotton, silk, wool and linen must be chemically bleached in order to achieve a satisfactory stable whiteness.[8,64] Hydrogen peroxide under controlled alkaline conditions is normally used in pad-steam-wash off, pad-batch-wash off or immersion bleaching treatments, although other oxidising agents such as peracetic acid, cold alkaline sodium hypochlorite or sodium chlorite under acidic conditions may also be used.

However, chlorine-based bleaching agents give a poor bleaching environment and chlorine is retained by the fibre, necessitating an antichlor aftertreatment with a reducing agent (e.g. sodium sulphite) followed by washing to remove any residual odour in the fabric. Retained chlorine from chlorine-based bleaches or from chlorinated water used for dyeing can give rise to shade changes when dyeing cotton with reactive dyes. Regenerated cellulosic fibres such as viscose, cuprammonium, polynosic, modal, high wet modulus and lyocell fibres are marketed by the fibre producers with a satisfactory whiteness for dyeing and printing.

9.6.6   Fluorescent brightening
If high whites are required, both natural and regenerated cellulose fibres may be chemically bleached and treated with a fluorescent brightening agent.[15,16] Fluorescent brightening agents are based upon diaminostilbene derivatives, triazoles, aminocoumarins and many other organic compounds, and are absorbed by the fibre.

Fluorescent brightening agents are organic compounds that absorb the ultraviolet radiation present in daylight and re-emit light in the blue–violet region of the visible spectrum. During the absorption and re-emission processes, some energy is lost and hence the light emitted is shifted to a longer wavelength. The effect is to add brightness to the whiteness produced by chemical bleaching. Alternatively, blue tints may be used, for example ultramarine.

9.6.7 Mercerization

Mercerization of cotton is a fibre swelling/structural relaxation treatment that may be carried out on yarns, but more usually on fabrics.[69,70] Hank or warp mercerization of yarns often creates dyeability differences because of yarn tension variations that pertain during mercerization. During mercerization in 22–27% caustic soda solution, both mature and immature cotton fibres swell so that the secondary wall thickness is increased. The fibre surface appearance and the internal structure of the fibre are modified. This improves the uniformity of fabric appearance after dyeing and there is an apparent increase in colour depth after mercerization which has been claimed to give cost savings of up to 30% on pale colours (1–2% dye owf, on weight of fabric) and even 50–70% on heavy depths when using some reactive dyes.[71,72] Dead cotton fibres (i.e. those with little or no secondary wall) are, however, not improved after mercerization.

Woven fabric mercerization is normally carried out under tension on chain or chainless fabric mercerizing ranges,[70] whereas tubular fabric mercerizing ranges are widely used for weft knitted cotton fabrics.[73] Mercerization leads to a number of changes in fibre and fabric properties:[69–73]

- a more circular fibre cross-section
- increased lustre
- increased tensile strength, a major factor for technical textile fabrics
- increased apparent colour depth after dyeing
- improved dyeability of immature cotton (greater uniformity of appearance)
- increase in fibre moisture regain
- increase in water sorption
- improved dimensional stability.

After mercerization, the structure of native cotton fibres, cellulose I, is converted into cellulose II which is the stable fibre form after drying.[72] The sorptive capacity of mercerized cotton is greater where the fabric is mercerized without tension (slack mercerizing) to give stretch properties to the fabric. An increase in drying temperature can also decrease the sorptive capacity, especially at temperatures above 80 °C.[74]

9.6.8 Anhydrous liquid ammonia treatments

This form of cotton fabric pretreatment is much less common than mercerizing and is most widely used in Japan.[72,75] Impregnation in anhydrous liquid ammonia at −38 °C in an enclosed machine followed by a swelling/relaxation stage, and removal of the ammonia by thermal drying and steaming, converts the cellulose I crystalline form back to either cellulose I or into cellulose III, depending upon the structural collapse of the fibre while the final traces of ammonia are removed in the steamer.

This ammonia-dry-steam process can be used to give better improvements in cotton fabric properties than mercerization, although the increase in colour depth after dyeing is usually somewhat lower than that achieved after mercerization. The high capital cost of the machinery for anhydrous liquid ammonia treatment and ammonia recovery, and environmental considerations, have limited the wider exploitation of this technique.

9.6.9   Heat setting

Synthetic thermoplastic fibres, yarns and fabrics may be heat set, steam set or hydro set in order to obtain satisfactory dimensional stability during subsequent hot wet treatments.[76] Fabrics may be preset prior to coloration or postset after coloration.[31] Hydrosetting in hot water is rarely carried out, but false twist textured yarn can be steam set in an autoclave using a double vacuum-steam cycle to attain satisfactory removal of air and hence uniformity of temperature in the treatment. Steam setting avoids the slight fibre yellowing that can occur in fabric form through fibre surface oxidation during hot air setting on a stenter, and the handle is softer.

Heat setting on modern stenters is often carried out by first drying and then heat setting in one passage through the stenter. The temperature and time of heat setting must be carefully monitored and controlled to ensure that consistent fabric properties are achieved. During heat setting, the segmental motion of the chain molecules of the amorphous regions of the fibre are generally increased leading to structural relaxation within the fibre structure. During cooling, the temperature is decreased below the fibre glass transition temperature (T_g) and the new fibre structure is stabilised. Because the polymer chain molecules have vibrated and moved into new equilibrium positions at a high temperature in heat setting, subsequent heat treatments at lower temperatures do not cause the heat-set fibres to relax and shrink, so that the fabric dimensional stability is high.

Presetting of fabric prior to dyeing alters the polymer chain molecular arrangement within the fibres, and hence can alter the rate of dye uptake during dyeing.[23,31,53] Process variations (e.g. temperature, time or tension differences) during heat setting may thus give rise to dyeability variations that become apparent after dyeing. Fabric postsetting after coloration can lead to the diffusion of dyes such as disperse dyes to the fibre surface and to sublimation, thermomigration and blooming problems, all of which can alter the colour and markedly decrease the colour fastness to washing and rubbing of technical textiles containing polyester fibres.[56]

9.6.10   Quality control in pretreatment

In all the pretreatments given to fabrics, it is necessary to control the process carefully in order to minimise fibre degradation and yellowing.[8] Mechanical damage (i.e. holes, poor dimensional stability and fibre damage through overdrying) must also be avoided. Fibre yellowing makes it very difficult to dye pale bright colours while any fibre degradation may be subsequently increased during dyeing and printing treatments and result in inferior physical properties (e.g. low tensile strength, tear strength and abrasion resistance) or to poor colour fastness performance. Inade-

quate pretreatment can lead to poor wettability, uneven coloration and inferior adhesion of coatings in technical textiles.

9.7   Total colour management systems

9.7.1   Specification of colours and colour communication

The time-honoured method of specifying colours involves sending physical standards (e.g. dyed or coloured patterns) to the dyehouse followed by dyeing samples to match the colour in the laboratory.[77] The samples are submitted to the colour specifier for acceptance or rejection. If they are not accepted by the colour specifier, this process must be repeated in order to obtain satisfactory colour matching to the standard. The approved laboratory sample will then be used as the basis for the initial dye recipe for bulk dyeings. A sample from bulk dyeing may then be submitted to the specifier for final approval prior to delivery. Similar principles apply to the production of laboratory strike-offs of each colour in a print for approval by the colour specifier prior to machine printing.

All this is a time-consuming procedure which has now been shortened considerably in order to avoid colour changes through storage and handling of physical samples and to achieve a quick response and provide just-in-time delivery to the customer. The use of a colour specifier program can dramatically decrease the cycle time for approval. This involves the use of instrumental colour measurement for formulation and quality control, accreditation procedures to enable self approval of colours and colour specification using reflectance data.[77–79] In the most advanced colour management systems it is now possible to visualise a colour on a colour monitor so that colour communication between the colour specifier and the dyer is vastly simplified. A number of standardised colour specification systems, for example Pantone, Munsell Chip systems, can also be used.[79]

9.7.2   Colour measurement

Objective colour matching using a spectrophotometer for colour measurement is superior to visual colour matching assessment because instrumental colour measurement allows the colour to be specified in terms of reflectance data and the precision of colour matching to the standard reflectance data can then be calculated numerically in colour difference units (ΔE).[80]

Colour tolerancing systems can be used to provide better agreement between visual assessment and the instrumentally measured colour difference, and colour acceptability limits can be agreed in advance in order to facilitate decisions on colour.[80–82] Colour acceptability limits are numerical values at which the perceived colour differences become unacceptable to the specifier, that is, single number shade passing systems. Instrumental shade sorting systems are widely used to separate fabric lengths on fabric rolls into similar colours.[83]

The spectrophotometers currently in use may give different measured reflectance values according to the instrument design. The geometry, wavelength scale, bandwidth or light source may differ between different makes of spectrophotometer.[77,80,81] The two most common geometries used for direction of illumination/

direction of view are: diffuse /8° and 45°/0°. Readings given by these two geometries are not compatible unless the ideal perfect diffuser is measured. Illumination is provided either by a tungsten filament halogen cycle incandescent lamp or by a pulsed xenon discharge lamp.

Tungsten filament lamps do not have significant ultraviolet emission compared with pulsed xenon discharge lamps. The measurement of samples containing fluorescent brightening agents or some fluorescent materials is thus affected by inclusion or exclusion of the ultraviolet component of the illumination.[77]

Spectrophotometers use either single-beam, double-beam or dual-beam optics. The latter are now more widely used to compensate for the variability of the spectrum of pulsed xenon discharge lamps.[77,84] The collection optics may gather light across the sample image, focussing it on to the spectrophotometer aperture, or alternatively it is imaged at infinity, gathering light along a narrow range of angles. This latter method is claimed to provide a greater depth of field and insensitivity to sample surface imperfections. Considerable progress has been made by the manufacturers of spectrophotometers to ensure that the instruments give reliable, repeatable measurements, and the inter-instrument agreement (i.e. the colour difference values for a set of colour standards measured with two or more instruments of the same model) is now very low (typically 0.04 ΔE). Inter-instrument agreement and precision of colour measurement are now very important for the colour measurement of some technical fabrics where the colour matching has to be very close to the standard, as in automotive fabrics where reproducibility to within 0.3 ΔE is typically demanded.

The spectrophotometers in use may utilise 16 data points at 20 nm intervals over the 400–700 nm range, 31 data points from 400 to 700 at 10 nm intervals, or 40 data points from 360 to 750 nm at 10 nm intervals.[77] In addition, the bandwidth may be 20 nm or 10 nm or less. As a result, it is difficult to convert measurements from one format to the other. Although conversion is possible, the colour difference measured at two different bandwidths on the same sample can be as high as 2.0 CIELAB units. However, the largest aperture should be used for colour measurement because this should provide more repeatable measurements.

Colour measurement of dyed textiles should be carried out on conditioned samples because the colour may change with temperature and moisture content and the colour change may exceed the pass/fail tolerance.[77] The sample presentation should also specify the number of fabric layers and the backing material to be used because these factors also affect the perceived colour. Colour measurement of loose fibres generally gives rise to greater variations in measurement than on woven fabrics so that it is advisable to use multiple measurements to improve the repeatability. There are considerable differences in colour between cut and uncut pile yarn, where measurements are made on the fibre tips of a cut hank of yarn or on the side of the yarn.[80]

Portable colour measurement systems utilise hand-held spectrophotometers with data storage and extensive memory capacity for monitoring the colour batch-to-batch and within batch (e.g. side-centre-side, and end-to-end colour variations within a fabric roll).[85] These are very convenient for quality control purposes both within the laboraratory and in the production plant, but sophisticated on-line colour measurement systems are also employed on continuous fabric dyeing ranges.[86] A typical total colour control system is illustrated in Fig. 9.2.[80]
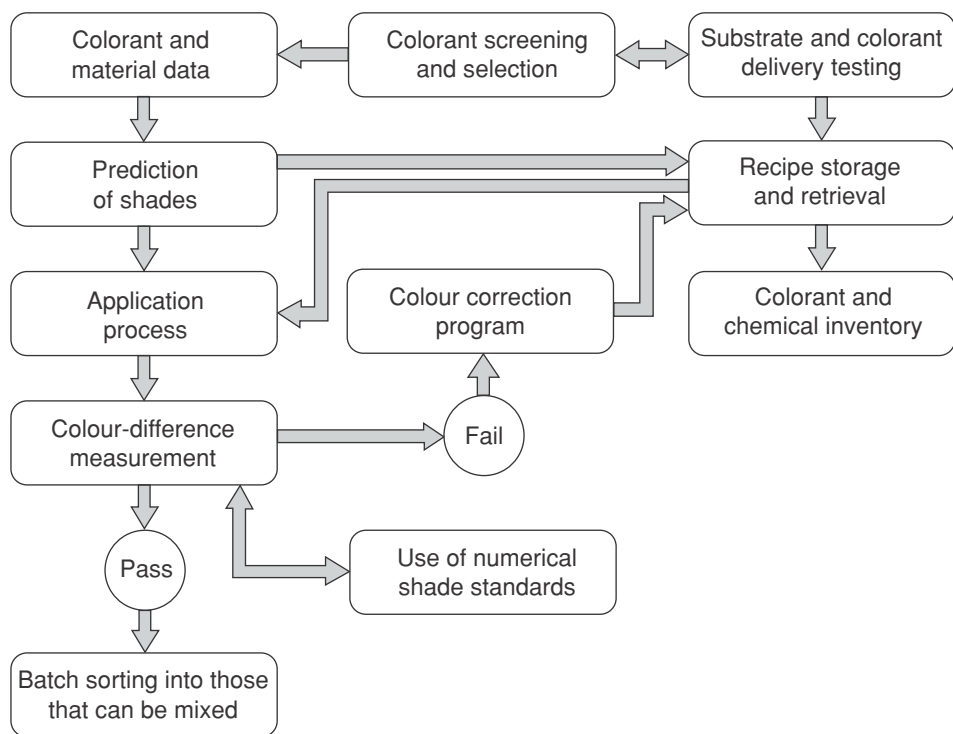
9.2   Total colour control (source: see ref 80, p. 45).

9.7.3   Laboratory matching

In the modern dyehouse, dyestuffs and chemicals are purchased to an agreed quality standard.[19,80] Dyestuffs for use in laboratory matching in many dyehouses are dissolved or dispersed in stock solutions above an automated laboratory dispensing unit. The colour specifier may supply a physical sample, the reflective curve of which is measured on the spectrophotometer in the laboratory or reflectance data are supplied directly to the laboratory. Computer match prediction is then carried out using the appropriate database of the dyes used in the dyehouse on the substrate to be dyed.[80] If the substrate to be dyed in bulk has a different dyeability to that originally used to construct the database, adjustment of the recipe must be made. The colorist in the laboratory must then select from the computer match prediction the most appropriate recipe, taking into account such factors as recipe cost, the anticipated technical performance in bulk dyeing, colour fastness, metamerism, and the closeness of the predicted colour match to the specified colour.

The appropriate dye recipe is then dispensed manually or on a laboratory dye dispensing unit and a sample of the material is then dyed in an automated laboratory dyeing machine under conditions that will simulate those to be used in bulk dyeing, for example the same pH, chemicals and auxiliaries, liquor ratio and temperature–time relationship. The laboratory matching is given the same rinsing or after-treatment that will be used in bulk dyeing, and is dried, conditioned, and the colour measured on the spectrophotometer. If the colour is a commercial match to the specified colour, then bulk dyeing is initiated. If the colour is outside the com-

mercial colour tolerance owing to differences in substrate dyeability and so on, a corrected recipe is predicted and the process repeated to obtain a commercial colour match followed by bulk dyeing.[80,81,87]

Where there is close control over the colour strength of the dyestuffs and consistent substrate dyeability, it is often possible to operate so-called 'blind dyeing' in which the computed dye recipe in the laboratory is used immediately for bulk dyeing.[87] This shortens the time required, decreases dyehouse costs and offers quick response and rapid delivery to customers. Where repeat dyeings of the same colour are required, it is usually possible to input the reflectance data gained from bulk dyeings in order to refine the database and thereby achieve a greater level of right-first-time dyeings. Right-first-time, right-on-time, right-every-time dyeing is the goal of the dyer, because this is the lowest cost dyeing system that provides quick response for customers.[87]

If a bulk dyeing proves to be off-shade and the original recipe requires a correction (i.e. an addition) that results in extending the dyeing time, the dyer suffers a considerable financial penalty. If the colour is too dark and the bulk dyeing must be stripped and redyed, this imposes further cost penalties and often impairs the quality, physical properties and surface appearance of the dyed material. In general, the shorter the processing time under hot wet conditions in the dyebath, the lower will be the fibre degradation and hence the quality of the dyed material will be superior, all important considerations for many technical textiles.

9.8   Dyeing machinery

Apart from mass coloration that has been discussed in Section 9.5, conventional dyeing machinery is used for the dyeing of technical textile materials in the form of all types of fibres, tows, yarns (e.g. warp, hank, package), fabric, garments, carpets and so on.[13,88–91] Fabric may be dyed in rope form (i.e. as a strand) or at open width (i.e. flat), or circular weft knitted fabrics may be dyed in tubular form. Modern trends are to dye in yarn or fabric form because this allows the decision on colour to be made later in the manufacturing chain and the cost of dyeing is lower. Many technical fabrics are dyed at open width to avoid inserting creases into the fabric. Such creases can be difficult to remove in synthetic fibre fabrics because of hydrosetting occurring during dyeing.

9.8.1   Batch dyeing machinery for exhaust dyeing

In conventional exhaust dyeing, dye molecules are transported to the fibre surface where the substantivity of the dye for the fibre ensures that adsorption takes place to produce a higher surface concentration of dye.[92] This promotes dye diffusion into the fibre, the rate of dye diffusion being dependent upon the dye concentration. Dye molecules diffuse within the disordered regions of the fibres, to provide adequate fibre penetration.[21] Level dyeing is attained through the migration of dye, by desorption from inside the fibre back into the dye liquor and thence adsorption and diffusion in another part of the fibre, this levelling process being aided by the relative motion of the dye liquor and the fibre. After an appropriate time, a level, well-penetrated dyeing is obtained. This process is facilitated if compatible dyes, that is, dyes that diffuse at the same rate, are initially selected for use together with a
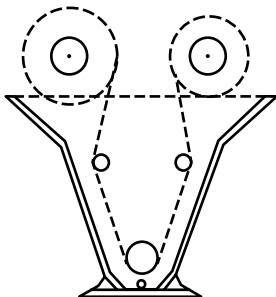
9.3   Jig dyeing machine (source: see ref 89, p. 29).

selected levelling agent. Dye fixation is ensured either through (i) electrostatic attraction between the dye and dyesites inside the fibre, (ii) by covalent bond formation between the dye and the fibre, (iii) by increasing the size of the dye or by dye aggregation leading to mechanical entrapment, or (iv) by conversion of the water-soluble dye into a water-insoluble form.

The three types of dyeing machinery for batch or exhaust dyeing are based on machines in which:[88,89,91]

1   the material moves, but the liquor is stationery, e.g. jig and winch (beck) machines for fabric dyeing
2   the liquor moves, but the material is stationery, e.g. hank or package dyeing of yarns and beam dyeing of fabrics
3   both the liquor and the material move, e.g. jet, softflow and overflow jet dyeing machines for fabrics.

In general, a lower liquor ratio decreases the water and energy consumption and decreases the volume of waste water, decreasing effluent treatment costs. It can also facilitate a more rapid dyeing cycle and increase the dye exhaustion on the fibre, because the total dye liquor is circulated more rapidly.

In the jig (or jigger), fabric is dyed at open width by traversing fabric from one roll through a dyebath and on to a second roll (see Fig. 9.3).[89] When the second roll is full, the rolls are stopped and the fabric motion is reversed, and the procedure repeated as required. The dye liquor is added in portions to ensure satisfactory levelness from end-to-end of the fabric. A hood prevents the release of steam and helps to maintain the fabric temperature on the rolls where the majority of the dyeing takes place. Most jigs operate at 98–100 °C (i.e. under atmospheric conditions) but pressurised jigs operating at up to 140 °C are used for some technical fabrics, for example polyester sailcloths. In the latter machine, the rolls and the dyebath are enclosed in an autoclave (i.e. pressure vessel) which can be closed with a ring seal. Jig dyeing operates at a liquor ratio of 3–5:1 and rinsing/washing off is more rapid on modern twin bath jig designs in which a combination of water spray and vacuum is used for removal of loose dyestuff.[93]

Jig dyeing is particularly suitable for technical fabrics that may be subjected to creasing and hence are preferably dyed at open width. In addition it is preferred for many technical fabrics that have a dense structure and where it is difficult to pump
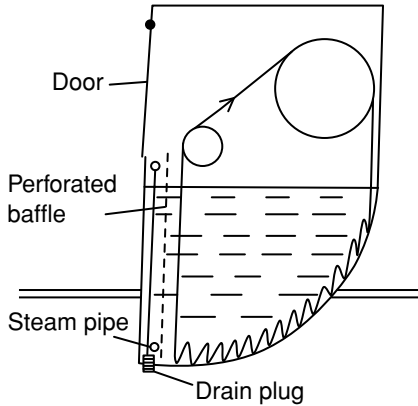
**9.4**   Winch dyeing machine (source: see ref 89, p. 38).
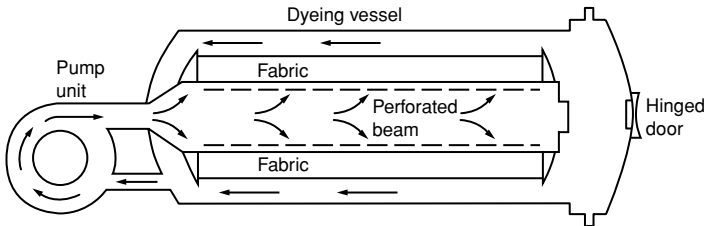
9.5   Sectional diagram of a high temperature beam dyeing machine (source: see ref 27, p. 117).

dye liquor through multiple fabric layers, as in beam dyeing (e.g. sailcloths, filter fabrics etc.).

The winch or beck dyeing machine may be used for dyeing in rope form, normally at temperatures of up to 98–100 °C (see Fig. 9.4).[89] High temperature winches have also been used in the past, but have now been replaced by high temperature (i.e. pressurised) jet dyeing machines. The latter are less likely to give rise to fabric creasing and have improved liquor interchange which aids the more rapid attainment of level dyeing by promoting dye migration.

In beam dyeing, the fabric is wound at open width on to a perforated stainless steel beam, and kept in place by the use of end plates (see Fig. 9.5).[89] Dye liquor is pumped through the multiple layers of fabric, usually from out to in, but in-to-out flow is also used. The fabric winding tension must be low to avoid stretching the fabric, and to avoid high pressure being applied to the innermost fabric layers, otherwise the fault known as watermarking or moiré may be observed. This is usually seen as a shimmering surface pattern on dark colours, the pattern changing with the orientation of the fabric relative to the observer. Too low a winding tension can, however, lead to telescoping and movement of the fabric on the beam. It is normal to wind a fent (or short sacrificial fabric length) on to the beam first to prevent perforation marks on the fabric layers next to the beam. These show as a pattern of dark spots corresponding to the perforated holes in the beam and are often caused
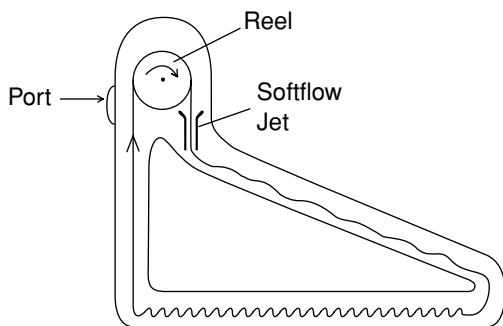
9.6   Softflow jet dyeing machine.

by poor dispersing or aggregation of disperse dyes. The liquor ratio in beam dyeing is around 10:1 although this can be decreased by the use of spacers, and most beam dyeing machines are pressurised machines capable of dyeing at temperatures of 130–140 °C. Beam dyeing is particularly effective for dyeing thin permeable fabrics composed of synthetic filaments, e.g. nylon 6.6 and polyester fabrics.

Pressurised machines are generally used for dyeing technical textiles composed of synthetic fibre materials. Softflow jets provide a more gentle mechanical action on the fabric rope, the main fabric transportation being carried out over a winch reel followed by a softflow jet system (see Fig. 9.6).[89,94] In some jet dyeing machinery, the liquor flow is split between two jets which exert a lower pressure on the fabric. This is claimed to decrease linting (loss of fibre) in staple fibre fabrics, and surface distortion. Garments are generally dyed in atmospheric or pressurised rotary drum machines or in atmospheric overhead paddle dyeing machines.[89,95]

Aerodynamic fabric transport systems utilise a blower to aid the fabric circulation through the jet dyeing machine. These enable liquor ratios as low as 1.3:1 to be used on hydrophobic filament fabrics such as polyester, although higher liquor ratios in the range 5–10:1 are used in conventional jets on hydrophilic cellulosic fabrics.[94]

9.8.2   Pad-batch dyeing

Both woven and knitted fabrics can be dyed using this method with the padding (impregnation) stage being conducted under ambient or hot conditions.[41,96] With reactive dyes, fabric prepared for dyeing is usually padded under ambient conditions and then wound up on a roll rotating on an A-frame. The dye concentration and the pick up of dye liquor by the fabric must be controlled to ensure uniform fabric coloration. The length of padded fabric on the roll may be covered with polyethylene film to prevent evaporation and is then rotated slowly (to avoid migration of the dye liquor to the outer layers of the fabric roll) for an appropriate time to achieve dye fixation. The time required is dependent upon the depth of colour, the reactivity of the reactive dye, the temperature and the alkalinity, but is generally in the range 4–24 hours (often conveniently overnight). This is then followed by a thorough hot wash off to remove the unfixed dyestuff and the alkali, and the fabric is then dried.

9.8.3   Continuous dyeing machinery

Continuous dyeing can be carried out by dye impregnation, fixation, washing off and drying on ranges designed for handling woven fabrics at open width, and there are also carpet and warp dyeing ranges.[90] Continuous dyeing was originally designed for efficient and economical dyeing of long runs of fabric, and many modifications have been made to facilitate more rapid turn around and less downtime in between a greater number of shorter production runs per colour. Automatic metering of liquid dyes to control the dye concentration in the dyebath and intelligent padding systems are used to control the pick up of dye liquor by the fabric. Thermofixation (dry heat), superheated steam or saturated steam fixation units in which the temperature is monitored and controlled may be used to obtain dye fixation. Reproducible colour is obtained after washing off loose dyestuffs and drying. Colour change during a production run is accomplished on-line within minutes using automated wash down systems. Continuous colour monitoring on the output dyed fabric on some ranges can be utilised to adjust the colour being dyed on the input fabric. Either the whole width of the fabric may be continuously monitored, or a traversing spectrophotometer measuring side-centre-side variations may be employed.

For the continuous dyeing of woven polyester/cotton fabric, the polyester fibres are first dyed with disperse dyes using a pad-dry-thermofix treatment.[90] The cotton is then dyed using direct, reactive or vat dyes using a pad-steam process. The dyed fabric is cleared of loose surface dyestuff by treatment on an open width washing range and then dried over steam-heated cylinders and batched. A scray is used at the fabric entry to the range to accumulate fabric so that the range continues to run at 50–150 m min^{-1} while the next roll of fabric is sewn on to the fabric being dyed.

9.9   Printing

9.9.1   Printing styles

Printing leads to the production of a design or motif on a substrate by application of a colorant or other reagent, usually in a paste or ink, in a predetermined pattern. In printing, each colour is normally applied separately and a wide variety of printing techniques is used. In direct printing, dyes are applied in a print thickener containing auxiliaries and are diffused into the fibres and fixed in a steamer or high temperature steamer.[57] Surface dye and thickener are then thoroughly washed off in a continuous open width washer, and the materials dried.

In pigment printing, water-insoluble pigments are applied with a heat-curable binder system, followed by drying and curing, and the physical properties of the pigment print depend greatly upon the adhesive properties of the print binder system. Pigment printing is a simple, popular method particularly for printing blended fibre fabrics.[7,57]

Two other major styles of printing are employed, namely, discharge and resist printing.[97] In discharge printing, a dyed fabric is printed with a discharging agent (a reducing agent) which decolorises the dye leaving a white motif against a dyed ground. Alternatively, a dye resistant to discharging can simultaneously be applied to give a second colour in the discharged area of the motif. In resist printing, the resisting agent (which may act mechanically or chemically) is printed on to the

undyed fabric. This prevents the fixation of the ground colour which is then developed by dyeing, padding or overprinting. A white resist, or a coloured resist, can be achieved if a selected dye or pigment is added to the resist paste and is then subsequently fixed.

9.9.2   The print image

The design image may be painted by hand on to transparent film for photographic development of diapositive images, or sophisticated CAD (computer-aided design) systems are used in conjunction with a design input scanner. The design image is then manipulated on screen, the colours are electronically separated and the digitised design images for each colour transferred to an engraving system for transfer on to a rotary or flat screen, or for direct use in digital ink jet printing.[98]

9.9.3   Fabric printing machinery

Rotary screen printing is the dominant printing method now employed for 60–70% of printed fabric production.[99] The design motif for each colour is developed as open mesh on the rotary screen by the use of film, laser or black wax engraving systems. Both lacquer screen and galvano screens are used. Each rotary screen secured in end rings is fixed in bearings and rotated in precise register and in a predetermined sequence. A separate colour is supplied to each rotary screen and pushed by a squeegee (e.g. a blade or a roller) through the open mesh of the screen on to the fabric which is temporarily gummed on to a print table with a moving blanket (apron).[100] Machines capable of continuously printing up to 24–36 colours are available, although most designs involve less than eight colours, and rotary screen printing on textile materials up to 5 m in width can be carried out, at speeds up to 80 m min^{-1}, but typically at 40 m min^{-1}.

Automatic or semiautomatic flat screen (flat bed) printing is used for many designs where very precise images are required, using polyester, polypropylene or polyamide monofilament fabric as the screen material.[100] In automated flat screen printing, the fabric is gummed to the print table and progressed forward intermittently, one design repeat at a time, after the lowering, printing and lifting of the screens, to print all the colours sequentially, using a squeegee system to force the print paste into the fabric. The printing speed is lower than that normally obtained in rotary-screen printing. Modern rotary and flat screen printing machines may be supplied with enough colour for each screen, with all the operations of weighing, metering, dispersing and mixing of dyes and auxiliaries with stock thickener (suitably diluted), or of pigments with binders and softeners controlled by a robotised colour kitchen based upon a computed print recipe. The colours are supplied in drums and supply pipes are used to furnish the colour for each screen in rotary screen printing.

At the end of the print run, excess print paste is removed and stored, and this may then be reused in a subsequent print run, or disposed of to landfill. Print monitoring systems are available for monitoring and comparing the fabric print with the electronically stored digitised design image. In the most sophisticated machines, it is possible to use such monitoring systems for correction of faults on-line, and many machines are designed for quick changeover of colours, for example by screen and blanket washing and drying facilities on-line, and also for rapid

changeover of screens at a design change.[101] Automated setting up, monitoring, control and correction systems and washing and drying on-line have all dramatically improved the productivity and repeatability in rotary and flat screen printing.

The latest advance in textile printing is the introduction of digital ink jet printing machines, capable of printing fabrics up to 2 m in width using acid, reactive or disperse dye inksets.[102–104] The fabric is normally pretreated and placed in the machine in roll form, printed and then the dyes are fixed, usually by steaming in a separate machine, washed off and dried. Both piezoelectric and bubble jet printing systems may be used, with any unused colour being diverted back to the ink reservoir and recycled. Generally four, seven–eight, and up to 12 colours may be printed; the greater the number of colours the greater the colour gamut that can be printed.

In general, digital ink jet printing systems are designed principally for use with natural fibres, (e.g. cellulosic, wool and silk fabrics) and also polyester fabrics.[102–104] On some machines, the inkjets are periodically cleaned with solvent, automatically, to avoid jet blockage, particularly with disperse dye systems. Such printing machines may be run overnight without operator supervision, the design images being preloaded, and design changeover being essentially instantaneous. Other systems are already being used for printing flags and banners and clearly have great potential for printing short production runs of advanced technical textile fabrics.[105] Ultimately, some form of reprographic printing method may be developed and research and development along these lines is continuing.[106]

Transfer printing may be carried out by sublimation transfer, melt transfer or film release methods.[55] In sublimation (or dry heat) transfer printing, volatile dyes (typically disperse dyes) are preprinted on to a paper substrate and are heated in contact with the textile material, typically polyester fabric. The dyes sublime and are transferred from the vapour phase into the fabric in this dry-heat transfer printing method. This may be assisted by the application of a vacuum. Melt transfer is principally used on garments whereby a waxy ink is printed on paper and a hot iron applied to its reverse face to melt the wax on to the fabric surface. In the film release method, the print design is held in an ink layer which is transferred completely to the textile from a release paper using heat and pressure. The design is held on to the textile by the strong forces of adhesion between the film and the textile.

9.10 Colour fastness of technical textiles

The performance of a dyed or printed technical textile when exposed to various agencies during end-use is normally assessed by appropriate colour fastness testing.[107,108] High standards of quality and performance in such tests are often related to the higher cost of the dyes and pigments used which possess superior colour fastness properties. There are national standards, for example British Standards (BS), European Standards (EN) and International Standards (ISO), but within most countries now there is a move towards harmonisation of test methods and performance standards, so that EN ISO standards will be used in the future. In North America, there are ASTM (American Society for Testing and Materials) and AATCC (American Association of Textile Chemists and Colorists) test methods. In

addition, there are also test methods that have been devised by industry for use for specific applications, for example automotive textiles.

Many colour fastness tests have been devised to simulate the likely end-use conditions, and the Society of Dyers and Colourists in the UK and the AATCC in the USA have been at the forefront of colour fastness testing developments. The colour fastness test usually defines a standard test method to be followed, and gives the method of assessment to be used, but the performance level which is satisfactory for the end-use has to be agreed between the dyer or printer and the colour specifier. Companies often set their own in-house performance criteria for their ranges of dyed or printed technical textiles, based upon their general working knowledge and experience in the field, through technical liaison with dye makers, through field testing under actual end-use conditions and by assessment of materials which are the subject of complaints.

It is not possible to discuss the many colour fastness tests that are now in use worldwide, but complete details are available in many other publications, which give details of a wide range of standard tests.[107,108] The major types of colour fastness test relate to the colour fastness to wet treatments, (e.g. to washing), and to light and weathering, to rubbing (crocking), atmospheric contaminants, and organic solvents, (e.g. dry cleaning).

The colour fastness performance in standardised wash tests is rated by visual assessment of the change in colour of the coloured material and the degree of staining on to adjacent materials in the wash liquor (e.g. a multifibre fabric test strip,[109] or specific adjacent fabrics), using ISO Grey Scales under standardised lighting conditions against a neutral grey background in a viewing cabinet. The Grey Scale ratings range from 5 (no change, i.e. excellent performance) through half point ratings, for example 4–5, down to 1 (large change, i.e. poor performance). The colour change may also be measured objectively using a spectrophotometer and the colour difference converted into a Grey Scale rating.[110]

Colour fastness to light is normally assessed using a high intensity filtered xenon arc lamp to simulate natural daylight, sample strips being mounted, part covered, on cards which can be individually rotated in a bank of holders that may be rotated around the accelerated fading lamp, depending on the type of machine, in an atmosphere of controlled temperature and relative humidity. A set of blue wool standard fabric strips that fade at known rates must also be used in each test. The set-up conditions for specific test methods used for many types of technical textiles are preprogrammed on modern light fastness testing machines.[111]

The degree of fade in British and European Standards is based upon visual assessment of the degree of colour fade on the test sample compared with the equivalent degree of fade on the blue wool samples. The light fastness rating changes from 8 (highest) down to 1 (lowest). Because of difficulties with the supply of blue wool standards, the Society of Dyers and Colourists is introducing a set of blue pigment-printed light fastness standards that will replace the blue wool standards, but in addition may also extend the light fastness rating range beyond 8 and below 1.[112] Weathering may be conducted in field trials, with samples exposed to sunlight either covered or uncovered by glass, or alternatively by exposure for a standard number of hours in an accelerated fading machine.

Colour fastness to rubbing (crocking) is assessed by rubbing a standard white fabric against the dyed sample under a constant pressure for an agreed number of strokes. The test may be conducted under wet or dry conditions, and the machine

may be operated by hand, or in the latest machines performed automatically.[113] Assessment of the degree of staining on the white fabric is assessed using the ISO Grey Scale for staining. For pigment printed materials, the rub fastness is dependent upon the properties of the adhesive binder used.

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10

Heat and flame protection

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10.1   Introduction

With industrialisation, the safety of human beings has become an important issue. A growing segment of the industrial textiles industry has therefore been involved in a number of new developments in fibres, fabrics, protective clothing.[1–10] Major challenges to coatings and fabrication technology for production in the flame-retardant textile industry have been to produce environmentally friendly, non-toxic flame-retardant systems that complement the comfort properties of textiles.[11–14] The 1990s, therefore, saw some major innovations in the development of heat-resistant fibres and flame-protective clothing for firefighters, foundry workers, military, aviation and space personnel, and for other industrial workers who are exposed to hazardous conditions.

For heat and flame protection, requirements range from clothing for situations in which the wearer may be subjected to occasional exposure to a moderate level of radiant heat as part of his/her normal working day, to clothing for prolonged protection, where the wearer is subject to severe radiant and convective heat, to direct flame, for example the firefighter's suit. In the process of accomplishing flame protection, however, the garment may be so thermally insulative and water vapour impermeable that the wearer may begin to suffer discomfort and heat stress. Body temperature may rise and the wearer may become wet with sweat. Attempts have therefore been made to develop thermal and flame protective garments which can be worn without any discomfort.

In this chapter, various factors affecting the flammability, development of new inherently heat-resistant fibres, and the flame-retardant finishes for both natural and man-made fibre fabrics along with the relevant test methods are described.

10.2   What constitutes flammability?

Ease of ignition, rate of burning and heat release rate are the important properties of textile materials which determine the extent of fire hazard. The other factors that influence the thermal protection level include melting and shrinkage characteristics of synthetic fibre fabrics, and emission of smoke and toxic gases during burning. So, while selecting and designing flame protective clothing, the following points should be kept in mind:

- the thermal or burning behaviour of textile fibres
- the influence of fabric structure and garment shape on the burning behaviour
- selection of non-toxic, smoke-free flame-retardant additives or finishes
- design of the protective garment, depending on its usage, with comfort properties
- the intensity of the ignition source
- the oxygen supply.

10.3   Thermal behaviour of fibres

The effect of heat on a textile material can produce physical as well as chemical change.[8,15,16] In thermoplastic fibres, the physical changes occur at the second order transition (T_g), and melting temperature (T_m), while the chemical changes take place at pyrolysis temperatures (T_p) at which thermal degradation occurs. Textile combustion is a complex process that involves heating, decomposition leading to gasification (fuel generation), ignition and flame propagation.

A self-sustaining flame requires a fuel source and a means of gasifying the fuel, after which it must be mixed with oxygen and heat. When a fibre is subjected to heat, it pyrolyses at T_p (Fig. 10.1) and volatile liquids and gases, which are combustible, act as the fuels for further combustion. After pyrolysis, if the temperature is equal to or greater than combustion temperature T_c, flammable volatile liquids burn in the presence of oxygen to give products such as carbon dioxide and water. When a textile is ignited, heat from an external source raises its temperature until it degrades. The rate of this initial rise in temperature depends on the specific heat
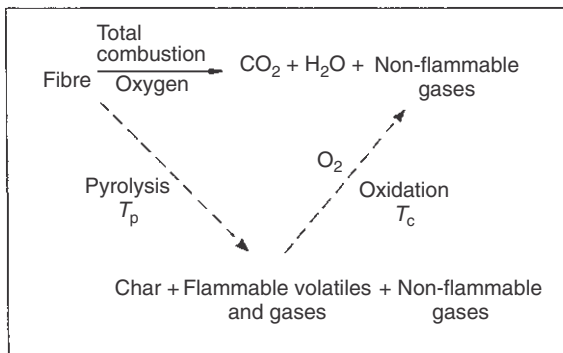
10.1   Combustion of fibres.

of the fibre, its thermal conductivity[17] and also the latent heat of fusion (for melting fibres) and the heat of pyrolysis.

Frank-Kamenetzky[18] demonstrated the influence of the nature of a reactive (flammable) material and its environment. The heat generation and heat loss was plotted as a function of temperature (Fig. 10.2). The plot shows that the loss of heat is approximately proportional to the difference in temperature between the combustion zone and the environment, and can be represented by an approximately straight line. The equilibrium between the heat generation and the heat loss is realized at the points of intersection of I and II (Fig. 10.2(a)). Point A represents the ambient temperature, point C represents the stationary temperature and both are stable while B is unstable. To the left of B, the heat loss exceeds the heat generation, while to the right of B this is just the reverse. Therefore, the temperature corresponding to B is the ignition temperature. During a fire accident, the material must be heated to such an extent that it reaches the ignition temperature. The temperature at B is also considered to be the self-extinguishing temperature; at lower temperatures heat loss exceeds heat generation. Figure 10.2(b) shows three materials with different degrees of flammability but in the same environment. The first (Ia) is highly flammable, the second (Ib) moderately flammable while the third (Ic) is flame resistant under these conditions. Figure 10.2(c), on the other hand, represents a material in different environments. An increased heat loss may be caused by a higher rate of air flow, less insulation and so on. From the above, it is thus evident that the flammable material may be barely flammable or even non-flammable under different environments.
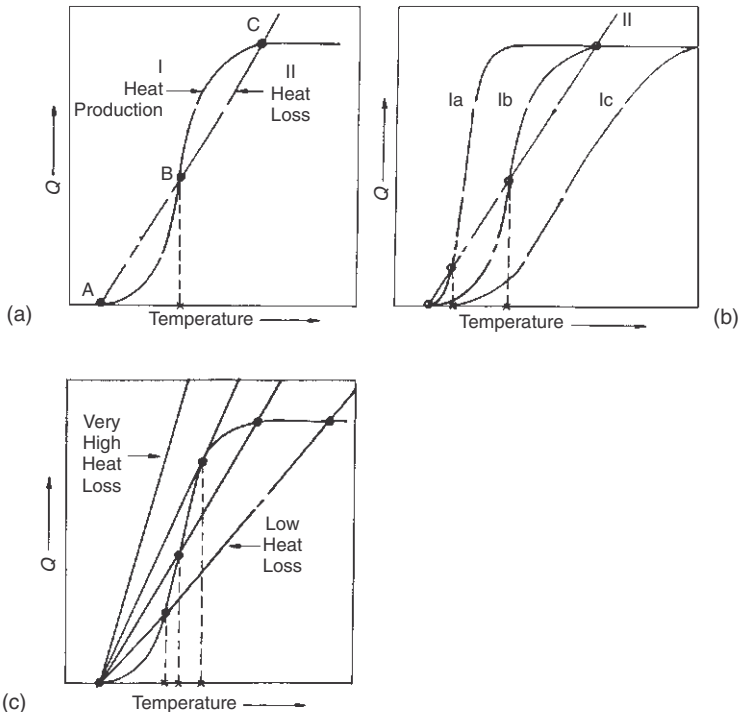
10.2   Schematic Stability diagram of Combustion. (a) Flame stability diagram, (b) three degrees of flammability, (c) four different surroundings.

In protective clothing, it is desirable to have low propensity for ignition from a flaming source or, if the item ignites, a slow fire spread with low heat output would be ideal. In general, thermoplastic-fibre fabrics[19,20] such as nylon, polyester fibre, and polypropylene fibres fulfil these requirements because they shrink away from flame and, if they burn, they do so with a small slowly spreading flame and ablate. For protective clothing, however, there are additional requirements, such as protection against heat by providing insulation, as well as high dimensional stability of the fabrics, so that, upon exposure to the heat fluxes that are expected during the course of the wearer's work, they will neither shrink nor melt, and if they then decompose, form char. The above mentioned requirements cannot be met by thermoplastic fibres and so recourse must be made to one of the so-called high-performance fibres such as aramid fibre (e.g. Nomex, DuPont), flame-retardant cotton or wool, partially oxidised acrylic fibres, and so on. It may also be noted that the aramid fibres, in spite of their high oxygen index and high thermal stability, have not been found suitable for preventing skin burns in molten-metal splashes because of their high thermal conductivity.

From the foregoing discussion, it may be noted that the mode of decomposition and the nature of the decomposition products (solid, liquid, and gaseous products) depend on the chemical nature of the fibre, and also on the type of finishes or coatings applied to the fabrics. If such decomposition products are of a flammable nature, the presence of atmospheric oxygen gives rise to ignition, with or without flames. When the heat evolved is higher than that required for thermal decomposition, it can spread the ignition to cause the total destruction of the material (Fig. 10.3).

In addition to the fibre characteristics and fabric finish, several garment characteristics also influence thermal protection. For a given fabric thickness, the lower the density, the greater the thermal resistance. This applies to fibres such as cotton, wool, and so on, which produce an insulating char on heating. Hence, thicker fabrics made from cotton, wool and other non-melting fibres give good thermal protection, whereas the thicker thermoplastic-fibre fabrics produce more severe burns.

Flame retardance of materials is normally expressed as oxygen index:[16]

$$(OI) = (OI)_m + f(FR) \tag{1}$$

where $(OI)_m$ is the oxygen index of the virgin material, and $f(FR)$ is the function of the flame retardant. Thermal properties of textile fibres including OI values are given in Table 10.1.

Miller *et al.*[21] have also studied the extinguishability of fabrics by determining the burning rate as a function of the environmental oxygen concentration. They quoted the intrinsic oxygen index, $(OI)_o$, values at extrapolated zero burning rates for cotton, wool, modacrylic, and aramid fibre for top ignition of vertically oriented samples, and for bottom ignition of both vertically oriented and 45°-inclined samples. Intrinsic oxygen index values were, however, lower than normal limiting oxygen index (LOI) values, for example, $(OI)_o$ for top-ignited cotton is 13 whereas the normal LOI is 18.

In another study, Van Krevelen[16] has established a good correlation between the chemical composition and the LOI value of the polymers. According to him, the composition parameter (CP) describing the combined effect of hydrogen and halogen content should be less than one for flame retardant materials. Figure 10.4 shows the relationship between CP and LOI for some textile materials
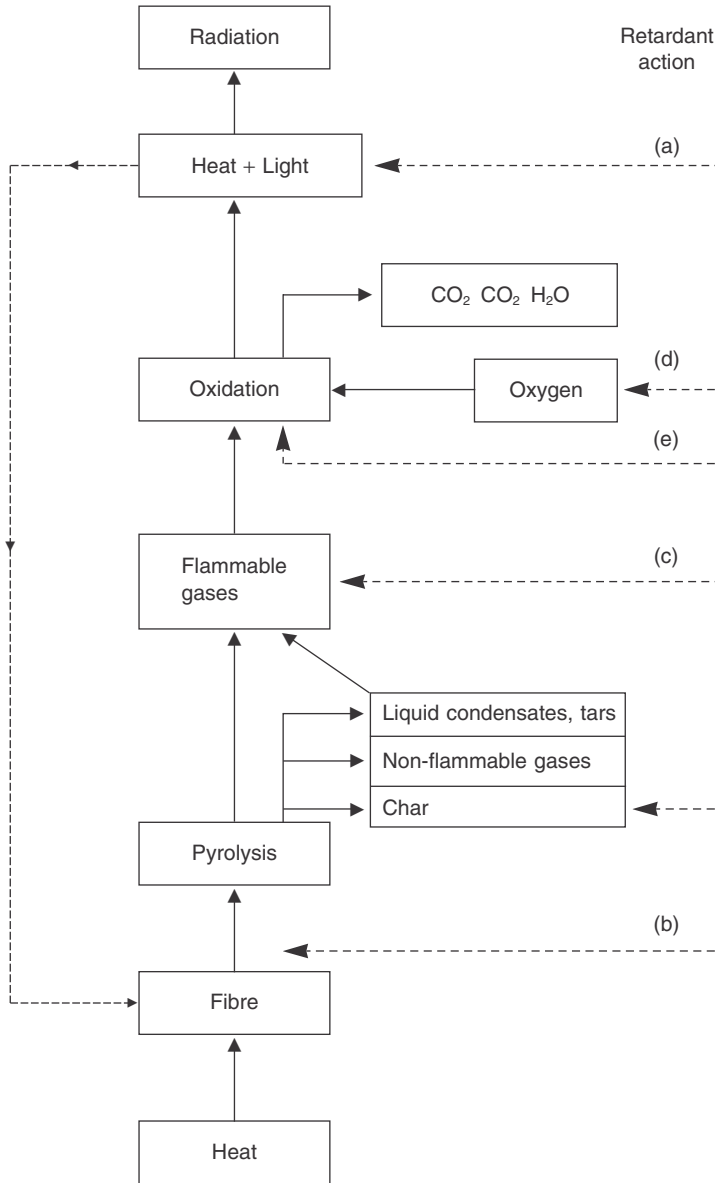
10.3   Combustion as a feedback mechanism.

$$CP = (H/C) - 0.65(F/C)^{1/3} - 1.1(Cl/C)^{1/3} - x(Br/C)^{1/3} \qquad (2)$$

where (H/C), (F/C) and (Cl/C) are the atomic ratios of the respective elements in the polymer composition, and coefficient x is probably 1.6, but is still uncertain owing to the lack of sufficient data. Although there is some data scatter, as shown in Fig. 10.4, there is a correlation between the LOI and CP.

- if CP $\geq$ 1 then LOI $\approx$ 17.5
- if CP $\leq$ 1 then LOI $\approx$ 42.5 to 60.

Table 10.1 Thermal and flame-retardant properties of some fibres[8]

Fibre	T_g (°C) Glass transition	T_m (°C) Melt	T_p (°C) Pyrolysis	T_c (°C) Combustion	LOI (%)
Wool	–	–	245	600	25
Cotton	–	–	350	350	18.4
Viscose	–	–	350	420	18.9
Triacetate	172	290	305	540	18.4
Nylon 6	50	215	431	450	20–21.5
Nylon 6,6	50	265	403	530	20–21
Polyester	80–90	255	420–477	480	20–21.5
Acrylic	100	>320	290	>250	18.2
Polypropylene	–20	165	469	550	18.6
Modacrylic	<80	>240	273	690	29–30
PVC	<80	>180	>180	450	37–39
PVDC	–17	180–210	>220	532	60
PTFE	126	>327	400	560	95
Oxidised acrylic	–	–	>640	–	55
Nomex	275	375	310	500	28.5–30
Kevlar	340	560	590	>550	29
PBI	>400	–	>500	>500	40–42

PBI = polybenzimidazole. For other abbreviations, see Fig. 10.4.
T_g is the second order transition, T_m is the melting transition, T_p is the pyrolysis temperature, T_c is the combustion temperature.
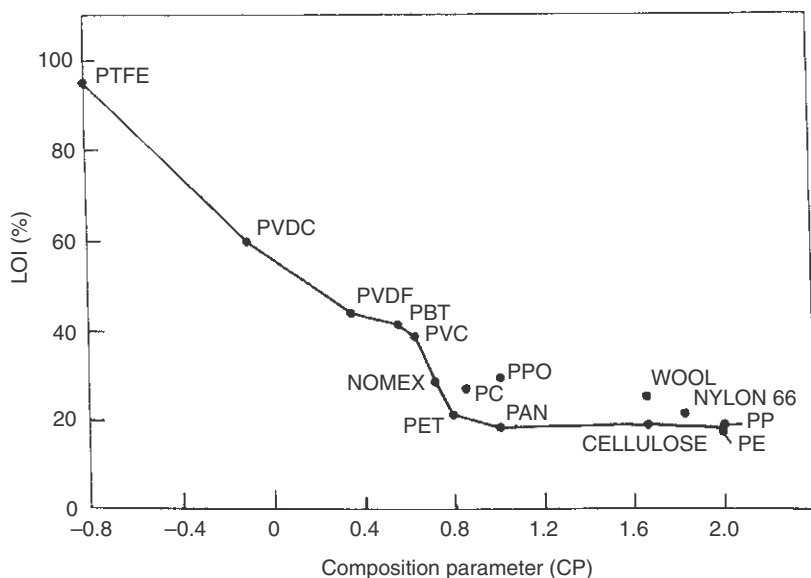
10.4 Correlation between oxygen index and elemental composition. PTFE = poly(tetrafluoroethylene), PVDC = polyvinylidene chloride, PBT = poly(butylene terephthalate), PVDF = polyvinylidene fluoride, PVC = poly(vinyl chloride), PET = poly(ethylene terephthalate), PC = polycarbonate, PPO = poly(phenylene oxide), PAN = poly(acrylonitrile), PP = polypropylene, PE = polyethylene.

(H/C) could be considered as a measure of the 'aromaticity' in polymers not containing halogen. This indicates that flame-retardant (FR) polymers and fibres should be intrinsically aromatic in nature with a CP value of <1.

Dependence of LOI on the environmental temperature, sample thermal history, moisture content, fabric sample dimensions, fabric area density and so on has been well documented. Horrocks *et al.*[22] have demonstrated the use of extinction oxygen index (EOI) rather than the LOI as a measure of textile flammability. By considering the potential fabric extinguishability in terms of an EOI parameter, the authors showed that the influence of ignition may be removed by simple extrapolation to zero ignition time to generate $(EOI)_o$.

10.4   Selection of fibres suitable for thermal and flame protection

The fibres could be classified into two categories:

- Inherently flame-retardant fibres, such as aramid, modacrylic, polybenzimidazole (PBI), Panox (oxidised acrylic) or semicarbon, phenolic, asbestos, ceramic etc.
- chemically modified fibres and fabrics, for example, flame retardant cotton, wool, viscose and synthetic fibres.

10.4.1   Inherently flame-retardant fibres

For some 2000 years, there was only one type of naturally occurring mineral fibre, asbestos which could not be completely destroyed by fire. Asbestos has many desirable properties and is cheap as well. However, the fibres are so fine that they can be breathed into the lungs and can promote fatal cancerous growth.

Glass fibres are also heat-resistant materials. In earlier times such fibres were used for printed circuit boards. Now developments in the texturing of glass fibres have provided a material that could substitute for the asbestos fibres to some extent. Unlike asbestos fibres, glass fibres with high diameter are non-respirable. They have an upper temperature resistance of about 450 °C. They spin well, knit or braid easily and can be coated with rubber, polyacrylate or silicones. Glass fibres have also good electrical and insulation properties. However, they cause skin irritation, which limits their application in protective clothing.

A number of ceramic fibres, SiC, silicon or boron nitride, polycarbosilicones, alumina and so on, have been developed. These ceramic fibres can withstand temperatures between 1000–1400 °C. However, the biggest problem with ceramic in staple form is that it is very abrasive and may wear out the processing machinery at a very high rate. Ceramic fibres generally contain a mixture of components, for example, Nicalon (Nippon Carbon Co.) is silicon carbide fibre containing up to 30% of silica, and carbon, while Nextel (DuPont) is a 70/28/2 mixture of $Al_2O_3/SiO_2/B_2O_3$. Tyranno (Ube Industries Ltd., Japan) is a ceramic fibre composed of silicon–titanium, carbon and oxygen (Si-Ti-C-O), which is reported to have a non-crystalline microstructure. Altex (Sumitomo, Japan) produces continuous α-alumina fibres with a diameter of 8–10 μm. The tenacity of these commercial ceramic fibres is in the range of 0.32–3.2 N tex^{-1} and breaking extension is only 0.4–5.4%. An important aspect of high temperature fibres that should be considered is their ability to insulate from thermal flux or conductivity. Silica-based fibres have high rates of thermal

conductivity, a property that may be valuable in heat dissipation in some uses but in situations like hot metal splashes, where the heat is transmitted to the person by conduction, they will cause more burn injuries instead of protecting the skin. Thus, the selection of the fibre for making thermally protective clothing should be decided on the basis of the environment to which a worker is exposed, namely, whether the heat will be transmitted to the person by conduction, convection or radiation. Despite their high temperature resistance, ceramic fibres have poor aesthetic characteristics, high densities and are difficult to process.

10.4.1.1   *Aramids*[23–29]

Aromatic polyamides such as poly(metaphenylene isophthalamide) char above 400 °C and may survive short exposures at temperatures up to 700 °C. Nomex (DuPont), Conex (Teijin), Fenilon (Russian) and Apyeil (Unitika) meta-aramid fibres have been developed for protective clothing for fighter pilots, tank crews, astronauts and those working in certain industries. Para-aramid fibres like Kevlar (DuPont), Twaron (Akzo Nobel) and Technora (Teijin) are also being used for ballistic and flame protection. Nomex nonwovens are used for hot gas filtration and thermal insulation.

Aramids are resistant to high temperatures, for example at 250 °C for 1000 hours the breaking strength of Nomex is about 65% of that before exposure. They begin to char at about 400 °C with little or no melting. Generally, meta-aramids are used in heat protective clothing, however, in intense heat, Nomex III (a blend of Nomex and Kevlar 29 (95:5 by wt) is preferred, in order to provide a greater mechanical stability to the char. Teijin[23] has introduced a new fabric, X-fire, a combination of Teijin Conex (meta-aramid) and Technora (para-aramid) fibres. This fabric is capable of resisting temperatures up to 1200 °C for 40–60 s.

Nomex can also be blended with FR fibres, for example FR wool and FR viscose. Karvin (DuPont) is a blend of 30% Nomex, 65% FR viscose and 5% Kevlar. Kevlar blends were formerly used by Firotex Co. UK (now defunct) with partially carbonised viscose in fabric form. This blend was developed as a fire blocking fabric for aircraft seats but found little favour because of the poor abrasion resistance of the carbonised viscose component (see Section 10.4.1.6 on semicarbon fibres).

Other examples of such blends include Fortafil and Fortamid needle felt NC580, which comprise aramid and FR viscose. This material is useful for gloves and mittens in which temperatures may reach up to 350 °C. The outer working surface of the aramid fibre is needled through a reinforcing polyester fibre scrim over an inner layer of FR viscose.

Another aromatic copolyamide fibre developed by Lenzing AG is P84. This fibre does not melt but becomes carbonized at temperatures in excess of 500 °C and has an LOI value of 36–38%. The basic fibre is golden yellow in colour but Lenzing AG offers it as spun material dyed in limited colours. P84 fibres have irregular cross-section, which provides a higher cover factor at lower weights of fabrics made from it. Its extensibility is >30% with good knot and loop strength. The applications of high performance P84 include protective clothing, as a sealing or packing material, for hot gas filtration and in aviation and space including covers for aircraft seats.[28] Mitsui Toatsu Chemical Co. has also claimed the development of a more heat-resistant aramid fibre. This fibre has been made from an aromatic isocyanate and an aromatic carboxylic acid.

Table 10.2 Properties of selected high temperature fibres[10]

Fibre properties	Aramid[a]	Carbon[b]	Glass (type)	PBI	Novoloid phenolic	PPS	Polyacrylate	PTFE	Polyimide	Polyamide-imide
Tensile and physical properties										
Tensile strength (Gpa)	0.6 M 3.4 P	4	3.5 E 4.6 S	0.37	0.26	0.42	0.22	0.18	0.35	0.32
Modulus (Gpa)	17.0 M 99 P	230	72 E 87 S	5.7	3.0	7.3	4.36	4.5	6.2	N/A
Elongation at break (%)	22 M 3.0 P	1.8	4.8 E 5.4 S	30	30	40	20–30	19–140	19–21	15–20
Moisture regain (%)	6.5 M 4.0 P	9	<0.1	15	6–7.3	0.6	12	0	3.0	3.4
Density	1.38 M 1.45 P	1.40	2.55 E 2.48 S	1.43	1.27	1.37	1.50	2.10	1.41	1.34
Abrasion resistance	Good M Poor P	Poor	Poor	Good	Poor	Good	Fair	Good	Good	Good
Resilience	Excellent	Poor	Poor	Excel	Fair	Good	Good	Poor	Fair	N/A
Chemical resistance										
Acids concentrated	Fair P	Poor	Excel	Excel	Poor	Good	Excel	Excel	Excel	Fair
Alkalis concentrated	Good P	Poor	Fair	Good	Excel	Excel	Excel	Excel	Poor	Good
Ultraviolet	Poor	Good	Excel	Good	Excel	Excel	Excel	Excel	Good	Good
Thermal properties										
LOI	30 M 29 P	55	>100	38	33	34	43	>95	40	32
Thermal conductivity (BTU-in hr^{-2}°F^{-1})	0.26 M 0.30 P	<0.03	7.20	0.26	0.28	0.30	0.31	0.20	N/A	0.08
Usable temperature (°C)	315–370	V.High	V.High	>595	400	260	[c]	430	<485	>420
Short term continuous	230	500	315	315	205	205	160	288	260	250
Smoke emission density	1.0	N/A	Low	Trace	<0.30	NA	Trace	Low	<1.0	<2.0

PPS = Poly(phenylene sulphide).

[a] M = poly meta-aramid (Nomex); P = poly para-aramid (Kevlar129); modulus (GPa) = (gpd × density) /11.33. [b] Celion 3000 (HS). [c] Auto ignition at 450 °C and 100% oxygen.

10.4.1.2   Poly(amide-imide) fibres

Rhone-Poulenc produces polyamide–imide fibre called Kermel. This is available in two forms: 234 AGF and 235 AGF. Type 234 is a staple fibre for use in both cotton and worsted spinning systems, and is produced in five spun-dyed colours. Type 235 is intended for nonwovens applications. In France, Kermel is used by firefighters and military personnel where the risk of fire is higher than usual. Its LOI is 31–32%, and it resists up to 250 °C exposure for a long duration. At 250 °C after 500 hours exposure, the loss of mechanical properties is only 33%. Kermel fibre does not melt but carbonises. During its carbonization it generates very little opacity. Blends of 25–50% Kermel with FR viscose offer resistance to ultraviolet (UV) radiation and price advantage also compared with 100% Kermal fabrics. Blending with 30–60% wool also produces more comfortable woven fabrics with enhanced drape. In the metal industry, the 50:50 blend gives very good results, but a 65:35 Kermel/viscose blend is preferred for such applications. Kermel-based fabrics are now used both on-shore and off-shore by leading petrochemical groups. The army, navy and air-forces are also using Kermel in woven and knitted forms.

10.4.1.3   Polybenzimidazole (PBI) fibres

Celanese developed PBI,[28,30,31] a non-combustible organic fibre. Its LOI is 41% and it emits little smoke on exposure to flame. PBI can withstand temperatures as high as 600 °C for short-term (3–5 s) exposures and longer term exposure at temperatures up to 300–350 °C. It provides the same protection as asbestos while weighing half as much. It also absorbs more moisture than cotton. The current area of interest in PBI is in the replacement of asbestos-reinforced rubbers used in rocket motors and boosters to control ignition. Its other applications include fire blocking fabrics in aircraft seats, firefighter suits and racing-car driver suits. Studies of subjective wearer evaluations have shown that PBI fibre exhibits comfort ratings equivalent to those of 100% cotton.

Ballyclare Special Products, UK[31] has recently developed a fire-resistant garment assembly for firefighter's safety. The outer fabric of the garment is made from Pbi Gold(R), a fire-resistant fabric from Hoechst Celanese. This fabric, which was originally developed for the US Apollo space programme, combines the comfort, thermal and chemical resistance of polybenzimdazole (PBI) with the strength of aramid fibre. Pbi Gold is stable even under simulated flash conditions at 950 °C. The fabric is also resistant to puncturing, tearing and ripping.

10.4.1.4   Poly(phenylene sulphide) PPS fibres

Ryton (Sulfar) fibres (Tm 285 °C) produced by Amoco Fabrics and Fibres Co. are nonflammable. They do not support combustion under normal atmospheric conditions, and the LOI is 34–35%. Chemical resistance and the ability to retain physical properties under extremely adverse conditions make the fibre valuable for protective clothing.

10.4.1.5   Polyacrylate (Inidex)

Polyacrylate[10,30] is a crosslinked copolymer of acrylic acid and acrylamide. Its LOI is 43%, and when subjected to flame, it neither burns nor melts. It emits virtually no smoke or toxic gases. Because of its low strength and brittleness, it can be used in nonwovens although the durability of fabrics made from this fibre may not be adequate for some apparel uses. As Inidex also offers protection from attack by

chemicals, including strong acids and alkalis, it may be found useful in filtration of liquids and hot gases.

10.4.1.6   Semicarbon/Panox fibres

These fibres[32] are produced by thermal treatment (thermo-oxidative stabilization) of either viscose or acrylic fibres. Asgard and Firotex are produced from viscose while Panox, Pyromex, Fortasil, Sigratex and so on are made from acrylic precursors. The acrylic fibres can be oxidised in the fibre, filament or fabric form at 220–270 °C in air, but the viscose fibres are generally partially carbonized in the fabric form in a nitrogen atmosphere.

These semicarbon fibres have excellent heat resistance, do not burn in air, do not melt and have outstanding resistance to molten metal splashes. After exposure to flame, there is no afterglow and fabrics remain flexible. In view of their outstanding properties, the Panotex fabrics (Universal Carbon Fibres) made from Panox (RK Textiles), for example, are ideal for use in protective clothing where protection against the naked flame is required. Currently, this range of fabrics is probably the most common and versatile of oxidised acrylic-based materials. Panotex fabrics can withstand flame temperatures in excess of 1000 °C, display very little shrinkage and yet, breathe like wool. However, the fabrics have relatively poor abrasion resistance. Therefore, a blend of oxidised acrylic fibre and an aramid used in a honeycomb woven fabric has been considered an ideal material as a fire blocker for aircraft seats and military tank crews. The honeycomb weave, which is intermittently tight and slack in construction, provides a spongy stretch fabric, which is easy to cut and fit around difficult shapes.

Panox/wool blends are suitable for flying suits. However, Panotex fabrics have high thermal conductivity and are non-reflecting. It is, therefore, necessary to have a suitable underwear to protect the skin while using Panotex in the outer layer of protective clothing. For this purpose a 60% Panox 40% modacrylic fibre double jersey fabric and a 60% wool 40% Panox core fibre have been recommended. In some cases, the heat conduction of Panotex fabrics can be of advantage in the construction of covers for aircraft seats; a fabric with a Zirpro-treated wool face and Panox back will probably spread the heat from a localized igniting source thereby delaying the ignition of underlying foam.

To prevent transfer of radiant heat, Panotex fabrics may be aluminized. An aluminized Panotex fabric is thus suitable for fire-proximity work but not for fire entry. It has been demonstrated that with a heat flux of $3\,W\,cm^{-2}$, an aluminium coating will ignite, but a stainless steel coating can withstand such a situation for a prolonged period. Multiple layers of Panotex fabric tend to protect a polyvinyl chloride (PVC)-simulated skin against irradiance as high as $170\,W\,cm^{-2}$ applied for 2 s.

Another advantage of Panotex outer fabric is the shedding of burning petrol, and it can even withstand several applications of napalm.

10.4.1.7   Phenolic or novoloid fibres

Kynol is a well-established novoloid heat-resistant fibre which is produced by spinning and postcuring of phenol formaldehyde resin precondensate. The fibre is soft and golden coloured with a moisture regain of 6%. When strongly heated, Kynol fabric is slowly carbonised with little or no evolution of toxic gases or smoke. However, its poor strength and abrasion properties preclude its application for

making apparel. To upgrade its mechanical properties, Kynol fibres can be blended with Nomex or FR viscose to produce flame-protective clothing.

Another phenolic fibre, Philene has also been developed, for example Philene 206 (0.9 den) and Philene 244 (2.1 den). The moisture regain of the fibre is 7.3% and is said to be non-flammable and self-extinguishing, with an LOI of 39%. It does not show any change in tensile properties after being heated for 24 hours at 140 °C (or for 6 hours at 200 °C). A charred Philene fabric is claimed to form a thermal insulating barrier that retains its initial form.

BASF[33] has also developed Basofil melamine staple fibres of 2.2 dtex with a tenacity of 2–4 cN dtex^{-1} and an elongation of 15–20%. It has LOI values of 31–33 and moisture regain is about 4%. Basofil can be used in continuous service at 200 °C. Above 370 °C, thermal degradation results in char formation rather than a molten drip. For protective wear, DREF-2 yarns comprising a 34 tex glass-fibre core is spun to Nm 12/2 (83 tex/2), sheathed with a blend of Basofil and para-aramid (80/20) to produce 400 g m^{-2} or 580 g m^{-2} fabrics required for foundries where these are constant hazards from molten metal splashes and sparks. Such materials may also be used to make proximity suits to protect against intense radiation or to make entry suits.

Kotresh et al.[34] have developed a flame-retardant fabric from DREF-2 friction spun core yarn of kevlar and FR viscose for anti-G suits (AGS) outer garment applications. This fabric has also been recommended for firefighters.

10.4.1.8   Modacrylic

Flame-retardant modacrylic under different brand names, such as Velicren FR (Montefibre, Italy) and SEF (Solutia Inc.) is a copolymer of acrylonitrile, vinyl chloride or vinylidene chloride in the ratio of 60:40 (w/w) along with a sulphonated vinyl monomer. It has an LOI in the range of 26–31%.

Kaneka Corporation has also developed Kanecaron, an FR modacrylic with an LOI value in the range of 30–35%. Fabrics from Kanecaron (e.g. Protex M) blended with cotton meet the requirements of BS 6249 Index B, while maintaining the softness and comfort of cotton.

10.4.1.9   Chlorofibre

Rhone-Poulenc's chlorofibre, Rhovylon FR and Clevyl is used in furnishing fabrics, nightwear and institutional blankets. It has quite a high LOI value of around 45%. Extensive testing has shown that chlorofibre meets International Standards for furnishing fabrics and it is in use in French high speed trains (TGVs) and a passenger liner (QE2).

10.4.2   Flame retardation of conventional textile fibres

10.4.2.1   FR viscose

Inherently flame-retardant viscose fibres are produced by incorporating FR additives/fillers in the spinning dope before extrusion. For example, Sandoflam 5060 (Sandoz), polysilicic acid or polysilicic acid and aluminium (Sateri).

Sandoflam 5060 contains both phosphorus and sulphur as shown in Structure I, bis (2-thio-5,5-dimethyl-1,3,2-dioxaphosphorinyl) oxide, below:
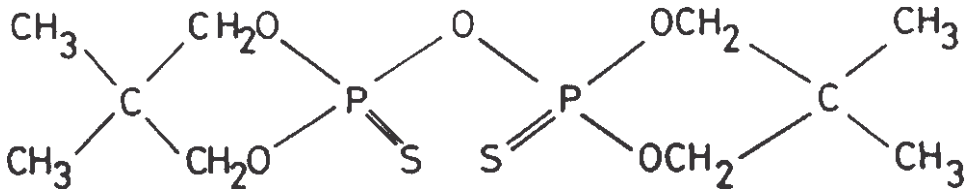
Structure I

Aqueous dispersions of pyro(thio)phosphates(II) containing polyoxyalkylenes have also been used as dope additives (15.8 parts) in 200 parts of 9% cellulose xanthate. The rayon produced from this mixture had an LOI value of 27.5 compared with 18 without the phosphate (II) dispersion (see Structure II).
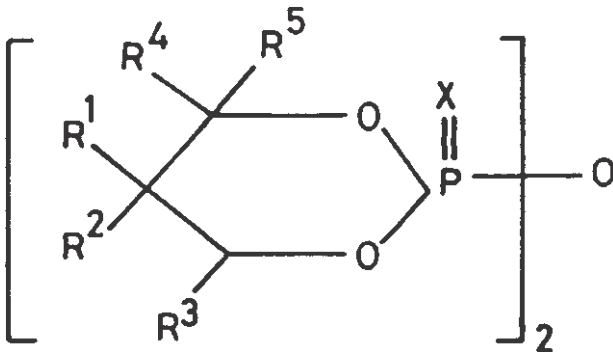
Structure II

R^1, R^2 = H, alkyl, CH_2Cl, CH_2Br, alkoxymethyl or R^1 = phenyl, R^3, R^5 = H, alkyl, R^4 = H, Me, X = O or S

Hoechst AG has previously offered an FR viscose staple fibre under the brand name Danufil CS. Here the FR additive was Sandoflam 5060 used in the viscose dope before wet spinning. The products offered were 1.7 and 3.3 dtex for short-fibre spinning and 4.0 dtex for long-fibre spinning. Its LOI value was 27%.

In 100% form, the fibre can be used for mattress covers and fire extinguishing blankets. A blend with aramid is suitable for protective clothing, such as army and fire service uniforms. Further, blending with wool shows a synergistic effect, and this blend is used for upholstery fabrics.

Lenzing AG currently produces Lenzing Viscose FR which contains Sandoflam 5060. It has been demonstrated that a wool/viscose FR blend performs better than either fibre alone and this is being used as seat covers in the Airbus 310.

DuPont and Lenzing AG have jointly developed a special blend consisting of 65% Viscose FR, 30% Nomex and 5% Kevlar for industrial wear under the brand name of Karvin[R].

Sateri (formerly Kemira) Fibres, Finland has developed an environmentally friendly hybrid viscose fibre containing cellulose and polysilicic acid under the brand name Visil[R], and viscose containing polysilicic acid and aluminium under the name

VisilAP$^{(R)}$. This hybrid fibre is a cellulosic fibre containing molecular chains of poly-silicic acid produced by wet spinning of water glass and alkaline cellulose xanthate during the coagulation process, the cellulose component is regenerated simultane-ously with the polymerization of polysilicic acid; $nSi(OH)_4 \rightarrow$ polysilicic acid.

The incorporation of polysilicic acid enhances the fire resistance of the hybrid by the following mechanism:[35–37]

- An inherently incombustible char is formed on the fibre surface.
- The temperature at which water is released from the fibre is lowered.
- The hydrated nature of the inorganic component suppresses the flame and exerts a self-extinguishing effect.

In another patent,[38] it is stated that polysilicic acid that contains aluminium silicate sites, a blend of viscose and water glass, after spinning, tow stretching and subse-quent washing with $40\,gl^{-1}$ Na aluminate solution and carding, showed an LOI value of 32. Properties of Visil fibre are given in Table 10.3.

Anand and Garvey[39] have also demonstrated the use of Visil/modacrylic and Visil/wool blends for use in protective clothing. In Visil/modacrylic blends, it has been shown that the level of flame retardancy is dependent not only on the fibre content, but the physical structure of the yarn as well. The blended ring spun yarn fabrics exhibited synergism relative to rotor spun yarn fabrics at each blend ratio (Visil/modacrylic: 16.7/83.3 to 83.3/16.7) in both char and LOI values. In contrast, Visil/wool blended fabrics failed in the BS 5438 strip test despite the higher LOI values (25.7–36%) of the blends. This anomalous behaviour has been attributed to the lofty wool structures which are known to burn extensively because of high oxygen accessibility to the fibre surface in the blended fabrics. Further, it may also be noted that in the LOI test, burning of the fabric takes place downward but in the vertical strip test upward burning conditions apply, which would favour the enhanced access of oxygen from the convective effects of the flame.

In another paper, Horrocks et al.[40] have shown that flame-retardant textiles can be developed in composite structures having fibre-intumescent interactive systems. The interactive pyrolysis of both components creates a fibrous char-reinforced intu-mescent charred derivative of the original structure, which offers a toughened and oxygen impermeable barrier to heat, flame and subsequent oxidation. The compos-ite structure comprised a nonwoven core ($200\,gm^{-2}$) of Visil in which an ammonium polyphosphate-based intumescent was dispersed and resin bonded up to 50% w/w. This core was sandwiched between a flame-retardant cotton face and backing woven fabric (Fig. 10.5). Exposure of this composite structure at around 500 °C in a furnace

Table 10.3 Physical and mechanical properties of Visil[36]

Linear density (dtex)	1.7, 3.5, 5.0, 8.0
Length (mm)	40 and 80 currently available
SiO$_2$ loading (%)	30–33, depending on grade
Cross-section	Kidney bean, irregular
Tenacity (cN/dtex)	1.5–2.0
Elongation-at-break (%)	22–27
Moisture regain (%)	9–11
Water imbibition (%)	50–60
Limiting oxygen index (%)	26–33, depending on grade or textile structure
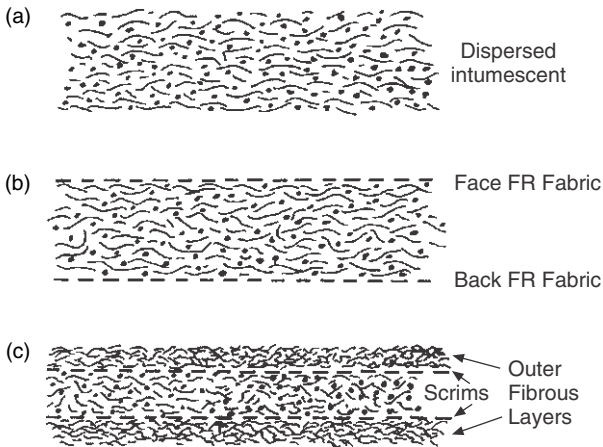
10.5   Textile/fibre applications of intumescent systems. (a) Random fibre web with dispersed intumescent, (b) same as (a) plus front and back FR fabrics, (c) similar to (b) but with fabrics located as reinforcing scrims.

showed that both the intumescent and organic cellulose component of the Visil charred along with the FR facing and backing fabrics. Simultaneously expanding the intumescent increased the thickness of the core fabric by a factor of 2. On further heating above 500 °C, the carbonized expanded composite slowly oxidised and the polysilicic acid content of the Visil was converted fully to silica.

These charred residues could survive 10 min exposure at 1100 °C while leaving the coherent inorganic silica residue at a similar thickness to that of the original fabric. The authors[41] also cite their patent in which they have disclosed the unique nature of such a composite structure for thermal protection, constructed from five layers as follows:

1   200 g m^{-2} Visil web,
2   120 g m^{-2} FR cotton woven fabric,
3   200 g m^{-2} Visil web containing the intumescent,
4   120 g m^{-2} FR cotton woven fabric,
5   200 g m^{-2} Visil web.

The intumescent content was varied from 100–250 g m^{-2} and the bonding resin (10% w/w on the basis of intumescent concentration) was added to it to produce the 'sandwich' structure.

10.4.2.2   Flame-retardant polyester

There are three methods of rendering synthetic fibres flame retardant:

- use of FR comonomers during copolymerization,
- introduction of an FR additive during extrusion,
- application of flame retardant finishes or coatings.

The first two methods would give inherently flame-retardant polyester fibres.

Trevira CS$^{(R)}$ and Trevira FR$^{(R)}$ produced by Hoechst are flame-retardant polyesters. Both are manufactured by copolymerizing a bifunctional organophosphorus compound based on phosphinic acid derivative (Table 10.4):

Table 10.4   Flame-retardant additives for polyester fibres[4]

Additives/Co-monomor	LOI	Reference
Phosphorus-based		
Phosphinic acid derivative (Trevira CS)	29–30	81
HO-P(O) XYCOOH		
X = H or alkyl		
Y = alkyl		
Bisphenol S oligomer (Toyobo GH)	28	81
Cyclic phosphonate (dimeric)	27–28	
(Antiblaze 1045)		
37.5: bisphenol S +	29	
55.35: Neopentyl glycol		JP 79,80,355(1979)
chlorophosphate →		*Chem. Abstr.* **91**,
5 parts FR ester + PET (100)		194591r (1979)
100 parts: PET	Good FR with no	50
7 parts: cresyl diphenyl phosphate	dripping fibre web	
5 parts: triallyl cyanurate	irradiated with	
	electron beam	
100 parts: PET	Resistant to	51
7 parts: diphenyl cresyl phosphonate	heating and melting	
[2,5-bis(2-hydroxyethoxy) phenyl]-	30	*Chem. Abstr.* **122**,
diphenyl phosphine oxide		83672h (1995)
mpt 195 °C		
Tetrakis (hydroxymethyl) phosphonium	28	*Chem. Abstr.* **122**,
chloride		12081c (1995)
Halogen-based		
p-bromophenoxycyclophosphazene	28	*Chem. Abstr.* **112**,
		8647t (1990)
Decabromodiphenyl oxide	29	*Chem. Abstr.* **99**,
		6796e (1983)
Neopentyl glycol chlorophosphate	29	*Chem. Abstr.* **91**,
		194591r (1979)

The LOI of Trevira CS fabric, having 0.6% phosphorus, is 28% and the burning fabric does not give rise to burning molten droplets. Subject to fabric construction, dyeing and finishing processes, interior textiles made from flame retardant Trevira (containing 0.6% w/w phosphorus) can be anticipated to pass all the stringent international test standards[42], such as BS 5867 part 2 type C for textiles, curtains and drapes.

Hoechst claims that the production of flame retardant Trevira is environmentally a clean process compared to other artificial and natural fibre fabrics. Tests on the toxicity of burning fabrics at increasing temperatures demonstrate the superiority of Trevira CS polyester fabric which is even less toxic as compared to treated FR cotton (Fig. 10.6). Trevira CS and FR are chlorine-free, unlike modacrylics (which contain up to 50% PVC) and PVC chlorofibres. They also liberate extremely low levels of toxic gases and smoke when exposed to an ignition source. There is zero hydrogen cyanide released, for example, in marked contrast to both smouldering and flaming FR wool, or modacrylics. Hence fumes released from Trevira polyester when it is subjected to 700 °C temperature, indicate a mortality rate of only 8% com-
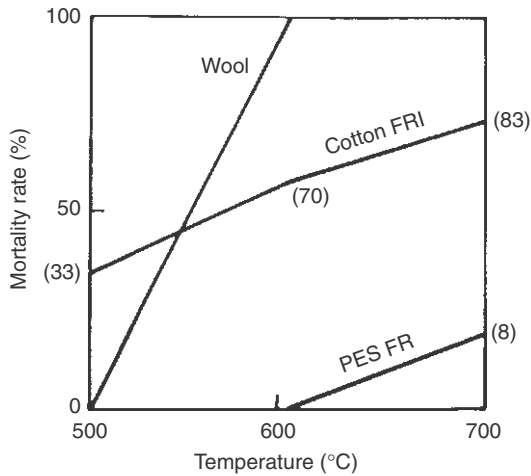
10.6   Toxicity of fabrics at different burning temperatures. PES = polyester.

pared with cotton FR which results in a mortality rate of 83% in experimental animal tests. Thus, Trevira CS/FR has been approved for the Oeko-Tex standard 100 certificate as containing no harmful substances.

Toyobo GH also licensed a flame retardant polyester to Montefibre, which is believed to be a sulphone–phosphonate copolymer. Ma *et al.*[43] have reported the synthesis and properties of intumescent, phosphorus-based flame-retardant poly-esters. Spirocyclic pentaerythritol di(phosphate acid monochloride) was used as a comonomer (Structure III):
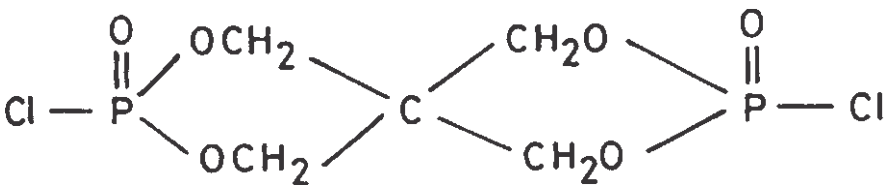
Structure III

The LOI value was found to be 27–30 and the analysis of the SEM photographs of the copolymer chars indicated the presence of solid phase intumescence.

Unitika[44,45] has also developed new flame-retardant melt spun polyester using [2,5-bis(2-hydroxyethoxy)phenyl]diphenyl phosphine oxide and bis(β-hydroxy ethyl)terephthalate copolymer. The filament is of the sheath–core type with regular polyester as the sheath and copolymer polyester as the core. This sheath–core struc-ture provides stability to heat in the texturing process and facilitates texturing. The LOI value of this FR polyester is 30%. It resists burning as it has a self-extinguish-ing property. Moreover, it generates no hazardous gases while burning.

Horrocks *et al.*[46] have developed an analytical model for understanding the envi-ronmental consequences of using flame-retardant textiles. An environmental rank value is given at each stage in the manufacturing process and product life of each

flame-retardant fibre textile. The results show that each of the eleven generic fibres analysed showed an environmental index value within the range of 32–51%, where 100% denotes the worst environmental position possible.

Zubkova[47] has recommended the use of poly(vinyltriethoxy)silane microencapsulated T-2 fire retardant in polyethylene terephthalate (PET) melt prior to extrusion, to reduce the combustibility of polyester and its blends.

In the patent literature, Japan Exlan Co.,[48] has also disclosed the production of flame-retardant polyester conjugate fibres. These are polyesters containing 0.5–5.0 mol% (based on total acid components) inorganic boron compounds as the core and polyester containing phosphorus, Mg or Si compounds as the sheath. Thus, ethylene glycol (I) and terephthalic acid (II) were esterified and polymerized in the presence of 1.5 mol% (on the basis of total acid component) B_2O_3 to give polyester (III), and I was polycondensed with II in the presence of 1.5 mol% $Mg(OAc)_2$ to give III. Then III containing B_2O_3 as core and III containing $Mg(OAc)_2$ as sheath were cospun at 295 °C and drawn to give conjugated fibres with excellent fire resistance even after washing.

Japan Exlan[49] has also disclosed the use of OH-terminated poly(dimethyl siloxane) or silane coupling agents as the sheath component for producing FR polyester bicomponent fibres.

Unitika[50,51] recommended the use of cresyl diphenyl phosphate or phosphonate (7 parts) and triallyl cyanurate (5 parts) in 100 parts PET prior to melt spinning. The fibres were then woven and irradiated with electron beam to 20 Mrad dose which showed good flame retardance and no dripping. Some of the FR additives/comonomers disclosed in the patent literature for polyester are listed in Table 10.4.

10.4.2.3   Flame-retardant nylon

Nylons have a self-extinguishing property due to extensive shrinking and dripping during combustion. Problems arise in blends with natural fibres like cellulosics which will char and form a supporting structure (the so-called scaffolding effect) which will then hold the molten polymer.

Introduction of flame or combustion retarders into polyamide melts before spinning appears to be an economical and feasible process if they are stable. Butylkina *et al.*[52] compared the performance of non-melting type compounds (e.g. lead methylphosphonate and a complex of alkylphosphonic acid and antimony) with highly viscous FR compounds like phosphorylated pentaerythritol (Fostetrol(R)) and phosphorus-based Borofos(R) as dope additives during melt spinning of nylon 6. The oxygen index value of about 50% was found in FR nylon 6 having (2 w/w% of antimony) as an antimony complex of alkyl phosphonic acid but the carbonized residue/char was found to be highest when Borofos was used as melt additive.

In another study, Tyuganova *et al.*[53] have used a ternary system of flame retardant, namely, boric acid, brominated pentaerythritol and antimony oxide mixed into the polymer melt prior to extrusion. It has been demonstrated that boron compounds display condensed phase active mechanisms and increase the yield of water and carbonized residue, while halogen-containing compounds are effective inhibitors of free radical reactions in the gas phase. A nylon sample having 2.28 w/w% Boron, 3.09 w/w% Br and 2.26 w/w% Sb showed the LOI value of 29.2.

Allied Signal[54] has disclosed in a patent the use of zinc (0.01–2.9 w/w%), molybdenum (0.002–0.58 w/w%) as calcium zinc molybdate and 0.05–1.3 w/w% chlorine, as chlorinated ethylene in nylon 6 melt for producing flame-retardant fibre for

carpets. The dyed carpets were backed with regular SBR latex and Actionbak secondary backing. Flammability was tested by the ASTM E-648 Flooring Radiant Panel Test. The sample with compound B (as Kem Gard^{TM} 425) from Sherwin-Williams as molybdenum-based flame retardant (0.3 w/w%) and compound A (chlorinated polyethylene with 25% chlorine) at 0.7 w/w% had an average of greater than 1.13 W cm^{-2} compared to 0.43 W cm^{-2} for the control carpet. Thus, FR carpet developed by Allied Signal was a class I carpet, while the control was a class II carpet as per the ASTM-E 648 test method.

Day et al.[55] have made a systematic study of the role of individual constructional components in the flammability characteristics of carpets. It was shown that carpets that are glued to cement asbestos board are less easy to ignite, burn at a slower rate, and give off less smoke and heat compared to carpets not glued down.

Stoddard et al.[56] have also studied the effect of construction parameters, face yarn additives and backing materials on the flame retardancy of nylon 6.6 carpets. A number of halogen-containing FR additives were introduced into nylon 6.6 melt before extrusion. The melt-stable additives were Dechlorane+25^R, hexabromobiphenyl and decabromobiphenyl oxide. Alumina trihydrate in the carpet latex and application of polyvinyl chloride to the face side of the primary backing were also used. It has been observed that FR carpets containing lower levels of Dechlorane/antimony oxide (2/1 w/w%) burnt for longer periods but extinguished between 2–9 min, while carpets containing 3 w/w% decabromobiphenyl oxide under similar test conditions extinguished in 5.5–10.5 min.

Organophosphorus compounds were also used as melt additives in nylon 6.6. These phosphorus derivatives in most cases reduced polymer viscosity to too low a degree for fibre formation and they also had very poor wash resistance.

Reduced flammability of nylon by use of potassium iodide[57] has also been disclosed. KI (<5 w/w%) as an additive in nylon textile fibres improved the heat, light and dye stability of fibres. The iodides used are Na, Li and other inorganic iodides and a combination of antimony oxide and inorganic iodides and inorganic phosphates.

Phosphorus-containing polyamide fibres with increased stain and fire resistance have also been disclosed by Monsanto Co.[58] Thus, bis(2-carboxyethyl)phosphinic acid neutralised with NaOH, was polymerized with nylon 6.6 salt and hexamethylenediamine to give phosphorus-containing polyamide fibres with enhanced flame resistance.

Levchik et al.[59] have suggested the role of inorganic fillers (talc, CaCO$_3$, ZnCO$_3$, MnO$_2$) in improving the flame retardance of a nylon 6/ammonium polyphosphate (APP) blend. It has been observed that MnO$_2$ oxidises nylon 6 thereby enhancing the char yield from the polymer. Furthermore, these fillers react, which increases the solid residue, improves thermal shielding of the char and gives inorganic glasses, which hinder propagation of the flame by combustible gases.

10.4.2.4   Flame-retardant acrylic fibres

Like other synthetic fibres, acrylic fibres shrink when heated, which can decrease the possibility of accidental ignition. However, once ignited, they burn vigorously accompanied by black smoke. Thus, many efforts have been devoted to improve the flame resistance of acrylic fibres.[60–67] Among these studies, halogen-based and particularly bromine derivatives or halogen- or phosphorus-containing comonomers, are the most effective flame retardants used in acrylic fibres.

Self-extinguishing modacrylic fibres have been produced from vinylidene chloride and acrylonitrile copolymers or terpolymers.[68–69]

A number of spinning dope additives are also known to render acrylic fibres flame retardant (Table 10.5), for example esters of antimony, tin and their oxides, SiO_2, halogenated paraffins, halogenated aromatic compounds, phosphorus compounds,[70–74] and so on. Bromine compounds have been found to be most effective flame retardants for acrylic fibres. The flame-retardant mechanism of these halogen compounds is believed to be associated with the interaction of halogen with reactive moieties of the flame itself.

While it is often considered that hydrogen halide reduces the concentration of the free radicals $OH^.$ and $H^.$, which help in propagation of the flame, thus following a gas phase reaction mechanism, this seems not to be the case following the pyrolysis of PAN (polyacrylonitrile) and its copolymers under burning conditions. Hall et al.[66] have demonstrated the role of various inorganic and organic phosphorus and nitrogen, or sulphur or halogen-containing derivatives with or without antimony oxide (Table 10.6). From thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and residual char-forming techniques, they have shown that flame retardancy relates directly to char-forming tendency for all the flame retardants and their ability to reduce the flammable volatiles formed during the first stage of acrylonitrile copolymer pyrolysis. Ammonium dihydrogen phosphate has been found to be the most char-forming flame retardant.

Various stages of acrylic polymer pyrolysis have been systematically studied by the same authors.[66] It is interesting to note that apparent activation energies of the acrylonitrile polymer cyclization reaction have been reduced and the lowest values are for $NH_4H_2PO_4$ containing copolymers. This suggests that the more effective, char-promoting flame retardants may initially modify the cyclization reaction to favour production of char-forming precursors. From the thermal data, a positive linear relationship between LOI and the char yield obtained at 500 °C at respective LOI values (Table 10.7) has been observed (Fig. 10.7) using the following linearly regressed equation under isothermal conditions

$$LOI = 17.0 + 0.40 \ (\text{char w/w\%}) \tag{3}$$

**Table 10.5**   Possible dope additive for making flame-retardant (FR) acrylic fibres[8]

Polymer	Additive	Property	Reference
P(AN-vinyl chloride)	5% Dibutyl tin ethyl maleate	FR fibres	8
Acrylonitrile (AN) copolymer with 3.5% Cl (chlorinated aliphatic acid ester)	0.6% Sb_2O_3 and 0.07% Bu_2SnO	FR fibres with good dyeability, strength and transparency	8
PAN	Finely divided inorganic tin compound	FR fibres with improved gloss, transparency, whiteness, and dyeability	8
P(AN-vinylidene chloride)	$SnCl_4$ and NaOH	Fibres with good transparency and lustre	8

Table 10.5 *Continued*

Polymer	Additive	Property	Reference
P(AN-vinylidene chloride-vinyl chloride)	Compounds containing Sb, Al, Sn, or Zn	FR fibres	8
P(AN-vinylidene chloride-vinyl chloride)	Dispersion of Sb_2O_3 particles in the dope	FR fibres	8
Polymer with AN $\geq$ 50%	15–50% of a metal oxide filler with mean particle size 1–10 nm	FR fibres	8
PAN	Cyanoethyl (*N,N*-dimethyl amido)-phosphate, tris(β-chloroethyl) phosphate	FR fibres	8
P(AN-methyl acrylate-sodium methallyl sulphonate)	0.5–5.0 wt% of cyclic phosphonitrile compound containing phenoxy groups	LOI = 24.1	8
PAN	12.5% Tetrabromobisphenol A	LOI > 30	8
PAN	Polychlorotrifluoroethylene	Fibres with low flammability	8
P(AN-vinyl acetate)	Bu_3PO_4 Tris(dibromopropyl) phosphate or $Al(OH)_3$ gel	LOI ~ 29 synergistic flame retardant	64
P(AN-vinylidene chloride)	Ca phosphate and Sb_2O_3		
P(AN-vinyl acetate)	15% Hexabromocyclododecane (Great Lakes CD-75P) 15% poly(dibromostyrene) (Great Lakes PDBS)	LOI 41–45.5 LOI 43–48	67
P(AN-vinyl chloride and/or vinylidene chloride/sodium methallyl sulphonate) 70 parts + 15 parts cellulose diacetate	37.5 parts colloidal soln. of Sb_2O_5 in dimethyl acetamide + 380 parts dimethyl acetamide	LOI = 36 Ts = 2.8 g/d Elongation = 36%	71
P(AN-Na styrene sulphonate – vinyl chloride – vinylidene chloride) 30% solution in Me_2CO	30% SnO_2 (av. diameter 0.05 μm) + 4% HCl + 0.15 part bisphenol-A-diglycidyl ether	LOI 35.5	72, 73

Table 10.6   Selected flame retardants[66]

Flame retardants	Flame-retardant elements
Ammonium polyphosphate (APP) (Amgard MC) (Albright & Wilson Ltd.)	P and N
Ammonium dihydrogen phosphate (ADP)	P and N
Diammonium hydrogen phosphate (DAP)	P and N
Proban cc (NH_3 condensate of THPC urea) (Albright & Wilson Ltd.)	Organic P and N
Sodium dihydrogen phosphate	P
Hexabromocyclododecane (hexa) (Schill & Seilacher Ltd.)	Aliphatic Br
Decabromodiphenyloxide (deca) (Schill & Seilacher Ltd.)	Aromatic Br
Antimony trioxide (Aldrich Chemical Co.)	Sb
Ammonium thiocyanate	S and N
Urea	N
Melamine	N
Sandoflam-5060 (Sandoz)	S and P
Ammonium chloride	Cl and N
Thiourea	S and N
Red Phosphorus (Amgard CRP) (Albright & Wilson Ltd.)	P
Diammonium sulphate	S and N
Zinc phosphate (Aldrich Chemical Co.)	P and Zn
Zinc borate (Aldrich Chemical Co.)	B and Zn
Flacavon-TOC (Schill & Seilacher Ltd.)	organic Br + Sb
Amgard CUS (Albright & Wilson Ltd.)	P and N
Phosphonitrilic chloride trimer (Aldrich Chemical Co.)	P, Cl and N
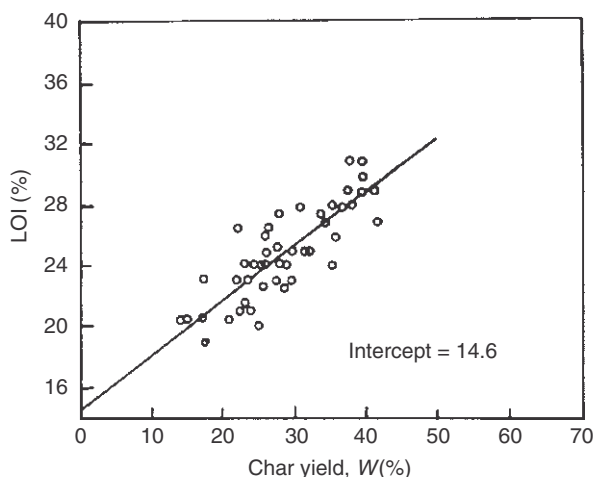
10.7   LOI–char relationship of acrylic polymers with various flame retardants under LOI burning conditions.

Table 10.7 LOI values and char production of acrylic polymers with various flame retardants[66]

Polymer (100 parts)	Flame retardant (parts)	LOI %	Char yield at LOI	Char yield at 31% O_2	Char yield[a] at 500 °C
PAN	–	19.0	17.3	11.8	19.7
PAN	Ammonium dihydrogen phosphate (15)	27.0	34.4	32.0	–
P(AN-VA), 10% VA (vinyl acetate)	–	20.4	14.9	13.2	22.0
	Ammonium dihydrogen phosphate (15)	31.0	39.8	39.8	52.0
	Ammonium polyphosphate (15)	31.0	38.1	38.1	62.1
	Diammonium hydrogen phosphate (15)	30.0	–	–	47.5
	Sandoflam-5060 (15)	27.0	–	–	42.5
P(AN-MA) 10% MA (methyl acrylate)	–	20.4	20.8	15.9	27.7
	Ammonium polyphosphate (15)	29.0	39.1	37.7	65.2
	Ammonium dihydrogen phosphate (15)	28.0	36.7	35.0	58.9
	Diammonium hydrogen phosphate (15)	27.0	41.7	40.0	60.4
	Antiblaze CUS (15)	27.0	34.3	33.0	–
	Red phosphorus (15)	26.5	22.0	20.6	40.1
	Sandoflam-5060 (15)	26.0	35.8	33.3	40.3
	Flacavon-TOC (15)	26.0	29.6	27.3	42.5
	Proban CC (15)	24.0	28.9	27.8	43.6
	Urea (15)	23.0	17.0	16.1	36.6
	Sodium dihydrogen phosphate (15)	23.0	21.9	20.4	29.2
	Thiourea (15)	23.0	26.0	25.0	42.5
	Zinc phosphate (15)	22.7	23.0	22.0	–
	Zinc borate (15)	22.6	24.5	23.5	–
	Hexa[b] (10) + antimony oxide (III) (5)	27.5	27.8	–	41.5
	Hexa (15)	26.5	26.4	–	33.0
	Deca[c] (15)	25.0	26.2	–	33.5
	Deca (10) + antimony oxide (III) (5)	25.2	27.6	–	40.0

[a] Char yield obtained from isothermal pyrolysis at 500 °C and calculated at 200 s. [b] Hexabromocyclododecane. [c] Decabromodiphenyl oxide.

On this basis, it may be concluded that char-promoting flame retardants, such as ammonium phosphates, are more effective than vapour phase inhibiting bromine-containing flame retardants.

Fire-resistant acrylic fibres[74–76] have also been manufactured by coating partially oxidised acrylic fibres (heated in air at 250 °C under tension for 15 min) with
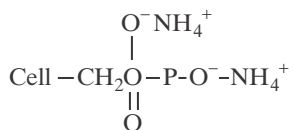
phosphoric acid (2.0 vol% in methanol) or 2.5% guanidine phosphate. After coating with the latter the LOI increased to 42. In another patent, Japan Exlan disclosed the use of hydrizine hydrate ($30 \text{g} \text{l}^{-1}$) for crosslinking with $ZnCl_2$ after hydrolysing the fibres with 30% NaOH. The fibres, P(AN-MA) (poly(acrylonitrile–methylacry late)) thus cross-linked with 5% $ZnCl_2$ solution for 30 min at 20 °C gave fibres with an LOI value of 34.
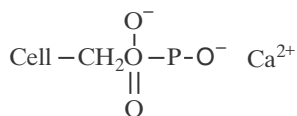
10.5   Fire-retardant finishes

A number of fire-retardant finishes and their modes of application have been well documented by Drake and Reeves,[77] Holme,[78] Wakelyn et al.,[79] Barker and Drews[80] and Horrocks.[81]

10.5.1   Cellulosic fibre fabrics

An early review of cellulose phosphorylation by Reid and Mazzeno[82] showed the typical structure of cellulose phosphate ester, Structure IV:

$$\text{Cell} - \text{CH}_2\text{O} - \overset{\overset{\displaystyle \text{O}^-\text{NH}_4^+}{|}}{\underset{\underset{\displaystyle \text{O}}{||}}{\text{P}}} - \text{O}^- - \text{NH}_4^+$$

However, exchange with hardness ions such as Ca^{2+} and Mg^{2+}, available in hard water, gave a salt, Structure V:

$$\text{Cell} - \text{CH}_2\text{O} - \overset{\overset{\displaystyle \text{O}^-}{|}}{\underset{\underset{\displaystyle \text{O}}{||}}{\text{P}}} - \text{O}^- \quad Ca^{2+}$$

This salt is stable and prevents the release of phosphoric acid on heating, the effectiveness of the flame-retardant finish thereby being reduced.

Phosphorylation of cellulose by means of diammonium phosphate (DAP)/urea gives rise to a finish that resists exchange of Ca^{2+} ions, although it is saponified by alkaline washes. The use of titanium, zirconium, or tin salts as a post-treatment of phosphorylated cotton also minimizes the exchange with hardness ions.[83]

The application of various finishes has been summarized well by Horrocks[81] (Table 10.8). The commercially most successful finishes are the N-methylol dialkylphosphonopropionamides, from which Pyrovatex CP (Ciba-Geigy) is derived.

Another product, Pyrovatex7572[(R)] (N-dimethylol dimethylphosphonopropionamide) has also been developed to obtain improved reactivity with the fibre. With environmental and safety issues in mind, an improved Pyrovatex CP reduces formaldehyde emissions during processing by over 50% and there is a remarkable reduction of tar build-up in the stenter/curing chamber during curing. This finishing agent carries the PA111 certificate and also meets the international Oekotex Standard 100.

Table 10.8 Selected retardant-finish formulations for cotton[8,81]

Finishes and coatings	Application
Finishes	
$(CH_2OH)_4P^+X^-$ tetrakis(hydroxymethyl)-phosphonium (THP) salts, where $X = Cl$, OH, $(1/2)(SO_4)^{2-}$ often as a condensate with urea, e.g. THPC-urea-NH$_3$, Proban CC (Albright and Wilson)	(i) Apply with trimethylolmelamine, heat cure at 160 °C (ii) Apply and cure with ammonia gas and oxidise with H$_2$O$_2$
$(CH_3O)_2POCH_2CH_2CONHCH_2OH$ *N*-methylol dimethyl phosphonopropionamide, Pyrovatex CP (CIBA)	Apply with melamine resins, cure at 160 °C
Pyrovatex 7572	Pad-dry-cure, chemical cross-linking
Ammonium polyphosphate	Non- or semidurable depending on '*n*'
Diammonium phosphate	Non-durable
Ammonium sulphamate + urea or urea-based cross-linking agent	Curing at 180–200 °C for 1–3 min. Treated fabrics pass the vertical flame test (VST) even after 50 hard alkaline launderings
Coatings	
Sb$_2$O$_3$/chlorinated paraffin wax	Apply from solvent
Sb$_2$O$_3$ or Sb$_2$O$_5$ + decabromodiphenyl oxide or hexabromocyclododecane + acrylic resin e.g. Myflam (B F Goodrich, formerly Mydrin)	Semi to fully durable

Other durable treatments include the use of ProbanCC$^{(R)}$ (Albright & Wilson). It involves padding of tetrakis (hydroxymethyl) phosphonium chloride (THPC)/ urea solution onto the fabric, curing with ammonia in a specially designed reactor to generate a highly crosslinked phosphorus–nitrogen three-dimensional polymer network. Cotton fabric finished with ProbanCC is subsequently treated with hydrogen peroxide which converts the P^{3+} to the P^{5+} state and enhances the durability of the finish. Pyrovatex CP is generally used for curtains while ProbanCC, which retains greater strength, is used for hospital bed sheets and so on. However, Le Blanc[84] has observed the loss of phosphorus content in Pyrovatex CP new treated cotton during storage at room temperature and after steam sterilization. It is assumed that the loss of phosphorus, consequently leading to failure in flame retardant properties, could be due to the following:

- Hydrolysis of the methyl ester groups of *N*-methylol dimethylphosphonopropionamide (MDPPA) molecules, which are not attached to cellulosic hydroxyl groups, producing – H$_2$C P(O)(OH)$_2$ groups which are acidic in nature.
- Acidity of these groups further accelerates the hydrolysis of more methyl ester groups and also cleaves the ether linkages between the MDPPA and cellulose.

The fabrics treated by modified process retained their FR properties, even up to 100 launderings. Morrison from Albright & Wilson Ltd. has given an excellent report concerning the application of FR treatments after the introduction of flammability regulations in the UK for furnishing fabrics.

Both Proban and Pyrovatex can satisfy the requirements of the UK Furniture and Furnishings (Fire Safety) Regulations, 1990 when applied at lower application levels. Pad bath additives normally consist of Pyrovatex CP new, orthophosphoric acid catalyst, and a low formaldehyde melamine resin and a softening agent. However, for some furnishing fabrics, a combination of melamine resin and a tetramethylol acetylene diurea-based resin is added to the pad bath.

New systems which provide extended durability to soaking include Amgard LR1[(R)] and Amgard LR2[(R)] for application to cellulosic or cellulosic-rich blends. Pad bath solutions consist of Amgard LR1 (ammonium polyphosphate-based solution), a fluorocarbon, water and soil repellent, softening agent and volatilisable wetting agent and water.

Many coating systems have also been recommended for the production of FR upholstery fabrics. New generation coating systems include Amgard LR4[(R)] and Amgard LR3[(R)] phosphorus-based flame retardants that are halogen and heavy metal free. The Amgard LR4[(R)] system is a mixture, a low solubility ammonium polyphosphate and Amgard LR2 (ammonium polyphosphate-based solution), applied in combination with an antifoaming agent and an acrylic-based latex.

Horrocks and co-workers[81,85] have demonstrated the role of char-forming and intumescent systems in the flame retardation of textiles. It is interesting to note that the majority of intumescent systems are based on ammonium polyphosphate (an acid source), melamine and its derivatives (as blowing agents) and pentaerythritol derivatives as char-forming agents.

Camino and Costa[86] studied the mechanism of intumescent char formation of ammonium polyphosphate (APP), pentaerythritol and pentaerythritol diphosphate combination. According to them,

1   APP starts decomposing at 210 °C onwards and phosphorylation of polyol occurs without elimination of gaseous products.
2   Subsequent phosphorylation produces cyclic phosphate esters.
3   Between 280–330 °C, the polyol phosphates decompose to char with considerable formation of phosphoric acid, which subsequently polymerises to polyphosphoric acid.

The degree of char expansion depends on the rates of gas/volatiles evolution, the viscosity of the liquefied pyrolysis products and the transformation of the latter to solid char which acts as a barrier.

Char studies of flame-retardant cellulose have indicated that most phosphorus remains in the char. However, Drews and Barker[87] showed that the phosphorus retention in chars depends on the reactivity of phosphorus moieties with cellulose.

Faroq et al.[88] have also established that the simple competitive pyrolysis mechanism in cellulose proposed by Kilzer and Broido[89] is influenced by the nature of the flame retardants. Figure 10.8 shows this modified mechanism and includes the 'activated cellulose' intermediate state as postulated by Bradbury et al.[90] Lewin[91] has reported the use of sulphamates as flame retardants. Cotton fabrics were treated with ammonium sulphamate in conjunction with urea or a urea based crosslinking agent, as a coadditive by pad dry cure method. Treated fabrics, both cotton and woollens passed the vertical strip test (VST) even after 50 hard water alkaline launderings.
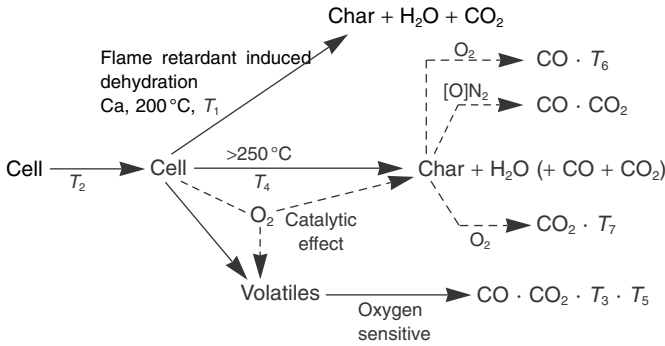
10.8   Modified Kilzer and Broido mechanism for cellulosic pyrolysis; for values of T_1–T_7 see Kandola *et al.*[85]

El-Alfy *et al.*[92] have reported the application of semidurable flame retardants for cotton. Urea ($400 \, \text{g} \, \text{l}^{-1}$)-phosphoric acid ($100 \, \text{g} \, \text{l}^{-1}$) solution was applied to cotton in the presence of various catalysts by the pad dry cure method. The catalytic efficiency was found to be in the following order: ammonium molybdate > zinc acetate > copper sulphate.

In another communication, Kurose and Shirai[93] have studied the flame retardation of cotton fabric treated with Ni^{2+}-phos-PVA ($30 \, \text{mol}\%$ phosphorus). In particular, cotton fabric treated with Ni^{2+}-phos-PVA (polyvinyl alcohol) complex (molar Ni^{2+}/phos-PVA ratio $= 1.25 \times 10^{-1}$) showed the LOI value of 57.5.

Use of Caliban FR/P-44, one of the first antimony trioxide/DBDPO (decabromodiphenyl oxide) retardants used in a resin category, has also been made in producing durable FR cotton and polyester fibre blends. They are used as flame-retardant protective garments for aluminium foundry workers.

10.5.2   Flame-retardant finishes for polyester

There has been some developments in flame retardant finishes[94–98] for polyester fabric and its blends. Flame-retardant finishes for synthetic fibres should either promote char formation by reducing the thermoplasticity or enhance melt dripping so that the drops can be extinguished away from the igniting flame. For protective clothing, char forming finishes would be desirable.[80]

Day and co-workers[94,95] have studied in depth the flammable behaviour of polyester fibre by using a series of phosphorus- and bromine-containing flame retardants as both additives and finishing agents. Alternatives to Tris-BP (tris(2,3-dibromopropyl) phosphate), a known carcinogen, were applied from tetrahydrofuran solution. The chemicals used were tris(2,3-dibromo-2-methyl propyl)phosphate, tris(2,3-dibromo-3,3-dimethylpropyl)phosphate, and so on. The pyrolysis and gaseous combustion of PET incorporating poly(4-bromostyrene), poly(vinyl bromide) and poly(vinylidene bromide) applied via topical treatment or radiation grafting showed significant release of HBr, which is capable of inhibiting gas-phase combustion reactions. Condensed phase interactions that are capable of altering gaseous pyrolysates were also noted.

Thermal stability data of the above-mentioned flame-retardant systems suggest that, although the aliphatic bromides are excellent sources of HBr, they cannot be
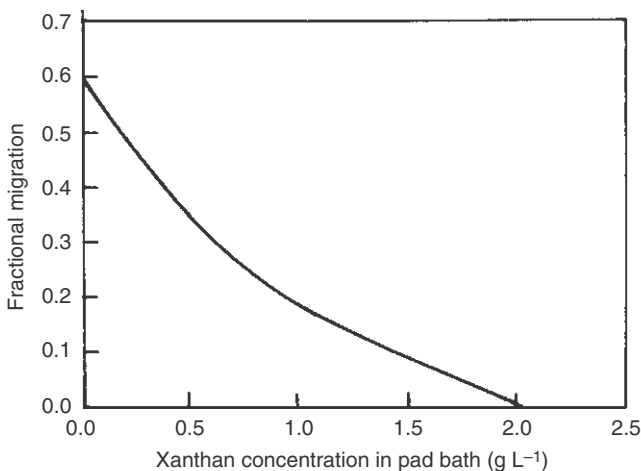
10.9   Fractional migration of liquid flame retardant on 100% polyester fabric as a function of xanthan concentration in a pad bath.

considered ideal flame retardants because of the toxicity of halogen halides. Furthermore, they are not char forming.

Mischutin[96] has recommended the application of low melting solid or liquid brominated compounds in combination with colloidal antimony oxide and a suitable binder by a coating technique – Caliban FR/P-44 is an example here. Simultaneous dyeing and flame retardation of 100% polyester fabric on a Beck dyeing machine or by the thermosol process have also been suggested. Flame-retardant treatments applied by the thermosol process are found to be extremely durable and they can withstand multiple launderings and dry cleanings. In a classical paper,[97] the problem of migration of liquid flame retardant in continuous thermal fixation finishing of polyester fabric by the pad-dry-cure process has been addressed. The experimental results reveal that migration control occurs by a gel formation mechanism and not by the particle flocculation mechanism that exists in the thermal fixation of disperse dyes. Xanthan gums have been suggested to control the migration of liquid flame retardants onto polyester fabrics (Fig. 10.9).

Toray Industries[98] and Nikka Chemical Industry[99] have used tetraphenoxydiaminocyclotriphosphazene dispersions in the dyeing bath,[98] and hexa bromocyclododecane along with Disperse Red 127 for simultaneous dyeing and flame retardance.[99] Akovali and Takrouri[100] have recommended the generation of crosslinking reactions by cold plasma treatment of polyester fabric in the presence of several flame-retardant volatile monomers (Fig. 10.10). Unitika[101] has also demonstrated the application of low temperature oxygen plasma onto polyester fabric padded with 10% polysiloxane, PSR-10(R) solution. After heat treatment, the fabric exhibited good resistance to melting in contact with a burning cigarette for 5 min.

10.5.3   Flame-retardant finishes for polyester/cellulosic blends
Flame-retardation of polyester/cellulosic blends is still a complex problem owing to the differential thermal behaviour of polyester and cellulosic components. Most of the approaches documented in the literature[102–104] have limitations because of toxi-
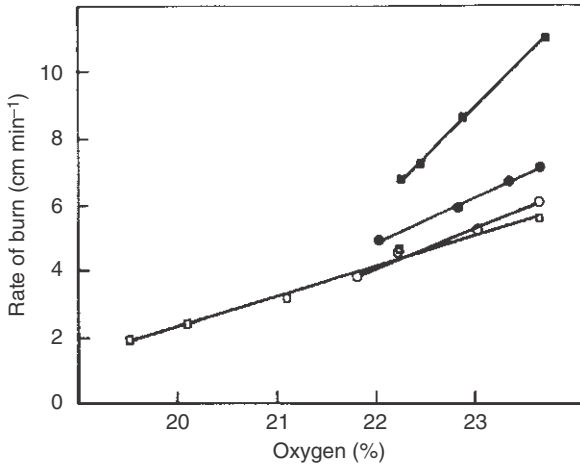
10.10   Rate of burning as a function of environmental oxygen concentration for untreated polyester fabric and plasma treated fabric at 20 W, 60 min. ■, untreated polyester fabric; ●, plasma treatment under vacuum; ○, tetrachloroethylene plasma-treated fabric; □, HMDS plasma-treated fabric (see Akovali and Takrouri[100]).

city, or difficulty in maintaining desirable aesthetic and performance properties. Miller *et al.*[102] observed that for a combination of untreated polyester and cotton, the system ignites sooner, burns faster, and evolves more volatile hydrocarbons than would be anticipated from the individual behaviour of polyester or cotton independently. On ignition cellulose chars and provides a scaffold for the molten polyester, preventing its escape from the flaming zone. It has been suggested that the interaction could be of a chemical nature (based on vapour phase interaction of pyrolytic products) or of physical origin, which alters the heat transfer characteristics.

Flame retardants that are active in both the condensed phase and vapour phase have been found to be very efficient on polyester/cotton blends. The performance of various phosphorus, nitrogen and antimony/halogen compounds on the flame retardance of polyester/cellulose blends has been reported by Bajaj *et al.*,[104] Holme and Patel,[105] Horrocks *et al.*,[4] Shukla and Singh.[106]

10.5.4   Flame-retardant finish for wool

Wool is not as flammable as cotton, and wool fabric was the traditional material for thermal protection except for the more arduous conditions where asbestos was required. However, for thermal protective clothing a Zirpro(IWS) finish,[8] based on hexafluorotitanates and hexafluorozirconates, has been developed, which is extremely stable in acid solutions and exhausts onto wool well below the boil. The Zirpro finish produces an intumescent char, which is beneficial for protective clothing, where thermal insulation is a required property of a burning textile. Work attributed to Benisek[107] has been reported to the effect that the addition of tetrabromophthalic acid (TBPA) to the basic Zirpro treatment produces a finish suitable for end-uses in which low afterflame times are required. However, TBPA increases the smoke density. A multipurpose finish incorporating both Zirpro (as a titanium

complex) and fluorocarbon in a single bath application that makes wool flame-retardant, as well as oil, water and acid repellent, has also been developed.

In one study, shirts made from 100% cotton, Firestop cotton, Flampro wool, and Nomex III were evaluated for their protective and wear-life performance. The greatest protection was provided by fire-resistant cotton and wool fabrics. Nomex aramid-fibre fabrics gave less protection and untreated cotton gave the least.

10.5.5   Glass-fibre fabrics

Haigh[108] has dealt with the special finishes for glass fabrics and heat reflective coatings. In one finishing treatment, colloidal graphite was used, together with silicone oil, to provide protection at higher temperatures. Clothes treated in this way can be used at 400 °C or higher if exposure times are in minutes rather than days or in the absence of oxygen.

Another feature of glass fibre is that it melts at around 1000 °C, so that in the untreated form, it is unsuitable for applications at higher temperatures. However, it can be treated to improve its resistance to such temperatures, by incorporating finely dispersed vermiculite and another involving aluminium salts. At high temperatures, the aluminium will react with the glass fibre to raise its melting point above 1500 °C.

Most hot environments are created by a mixture of convective and radiant heat. Glass fabrics provide good protection against the former, because they generally have low coefficients of thermal conductivity (around $0.6\,W\,m^{-1}\,K^{-1}$). Their performance against radiant heat can be greatly improved by the application of an aluminium reflective layer to one surface. It can be applied directly to the fabric, either as a very thin foil or supported on a thin polyester film.

The market for FR coatings is growing because back coating is proving to be one of the most versatile techniques for producing FR furnishing fabrics.[109]

In order to understand the environmental impact of FR systems, BTTG's Fire Technology Services division is actively engaged in modifying the existing FR systems in order to minimise the toxic emissions during end-use, and also to develop new FR systems employing less hazardous materials.

10.6   Flame-retardant test methods

It is important to test fabrics to ascertain if they are likely to be suitable for the application for which they are required. ASTM and BSI methods are available for such tests, in some cases, ISO standards also exist.

The first group of tests answer the question 'does the fabric burn when a flame is applied to it?' Both ASTM and BSI have a vertical specimen test for fabrics for thermal protection. ASTM D3659 resembles BS 3119, which has been virtually replaced by BS 5438. If the fabric ignites, these tests can determine the spread of flame and the burning rate. Fabrics for thermal protection should not ignite, so the other aspects are not needed. Tests to determine the critical oxygen content of textiles or LOI are ASTM D2863, which is identical to Method 141 of BS 2782.

The second group of tests answer the question 'how well will fabric protect a person wearing it?' ASTM D4108 and BS 3791 deal with this aspect. ISO6942 test has been drafted for gas-heated radiant panels. The ASTM test uses convective heat while the ISO test uses purely radiant heat.[108]

10.6.1   Standards

The formulations of fire safety standards within Europe[109,110] and the new construction products directive operative within EU member countries have been discussed, and this was followed by a review of the CEN/TC 127 fire safety in buildings in the Technical Committee. Some of the important test methods/standards are discussed below:

10.6.1.1   Vertical strip test

The vertical strip test has achieved the widest acceptance for determining flammability. British Standard[111] BS 5438:1989 describes the test method for measuring the ease of ignition and rate of flame spread of vertically oriented test samples. A specified small butane flame is applied to the bottom edge of a vertical test specimen (200 mm long × 80 mm wide) for prescribed times and the minimum ignition time is determined. In another set of experiments, a small igniting flame is applied for 10 s to the bottom edge of a vertical test specimen and flame spread times are measured by recording the severance of marker threads in seconds (Test 3b).

10.6.1.2   Fire tests for upholstered composites and mattresses

BS 5852 (part 1) describes the test method[112] for assessing the ignitability of material assemblies of upholstered composites for seating when subjected to either a smouldering cigarette or a lighted match. The test materials shall be representative of cover, filling and any other components used in the final assembly. The cover size needed for each test is 800 ± 10 mm × 650 ± 10 mm. The upholstery filling required for each test is two pieces, one 450 × 300 × 75 mm thick and the other piece 450 × 150 × 75 mm thick. Some cushioning assemblies may consist of several layers of felt, wadding or different foams. In these cases the test pieces shall reproduce the upper 75 mm of the cushioning assembly.

A smouldering cigarette is placed along the junction between the vertical and horizontal test pieces, allowing at least 50 mm from the nearest side edge to the cigarette. The progress of combustion is observed using the clock and any evidence of progressive smouldering or flaming in the interior and/or cover is recorded.

BS 5852: Part 2:1982 covers ignition sources between 2 and 7, although in practice 5 and 7 are specified (two butane flames and four burning wooden cribs), which together with the butane flame source of BS 5852: Part 1, form a sequence of increasing thermal output from that approximating to a match burning to four sheets of full size newspaper burning.[112]

The objective of this test is to subject an assembly of upholstered composites, arranged to represent the junction between a seat and back, as is typical in chairs, to six flaming sources selected to cover the intensities of actual sources that might be encountered in various end environments.

Progressive smouldering failure can be detected for any composite that produces externally noticeable amounts of smoke, heat or glowing for 30 min after the removal of the burner for sources 2 or 3. However, for sources 4, 5, 6 and 7, any composite that produces externally detectable amounts of smoke, heat or glowing for 60 min after ignition of the crib.

British Standard BS 6807:1996 describes the method for assessing the ignitability of mattresses, upholstered divans and bed bases when subjected to flaming types of primary and secondary ignition sources of different severities.[113]

Holme cites the review of Bryson which considers these standards from the fabric producer's viewpoint. According to Bryson the basic standards, BS 5852 Part 1 (for cigarette and match ignition) and BS 5852 Part 2 (covering ignition sources anywhere between 2 and 7, but in practice 5 and 7), state that the cigarette test could be carried out over the infill used in the furniture, but the match test has to be carried out over $22 \, kg \, m^{-3}$ polyurethane foam, which could not legally be used in domestic furniture. However, BS 5852 Part 2 might be carried out over any foam. Water soak tests and the use or non-use of interliners create further complexities.

Peter Cook International[115] has also claimed that the development of the Partex System for upholstery fabrics, interlinings, drapes, workwear fabrics and mattress tickings meets the fire retardancy regulations. This system allows for fabric treatment to meet BS 5852 Part 1 (after the soaking test) and can take natural fabrics through to Crib 5.

Cigarette ignition of upholstered chairs has been analysed by Braun *et al.*[116] at the National Bureau of Standards, Washington DC. The objective of this work was to observe the smouldering behaviour of upholstered chairs varying in cover fabrics and filling materials, after cigarette ignition. The chairs which smouldered only contained polyester batting under the cover fabric in the area where the cigarette was placed, those which first smouldered and then burst into flames contained polyurethane foam or cotton batting.

10.6.1.3   Ignitability of fabrics used in tented structures

British Standard BS 7157:1989 describes the method for testing the ignitability of fabrics used in the construction of tented structures such as marquees, large tents, awnings or flexible membrane.[117]

The range of ignition sources used in this test are pinewood cribs: ignition source 4 to 7 as described in BS 5852:Part 2. The test frame consists of a metallic rod arranged to represent the main and side walls and roof of the tent structure. The frame shall be constructed slightly smaller than the test specimen (as a mini tent) but by not more than 10 mm less than any dimension. The fabric specimens and the cribs shall be conditioned before performing the test for 72 hours in indoor ambient conditions. The ignitability test should be performed in a draught-free environment with a temperature of $20 \pm 5 \, °C$ and a relative humidity of $55 \pm 20\%$.

The crib is ignited as described in BS 5852:Part 2 and progress of combustion is recorded along with the formation of flaming droplets or glowing, if any.

10.6.1.4   Ignitability of bedcovers and pillows by smouldering and flaming

In this test (BS 7175:89),[118] the test specimen is placed on a mineral wool fibre pad (MWFP) and subjected to smouldering and flaming ignition sources placed on top of and/or below the test specimen. A cigarette and the test specimen are placed on the MWFP so that the cigarette lies adjacent to the pillow. Light the cigarette and draw air through it until the tip glows brightly. Light another cigarette and place it on the upper surface of the pillow. Start the clock and observe the specimen for progressive smouldering or concealed smouldering. In the case of a quilt, observation continues for 60 min after the placement of a third cigarette.

If ignition of the test specimen is observed, extinguish the text specimen and record that ignition occurred for the ignition source used. For ignition sources 1 to 3, a butane flame test is used.

The requirements for contract upholstered furniture in the UK have generally been that the cover fabric, in conjunction with the actual filling to be used, be able to pass an ignitability test to BS 5852 source 5 (flaming wood crib) level. With a wide range of different fabrics, and to a lesser extent fillings, available on the contract market, manufacturers have been put in the difficult position of having to test very large numbers of fabric-filling combinations.

However, BS 7176:1995, the 'predictive testing' approach used in this method, recommends the use of a particular grade of non-FR polyurethane foam.[119] The rationale is that if a fabric will pass for ignition source 5 test over this foam, it should pass over any CMHR (combination modified high resilience) foam.

BS 7176 also lists four hazard classes categorised as low, medium, high and very high[120] (Table 10.9). The examples cited in Table 10.9 for each hazard category[120,121] cannot be exhaustive and some of the examples appear in more than one hazard category. This reflects the range of the hazards possible under different circumstances.

10.6.1.5   Evaluation of textile floor coverings

Assessment of the textile floor coverings tested in accordance with BS 4790 is valuable in determining the ease with which the textile floor covering will ignite when a burning cigarette, a hot coal or a similar source of ignition is dropped on it.[122,123] It is applicable to all types of textile floor coverings used in the horizontal position. BS 4790 is not intended to give an overall indication of the potential fire hazard under actual conditions of use. The radiant panel test described in ASTM-E648:1978, however, can be used to assess the performance of textile floor coverings in a fire situation.

Table 10.9 BS7176:1991 Hazard Classifications and Ignitability Performance Requirements[120]

	Low hazard	Medium hazard	High hazard	Very high hazard
Test methods	Section 4 of BS5852:1990	Section 4 of BS5852:1990	Section 4 of BS5852:1990	Section 4 or Section 5 of BS5852:1990 (or other as specified)
Requirements	Resistant to ignition sources 0, 1	Resistant to ignition sources 0, 1, 5	Resistant to ignition sources 0, 1, 7	At the discretion of the specifier but at least high hazard requirements
Typical examples	Offices, schools, colleges, universities, museums, exhibitions, day centres	Hotel bedrooms, public buildings, restaurants, services' messes, places of public entertainment, public halls, public houses, bars, casinos, hospitals, hostels	Sleeping accommodation in certain hospital wards and in certain hostels, offshore installations	Prison cells

Three methods (loose-laid, fully adhered or loose-laid with underlay) for mounting the samples can be used for testing floor coverings. The selection of which method will depend on how the floor coverings are laid in actual use. According to its observed behaviour, a specimen can be considered satisfactory if the radius of the affected area is not greater than 75 mm.

The hot metal nut method[122] has also been used in BS 4790:1987 to study the effect of a small source of ignition on textile floor coverings. In this test, the nut is heated to a temperature of $900 \pm 20\,°C$ in a muffle furnace. It is then placed centrally on the specimen in a chamber within 3 s of its removal from the furnace. The sliding panel is opened and the nut removed from the specimen after it has been in contact with it for 30 ± 2 s. The sliding panel is closed after all the effects of ignition have ceased.

In another British Standard, BS 6307:1982, the methenamine tablet test has been used to study the influence of a small source of ignition on textile floor coverings.[124] However, this method is used only to assess the properties of materials in response to heat and flame under controlled laboratory conditions. This method is generally used for acceptance testing in the trade.

10.6.1.6   Evaluation of protective clothing

The European Committee for Standardization has recommended the EN366:1993 standard for evaluation of materials and material assemblies exposed to a source of radiant heat, while EN367:1993 is for determination of the heat transmission on exposure to flame. EN532:1993 standard has been used to test the specimens for limited flame spread. The requirements and test methods for protective clothing for firefighting[125] have been covered in EN469:1995. This standard specifies the requirements for clothing to be worn during structural firefighting operations. Heat transfer (flame) by multilayer clothing assemblies for firefighters tested as per EN367 standard shall give a mean heat transmission index, $HTI_{24} \geq 13$, while heat transfer (radiation) is measured in accordance with Method B of EN366 at a heat flux density of $40\,kW\,m^{-2}$, and after the pretreatment should give a mean $t_2 \geq 22$ s and a mean transmission factor $\leq 60\%$.

The complete garment assembly may be additionally tested for typical scenarios encountered by a firefighter under the conditions given in Table 10.10.

However, testing under emergency conditions must be carried out on an instrumented mannequin.

Krasny et al.[126] have also discussed the heat flux conditions measured in seven room fires for protecting firefighters. The fires ranged from just short of flashover through rapid build-up to considerable postflashover burning. The standard, NFPA 1971, Protective Clothing for Structural Fire Fighting, requires that the turnout coat or pants assembly must protect the wearer against second degree burns when a heat flux of $84\,kW\,m^{-2}$ is applied to its outside surface for a minimum of 17.5 s. The

Table 10.10   Firefighting scenarios

Conditions	Exposure time	Temperature (°C)	Heat flux density (kW m^{-2})
A. Normal	8 h	40	1
B. Hazardous	5 min	250	1.75
C. Emergency	10 s	800	40

results imply that firefighters have only 10 s or less to escape under most flashover conditions.

Welder's protective garments requirements and evaluation[127] has been discussed in EN470-1(1995). Welder's protective garments may be designed to provide protection for specific areas of the body, for example, sleeves, aprons, and gaiters. Electrical conduction from the outside to the inside of the garment should also be avoided. As per this standard, the garment when tested for flame spread in accordance with EN532 after washing/dry cleaning shall meet the following requirements:

- No specimen should give flaming to the top or either side edge.
- No specimen should produce a hole or give flaming or molten debris.
- The mean value of after flame time and afterglow time shall be ≤ 2 s.

European Standard EN531:1995 is applicable to protective clothing for industrial workers exposed to heat[128] (excluding firefighter's and welder's clothing). The heat may be in the form of convective heat, radiant heat, large molten metal splashes or a combination of these heat hazards. This European Standard specifies the performance requirements and methods of test and gives design recommendations for the clothing wherever necessary. When tested in accordance with EN366 method B at a heat flux density of $20\,kW\,m^{-2}$, all clothing assemblies offering protection against radiant heat shall meet at least level C_1, that is, mean time to level t_2 between 8 s (min) to 30 s (max). For convective heat protection, the clothing assemblies if tested as per EN367 shall meet at least B1, that is, the range of HT1 values should be between 3 min (minimum) and 6 min (maximum).

The performance requirements of limited flame spread materials and material assemblies used in protective clothing[129] are given in EN533:1997. All material assemblies claiming compliance with this European Standard should have a limited flame spread index of 2 or 3 when tested in accordance with EN532 with the flame applied to the outer face and to the inner face.

Whiteley[130] has made some important observations on the measurement of ignitability and on the calculation of 'critical heat flux'. According to him there is no universally accepted model for the correlation of ignition time with incident radiant heat flux.

Whiteley et al.[131] and others[132,133] have demonstrated the use of a cone calorimeter test in studying the heat release from flame-retardant polymeric materials. This test gives a better correlation between room scale testing and large scale fire testing and provides a pyrolysis profile under ambient oxygen conditions.

In an excellent review, Weil et al.[134] have commented on the oxygen index test for evaluating the flammability of polymeric materials and discussed what the oxygen index correlates to. According to them, this test can be improved by using it with bottom ignition rather than with standard top ignition.

10.6.1.7   British Textile Technology Group manikin test systems, RALPH

The influence of external heat flux is observed in various manikin tests. These methods are typified by the manikin developed by the British Textile Technology Group (BTTG) known as RALPH (Research Aim Longer Protection Against Heat). Improved standards for fire protective clothing are the objective of BTTG (Fire Technology Services). The reported differences between RALPH II and DuPont's Thermo-man are part of the debate for a possible European standard based on manikin testing for heat and flame protective clothing.[135,136]

The basis of the RALPH manikin was a 'shop' display manikin composed of glass fibre/polyester resin. This composition is insufficiently inert to direct flame contact and was therefore coated with a ceramic material of approximately 5 mm thickness that also served to create greater thermal inertia. This coating was chosen, after comparison with other materials, because it had the best combination of flame retardancy, resistance to cracking when heated/cooled, ease of application and adhesion to the glass fibre/polyester resin. The coated manikin was then painted with an intumescent material to impart further protection.

The heat sensing equipment consists of 32 linearized thermocouple amplifiers connected to a computer. Each sensor was a Type T copper–constantin thermocouple soldered to a copper disc 8 mm in diameter and of 0.2 mm thickness. These sensors were then implanted into the manikin with all wiring exiting via the head to the amplifier/computer.

RALPH II carries a total of 57 heat sensors, instead of the original 32. Improved computer manipulation and display of data with the existing RALPH facility permits any half of the manikin to be exposed to flames at approximately $60\,kW\,m^{-2}$. The facility has been extended to increase this to at least $84\,kW\,m^{-2}$, by adding a second array of burners so that RALPH can be enveloped in flames, and to provide an alternative purely radiant heat source.

To calibrate the sensors, two approaches were adopted. For 'time to pain' the pain response of volunteers was measured for heat fluxes of $1–31\,kW\,m^{-2}$, this data then being compared with the temperature recorded by a single sensor when covered with various types and thicknesses of thermoplastic tape. By this method, the tape producing the best 'match' response with volunteers' 'time to pain' was achieved. For burn injury prediction, reference was made to the work carried out by Stoll and Chianta for the US Air Force.[137]

The University of Alberta has also developed mannequin (nicknamed 'Harry Burns') with its accompanying flash fire system.[138] The male mannequin, size 40R, is made of 3 mm thick fibre glass to provide sufficient strength for handling and to have a thick layer for easy mounting of heat flux sensors. The thermal protective quality of a garment is judged on estimates of the extent of skin damage resulting from a controlled flash fire.

It has been claimed that with the mannequin and flash fire system, real life exposure conditions can be more closely simulated, and the whole garment assembly can be tested together, taking into account many variables which otherwise cannot be included in small scale testing.

10.7   Summary

Most flame-retardant textiles are designed to reduce the ease of ignition and also reduce the flame propagation rates. Conventional textiles can be rendered flame retardant by chemical after-treatments as co-monomers in their structures or use of FR additives during extrusion. High performance fibres with inherently high levels of flame and heat resistance require the synthesis of all aromatic structures, but these are expensive and used only when performance requirements justify cost. In addition, while heat and flame-resistant textiles have been reviewed and compared, the mechanisms of char formation and the role of intumescents and plasma treatment have also been highlighted. The increasing need to use environmentally

friendly FR finishes has been emphasized. Improved standards for fire and heat protective clothing including more realistic tests, such as instrumented manikins, have also been discussed.

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