

Chapter 4

Overview of traditional flame retardant solutions including coating and back-coating technologies

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4.1 Introduction

Within recent years there has been a number of comprehensive reviews that not only have critically reviewed the research period up to about 1980 during which period most of the presently used commercial flame retardants for fibres and textiles were developed excluding back-coatings [1, 2] and references within these direct the reader to more contemporary specific reviews of particular fibre types. Further reviews have considered developments since that time [3-5]. During the period up to about the 1960-80 period, the established durable and flame retardant treatments for cotton and wool fibres as well as those additives and comonomers introduced into both regenerated (e.g. viscose) and synthetic (notably polyester, polypropylene and the modacrylics) fibres during manufacture were synthesised and developed into commercially-acceptable products, many of which are still available today (*see Chapter 5*). The years 1975-1980 were the period when back-coatings were also first developed and have become extremely commonly used in certain applications, particularly furnishing fabrics where their use prevents the front fabric face aesthetics being influenced by their presence [6]. In fact it is probably true to say that the majority of currently available flame retardants for textiles and fibres reviewed recently by Weil and Levchik in 2008 [5] derive from chemical developments prior to 1980. A major reason for the significant drop in research into novel flame retardants after this period was the report in 1977 the very efficient flame retardant tris(2,3-dibromo propyl) phosphate failed clinical tests resulting in carcinogenic behaviour and in the following years many other products were also

withdrawn on health and safety grounds [7, 8]. The history of their development during this period has been reviewed by Horrocks more recently [9].

This chapter will focus on semi- and fully durable flame retardant methods and application technologies for textile fabrics having little if any inherent flame resistant properties. It will concentrate on those flame retardant technologies that are well-established and in current use world-wide and will include textile coating technologies which have technical textile applications. It will not consider more recent potentially commercial processes that have yet to be fully accepted and proven – these have been reviewed by both Weil and Levchik [5] and myself [9] previously. Examples of such exclusions are the recently developed phosphorus-based Fyroltex[®] HP (Akzo) and Noflan[®] (Firestop Ltd) products which while claiming to be commercially viable, and according to the author's knowledge, have yet to be fully accepted into the market place as fully durable flame retardants for cotton although the former claims to withstand up to 25 home launderings [5].

Non-durable flame retardants have changed little over recent years, have been reviewed in cited references above [2, 3], comprise in the main soluble salts of ammonia and organic bases (e.g. urea, guanidine) and phosphorus oxyacids (sometimes augmented by the presence of ammonium bromide) and may be applied by simple pad-dry techniques and spraying. Typical methods for applying most flame retardants in which open width cloth may be commercially processed are schematically presented in **Figure 4.1** and will be referred to in more detail in the text below.

Figure 4.1

Durable flame retardants may only be applied if the retardant species interacts with fibre chemical structure and thus forms strong chemical bonds, creates an interpenetrating

polymeric network within a fibre structure thereby “locking in” the flame retardant species or is contained within a surface coating or back-coating. Synthetic fibres generally have little chemical reactivity and are very polycrystalline, impenetrable structures and so, unless they contain a comonomer with inherent flame retardancy or an additive introduced during their production, may only be effectively flame retarded by the presence of a surface treatment or by flame retardant activity transfer from a co-blended natural fibre already containing a flame retardant.

This chapter will comprise, therefore, the following main textile types:

- (i) Durable flame retarding of cellulose-containing (usually cotton) textiles and cellulose blends;
- (ii) Durable flame retarding of wool and wool blends;
- (iii) Durable flame retarding of man-made fibre-containing fabrics; and
- (iv) Coating and back-coating both natural fibre-containing and synthetic fibre-containing fabrics.

4.2 Durable flame retardant treatments for cellulose-containing textiles

Textile finishes having semi- or at least 50 domestic wash durability applied to cotton and its blends, unless applied as a coating or back-coating (*see Section 4.5.2* below), comprise phosphorus-containing species. Generally, these are considered to release phosphorus acids on heating which act as Lewis acids and promote the char-formation [1, 2, 10]. This release of Lewis acidic properties should not occur significantly below 150°C if the treated textile is to resist normal drying and curing temperatures. Often the simple non-durable salt finishes start to decompose about this temperature and so any drying treatments should not exceed about 130°C. However, in the case of the soluble ammonium phosphates (explained more fully in ref. 3), careful heating at about this temperature enables some phosphorylation of

cellulose to occur and hence some level of durability. Simultaneous acid degradation of the cellulosic chains may be reduced by the presence of an organic base such as urea which both increases cotton fibre penetration and buffers the overall acidity during this curing process. Urea-ammonium phosphate flame retardant treatments for cotton have in fact a considerable history with the earliest reviews appearing in the late 1940s [11, 12]; a number of commercial versions appeared during the 1950-60 period but these have been superseded by the subsequently developed organophosphorus chemistries (*see below*). The main drawback of these relatively simple chemical treatments was the ion exchange with calcium ions during laundering in hard water. The formation of calcium cellulose phosphate stabilises the phosphate and prevents formation and release of phosphoric acid and hence inhibits char formation and flame retardancy properties. However, where wash durability is not a problem, an acceptable level of water-soak durability is achieved and this system applied to cotton interliners is claimed to be able to pass the 30 min, 40 °C water soak test according to BS 5651 as required by the UK Furnishing and Furniture (1988) regulations [13] when testing to BS 5852:1979:Part 1, Sources 0 (cigarette) and 1 (simulated match).

Higher durability requires either the use of functional finishes based on organophosphorus compounds typified by the alkylphosphonamide derivatives pioneered by Ciba and now manufactured and marketed by Huntsman under the Pyrovatex[®] brand or tetrakis (hydroxy methyl) phosphonium salt (THPX) condensates, principally Proban[®] invented by the former Albright & Wilson and now produced by Rhodia.

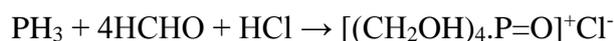
Most of these treatments have become well-established during the last forty plus years and few changes have been made to the basic chemistries since that time [1, 2]. Those that have been made often involve minor changes which influence properties such as handle [14] or decreased levels of formaldehyde release during application as seen, in Pyrovatex[®] LF [15], for example. However, during the same period, many other flame retardants based on

phosphorus chemistry and reviewed extensively elsewhere [2], in the main, have ceased to have any commercial acceptability for reasons which include toxicological properties during application or during end-use, antagonistic interactions with other acceptable textile properties and cost. The examples cited above may be considered to be those which continue to satisfy technical performance and enable flammability regulatory requirements to be met, while having acceptable costs and meeting current health and safety and environmental demands.

While the chemistry of functional organophosphorus finishes is quite complex [1, 2, 5], it is important to consider those important chemical features which influence the application process and the overall flame retarded textile performance.

4.2.1 Tetrakis (hydroxy methyl) phosphonium salt (THPX) condensates

These were developed in the 1950s by Albright and Wilson in the UK and Hooker Chemicals in the USA and the essential chemistry was undertaken by US Department of Agriculture Southern Regional Research Laboratory. With regard to the underpinning research, Vail and co-workers published a number of papers regarding the chemistry of THPX phosphonium salts where X may be OH⁻, Cl⁻ or SO₄⁻ [16, 17]. Tetrakis (hydroxy methyl) phosphonium chloride (THPC) is the most important of these and although described first in 1921 by Hoffman [18], its commercial potential was realised by Reeves and Guthrie in 1953 [19]. THPX salts. THPC is prepared as follows [20]:



but by itself it cannot confer flame retardancy unless a nitrogen-containing species and hence P/N synergy are present. Sources of nitrogen include urea, thiourea, trimethylol melamine

(TMM), cyanamide and others which have been reviewed by Horrocks [2] and these bases form THPX complexes which are the precursors for flame retardant formation. The chemistry of application and finishing of these have also been reviewed in detail by Vail et al [21, 22].

While heating THPX with cotton causes some cross-linking to the cellulose molecules in the presence of an amine-ended species, polymerisation of the THPC-base complex is the favoured reaction; however, control of pH is essential if excessive degradation is not to occur [23]. This property of THPX-based polycondensation and the subsequent development of ammonia as a cross-linker by Albright and Wilson led to the currently successful Proban[®] process [24]. The result of such polycondensation is a polyphosphine in which the unstable P(III) must be oxidised to the stable P(V) state giving rise to the final poly(phosphine oxide) which has the combination of flame retardancy and durability [25].

The former Hooker Chemical process used THPOH while the Proban[®] process has always involved the formation of a THPC condensate. The Proban[®] nomenclature can be quite confusing since it has changed with time. The current position is that Perform is the generic name for the THPC-urea monomers or precondensates of which Rhodia market two variants:

- Perform CC[®] which is the standard finish monomer, precondensate of urea and THPC, formerly Proban[®] CC, and
- Perform STi[®] which is a soft handle finish based on a modified monomer precondensate of urea and THPC, formerly Proban[®] STi.

The generic brand Proban[®] is used to refer to the polymer, related processing technology and the downstream finished fabrics.

Figure 4.2 outlines the essential chemical and processing stages (shown schematically also as process (iii) in **Figure 4.1**) for the Perform[®] CC THPC-urea complex in which the THPC and urea are probably in a 2:1 molar ratio with a molar P:N ratio of 1:1.

The chloride is generally preferred relative to other salts, such as the sulphate (THPS), because as a univalent anion, the salt-urea complex achieves a higher degree of penetration into the fibre microstructure. Experience has shown that the divalent sulphate complex, which is considerably larger, leads to lower levels of penetration with consequent reduction in durability.

Figure 4.2

The THPC-urea complex solution is applied by a pad or foam application method (*see Figure 4.1*, process (iii)) in the presence of wetting and softening agents. To ensure a high degree of penetration, the cotton fabric must have been scoured and bleached to a high degree of absorbency. After application (at a level commensurate with 2.0 – 3.0% (w/w) P on the final cloth), the fabric is dried to about 8-10% moisture level. This dried fabric is passed in open-width form to an ammonia-cure reactor into which ammonia gas is fed at a controlled rate. An exothermic cross-linking reaction occurs, preferably within the component fibre microstructure, yielding an insoluble polymeric phosphine having a molar P:N ratio of 1:2. This ratio yields a high degree of synergy, which if P > 2 wt.-% with respect to fabric, gives an acceptable level of flame retardancy for most applications. It must be emphasised that the final polymeric structure is not grafted on to the supporting cellulose molecular structure but more of an interpenetrating network of cross-linked Proban[®] polymer within a microfibrillar cotton cellulose structure. Its extreme durability derives from the intimacy of this interpenetrating network character.

As stated above, in order to stabilise the highly reducing phosphine polymer, after ammonia curing fabric is passed through a dilute hydrogen peroxide bath to oxidise the polymer to a

poly(phosphine oxide) [26, 27]. After this the fabric is washed and dried. If the fabric has been correctly prepared and impregnated and the ammonia cure controlled, then the final fabric will have a durable finish with little surface deposits and good handle. Finished softness is improved by inclusion of softeners such as long chain fatty amines [28] but increases after laundering as surface polymer is removed [29].

The final properties both good and bad are summarised in **Table 4.1**.

Table 4.1

The main advantages are its exceptional durability to laundering where it will withstand over 100 75°C (hospital) washes [29]. After application there are minimal losses in fabric tensile and tear properties and there are no reported significant emissions of formaldehyde in use (*see* below). In fact, any emission of HCHO is a consequence of poor final oxidation of the polyphosphine oxide stage since there is no known chemistry that would release this gas from the poly(phosphine oxide) polymer. At best the emissions are less than 20 ppm.

The major disadvantages of this treatment are that the application process cannot be simply carried out on normal textile heat curing equipment and a specialist ammonia gas cure unit is essential and is a part of the Proban[®] licensed process. The former Hooker THPOH-NH₃ process suffers from the same problem and this treatment is believed to be still undertaken by a number of US finishers. The extremely reducing character of the ammonia cure process ensures that there can be adverse reactions with some dyes e.g. sulphur dyes, and as stated above, there is often a requirement for softeners to improve fabric handle. While attempts have been made to reduce or remove the need for ammonia gas curing [2, 3, 5], none has been able to be an effective replacement at the commercial level.

4.2.2 Phosphonamide finishes

The basic chemistry of these finishes are based on the N-methylol dimethyl phosphonamide, $(\text{CH}_3\text{O})_2\text{PO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{OH}$ and the associated chemistry described by Aenishaenslin et al in 1969 [30] on behalf of the then Ciba-Geigy company. This molecule, synthesised from methylolating the adduct from dimethyl phosphate and acrylamide, does not have the required reactivity with cellulose required for achieving an effective and durable flame retardant finish. It may only bond to the cellulose molecules via a methylolated resin bridge molecule (*see Figure 4.3*). Typically, this is a methylolated melamine derivative or dihydroxydimethylol ethylene urea (DHDMEU) in the presence of an acidic catalyst. Orthophosphoric acid has been shown to be the most effective catalyst in that it is sufficiently acidic to promote cross-linking reactions and yet it is not too acidic to create excessive hydrolytic degradation of cellulose chains and hence undesirable decrease in both the fabric tear and tensile strengths. However, if an effective finish with minimum stiffness and surface deposits is to be achieved as for the Proban[®] finishes above, a well-prepared fibre is essential and careful padding or foam application of the formulation is essential in order to maximise penetration (*see Figure 4.1*, process (ii)). A typical formulation for application to a 150-200 gm⁻² cotton fabric at 80% expression or wet pickup is shown in **Table 4.2**. The advantage of this overall process compared with the THPC-urea/ammonia cure process above is that it may be undertaken on a conventional open-width, pad-dry-cure-wash-off (*see Figure 4.1*, process (ii)) range. A more detailed schematic is shown in **Figure 4.4**.

Table 4.2

Figure 4.3 and Figure 4.4

After application, the padded fabric is dried at 130 °C and then passed to a curing oven or baker at 150 °C for 4.5 min or 170 °C for 1 min. Generation of gaseous formaldehyde is a serious problem and must be contained, extracted and removed by water scrubbing along with other emitted volatile organic compounds (VOCs); work by the author and his colleagues [31, 32] has indicated that formaldehyde emission can be decreased by optimising the bath formulation (*see* below, **Section 4.2.3** and **Table 4.1**). A secondary effect of the high possible levels of HCHO release during curing is the formation of highly intractable tarry deposits on the inside of the curing chamber which necessitates removal unless volatiles are removed from the curing oven air. Lower temperature curing and higher concentrations of phosphoric acid catalyst also reduce tar levels but this may reduce levels of fixation and promote greater loss in tensile properties respectively.

Curing must be followed by an immediate alkaline (caustic soda, NaOH, or soda ash, Na₂CO₃) neutralisation at 40-45 °C, if acid tendering is to be minimised. This neutralisation removes all residual phosphoric acid catalyst, uncross-linked phosphonamide and some surface cross-linked polymer. Subsequent water washing-off and drying completes the process.

If controlled, the finishing process will yield high levels of durable flame retardancy at phosphorus levels of 1.5 – 2.0 wt.-% (*see* **Table 4.1**), and a fabric which has some degree of crease resistance, minimal losses in tensile and tear strengths (about 20-25%) and acceptable handle. Disadvantages are the need to minimise formaldehyde emissions and tensile property loss plus high losses of active flame retardant from poor fixation and reagent purity. Because of the influence of two of these factors upon effluent discharges, they will be explored in greater detail in **Section 4.2.4**.

Compared to the THPC-ammonia cure systems, the cured phosphonopropionamide flame retardant has better dye compatibility (hence its preferred use on printed upholstery fabrics)

and better flame retardancy per unit level of phosphorus, but yields inferior tensile properties and poor resistance to bleaches during laundering. Furthermore, during storage there may be both slow release of HCHO to the environment as well as loss in tear and tensile strength through acid hydrolysis. This is because the condensation reactions involved (*see Figure 4.3*) are equilibria, catalysed by acids and formaldehyde present during both application and regenerated during service life. The presence of atmospheric moisture and acidic residues (which will increase in concentration with the degree of hydrolysis) present in cotton especially favour the reverse reaction and hence generation of formaldehyde during storage and service [33]. This hydrolysis may be minimised by careful neutralisation during the washing-off stage after curing. Periodic washing of treated fabrics such as FR curtains will remove acidic residues and so reduce or even eliminate fabric tendering during service life. However, it is because of this ubiquitous presence of HCHO, even though Pyrovatex[®]-treated fabrics can achieve HCHO levels < 75 ppm and so pass stringent levels such as Japanese Law 100 and Oeko-Tex requirements for skin contact [34], manufacturers like Huntsman will recommend that their Pyrovatex[®] products should not be used to treat children's nightwear.

Table 4.2 summarises the comparative advantageous and disadvantageous characteristics of both types of durable FR treatments for cotton. One particular additional advantage over THPC-based finishes is the ability to apply concurrently other finishes such as soil releasing agents which may be co-cured during the normal oven curing process [35].

Table 4.2

While the Pyrovatex[®] brand was developed by Ciba-Geigy, it is currently owned by Huntsman and two products are available namely Pyrovatex[®] CP New and Pyrovatex[®] CP-LF where LF stands for low formaldehyde (*see below*) [35]. Other commercial examples of

N-methylol dimethyl phosphonamide include Thor Chemicals' Aflammit[®] KWB and Clariant's Pekoflam DPM.

4.2.3 Effluent and water minimisation

As a consequence of current environmental legislation across the EU (e.g. UK Environmental Protection Act, 1990) demands for stricter controls over effluent discharge have identified a number of problems associated with textile flame retardant applications during the last 20 years or so. These relate to the following:

- effects of discharge to effluent of unused flame retardant liquors;
- effects of emissions of formaldehyde to the atmosphere, especially during curing (currently required to be ≤ 20 ppm);
- emissions of VOCs (currently ≤ 50 ppm);
- use and emission of ammonia in THP-based treatments; and
- discharge of unfixed flame retardants from washing-off effluent.

While the Proban[®] process comprises a conventional padding process followed by a specialised ammonia cure process followed by oxidation and washing off, excessive release of phosphorus- and nitrogen-containing species into effluents and the atmosphere has not generally been seen to be a problem, perhaps because of the closed nature of the patented ammonia cure process [26, 27] and the effectiveness of the cross-linking process. However, this was significant problem during the early 1990s in particular for the N-methylol dimethyl phosphonopropionamide finishes which stem from the impurity of the reagent itself and the difficulty of optimising the chemistry to minimise formaldehyde release. Research by Kapura [36, 37] showed that the percentage solids active species in commercial Pyrovatex[®] CP during this period was as little as 27 wt.-% with the methyl ether derivative of N-methylol dimethyl phosphonopropionamide $((\text{CH}_3\text{O})_2\text{PO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{OCH}_3)$ present at 28

wt.-%. If these are considered to be similarly effective in their ability to chemically react, this is equivalent to a total effective solids content of still only 55 wt.-%. Remaining components include the non-methylolated form, $(\text{CH}_3\text{O})_2\text{PO.CH}_2\text{CH}_2\text{CO.NH}_2$, (8%, w/w) and the dimer, $[(\text{CH}_3\text{O})_2\text{PO.CH}_2\text{CH}_2\text{CO.NH.CH}_2]_2\text{O}$, (37 wt.-%). In 1990, Ciba introduced a purer version, Pyrovatex[®] CP New, which according to Kapura, comprises 61 wt.-% main reagent $\text{R.CO.NH.CH}_2\text{OH}$, 10 wt.-% of the methylated derivative, 21 wt.-% of the non-methylolated form and a much decreased dimer content of 8 wt.-%. This product has given higher levels of fixation after curing and decreased levels of resin deposits in the curing/baking zones. More recently, Ciba introduced Pyrovatex[®] 757 during the 1990s, possibly the dimethylolated derivative $(\text{CH}_3\text{O})_2\text{PO.CH}_2\text{CH}_2\text{CO.N}(\text{CH}_2\text{OH})_2$, to increase fixation further although current Huntsman literature suggests that this does not form the basic chemistry of the current Pyrovatex[®] New product [35]. An alternative product, Pyrovatex[®] 7620, was also developed with decreased formaldehyde emissions and it is possible that this is the forerunner of the current Pyrovatex[®] CP-LF finish.

Research by the author under a UK Environmental Technology Best Practice Programme [31, 32, 38] has shown that during the application of Pyrovatex[®] CP, decreases in formaldehyde emissions by up to 75% are achievable together with reductions of effluent phosphorus levels by improved finish fixation. This work showed that application of a chemometrics software package to the five variable component liquor (*see Table 4.1*) could be analysed in terms of identifying those component concentrations which significantly affected flame resistance (measured as LOI), formaldehyde emission levels and degree of fixation. From this an optimised recipe could be predicted and tested. The standard and optimised recipe with associated fabric properties and formaldehyde levels measured at the curing stage are presented in **Table 4.1** for laboratory-based experiments. While the optimised recipe is little different from the standard formulation, the analytical software predicted and demonstrated

that the latter is on a "knife edge" with regard to sensitivity of the concentration of formaldehyde emission. Scaling up to full plant scale at 3 UK installations reduced the four-fold decrease in formaldehyde from 20 to 5 ppm previously obtained under laboratory conditions shown in **Table 4.1** to between 36 and 59% reductions when measured at point B in the production line in **Figure 4.4**.

4.2.4 Durable flame retarding of cotton/synthetic fibre blends

Experience has shown that flame retardants which are effective on one fibre, when in contact with a second differently flame retarded fibre, may prove to be antagonistic and render the blend flammable [2]. Consequently, the current rules for the simple flame retarding of blends are either to apply flame retardant only to the majority fibre present or apply halogen-based back-coatings, which are effective on all fibres because of their common flame chemistries in the vapour phase.

The widespread use of polyester-cotton blends coupled with the apparent flammability-enhancing interaction in which both fibre components participate (the so-called *scaffolding effect*, reviewed elsewhere [2]) has promoted greater attention than any other blend. However, because of the observed interaction, only halogen-containing coatings and back-coatings find commercial application to blends which span the whole blend composition range; the earlier (1975) Caliban F/R P-44 decabromodiphenyl oxide and antimony III oxide in a 2:1 mass ratio (equivalent to a molar ratio of Br:Sb = 3:1) in a latex binder [39] has been the model for current coating and back-coating formulations for polyester-cotton blends as well as for back-coatings in general [6] (*see* below, **Section 4.5**). While the presence of a binder may adversely affect fabric handle and the usually off-white particles of the organobromine flame retardant and antimony III oxide yield a surface chalkiness with consequent effect on depth of shade of any dye present, such fabrics in workwear

applications have been found to be advantageous in some off-shore applications where they possess an oil-shedding property.

In the case of durable, phosphorus-containing cellulose flame-retardants, they are generally only effective on cellulose-rich blends with polyester because while they may have some positive effect on the polyester component, they are only substantive on the cellulose component. THPC - based systems like Proban[®] are effective on blends containing no less than 55% cotton if a combination of flame retardation and acceptable handle is required. This is because the THPC condensate is substantive only on the cellulose content, which would require over 5 wt.-% phosphorus to be present on this component in order to confer acceptable flame retardancy to the whole blend. However, high phosphorus and hence finish levels lead to excessive surface deposits on fibres, decreased durability to laundering and create unacceptable harshness of handle. Furthermore, such applications only work well on medium to heavy weight fabrics (> 200 gm⁻²) and so are particularly effective for protective clothing applications. The use of a cotton-rich blend here is particularly advantageous because the lower polyester content confers a generally lower thermoplastic character to the fabric with less tendency to produce an adhesive molten surface layer when exposed to a flame.

In order to achieve the high finish levels necessary, often a double pass pad (or foam)-dry stage is required before the THPC-urea-impregnated fabric is ammonia-cured in the normal way. If a lower degree of durability is required then cheaper semi-durable flame retardant combinations are feasible. For example, combination of an oligomeric ammonium polyphosphate/urea formulation (e.g. Antiblaze[®] LR2, Rhodia) at phosphorus levels of about 6 wt.-% with respect to the cotton component together with 5-6 wt.-% of the monomeric cyclic phosphonate exemplified by Antiblaze[®] CU/CT (Rhodia) or Aflammit[®] PE (Thor) with respect to the polyester component applied to cotton and polyester components

respectively in the blend will give a 40 °C, 30 min water soak-resistant finish as required for UK domestic upholstery fabrics [13].

Application of methylolated phosphonamide finishes (e.g. Pyrovatex[®] CP) is effective on blends containing 70% or less cellulose content. This is because the phosphorus present is less effective on the polyester component than in THP-based finishes [2]. The reasons for this are not clear but are thought to be associated with some vapour-phase activity of phosphorus in the latter finish on the polyester component [40].

While blends of cotton with polyester comprise the majority of cotton/synthetic fibre mixtures, in the USA especially, majority cotton blends with nylon are quite common for workwear where the latter is present to increase abrasion resistance. In this respect, Weil and Levchik [5] cite blends of 88% Proban[®]-treated cotton with 12% high tenacity nylon sold by Westex as Indura[®] Ultra Soft fabric for high comfort work clothing. Within the UK, Carrington Workwear market a range of 88% Proban[®] cotton/12% nylon fabrics under its Flamgard range with specific examples being Flamtuff[®] 200, Flamtuff[®] 250 and Flamtuff[®] 330 where the number relates to the area density in g/m². They also market antistatic versions comprising 88% Proban[®]/12% nylon/1% antistatic nylon. The nylon component may be increased and the US Alexium International Group claims to have a durable flame retardant treatment that will be effective on 50/50 blends with applications in military fatigue fabrics [41]. No information regarding the flame retardant system used is available but for high nylon contents one Burlington Industries patent [42], for instance, claims that for nylon contents between 10 and 65%, THPX finishing of cotton combined with either a monomeric cyclic phosphonate (e.g. Antiblaze CU/CT, Rhodia) or hexabromocyclododecane are required to achieve acceptable levels of flame retardancy. The process must be carried out in two stages where the first is application of the THPX/ammonia finish and followed by padding on

and heat curing of the second agent. Other similar Burlington Industries patents of a similar type for cotton/nylon blends have been cited and reviewed by Weil and Levchik [5].

4.3 Durable flame retardant finishes for wool

Of all conventional fibres, wool has the lowest inherent flammability and for some end-uses, where high density of structure and horizontal orientation (e.g. carpets) are required in the product, wool fabrics will pass the required flame retardancy tests untreated. Its relatively high LOI value of about 25%, high ignition temperature of 570-600 °C and low flame temperature of about 680 °C is a consequence of its higher moisture regain (8-16% depending upon relative humidity), high nitrogen (15-16%) and sulphur (3-4%) contents and low hydrogen (6-7%) content by weight. While organo-sulphur compounds are generally flame retardant to some degree, the disulphide cystine links are easily oxidisable and so this can offset some of the anticipated natural flame retardancy. Pre-oxidation of wool and hence cystine to cysteic acid residues restores this expected activity and oxidised wools can have greater inherent low flammability.

Notwithstanding the above, if wool is to be effective in applications such as curtains, upholstery, protective clothing and barrier fabrics, flame retardant finishing is essential, although durability often needs only to extend to dry cleaning in most instances. When heated wool, like cellulose, tends to form a char and this reaction is highly favoured in untreated wool. Furthermore, because wool chars via a semi-liquid state, char-formation is accompanied by intumescence to give an expanded, though brittle char which is often thicker than the original fabric. Thus the charred structure provides an equivalent, if not superior thermal barrier, provided that the char remains coherent, relative to the original fabric. This makes wool an ideal fibre for use in protective clothing, especially where the hazard of molten metal splash exists, because the intumescent char provides a thermal barrier to the

solidifying metal splash (and its associated emission of latent heat of fusion), and the mass of the metal enables it to fall away as the weak encapsulating char fractures. An added advantage of the char is that following its formation by a point ignition source of short duration (e.g. brief cigarette or match contact), it can be brushed away leaving little if any sign of damage assuming that only the fabric surface has been exposed. Finally, the absence of significant inorganic salt concentration in natural wool, gives few if any afterglow problems, which can be a feature of cellulosic textiles.

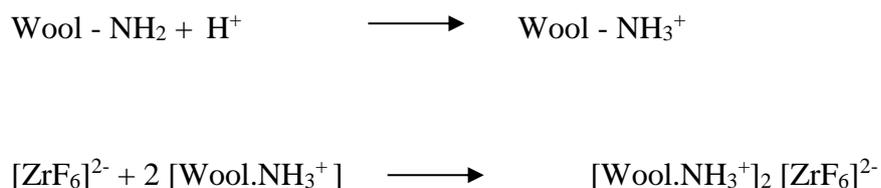
The review by Horrocks [2] comprehensively discusses developments in non-durable and durable flame retardants for wool up to 1986 and very little has changed since that time. Readers should consult this and its many cited references for a more detailed understanding of flame retardant treatments for wool.

It is significant that the nominally non-durable ammonium phosphates and derivatives, which function as Lewis acids, release phosphorus acids and promote the deamination of wool protein and so encourage char promotion, when dried and cured at temperatures up to 130 °C, will give dry clean durability up to as many as 10 cycles. Even the highly water soluble ammonium bromide can give some degree of dry-clean durability on wool.

As detailed in reference 2, in spite of considerable research into the use of functional phosphorus-based finishes, including the more recent study of the effectiveness of methylolated phosphonamides (e.g. Pyrovatex® CP) by Hall and Shah [43], and substantive halogenated species like chlorendic, tetrabromophthalic and dibromo-maleic anhydrides and brominated salicylic acid derivatives, the most commonly used durable flame retardants are based on Benisek's Zirpro® system [2 and references cited therein] initially developed and marketed by the International Wool Secretariat (IWS). Major advantages of this treatment are the absence of any discoloration or other effect on wool aesthetics, coupled with its application via a simple exhaust process usually during the normal acid-dyeing process.

The Zirpro[®] process is based upon the exhaustion of negatively charged complexes of zirconium or titanium on to positively charged wool fibres under acidic conditions ($\text{pH} \leq 3$) at a relatively low temperature of 60°C. Zirpro[®] treatments can be applied to wool at any processing stage from loose fibre to fabric using exhaustion techniques either during or after dyeing. The relatively low treatment temperature is an advantage because this limits the felting of wool.

The processor has the choice of potassium hexafluorozirconate (K_2ZrF_6) or a mixture of this and potassium hexafluorotitanate (K_2TiF_6). Both components are stable metal fluoride complexes which are substantive to wool. Exhaustion is rapid achieving 80% or so after 30 minutes. The simple chemistry of application is:



Some hydrolysis of the complex does occur but Benisek demonstrated that acceptable flame retardancy occurs if the molar ratio $\text{F}:\text{Zr} \geq 5$ when maximum exhaustion occurs [44] and the zirconium concentration on the fabric is 2.3 wt.-%. The use of the titanium complex, because of the smaller ionic size and hence the greater penetrative character of titanium, enables an equivalent or higher level of flammability to be achieved at similar bath concentrations. K_2TiF_6 , however, causes discoloration and so it is used as a mixture with K_2ZrF_6 to minimise this and decrease both concentrations and cost [2].

It is important to maintain a low $\text{pH} (\leq 3)$ in order to maximise fibre penetration and wash-fastness to as many as 50 washes at 40 °C or 50 dry cleaning cycles in perchloroethylene. Acids like hydrochloric and formic acid are preferred because, unlike sulphuric acid, for

example, they do not have anions which compete with the metal fluoride ions for protonated amino groups in wool. However, the general simplicity of the whole process enables it to be used either concurrently with 1:1 premetallized and acid levelling dyes or after dyeing when applying acid milling reactive 1:2 premetallized and chrome dyes. Furthermore, the treatments are compatible with shrink-resist, insect-resist and easy-care finishes.

Should smoke emission be a problem, then because the above Zirpro[®] treatments can increase smoke generation with respect to untreated wool, a low-smoke variant may be used which comprises a fluorocitratozirconate complex. This is applied from formic acid to achieve a molar ratio F:Zr = 2 and a zirconium concentration of at least 2-3 wt.-%.

The effectiveness of the Zirpro[®] treatment is not fully understood from the mechanistic point of view and while Benisek [45] attributes it to enhanced intumescent char formation, Beck et al. contest this view [46] and state that the treatment promotes peptide bond scission with increased mass loss. Clearly, however, its ability to create extremely effective flame and heat barrier properties at high heat fluxes is associated with the char structure generated.

Zirconium hexafluoride as the fluorozirconate salt was in the recent past supplied by MEL Chemicals, UK, although its web-site now suggests otherwise. However, Thor have their product Aflammit[®] ZR, which comprises potassium hexafluorozirconate, as a suitable flame retardant to achieve the Zirpro[®]-type finish. They also have a product Aflammit[®] ZAL comprising zirconium acetate solution which when used together with Aflammit[®] ZR claims to give a reduced smoke flame retardant finish to wool fabrics. The Avocet Dye and Chemical Company (UK) produce respectively similar flame retardant formulations, namely Cetaflam[®] PHFZ and Cetaflam[®] ZAS for normal and low smoke Zirpro[®]-type finishes. They also supply Cetaflam[®] DTB to reduce afterflaming times in conjunction with the previous formulations – this is probably tetrabromophthalic acid or a similar chemical (*see* below).

Recently the Zirpro[®] process has come under the critical eye of environmentalists as a consequence of the release of heavy metal ions into effluent discharges. In attempts to decrease effluent problems, replacement of the exhaust method by padding methods has not been successful because both the potassium metal fluoride complexes are not very soluble (~10 g/l) at room temperature.

In some applications, such as transport seating fabrics, where excess afterflame is seen to be a problem, the Zirpro[®] treatment may be combined with a bromine-containing agent such as tetrabromophthalic acid (TBPA) which has a substantivity for wool under acid conditions [47]. This enables slightly lower concentrations of zirconium to be used but this is offset, from an environmental point of view, by the addition of bromine present.

In spite of these concerns, research during the last fifteen years or so has been limited. For instance, Lewin and Mark [48] have demonstrated that sulphation with ammonium sulphamate followed by curing at 180-200 °C in the presence of urea can give a 50 hard water wash-durable finish for wool fabrics with little change in handle. Research by the author into the possibility of using treatments based on intumescent has shown that enhanced barrier properties are possible and this occurs for both flame retarded (Zirpro[®]) and unretarded wool fibres present [49, 50].

One final point to be mentioned concerns the need to impart a number of finishes to wool fabrics if they are to achieve the many performance requirements demanded by protective clothing and aircraft (and other transport) upholstery applications, for instance coupled with the need for easy-care properties. Developments in this area have been reviewed [2] and certain factors are worthy of note:

- oxidative shrink-resist treatments should be applied before Zirpro[®] treatment;
- insect resist treatments should be added to a Zirpro[®] bath first;

- resin-based shrink-resist treatments can promote flammability unless, like the Hercosett (Hercules) resin, they contain elements like chlorine and nitrogen; such resins should be applied after Zirpro[®] treatment; and
- co-application of water-repellent (e.g. resin-wax dispersions) and oil-repellent (eg fluorocarbon) finishes should follow Zirpro[®] treatment, for example by a pad-dry-cure-rinse-dry process.

When processing wool blends, given the position of the Zirpro[®] process as the currently major durable flame retardant treatment, its specificity ensures that little if any transferability of both the zirconium complex or its flame retardant activity occurs to other fibres present. Furthermore, Benisek reported antagonisms between Zirpro[®] and other flame retardant fibres, principally Trevira[®] CS in 1981 [51]. In the absence of any back-coating treatment acceptable flame retardancy of Zirpro[®]-treated blends are obtainable in 85/15 wool/polyester or polyamide combinations although synthetic fibre content may be increased to about 25% if the zirconium tungsten modified treatment is used. For lower wool contents in blends and without the possibility of using alternative flame retardant treatments, flame retardance can be maintained only if some of the Zirpro[®]-treated wool is replaced by certain inherently flame retardant fibres, except for Trevira[®] CS polyester [51]. Chlorine-containing fibres such as PVC and modacrylics are particularly effective in this respect.

4.4 Flame retardant finishes for man-made fibres

Man-made (including regenerated and often-called chemical or synthetic) fibres may be rendered flame retardant during their production thereby creating a degree of inherent flame retardancy. Apart from viscose and, more recently, lyocell fibres, the conventional synthetic fibres are hydrophobic with physical structures inaccessible to the salt-like materials used for semi-durable flame retardants and even the most reactive precursor organophosphorus agents.

Consequently, only regenerated cellulose fabrics and blends are amenable to durable flame retardant finishing with treatments used for cotton. Viscose, in particular, is more delicate than cotton and lyocell fibres, and so must be finished with care to avoid undue strength losses during drying and curing. Very rarely, to the author's knowledge are viscose fibres durably flame retardant treated since there are inherently flame retardant alternatives such as Lenzing's flame retardant viscose available and these more commercially attractive (*see Chapter 5*).

The remaining common synthetic fibres, namely polyamide, polyester, polyacrylic and polypropylene, may be semi-durably and durably flame retarded and **Table 4.3** lists examples of those currently available for polyester and polyamide (and blends).

Table 4.3

In the case of acrylics, because of the difficulty of finding an effective flame retardant finish, modacrylic fibres are preferred.

The low melting point, non-functionality and high hydrocarbon fuel content (*see Table 4.3*) of polypropylene are three factors that have created problems in finding an effective durable flame retardant finish and also pose difficulties in the design of effective back-coatings (*see Section 4.5*).

This leaves only polyamides and polyesters as possible candidates for durable flame retardant treatments. While the scientific literature contains a number of possible solutions [2], few have entered the commercial arena as examples in **Table 4.3** show [3].

The Antiblaze[®] CU product (formerly Antiblaze[®] 19 [2]) based on the cyclic phosphate formula in **Table 4.3** is claimed to be effective on polyamides and polypropylene as well as polyester, for which it was initially developed. It is essentially monomeric although has been

available as the high boiling dimer, Antiblaze® P45 for use as a melt additive. Antiblaze® CU has a high phosphorus content (21.5 wt.-%) and is a clear viscous liquid which is applied to polyester at 3 to 6 wt.-% add-on buffered at pH 6.5 with disodium phosphate and a small amount of wetting agent. After padding at about 40-60% expression or wet pickup, fabric is dried at 110-135°C followed by thermofixation at 185-205°C for 1–2 min. Thermofixation usually only results in about 80% retention of the original finish because of its volatility at high temperature. After rinsing and drying, the finish should resist 50 washes at 60°C or 10 dry cleaning cycles with 90% retention.

This same finish may be incorporated in a resin for coating for polyester and its blends. Durability is not as great but loss does not occur during processing as in the thermofixation treatment. Inclusion of melamine increases the finish effectiveness on 100% polyester. A typical binder mass ratio of Antiblaze CU : melamine : binder would be 8 : 13 : 34 with the residual weight made up of water and a viscosity modifier. Thor's Aflammit PE and Schill & Seilacher's Flacavon AZ are believed to have a similar chemical composition if not the same as Antiblaze CU.

Of the other durable FR finishes for polyester listed in **Table 4.3** are those that may be applied directly from the dyebath and these include Cetaflam® DB 9 and DbeXL (Avocet, UK) and the very recently introduced TexFRon® 3000 (ICL-IP), both of which have undisclosed chemistries.

For the flame-retardant treatment of nylon fabrics few treatments are satisfactory. While application of 10 wt.-% ammonium bromide or 18 wt.-% ammonium dihydrogen phosphate by a pad-dry route is effective but non-durable, the use of urea-formaldehyde resins or aminotriazine-aldehyde condensates can be used with ammonium bromide using a pad-dry-cure process to improve the durability of the finish. Durable but fabric-stiffening flame retardant finishes based upon methylated urea-formaldehyde with thiourea- formaldehyde

have been successfully applied to nylon nets for evening wear and undershirts. For example Thor's Aflammit[®] NY comprises two components, Aflammit[®] NY 1 based on an organic nitrogen/sulphur compound, probably a thiourea derivative and Aflammit[®] NY 2, the cross-linking methylolated urea component. Typically for such formulations, about 15-20 wt.-% thiourea-formaldehyde precondensate is padded with ammonium chloride (1 wt.-% on the weight of the resin) as a latent catalyst followed by low temperature drying and then curing at 170°C for 1 min. Examples of these finishes are included in **Table 4.3**, although the exact chemical constitutions of polyamide-specified retardants are not available.

4.5 Flame retardant coatings and back-coatings

Coating technologies have been around for many years and the review by Woodruff [52] shows that main applications are for technical and industrial textile applications which may involve the need for flame retardancy. Back-coatings are more usually applied to the reverse faces of furnishing fabrics and so have applications in both consumer and contract markets. The whole area of flame retardant textile coatings and back-coatings has been recently reviewed by the author [53] and readers are invited to read this reference for greater detail, especially into recent research and innovations in these areas.

4.5.1 Flame retardant coatings

Given the detailed reviews cited above [52, 53], this section will focus only on currently used flame retardant coatings with certain service applications in mind. Flame retardant coated textiles include a wide range of materials in which flame retardancy is only one property (e.g. tarpaulins, awnings and outdoor textiles which also require waterproof and weather resistant properties). This area also overlaps the area of laminated textile materials (e.g. airbags and seating composites for automotive and other transport applications, decorative textile

laminates, etc.). Coating technologies are quite numerous and varied [52] and from the applied polymeric formulation viewpoint they include the following:

- solvent-based systems
- chemically-cured systems and
- hot melt processes.

With the need for reduced volatile organic species produced in the workplace and rising costs of solvents, chemically-cured and hot melt formulations have become more popular in recent years. Furthermore, the former are often applied as polymer dispersions in aqueous media. In the main, flame retardant coating formulations are applied to conventional fibre-containing fabrics such as cotton, polyester, polyamide, etc., unless very high levels of fire resistance are required and then glass fabrics are often the textile substrate. **Table 4.4** lists a selection of the coating polymers used alongside their respective limiting oxygen index values from which it may be seen that those with $LOI \geq 25\%$ have some degree of inherent flame resistance.

Table 4.4

Flame retardancy or enhanced flame resistance is usually introduced by means of additives which fall into one or more of the following groups:

- Phosphorus-containing agents;
- Halogen-containing agents;
- Intumescent;
- Synergists only in the case of halogen-containing coating polymers;
- Inorganic agents.

Ideally those selected should be liquids so that polymer coatings remain flexible (and indeed may be plasticised) and retain desirable surface properties. This is not possible when

intumescent or synergists like antimony III oxide are used because of their usually white (or off-white) particulate characteristics.

Table 4.5 and Table 4.6

Phosphorus-containing agents: **Table 4.5** lists typical examples of acceptable flame retardants including the long chain alkyl/aryl-substituted phosphate examples where plasticisation is also required. While **Table 4.5** concentrates on single chemical entities, many commercial proprietary flame retardants are formulated mixtures or blends which are especially easily achievable when components are liquids. Such blends enable balances of flame retardancy to be achieved while offering acceptable processing and end-product performance.

Halogen-containing flame retardants: Within this group (*see Table 4.6*), bromine-containing agents predominate because not only are they more efficient than similar chlorine-containing species, but also the high atomic weight of bromine ensures that it is present in a high mass fraction within most organo-bromine compounds. Typically for many polymers acceptable levels of flame retardancy are achieved if at least 5 wt.-% bromine is present in the final formulation. For example, the very commonly used decabromodiphenyl ether (DecaBDE; *see Table 4.6*), where the bromine content is 83 wt.-%, its presence is often less than 10 wt.-%, which is quite low compared with most flame retardant polymers containing other additive flame retardants. However, the synergist antimony III oxide (ATO) is usually present [54] and assuming a bromine:antimony molar ratio Br:Sb = 3:1 (reflecting the possible formation of SbBr_3 as an intermediate), this equates to a mass ratio ATO:DecaBDE = 1:2, thereby ensuring that the total flame retardant concentration present in the polymer may be as high as 15 wt.-% or so. Similarly high total formulation levels are seen for other brominated flame

retardants, although still often less than the >20 wt.-% levels required by phosphorus-containing FRs and >50 wt.-% levels for some inorganic agents (*see below*). Recently, a number of tin compounds including zinc stannate (ZS) and zinc hydroxystannate (ZHS) have been shown to be synergistic with halogen-containing flame retardants, but unlike ATO, bromine-containing FR/ZS or ZHS combinations have to be selected for maximum efficiency [55, 56]. These are also briefly discussed in the following sections on synergists and inorganic flame retardants.

Intumescent systems: Intumescent flame retardants are those that form a highly expanded, insulative chars on heating and so offer high levels of flame barrier properties [57, 58] within the polymer. These are especially beneficial in polymers such as the polyolefins and polyesters which lack any char-forming ability and where the intumescent char provides a supportive network preventing melt dripping and restricting the overall burning process. Such formulations may be intumescent in their own right and generate carbonaceous chars independently of the surrounding polymer matrix or they may interact with the matrix so that the flame retardant-polymer together give rise to an expanded, intumescent char when exposed to heat and flame. The majority of these are based on ammonium polyphosphate (APP) and melamine chemistries and selected examples are presented in **Table 4.7**.

Table 4.7

All are particulate solids, of which one or more components may be water soluble, and so for water soak or wash durability they may only be used in hydrophobic polymeric coating matrices which may create dispersion problems during processing. Hence, many commercial particulate examples are coated or microencapsulated either to reduce water solubility and/or to improve polymer matrix compatibility. Furthermore, as seen in **Table 4.7**, manufacturers

like Budenheim are offering variations with reduced particle sizes as shown for APP and melamine phosphates in particular.

While APP is not an intumescent in its own right, it is a powerful char-former when in the presence of oxygen-containing polymers and copolymers and so is particularly effective on cellulosic and polyamide textiles. To ensure intumescent action, it is used in combination with other agents such as pentaerythritol and melamine [57]. The melamine phosphates shown in **Table 4.7** do have a greater degree of inherent intumescent activity since the acid-forming component phosphate is chemically combined with the gas-forming melamine. They also have superior water insolubilities often $<1 \text{ g}/100\text{cm}^3$ before any subsequent coating or microencapsulation. Particle sizes are often less than normal APP samples and may have particle diameter values of $D_{50} \leq 8 \text{ }\mu\text{m}$.

Of all flame retardant coating innovations of the last few years, it is probably true to say that those incorporating intumescent flame retardant agents have been the most commonly reported [57-59]. Indeed the recent demand for halogen-free, flame-resistant barrier fabrics in US markets driven by Californian regulations for furnishings (TB 133) and mattresses (TB 129 and 630) and federally by the US Consumer Product Safety Commission (CPSC 16 CFR 1633) for mattresses [60] has encouraged the development of intumescent coatings applied to inherently fire resistant fibre-containing fabrics, including glass which are exemplified by the established Springs Industries products [61] and fabrics from Sandel International Inc., USA.

Synergistic additives: While pure PVC has an LOI in the region 45-47%, in the presence of a typical plasticiser such as di-isononyl phthalate, the LOI reduces to between 23 and 25%. If the plasticised polymer is to achieve acceptable levels of flame retardancy then either the plasticiser is replaced by a similar flame retardant with plasticising properties such as a phosphate ester such as isodecyl diphenyl phosphate (e.g. Phosflex[®] 390, Supresta) (*see Table 4.5*) or a synergist like antimony III oxide is added to act together with the chlorine

present and so raise the LOI to above 30% or so. In practice, addition of ATO is the cheaper option and so more often used for a variety of flame resistant PVC-coated textiles such as awnings, carpet backings and tarpaulins. It is possible to replace the ATO by zinc hydroxyl stannate, which although slightly more expensive, has no associated toxicological risk factors [56].

Inorganic flame retardants: These are typified by compounds such as the hydrated aluminium and magnesium oxides. The former is often referred to as alumina trihydrate (ATH) or aluminium hydroxide and the latter, magnesium hydroxide (MDH) [62]. Both release water when heated and this increases the overall endothermicity of the flame retardant polymer and generates water vapour which then dilutes the flame, thereby promoting flame extinction. However, both hydroxides require to be used at high mass concentrations, typically above 50 wt.-% and then may promote stiffness and chalkiness when used in coatings. They have different sensitivities to heat with aluminium hydroxide releasing water (up to 34.6 wt.-% of initial mass) when heated above 200 °C and so may only be used in low melting fusible polymers such as polyethylene and EVA. On the other hand, magnesium hydroxide, which is more expensive, is stable up to 300 °C and so may be used in many higher-temperature processed polymers such as polypropylene, polyamides and fluorinated copolymers. Neither hydroxide may be used in thermoplastic polyesters since they can catalyse decomposition. When used in textile coatings, particle size control is essential and while the coarser grades produced by grinding may have average diameters as high as 35 µm or so, the finer grades, in particular of ATH, are preferred. These are produced by precipitation and can have diameters below 5 µm. The finest grades of ATH at about 1 µm are preferred for coating fabrics while the coarser grades between 3 and 12 µm find application in polyethylene carpet backing formulations [63]. In order to improve dispersion and rheology, surface-coated variants are generally commercially available.

Other well-established inorganic flame retardants like zinc borate (e.g. Firebrake[®] ZB, Rio Tinto), while being used primarily in bulk polymeric applications, may be used as an antimony III oxide (ATO) synergist replacement in flexible PVC in waterproof coatings (e.g. tentage, awnings) and carpet backings. Its presence also has a smoke-reducing effect as do ATH and MDH when present in coating formulations. Other inorganic salts used as ATO-replacement synergists include zinc stannate (Flamtard S, William Blythe, UK) and zinc hydroxystannate (Flamtard H, William Blythe, UK), both of which have the advantage of very low particle size (1-2 µm) as well as suppressing smoke.

In conclusion, while most major flame retardant manufacturers are offering non-halogen coating formulations, they do not disclose which of the above non-halogen methodologies are used. For example, ICL Industrial Products market their TexFRon 9020 and 9025 low melting coating formulations as being alternatives to DecaBDE and HBCD with better efficiency in terms of percentage bromine requirement. This suggests that bromine is still present and that it is a bromo-containing polymer based on this company's having developed a range of such products as being ecotoxicologically superior. These are typified by their portfolio of brominated polystyrene (FR803), brominated epoxy (FR 2400) and brominated benzyl acrylate (FR1025) products [64]. Of these, it is likely that poly(pentabromobenzyl acrylate) forms the basis of their latest TexFRon P and P+ coating and back-coating formulations (*see Section 4.5.2*) [65]. TexFRon P+ also contains a phosphorus-containing agent as well as the bromine-containing polymeric binder which enables less antimony III oxide to be required in comparison with DecaBDE/HBCD-based formulations.

4.5.2 Flame retardant back-coatings

Back-coating describes a family of application methods which has grown in importance since the 1980s where the flame retardant formulation is applied in a bonding resin to the reverse

surface of an otherwise flammable fabric (*see* **Figure 4.1**, process (iv), and **Figures 4.5** and **4.6**). During the last 30 years, they have come to dominate the UK furnishing fabric market as a consequence of the UK furnishing regulations first of 1979 (amended in 1983 [66]) and then 1988 [13]. Their success has been due to their relative cheapness and the fact that they can be applied to the reverse of any fabric structure comprising of any fibre type(s) without affecting the aesthetics of the front face of these fabrics. Careful use of viscosity modifiers and general back-coating application variables ensures that "grin-through" is minimised and low second order transition resins ($T_g < 10^\circ\text{C}$) are to be recommended if fabric handle effects are to be minimised. Application methods include doctor blade or knife-coating methods [52] and the formulation is as a paste or foam. These processes and finishes are used on fabrics where aesthetics of the front face are of paramount importance, such as furnishing fabrics and drapes. **Figures 4.5(a)** and **4.5(b)** show schematically, blade-in-air and blade-over-roll methods respectively. **Figure 4.6** shows a schematic diagram of the whole back-coating process from application, oven curing and final fabric wind-up.

Figure 4.5 (a and b) and Figure 4.6

The underlying scientific principles of back-coating have been little studied and work in the author's laboratory in 1999 attempted to analyse the important variables involved [67]. In this study, the effect of coating parameters of a typical DecaBDE/ATO formulation (*see* below) on the levels of penetration within a cellulosic upholstery fabric was investigated with the overall aim of improving the effectiveness of the antimony/bromine-free flame-retardants present. Three variables were studied using a blade-over-air coating technique which were blade angle, blade height and coat formulation viscosity. It was seen that a low viscosity, as might be expected, allowed best penetration as did a low blade height which increases the

force exerted on the coating and so help push it through the fabric. An optimum blade angle of 10° was observed suggesting that in any back-coating process, selection of the blade variables is crucial if optimal coating and penetration are to be achieved.

The vapour phase activity of the typical halogen-containing/antimony III oxide synergised flame retardant formulations discussed above [54] ensures their effectiveness since their activity may transfer easily from the coating on the rear face of the fabric to the front face where an igniting source such as a match or cigarette will impinge. Within the UK's furnishing textile back-coatings market, the standard formulations based on antimony III oxide and brominated hydrocarbons, notably decabromodiphenyl ether or oxide (DecaDBE), still dominate in spite of environmental concerns, although these are becoming increasingly active with the likelihood of its being withdrawn during 2016 (*see* below). A typical back-coating formulation is based on the recipe:

Decabromodiphenyl ether or oxide	33 wt.-%
Antimony III oxide	17 wt.-%
Acrylic binding resin	50 wt.-%

applied to the back of the fabric at 20-30 wt.-% total solids add-on. As for coating formulations discussed above, the above mass ratio for ATO : DecaBDE of 1 : 2 relates to an elemental mole ratio for Sb : Br of 1 : 3 and a bromine concentration of about 5-10 wt.-% on fabric. Such a back-coating application equates with dry coating weights of 70-80 gm⁻² for velour pile fabrics, 30-40 gm⁻² for cotton woven fabrics and 40-50 gm⁻² for other flat woven furnishing fabrics in which the solids content of DecaBDE equates with 30-40 wt.-% of the dry coating weight as shown above [68]. For all synthetic fibre-containing fabrics, back-coating levels are much greater because the char-forming character of the resin needs to

offset the shrinking back and melting of the face fabrics which would otherwise reveal the underlying filling to the igniting source. Back-coating levels here may be in the region of 50-100 wt.-%.

When DecaBDE came under environmental scrutiny some years ago [3], hexabromocyclododecane (HBCD) was considered to be a viable alternative and used during the late 1990 and early 2000 period. However, while both DecaBDE and HBCD were considered to have low toxicological risk in the US National Academy of Sciences risk analysis in 2000 [69], subsequent EU risk analyses [68, 70] while finding no significant risk for DecaBDE, did so with HBCD. This latter risk assessment [68] concluded that HBCD is persistent, bioaccumulative and toxic and while there is no risk to consumers, either by exposure to products containing HBCD or via the environment, there are possible risks to the workforce during processing. As a consequence, HBCD will be phased out from use in Europe by October 2015. During this same period and especially in the USA, DecaBDE has continued to be subjected to environmental interest pressures to the extent that the two US manufacturers ceased production by 31 December 2012 and the three major US suppliers have agreed to cease supply by 31 December 2013. In the EU, similar pressures have increased to the extent that at on 19 December 2012 [71], DecaBDE was included on the European Chemicals Agency list of Substances of Very High Concern (SVHC) under Article 57 of the EU Reach regulation [72] as persistent, bioaccumulative and toxic (Article 57d:PBT) and very persistent and very bioaccumulative (Article 57 e: vPvB). Thus it is under increasing pressure to be withdrawn from use in Europe and this will most likely occur during 2016. Consequently, a number of companies are marketing bromine-containing alternatives such as decabromodiphenyl ethane (or ethane 1,2 -bis(pentabromophenyl) marketed as Great Lakes Emerald 1000 and by Albemarle as Saytex 8010. While having a similarly high bromine content (82.3 wt.-%) as DecaBDE it is claimed to have no adverse

toxicological and ecotoxicological effects. Similarly, DecaBDE alternatives are being marketed by ICL-IP under the TexFRon 9000 as an immediate DecaBDE replacement in back-coating formulations as well TexFRon 9020 and 9025 as discussed in **Section 4.5.1** above.

While coating methods generally, unlike those requiring impregnation (*see Figure 4.1*, processes (i) – (iii)), lead to little or no waste of application chemical formulation and hence effluent problems, there remain increasing pressures to replace antimony-bromine formulations by less environmentally-questionable retardants based on phosphorus. In these respects the use of halogen-containing resins, such as PVC-vinyl acetate and PVC-ethylene-vinyl acetate copolymers and poly(pentabromobenzyl acrylate) [64, 65] may be used to decrease the amount of the less effective, alternative phosphorus-containing replacement retardants required and hence maintain acceptable coating application levels.

At the current time, while there are a number of commercial halogen-free back-coating formulations available, they tend to be fabric-specific and less effective than the antimony-bromine ones they replace. Of these so-called halogen-free alternatives, the majority will most likely contain ammonium polyphosphate (APP) which has the significant advantages that, not only is it effective on most cellulose, wool and even acrylic-containing fabrics, but also its solubility is less than the simple phosphates which would fail to pass the UK regulatory 40°C soak test prior to testing to BS 5852:Part 1:1979 [13]. However, the solubility of the simpler APP types is often insufficient to withstand this durability requirement and it depends on the degree of polymerisation of the linear $-\text{[P(O).(ONH}_4\text{).O]}_n-$ chains and the type of crystalline structure. **Table 4.7** also lists a range of commercial currently and formerly available ammonium polyphosphate types and associated solubility, average particle size and thermal data where available. Encapsulation of APP can also increase insolubility and a number of commercial examples are also listed in **Table 4.7**. In

A.R. Horrocks. Overview of traditional flame-retardant solutions, in: *Update on Flame Retardant Textiles: State of the Art, Environmental Issues and Innovative Solutions*, J. Alongi, A.R Horrocks, F. Carosio and G. Malucelli (Eds), pp.123-178, Smithers Rapra, Shawbury, UK (2013)

addition, APP has a phosphorus content of about 32 wt.-% and so add-ons of 5–15 wt.-% are required to achieve phosphorus levels of about 1.5–4.5 wt.-%.

Of the commercial variants available not marketed under an APP umbrella, Devan Chemicals' (Belgium) Eco-flam series of products were pioneers in this area. For example the company recently claims that its products Ecoflam[®] PU 222, PU254 and PU when applied to upholstery comply with EN 597-1 cigarette and EN 597-2 match tests as well as achieving M1 of the French NF 92504 test after water soaking [73]. Thor also have two non-halogen-based, Aflammit[®] UCR and Aflammit[®] FMB which are based on phosphorus and nitrogen compounds and after pad-cure application are claimed to yield 40 °C water soak durability and passes to BS 5852:Part 1:1979 furnishing regulatory requirements. It is important to note, however, as stated above that whereas the bromine-antimony formulations function on all fabric /fibre types, the non-halogen alternatives are fibre/fabric specific with the Thor products, for example, being recommended only for fabrics containing high percentages of cellulosic fibres.

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Table 4.1: Comparison of the strengths and weaknesses of tetrakis(hydroxymethyl) phosphonium salt condensate- and N-methylol N, N' dimethylpropionamide derivative-based flame retardants for cotton

Flame retardant	Advantages	Disadvantages
THPX condensates	<p>Durable to over 100 75°C (hospital) washes</p> <p>Minimal losses in fabric tensile and tear properties</p> <p>No reported significant emissions of formaldehyde in use</p>	<p>Requires specialist ammonia gas cure unit</p> <p>Can react adversely with some dyes e.g. sulphur</p> <p>May require softeners to improve fabric handle</p>
N-methylol dimethylpropionamide derivatives	<p>Durable to over 100 75°C (hospital) washes in the absence of bleach only.</p> <p>Applied by normal pad-cure methods.</p> <p>Compatible with all dyes, hence ideal for prints.</p> <p>My be applied and co-cured together with other finishes such as soil release agents.</p>	<p>Significant losses in tensile (typically up to 20%) and tear (up to 50%) strengths.</p> <p>Often forms tarry deposits in curing plant.</p> <p>Poor abrasion resistance.</p> <p>Formaldehyde release is a problem during application and end-use.</p> <p>Autocatalytic hydrolysis during storage releases formaldehyde</p> <p>Cannot be used in sensitive applications such as children's nightwear</p>

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Table 4.2: Pyrovatex CP standard and optimised application recipes and pilot-scale results [28, 29]

	Standard Recipe	Optimised Recipe
Recipe Component, g/litre		
Pyrovatex CP	280	260
Melamine resin	35	32
Softener	25	27
Acid catalyst	20	15
Wetting agent	1.25	1.25
Fabric Response, %		
LOI	28	30
Phosphorus on fabric	1.9	2.0
Emission level after curing stage, ppm		
HCHO, formaldehyde	20	5

Table 4.3: Durable finishes for synthetic fibre-containing textiles [3]

Chemical Constitution/Comments	
Rhodia	
Antiblaze CU/CT	$(\text{CH}_3\text{O})_{2-n} \cdot \text{P} \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{OCH}_2 \cdot \text{C} \begin{array}{l} \text{CH}_2\text{CH}_3 \\ \text{CH}_2 \cdot \text{O} \\ \text{CH}_2 \cdot \text{O} \end{array} \text{P} \cdot \text{CH}_3 \\ \parallel \\ \text{O} \\ \text{CH}_3 \end{array} \right]_n$ <p>N=1; cyclic oligomeric phosphonate; pad-dry(110-135°C)-cure(185-200 °C) Primary use: polyester Secondary uses: polyamide, polypropylene</p>
Thor	
Aflammit PE Aflammit NY	As above for Antiblaze CU, polyester Organic nitrogen and sulphur compound (probably a thiourea derivative) and a reactive cross-linking compound; polyamide. Cure at 150-170°C for 45-60s.
Schill & Seilacher	
Flacavon AM	Nitrogen and sulphur-containing compound (thiourea derivative?); polyamide; 100-110°C dry only; durable to dry cleaning
Flacavon AZ	Organic phosphorus compound (as for Antiblaze CU?); polyester
Flacavon H14/94	Antimony oxide + bromine compound (+ binder); all fibres especially polyester-cotton blends
Clariant	
Pekoflam PES new liq.	Cyclic organic phosphorus compound (as for Antiblaze CU?); polyester
Apexical (US)	
Apex Flameproof 1506	Organohalogen compounds: polyester
Apex Flameproof 1528	Non-toxic, durable non-halogen flame retardant: polyester and polyamide
Apex Flameproof 2952	Durable FR for 100% polyamide
Avocet (UK)	
Cetaflam® DB 9 and DBeXL	Non-halogen, phosphorus-containing, dDyebath applicable durable FRs for polyester

Table 4.4: Typical coating resins and their limiting oxygen index values [51]

Polymer or resin	Acronym or trivial name	LOI,vol% oxygen
Natural rubber		19-21
Synthetic rubbers:		
polyisobutylene	butyl rubber	20-21
styrene butadiene	SBR	19-21
poly(butadiene-acrylonitrile)	nitrile rubber	20-22
poly(chloroprene)	neoprene	38-41
chlorosulphonated polyethylene,		26-30
poly(fluorocarbon)		>60
silicone elastomers.		26-39
Poly(vinyl chloride)	PVC unplasticised	45-47
	PVC plasticised	23-25
Poly(vinyl alcohols) and poly(vinyl acetate)	PVA	19-22
Formaldehyde resins:		
phenolic		21-22
urea		~30
melamine		~30
Acrylic copolymers	acrylics	17-18
Polyurethanes	PURs	17-18
Silicones		≥26
Ethylene-vinyl acetate and related copolymers (emulsions); vinyl chloride presence will increase	EVA; EVA-VC	≥19-20
LOI		
Poly(fluorocarbons):		
Poly(tetra fluoroethylene)	PTFE	98
Fluorinated ethylene polymer	FEP	~48
Poly(vinyl fluoride)	PVF	23
Poly(vinylidene fluoride)	PVDF	44
Fusible/powders:		
low density poly(ethylene)	LDPE	17-18
high density poly(ethylene)	HDPE	17-18
polyamides	PA6, PA66	24-26
polyesters	PES	20-21
ethylene-vinyl copolymers	EVA	19

Table 4.5: Selected phosphorus-containing flame retardants for use in coating [51]

Chemical formula/name	Commercial examples	Comments
Triaryl phosphates	Reofos 35-95; Chemtura Phosflex 71B; Supresta	Proprietary formulations with 7.6-8.0%P
Cresyl diphenyl phosphate	Kronitex CDP; Chemtura	9.1% P
Tricresyl phosphate	Kronitex TCP; Chemtura	8.4% P
Trixylyl phosphate	Kronitex TXP; Chemtura Phosflex 179; Supresta	7.8% P
Triethyl Phosphate	Fyrol TPE; ICL	17% P
Isodecyl diphenyl phosphate	Phosflex 390; Supresta	Functions as plasticiser in PVC; 7.9% P
Oligomeric phosphate-phosphonate	Fyrol 51; Supresta	Textile back-coatings; 20.5% P
Cyclic organophosphates and phosphonates	Antiblaze CU; Rhodia Pekoflam PES; Clariant Aflammit PE ; Thor	Substantive to PES fibres but may be incorporated in most coating resins; 17% P
Nitrogen-containing polyol phosphate	Exolit OP 920; Clariant	Non-halogen FR for lattices with plasticising effects; 16% P, 9% N

Table 4.6: Halogen-containing flame retardants for coatings and laminates [51]

Chemical formula/name	Commercial examples	Comments
Dibromostyrene	Great Lakes DBS ; Chemtura	59% Br
Decabromodiphenyl ether	Great Lakes DE-83R; Chemtura FR-1210; ICL Saytex 102E; Albemarle Myflam and Performax; Noveon	Principal FR for textile back-coatings; 83% Br
Hexabromocyclododecane (HBCD)	Great Lakes CD-75; Chemtura Flacavon H14; Schill & Seilacher FR-1206; ICL Saytex HP-900; Albemarle	Competes with decaBDE in textile back-coatings; 73% Br
Tetrabromophthalic anhydride and diol	Great Lakes PHT4 and PHT4-DIOL; Chemtura Saytex RB-49; Albemarle	68% Br 46% Br 68% Br
Tetrabromobisphenol A (TBBA)	Great Lakes BA-59; Chemtura FR-720; ICL	59% Br
Dedecachloropenta- cyclooctadecadiene	Dechlorane; Occidental	Used in elastomeric coatings (synthetic and silicone); 65% Cl

Table 4.7: Selected intumescent and intumescent component flame retardants [51]

Chemical formula/name	Commercial examples	Comments
Ammonium polyphosphate	<i>Phase I types*</i> :	
	Antiblaze MC; Albemarle	Water solubility ~4 g/100cm ³
	Exolit AP 412; Clariant	
	FR CROS 480-485 ; Budenheim	
	<i>Phase II* types</i> :	
	Exolit AP 422 ; Clariant	Water solubility ~4 g/100cm ³
	FR CROS 484; Budenheim	
	<i>Coated Phase II types</i> :	
	Exolit AP 462 & 463	Microencapsulated version of AP 422; water solubility <0.5 g/100cm ³
	FR CROS 486 ; Budenheim	Silane coated: melamine-formaldehyde
FR CROS 487 ; Budenheim	(MF) coated: water solubility ~ 0.1g/100cm ³	
FR CROS C30/C40/C60/C70/489; Budenheim	Surface reacted MF, varying particle sizes D ₅₀ =7-18 µm; water solubility ≤0.1 g/100cm ³	
Melamine phosphates	BUDIT 310; Budenheim	Dimelamine orthophosphate
	Antiblaze ND; Albemarle	Dimelamine orthophosphate
	BUDIT 311; Budenheim	Dimelamine pyrophosphate
	BUDIT 312; Budenheim	Melamine phosphate
	Antiblaze NH; Albemarle	Melamine phosphate
	Melapur MP; Ciba	Melamine phosphate
	Antiblaze NJ; Albemarle	Melamine pyrophosphate
	Melapur 200; Ciba	Melamine polyphosphate
BUDIT 3141; Budenheim	Melamine polyphosphate	
Other melamine salts	BUDIT 313; Budenheim	Melamine borate
	BUDIT 314/315	Melamine cyanurate
	Melapur MC; Ciba	Melamine cyanurate
Other pentaerythritol derivatives	Great Lakes NH 1197; Chemtura	Phosphorylated pentaerythritol
	Great Lakes NH 1511; Chemtura	Phosphorylated pentaerythritol/melamine salt
	BUDIT 3077 and related products; Budenheim	
Intumescent blends	Antiblaze NW; Albemarle	Melamine phosphate and dipentaerythritol

*Phases I and II refer to different levels of molecular weight, cross-linking and hence crystalline characteristics. Phase I APP variants have much lower degrees of polymerisation and cross-linking and greater water solubility,

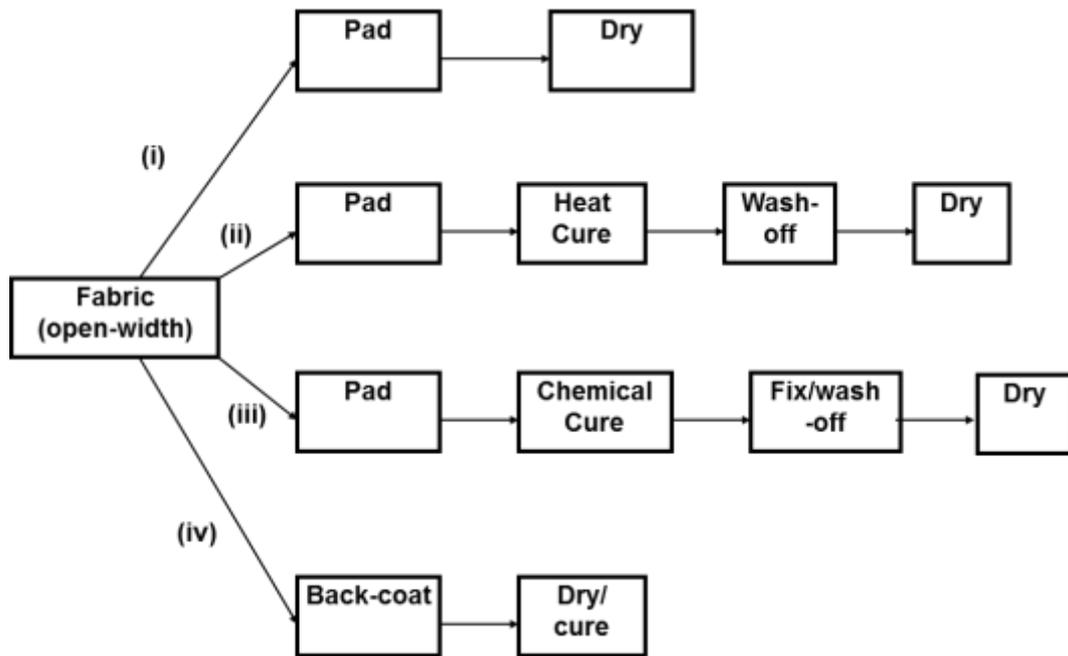


Figure 4.1. Schematic representations of the various common flame retardant application technologies for open-width fabric processing

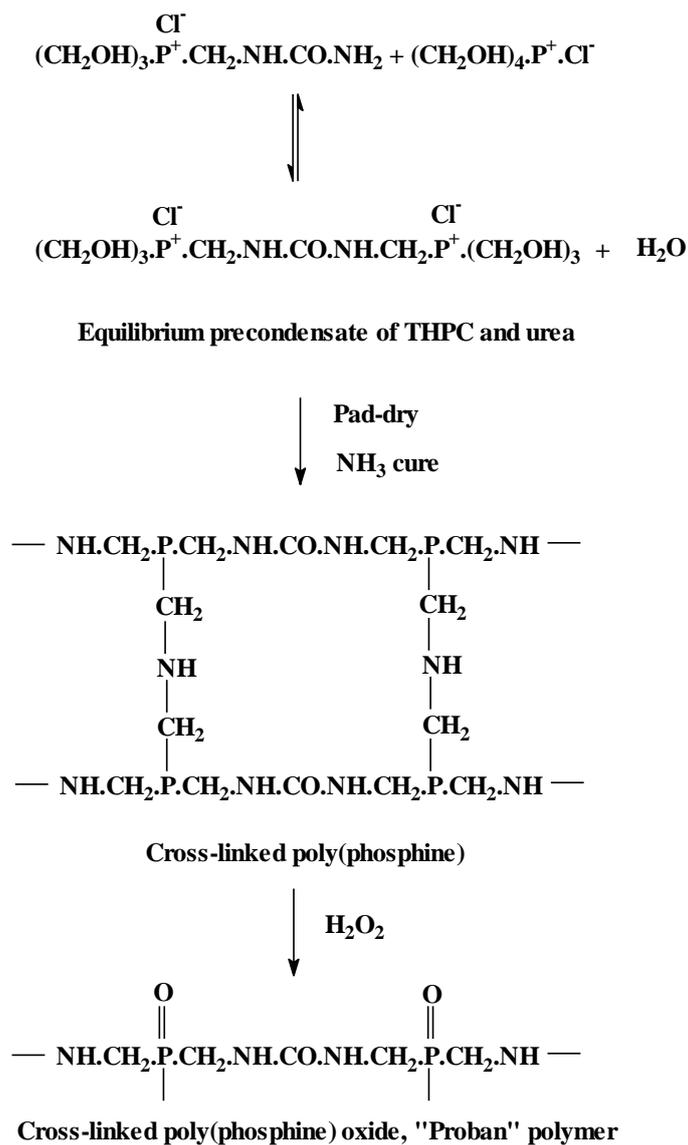


Figure 4.2. The chemistry of the Proban[®] process

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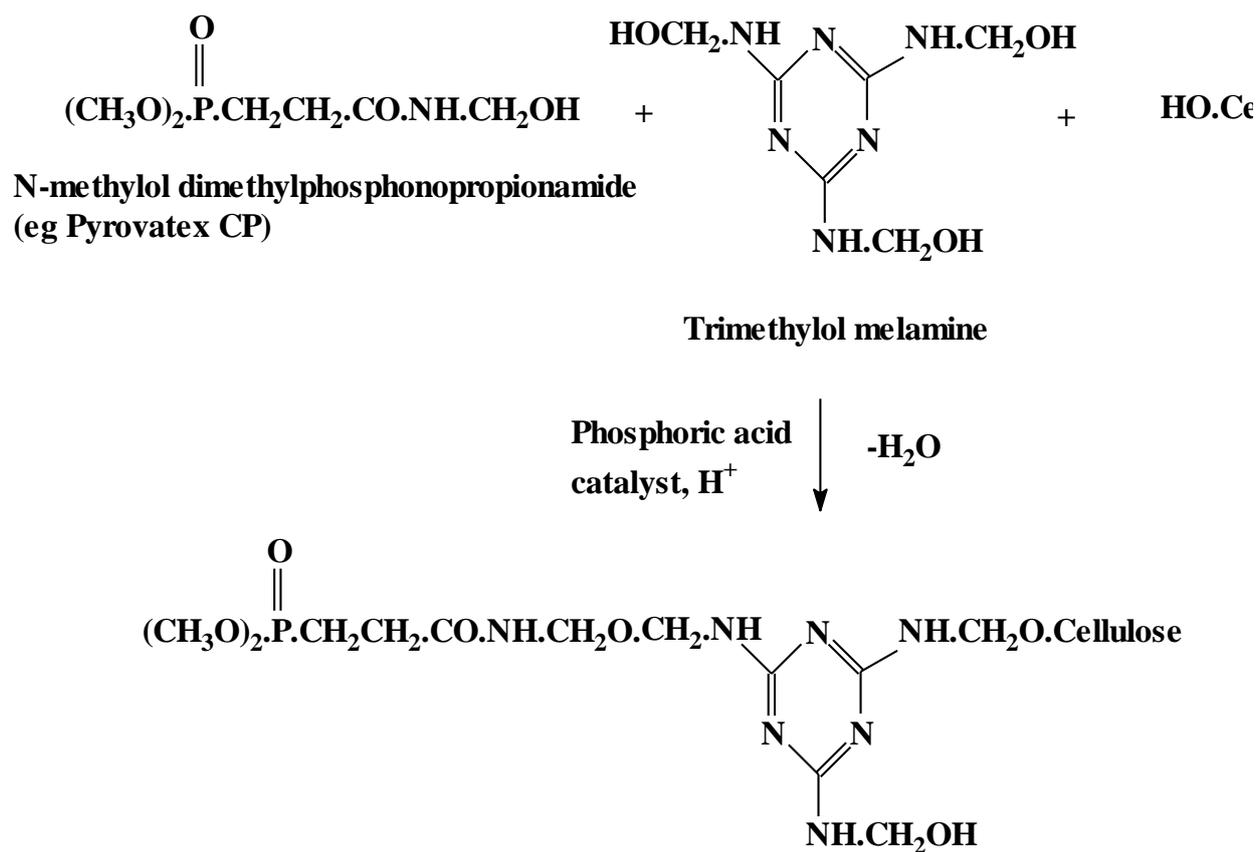


Figure 4.3. Chemistry of the Pyrovatex[®] (and similar phosphonamide) finishes

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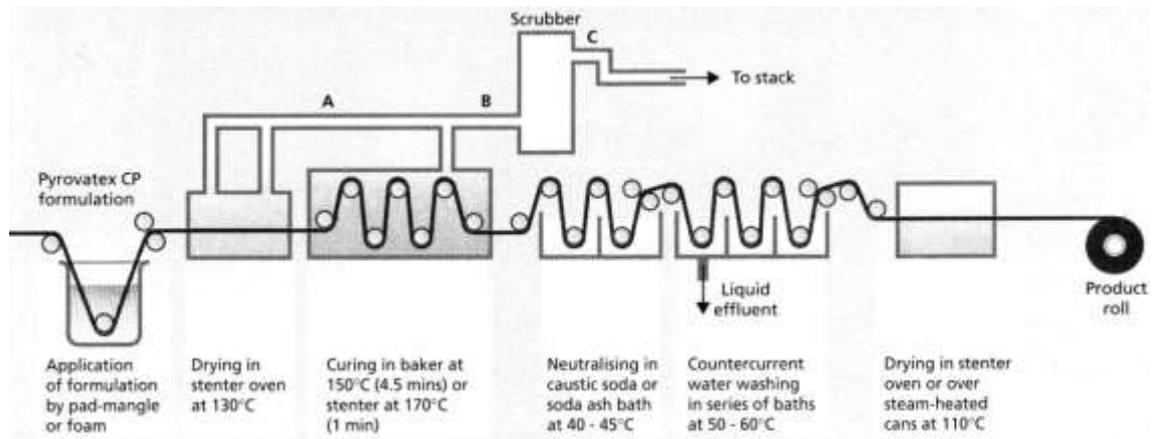
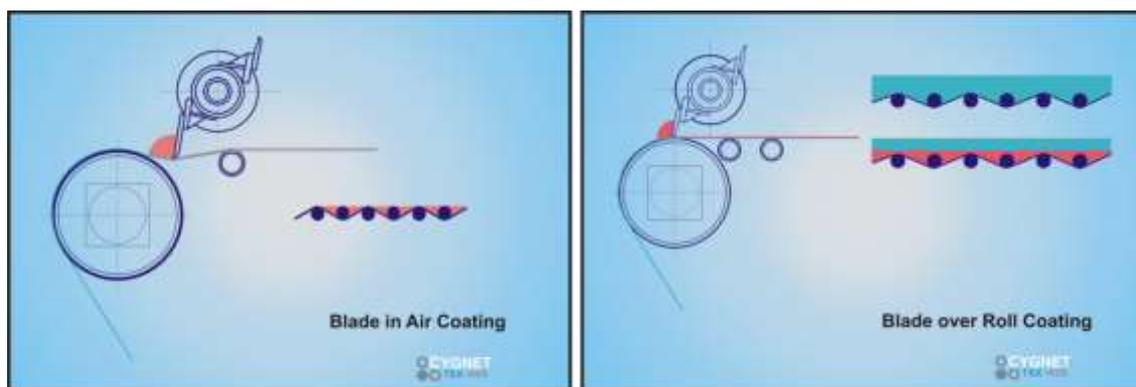


Figure 4.4. A detailed scheme of the overall Pyrovatex® CP application process [36]



(a)

(b)

Figure 4.5. Schematic diagrams of (a) blade-air-air and (b) blade-over-roll methods (single or double layer coating)
(figures courtesy of Cygnet Tex-Web, UK)

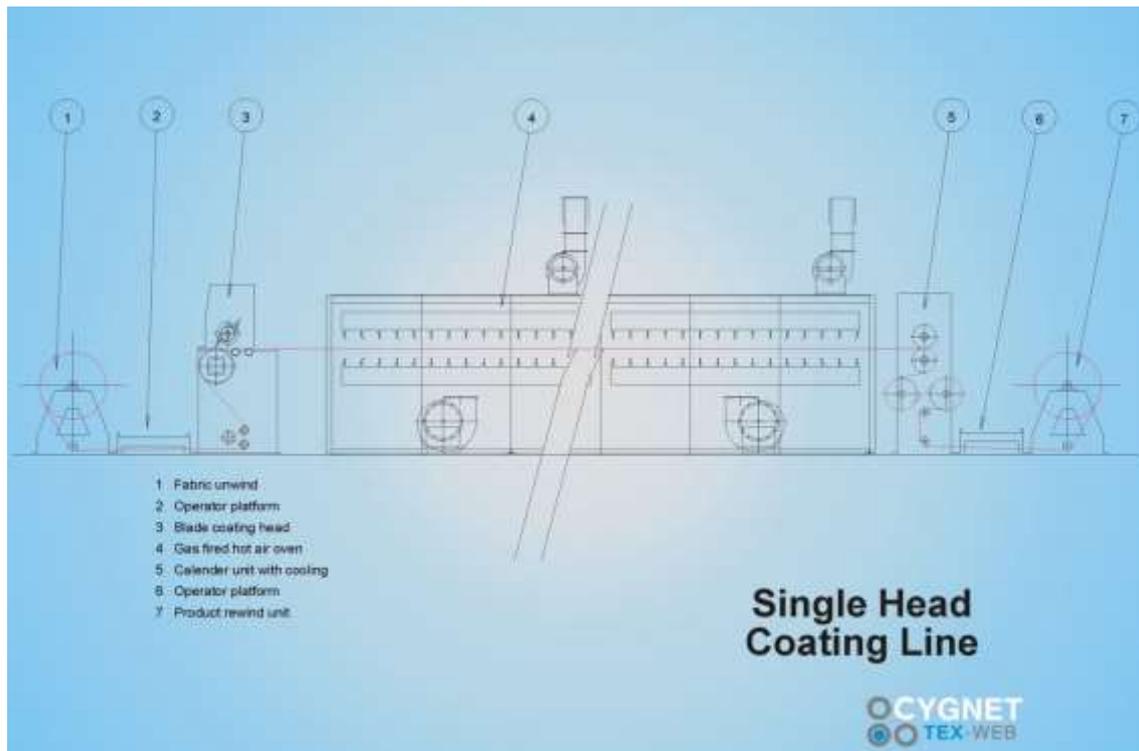


Figure 4.6. Schematic diagram of a typical complete back-coating line (figures courtesy of Cygnet Tex-Web, UK)