Chapter 6: Flame Retardant Issues and Environmental Issues

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6.1 Introduction

Apart from the inevitable pressure to reduce costs throughout the textile industry and use the most cost-effective finishes and application processes available, a major issue of the last 25 years or so has been the influence of environmental factors and the related current concerns levelled at the use of flame retardants in general.

Environmental concerns became significant issues during the late 1980s with regard to the following:

  i.   Effluent and water minimisation,

  ii. Reduction and/or removal of formaldehyde as an agent during flame retardant manufacture and processing, and

  iii. The potential environmental risks associated with halogen-containing flame retardants.

6.2 Effluent and water minimisation

The EU directives Environmental Impact Assessment 85/337/EC, 1985 (amended by the directive 97/11/EC, 1997) and Integrated Pollution Prevention and Control (IPPC) Directive 96/61/EC, 1996, demanded strict controls over effluent discharge and their embodiment in national legislation occurred across the community during the 1990-2000 period. As stated briefly in Chapter 4 within the UK, the consequence of this was the Environmental Protection Act, 1990 which identified the need for the following controls associated especially with flame retardant applications involving formaldehyde:

- emissions of formaldehyde to the atmosphere, especially during curing (currently required to be ≤ 20ppm);

- emissions of volatile organic compounds (VOCs) (currently ≤ 50ppm);

- discharge of unfixed flame retardants from washing-off effluent.

How these regulations have impacted on commercial finishers applying either THPX- or phosphonamide-type flame retardant treatments has already been discussed in **Chapter 4**. In addition to optimising the chemistry so that by-product formation is minimised [1, 2], for most commercial textile finishers to achieve acceptable formaldehyde and VOC emissions when applying formaldehyde-based finishes such as Pyrovatex® CP and its analogues, gaseous exhausts from the drying and curing stages must pass through scrubbers before release into the environment. Liquid effluents require neutralisation and dilution before release. Not surprisingly, use of techniques such as controlled impregnation technologies, low formaldehyde finishes and recycling of wash waters were found to not only reduce effluents but save money and so became economically attractive to finishers. It has been a requirement since this time that all UK textile finishing plants account for all effluents, seek agreed permissions for chemical discharges and are charged accordingly for their disposal and this has encouraged them to adopt minimum and even zero waste strategies.

In a not-unrelated similar manner, flame retardant users of DecaBDE and similar bromine-containing flame retardants have adopted the Voluntary Emissions Control Action Programme, VECAP^{TM}, system now operated under the auspices of the European Flame retardants Association (EFRA) to ensure that none of these chemicals are released into the environment (see Section 6.4 below) [3].

6.3 Attempts to reduce/remove formaldehyde from textile flame retardants

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As is evident from Chapter 4, the main targets for replacement are the two major and commercially dominant generic types of durable flame retardants for cotton and cotton-rich blends, namely those based on tetrakis(hydroxymethyl) phosphonium salt (THPX) condensates and those based on N-methylol dimethylpropionamide derivatives. Surprisingly, while THPX-ammonia-cured treatments are one of the targets here, there is no formally published evidence that formaldehyde release is a problem either during the application of the flame retardant or during service life. However, there is commercial evidence that some formaldehyde may be released during use but at levels much less than in cured N-methylol dimethylpropionamide derivatives. This would only be possible if that after ammonia-curing, the subsequent oxidation of the polyphosphine structure to the stable poly(phosphine oxide) form with an idealised generic structure $-CO-NH-CH_2-P(=O).(CH_2-NH-)_2-$ were not 100% efficient. Otherwise it is difficult to visualise how significant quantities of formaldehyde could be released from this structure during normal use.

However, this is not the case with N-methylol dimethylpropionamide as explained in Chapter 4 since the condensation reactions involved are equilibria in which formaldehyde is a product and hence always present in a finished fabric, albeit at very low levels if correctly applied.

Notwithstanding this formaldehyde issue, in order to be able to replace either of these products and their derivatives, then it is most likely that any flame retardant must be cellulose-reactive which usually means in the first instance reaction via the anhydroglucopyranose C(6) hydroxyl group. Possible alternatives to phosphonamide and THPX-based finishes to be discussed in detail below have to be cognisant of their respective been previously strengths and weaknesses which were summarised in **Chapter 4, Table 4.1**. It is instructive to note that many recent research papers assume only the worst properties of both these finishes as being reasons for their replacement and in doing so, ignore their

respective strengths, not least their exceptional durabilities that can exceed 100 domestic and even commercial wash cycles [4]. Therefore, for any new durable flame retardant for cotton to become accepted and compete with these two market leaders requires they have the majority, if not all, of the following properties:

- equivalent or superior ease of application,

- zero formaldehyde-releasing properties,

- comparable textile service-life properties in terms of durability, effect on handle and tensile properties,

- overall comparable cost-effectiveness and preferably be cheaper and

- equivalent or superior toxicological and environmental impacts.

Because of the formaldehyde issue and in spite of its apparent absence from ammonia-cured-THPX treatments, a considerable literature has appeared in attempts to develop formaldehyde-free flame retardant replacements. While this review is not intended to be a comprehensive review of all research undertaken in this area [4, 5], some of the more salient alternatives will be briefly discussed with a focus on those research areas that might have some chance of commercialisation. Furthermore, **Table 6.1** summarises the chemical character of each of the examples discussed below where there is greatest promise of effective levels of flame retardancy coupled with durability which implies cellulose-flame retardant chemical interaction.

Table 6.1

Oligomeric phosphate-phosphonate: In 2002 Akzo Nobel re-introduced their former Fyrol 51 product (an oligomeric phosphate-phosphonate: $H-(O.CH_2.CH_2.O.P(O)(OCH_3))_{2x}.(O.CH_2.CH_2.P(O)(CH_3))_x.O.CH_2.CH_2.OH)$ as Fyroltex HP [5, 6] which has the potential for being a durable flame retardant for cellulosic textiles. Since then these workers have

undertaken further research which has shown [7-12] that if it is to achieve acceptable levels of multiple laundering durability, its application requires the presence of an aminoplast or principally a methylolated resin species like dimethylol dihydroxyethylene urea (DMDHEU) or methylated formaldehyde-urea. These publications show that up to 12 launderings are feasible if the correct cross-linker is chosen although the problem of formaldehyde release will still remain. Subsequent publications claimed up to 40 wt% retention and 50 laundering durability for a Fyroltex/TMM/DMDHEU combined finish applied to 50%/50% nylon (6 or 6.6)/cotton blends [12] and this whole area has recently been reviewed by Yang [13].

Butyl tetracarboxylic acid (BTCA): In the USA interest in char-forming polycarboxylated species like butyl tetracarboxylic acid (BTCA) along with other functional species has shown that they may interact with cellulose in particular to generate levels of flame retardancy acceptable for certain textile applications such as carpets with moderate levels of durability to washing [14]. Unfortunately, because of the ease of hydrolysis of the BTCA-cellulose ester links formed, durability to domestic laundering is limited, and so flame treatments based on this chemistry may only lead to semi-durability. Subsequent work by Yang and colleagues has combined BTCA as the cellulose bridging species with phosphorylated species such as the hydroxyalkyl organophosphorus oligomer, Fyroltex HP, discussed above to enhance both flame retardancy, and durability [6, 15]. While the BTCA forms a bridge between the oligomer, and cellulose molecules, and durability is somewhat improved, the ease of ion exchange between free carboxylic acid group hydrogen ions with calcium ions during washing in hard water is accompanied by a loss in flame retardancy as a consequence of calcium salt formation [10]. Addition of triethanolamine (TEA) reduces the calcium ion pick-up as a consequence of free carboxylic acid group esterification and, using a Fyroltex/BCTA/TEA combination applied to a 35%/65% cotton/Nomex® blend, acceptable levels of durability were achieved with vertical strip test (ASTM D6413-99) passes after 30

home launderings [15]. A subsequent publication extended this work to show that the mixed Fyroltex/BCTA system may be applied to silk to yield a 15 hand-wash level of durability [16] while more recent work re-examined the possible role of Fyroltex and BCTA in 100% cotton fleece which when TEA is present also achieves Class I after multiple home launderings [17].

It is in the cotton fleece fabric area where the use of polycarboxylic acid species like BCTA can find application where the conventional THPX- and N-methyl phosphonamide - based durable finishes cannot be used because of associated stiffness and or processing difficulties and where limited durability is required [18]. Yang's research team developed this idea further and reported that treatment of cotton fleece with maleic acid and sodium hypophosphite enables Class 1 passes to 16 CFR 1610 (US Federal Standard for the Flammability of Clothing Textiles) to be achieved when exposed to the 45° ASTM D1230-94A apparel test after 20 home launderings [19]. These authors propose that the hypophosphite anion interacts with the maleic acid entity to form a cross-link of the type:

Cell-O-CO-CH_2-CH(COOH)-P(O).(O^-)-CH(COOH)-CH_2-CO-O-Cell. Subsequent work has extended this to include the dicarboxylic acids succinic, malic and tartaric acids [20] and polycarboxylic acids like BCTA and citric acid (CA) to yield similar flame retardant performance [21]. This latter work shows that for acids with 3 or more carboxylic acid groups (CA, BCTA) increase the level of cellulose cross-linking which increases fabric dimensional stability and stiffness.

Their work with maleic acid has been extended to include phosphorus-containing maleic acid (MA) oligomers (PMAO) synthesized by aqueous free radical polymerization of maleic acid in the presence of potassium hypophosphite. PMAO is considered to be a mixture of species having the general formulae : H-P(O) (OMA).$[MA]_x$-H, H-$[MA]_x$ - P(O) (OMA).$[MA]_y$-H and HO-P(O) (OMA).$[MA]_x$-H where x and y are between 3 and 5. This mixture is applied to

cotton fleece fabrics again in the presence of sodium hypophosphite with no significant changes in fabric properties [22]. Following on from this work, they have demonstrated that the maleic acid/sodium hypophosphite system can form ester cross-links between cellulose chains conferring both wrinkle resistance [23] and improved fire performance [24] as already described above [19].

Alkyl phoshoramidate adduct: Quite different from the above approaches is the recently introduced Firestop product Noflan, a phosphorus-, and nitrogen-containing molecule reported to have the structure $[CH_3\text{-}P(O).(ONH_4)\text{-}NH_2]\ NH_4Cl$ in which an alkyl phoshoramidate is stabilized as a salt adduct with ammonium chloride [25]. While this is obviously a formaldehyde-free molecule, it may react only with cellulosic substrates via the phosphoramidate - NH_2 group, which is not very reactive. It is most likely that for this to be effective in cellulosic-based textiles, it must be applied either in a resin binder or cross-linked using a methylolated resin. It is claimed to be effective on cotton and cotton-polyester blends with reasonable levels of durability. When applied to wool, it can survive dry cleaning treatments and finds application in technical end-uses such as aerospace interior fabrics.

Organophosphoramidates: In a not-unrelated paper, work by the Swiss research team [26] has investigated the particular value of organophosphoramidates as flame retardants for cellulose which are claimed to be not only easily synthesised from chlorophosphates but also exert high levels of flame retardancy because of nitrogen-phosphorus synergy which may be varied depending on the level of nitrogen-containing moiety substitution. The research focussed on the behaviour of secondary organophosphoramidates since a previous study by Pandya et al over 30 years ago [27] suggested that they were superior to tertiary analogues. These specially synthesised structures having the general formula $(C_2H_5.O)_2\text{-}P(O)\text{-}NH\text{-}R$, where R = -H, -$C_2H_5$, -$C_2H_4.OH$ and –$C_2H_4.O.CH_3$ demonstrated high levels of condensed

phase activity [28] although no attempt was made to assess or improve their poor durability. The study therefore remains academic although poses the question of whether or not suitable cellulose reactivity can be introduced to confer the necessary levels of durability for commercial exploitation.

Phosphonyl cyanurates: An interesting and novel approach has been published by Chang et al., [29] from the USDA Southern Regional Research Centre in New Orleans where much of the pioneering research into durable flame retardant finishes for cotton was undertaken during the 1950-70 period [4]. This group has synthesised two new monomers (2-methyl-oxiranylmethyl)-phosphonic acid dimethyl ester and 2-(dimethoxy-phosphorylmethyl)-oxyranylmethyl]-phosphonic acid dimethyl ester which together with dicyandiamide ($NH_2.C=NH.NH.CN$) and citric acid impart flame resistance to woven 100% cotton and 80/20 cotton/polyester fleece fabrics. The resulting mono- and bis-(dimethoxy-hydroxymethyl phosphonyl) cyanurate derivatives may be padded on to fabrics and while the former can give rise to LOI values up to 25.5 % at about 21 wt.-% add-on, higher LOI values above 28 % were obtained when the latter was applied at add-ons below 20 wt%. Fabrics passed the standard 45° and vertical strip tests ASTM D1230-94 and D6413-99 before laundering. Durability is not, however, very good with only about 5 wash cycles being achievable whilst maintaining acceptable levels of flame retardancy in spite of the claimed cellulose reactivity of cyanurate derivatives.

Cellulose-phosphoramidate ester interchange: This same group of researchers [30] have recently extended their work to include further work on phosphoramidates, specifically diethyl 4-methylpiperazin-1-ylphosphoramidate. This molecule, similar to those synthesised by Gaan et al [26] and where R= $-C_4H_8N_2.CH_3$, was applied to cotton and cured at 160°C for

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5 min. They propose that bonding to cellulose may occur by the transesterification in Scheme I.

$$Cell.OH + (C_2H_5.O)_2\text{-}P(O)\text{-}NH\text{-}C_4H_8N_2.CH_3 \rightarrow Cell.O.\ P(O)(C_2H_5.O)\text{-}\ C_4H_8N_2.CH_3$$

Scheme I

The reaction is sensitised in slightly alkaline conditions similar to those within the mercerised cotton fibres present in the fabrics studied. They claim LOI values >27% and in some cases 31% at phosphorus levels of 2.1 and 2.7% respectively with significant char formation and absence of afterflame and afterglow. Although formal durability trials were not undertaken, after washing in water at 40°C for 10 minutes, original add-ons reduced to about 83-84% of the original values which remained the same after a third wash. Clearly, durability has improved with regard to the earlier work on phosphoramidates but these authors claim that it is the focus of future research.

Cellulose-chloro triazinyl derivative condensation: One means of achieving strong bonding to cellulose and so high levels of durability, is to exploit reactive dye chemistry where strong covalent Cell.O.Dye bonds having extremely good washfastness are achieved [31]. The more common reactive species within a reactive dye is the 6-chloro-1,3,5-triazine group, in which the chlorine replaces the anhydroglucopyranose repeat group C (6) primary –OH group hydrogen under alkaline conditions to create a strong Cell.O.N bond which is resistant to hydrolysis under normal laundering conditions. While to the author's knowledge there has been no academic study, until recently [32], of this possibility, there were some attempts by the former ICI Dyestuffs Division during the 1980s, the inventors of reactive dyes and the famous Procion® range of dyes (now produced by Dystar Colours GmbH), to develop a
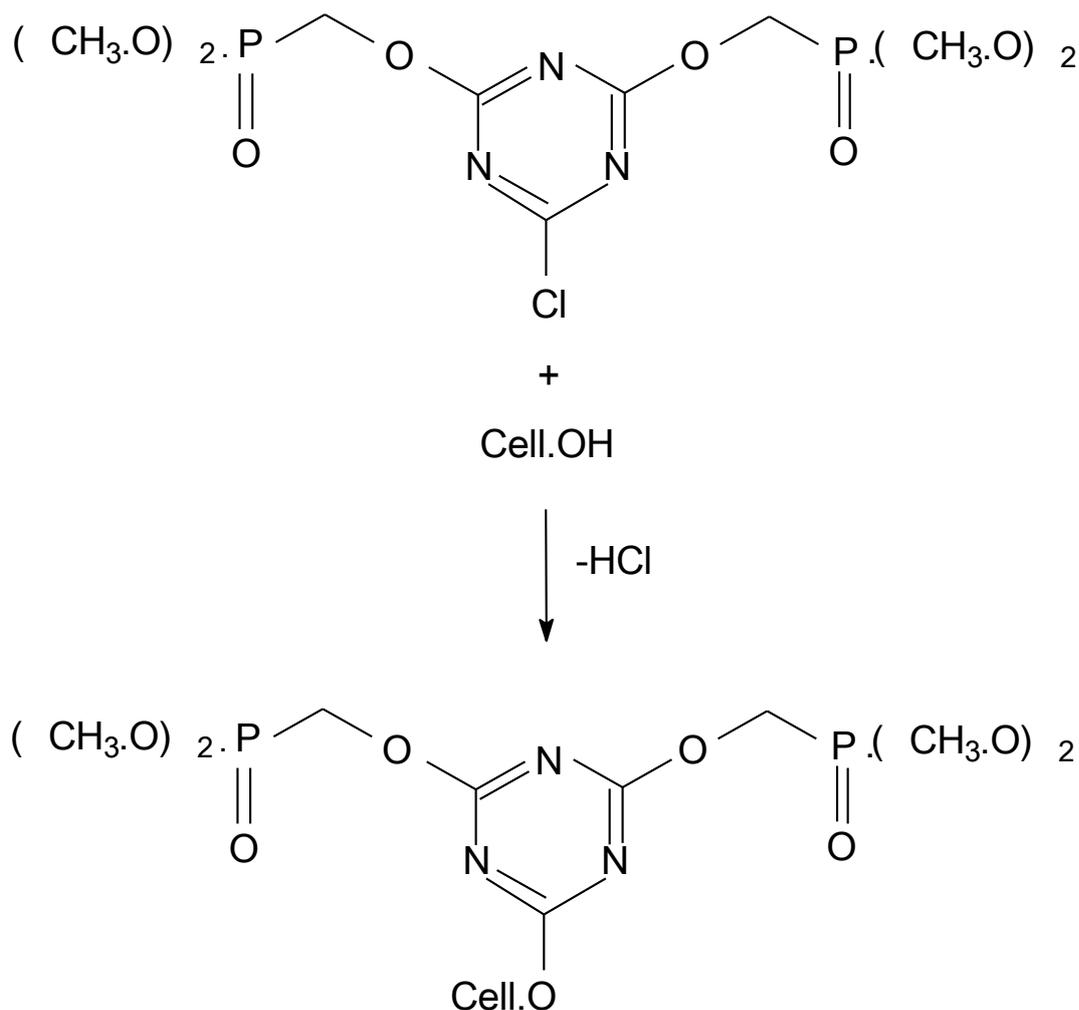
flame retardant based on this chemistry. To the author's knowledge no patents arose from these studies and no commercialised products were developed.

This is perhaps because the major challenge is the limited accessibility of the potentially reactive primary C(6) CH_2OH groups in the polycrystalline cotton fibre and the fact even the highest dyes uptakes were rarely above about 5wt.-% for the deepest shades. This coupled with the fact that most phosphorus-containing flame retardant species rarely contain over 20wt.-% phosphorus means that obtaining more than 1wt.-% phosphorus bonded would require at the very least 5wt.-% or greater bonding of the reactive species to the accessible cellulose within cotton fibres is; this poses a significant challenge.

This challenge has been recently addressed, however, by Chang and coworkers, again at the USDA Southern Regional Research Centre [32], who reported in 2012 the synthesis and reaction with cotton of tetramethyl (6-chloro-1,3,5-triazine-2,4,diyl)bis(oxy)bis(methylene) diphosphonate as below in Scheme II.

$(CH_3.O)_2.P$ — O —(triazine ring, N)— O — $P.(CH_3.O)_2$

with $=O$ on each P, and the triazine bearing Cl

+

Cell.OH

$\downarrow$ -HCl

$(CH_3.O)_2.P$ — O —(triazine ring, N)— O — $P.(CH_3.O)_2$

with $=O$ on each P, and the triazine bearing Cell.O

Scheme II

This reagent was padded on to cotton in 50% aqueous isopropanol, dried at 100°C for 5 min

and cured at 140°C for 5min at add-ons from 5 to 19 wt.-%. Treated fabrics were white and

only the highest add-ons (17 and 19 wt.-%) were self-extinguishing with LOI>35%.

Phosphorus and nitrogen analyses showed great variability across the 19wt.-% add-on sample

with average values of about 2.4 and 6.4% respectively. SEM photographs indicate

significant presence of surface deposits and no attempts were made to assess the durability of

the treatment but the authors stated that this was their immediate priority. Thus at the present

stage, there is no indication of what level of the flame retardant is firmly covalently bonded to the cellulose within the cotton fibres' microfibrillar, polycrystalline interiors.

Phosphorus acid derivatives of cellulose: As yet unpublished research undertaken at the University of Leeds over the last ten years has given rise to a number of significant patent applications through its company Perachem Ltd., that describe the basis of a durable flame retardant treatment for cotton involving phosphorous acid [33, 34, 35]. The 2009 application [34] discloses the interaction between cellulose, urea and phosphorous acid as the potassium or sodium salt at pH 8-10 to yield cellulose phosphonate (Cell-HPO_3^-) and/or the dimer, Cell-O-PH(O)-O-Cell formation which gives rise to a wash durable FR treatment. The earlier 2007 application describes the application to cotton of H_3PO_3 or the phosphate followed by potassium cyanate, cyanamide or derivative and then curing at 200^oC to yield a wash durable, flame retardant finish. In 2010 a third application has extended the claims to include a first component selected from a phosphorous-containing acid or a salt of a phosphorous-containing acid and a second compound selected from an isocyanic acid, a cyanate salt, a thiocyanate salt or isothiocyanate precursor, dicyandiamide, cyanamide or carbodiimide precursor. While the exact chemistry has not been published, there is an obvious reaction between the cellulose phosphonate moiety and the cyanate (or other disclosed nitrogen-containing derivative) which then introduces the necessary synergistic nitrogen into the structure. However, it has been previously recorded that replacement of hydrogen in the phosphonic residue by 2-cyanoethyl and 2-carboxyethyl groups retarded dehydration of cellulose and so it is likely in the chemical mechanism that substitution of the P-H group by an electron-withdrawing group does not occur [36]. If the resulting treatment is to have the claimed washfastness and resistance to calcium ion exchange, then the removal of the acidic P-OH moiety is essential and possible products of P-OH interaction with CNO^- ion, for

example, should offer both P-N synergy and hydrolysis resistance providing that either a strong P-N, P-O or P-C bond is formed as a result. The processes described have provoked sufficient commercial interest for its licensing to Clariant who have announced a commercial version called Pekoflam®ECO/SYN claimed to be applicable to 100% cotton and cotton/synthetic blends and offering high durability. While the number and type of wash cycles has not been disclosed, treatments prove to be resilient to wash fastness tests in 5g/l Na_2CO_3 at 60°C for 12min repeated up to 12 times after which they continue to pass standard vertical strip tests by demonstrating self-extinction and char lengths <15cm in length [33, 35]. They also claim the product to be free of any Oeko-Tex® restricted chemicals such as formaldehyde.

Phosphorus-nitrogen-silicon developments: Recent interest has also been shown in the potential for combining phosphorus, nitrogen and silicon on to cellulose substrates to create the potential for carbonaceous and silicaceous char-forming characteristics. Lecoeur et al [37, 38] have combined monoguanidine diphosphate (MGDP) and 3-aminopropyltriethoxysilane, $NH_2(CH_2)_3Si(OC_2H_5)$, applied in the presence of phosphoric acid which is a required catalyst if water soak durability (20 min in hard water at room temperature) is to be achieved. Treated cottons behave typically of those containing char-promoting flame retardants in that flame retardancy is improved (M1 rating to NF P 92-503), PHRR reduces and residual char increases. The level of durability achieved is a consequence of MGDP phosphorylating cellulose during the 180°C cure and the polymerisation of the silane and its partial reactivity with cellulose. Again, the challenge remains of developing a reactive flame retardant species that effectively bonds to cellulose through the hydroxyl groups, is hydrolysis resistant and withstands normal textile processing conditions.

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One final recently reported work is in contrast to the above which attempt to bond reactive agents directly to cellulose is that of Yang et al [39] who created a polymer network within the cotton microfibillar structure, not unlike that observed in the THPX condensate-ammonia cured finishes. However, here cotton is first treated with a solution of a branched poly(ethylene diamine) followed by a condensate of phosphonitrilic choride ($N_3P_3Cl_6$)and acrylamide to yield the hexasubstituted product $N_3P_3(NH.CO.CH=CH_2)_6$ and then dried at 80°C. The resulting treatment appears to yield fibres with little or no surface deposits observable by SEM and fabrics that show self-extinguishing properties even after 30 49°C standard AATCC washes. While this recent research appears to be novel, the use of and possible release in use of acrylamide needs to be questioned as does the presence of a phosphonitrilic or phosphazene component on both potentially commercial [40] and health and safety grounds given that some earlier flame retardants like the now-obsolete Fyrol 76 [4], which comprised acrylonitrile, were withdrawn for similar reasons.

6.4 The halogen (bromine) – antimony question

Concerns regarding halogens in flame retardants started some years ago with an initial focus regarding the possible formation of polybrominated dioxins associated with incineration of organobromine compounds, especially those based on polybrominated diphenyls and diphenyl oxides [41].

Without wishing to enter into extreme detail, following the initial concern in Germany in 1986, the EU published in 1991 a draft amendment to EC Directive 76/769/EEC, which would essentially ban use of all polybrominated diphenyl oxides (PBDPO) or ethers within five years. In 1994 this Directive was withdrawn as subsequent studies cast doubt on the earlier concerns. Simultaneously, other organisations (e.g. US Environmental Protection

Agency, OECD) initiated risk analyses of these compounds. At the same time the World Health Organisation initiated an evaluation of the risk to health of PBDPOs which in 1994 indicated that they did not pose a significant hazard. While the full details of the OECD programme are complex [42], one outcome was an industrial commitment to address environmental exposure and purity of these agents and minimisation of the presence of non-commercial congeners.

 During this same period, the role of antimony III oxide in "cot deaths" or sudden infant death syndrome (SIDS) was raised on UK Television in 1994 and although refuted [43] and subsequently shown to be without foundation [44] the image of antimony/bromine flame retardant formulations and especially back-coatings in general became increasingly questioned within the media and environmental circles.

 In 1997 Stevens et al published work funded by the then UK government Department of Trade and Industry [45] which reviewed the fire safety value and effectiveness of flame retardants in consumer products and assessed the risk benefits of the latter. A major conclusion was that, based on the information available at the time, any risks to health and the environment were more than offset by their benefits in terms of lives saved and reduced fire injuries. This study was followed by an analysis of the effects of the UK furnishings regulations of 1988 in terms of their ability to reduce domestic dwelling fire casualties [46, 47]. These authors estimated that implementation of these domestic fire regulations saved on average 140 lives per annum and the decrease in UK fire casualties since 1990 discussed in Chapter 1 are reflected in the overall reduced fire death figures (see **Figure 1.3, Chapter 1**). A subsequent and more recent study commissioned by the UK Government [48] concluded that over the period 2003-2007, the implementation of these regulations continued to save 54 lives with 780 fewer casualties each year. It is likely that the lower casualty numbers compared with those in the previous report [46] are in part be due to the reductions in fire

casualties in UK dwelling fires and hence increased safety of furniture and furnishings in the home as a consequence of the regulations during the period 1990-2003. The wider area of risks and benefits of flame retardants has been recently more fully reviewed by Emsley and Stevens to extend their previous studies [49].

Meanwhile in the USA during the late 1990 period as a result of pressures in the main from the US National Association of Fire Marshalls regarding concerns about domestic fire deaths of children as a result of playing with matches, the US Consumer Product Safety Council (CPSC) planned to introduce a small ignition source test for furnishing fabrics similar to BS5852: Part 1:1979. However, it was realised that the use of flame retardant furnishing fabrics across the US would become mandatory if any resulting US Federal regulations were implemented in which such a test was defined,. Because of concerns raised with regard to health and safety and the environment as a consequence of introducing the presence of flame retardants into the home, in 1999 the US Congress directed CPSC to arrange an independent study by the National Research Council (NRC) to assess the risks of flame retardants in furnishings. In turn the NRC passed this request on to its Committee on Toxicology which set up a Sub-committee to undertake this work. The report from this Sub-committee was published in 2000 and while this may be considered to be somewhat out of date, it remains the most authoritative risk analysis of the 16 selected flame retardant chemicals to date [50]. Table 6.2 lists these and whether or not they are actually useful for flame retardaning furnishing fabrics based on UK experience. Those in the upper half of the table were deemed to be toxicologically safe while those in the lower half were deemed to have unacceptable risks and required further research.

Table 6.2

Of especial significance at this time was that, contrary to many contemporary EU member state and pressure group viewpoints, this study exonerated the bromine-containing retardants decabromodiphenyl ether (DecaBDE) and hexabromocyclododecane (HBCD) and yet signalled a risk to the use of antimony III oxide and other antimony-containing synergists used in these same finishes. One major issue that caused concern within this study was that while they had been instructed specifically to undertake risk analyses of the designated 16 chemicals, when present within a textile finish or back-coating some of these flame retardants were actually precursors which become chemically very different when present in a flame retarded fabric (eg THPX-condensates are present as polyphosphine derivatives and phosphonamide derivatives are cross-linked to cellulose molecules, see **Chapter 4**). Furthermore, even the free chemicals would be embedded in a resin which would severely reduce their mobility and release into the environment.

This risk assessment indeed promoted further research which is continuing toady. In particular, there has been increasing activity both in the USA and Europe to define more effectively the environmental risks posed by the use of brominated flame retardants in particular. Wakelyn has reviewed both US and EU positions up to 2008 [51] including the particular concerns over the use of the polybrominated diphenyls and both penta- and octabromodiphenyl ether and their subsequent bans since August 2004 on both health and bioaccumulation grounds. While these flame retardants had little if any application to textiles, their ban increased focus of attention on DecaBDE and HBCD as already outlined in **Chapter 4** and which, as previously described in **Section 4.5.2**, have now led to their phasing out in Europe by 2016 and 2015 respectively.

However, to more fully understand the background of the processes leading to these withdrawals from use, it is worth discussing the various parallel activities during the 2000-

2010 decade, which contributed to the environmental debate and subsequent actions. It also needs to be understood that while the focus was on these two major retardants, it continued with regard to all other brominated flame retardants in general use as well as those being applied specifically to textiles.

The EU risk assessments undertaken on DecaBDE [52] found no real cause for this flame retardant to be controlled because of any toxic factor whereas that for HBCD [53] did find possible health risks to workers during its processing. As stated earlier (see **Chapter 4**), the major cause for banning DecBDE is because of its claimed persistence and bioaccumulation in the environment. Any claimed toxicity is associated with possible debromination during UV degradation to yield products which include the known toxic congeners penta- and octabromodiphenyl ether although this is disputed and appears to depend on whether or not an oxidative or anaerobic environment is present. While this chapter is not intended to present a review of this whole contentious area, a few recent and pertinent references may be cited regarding the above debate [54-60].

The expected ban on DecaBDE, rather than based on firm scientific evidence, is one that appears to be based on a precautionary principle that future science may in fact conclude more definitely in favour of a ban. What is rarely considered is that while analytical methods become increasingly sensitive leading to the discovery of many chemicals in the environment at very low levels often at ng/g level, the levels found must be related to known toxicological dose data. This whole area has been discussed by Stevens et al. [61] together with service-life simulation data regarding the possible release of both HBCD and DecaBDE from back-coated textile furnishing fabrics. In this work, particulate debris from fabrics abraded in a modified Martindale Abrasion Tester, was analysed for size distribution and morphology using SEM and EDX. Results showed that much of the debris produced is in the form of short

fibres arising both from the target cotton fabric and the wool wear abradant material. Only after 30,000 rubs, after which the top fabric surface had started to fail and to reveal the underlying fibres and back-coating, were particles produced which were associated with the back-coating and these were released as agglomerates having sizes ranging from 2 to 5µm up to 50 to 100µm. Even then, the observed particles containing flame retardant were surrounded by the back-coating resin and no evidence was found of free Br or Sb particles and hence free flame retardant.

In an attempt to reduce possible release of bromine-containing flame retardants following the publication of the European Commission risk assessment of decabromodiphenyl ether completed in 2004 [52], the Bromine Science and Environment Forum (BSEF) launched in 2004 the Voluntary Emissions Control Action Programme or VECAP™ [3] (later adopted by EFRA (see Section 6.2)), to reduce levels of DecaBDE in the environment. Under this programme, manufacturers and users of DecaBDE for textiles and plastics formed a voluntary action group that agreed to limit releases of the flame retardant into the environment by providing data on the use of the chemical and establishing and demonstrating control over processing waste. VECAP™ advises manufacturers, processors and users of brominated flame retardants by sating the following actions [3]:

- Increasing understanding of chemicals management in the value chain beyond existing legislation

- Promoting and facilitating open and constructive dialogue with all interested parties, such as industry, regulators and other stakeholders

- Raising awareness among all those involved in the process, from the shop floor to the boardroom

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- Implementing best practices identified through the progressive development of the programme.

In so doing, all interested parties may work together to establish and implement best practices on managing brominated flame retardants to reduce and prevent emissions to the environment. The VECAP™ process is schematically shown in **Figure 6.1** in which the user procedures and self audit processes are present followed by mass balance calculation and emission reporting [3]. External auditing of the process overseen by EFRA is undertaken after which an improvement plan is developed and implemented. A VECAP™ initiative specific to DecaBDE was introduced in the United Kingdom in 2004, extended to other European Union countries in 2005 and then launched in the United States and Canada in 2006. During the early years of the programme, there was an exclusive focus on emissions to air and water, mainly following a request from EU regulators to the producers of brominated flame retardants to monitor and report progress in this area of handling of chemicals. Subsequently the programme was extended to cover all bromine-containing flame retardants. VECAP™ issues annual reports to indicate the progress of this initiative [62]. **Table 6.3** presents the data from 84% of DecaBDE sold by EFRA members for the years 2008-2012 in terms of the consumption versus emissions and based on audit data undertaken in 2011. In spite of the reductions of DecaBDE emissions and other flame retardants into the environment which VECAP™ has caused, there still remained the concerns over DecaBDE in particular and hence the expected ban by 2016 suggests.

Last but not least of the environmental influences on flame retardants for textiles are the European Union's Registration, Evaluation, and Authorization of Chemicals (REACH) legislation which came into force in 2007 [63]. REACH requires that manufacturers of chemicals that are made in or imported into the European Union in large volumes, such as

brominated flame retardants, register those chemicals and provide information about how they can be safely used. REACH is a complex piece of legislation that is having an impact on a vast spectrum of substances contained within materials, which are made, sold, used, and disposed of across the EU. Registration of chemicals must be made by manufacturers or importers of more than one metric ton of a chemical substance per year with the European Chemicals Agency. For each qualifying chemical they must provide all information regarding the properties, uses and safe handling of the substance. REACH provisions, phased in over 11 years from 1st June 2007, should be complete by June 2018. However, the regulations only cover molecular substances having a diameter < 100nm and which are deemed as being small enough to penetrate a human cell wall. This, therefore, excludes polymers and this is why most bromine flame retardant manufacturers are now focussing on the development of polymeric bromine-containing flame retardants as discussed in **Chapter 4** with regard to alternatives to HBCD and DecaBDE.

In conclusion, it is evident that the pressures from health and safety and environmental sectors are not going to reduce in future years and the flame retardant industry must continue to react constructively to these. However, in the continuing debates, the current safety advantages in terms of reduced fire casualties that the application of flame retardants to fibres and textiles confers are often lost and the concept of risk-benefit ignored. So much so is this happening at the present time, that in the USA and as discussed in **Chapter 3, Section 3.3.2,** the proposed US standard CPSC 16 CFR Part 1634 for the resistance of residential furniture to a smouldering and open flame ignition source is currently under scrutiny so that compliance may be achieved without the need for flame retardant chemicals. Whether or not this can be achieved without simply eliminating the open flame requirement remains to be seen.

A. R. Horrocks. Flame retardant and environmental issues, 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.207-238, Smithers Rapra, Shawbury, UK (2013)

References:

1. A. Edmond and A. R. Horrocks, *Environmental Best Practice Programme, FP 70,* Harwell, UK, ETSU, 1997.

2. M. Hall, A.R. Horrocks, D. Roberts in *Proceedings of Ecotextile'98: Sustainable Developments*, Ed., A.R. Horrocks, Woodhead Publishing, Cambridge, 1998, p.63.

3. European Flame retardants Association (EFRA), The Voluntary Emissions Control Action Programme, VECAP^{TM}, EFRA web-site: http://www.cefic-efra.com/index.php?option=com_content&view=article&id=98&Itemid=238

4. A.R. Horrocks, *Reviews in Progress in Textile Colouration,*1986, **16**, 62-101

5. E.D. Weil, S.V. Levchik , *Journal of Fire Sciences,* 2008, **26**, 243-281

6. J.K. Stowell, E.D.Weil, W.L. Coble , C.G. Yang, (assigned to the University of Georgia Research Foundation and Akzo Nobel), United States Patent 6,365,070, 2 April 2002

7. C.G. Yang, W. Wu, J.K. Stowell, E.D.Weil, (assigned to the University of Georgia Research Foundation and Akzo Nobel), PCT Appl. WO 2004/001121, 2004

8. W. Wu, C.Q. Yang in *Proceedings of 14th conference Advances in Flame Retardant Polymers*, Norwalk, CT: Business Communications Inc., 2003

9. C.Q. Yang, W. Wu, *Fire and Materials,* 2003, **27**, 223-238

10. C.Q. Yang, W. Wu, *Fire and Materials,* 2003, **27**, 239-251

11. W. Wu, C.Q. Yang, *Journal of Fire Sciences,* 2004, **22**,125-143

12. H. Yang, C.Q. Yang, *Polymer Degradation and Stability,* 2005, **88***, 363-370

13. C.Q. Yang in *Handbook of Flame Retardant Textiles,* ed. F. Selcen Kilinc, Woodhead Publishing, Cambridge, 2013.

14. E.J. Blanchard, E.E.Graves, *Textile Research Journal,* 2002, **72**, 39-43

A. R. Horrocks. Flame retardant and environmental issues, 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.207-238, Smithers Rapra, Shawbury, UK (2013)

15. H. Yang, C.Q. Yang, *Journal of Fire Sciences,* 2007, **25**, 425-446

16. J. Guan, C.Q. Yang, G, *Polymer Degradation and Stability*, 2009, **94**, 450-455

17. X. Cheng, C.Q. Yang, *Journal of Fire Sciences*, 2009, **27**, 583-600

18. E.J Blanchard, E.E Graves, *AATCC Review*, 2005, **5,** 5, 26–30

19. *Journal of Fire Sciences,* 2008, **26**, 351-368

20. C.Q. Yang, X. Wu, *Journal of Fire Sciences*, 2009, **27**, 431-444

21. X. Wu, C.Q. Yang, *Cellulose,*2010, **17**, 4, 859-870

22. X. Cheng, C.Q. Yang, *Fire and Materials,* 2009, **33**, 365-375

23. C.Q. Yang, D. Chen, J. Chan, Q. He, *Industrial and Engineering Chemistry Research,* 2010, **49**, 18, 8325-8332.

24. C.Q. Yang, Q. He, B. Voncina, *Industrial and Engineering Chemistry Research,* 2010, **50**, 10, 5889-5897.

25. L.S. Galbraikh, N.S. Zubkova, N.G. Butylkina, A.A. Berlin, N.A. Khalturinsky, (assigned to Isle Firestop Chemicals) United States Patent 6,541,068, 1ˢᵗ April, 2003

26. S. Gaan, P. Rupper, V. Salimova, M. Heuberger, S. Rabe, *Polymer Degradation and Stability*, 2009, **94**,1125- 1134

27. H.B. Pandya, M.M. Bhagwat, *Textile Research Journal,* 1981, **51**(1): 5–8

28. S. Gaan, P. Rupper, V. Salimova, M. Heuberger, *Journal of Analytical and Applied Pyrolysis,* 2010, **87**, 93-98

29. S-C. Chang, N.D. Sachinvala, A.P. Sawhney, D.V. Parikh, W.A. Jarrett, *Polymers for Advanced Technologies,* Grimm C, 2007,**18**, 8, 611-619

30. T-M. D. Nguyen, S-C. Chang, B. Condon, M. Uchimiya and C. Fortier, *Polymers for Advanced Technologies,* 2012, **23**, 1555-1563

31. P. Rhys, H. Zollinger, in *The Theory of Coloration in Textiles, Second Edition,* Ed. A. Johnson, Society of Dyers and Colourists, Bradford, UK, 1989, pp428-476

A. R. Horrocks. Flame retardant and environmental issues, 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.207-238, Smithers Rapra, Shawbury, UK (2013)

32. T-M. D. Nguyen, S-C. Chang, B. Condon, M. Uchimiya, E. Graves, J. Smith, M. Easson and P. Wakelyn, *Polymers for Advanced Technologies,* 2012, **23**, 1034-1044

33. P. Webb, D.M. Lewis, J.A. Hawkes, A.E. Bayliff, (assigned to Perachem Ltd, Leeds Innovation Centre), PCT/GB2007/00738 and WO2007099343A1; 2 March 2007, granted as EP1991638A1, 16 September 2010.

34. J.A. Hawkes, P. Webb, D.M. Lewis, A. Bayliff, (assigned to Perachem Ltd, Leeds Innovation Centre), PCT/GB2008/050776, 3 September 2008; EP2188350 A1, granted 8 February 2012.

35. P. Webb, D.M. Lewis, J.A. Hawkes, A.E. Bayliff, (assigned to Perachem Ltd, Leeds Innovation Centre), PCT/GB2010/ 0233925, 16 September 2010

36. N. Inagaki, S. Nakamura, H. Asai, K. Katsuura, *Journal of Applied Polymer Science,* 1976, **20**, 2829-2836

37. E. Lecoeur, I. Vroman, S. Bourbigot, T.M. Lam, R. Delobel, *Polymer Degradation and Stability,* 2001, **74**, 487–492

38. E. Lecoeur, I. Vroman, S. Bourbigot, R. Delobel, *Polymer Degradation and Stability,* 2006, **91**, 1909-1914

39. Z. Yang, X. Wang, D. Lei, B. Fei, J.H. Xin, *Polymer Degradation and Stability,*2012, **97**, 2467-2472

40. E.D. Weil, in *Recent Advances in Flame Retardancy of Polymeric Materials, Vol. 2,* Eds. M. Lewin, G.S. Kirschenbaum, Business Communications Co., Norwalk, CT, USA,1991, 15-32.

41. D L McAllister in proceedings of Flame Retardants '92, Interscience Communications, London, (1992), p.149

A. R. Horrocks. Flame retardant and environmental issues, 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.207-238, Smithers Rapra, Shawbury, UK (2013)

42. M.C. Hardy, in *Recent Advances in Flame Retardancy of Polymer Materials, Vol. 8*, Ed. M. Lewin, Business Communications Co., Norwalk, CT, USA, 1997.

43. P.J. Wragg , in *Ecotextile'98 – Sustainable Development, E*d. A.R. Horrocks, Woodhead Publishing, Cambridge, UK, 1999, pp247-258.

44. Anon, , *Chem. Brit.,* 1998, **34,** 7, 8; *Expert Group to Investigate Cot Death Theories: Toxic Gas Hypothesis,* London, UK Department of Health; http://www.open.gov.uk/doht.limer.htm

45. G.C. Stevens and A.H. Mann, *Risks and Benefits in the Use of Flame Retardants in Consumer Products,* UK Department of Trade and Industry Report, URN 98/1026, January 1999

46. G.C. Stevens and A.E. Emsley, *Effectiveness of the Furniture and Furnishing (Fire) (Safety) Regulations 1988*, UK Department of Trade and Industry Report , URN 00/783, June, 2000.

47. G.C. Stevens, A. Emsley, L. Lim and P. Williams, The benefits of fire measures in the UK and Europe from a consideration of UK and International Statistics, in the *Proceedings of Flame Retardants 2006*, Interscience Publications, London, 2006, pp. 235.

48. *A Statistical Report to Investigate the Effectiveness of the Furniture and Furnishing (Fire) (Safety) Regulations, 1988,* Greenstreet Berman Ltd., 2009

49. A.M. Elmsley, G.C. Stevens, in *Advances in Fire Retardant Materials,* Eds A.R. Horrocks, D. Price, Woodhead Publishing, Cambridge, 2008, pp363-397.

50. National Academy of Sciences. Toxicological risks of selected flame-retardant chemicals. Sub-committee on Flame-retardant Chemicals of the United States National Research Council, Washington, DC. Washington: National Academy Press, 2000.

51. P.J. Wakelyn, in *Advances in Fire Retardant Materials,* Eds A.R. Horrocks, D. Price, Woodhead Publishing, Cambridge, 2008, pp188-212

A. R. Horrocks. Flame retardant and environmental issues, 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.207-238, Smithers Rapra, Shawbury, UK (2013)

52. European Union Risk Assessment Report for bis(pentabromodiphenyl) ether, European Chemicals Bureau,2003 (closed 26th May 2004) : www.bsef.com

53. European Union Risk Assessment Draft Report for hexabromocyclododecane, European Chemicals Bureau (October 2007): www.bsef.com

54. H.M. Stapleton, N.G. Dodder, *Environmental Toxicology and Chemistry*, 2008, **27**, 2, 306-312

55. A. Christiansson, J. Eriksson, D. Teclechiel, Å . Bergman, *Environmental Science and Pollution Research*, 2009, **16**, 3, 312-321

56. L.G. Costa, G. Giordano, *NeuroToxicology,* 2011, **32**, 1, 9-24

57. S. Ravnum, K.E. Zimmer, H. Keune, A.C. Gutleb, A.J. Murk,J.G. Koppe, B. Magnanti,J.L. Lyche, G.S. Eriksen, E. Ropstad, J.U. Skaare, M. Kobernus, A. Yang, A. Bartonova, M. Krayer Von Krauss, *Environmental Health: A Global Access Science Source*, 2012, **11** (SUPPL.1), art. no. S7.

58. J. Wang, S. Chen, X. Nie, M. Tian, X. Luo, T. An, B. Mai, B. *Chemosphere*, 2012, **89**, 7, 844-849.

59. A.P. Cousins, *Science of the Total Environment*, 2012, **438,** 233-241.

60. C. Sun,W. Chang, W. Ma, C. Chen, J. Zhao, *Environmental Science and Technology*, 2013, **47**, 5, 2370-2377

61. G. C. Stevens, R. Ghanem, J.L. Thomas, A.R. Horrocks, B. Kandola, in *Flame Retardants 2004,* Interscience Communications, London, 2004, pp

62. VECAP, *Maintaining the Momentum, European Annual Progress Report 2012*, EFRA and BSEF Secretariat, Belgium, www.vecap.info

63. REACH, 2007. http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm

Table 6.1: Cellulose-reactive and potentially-reactive flame retardant bonding types discussed in **Section 6.3**

Bond	Structure	Comments	Refs
N- Methylol species	Cell.O.CH$_2$.NH-	Resists hydrolysis but releases HCHO during storage	4 and see **Chapter 4**
Cellulose ester with Fyroltex HP	Cell.O. CH$_2$.CH$_2$.(O.CH$_2$.CH$_2$ .O.P(O)(OCH$_3$))$_{2x}$. (O. CH$_2$.CH$_2$ .P(O)(CH$_3$))$_x$. CH$_2$.CH$_2$.OH	Poor wash stability	7-12
Cellulose ester with BCTA (and/or Fyroltex HP)	Cell.O.CO.CH$_2$.CH(COOH).CH(COOH).CH$_2$.CO.R where R=O.Cell or .FR (eg Fyroltex HP)	Poor hydrolysis and wash resistance	14, 15
Cellulose/BCTA link stabilisation: Effect of triethanolamine (TEA)	Cell.O.CO.CH.CH(CO$_2$)$^-$.CH(COOH).CH.CO.R (CH$_2$.CH$_2$.O)$_3$.NH$^+$ Cell.O.CO.CH.CH(CO$_2$)$^-$.CH(COOH).CH.CO.R (CH$_2$.CH$_2$.O)$_3$.NH$^+$	Claimed 30 wash durability for Fyroltex/TEA/BCTA on 35/65 cotton/Nomex® blend.	15, 17
Cellulose-diacid-hypophosphite link; where diacid is maleic, succinic, malic or tartaric acids.	Cell-O-CO-CH$_2$-CH(COOH)-P(O).(O$^-$)-CH(COOH)-CH$_2$-CO-O-Cell Note that with 3 or more –CO.OH groups in a polycarboxylic acid, evidence of increased cellulose chain cross-linking is observed.	20 home wash cycles	19-24

Cellulose-phosphoramidate systems	$(C_2H_5.O)_2$-P(O)-NH-R, where R = -H, $-C_2H_5$, $-C_2H_4.OH$ and $-C_2H_4.O.CH_3$	No reactivity with cellulose	26, 27, 28
Cellulose-phosphoramidate ester interchange	Cell.O. P(O)($C_2H_5.O$)- $C_4H_8N_2.CH_3$; linkage to cellulose following heat curing at 160°C in slight alkaline conditions.	Some water soak (40°C) durability	30
Cellulose-chloro triazinyl condensation.	where R= -O.CH_2.PO(OCH_3)$_2$	Durability as yet unknown	32
Cellulose phosphonate and derivatives	Cell.OH + HO.PH (O).O^-M^+ → Cell.O.PH (O). O^-M^+ + H_2O Cell.O.P(O)H. O^-M^+ + HO.Cell → Cell.O.PH(O).O.Cell + M^+OH^- where M^+ = Na^+ or K^+, plus MOCN, CN.NH_2 and derivatives	Durable to at least 30 washes	33-35

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Table 6.2: Risk analysis of 16 selected flame retardants [51]

Risk	Chemical	Use in Furnishings
Acceptable	Hexabromocylcododecane	√
	Decabromodiphenyl oxide	√
	Alumina trihydrate	√
	Magnesium hydroxide	√
	Zinc borate	X
	Ammonium polyphosphates	√
	Phosphonamide ("Pyrovatex" type)	√
	Tetrakis(hydroxymethylol) phosphonium derivatives ("Proban" type)	√
Unacceptable	Antimony III oxide	√
	Antimony pentoxide and antimonates	√
	Calcium and zinc molybdates	X
	Organic phosphonates	√
	Tris (1, 3-dichloropropyl 1-2) phosphate	X
	Tris (monochloropropyl) phosphates	X
	Aromatic phosphate plasticisers	X
	Chlorinated paraffins	X

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Table 6.3: Usage versus emission data published by EFRA under VECAP[TM] [62]

Tonnes\Year	2008	2009	2010	2011	2012
Total 2011 volume sold, tonnes	5,000-7,500	5,000-7,500	5,000-7,500	7,500-10,000	2,500-5,000
Total emissions, tonnes	<4	<1.5	<1.5	<0.5	<0.3

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A. R. Horrocks. Flame retardant and environmental issues, 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.207-238, Smithers Rapra, Shawbury, UK (2013)

Figure 6.1: The VECAP^{TM} Process