OAKDENE HOLLINS LTD

University of Bolton
Professionals in Practice

gnosysuk

Defra Contract No: SPMT09_011

Fire Retardant Technologies: safe products with optimised environmental hazard and risk performance

Annexe 3

Review of Alternative Fire Retardant Technologies

defra
Department for Environment Food and Rural Affairs

For the attention of the Project Steering Group

ISOQAR QUALITY ASSURED FIRM ISO 9001 4077/03

UKAS QUALITY MANAGEMENT 026

Fire Retardant Technologies: safe products with optimised environmental hazard and risk performance

Annexe 3

Review of Alternative Fire Retardant Technologies

Authors:

Professor Gary Stevens	GnoSys
Dr Alan Emsley	GnoSys
Dr Linda Lim	GnoSys
Professor Baljinder Kandola	University of Bolton
Professor Dick Horrocks	University of Bolton

GnoSys Report No: GR233

GnoSys UK Ltd, University of Surrey, Guildford, Surrey, GU2 7XH

tel: (+) 1483 689599, fax: (+) 1483 9555, web: www.gnosysuk.com

Summary

This report examines a number of alternative FR technologies for each of the primary consumer products categories being considered: (a) Furniture and Furnishings, (b) Clothing textiles, and (c) Electronic and Electrical Equipment (televisions and computers both personal (desktop) and portable (laptop and notebooks). The source information from this is drawn from a wide range of industrial and academic sources in the UK, Europe and the US. Use is also made of the results of an FR Technology survey carried out during the study.

There are many potential alternative technologies and substitution options available for a number of the leading chemical FRs that are in current use and which have been, or are being, considered for ban or voluntary removal in Europe.

While some of these alternatives have been well researched and are fit for purpose, there are many that, although they may be chemically classified, have not been adequately assessed technically for their long term performance or for their potential impact on exposure to humans and the environment through rigorous risk assessment.

This is particularly the case for alternative chemical FR technologies for printed circuit boards, where the manufacturing demands are stringent and the industry experience of moving to new lead free solder is relatively new.

There are also a number of emerging FR technologies that are at the research stage and cannot currently be offered commercially.

It is clear from the current debate on the potential removal of bromine and chlorine containing compounds from some consumer products that sound technical and scientific information must be considered in parallel with careful application of the precautionary principle.

There is a need for greater scrutiny of proposals for substitution and replacement of certain chemical FRs in the belief that better alternatives exist. It is necessary to ensure that candidate substitute technologies are proven, be they chemical or physical. These must be shown to be capable of meeting all relevant and important criteria to ensure the materials/component/products that use them are fit for purpose and capable of meeting both Ecolabel criteria and product manufacturing and lifetime requirements, including fire performance.

Contents

SUMMARY 3

PART 1: GENERAL INTRODUCTION ON FLAMMABILITY AND FIRE RETARDANT TECHNOLOGIES 8

1 GLOBAL AND EUROPEAN FIRE RETARDANT MARKET 8

1.1 USA, Europe and Asia 8

1.2 Europe 10

2 FLAMMABILITY OF POLYMERS 11

3 FIRE RETARDANT STRATEGIES FOR TEXTILES 11

3.1 Surface treatments 11

4 FIRE RETARDANT ADDITIVES / COPOLYMERS IN SYNTHETIC POLYMERS AND FIBRES 12

5 ALTERNATIVE FIRE RETARDANTS 13

5.1 NanoComposites 13

5.2 Heat resistant and inherently fire retardant polymers and fibres 14

5.3 Fibre blending 15

5.4 Composite assemblies – design issues 15

PART 2 : FIRE RETARDANT TECHNOLOGIES FOR SPECIFIC APPLICATIONS 16

6 NIGHTWEAR 16

6.1 Children nightwear 16

6.2 Adult nightwear 16

6.3 Future FR Technology Challenges for nightwear 17

7 FURNITURE AND FURNISHINGS 18

7.1 Covering fabrics 18

7.2 FR technology where inherent fire retardant fibres are not used: 19

7.3 Foams and filling materials 20

7.4 Fire-blockers and Interliners 20

7.5 Bedding 21

7.6 Curtains and Drapes....21

7.7 Floor coverings 22

7.8 Tents and marquees....22

7.9 Ecolabel and Green Procurement issues and Alternative FR Technology in Furnishings....22

8 TELEVISIONS, PERSONAL AND MOBILE COMPUTERS (INCLUDING ENCLOSURES AND PRINTED CIRCUIT BOARDS)....23

8.1 TV and Computer Enclosures Plastic Content 23

8.2 Overview....24

8.3 More Recent Chemical FR Alternatives to BFRs....26

8.4 Electronic Product Supply Chain Initiatives....26

9 ALTERNATIVE FR TECHNOLOGIES FOR ELECTRONIC PRODUCTS 27

9.1 Alternative PCB Materials 28

9.2 Alternative Chemical Fire Retardants in PCBs 29

9.3 FR Substitution in Enclosure Materials....30

10 US EPA DESIGN FOR THE ENVIRONMENT PROGRAMME – CLEANER TECHNOLOGY SUBSTITUTES ASSESSMENT 31

10.1 Furniture Flame Retardancy Partnership 32

10.2 Fire Retardants in Printed Wiring Boards Partnership 35

10.3 Lowell Centre for Sustainable Production Substitutes Programme – a summary 36

11 IN SUMMARY 37

APPENDIX 1 FLAMMABILITY OF POLYMERS 38

Bulk polymers....38

Polymer fibres 38

APPENDIX 2 FIRE RETARDANT STRATEGIES FOR TEXTILES....42

APPENDIX 3 OXYGEN INDEX AND UL94 TESTS AS A BROAD INDICATION OF THE FLAMMABILITY PERFORMANCE OF A MATERIAL....45

APPENDIX 4 FINDINGS OF THE FR TECHNOLOGY SURVEY 47

SUMMARY 47

SURVEY STRUCTURE AND PARTICIPATION 47

SUMMARY OF FINDINGS AND RESPONDENT COMMENTS 48

FR Producers 48

Product Producers 49

FR Technology Costs 50

EU Ecolabel Scheme 51

Respondent's General Comments 52

Participants by Organisation 55

APPENDIX 5 LOWELL CENTRE FOR SUSTAINABLE PRODUCTION SUBSTITUTES PROGRAMME – FR SUBSTITUTE STUDIES 58

APPENDIX 6: ELECTRONIC PRODUCT OEM STATEMENTS REGARDING CHEMICAL SAFETY, BROMINATED FIRE RETARDANT PHASE-OUT AND HALOGEN COMPOUND REDUCTION 64

Glossary

BIS Department of Business, innovation and Skills
BSEF Bromine Science and Environment Forum
CAA (US) Clean Air Act
CAA (US) Clean Air Act
CHIP Chemicals (Hazard Information and Packaging for Supply) Regulations
CLP Regulation on classification, labelling and packaging of substances and mixtures
COSHH Control of substances Hazardous to Health
CPSA (US) Consumer Product Safety Act
CPSC (US) Consumer Product Safety Commission
Deca-DBE decabromodiphenyl ether
DPD Dangerous Preparations Directive 1999/45/EC
DSD Dangerous Substances Directive 67/548/EEC
EBFRIP European Brominated Flame Retardant Industry Panel
ECHA European Chemicals Agency
EFRA European Flame Retardants Association
EPA (US) Environmental Protection Agency
ESR Existing Substances Regulation (Council Regulation (EEC) No 793/93)
EUP Energy Using Products (EUP) Directive 2005/32/EC
FFA (US) Flammable Fabrics Act
FHSA (US) Federal Hazardous Substances Act
FR fire retardant
GPSD General Product Safety Directive
HBCD hexabromocyclododecane
HELO Hungarian Eco-labelling Organisation
IPPC Directive on Integrated Pollution Prevention and Control, 2008/1/EC
NFPA (US) National Fire Prevention Association
NONS Notification of New Substances Regulations (Council Directive 67/548/EEC)
Octa-DBE octabromodiphenyl ether
PBB polybrominated biphenyl
PBDE polybrominated diphenyl ether
Penta-DBE penta-bromodiphenyl ether
REACH Registration, Evaluation, Authorisation and Restriction of Chemicals
RoHS **R**estriction **o**f the use of certain **H**azardous **S**ubstances
TBBPA tetrabromobisphenol A
TSCA (US) Toxic Substances Control Act
WEEE Waste Electrical and Electronic Equipment directive
WFD Water Framework Directive Directive 2000/60/EC

Part 1: General introduction on flammability and fire retardant technologies

Fire retardants (FRs) have been in volume use for nearly 60 years since it was found that they could effectively reduce the combustibility of most carbon based materials including natural and synthetic polymers. FRs have been used in the areas at highest risk to ignition and flame spread or at greatest fire risk to humans. As discussed in Annexes 1and 2 of this report, FRs may be required to meet regulatory and legislative requirements which are usually fire performance related rather than prescriptive for the use of chemical FR systems.

It has been estimated that historically there were between 300 and 400 chemical FR systems produced commercially for application to a variety of consumer and commercial products .[1, 2.] There has been some reduction in the number of commercially available chemical FRs in the last decade and, increasingly, a shift toward polymeric and phosphorous based chemical FRs largely to address the need for improved environmental performance.

1 Global and European Fire Retardant Market

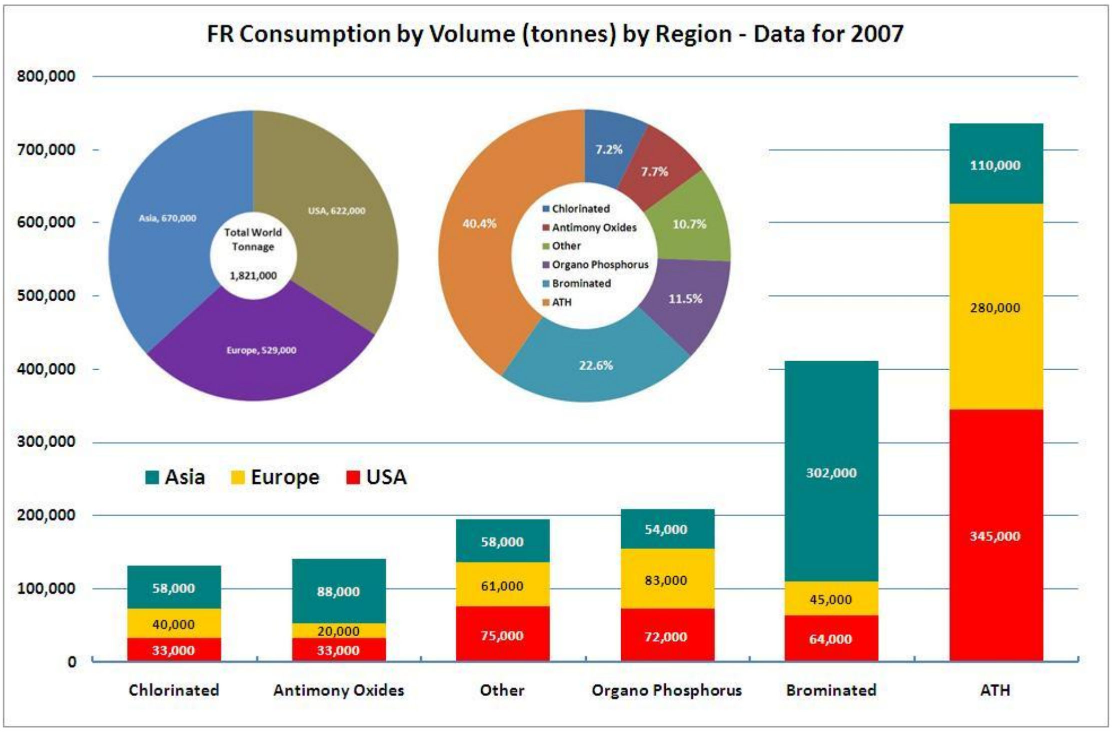
1.1 USA, Europe and Asia

According to a survey carried out by SRI Consulting[3], the total market for FRs in the United States, Europe and Asia in 2007 amounted to about 1.8 million metric tons, Figure 1 and was valued at $4.2-4.25 billion, Figure 2. This market was expected to grow at an average annual rate of about 3.7% per year on a volume basis over the period 2007-2012.

In terms of tonnage, brominated FRs are second only to the inorganic compounds such as alumina trihydrate (ATH), although this is totally due to the large use of these compounds in Asia. Brominated flame retardants do, however, have the greatest market value as shown in Figure 2.

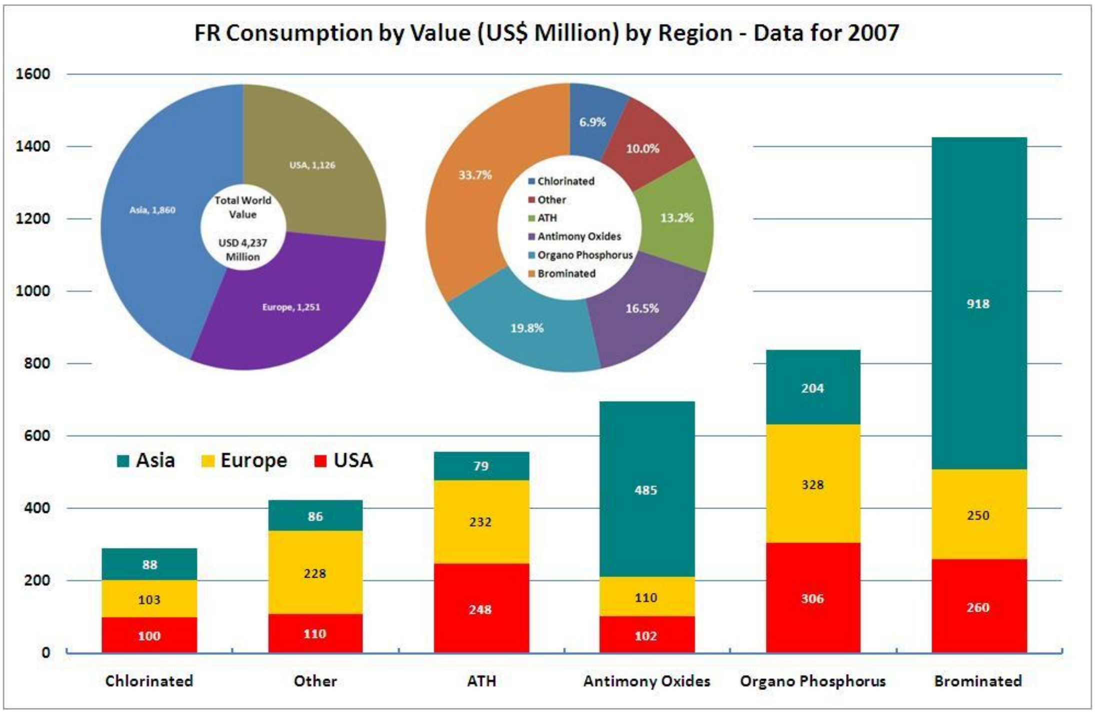
[1] *Risks and Benefits in the Use of Flame Retardants in Consumer Products,* DTI report URN 98/1026; produced by the Polymer Research Centre, University of Surrey;, G. C..Stevens and A.H. Mann, 1999.
[2] *Prioritisation of Flame Retardants for Environmental Risk Assessment,* Environment Agency report, 2003; ISBN: 978-1-84432-956-4; authors: P R Fisk, A E Girling and R J Wildey
[3] SRI Consulting Report on Flame Retardants Published December 2008

Figure 1: Volume consumption of fire retardants in the USA, Europe and Asia



Data Source: SRI Consulting

Figure 2: Value of fire retardants worldwide



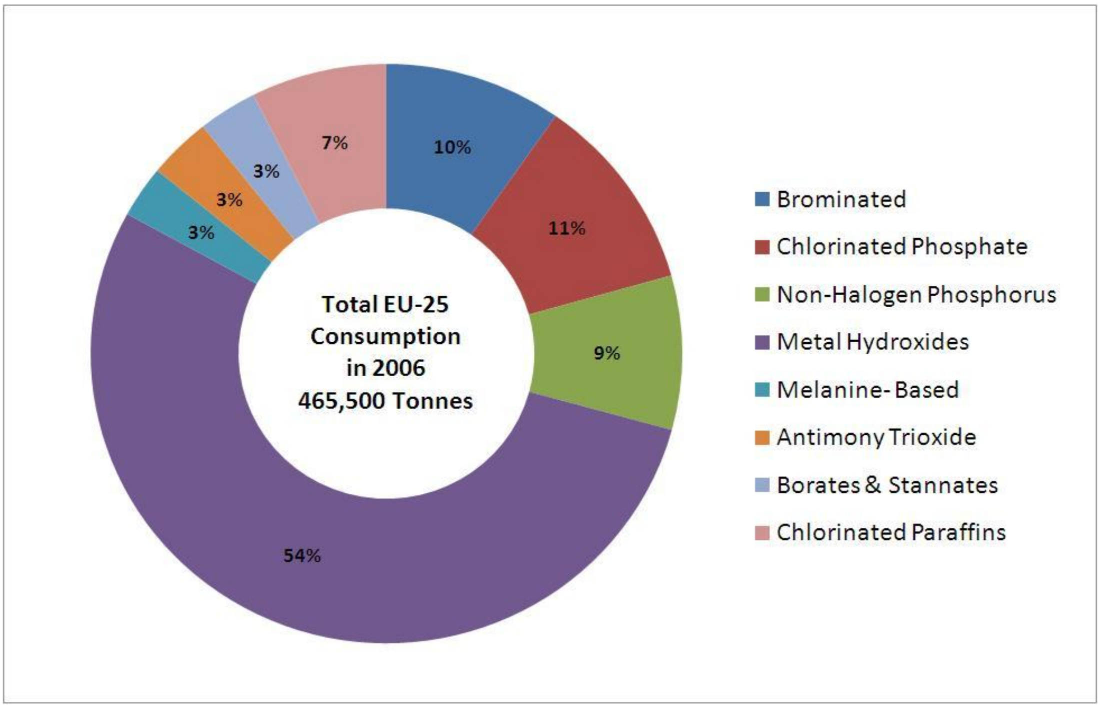
Data Source: SRI Consulting

1.2 Europe

With regard to the European Union (EU-25), an EFRA[4] members survey carried out in 2007 gave an estimated consumption of FRs for 2006 of about 465,000 tonnes. The breakdown of FR types is shown in Figure 3. The SRI study reported an estimated FR consumption of 580,000 tonnes in 2007, which was approximately a 25% increase on the 2006 data produced by EFRA. The SRI study also gave a breakdown of consumption for the Western European countries (EU-15) and the Eastern European/Russian countries of 530,000 tonnes and 50,000 tonnes respectively.

It was expected that the Eastern European countries would have a greater increase in consumption than the Western European countries over the period 2007-2012 due to rising safety standards and harmonization with EU legislation.

Figure 3: Types and proportions of fire retardants used in the EU-25 in 2006



Data Source: EFRA Members Survey 2007

Clearly, the largest FR category in terms of EU tonnage is that associated with inorganic compounds such as aluminium trihydroxide (ATH) and magnesium hydroxide (MDH). These compounds are generally used in combination with other fire retardant synergists such as antimony trioxide and zinc stannates and are classified as 'additive' fire retardants. Under the new EU Ecolabel criteria for textiles this sector of the fire retardant market would not be acceptable.

There is little doubt that the use of FRs will increase in the future, but it is likely that the consumption profile of the various FR types will change significantly, because of an increasing awareness of the human, environmental and ecological impact of certain fire retardants throughout the complete life cycle

[4] European Flame Retardants Association

of fire retarded products. Growth rates for the individual groups of fire retardants vary widely, between 5% growth (ATH, MDH, APP, zinc stannates, melamine derivatives) and 5-10% decline (TBBPA/ATO), depending on developments in government regulations, replacement of one (halogenated) fire retardant chemical by another (non-halogenated) compound and new product applications.

2 Flammability of polymers

The following is a brief summary of the key aspects of polymer flammability and FR strategies to combat flame spreading. For a more complete discussion please see Appendix 1.

The burning behaviour of bulk polymers and fibres depends upon their physical and chemical properties and is essentially a three phase process - heating, thermo-pyrolytic decomposition and finally ignition. Thermoplastics tend to soften/melt at 100 - 250 ^{o}C, which causes them to distort, in some cases away from the heat source. In other cases, the polymer degradation products are volatile and flammable and self ignite. Natural fibres tend to decompose at 250 - 500 ^{o}C, sometimes forming char by recombination of the degradation products, which slows the spread of the flame. The melting, pyrolysis and combustion behaviour of polymeric materials is discussed further in Appendix 1 and summarise in Table 1-1. Where polymer fibres are used in apparel, the most important characteristics of burning are time-to-ignition, rate of flame spread and rate of heat release and these are summarised for commonly used fibres in Table 1-2 of Appendix 1.

FR strategies to reduce flammability act in one (or more) of the following ways:

- retard the development of the flame by interfering with radical chain branching reactions in the gas phase
- dilute the flame with water or inert gases.
- absorb heat in the bulk polymer
- reduce the supply of fuel from the bulk to the gas phase by encouraging carbon formation (charring)
- add an intumescence promoter to produce a carbon barrier layer at surface.

3 Fire retardant strategies for textiles

3.1 Surface treatments

Surface treatment is the oldest method of fire retarding the textiles. There are two types of surface treatments - finishes and coatings. Finish is applied by impregnating the fabrics in an aqueous solution of the chemical. Coating on the other hand is the application of a continuous or discontinuous layer on the surface of the fabric generating a heterogeneous fabric/polymer composite. Some treatments are non-durable to laundering, others may be semi-durable and withstand a single water soak or dry cleaning process. Durable coatings are defined as able to withstand 50 wash cycles. Durability requirements are usually determined by the application and specified by associated regulations. Typical chemical finishes involve the use of phosphates and polyphosphates, phosphorus amides, phosphonium derivatives, borax and boric acid or halogenated FRs. Typical coatings use, for instance natural and synthetic rubbers, poly(vinyl chloride), poly(vinyl alcohols), formaldehyde-based resins, acrylic copolymers, polyurethanes, silicones and fluorocarbons etc. Fire retardants used for coatings include phosphates and phosphonates, eg, triaryl phosphate, cresyl diphenyl phosphate or phosphinate. Brominated derivatives such as decabromodiphenyl oxide (DBDPO) and hexabromocyclododecane (HBCD) may be applied as a back-coating in the form of a paste or foam.

Modern alternatives to the traditional treatment techniques are being developed. These include plasma-induced-graft-polymerization to graft and phosphate and phosphinate FRs to the surface and embedding nanoparticles on to textile substrates by a plasma polymerization / co-sputtering process. Neither process is yet commercially available.

Finishes and coatings for different material types are discussed in detail in Appendix 2 and nanocomposite FRs are discussed below.

4 Fire retardant additives / copolymers in synthetic polymers and fibres

As the title suggests, this approach is applicable to synthetic fibres only where either one of the monomer / homopolymer can be fire retarded or the FR molecules can be attached to the polymer chain during polymerization, or FR additives can be in the polymer melt or in solution prior to extrusion. In the case of synthetic fibres these are sometimes classified as inherently fire retardant. Some exemplar fibres are discussed here.

Viscose or rayon: A well known inherently fire retardant viscose fibre is Viscose FR, marketed by Lenzing GmbH, (Austria). The fibre is produced by adding Sandoz 5060 (Clariant 5060) - bis(2-thio-5,5-dimethyl-1,3,2-dioxaphosphorinyl)oxide in the spinning dope before extrusion. As this additive is phosphorus based, it is similar to other phosphorus- based fire retardants in terms of mode of action (condensed phase). The second example is Visil fibre, developed in Finland by Säteri Fibres (formerly Kemira and now no longer manufactured) by adding polysilicic acid (Visil®) and aluminum (Visil AP®).

Polyester: One of the most successful commercially available fire retardant polyester fibre is Trevira GmbH (Germany), which is produced by incorporating a comonomeric phosphinic acid unit into the PET polymeric chain. Examples of fire retardant additives used in polyester are bisphenol-S-oligomer derivatives (Toyobo GH), cyclic phosphonates (Antiblaze CU and 1010, Rhodia) and phosphinate salts (Clariant). All these fire retardants do not promote char formation.

Polypropylene: Although in principle, phosphorus-containing, halogen-containing, silicon-containing, metal hydrate and oxide are effective in rendering PP fire retardant, invariably these fire retardants are required in high levels, typically >20% w/w, to achieve specified level of fire retardancy. However, such high levels render the processing of compounded polymer into fibres difficult and the resulting fibre properties unsuitable for textile applications. Apart from antimony–halogen or in some cases, tin–halogen formulations only one single fire retardant system, tris(tribomoneopentyl) phosphate (FR 372, ICL) is presently effective in polypropylene when required for fibre end-uses.

***Polyamides*:** It is very difficult to incorporate additives in polyamides because of their melt reactivities.

5 Alternative fire retardants

5.1 NanoComposites

Although there has been considerable amount of research going on in area of polymer nanocomposites, there has been only limited success in developing textile structures out of them. Indeed, our survey of FR technologies found that no FR manufacturer who responded is supplying FRs based on nanotechnology albeit some FRs are believed to be commercially supplied in the nanoparticulate size rage 1 to 1000nm. For fire retardant properties, it is believed that the presence of nanoclays in a polymer promotes carbonaceous - silicate particle build up on the surface during burning, which insulates the underlying material [5,6] . The accumulation of silicate layers on the surface is due to gradual degradation and gasification of the polymer; it may also be facilitated by surface melting - according to other theories the migration of silicates to the surface is due to the lower surface free energy of the clays and by convection forces, arising from the temperature gradients, perhaps aided by movement of gas bubbles present during melting of the thermoplastic polymers.[7]

This mechanism works fine for thick polymer sections. However, for physically and thermally thin samples like textiles, there is not enough time to make a thermal barrier and hence the nanoclays in textiles are not as effective as seen in bulk polymers. The other important issue is that although nanoclays reduce peak heat release rate during cone calorimetric testing, they have no effect on time-to-ignition. Most often simple techniques such as limiting oxygen index show that the addition of nanoclays and other nanoparticles do not significantly increase LOI values unless their presence modifies the burning behavior by reducing melt dripping character of the polymer.[8] They however, do promote char formation in otherwise non-charring polymers, which is an advantageous effect. There are still no commercially available inherently fire retardant polymer-nanocomposite fibres. Most of the work is still on the lab scale, as summarised below.

Cotton: the only reported cotton-clay nanocomposites work is by White[9] where cotton with MMT clay in a 50% solution of 4-methylmorpholine N-oxide (MMNO) was produced in the form of large plaques. However, no fiber or textile structures could be obtained.

Polylactic acid: (PLA) -clay nanocomposites fibres [10] by melt blending organomodified (OM)-MMT (1 to 4 wt.-%) with PLA and then melt spinning into multifilament yarns have been reported.

Polyester: the reported work [11] done in Sichuan University of China, involves adding montmorillonite clay in a copolymer of poly(ethyleneterephthalate), which with a phosphorus-containing monomer could

---

5 Bourbigot, S., Gilman, J. W. and Wilkie, C. A. 2004. Kinetic analysis of the thermal degradation of polystyrene–montmorillonite nanocomposite. *Polym. Degdn. Stab*. 84(3): 483-492.

6 Gong, F., Feng, M., Zhao, C., Zhang, S. and Yang, M. 2004. Thermal properties of poly(vinyl chloride)/montmorillonite nanocomposites. *Polym. Degdn. Stab*., 84(2): 289-294.

7 Lewin, M. 2003. Some comments on the modes of action of nanocomposites in the flame retardancy of polymers**.** *Fire Mater***.** 27 (1): 1-7.

8 Horrocks, A.R. and Kandola**,** B.K. 2007. Potential applications of nanocomposites for flame retardancy. Chapter 11 in *Flame retardant polymer nanocomposites*, ed. Morgan, A.B. and Wilkie, C.A. Wiley-VCH, Verlag GmbH & Co, KGaA.

9 White, L.A. 2004. Preparation and thermal analysis of cotton - clay nanocomposites. J. Appl. Polym. Sci., 92(4): 2125–2131.

10 Solarski, S., Mahjoubi, F., Ferreira, M., Devaux, E., Bachelet, P., Bourbigot, S., Delobel, R., Murariu, M. , Da Silva Ferreira, A., Alexandre, M., Degée, P. and Dubois, P. 2007. (Plasticized) Polylactide/clay nanocomposite textile: thermal, mechanical, shrinkage and fire properties. *J. Mater. Sci.*, 42 (13): 5105 – 5117.

produce PET with higher thermal stability and char-forming tendency. However fibres were not produced from this PET-nanocomposite polymers.

Polypropylene: One of the difficulties of incorporating nano clays into polypropylene is the lack of polar groups in the polymer chain which makes direct intercalation or exfoliation almost impossible. Most often maleic anhydride - grafted polypropylene is used as a compatabilizer. Nanoclays on their own however, are not sufficient to impart required fire retardancy, but in the presence of a conventional fire retardant, can shown good results[12,13]. The effect of the fire retardants ammonium polyphosphate, melamine phosphate, pentaerythritol (PER), pentaerythritol phosphate, cyclic phosphate, intumescent mixtures of APP, PER and melamine etc in the presence and absence of nanoclay has been studied in the literature.[13] Other nanoparticles used for PP include poly(vinylsilsesquioxane) (POSS) [14] and multi-walled carbon nanotubes (MWNT) (1 and 2% by mass).,[15], [16,]

Polyamides: A number of research groups have reported the flammability performance of nylon 6 and nylon 6.6 / clay hybrid fibres made by melt blending and by melt spinning[78] and confirmed that nanoclays on their own will not be able to fulfil all the required features of an ideal fire retardant such as conferring ignition resistance, self extinguishability and char-forming propensity. However, they may increase the effectiveness of more normal FRs and thus enable lower quantities to be used, an especially important requirement in synthetic fibre production and processing.

5.2 Heat resistant and inherently fire retardant polymers and fibres

Inherently fire and heat resistant polymers and fibres are either all-aromatic polymeric structures or inorganic and mineral based. Aromatic polymer fibres are mostly used for apparel applications as protective clothing. Some commonly used fibre types are given in Table -1. These are non-thermoplastic, combustion-resistant with decomposition temperatures above 375^0C and with LOI values 30 vol-% or more. Moreover, they have char-forming tendency.

---

[11] Wang D-Y, Wang Y-Z, Wang J-S, Chen D-Q, Zhou Q, Yang B , Li W-Y. 2005. Thermal oxidative degradation behaviours of flame-retardant copolyesters containing phosphorous linked pendent group/montmorillonite nanocomposites. *Polym. Deg. Stab.*, 87: 171-176.

[12] Horrocks, A.R., Kandola, B.K., Smart, G., Zhang, S., Hull, T.R. 2007. Polypropylene fibers containing dispersed clays having improved fire performance. I. Effect of nanoclays on processing parameters and fiber properties. *J Appl. Polym. Sci.***,** 106 (3): 1707 - 1717.

[13] Smart, G., Kandola, B.K., Horrocks, A.R., Marney, D. 2008. Polypropylene fibers containing dispersed clays having improved fire performance Part II : Characterisztion of fibers and fabrics from PP - nanoclay blends', *Polym. Adv. Techn.,* 19: 658 - 670.

[14] Bourbigot, S., Le Bras, M., Flambard, X., Rochery, M., Devaux, E. and Lichtenhan, J. 2005. Polyhedral oligomeric silsesquioxanes: Application to flame retardant textiles. *Fire Retardancy of Polymers: New Applications of Mineral Fillers* , ed., Le Bras, M., Bourbigot, S., Duquesne, S., Jama, C. and Wilkie, C.A., Royal Society of Chemistry (Pub), pp 189-201.

[15] Bellayer, S., Bourbigot, S., Flambard, X., Rochery, M., Gilman, J. W., Devaux, E. 2004. Polymer/MWNTs nanocomposite yarns and fabrics: processing, characterization and flammability and thermal properties. *Proceedings of the 4th AUTEX Conference*, ENSAIT, Roubaix 2004, O-3W1.

[16] Bourbigot, S. 2008. Flame retardancy of textiles: new approaches. Chapter 2 in *Advances in Fire Retardant Materials,* ed. Horrocks A.R. and Price, D. Woodhead Publishing Ltd, Cambridge, England, pp 9 – 40.

5.3 Fibre blending

Fibre blending is a very common method of reducing the flammability of flammable fibres. Polyester is usually blended with cotton and this poly-cotton, if it has lower than 50% polyester content can pass the simple vertical strip flammability test. With higher polyester content, sometimes the blended fibre is more flammable than the individual components. This is called a wicking effect where the cotton acts like a wick, holding the polyester component together, which burns. Cotton-nylon blends are also quite commonly used to reduce flammability of cotton.

Wool and Visil fibre are blended to improve the latter's fibre properties, but the flammability of the blend is also reduced. Cotton - wool blends are quite common as well. Aramids are blended with many fibres for different applications. Nomex can be blended with FR viscose and FR wool to produce fire blocking fabric, eg for aircraft seats.[17] Nomex blended with Kevlar shows better performance than 100% Nomex in fire fighters' outer protective garments[18] Various blends of glass fibres with aramids, melamine fibres, PVC fibres and polyester have been reported for use in fire-protective non-woven veils for upholstery and mattresses.[19]

5.4 Composite assemblies – design issues

The flame resistance of a fabric not only depends upon the nature of components and the FR treatments applied, but also on fabric area density, construction, air permeability and moisture content. Nonwovens for example will have superior properties to woven or knitted structure, even if all other variables are kept the same.[20] The air entrapped within the interstices of any fabric structure and between layers of fabrics within a garment assembly provides the real thermal insulation. For effective thermal and fire resistance in a fabric structure, these insulating air domains need to be maintained. In general, for protective clothing and fire-block materials, for best performance multilayered fabric structures are employed. The assembly structures can be engineered to maximize their performance.

---

[17] Bajaj, P. 2000. Heat and Flame Protection, In *Handbook of Technical Textiles*, ed. Horrocks, A. R. and Anand, S. C., Woodhead Publishing Ltd., Cambridge, England, pp. 223-263.

[18] Weil, E.D. and Levchik S. 2008. Flame retardants in commercial use or development for textiles. *J.Fire Science*, 26: 243 - 281.

[19] Weller, D.E. 2007. (to Owens Corning), European Patent Appl. 1,771,615

[20] Lee, Y.M., Barker, R. 1987. Thermal protective performance of heat-resistance fabrics in various high intensity heat exposures. *Text Res J*, 57 (3): 123 - 132

Part 2 : Fire retardant technologies for specific applications

6 Nightwear

This section should be read in conjunction with Table 4-4 of Annex 4 – a matrix of fire retardant use in sleepwear.

6.1 Children nightwear

Children's nightwear fabrics generally include polyester and polyester/cotton or viscose blend, which meet current Ecolabel requirements. For adults, most commonly used fabrics are polyester/cotton blends, polyester, cotton, viscose, nylon, silk fibres and their blends. They are low flammability materials and generally assessed as low hazard, but there is limited choice of FR grades in each fibre type.

FR technology used:

For children nightwear in UK polyester fabric is usually used. 100% polyester (free of all impurities) can usually pass the BS 5722:1984 test if yarn and fabric structural characteristics are controlled and hence, no further fire retardant application is required.

Since there are no EU regulations and few in member states, it is likely that pure polyester, cotton, polyester/cotton are used in most of the European countries.

For the US market polyester will need further treatment, for which either polyester/polyester Trevira CS blend (some percentage of Trevira) is used. Trevira CS is produced by incorporating a **comonomeric** phosphinic acid unit into the PET polymeric chain, hence is an **inherently fire retardant** fibre.

Alternatively **phosphorus-based** durable **chemical finishes** of the cyclic ologomeric phosphonate type (eg, Antiblaze CU, Rhodia Specialities Ltd; Aflammit PE, Thor) is applied by pad- dry-cure method.

Polyester/cotton blends would require fire retardant treatment, for which **phosphorus and nitrogen based durable finishes** are applied. The most commonly used durable commercial finishes are : Tetrakis hydroxyl methyl phosphonium chloride-urea condensate (eg, Proban, Rhodia Specialities Ltd) and N-methylol dimethyl phosphonopropionamide (eg Pyrovatex, Huntsman, formerly Ciba).

6.2 Adult nightwear

In the UK most of the adult nightwear fabrics are made of polyester/cotton. According to the Nightwear (Safety) Regulation 1985, the adult nightwear do not need to pass the BS 5722:1984 test and must carry the safety label, 'KEEP AWAY FROM FIRE', no further treatment to the fabrics is done.

Where required, eg hospitals, etc, for cotton and cotton-rich polyester blend fabrics for nightwear, **phosphorus and nitrogen based durable finishes** are applied. The most commonly used durable commercial finishes are : Tetrakis hydroxyl methyl phosphonium chloride-urea condensate (eg, Proban, Rhodia Specialities Ltd) and N-methylol dimethyl phosphonopropionamide (eg Pyrovatex, Huntsman, formerly Ciba).

6.3 Future FR Technology Challenges for nightwear

For nightwear fabrics the current design challenges to eliminate FRs are:

- To minimise thermoplastic and melt drip effects and enhance char-promotion in synthetics
- To avoid finishes (including non-fire retardant finishes such as easy-care treatments) that may release formaldehyde, especially for children where skin sensitivity is greatest. Japan have minimum formaldehyde release requirements and phosphonopropionamide-based finishes are banned for use on children's nightwear in the USA because of their formaldehyde-releasing potential
- To use technologies having lower environmental impact in terms of reduced water and energy usage
- Certain additive compounds are excluded by risk phrase, but a significant choice of additives still remains.

Minimisation of thermoplasticity of synthetics

For polyester (and other synthetic fibres) rich fabrics, reducing their thermoplasticity is a big challenge. Although the fabric passes the BS5722:1984 test, the drips can inflict serious burns to wearer's skin. To that effect, the use of polymer layered silicate nanocomposites in combination with nominal amounts of phosphorus based fire retardants is a way forward. The phosphors based fire retardant could be a comonomer with layered silicates added by melt blending or in-situ polymerisation. Alternatively the clays can be added in the surface finish, by nanodispersing in one of the component of the finish.

Avoidance of formaldehyde releasing finishes

The formaldehyde factor reduces significantly the potential for conventional reactive finishes to be used in nightwear and the alternatives of 100% polyester remove this factor. Alternatively, the use of inherently fire resistant fibres such as Trevira CS polyester, Kaneka's Kanecaron modacrylic (Kaneka, Japan) and Lenzing's FR Viscose (Lenzing GmbH, Austria) offer alternatives if higher levels of fire retardance are required.

Technologies with lower environmental impact

Industry is very keen to replace the conventional water-based finishing process with the plasma process to add reactive fire retardant groups to the surface. Although much research is being done in this area, most of the efforts to date are on a laboratory scale and are not yet commercially exploited. One system that has been adopted by UK industry is the VECAP system promoted by the Bromine Science and Environment Forum (BSEF) which is designed primarily to minimise waste bromine-containing fire retardants used in back-coating formulations entering the waste effluent streams. While this system is best used by furnishing fabric manufacturers, it merits mention here to illustrate how textile processing plants have been able to respond to environmental concerns.[21]

---

[21] bsef.com and P Wakelyn, ' Environmentally friendly flame resistant textiles' in *Advances in Flame Retardant Materials,* Horrocks AR and Price D (editors), Woodhead Publishing, Cambridge, 2008, p185-212

With the plasma technology novel nanocoatings having the desired thermal shielding effects can also be achieved. Nanoparticles with homogeneous size can be embedded on textile substrates by plasma polymerization / etching process or by plasma polymerization / co-sputtering process. However, while such processes are low in use of water or solvents they do consume electrical energy. Whether this input is less than that saved by eliminating current drying process used in aqueous-based fire retarding processes remains to be seen should commercialisation occur.

7 Furniture and Furnishings

This section should be read in conjunction with Table 4-6 of Annex 4 – Matrix of fire retardant use in interior furnishings.

Upholstered furniture contains covering material, foam and a frame assembly and in the UK the test method BS 5852: 1979: Parts 1 and 2 and its subsequent editions and EN/ISO variant reflect this structure. As stated in the regulatory section, the test methodologies for furnishings in different risk categories are defined in BS7176:1995 (now 2007). For seats in transportation, sometimes other interior materials are used beneath the covering fabric for more comfort. The foam used for furniture is always fire retarded. In some cases so-called fire-blocker materials are used between the face fabric and the foam. Fire-blockers, made from inherently fire retardant fibres like oxidized acrylics and aramids, were first used for aircraft seats and now being increasingly used on trains, buses and coaches. In the US such fire-blockers may also comprise glass-cored yarns about which are wrapped with inherently fire resistant fibres. This reduces the overall costs of fabrics because of the relatively low costs of glass filament yarn components.

For bed mattresses covering materials or tickings are tested over a filling foam which is supported on a metal frame. For example, within the UK bedding is assessed for ignitability to cigarettes and small fires using test methods in BS EN ISO 12952-1/2/3/4:1999 and to specified performance standards in BS 7177:2008.

7.1 Covering fabrics

For foam-containing upholstered furniture (domestic and office) covering textile material is usually made of polypropylene, wool, polyester and cotton/polyester blends. All of these fibres being flammable, need fire retardant treatment to attain a satisfactorily low level of flammability and a low hazard assessment. The use of inherently FR materials tends to prohibitively expensive. Most often covering textile contains more than 2 fibres and often more than 4 different fibres. For example, a typical jacquard system will use polyester in the warps and polyester/cotton, polyester, polypropylene or acrylic may be used for design and cross coloured effects. It is very difficult to treat such fabrics as fire retardant treatment for one fibre type may not be effective on the other one, and in some cases might result in an antagonistic effect. Wool although considered inherently fire retardant, is only relatively less flammable (LOI = 25%, Table 1-1 of Appendix 1) than cotton (LOI = 18.4%), polyester (LOI = 21%), etc. Hence, to pass certain flammability tests, will require further FR treatment although fabrics having very high area densities (>600 gsm) may not require treatments for certain furnishing applications or if they do, require them at low concentrations.

In transport applications most of the passenger car interiors including car seats are made of polyester fibre (90% of the world market), and in some cases polypropylene fibre. The flammability testing of fabrics used in motor vehicles, in particular cars are not mandatory due to the fact that fire incidents in motor vehicles are rare and, moreover, fire spreads relatively slowly. Most manufacturers test seating covers and carpets conform to the US FMVSS (Federal Motor Vehicle Safety Standard) 302 test, which is a simple horizontal flame spread test. Other similar standards are German DIN 75 200, British, Australian BS AU

169 and Japanese JIS D 1201 automotive standards. Polyester and polypropylene fabrics used for car seats, pass these tests, hence no further treatment is required.

Furnishing fabrics used in railway seatings are tested in European countries as a complete assembly with UIC (Union Internationale des Chemins de. Fer.) 564.2. In the US, ASTM E 1537-98 and in the UK, ceiling lining materials are tested according to BS 476. Furnishing fabrics used in railway seatings are mainly 85% wool /15% nylon or polyester of FR grade (eg Trevira CS).

Seats for commercial aircraft need to conform to highest standards of fire safety. Flammability testing of all textile materials is regulated by the US Federal Aviation Administration (FAA) under Federal Aviation Regulations (FAR) and these latter extend to all commercial airliners operating across the world internationally. All textiles present in an aircraft have to pass the test requirements defined in FAR 25.853(b) in which a Bunsen burner flame impinges upon the bottom edge of a vertically oriented sample. For seats, the complete seat assembly is tested according to FAR 25.853 (Part II, Appendix F) in which the seat assembly is subjected to a kerosene burner of 120 kW/m^2 heat flux for 10 min. Commercial aircraft seat covers are usually made from wool (Zirpro-treated), wool/nylon blends or leather. Sometimes, fire-blockers may be included if required and allow the cover fabric to be less fire resistant.

7.2 FR technology where inherent fire retardant fibres are not used:

- For outer coverings, the most common method of fire retardation is by the technique of **back-coating** since this method enables the reverse side of any fabric to be treated in a manner that has minimal effect on the front face where aesthetic properties are the prime factors. Chemicals used for back-coatings are antimony-halogen (mostly bromine)-based, eg decabromodiphenylether (decaBDE) and antimony trioxide as synergist, and hexabromocyclododecane (HBCD) and antimony trioxide. These can be applied to any fibre/fabric types, including blends and because they are not chemically bonded to the fibre, they must be bonded **physically** using typically an acrylic, ethylene-vinyl acetate (EVA) or PVC based resin, this last having an inherent fire resistant property.

  The back-coating functions as a **barrier** layer, resisting ignition to sources impinging upon the front face of the fabric. Levels of application are typically in the range 25-30 wt% (dry weight) on fabric of which the fire retardants comprise about 60-70 wt%. Typically the brominated fire retardant: antimony oxide mass ratio is about 2:1 suggesting that total bromine fire retardant content is about 12-15 wt%. Since decaBDE and HBCD comprise high concentrations of brome (~80%) then this means that back-coated fabrics may comprise about 8-10wt% bromine itself.

  The advantage of the bromine-containing **back-coating** formulations is that they function on any fabric composition. The main challenge in replacing bromine-containing FRs lies in the reduced efficiencies of possible alternative non-halogen FRs coupled with their fibre specificity. For example phosphorus-based fire retardants work best on hydroxyl-containing fibre-forming polymers such as cellulose and hence cotton and viscose. Nevertheless, there are some halogen-free back-coating formulations available on the market, eg, MelaphosFR™ Dartex coatings, although at present these are few and far between.

- For polypropylene usually **halogenated** fire retardants (eg, tris(tribomoneopentyl) phosphate (FR 372, ICL) are used, introduced in the polymer by **melt blending,** prior to extrusion into fibres. These too have been traditionally used in the presence of antimony oxide as a synergist although more recently this has been replaced by the novel hindered amine stabiliser such as NOR116 (Ciba).

- For polyester fabrics cyclic oloigomeric phosphonate (eg, Antiblaze CU, Rhodia Specialities Ltd; Aflammit PE, Thor) is applied as a **chemical finish** by pad- dry-cure method.

- For cotton rich fabrics (>80% cotton) ammonium polyphosphate (APP) based products are used, which on curing can provide soak durable treatments.

- For cotton and cotton/polyester fabrics, durable **chemical finishe**s such as Pyrovatex (Huntsman, formerly Ciba) or Proban (Rhodia) are applied. These finishes are phosphorus and nitrogen based. While Pyrovatex is covalently bonded to cellulose structure, the Proban-type finish is a highly cross-linked three-dimensional polymer network, enclosing the fibrillar structures.

- Wool is invariably Zirpro-treated by an exhaustion method often simultaneous with the application of dye in the dyebath, where negatively charged complexes of zirconium or titanium are ionically bonded to positively charged wool fibres.

- For artificial leather eg, polyurethane based, inorganic fire retardants such as borates are used as additives. However PVC based artificial leather does not require fire retardant treatment for domestic furniture, but may require other fire retardant additives to pass BS5852 Crib 5 or 7 tests, depending upon specific end use.

7.3 Foams and filling materials

Foam used in UK domestic furniture needs to pass BS 5852, crib 5 test, hence needs to be fire retardant. CME (combustion modified ether) foam is becoming one of the prevalent forms of foam available for the furniture industry, replacing CMHR (combustion modified high resilient) foam. CMHR foams are still available but not in such large quantities as previously. Both foams are forms of combustion modified polyurethane foam. Apart from the inclusion of melamine, commonly used fire retardants introduced into the foam during manufacture include the chlorophosphates (see below), Combinations of these are selected depending on the density and resilience of the foam required plus of course the need to pass the required ignition resistance test.

Another type of foam, commonly used is graphite impregnated foam (GIF), which is inherently fire retardant. Latex is also commonly used.

FR technology used:

As stated, most of the fire retarded foams contain melamine and halogenated fire retardant, added during foam preparation. The halogenated fire retardants include tris(1-chloro-2-propyl) phosphate (TCPP) and tris (1,3-dichloropropyl 1-2) phosphate (TDCP). TCPP is widely used for furniture foams, TDCP use is largely (probably completely) restricted to automotive and industrial applications.

7.4 Fire-blockers and Interliners

Interliners between the foam and face fabric are designed to eliminate or reduce the use of FRs in foam are usually made of cotton because of their non-thermoplasticity, low cost and they are easily fire retarded. Like the covering fabrics they must withstand a water soak durability test and hence a degree of fire retardant durability is required. Polyesters may be used but because of their thermoplasticity and inability to protect an underlying unmodified foam when exposed to BS 5852:1982 Sources 0 or 1 in the UK for example, they are only used in contract furnishings where this demand is not required. Interliners for use in UK domestic furniture have to pass BS 5852, Crib 5 test as defined by S.I. 1324 Schedule 3. In the US, the use of inherently fire retardant fibre-containing fabrics is made although can be expensive.

FR technology used:

- For cotton Pyrovatex- or Proban-type durable finishes are applied. While these finishes are fully durable in home laundering terms, some semi-durable finishes such as ammonium polyphosphate can be rendered sufficiently durable to water soaking at 40^{o}C if heat cured following padding application. Examples of these and others are marketed by Rhodia, Thor, Clariant and Huntsman.

- For polyester, phosphorus-based cyclic oligomeric phosphonate (eg, Antiblaze CU, Rhodia Specialities Ltd; Aflammit PE, Thor) or chlorine based, TCPP chemical finish could be applied. This will however, not pass the BS 5852, Crib 5 test, hence cannot be used in UK domestic furniture.

- The loose fillings are usually enclosed with polyester fabric. The polyester is either Trevira CS or treated with above mentioned finishes. Trevira CS is produced by incorporating a comonomeric phosphinic acid unit into the PET polymeric chain, hence is an inherently fire retardant fibre.

- Interliners from inherently fire retardants fibres can further reduce the flammability of the product. In general if the covering material is made of > 75% natural fibres, it does not need to be fire retarded if the interliner made of **inherently fire retardant fibres**, which can pass Crib 5 test of BS5852:Part 2:1989, is used.

7.5 Bedding

Mostly polyester, cotton and polyester/cotton fabrics are used for bedding tickings and sheets although the latter are not fire retarded using chemical after treatments. Regulations do not currently demand that bedsheets are fire retarded because of possible patient sensitivities and allergies.

FR technology used:

- Most fire retardant bedsheets are from inherently fire retardant polyester fibre such as Trevira CS.

- For tickings similar fabrics and fire retardants to those for fire-blockers and interliners are used (see above).

7.6 Curtains and Drapes

Curtains and drapes usually involve cotton, wool, silk, acrylic, modacrylic and polyester fibres. Nylon or polyamides are not used because of their UV sensitivities.

- Wool and silk being less flammable than other natural fibres, are not usually fire retarded for this application

- For polyester inherently FR version, Trevira CS polyester is used.

- On cotton durable phosphorus and nitrogen based chemical finishes are applied.

- Modacrylics are used as inherently fire retardant acrylics and whilst often quite expensive, offer the highest levels of UV stability.

7.7 Floor coverings

Cotton, viscose, nylon, polypropylene, acrylic, polyester or wool are generally used in carpets as the face or pile fabric over Neoprene latex.

FR technology used:

Carpets are usually fire retarded by back-coating with antimony-halogen system supported within a latex resin. The addition of alumina trihydrate may be used to reduce bromine/antimony concentrations.

7.8 Tents and marquees

Tents, marquees etc use textile materials as single layer of fabrics, mostly cotton, cotton-synthetic blends etc. The two relevant British Standard test methods are BS 5576:1998 for camping tents and BS EN 14115:2002 for large tents and marquees.

FR technology used:

While for cotton durable phosphorus and nitrogen based chemical finishes**,** such as Proban or Pyrovatex type finishes can be applied, traditionally the use of chlorinated paraffin wax-based coatings have been used because they confer water repellency. Use of these is being phased out because of associated toxicological hazards. In some cases PVC-based coatings may be used to confer both fire and water resistance.

Light tentings are now being replaced by nylons which require no fire retarding because of their thermoplasticity which enables them to pass any required fire test.

7.9 Ecolabel and Green Procurement issues and Alternative FR Technology in Furnishings

The current challenges faced by industry are :

- To replace both bromine-containing fire retardants (Br-FRs) and antimony trioxide in back-coatings

- To improve FR performance if current technologies are marginal in effectiveness, eg improving the current low efficiencies of BrFR substitutes; improved FRs for foams in terms of improved FR and reduced volatility/mobility

- To adopt technologies having lower environmental impact in terms of reduced water and energy usage

- To minimise thermoplastic and melt drip effects

To achieve these challenges, the following alternatives are proposed:

- The use of volatile and possible vapour phase-active, phosphorus-based fire retardant components in back-coating formulations. At present, research has shown this to be a viable solution but currently no commercial example is available.

- For upholstered furniture and mattress covering material, if synthetic fibres are used, adding nanocomposites in the polymers can reduce their thermoplasticity and enhance char formation. Research has shown that polymer-layered silicate nanocomposites in combination with nominal amounts of phosphorus and halogen-based fire retardants can provide self-extinguishing character to the synthetic fibre. These components can be added in the polymer melt by blending under shear, prior to extrusion into fibres. However, commercial exploitation has yet to be realised.

- The conventional water-based finishes could be replaced by surface modification by plasma technology. The interest in this has increased with the recent development of atmospheric plasma machines for processing wide widths of fabrics although no current fire retardant successful example exists at the present time.

8 Televisions, Personal and Mobile Computers (including enclosures and printed circuit boards)

In this section we consider the common materials used in the construction of TV and computer enclosures and casings (also referred to mechanical plastics) and the composite materials used for printed circuits boards. These present the largest component fire loads in these products.

8.1 TV and Computer Enclosures Plastic Content

It is not possible to obtain a reliable UK, European or US picture of the detailed formulations and tonnage of materials currently used in new TV and computer enclosures. It is possible to gain a historic view from data available from waste streams which are now being collected as part of the Waste from Electrical and Electronic Equipment (WEEE) Directive (2002/96/EC) – this has recently been reviewed by Stevens and Goosey[22].

However, current market analysis carried out by SOFRES does provide some insights. This work is carried out on behalf of the Association of Plastics Manufacturers in Europe (APME), now Plastics Europe [23], has provided information which has been used by the EFRA[24] and the related European

---

[22] G C Stevens and M Goosey "Materials Issues in Electronics", Electronic Waste Management: Design, Analysis and Application *by Ronald E. Hester (Editor), Roy M. Harrison (Editor) Chapter 2*

[23] http://www.plasticseurope.org/

[24] http://www.cefic-efra.com/

Brominated Flame Retardants Industry Panel (EBFRIP)[25] and the more recent Phosphorus, Inorganic and Nitrogen Flame Retardants Association (PINFA)[26].

Figure 4 illustrates the plastics demand in electrical and electronic equipment in Western Eurooe in 2007. Out of these materials, those in most use in TV and computer enclosures include high impact polystyrene (HIPS typically in 70 to 80% of TVs and 25% computers), acrylonitrilebutadienestyrene (ABS typically 5 to 10 of TVs and 40% computers), polycarbonate (PC typically 1% of TVs and 4% of computers) PC/ABS blends (PC-ABS typically 30% of computers), polyphenyleneoxide and related blends (PPO typically 5 to 7% of TVs and 6 to 12% of computers).

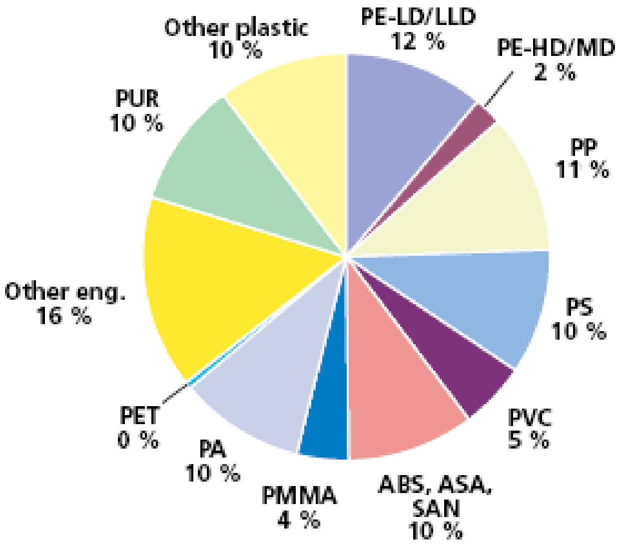


Figure 4 Plastics demand for electrical and electronics applications in Western Europe in 2007 (total of 2.1 million tonnes; source: PlasticsEurope)

PINFA estimate that 65% of all IT equipment and 55% of all consumer electronics are treated with FRs and this accounts for about 180,000 tonnes of FR treated plastics p.a. in Western Europe [27].

8.2 Overview

Traditionally, the materials used in PCBs and enclosures have been treated with chemical FR technologies to achieve fire safe products. As discussed in a recent review of materials in electronics [22] the most common historic and currently used FRs for enclosure materials include the following additive and reactive BFRs:

Tetrabromobisphenol A (TBBPA) – commonly used in PCBs as a reactive BFR

---

25 http://www.ebfrip.org/

26 http://www.pinfa.eu/

27 PINFA presentation to meetings in the European Parliament on the recasting of the ROHS directive, 23 March 2010

Hexabromocyclododecane (HBCD) – commonly used as additive BFR in engineering thermoplastics

Polybrominated diphenylethers (PBDE) – commonly used as an additive BFR in engineering thermoplastics – of these only deca-BDE has continued in common use.

In many cases the BFRs have been used in the presence of antimony trioxide (ATO) as a synergist.

However, under increasing pressure from consumer and environmental groups, consumer electronics companies have developed policies to phase out hazardous substances there is growing displacement of BFRs in the polymers used in electronic products.

Many electronic product OEMs believe that commercial alternatives to BFRs exist today and a number of companies have declared policies to reduce and remove the use of BFRs and bromine and chlorine containing compounds – a number of these are summarised in Table 1 below and some of the related public statements are shown in Appendix 6.

Table 1 Halogen-free commitments and timelines for various electronics OEMs based on the availability of suitable alternatives[28]

Halogen Specification	Br, Cl and their compounds	
OEM	***Specification***	***Timeline***
Nokia	Br < 900ppm, Cl <900ppm	All products by 2008
Sony-Ericsson	Br < 900ppm, Cl <900ppm Br+Cl <1500ppm	All new products by end of 2006
Lenovo		All products from 2009
Dell	Br < 900ppm, Cl <900ppm	All products from 2009
LG	Br < 900ppm, total halogen < 1500ppm	All products from 2010
Samsung		All mobile phone products from 2010
Toshiba		Begin 2009
Wistron	Br < 900ppm, Cl <900ppm Br+Cl <1500ppm	Begin 2008 3Q
Apple	Br < 900ppm, Cl <900ppm Br+Cl <1500ppm	All products by end of 2008
HP	Br < 900ppm	All new products from 2009

[28] Sourced from PINFA briefing on “Innovative Flame Retardants in E&E Application” – original source: Foxconn presentation and OEM announcements at Intel Halogen Free Symposium sponsored by IPC, 15 -16 January 2008

Intel	Not intentionally added	

8.3 More Recent Chemical FR Alternatives to BFRs

Most of the FR technology alternatives involve the adoption of alternative chemical FR systems many of which are based on organo-phosphorus FRs. BFR producers have also been developing new BFRs including polymeric BFRs to produce more contained and less labile FR systems for both additive and reactive chemical FR use. Examples of these include the following [29],[30]:

Poly (pentabromoacrylate) - for use in polybutylene terephthaltae (PBT) and polyamides

Brominated epoxy polymers - for use in styrenic copolymers and polycarbonate blends as well as in PBT and poplyamides

Brominated polystyrene – for use in PBT and polyamides

Tris (tribromophenoxy) triazine – for use styrenic copolymers and blends

Decabromodiphenylethane – as a replacement for deca-BDE in polycarbonate blends and with other FR blends in styrenic copolymers and blends

In the case of phosphorus based FRs the most common proposed for use in electronics include the aromatic phosphate esters for use with PC/ABS and PPE/HIPS blends [31]; examples include: triphenyl phosphate (TPP), resourciniol bis-(dipehnylphosphate) (RDP), bisphenol A bis-(diphenyl phosphate) (BDP) and resourcinol bis-(2,6-dixylenyl phosphate) (RDX). The same Pinfa source also mentions the potential use of the inorganic metal phosphinates in PC, PC/ABS and the sytrenics.

As discussed in the overview and as shown in Appendix 4, many electronics OEMs have adopted commitments to phase-out BFRs and other compounds including PVC. While in many cases the alternative technologies are satisfactory technically experience is still building on their long term performance. In the case of connectors and cables for electronic products options have been provide through the development of new halogen free polyamides and polyesters [32] .

8.4 Electronic Product Supply Chain Initiatives

Collective action across the supply chain to identify FR alternatives has been taken by HDP User Group International [33]. This group have completed 1 project and have 3 active projects related to halogen free materials technologies:

---

[29] R Borms et al, "Polymeric Flame Retardant Systems: A Step Forward to a Safer Environment, Proceedings of Flame Retardants 2006, p135- 142, Interscience Communications, London, February 2006.

[30] R Borms et al, "Implementation of Higher Fire Safety Requirements for European Televisions, Proceedings of Flame Retardants 2008, p135- 142, Interscience Communications, London, February 2008.

[31] Pinfa publication; "Innovative Flame Retardants in E&E Applications; 2nd Edition, June 2009, see www.pinfa.eu

[32] N Nimpuno et al; "Greening Consumer Electronics"; Chemsec publication, September 2009, http://cleanproduction.org/library/GreeningConsumerElectronics.pdf

[33] High Density User Group International (www.hdpug.org) was established as a not for profit organisation in 1994, it has a membership of around 30 companies including electronics OEMs and component manufacturers, materials

(i) Halogen-free Guideline – published

(ii) Haolgen-free Materials Database – definition stage

(iii) Halogen-free PCB Assembly – in progress

(iv) Halogen-free Assembly Reliability – in progress

In the discussion below on printed circuit boards and enclosure materials reference will be made to the HDPUG Halogen-free Guideline report [34]. This report was constructed with input from 25 member companies including several of those listed in Appendix 4 and others such as Tyco Electronics, Isola (PCB laminate producer) and chemical FR suppliers such as Albemarle, Clariant and ICl Industrial products.

The report covers alternative technologies for halogen laminate materials in PCB, the issues of processing Halogen free PCBs, chip CPU base materials, wire bond package and connector materials, cable base materials and so-called mechanical plastics such as those used in enclosures and casings and thermoplastic films. The transition to halogen free products and the issues that affect reliability are also addressed from an industry standpoint.

In addition to the structured work of the companies connected with HDPUG, the not for profit organisation Chemsec has been promoting non-bromine and non-chlorine containing materials in electronic products and have produced a variety of publications on green electronics [3231,35]. However, these reports appear not to adopt a rigorous approach to the collection and evaluation of information. Chemsec also produces the so-called SIN list (Substitute It Now list) along with a variety of green NGOs. The SIN List version 1.1 (updated in October 2009) consists of 356 chemicals that have been identified as Substances of Very High Concern where it is claimed that this has been done using criteria established by REACH – this list includes a small number of chemical FRs. The claimed purpose of this list is to lobby the legislative process and provide a tool that businesses and others can use to substitute hazardous chemicals with safer alternatives, ahead of legislation.

9 Alternative FR Technologies for Electronic Products

A variety of studies have considered potential alternative technology fire retardants with a view to replacing BFRs with more environmentally benign FRs but ones that are equally effective in protecting against fire. The focus below is on PCBs and enclosure materials.

---

and PCB laminate producers and chemical FR suppliers. HDPUG have completed some 60 projects which seek to reduce the costs and risks of utilising electronic packaging.

[34] HDPUG Halogen-free Guideline report, November 2008, available from HDP User Group International - www.hdpug.org

[35] Chemsec publication; "Electronics Without Brominated Flame Retardants and PVC – A Market Overview; May 2010; see http://www.chemsec.org/images/stories/publications/ChemSec_publications/

9.1 *Alternative PCB Materials*

PCBs are manufactured using copper clad glass fibre reinforced laminate materials in which the supporting insulator between the conductors is made from a reinforced polymer. For electronic products that require only a single layer of copper interconnection, the supporting dielectric material is often made from low cost materials such as paper-reinforced phenolic resins. While this type of laminate is widely used to produce large volumes of boards for consumer products such as televisions, there are also many applications such as PCs that require much more complex multilayer interconnect structures and better performance than these low cost materials can deliver.

Multilayer boards have traditionally been made from laminates based on epoxy resin chemistry and the most widely used material is known as FR4. FR4 is a glass fibre reinforced laminate that employs an epoxy resin system based on the diglycidyl ether of bisphenol A. FR4 laminates are also required to meet various fire retardancy performance standards (e.g. UL94-V0) and as such also contain appreciable quantities of brominated resins to impart the required degree of fire retardancy – the most common FR used for this is the reactive TBBPA.

Developments in new laminates for higher temperature non-lead based soldering require high thermal performance PCBs that now often need to be able to survive soldering temperatures that could be as high as 300°C. These new laminates may also offer improved fire performance but at higher cost than conventional FR4 laminates. Examples of these laminates include, amongst others, those based on polyimides, cyanate esters, allylated polyphenylene ethers, and the so-called BT-epoxy and tetrafunctional epoxy systems.

The properties of some example laminate types are shown in Table 2.

Table 2 Properties of some high performance laminates compared to FR4 taken from laminate manufacturer's literature

Laminate Material	Tg (°C)	Dielectric Constant (10 GHz)	Dissipation Factor (10 GHz)	Relative Price
Standard Tg epoxy	130-150	4.5	0.022	1
High Tg epoxy	170-180	4.4	0.02	1.15-1.25
Polyphenylene ether	175	3.4	0.009	3
Epoxy/Polyphenylene Oxide	180	3.9	0.013	1.7
Bismaleimidetriazine	180	4.1	0.013	2 to 3
Epoxy/Cyanate ester	210	3.6	0.014	
Cyanate Ester	240	3.8	0.009	2.5 to 4
Polyimide	280	4.3	0.02	2.8 to 4.5
Hydrocarbon/ceramic	>280	3.48	0.004	
Liquid Crystal Polymer	280	2.8	0.002	

9.2 *Alternative Chemical Fire Retardants in PCBs*

PCB laminates are required to meet flammability requirements such as those specified by the Underwriter's Laboratory in the UL94-V0 test. To meet this, the materials have traditionally been formulated with fire retardants. In the case of FR4 type epoxy resin based materials fire retardancy is achieved through the incorporation of brominated resins into the polymer matrix. By far the most widely used materials for this application are those based on tetra-bromobisphenol A based resins (TBBPA).

TBBPA reacts with the epoxy resin system so that it becomes covalently bound into the crosslinked polymer network. In this position the now chemically transformed FR is immobilised and only activated when the polymer matrix experiences thermal degradation at elevated temperatures. In recent years concerns about the impact of brominated chemical species on the environment and in particular their persistence in the environment have also cast doubt on TBBPA as a compound. While crosslinking of the epoxy matrix involves TBBPA transformation, this incorporation may not be complete and residual amounts of TBBPA monomer may remain as a labile fraction in the PCB. Small amounts (typically 17mg per kg of waste) of TBBPA have been shown to be released during the recycling of WEEE products and materials as shown in a detailed Swiss substance flow analysis of a recycling plant [36].

Brominated fire retardants were candidates for proscription in early iterations of the WEEE Directive, but the pertinent legislation for their management is now the RoHS Directive. At one point TBBPA based resins were specifically cited as a class of brominated fire-retardants that would be proscribed, but the legislation has evolved to become more specific and, at the time of writing, the FRs detailed for proscription belong to certain members of the non-reactive family of the PBDEs and the polybrominated biphenyls not reactive TBBPA. TBBPA is not specifically cited for proscription at this time, although the situation could change in the future if further studies of its impact reveal a problem.

The possibility that TBBPA type resins might also be banned and strategic pressure from consumer electronics companies to use non-brominated FRs (see Appendix 4) has prompted laminate manufacturers to develop alternative fire retardant systems. There are various approaches that have been adopted to provide viable bromine-free fire retardancy to laminates. These include the use of phosphorus, in various forms along with antimony trioxide, hydrated metal oxides and nitrogen containing organics. Hitachi has, for example, developed a laminate system based on the use of a new resin system containing a large quantity of nitrogen and a high inorganic filler content. In a recent review of current FR systems for epoxy resins[37] and phosphorus base FRs [38], Levchik and Weill drew attention to the introduction of reactive dihydrooxaphosphaphenanthrene oxide and various adducts and and hydroxyl-terminated oligomeric phosphorus-containing esters. A further approach is the modification of the epoxy resin by placement of aromatic groups between the glycidyloxyphenyl groups, and/or by use of a triazine-modified novolac crosslinking groups. These developments may also be supplemented with FR epoxy coatings which can make use of more conventioanl ammonium polyphosphate plus char-forming additives.

Phosphorus has been used in various forms to provide fire retardant properties to laminates. Phosphorus mainly works in the solid phase by producing char that stops the propagation of fire and in some cases its effectiveness is enhanced by the presence of nitrogen. Some phosphorus containing fire retardants also

---

[36] L S Morf et al, Brominated flame retardants is waste electrical and electronic equipment: substance flows in a recycling plant; Environmental Science and Technology Vol 39, No. 22, 2005, 8691- 8699.

[37] Edward D. Weil and Sergei Levchik; A Review of Current Flame Retardant Systems for Epoxy Resins; Journal of Fire Sciences, Jan 2004; vol. 22: pp. 25 - 40.

[38] Sergei V. Levchik and Edward D. Weil; A Review of Recent Progress in Phosphorus-based Flame Retardants; Journal of Fire Sciences, Sep 2006; vol. 24: pp. 345 - 364.

function in the vapour phase, where phosphorus free radicals are produced. Phosphorus, however is toxic when burnt and may create problems in processing. There have also been suggestions that free phosphorus can lead to the poisoning of plating baths used in electronics manufacturing, although specific references to this effect are elusive.

Phosphorus containing laminates may also be more sensitive to moisture absorption and thus there is the possibility of a laminate's electrical properties being degraded. Some laminate manufacturers claim to have overcome the issues associated with phosphorus by using new resins that have chemically bonded phosphorus (and sometimes nitrogen as well) in their polymer structures. The laminate manufacturer Isola has produced a base material similar to FR4 that is known as DURAVER. The resin matrix is based on a phosphorus-modified epoxy resin and conventional glass fabric is used for reinforcement. The material meets the requirements of UL94-V0 without the need for the addition of antimony compounds.

Whilst many of these alternatives may offer fire retardancy properties and better environmental performance it is noted that the alternatives may not have been critically assessed in their technical or from either an environmental or a human health and safety perspective. So, care must be exercised in the selection and assessment of alternatives. This point is stressed in the HDPUG report [34] and reinforced by the IPC - Association of Connecting Electronics Industries which represents the PCB and assembly manufacturers and has 2700 global members[39].

The HDPUG report identifies a number of issues related to so-called halogen free (HF) PCBs. While phosphorus based HF FR4 laminate is now widely available, it has less than 10% of the market and it is not suitable for substrate PCBs and there are concerns about its hygroscopic, the use of higher volumes which reduce the glass transition temperature and the problem of low copper adhesion. The processing of HF PCB laminates can also be problematic – see the HDPUG report for more details.

It is expected that the need to develop enhanced performance properties in laminates for non-lead soldering purposes may assist the development of enhanced fire performance laminates, some of which may be intrinsically fire retarded. There may also be new chemical strategies adopted that are viable technically and are shown to be environmentally safe.

9.3 FR Substitution in Enclosure Materials

The HDPUG report[34], the Pinfa review [31], the Danish EPA review of alternatives to decaBDE [40] and the Lowell study of alternatives [41] examined commercially available alternatives decaBDE and HBCD; all conclude that alternatives will most often have some disadvantages in comparison with the currently used BFRs. Collectively, they advocate that selection of alternatives for specific applications consider the following factors:

- Physical/chemical properties of alternatives during manufacturing.
- Physical/chemical properties of alternatives during use.

---

[39] http://www.ipc.org/default.aspx

[40] Carsten Lassen et al, Danish EPA report; "Deca-BDE and Alternatives in Electrical and Electronic Equipment"; Environmental Project No. 1141, 2006

[41] Lowell Institute – "Decabromodiphenylether: An Investigation of Non-Halogen Substitutes in Electronic Enclosure and Textile Applications", Lowell, 2005) – see also Appendix 3.

- Environmental and health risk of alternatives during manufacturing, use and disposal.
- Price of alternatives.
- Expenses of changes in tools and machinery.

In principle there will be alternatives to halogen-containing fire retardants for almost all applications - it depends on the costs and/or technical disadvantages the user is willing to accept.

The expenses of changes in tools and machinery may be a very significant restriction to the introduction of alternative plastic materials. If substitution can take place within the frame of the periodical renewal of machinery, the extra expenses will often be very limited. The Danish EPA study further considered that substitution of brominated fire retardants can then take place at three levels:

- The brominated fire retardant can be replaced by another fire retardant without changing the base-polymer.
- The plastic material, consisting of the base polymer with fire retardants and other additives, can be replaced by another plastic material.
- The product can be replaced by a different product, or the function can be fulfilled by the use of a totally different solution.

An example of the latter can be a solution where a reduction of the risk of fire spread in electronics is achieved by a metal sheet covering the plastic in contacts with current-carrying parts.

In Denmark as in the UK fire safety standards for consumer products do not set up material specific requirements. The object of the tests is the fire performance of the whole product and may be based on tests such as limiting oxygen index and the UL94 flammability rating. There is no simple relation between UL94 rating and oxygen index, but the oxygen index gives a broad indication of the flammability performance of the material.

Oxygen indexes (OI) of a number of base polymers and V-0 grade plastics based on the same polymers are discussed further in Appendix 3 and shown in Table 3-1.

10 US EPA Design for the Environment Programme – Cleaner Technology Substitutes Assessment

Under the EPAs Design for the Environment (DfE) Programme [42] which was established in 1991, the Cleaner Technology Substitutes Assessment (CTSA) [43] activity has specifically targeted industry sector partnerships to address issues related to reducing the risk to people and the environment by preventing pollution. It seeks to provide methodologies to anyone who can benefit from the increased efficiency and reduced environmental risk that results from using a cleaner product, process, or technology. It presents sources of data, analytical models, and previously published guidance that can be used in a CTSA.

The DfE program has three goals:

---

[42] http://www.epa.gov/dfe/pubs/
[43] http://www.epa.gov/dfe/pubs/tools/ctsa/index.htm

- Encourage voluntary reduction of the use of specific hazardous chemicals by businesses, governments, and other organizations through actual design or redesign of products, processes, and technical and management systems.

- Change the way businesses, governments, and other organizations view and manage for environmental protection by demonstrating the benefits of incorporating environmental considerations into the up-front design and redesign of products, processes, and technical and management systems.

- Develop effective voluntary partnerships with businesses, labour organizations, government agencies, and environmental/community groups to implement DfE projects and other pollution prevention activities.

The CTSA methodology is a means of systematically evaluating the comparative human health and environmental risk, competitiveness (e.g., performance, cost, etc.) and resource conservation of traditional and alternative chemicals' manufacturing methods and technologies.

Part of the CTSA strategy is “Building Partnerships for Environmental Improvement (EPA, 1995a) which, works through voluntary partnerships with industry, professional organizations, state and local governments, other federal agencies, and the public, including environmental and community groups.

Two activities in CTSA are relevant to this report:

1. Furniture Flame Retardant Partnership

2. Assessment of fire retardants in printed wiring boards

10.1 Furniture Flame Retardancy Partnership

The US EPA Furniture Flame Retardancy Partnership is a multi-stakeholder effort to investigate and disseminate information on alternative fire-retardant technologies for achieving furniture fire safety standards. Partners include the American Fire Safety Council (AFSC), the American Home Furnishings Alliance (AHFA), the Business and Institutional Furniture Manufacturers Association (BIFMA), the Consumer Product Safety Commission (CPSC), GreenBlue Institute (GreenBlue), and EPA’s Design for the Environment (DfE) Program.

As penta-BDE was voluntarily phased out in the US at the end of 2004, it was important to find environmentally preferable ways to achieve fire safety. The first product of the partnership was the report: “Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam”. It evaluates some leading chemical alternatives to pentaBDE for fire retarding low-density foam and it includes some commentary on other FR technologies, such as barriers or fabric backcoatings, which may be used in the future to meet a planned CPSC national flammability standard for residential upholstered furniture.

Some leading US FR chemical manufacturers identified 14 chemical FR formulations that are potentially viable substitutes for large-scale production of low-density flexible polyurethane foam. The FR substitutes are primarily additive FRs with some components which are reactive types and are shown in Table 3.

Table 3 Potential FR Chemical Formulations Substituting for Penta-BDE in Flexible Foam

Albemarle Corporation	
SAYTEX® RX-8500	proprietary D reactive BFR with proprietary B Aryl phosphate and triphenyl phosphate
SAYTEX® RZ-243	proprietary E tetrabromophthalate diol diester (*probably reactive)* with triphenyl phosphate
ANTIBLAZE® 180 and 195	Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)
ANTIBLAZE® 182 and 205	Proprietary A chloroalkyl phosphate with proprietary B aryl phosphate and triphenyl phosphate,
ANTIBLAZE® V-500	Proprietary C chloroalkyl phosphate with proprietary B aryl phosphate and triphenyl phosphate,
Ameribrom, Inc. / Supresta (ICL Industrial Products)	
FR 513	Tribromoneopentyl alcohol (*probably reactive*)
AB053	Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)
AC003	Proprietary I organic phosphate ester with triphenyl phosphate
AC073	Triphenyl phosphate with proprietary J, K and L aryl phosphates
Fyrol® FR-2	Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)
Great Lakes Chemical Corporation	
Firemaster® 550	Proprietary F halogenated aryl ester with proprietary G triaryl phosphate isaopropylated, triphenyl phosphate and proprietary H halogenated aryl ester
Firemaster® 552	Proprietary F halogenated aryl ester with proprietary G triaryl phosphate isaopropylated, triphenyl phosphate and proprietary H halogenated aryl ester

It is clear from Table 3 that some of the FR alternatives to penta-BDE are themselves brominated and many are organophosphorous FRs some of which are chlorinated; many are also complex mixtures. It is interesting that only five of these 14 FRs contained no “high hazard concern” scores – these were Antiblaze 180 and 195, FR513, AB053 and Fyrol FR-2 all of which contain halogens. None of the FRs had a scoring of “low hazard concern” for all of the hazard metrics chosen.

The US EPA assessed the hazards, potential exposures and tendency to bioaccumulate and persist in the environment for the chemicals in each formulation. EPA presented hazard concern levels for key toxicological and environmental endpoints based on experimental data where available, or estimated data. EPA also provided information on potential routes of exposure, based on physical and chemical properties.

The screening-level hazard and exposure information is presented in the report at three levels in an effort to meet the needs of a range of audiences and maximize transparency:

- A table showing a qualitative summary of each formulation that assigns a high, moderate, or low hazard concern level for each chemical according to the key human health and environmental endpoints.

- Quantitative summaries of the toxicity and exposure data from publicly available literature, EPA's confidential databases, chemical companies, EPA's New Chemicals Program, as well as the professional judgment of EPA staff.

- Detailed hazard data reviews with a summary of the availability and adequacy of data and a full data review by endpoint. References are included for chemicals that are not proprietary.

Despite the hazard review, the report did not attempt to rank the proposed FR formulations. The Partnership agreed that no single alternative is expected to provide an ideal solution to address every situation. While not providing full risk assessments or hazard ranking, the report provides screening-level information on the hazards of concern and potential routes of exposure associated with chemical components of fire-retardant formulations. It is noted however, that the fire retardants evaluated in the report, do not appear to be persistence or bioaccumulative in the environment.

10.1.1 Barrier Technologies

Barrier technologies have already been discussed in this report, but they are mentioned here as they form part of the alternative technology group that the US EPA Furniture FR Partnership examined. This group recognise that some furniture designs exclude the use of filling materials, and even fabric altogether. Design therefore, should be considered when evaluating alternative means for achieving fire retardancy in furniture.

Fire-retardant barrier materials or so-called "fire-blockers" can be a primary defence in protecting padding for furniture and mattresses. Manufacturers can layer barrier materials to improve the fire retardancy of their products. Multi-layering allows a product to maintain its fire resistance even if one layer is compromised.

There are many types of barrier materials available. Fabrics composed of natural fibers such as cotton that are chemically treated to make them fire retardant are fire-retardant barrier materials. The hazards of these chemical treatments have not been assessed in this report. Fabrics composed of synthetic fibers that are inherently fire retardant are also fire-retardant barrier materials. Plastic films derived from fire-retardant resins are also fire-retardant barrier materials. These materials are designed and manufactured to meet specific flammability standards. This also explains the large number of fire-retardant barrier materials that are available. Fire-retardant barrier materials can be characterized by cost, resulting in three primary groups.

The first group of fire-retardant materials is the chemically treated, primarily boric acid treated [44], cotton-based materials. These materials are the least expensive fire-retardant barrier materials available. Mattress manufacturers that base their material decisions predominantly on cost prefer these fire retardants.

The second group of fire-retardant materials is a blend of inexpensive natural fibers and expensive synthetic fibers. Synthetic fibers used in these blends include VISIL, Basofil, Polybenzimidazole,

[44] In Europe boric acid is a candidate by the Coordinated Chemical Risk Management Programme for classification as a Substance of Very High Concern (SVHC) – it is also water soluble and therefore non-durable.

KEVLAR, NOMEX and fiberglass. Smaller manufacturers of furniture and mattresses in niche markets use these materials. These blends are commonly used in bus and airplane seating.

The third group of fire-retardant materials is composed solely of expensive, high-performance synthetic fibers. They are generally used in industrial or high-performance applications such as firemen's coats and astronaut space suits.

One unique group of barrier materials is fire-retardant films. The films do not have the strength or texture to be used as an external barrier. The film can be used to wrap the foam cushions or it can be quilted with fire-retardant fabrics for added support and an extra layer of fire protection. Neoprene film is a common fire-retardant film. One type of material that competes with neoprene film is fiberglass fabric.

10.1.2 Graphite Impregnated Foams

Graphite impregnated foam (GIF) can be considered an "inherently fire-resistant foam" that is self-extinguishing and highly resistant to combustion. It is largely used in niche markets such as for general aircraft seating. GIF technology produces foam that can meet airline fire safety standards for the seats with a reduced dependency on fire-retarded fabric. By minimizing the expense associated with fire-retardant fabric, GIF modified foams can be priced competitively.

GIF technology reportedly allows the design and fabrication of complex, comfortable and aesthetically pleasing seating for private aircraft. While GIF foam seating promises the possibility of eliminating the need for barrier fabrics, there are tradeoffs. When the barrier is removed, comprehensive composite flammability testing will be required on each new seat design to meet current fire safety standards (Federal Airways Regulation Part 25 Appendix F).

10.1.3 Surface Treatments

Surface treatments are also used in some applications and niche markets and may be appropriate for some textile manufacturing and furniture manufacturing readers of this document. However, surface treatments may not be viable as industry-wide replacements for pentaBDE for use in low-density foam for the following reasons:

There have been many proposals to achieve good resistance to ignition by post impregnation of foam with a variety of additives including borates, phosphates, various ammonium salts, etc. In addition to durability concerns (many surface treatments wash off or degrade over time), there are other considerations that limit their use.

The main concern is difficulty in achieving uniform impregnation of a foam cushion, which may be 5 or 6 inches thick. In addition, many of these systems are water-based and the impregnated pieces then have to be dried, which is a slow and expensive process. The drying process also tends to produce a thin crust of the additive on the surface of the flexible polyurethane foam cushion. A variation of this approach has been to surface treat the finished upholstered cushion. This process must occur at the furniture assembly plants, which are not typically equipped for chemical processing. Some surface treatments can also leave an undesirable coating on the fabric cover or the cushion that is subject to disruption by friction during use.

10.2 Fire Retardants in Printed Wiring Boards Partnership

This partnership appears to be a recent addition CTSA programme and there is no information available on the EPA DfE website about its activities. However it has been referenced by Albermarle in a recent conference talk that mentioned that work is in progress (Susan Landry, September 2009 – see http://www.bfrl.nist.gov/info/conf/fireretardants/2-Landry.pdf).

It is useful to know that there is also a Wire and Cable Partnership that also appears to be considering fire retardants issues – but no information is available on their FR activities.

10.3 Lowell Centre for Sustainable Production Substitutes Programme – a summary

The Lowell Centre has been involved in an alternatives assessment approach that seeks to focus on solutions rather than the problem, and in stimulating innovation and prevention, in an effort to reducing several risks simultaneously. Within the programme they have devised an Alternatives Assessment framework for more rapid assessment of potential viable alternatives – however, it appears this was not reported until after the FR report cited below.

In 2005 the Lowell Center published a report on "Decabromodiphenylether: An Investigation of Non-Halogen Substitutes in Electronic Enclosure and Textile Applications" and in 2006 another report on "An Overview of Alternatives to Tetrabromobisphenol A (TBBPA) and Hexabromocyclododecane (HBCD)" and it considered application needs in textiles and electronic product enclosures.

These studies are reviewed in discussed in Appendix 5; the essential findings for deca-BDE are:

The report concluded that "based on an in-depth review of the literature for these applications and interviews with experts from industry, it appears that there are many non-halogenated alternatives to decaBDE available on the market today".

The report commented that its conclusions are based on the availability of substitutes and do not include an evaluation of their potential human health and environmental risks. Neither did the report provide evidence of equivalent fire performance being achieved. So care is required in accepting some of the conclusions reached in this work.

In contrast, in regard to TBBPA and HBCD the Lowell report concluded:

- For many of the potential FR alternatives, the existing health and environmental data may be more limited than for either TBBPA or HBCD. These data gaps should be identified and carefully considered before recommending specific alternatives. Sufficient care should be taken to ensure that the substitutes are less hazardous than the chemicals they are replacing.

- In this study a nominal review was carried out of pertinent standards associated with the various uses of TBBPA and HBCD. To better understand the fire retardance requirements for products using HBCD and TBBPA, a more thorough review of the pertinent regulations and standards that apply to electronics and building insulation products regionally, nationally, and globally could be conducted.

- Further research of TBBPA and HBCD alternatives could include a more detailed comparison of fire retardancy requirements as well as other key performance requirements for the various uses of TBBPA and HBCD. The alternatives could then be evaluated and compared as to how well they meet the various performance requirements for each use. It should be noted that TBBPA is used in some mission critical PWB applications such as military, aerospace, medical equipment, and telecommunications. Sufficient reliability data should be obtained for alternatives before their use is recommended.

- A comparison could be conducted of costs associated with using TBBPA and HBCD versus costs for using alternatives. The commercial availability of the alternatives could also be determined. This comparison was outside the scope of this study.

- Additional factors that may be investigated for the potential alternatives including the raw materials and manufacturing processes used to make the chemical/material, as well as the recyclability of the material at product end of life.

It is clear from these conclusions that the there is a need for greater scrutiny of proposals either calling for substitution or promoting such in the belief that alternatives are better. It is necessary to ensure that candidate substitute technologies, be they chemical or physical, are capable of meeting all relevant and important criteria to ensure the materials/component/products are fit for purpose and capable of meeting both application needs and fire performance requirements.

It is apparent that experience needs to be developed in this area and in a way that satisfies Design for Environment (DfE) principles, which in turn requires that for life cycle performance both environmental and economic impact assessment are applied.

11 In Summary

There are many potential alternative technologies and substitution options available for a number of the leading chemical FRs that are in current use and which have been, or are being, considered for ban or voluntary removal in Europe.

While some of these alternatives have been well researched and are fit for purpose, there are many that have not been adequately assessed technically for their long term performance or for their potential impact on exposure to humans and the environment through rigorous risk assessment despite being chemically classified.

This is particularly the case for alternative chemical FR technologies for printed circuit boards where the manufacturing demands are stringent and the industry experience of moving to new lead free solder is relatively new.

There are also a number of emerging FR technologies that are at the research stage and cannot currently be offered commercially.

It is clear from the current debate on the potential removal of bromine and chlorine containing compounds from some consumer products that sound technical and scientific information must be considered in parallel with cautious application of the precautionary principle,

There is a need for greater scrutiny of proposals for substitution and replacement of certain chemical FRs in the belief that better alternatives exist. It is necessary to ensure that candidate substitute technologies are proven, be they chemical or physical. These must be shown to be capable of meeting all relevant and important criteria to ensure the materials/component/products that use them are fit for purpose and capable of meeting Ecolabel criteria and product manufacturing and lifetime requirements including fire performance.

Appendix 1 Flammability of polymers

Bulk polymers

The burning behaviour of bulk polymers and fibres depends upon their physical and chemical properties. The burning of polymer/fibre is essentially a three phase process - heating, thermo-pyrolytic decomposition and finally ignition. The behaviour of a polymer during the initial or primary heating phase depends to a considerable extent upon the nature of its composition. FR strategies for bulk polymers include the production of chemical FR moieties in the gas phase which act to retard the development of the flame by interfering with radical chain branching reactions or by diluting of the flame with water or inert gases. FRs may also operate by heat absorption in the bulk polymer and the reduction of fuel supply from the bulk to the gas phase by encouraging carbon (char) formation. Intumescence promoters may also be used to produce carbon barrier layers at surfaces which act as physical and thermal barriers to insulate the bulk polymer from external heat sources.

The burning behaviour of bulk polymers and the detailed mechanisms of fire retardancy are well described in the literature[45] and are not repeated here. Some of the more recent developments in new approaches to fire retardancy are also considered in the literature [46]. The uninformed reader is encouraged to consult these sources. Greater attention is paid here to the general burning behaviour of fibres and textiles which has much in common with bulk polymers but also has distinctive behaviour peculiar to the materials and their geometry. The following review of fibre behaviour may be generalised to bulk polymers.

Polymer fibres

Thermoplastic fibres, because of their linear molecular chains, will generally melt in the temperature range of 100 - 250 ^{o}C and start to flow. Further pyrolysis and ignition is prevented, in some cases, because they move away from ignition source as a result of loss of rigidity. Natural fibres like cellulose, wool, silk on the other hand remain unchanged during this stage. Their three-dimensional cross-linked molecular structure prevents softening or melting and decomposition or pyrolysis occurs between 250 - 500 ^{o}C, depending upon the chemical composition of the fibre.

Pyrolysis or decomposition involves unzipping of the polymer chains to yield flammable monomers or the random elimination of small chemical fragments. Both types of products can sustain gas phase fire reactions. The flammable gases formed by pyrolysis mix with atmospheric oxygen, reach the lower flash point limit and are either ignited by an external flame, or if the temperature is sufficiently high, they self ignite. In some cases however, recombination of some of the decomposition chemical fragments may also occur in the solid phase and lead to the formation of an aromatic condensed ring system, called char which is stable under the pyrolytic conditions.

The major difference between fibres and bulk polymers is the small thickness of individual fibres, typically 15-30 μm in diameter, which yield yarns of 50-100 μm diameter and fabrics with thicknesses that vary from as low as 100 μm to several mm. The temperature gradient through the thickness of a fibre

---

[45] See for example: Fire Retardant Materials; Editors A R Horrocks and D Price, Woodhead Publishing, 2001; Proceedings of the annual and bi-annual conferences on Fire and Materials, Interflam and Flame Retardants organized by Interscience Communications;

[46] Fire Retardancy of Polymers: New Strategies and Mechanisms; T Richard Hull (Editor), Baljinder K Kandola (Editor); ISBN: 978-0-85404-149-7; RSC Publishings, 2008.

is very low, due to very high fibre surface-to-mass ratios, hence the reactions mentioned above occur very rapidly, leading to easy ignition. Melting, pyrolysis and combustion temperatures and flammability behaviour of different fibre types taken from literature are given in Table 1-1.[47,48,49] Also given are the limiting oxygen index (LOI) values, which are measures of the burning character of a material and expressed as percentage. Wool and silk have much higher ignition temperature and LOI values than cotton and hence are less flammable, but they are not inherently fire retardant. Synthetic fibres such as polypropylene, nylon, polyester are flammable. Aramid, oxidised acrylic, modacrylic and polyvinyl chloride fibres are inherently fire retardant. Aramid, oxidised acrylic and modacrylics because of their chemical structures on exposure to heat/fire char rather than burn. In polyvinyl chloride fibres, presence of chlorine imparts fire retardant character to the polymer.

In contrast to bulk polymers and fibres, the burning behaviour of fabrics depends upon many factors such as fibre type or fibre blend ratio, fabric area density, fabric structure (woven, knitted or non-woven, open structure or closely woven etc), finishes, garment design, point of ignition and the intensity of ignition source, orientation of fabric (vertical or horizontal) etc. Due to their thermally thin character and the open structure of textiles it is easy for air to circulate between the burning fibres. In the case of thermoplastics, some fabrics may shrink in one or more directions, curl, and hence, change geometry. Melting occurs in thermoplastics or blends with a high ratio of thermoplastic fibres, giving rise to often flaming molten drips.

From a "burning hazard" point of view, the important parameters are time-to-ignition, rate of flame spread and rate of heat release. These parameters for selective fabrics, most commonly used as apparels are given in Table 1-2[48]. Although the LOI values given in Table 1-1 are different for different fibre types, all fabrics ignite within 1- 3 s, when studied by the BS 5438 Test 1, indicating that all these fabrics are flammable to a certain extent. Flame spread results under different orientations show that the fire hazard is at a maximum when the fabrics are free hanging in the vertical direction. Light cotton as expected has the highest rate of flame spread. Acrylic has a much lower flame spread rate than other fabrics, but the highest peak and total heat release rate amongst all fabrics.

These results show that the flame spread rate is inversely proportional to the fabric area density. A similar conclusion that ' for a particular fibre type, the heavier the fabric the better it behaves in a fire' could also be drawn from a recent study by Hirschler et al[50], where they conducted a flammability study of 50 fabrics with different fibre types and different area densities using the NFPA 701 small-scale test.[51]

---

[47] Bajaj, P. 2000. Heat and Flame Protection, In *Handbook of Technical Textiles*, ed. Horrocks, A. R. and Anand, S. C., Woodhead Publishing Ltd., Cambridge, England, pp. 223-263.

[48] Horrocks, A. R. 2001. Textiles. In *Fire Retardant Materials*, ed. Horrocks, A. R. and Price, D., Woodhead Publishing Ltd./CRC, pp. 128-181.

[49] Kandola, B.K. Flame Retardancy Design for Textiles. Chapter 24. In *Fire Retardancy of Polymeric Materials*, Second Edition, Ed. A.B.Morgan and C.A.Wilkie, CRC Press, in press 2009.

[50] Hirschler, M.M., and Piansay, T. 2007. Survey of small – scale flame spread results of modern fabrics. *Fire Mater.*, 31 (6): 373 - 386.

[51] Davis, S., and Villa, K.M. 1989. Development of a Multiple Layer Test Procedure for Inclusion in NFPA 701: Initial Experiments, NISTIR 89-4138. National Institute of Standards and Technology: Gaithersburg, MD, August 1989.

Table 1-1 Thermal and flammability properties of some commonly used [46,47,48]

Fiber	Melting Temp (°C)	Pyrolysis Temp (°C)	Ignition Temp (°C)	LOI (%)
Natural fibres				
Cotton	-	350	350	18.4
Wool	-	245	600	25
Silk	-	320	600	23
Synthetic – thermoplastic				
Nylon 6	215	431	450	20 - 21.5
Nylon 6,6	265	403	530	20 - 21
Polyester	255	420 - 477	480	20 - 21.5
Polypropylene	165	469	550	18/6
Poly vinyl chloride	>180	>180	450	37 - 39
Synthetic – char formers				
Viscose	-	350	420	18.9
Acrylic	>320	290	>250	18.2
Modacrylic	>240	273	690	29 - 30
High performance fibres				
Meta-aramid (eg Nomex)	375	310	500	28.5 - 30
Para-aramid (eg Kevlar)	560	590	>550	29
Oxidized acrylic	-	>640	-	55
Polybenzylimidazole (PBI)	-	>500	>500	40 - 42
Polytetrafluorethylene (PTFE)	>327	400	560	95

Table 1-2 Ignition, flame spread and heat release properties of some commonly used fabrics as apparel' [48]

Fabric	**Ignition time using BS 5438, Test 1 (s)**		**Auto ignition**		**Flame spread rate using modified BS 5438 Test 3 (m/s)**			**Cone results at 35kW/m² heat flux**		
	Face Ign	Edge Ign	Ign. Temp (°C)	Ign time (s)	Vertical	45° angle	Horizontal	TTI (s)	PHRR (kW/m²)	THR (MJ/m²)

Light-weight cotton (87 g/m^2)	2	1	480	16	57	37	6	9	94	1.0
Heavy-weight cotton (180 g/m^2)	4	1	480	35	27	18	3	14	128	3.2
Polyester: cotton (65:35, 105 g/m^2)	2	1	574	20	37	24	9	10	154	1.9
Acrylic (118 g/m^2)	*		-	-	23	13	6	17	292	4.5
Light-weight silk (71 g/m^2)	2	2	909	3	***	***	***	***	***	***
Heavy-weight silk (174 g/m^2)	**	3	655	4	***	***	***	28	45	1.0
Wool (173 g/m^2)	3	3	746	3	23	12	14	16	171	2.9

* Flames extinguished when the flame was moved away
** Fabric melted away from the flame.
*** Test not performed.

Appendix 2 Fire retardant strategies for textiles

Fire retardant finishes

Most of the treatments and formulations were developed in the period 1950-1970 and, in terms of new chemistry, nothing much has changed since then. Finishes are usually applied by the "pad-dry method", where fabric is passed through the chemical formulation (mostly in aqueous form), then through rollers to squeeze out the excess and finally dried in an oven at 120 ^{O}C. This gives a non-durable finish. To get a semi-durable or durable finish, fabric is passed through another oven set at a higher temperature (usually 160 ^{O}C), where a curing stage allows a degree of interaction between the finish and the fibre. In some cases, the curing stage might also involve chemical treatment, the best example is the Proban process, which requires an ammonia gas curing process in order to polymerize the applied finish into the internal fibre voids. Finishes are generally applied to fabrics from natural fibre types, although there are some available commercially for synthetic fibres as well. Some generic types of finishes are discussed below, the details of which can be found elsewhere. [48,52,53]

Cotton: Ammonium phosphates like mono- or diammonium phosphates are most commonly used for non-durable treatments. Ammonium polyphosphates are used in combination with urea to provide semi-durable finishes and by curing at 160^{o}C, when some phosphorylation can occur. Semi-durable finishes are very useful for materials that may not need frequent washings, e.g., mattresses, drapes, upholstery, carpets, etc. Some commercial examples of semi-durable finishes include, Flammentin® FMB (Thor Specialities), Pyrovatim® PBS (Ciba, now marketed by Huntsman).[58]

Amongst the commercially successful durable finishes, one type is based on N- methylol dialkyl phosphonopropionamides, from which the well known product, Pyrovatex CP (Ciba) is derived. Pyrovatex CP (N-methylol dimethyl phosphonopropionamide) is applied with a methylolated melamine resin in the presence of phosphoric acid, which catalyses the formation of pyrovatex-resin-cellulose moeities via the C(6) OH group. Another commercial product based on similar chemistry is Thor's Aflammit® KWB.

Another most successful durable treatment is based on tetrakis (hydroxymethyl) phosphonium derivatives. Very well known brand marketed as Proban CC (Rhodia, previously Albright & Wilson) involves padding of tetrakis (hydroxymethyl) phosphonium chloride (THPC) urea solution onto the cotton fabric, curing with ammonia in a specially designed reactor to generate a highly cross-linked three-dimensional polymer network. The fabric is then treated with hydrogen peroxide which converts P^{3+} to the P^{5+} state. Another similar commercial product is Thor's Aflammit® P. Many combinations of tetrakis (hydroxymethyl) phosphonium derivatives with other salts have been reported in the literature, but the most successful so far has been the THPC-urea-NH_3 system discussed above.

Pyrovatex CP type treatments have more dye affinity, and hence, are used for curtains, apparels (nightwear), etc, whereas Proban CC, which retains greater strength, is used for hospital bed sheets, military applications, hotels, nursing homes etc. Some other durable treatments for cotton include Akzo Nobel's Fyrol® 51, now called Fyroltex® HP, Firestop's Noflan® (a phosphorus-chlorine based product).[58]

---

[52] Bourbigot, S. 2008. Flame retardancy of textiles: new approaches. Chapter 2 in *Advances in Fire Retardant Materials,* ed. Horrocks A.R. and Price, D. Woodhead Publishing Ltd, Cambridge, England, pp 9 – 40.

[53] Weil, E.D. and Levchik S. 2008. Flame retardants in commercial use or development for textiles. *J.Fire Science,* 26: 243 - 281.

Polyester : Tris(2,3-dibromopropyl) phosphate was the successful finish developed in 1970s for polyester fabrics, but was withdrawn from the market after a short time due to being carcinogenic. Since then, the major product used in the thermosol dyeing treatment of polyester fabric has been Rhodia's Antiblaze® 19 now Amgard CU, or Special Materials' SMC 688.**Error! Bookmark not defined.** Some other commercial products include Thor's Afflamit® PE, Zschimmer & Scharz Mohsdorf's (Germany) Flammex® DS and Chemtura's CD-75PM® (hexabromocyclododecane).[58]

Cotton-polyester blends*:* For fibre blends, finishes which are successful on one type of fibre, may prove to have antagonistic effects on other blends.[3] The general rule is to apply the finish appropriately to the majority fibre present or apply halogen-based coatings (see section below). Most non-durable finishes for cotton will function on cotton-rich blends with polyester, but not for the polyester rich blend unless some bromine is present.[47] Durable treatments such as Proban and Pyrovatex type finishes can be applied on higher cotton content fabrics, eg, 80:20 cotton/polyester.

Wool: Ammonium phosphates and polyphosphate, boric acid-borax, ammonium bromide can be successfully used in non-durable fire retardant finishes for wool. The most successful durable treatment for wool is Zirpro®, developed by Benisek, which involves exhaustion of negatively charged complexes of zirconium or titanium onto positively charged wool fibres under acidic conditions at 60°C. The treatment can be applied to wool at any processing stage from loose fibre to fabric using exhaustion techniques.

Silk : Silk although it is not very flammable (LOI 23%), needs fire retardant treatment for certain applications, eg nightwear garments, curtains, interior decoration of executive jet aeroplanes, etc. Non-durable finishes containing a mixture of borax and boric acid,[54] inorganic salts and quaternary ammonium salts, urea - phosphoric acid salt[55] have been reported to be effective on silk. Semi-durable finishes like organophosphorus fire retardant and trimethylolmelamine (TMM) 99], Pyrovatex CP (Ciba)[60] are also reported to be effective on silk.

Coatings

Fire retardant coatings can be applied on the surface of the fabric (including on the back) to confer fire retardancy to the overall fabric. Typical textile coating polymers include natural and synthetic rubbers (polyisobutylene, styrene butadiene, poly(butadiene-acrylonitrile), poly(chloroprene), etc), poly(vinyl chloride) or PVC plastisols and emulsions, poly(vinyl alcohols), formaldehyde-based resins, acrylic copolymers, polyurethanes, silicones and fluorocarbons, used for different applications such as water resistance, flexibility, moisture permeability and fire retardancy. Some coatings have varying levels of inherent fire retardancy (eg. PVC and other chlorine and fluorine-containing polymers), although the more commonly used polymers and copolymers are quite flammable and so the presence of fire retardants additives is necessary to fire retard both the coating matrix polymer and the underlying textile substrate. Fire retardants used for coatings include different phosphates and phosphonates, eg, triaryl phosphate, cresyl diphenyl phosphate, oligomeric phosphate – phosphonate etc. The commercial products of these chemicals are discussed by Horrocks in a recent review.[56]

Back-coating: Back-coating of textiles is a well established application method where the fire retardant formulation containing brominated organic species and antimony trioxide is applied in a bonding resin to the reverse surface of the fabric. Application methods include doctor blade or the knife-coating methods

---

[54] Zhou, H. 1995. Now and future of flame retardancy of fabrics. *Guangxi Textile Science Technology,* 24(2):35–39.
[55] Achwal, W.B. 1987. Flame retardant finishing of cotton and silk fabrics. *Colourage*, June:16–30
[56] Horrocks, A.R. 2008. Flame retardant textile coatings and laminates. Chapter 7 in *Advances in Fire Retardant Materials,* ed., Horrocks, A.R. and Price, D., Woodhead Publishing Ltd, Cambridge.

and the formulation is as a paste or foam. Most typical brominated derivatives are decabromodiphenyl oxide (DBDPO) and hexabromocyclododecane (HBCD). Such back coatings are effective on a wide range of fabrics, including nylon, polypropylene, polyester-nylon blends, acrylics, and many blends. Important applications are in domestic, industrial and automotive upholstered furniture, draperies for hotels and other public buildings. However, there are environmental issues about the use of antimony and bromine - containing chemicals and the risk analysis debate continues in organisations such as the US National Academy of Sciences, US Consumer Product Safety Commission (CPSC), EFRA and the Bromine Science and Environmental Forum (BSEF). All halogen and more specifically, bromine-containing fire retardants have come under scrutiny, and while some like penta- and octabromodiphenyl ether have been banned, others like decabromodiphenyl ether (DBDE) and tetrabromobisphenol A have been subjected to risk assessments and have been found to be safe.

Intumescent coatings: Intumescent additives and coatings may be applied to bulk polymers as well as fibres and fabrics. On heating these encourage the formation of a foamed char, which thermally insulates the underlying structure. In textiles although such coatings can be used on the fabric [57] it is usually applied in between different fabric layers, which are then needle-bonded to consolidate the whole structure.[58]

In carpets the intumescent layer can be applied between the tufting and the backing, or on the upper surface of the backing. The intumescing material also closes up the interstices of the fire-exposed fabric. Nylon carpets made with this backing are fire retardant and are said to meet airline standards for fire safety.[58]

Plasma coating: Plasma technology can be used for surface modification (etching) of fibres and fabrics, functionalization of the surface or surface coating by deposition of a thin layer on the surface followed by grafting. Cold plasma technology can simultaneously graft and polymerize monomers onto the surface of the textile substrate. In the so called plasma-induced-graft-polymerization process, the plasma is used to activate the surface and the plasma of an inert gas is used to initiate polymerization of the non-volatile or solid monomer on the surface of the substrate. Most of the work on plasma has been so far research based and to the best to our knowledge this is not commercially used. The surface grafting of rayon fabrics with phosphorus containing polymers has shown good results in the literature[59]. Phosphorus-containing acrylate monomers (diethyl(acryloyloxyethyl)phosphate (DEAEP), diethyl-2-(methacryloyloxyethyl)phosphate (DEMEP), diethyl (acryloyloxymethyl)phosphonate (DEAMP) and dimethyl (acryloyloxymethyl)phosphonate (DMAMP)) have been successfully grafted onto polyacrylonitrile fabrics. In a more recent work [60] polyethylene methacrylate phosphate was grafted on the cotton fabric. The LOI values rose from 21 vol.-% for the pure cotton to 32 vol.-% for the FR cotton. The treated fabric could achieve M2 rating, compared to M3 rating by pure cotton.

Nanoparticles with homogeneous size can be embedded on textile substrates by plasma polymerization / etching process or by plasma polymerization / co-sputtering process. To this effect, work is in progress in University of Bolton’s laboratory.

---

[57] Tolbert, T. W., Dugan, J.S., Jaco, P.J. and Hendrix, J.E., Spring Industries Inc., US Patent 333174, 4 April 1989.
[58] Von Bonin, W. and Von Gizycki, U., Bayer, A.G., Europ. Patent 91121065.6, 9 December 1991
[59] Simionescu, C.I, Dénes, F., Macoveanu, M.M., Cazacu, G., Totolin, M., Percec, S. and Balaur, D. 1980. Grafting of rayon fabrics with phosphorus containing polymers in cold plasma in order to obtain flame-retardant materials. *Cellulose Chemistry and Technology*, 14: 869-883.
[60] Vannier, A., Duquesne, S., Bourbigot, S., Delobel, R., Magniez, C. and Vouters, M. 2006. The use of plasma induced polymerization technology to develop fire retardant textiles. *Proceeding of International Conference on Textile Coating & Laminatin*g, Nov. 2006, 8-29, Barcelona (Spain).

Appendix 3 Oxygen index and UL94 tests as a broad indication of the flammability performance of a material

Fire performance of a product may be based on tests such as limiting oxygen index and the UL94 flammability rating. There is no simple relation between UL94 rating and oxygen index, but the oxygen index gives a broad indication of the flammability performance of the material. The oxygen indexes (OI) of a number of base polymers and V-0 grade plastics based on the same polymers are shown in Table 3-1.

Table 3-1 Limiting oxygen index of base polymers and V-0 grades of some plastics

Base polymer	Abb.	Limiting oxygen index of base polymer [1] (%)	Examples of oxygen index of V-0 grades [2]
Acrylonitrile butadiene styrene	ABS		31
Polystyrene	PS	18	26
Polyketone	PK	20	35
Polybutylene terephthalate	PBT	22	29-36
Polyamide	PA	24.5	28
Polyphenylene ether	PPE	28	37
Polycarbonate	PC	29	35
Polysulfone V-1 grade	PSU	29.5	36
Polyaryletherketone	PAEK	37	
Polyethersulfone	PES	38	45

Notes: [1] The list includes plastics listed in MatWeb, The Online Materials Information Resource (covering more than 50 suppliers of polymers). Information on flame retardants has been provided by producers of the plastics. [2] V-0 rating grade is only available for un-reinforced grades.

The OI of the polymers and plastics will vary somewhat and slightly different values can be found in different references. The index is also dependent on addition of reinforcement material. For example, the addition of inorganic fillers and fibres will lower the OI of the plastic material. Materials with a limiting OI of more than about 30% are self-extinguishing, i.e. they can be used as fire retardant grades without addition of fire retardants. In Table 3-1, three plastics, polysulfone, polyaryletherketone and polyethersulfone have high enough Limiting Oxygen Index (LOI) that fire retardant grades are obtained without addition of fire retardants.

The necessary loading of fire retardants required to obtain a certain flammability rating of a plastic material will depend on the flammability of the base polymer. As an example, the red phosphorus concentration required for UL94 V-0 rating for a number of polymers is shown in Table 3.2. The required concentration is broadly inversely proportional to the oxygen index of the polymer ranging from 15% in polystyrene (LOI $\approx$ 18) to 1.2% in polycarbonate (LOI $\approx$ 29).

Table 3-2 shows that a V-0 rating can be obtained for a variety of polymers using red phosphorus. The authors claim that similar results may be shown for other non-halogen fire retardants as magnesium hydroxide, melamine derivatives, organophosphorus compounds and zinc borate (probably in combination with another FR) [40].

Table 3-2 Red phosphorus concentration required for UL94 V-0 rating

Resin	Concentration (%)
Polystyrene	15
Polyethylene	10
Polyamide	7
Polyethylene terephthalate	3
Filled phenolic resin	3
Polycarbonate	1.2

Appendix 4 Findings of the FR Technology Survey

Summary

The FR Technology survey sought information on FR technologies from both a fire retardant producer's perspective and also that of product manufacturers as users. The survey sought information on the key chemical fire retardant technologies used in the consumer products of interest and alternative non-chemical fire retardant technologies currently used in different products in the UK and EU and to identify emerging chemical and non-chemical technologies. Product manufacturer's views on the EU Ecolabel scheme and FR related criteria were also sought.

A draft of the survey and a list of invited participants were produced and approved by Defra.

The questionnaire was scripted into an electronic survey tool. An invitation letter was issued under Defra letterhead along with a briefing note on the study objectives. The survey was conducted by web link, telephone and e-mail with all of the organisations that responded.

The survey closed 8 weeks after it was launched to enable slower organisations to respond and trade associations to engage their members. A number of relevant knowledge transfer networks KTNs were also used to promote participation in the survey.

Survey Structure and Participation

400 organisations from a wide range of fire retardant producers, product manufacturers, trade associations and other stakeholders were invited to participate in the survey and to make other organisations aware of the survey.

A list of the organisations that finally participated is given in below.

Invitations were sent out by email and personal invitations made by phone. The response was modest and the final number that completed the survey was lower than expected.

The total number of people who actually started on the survey was 101 but those who submitted completed forms numbered 57 (56% of the response cohort). The others left the survey or did not continue after registering. In all cases this followed the participants visit to the page containing Defra's confidentiality statement.

Those who completed the survey consist of:

1. Fire Retardant Producers 15
2. Product Producers 24
3. Others 18

Respondents in the Others category included:

- Stakeholder on DfE Flame Retardancy Partnerships
- NGO
- Government Department
- Ecolabelling organisation

- Members are Builders Merchants
- NHS Supply Chain runs tender process and manages supplier agreements for the NHS
- Distributors or suppliers of Fire retardant garments
- Product Designer
- Defence contractor
- Trade Association representing the interests of UK/European manufacturers
- Retailers
- Universities
- Non profit association dealing with EHS issues of 10 antimony substances

It is clear that a reasonable cross section of representation was obtained despite the low numbers that participated in this survey.

Summary of Findings and Respondent Comments

FR Producers

Supply of FRs

The chemical FR technology represented by responding FR producers in order of use were:

Phosphorous based

Inorganic and Polymeric

Organic - Brominated and Chlorinated.

It should be noted that many phosphorus FRs contain chlorine and many polymeric are brominated.

Other types not listed included:

Chemical FRs for fire/ explosion suppression,

Nitrogen based and

Reactive fire retardants.

EBFRIP indicated that their member companies produce all types of brominated FRs, some of which are polymeric. Respondents did not qualified what they mean by “Reactive” or “Polymeric” so we rely on the definitions provided in the survey guidance .

Most of the fire retardant producers who participated in the survey produce more than 1000 tonnes. The major FR types are supplied in solid form, but one company respondent indicated that they also produced Br-based and polymeric additives in liquid form.

Most companies indicated that their FR particles size was greater than 1000nm and only a few indicated that their products are nano sized with just two reporting particle sizes less than 10nm.

There is no clear indication as to whether the organic and polymeric fire retardants are mixtures with other functional groups or purely organic.

FRs in Consumer products

FR producers supply FRs to all of the structural components used in furniture; mainly foam followed by coverings. 5 producers also supply to the nonwoven felt and interliner markets.

The major application of FRs in textiles is in backcoating, followed by fabric treatment. Other components listed were vinyl coated fibre and woven fibre and finishing. In one case this includes FRs supplied to the transportation sector including automotive.

Two respondents in the consumer electronic products section indicated that virtually all electronic and electrical products including wires, cables and connectors are treated with fire retardants Most FR producers supply FRs to all of the equipment considered in the survey. Others that were specified by respondents include mobile phones, MP3 players, connectors, printed circuit boards, transportation, including automotive coating and instrumentation for cooling applications.

None of the FR producers that responded are supplying nanomaterial based FRs at this point in time.

Product Producers

The greatest number of producers who responded were textile manufactures followed by furniture and consumer electronics producers. This is in line with the level UK and European manufacturing in these sectors.

Furniture	8
Textiles	12
Consumer Electronics	5

No nightwear producers participated in the survey. However, two participants did complete the textile section in relation to nightwear. One of them claimed production of all the categories of nightwear while the other, who suppliers textiles to the furniture industry, also indicated that they produce synthetic fabrics for nightwear.

Furniture producers use FRs in all of their components: foam, covering, mattress filling, nonwoven felts and interliners.

Textile producers use FRs in all the primary components: fibre, fabric, backcoating, chemical finishes and lamination.

Consumer electronics producers use FRs in all of the products considered here with the leading product being LCD TVs. Portable computers came next followed by equal numbers of desktop computers, monitors and plasma TVs. This is line with findings from the FR producers.

Fire retardant technologies used in products

The technology most used is bulk addition, barrier layer technology is the next most popular followed by inherent FR fibres.

“Additive” chemical FR technologies are the most commonly used with phosphorus based FRs second and equally popular in furniture and electronics. The furniture industry seems to use the full range of the technologies listed except for nano.

Textiles scored highest with additive technologies but again this product set uses the whole range of technology listed except for nano. Similarly, the electronics sector scored on all the technologies except for intumescents and nano.

	Application	**Most popular**	**Second most popular**	**Third Choice**
Technology types	furniture and textiles	bulk addition	barrier layer	inherent FR fibre
	consumer electronics	bulk addition	product design, melt blending and barrier layer	
FR types	furniture and textiles	“Additive” chemical FR technologies	phosphorus based FRs	
	consumer electronics	“Additive” chemical FR technologies	phosphorus based FRs	

FR Technology Costs

Current Technologies

Actual Cost per Product Unit

Participants were asked to specify the costs, either actual or estimated, for each single unit of product (i.e. a single product or item or for 100m of textile) they produced. Eleven respondents answered this question; about two thirds of them quoting in £ pounds while the rest in € euro.

For **Actual Added Cost** per unit, the largest response was in the range £/€ 21-50 for furniture. The next highest category was between £/€.0-1 for consumer electronics. There were no respondents claiming costs greater than £/€50 per unit. The major technology used in both cases is brominated-FR (we assume in many cases with ATO as a synergist).

For **Estimated Cost** per unit the largest response was the range £/€2-5, with fewer in the ranges £/€0-1 and £/€6-10. Both chemical FR bulk addition and chemical FR phosphorus based were identified as major technologies in the estimated costing.

The majority of respondents claimed that the extra cost per unit of their product to be greater than 10% where bulk addition, bromine based and phosphorus based were identified as the major FR technologies used.

Future FR Technologies

Participants were requested to provide information on their estimated cost for future fire retardant technologies specifying Actual Estimated Cost, Estimated Expected Cost and Estimated % Additional Cost for the whole product.

The main FR technologies identified in this section were chemical FR bulk addition and chemical FR phosphorus based technologies which are now cited more than brominated FRs.

For **Expected Cost per product:** all the participating product producers indicated £/€ 0-1 only. These were for bromine based, bulk addition, and phosphorus based and chemical FR polymeric technologies.

The **Estimated Expected Costs** were generally higher than the Actual Expected Costs; 50% of the respondents indicated £/€ 2-5 per unit product followed by 40% at £/€ 0-1. The other 10% indicated £/€ 6-10. The higher cost may reflect uncertainty and caution when estimating costs.

The Estimated Percentage Addition to product cost reflected closely the Estimated Expected Costs in the FR technologies. The majority of product producers indicated 0-0.2% addition to their cost of product using future technology based technologies also featured.

Some Respondent Comments on Costs

One respondent commented that there is the potential for increased costs to their company resulting from the loss of certain retardant technologies arising from legislative concerns.

One participant from a trade association commented that he is completely unaware of any emerging technology that will render flexible PU foam compliant with UK flammability requirements. He stated that should innovators believe they have appropriate technology, it is important to establish not just economical viability but independent verification of compliance with current UK ignition resistance legislation and equivalent or better post-ignition characteristics. He concluded that it would also be important to verify other performance standards such as durability and acceptable HSE profile.

EU Ecolabel Scheme

Ecolabel for Textiles and Furnishings

There is a requirement in the current Ecolabel criteria for textile products, which include clothing, bed linen and indoor textiles and other products containing textiles such as furnishing fabrics, that no "additive" FRs are permitted, only reactive fire retardants are allowed.

The majority of respondents consider this Ecolabel criterion to be too restrictive and a barrier to applying for Ecolabel. About 14% thought it sensible while about 11% thought it was an effective way to reduce environmental impact.

This section of the survey provoked the most comments from respondents. Some of these are summarized below:

- The criteria do not distinguish between mono molecular and polymeric additives.
- It is better to have inherently fire retardant materials
- This participant's fire retardant is non hazardous and has no environmental impact

- There is confusion in the understanding of the definition of "reactive" between the ecolabel regulators and the textile industry. The regulatory requirements for fire protection in the UK and Ireland cannot be achieved for any products granted an ecolabel. Therefore the ecolabel system for textile products will not be usable in these countries.

Ecolabel for Electronic Products

In contrast to textiles and furnishings, the Ecolabel criteria established for electronic products, which include personal computers, portable computers and TVs, the use of fire retardants is restricted by certain Risk Phrases, but both additive and reactive fire retardants are allowed.

Again, the majority of respondents were of the opinion that the current Ecolabel criteria requirement for electronic products is too restrictive and a barrier to applying for Ecolabel. About 22% thought it sensible while about 11% thought it was an effective way to reduce environmental impact.

The main contributed comments in this section include:

- the need to distinguish between mono molecular and polymeric additives is not in the criteria.
- FRs should be assessed through a consistent comparative hazard assessment framework.
- both additive and reactive FRs should be permitted.

Comments were also made that the list of R-phrases is too restrictive and that they relate to hazard and not risk. There was concern that account had not been taken of the classification and labelling status of current commercial FR technologies - this was cited as a reason why ecolabel requirements cannot be achieved for most commercial FR systems.

Ecolabel for Bed Mattresses

In the criteria established for bed mattresses, there is a requirement that no additive fire retardants are used in PU and Latex foams. Only reactive fire retardants will be allowed.

The majority of respondents were of the opinion that the current Ecolabel criteria requirement for bed mattresses is too restrictive and a barrier to applying for Ecolabel. About 8% thought it sensible, the same number thought it was an effective way to reduce environmental impact.

Respondent's General Comments

- There is no commercial system which can meet the ecolabel criterion for foam, because the ecolabels regulators (Commission and the EUEB) seem to have a definition of "reactive" which is different from that used normally in the industry, and this may have led to confusion.

- The confusion over the definition of "reactive" also means that the regulatory requirements for fire protection in the UK and Ireland cannot be achieved for any bed mattresses granted an ecolabel. Therefore the ecolabel system for bed mattresses will not be usable in these countries.

- "Totally ill-conceived and impractical. No science has been presented in support of the new requirements, and because decision making lacked manufacturing industry consultation there is a complete un-awareness of what is industrially realistic. The new eco-label rules now exclude substances shown to be risk-free to consumers and environment. If fire retardants are now required to be chemically reactive why does the same not apply to all other substances in eco-labelled articles and why are naturally occurring CMR substances allowed to be present in naturally sourced products?

FIRA International Ltd

Effectiveness of the current domestic regulations.

The UK has the most stringent fire safety requirements for furniture in Europe. They have been proved to be truly effective in saving lives and are fully supported by the industry.

It estimated the effectiveness as saving 54 lives per annum (780 fewer non fatal injuries) and 1,065 fewer fires. This equates to a monetary saving of £140 m per annum. 60% of this saving was attributed to the fire retardants used with the fabrics.

Environmental effects of fires

The environmental impact of fires would increase if less effective fire retardants were used.

Not only is there an environmental impact in terms of CO2 emissions from the fire itself, but then also the additional impact of re-building/re-furbishing the buildings affected.

Fire retardant types

FIRA would recommend that fire retardant coatings are not used, as they can either be washed off, affected by cleaning or wear, and thus have their effectiveness reduced.

International Antimony Association

"Antimony trioxide has an R40 phrase because of the potential risk via inhalation of the fine Sb particles during production of the antimony trioxide itself. Once it is encapsulated in the resin (masterbatch form) and sold to the plastics or textile industry, the EU and OECD experts all concluded that there is no risk whatsoever".

Participants by Organisation

Name	Company
Adrian Foster	NHS Supply Chain
Adrian Hyner	3M
Albert Kronborg Hansen	K. Balling-Engelsen a/s
Barry Owen-Smith	Leggett & Platt Adjustables
Berni Rowland	Millbrook Beds Limited
Borms Rudi	ICL-IP Europe
Brian Halson	Eurotek Office Furniture Ltd
Carole Green	Builders Merchants Federation
Coopmans Karl	Campine NV
Craig Lauder	SMD CONTRACTS LTD
David Roe	
Dr D Crump	Cranfield University
Dr David Waite	British Plastics Federation
Dr John Williams	William Blythe Limited
Dr Phil Hope	EBFRIP
Dr. Adrian Beard	Clariant
Dr. Heiko Tebbe	LANXESS Deutschland GmbH
Dr. Phil Hope	EBFRIP (European Brominated Flame Retardant Industry Panel)
Dr. Thomas Futterer	Chemische Fabrik Buidenheim KG
Gareth Wood	EADS DS UK Ltd
Graham Berry	Camira Fabrics
Grayson Dyas	Hitachi Europe
Hans Wendschlag	Hewlett-Packard
Ian Flint	Quality Furniture ltd
Jakob Waidtløw	Ecolabelling Denmark
Jo Milnes	Dartex Coatings ltd

Kasturirangan Kannah	Chemtura Manufacturing UK Ltd
Keith Oakes	Gradus
L G Ulin	Yaaparra Limited
Lauren Heine	Clean Production Action
Lorraine Roberts	Westbridge Furniture Designs Ltd
Margot Clauss	Ciba Inc (Ciba is now BASF)
Mark Hambleton	PINEWOOD DRAPILUX UK LTD
Martin O'Hara	Danfoss Randall Ltd
Maurice Morgan	Alexandra plc
Mette Mørup	Mørup Stof
Mr A P Spalding	Fabric Flare Limited
Noel Taylor	Durapipe UK
Nora Harper	NHS Supply Chain
Norberto Gatti	Italmatch Chemicals spa
Patrycja Lewkowicz	PCC Rokita S.A.
Peter Evans	Sony United Kingdom Limited
Philip Allison	Enkev UK Ltd
Robert Andrews	George Clothing
Robert Turner	Pace plc
Robert Walton	Agua Fabrics
Roger Hoodless	BAE SYSTEMS Shared Services - PARC
Shaun Ambrose-Jones	Dartex Coatings
Sue Blacker	Blacker Sheep ltd
Suzanne McGroarty	Bute Fabrics Ltd
Terry Edge	Department for Business, Innovation and Skills
Terry Fuller	Ulster Supported Employment LTD
Tim Tatton	Invotec Group Limited
Van de Velde Karine	International Antimony Association

Van Ravestyn Pierre	Kaneka Belgium nv

The survey was also sent to the following Knowledge Transfer Networks (KTNs):

Jenny Marsden - The Environmental Sustainability - Jenny.Marsden@ctechinnovation.com

Mr Quarshie - Materials - materials.ktn@iom3.org

Ms Boyer-Spooner - Chemistry Innovation - enquiries@ciktn.co.uk

Mr Evans – Electronics - info@electronics-ktn.com

Appendix 5 Lowell Centre for Sustainable Production Substitutes Programme – FR Substitute Studies

The Lowell Centre has been involved in an alternatives assessment approach that seeks to focus on solutions rather than the problem, and in stimulating innovation and prevention, in an effort to reducing several risks simultaneously. Within the programme they have devised an Alternatives Assessment framework for more rapid assessment of potential viable alternatives – however, it appears this was not reported until after the FR report cited below.

In 2005 the Lowell Center published a report on "Decabromodiphenylether: An Investigation of Non-Halogen Substitutes in Electronic Enclosure and Textile Applications" and in 2006 another report on "An Overview of Alternatives to Tetrabromobisphenol A (TBBPA) and Hexabromocyclododecane (HBCD)" and it considered application needs in textiles and electronic product enclosures.

Decabromodiphenyl ether (decaDBDE) Substitute Study

This study was in response to many manufacturers claiming they wanted non-DBDE and non-BFR alternatives.

The purpose of the study was to:

1. Identify the primary sectors that use decaBDE in the U.S.
2. Identify substitute fire retardants and materials in electronic enclosures and textiles that meet fire protection standards
3. Assess the availability of these substitutes
4. Delineate examples of where these substitutes are currently used in commerce
5. Assess the costs of these substitutes where data are available.

A detailed review of the literature on exposure and human and environmental toxicity of fire retardants was beyond the scope of the study. Nonetheless, it was stated that a thorough consideration of the health and ecosystem risks of alternatives is an important aspect of any substitution process. The scope of this study was therefore limited to summarizing the known non-halogenated substitutes to replace the use of decaBDE in electronic enclosure and textile applications.

Electronic Enclosures

The major use of decaBDE in the U.S. is in electronics, with the primary use being the black plastic electronic enclosures used to enclose the rear of the TV. DecaBDE is used in TV enclosures because it is an inexpensive, highly efficient fire retardant that is very compatible with inexpensive high impact polystyrene (HIPS). In a TV enclosure, the back plastic panel and in some cases the front panel will be made from decaBDE HIPS containing roughly 12% decaBDE by weight in combination with antimony trioxide (ATO) at a ratio of roughly three parts decaBDE to one part ATO.

The study focused on the substitution in TV enclosures, but the results were claimed to be broadly applicable to enclosures using decaBDE and HIPS.

The chief fire safety standards for electronic enclosures are the UL 94 component standards. The UL 94 component standards range from UL94 HB (the lowest standard), which involves a horizontal burn, to successively more stringent vertical burning tests (Class UL 94 V-2, V-1, V-0 and 5V). DecaBDE is typically used in components that require high levels of fire retardancy, V-0 or higher. The default standard for replacement of components using decaBDE is almost always V-0.

Some enclosure manufacturers have been able to redesign their products and separate the voltage supply from ignitable plastics. While these products technically meet the UL standard, manufacturers in the U.S. and increasingly in Europe are still fire retarding the housings to protect them from external ignition sources.

The most cost-effective non-halogenated substitutes for decaBDE HIPS involve changing the resin system and the use of phosphorous-based fire retardants. The most cost-effective non-halogenated substitutes include:

- blends of polycarbonate and acrylonitrile-butadiene-styrene (PC/ABS)
- polycarbonate (PC)
- blends of high-impact polystyrene (HIPS) and polyphenylene oxide (HIPS/PPO)

Other substitutes such as metal, wood or enclosures based on polylactide are possible but not widely employed due to cost and performance issues. These substitute resin systems are commodity resin systems widely used in a variety of applications in the U.S. Of these three replacement systems, only HIPS/PPO is 100% halogen-free.

The PC/ABS and PC systems typically contain a very small amount of fluoro polymer(roughly 0.3%) for drip resistance. A fourth alternative system to decaBDE HIPS is straight ABS but this resin system requires brominated fire retardants to achieve a V-0 rating.

The cost of various fire retardant amorphous plastics for electronic housings varies tremendously, with fire retardant HIPS being the cheapest and HIPS/PPO blends being the most expensive. The raw material costs for resin enclosures depend on a number of factors including the cost of the resin itself, the cost of the fire retardant, and volume-related pricing. The cost of these substitute systems is roughly $0.40 to $1.00 per pound greater than decaBDE HIPS, which costs roughly $0.87 to $0.98 per, pound. To put these costs in perspective, the cost increase for an average 27-inch TV that sells for roughly $300 using PC/ABS rather than decaBDE HIPS in the rear enclosure would be roughly $4.40 to $7.50, or roughly 1.5 to 2.5% of total purchase price. Note that these costs are raw material costs only and do not include one-time switching costs such as new moulds or other cost increases or decreases due to changes in energy use, yield, or cycle time.

Throughout the report, PC/ABS and PC are referred to as “halogen-free”. This term applies to the fire retardants as opposed to the resin system which contains a small amount of fluoropolymer.

For TVs the report concluded that if market drivers existed for radical change in the US, nearly all manufacturers have the technology and know-how to meet the demand for decaBDE-free products that meet strict fire safety standards.

Textiles

Textiles are the second major use of decaBDE examined in this study. Unlike electronic enclosures for which there are a limited number of substitutes currently available, there are many different fire retardants, fibers, and barrier substitutes for textile applications. This makes summarizing the substitutes for textiles more difficult. Roughly 10 – 20% of U.S. decaBDE use occurs in the textile industry (Hardy 2003). Based on a literature review and an analysis of the U.S. Toxics Release Inventory (TRI), the primary textile uses appear to be in the mattress, drapery, commercial upholstered furniture, and transportation (automotive and airplane) industries. Other niche applications of decaBDE in textiles include tents, awnings, and related fabric applications.

Fire Safety: There are numerous federal, state and voluntary fire safety performance standards that drive the use of fire retardant textiles. The most significant of these include those promulgated by the State of California Bureau of Home Furnishings and Thermal Insulation (CA BHFTI) and the Consumer Product Safety Commission (CPSC). CPSC proposed a rule for mattresses in January 2005, and is in the process of developing regulations for furniture and bedding. According to the CPSC, the total use of fire retardant chemicals is expected to increase somewhat if such requirements are finalized (CPSC) 2005). DecaBDE is one of many potential fire retardants that are likely to be used to comply with these standards.

DecaBDE is typically applied to the back of textile fabric in a coating that contains antimony in an acrylic or ethylene-vinyl acetate copolymer matrix. Strategies for substituting decaBDE in textiles include the redesign of products to reduce their fuel load (i.e., eliminate the use of foam), fire retardant chemical treatment, inherently fire-resistant fabrics, and barrier layers.

There are limited examples of manufacturers reducing the fuel load of their product. For example, fabric office chairs such as the Aeron from Herman Miller contain no polyurethane foam. Providing comfort without contributing to the fuel load is a potential research and innovation area for the furniture industry.

There are several chemically applied decaBDE substitutes commonly available on the market for natural cellulosic fibers such as cotton, wool, rayon, and linen. The most common types of non-halogen decaBDE substitutes for cellulosics include dimethylphosphono (N-methylol) propionamide and tetrakis (hydroxymethyl) phosphonium salt (or chloride) compound with urea. For synthetic fabrics such as acrylic, acetate, nylon, and polypropylene, a halogenated fire retardant may be used such as decaBDE in an acrylic polymer coating. While some decaBDE substitutes are available on the market, they often have limited durability owing to their water solubility and tendency to wash out during laundering. In these cases, dry cleaning may be required. In some applications, blends of natural and synthetic fibers can be used since natural fibers can be fire retarded without halogens.

Fire-Resistant Fibres Inherently fire-resistant fibres can be used as decaBDE substitutes for synthetic fibres that require high durability. Some synthetic fibres are manufactured to be inherently fire resistant through the addition of non-halogen additives during the melt spinning process. Common examples include the use of phosphorus-based additives in polypropylene and polyester fibres.

Some fire-resistant fibres require no added fire retardants – their base polymers are inherently fire resistant. They have traditionally been used in high-performance apparel (e.g., fire fighter turnout gear), but have more recently been used in mattresses and upholstered furniture applications. Non-halogen examples include melamine, polyaramides, carbonized acrylic, and glass. Halogenated examples include modacrylic and polyhaloalkenes. Mixtures of inherently fire retardant and less fire-retardant fibres can be used to balance cost, comfort, and fire safety goals. Fire barriers are another substitution approach for decaBDE. Manufacturers use fire barrier technologies between the surface fabric and the interior foam core in furniture and mattress construction. Manufacturers also thermally or mechanically bond fire-retardant laminates to the back of fabrics to achieve compliance with fire standards.

To examine the substitute approaches in greater depth, the study examined three product applications that use decaBDE to meet fire performance standards: mattresses, upholstered furniture, and draperies.

Mattresses – deca-BDE has been traditionally used to fire retard the mattress fabric (known as ticking). Non-halogen substitutes based on phosphates are available on the market. To meet more rigorous fire safety standards for products sold in California and in institutional settings such as nursing homes, hospitals, and prisons, manufacturers have turned to fire barriers. According to the CPSC, although decaBDE has been suggested as a candidate for use in mattress ticking, it is not likely to be used to meet the proposed CPSC mattress standard (CPSC 2005). There are numerous mattresses on the market today that meet the most stringent open-fire flammability codes without the use of decaBDE or other brominated fire retardants. For example, the Comfort Care mattress manufactured by the Restonic Mattress Corporation uses a non-halogen inherently fire-retardant resin to meet the strict California mattress fire performance standard.

Upholstered Furniture - consists of complex composites of many component pieces including fabrics, cushioning, frame, and barrier layers. Chemical fire retardants are not necessary for panel and upholstery fabrics in order to meet the fire codes for residential upholstered furniture. However, for upholstered furniture sold in California or in certain institutional settings including high-rise office buildings, hotels, and other public places, some synthetic fabrics are treated with decaBDE. Substitutes for the use of decaBDE in office/commercial furniture include nonhalogen phosphorus chemically coated fire retardant systems and the use of fire barriers like those used in the mattress industry.

Draperies Drapes and curtains used in public places are required to meet certain fire retardant standards. Drapery manufacturers use both inherently fire retardant fibers as well as chemically applied finishes such as decaBDE to meet these requirements. The original report exemplified polyester as inherently fire retardant fibre, which is incorrect as polyester is flammable.

Generally, natural fibre fabrics are the best choice when choosing a drapery fabric to fire retard with chemicals. Natural fibres such as cotton, silk, linen, wool, etc. absorb the fire retardant readily and can be treated with non-halogen phosphate type treatments. Synthetic fibres are more difficult to treat for fire retardancy. Acrylics, acetates, nylons, and polypropylene fabrics are not recommended for drapery use. If these fabrics are used, a backcoating is typically applied (such as decaBDE/antimony in an acrylic polymer coating). Substitutes for decaBDE for polyester, polypropylene and rayon fibers involve the use of phosphate-type additives in the polymer/fibre manufacturing process. Blends of natural and synthetic fibers are common in draperies. The greater the natural fibre content, the better the results from chemical fibre treatment. High synthetic fibre blends may require backcoating to meet vertical flame tests.

There is little cost information on decaBDE substitutes in the literature. Data from one manufacturer showed that their chemically applied substitute for decaBDE was roughly 2 to 2.5 times more expensive on a per-pound basis. But the price of substitute fibres, inherently fire-resistant fibres and the use of fire barriers are very application specific and the information is closely guarded, making it difficult to generalize about substitution costs. For products such as mattresses, upholstered furniture, and draperies, there are numerous non-halogenated fibre, fabric, chemical treatment, and barrier product options that when carefully combined, can replace the use of decaBDE.

The report concluded that “based on an in-depth review of the literature for these applications and interviews with experts from industry, it appears that there are many non-halogenated alternatives to decaBDE available on the market today”.

The report commented that its conclusions are based on the availability of substitutes and do not include an evaluation of their potential human health and environmental risks. Neither did the report provide evidence of equivalent fire performance being achieved. So care is required in accepting some of the conclusions reached in this work.

TBBPA and HBCD Substitute Study

The Lowell Center for Sustainable Production was commissioned to review available information relative to the uses and potential alternatives for two brominated fire retardants, tetrabromobisphenol A (TBBPA) and hexabromocyclododecane HBCD. The objective of this study is to accomplish the following:

- Investigate TBBPA and HBCD product and application information that is available in the public domain.
- Identify potential alternatives to the products identified.
- Conduct a preliminary and qualitative review of potential alternatives.

Key Findings

This study presents a high level overview of the findings. No chemical analyses, toxicological studies, performance evaluations, or economic assessments were included as part of this study.

The report highlighted that on a global basis, the annual market demand in 2003 for TBBPA and HBCD was approximately 145,113 and 21,951 metric tonnes respectively. TBBPA and HBCD are used in a variety of applications. TBBPA is most commonly used as a reactive fire retardant in epoxy resins for printed wiring boards. HBCD is most commonly used for expanded polystyrene (EPS) and extruded polystyrene (XPS) insulation applications in the building and construction industry.

This report has identified numerous potential alternatives for both TBBPA and HBCD that are commercially available. Most of the potential alternatives identified are fire retardant substitutes, and some are resin/material substitutes.

For TBBPA use in printed wiring boards, this report identified potential alternatives in the following categories: other brominated compounds, red phosphorus, other phosphorus based compounds, metal hydroxides, non-flammable resins, polyimide resin, and other resins.

For HBCD use in expanded-PS and extruded-PS insulation applications, this report identified alternatives in the following categories: other brominated fire retardants, polyurethane and polyisocyanurate products, phenolic foam, and other insulation materials.

Consumer product manufacturers identified certain requirements that should be met before these substitutions can be made. (Scheifers, 2004) These requirements include:

- Equal or better fire retardance for the product/part
- Equal or better performance and physical properties for the product/part
- Less risk to environment and human health
- Cost
- Commercial availability

The report identified a number of key health, environmental, and performance concerns for each alternative but it posed no solution as insufficient information was available to make any firm recommendations. It did however recommend that additional research needs to be conducted on the TBBPA and HBCD alternatives identified in this report. This research will help to better determine if the substitution requirements are satisfied for the most common uses of TBBPA and HBCD and to determine if the materials discussed in fact represent safer alternatives.

Some Conclusions

The following conclusions reached by the authors reflect the lack of current knowledge on substitutes and the potential inadequacy of the alternatives:

- For many of the potential alternatives, the existing health and environmental data may be more limited than for either TBBPA or HBCD. These data gaps should be identified and carefully considered before recommending specific alternatives. Sufficient care should be taken to ensure that the substitutes are less hazardous than the chemicals they are replacing.

- In this study a nominal review was carried out of pertinent standards associated with the various uses of TBBPA and HBCD. To better understand the fire retardance requirements for products using HBCD and TBBPA, a more thorough review of the pertinent regulations and standards that apply to electronics and building insulation products regionally, nationally, and globally could be conducted.

- Further research of TBBPA and HBCD alternatives could include a more detailed comparison of fire retardancy requirements as well as other key performance requirements for the various uses of TBBPA and HBCD. The alternatives could then be evaluated and compared as to how well they meet the various performance requirements for each use. It should be noted that TBBPA is used in some mission critical PWB applications such as military, aerospace, medical equipment, and telecommunications. Sufficient reliability data should be obtained for alternatives before their use is recommended.

- A comparison could be conducted of costs associated with using TBBPA and HBCD versus costs for using alternatives. The commercial availability of the alternatives could also be determined. This comparison was outside the scope of this study.

- Additional factors that may be investigated for the potential alternatives including the raw materials and manufacturing processes used to make the chemical/material, as well as the recyclability of the material at product end of life.

It is clear from these comments that the there is a need for greater scrutiny of proposals either calling for substitution or promoting such in the belief that alternatives are better. It is necessary to ensure that candidate substitute technologies, be they chemical or physical, are capable of meeting all relevant and important criteria to ensure the materials/component/products are fit for purpose and capable of meeting both application needs and fire performance requirements. Experience needs to be developed in this area and in a way that satisfies Design for Environment (DfE) principles, which in turn requires that for life cycle performance both environmental and economic impact assessment are applied.

Appendix 6: Electronic Product OEM statements regarding chemical safety, brominated fire retardant phase-out and halogen compound reduction

Acer

“Acer defines a ”hazardous chemical substance” as one that is persistent, bio-accumulative, toxic, carcinogenic, or mutagenic, reproduces toxicity or causes environmental hormone disruption.”

“Acer’s prevention principles behove us to assess any potentially hazardous or chemical substance that may have a negative impact on the environment. Thus, Acer is committed to eliminating the use of hazardous chemical substances listed in OSPAR Plus. At the present stage, PVC and BFRs are priority hazardous chemical substances chosen for gradual elimination.”

http://www.acer-group.com/public/Sustainability/sustainability_main04-2.htm

“…Acer hopes that influential regulations can help to restrict PVC/BFRs; the EU directive RoHS might be the most important one. Regulations to prohibit halogen containing products are now critical. If such a regulation can be predicted, the supply chain and the market will go for non-halogen products before the effective date of regulation. This is the quick solution for widely accepted halogen-free products and for the problem that Acer encountered.”

http://www.acer-group.com/public/Sustainability/sustainability_main04-3.htm

Apple

“The greatest environmental challenge facing our industry today is the presence of arsenic, brominated retardants (BFRs), mercury, phthalates, and polyvinyl chloride (PVC) in products. In keeping with our philosophy over the last decade, Apple is not waiting for legislation to ban these substances.”

http://www.apple.com/environment/complete-lifecycle/

ASUS

“ASUS defines a hazardous chemical substance as a material characterized by persistent, bio-accumulative, toxic, carcinogenic, or mutagenic features, as well as possible reproductive toxicity or environmental hormone disruption.” “ASUS has defined many halogenated compounds such as BFR, CFR, TBBP-A and PVC as hazardous substances.”

“..if BFRs or CFRs contained end of life products are not properly treated and recycled, they will release dioxin and furan during the incineration process. Dioxin compounds are stored in biological fat, are hard to be metabolized, and will be cumulated through the food chain, thus they will lead to bio-genetic lesions.”

http://csr.asus.com/english/index.aspx#35

Cisco

“Material selection and chemical use in products is a growing concern of Cisco’s stakeholders and a key aspect of the global challenge of electronic waste. Cisco recognizes that hazardous substances pose a risk to the environment and our collective health and safety. Through Cisco’s Product Materials Management program, we seek to minimize the use of potentially hazardous substances in our products and operations, and ban certain substances as necessary.”

“Cisco is investigating substitutions for BFRs and PVC in our products.”

http://www.cisco.com/web/about/ac227/csr2009/the-environment/product-materials-content/index.html

Dell

“Dell believes that if reasonable scientific grounds indicate that a substance or group of substances could pose significant environmental or human health risks, it is a substance of concern. Dell will avoid using these substances of concern and will take precautionary measures…”

“If alternatives are not yet viable, Dell works with its industry partners to promote industry standards and the development of reliable, environmentally sound and economically scalable technical solutions.”

“In line with Dell’s Chemical Use Policy, the Precautionary Principle and with consideration for Chemicals for Priority Action identified by the Convention for the Protection of the Marine Environment of the NE Atlantic (OSPAR), Dell’s goal is to eliminate the use of all brominated fire retardant (BFR) chemicals and polyvinyl chloride (PVC) plastics in our products worldwide.”

http://content.dell.com/us/en/corp/d/corpcomm/earth-greener-products-materials.aspx

Electrolux

“Legislation is an increasingly applied mechanism to reduce the use of hazardous substances, primarily in the EU, Japan, China and California. Electrolux is concerned about potentially hazardous substances[…] chemicals may have a negative impact on health and the environment. Consumers demand products that are safe to use. Our objective is to deliver safe products and manage production safely, while protecting the environment.”

http://www.electrolux.com/node281.aspx

“The Electrolux Restricted Materials List specifies the chemicals that we classify as ”banned”, ”restricted” and ”substances of concern”. Through the Restricted Materials List (RML), Electrolux stipulates its group-wide position on chemicals in products. The RML is designed to facilitate compliance to legislation such as restrictions on hazardous substances (RoHS), and registration of chemicals (such as REACH) and upcoming stricter chemicals regulations in China and California. The purpose of the list goes beyond compliance -by monitoring the presence of chemicals that may potentially constitute a risk, the Group is equipped to respond to new scientific findings.”

Brominated fire retardants and PVC are listed on the Restricted Materials List.

http://www.electrolux.com/node214.aspx

Fujitsu

“Fujitsu group are committed to eliminating the use of harmful and potentially harmful substances in its products and production processes in order to minimize risk to end users and to the environment.” ”Fujitsu group sets the criteria of ”Fujitsu Group Specified Control Substances” and tries to avoid the use of substances that may be harmful even when their harmfulness has not yet been fully demonstrated.”

Brominated fire retardants and PVC are listed on the Fujitsu list of controlled substances.

http://www.fujitsu.com/global/about/environment/products/chemical/HCL

“HCL believes that if reasonable scientific grounds indicate a substance (or group of substances) could pose significant environmental or human health risks, even if the full extent of harm has not yet been definitively established, precautionary measures should be taken to avoid use of the substance(s) in products unless there is convincing evidence that the risks are small and are outweighed by the benefits. HCL considers these to be substances of concern that need to be eliminated in the long term and substituted or gradually phased out in the short term. HCL is strongly in favour of government legislation such as the Electronic Products Standard law which restricts/bans use of certain identified chemicals in Electronic Products. HCL identifies these substances with consideration for legal requirements as mandated by the Ministry of Environment and Forest, Government of India, international treaties and conventions, RoHS legislation etc…”

http://www.hclinfosystems.in/chemical_policy_precautionary_principles.html

Hitachi

“Hitachi will “investigate and examine the effect of its business operations on the environment and seek to introduce new technologies and materials with superior functionality regarding environmental safety, energy conservation and resource conservation.” As part of Hitachi’s efforts to reduce the usage of chemicals with an impact on the environment, the company is voluntarily controlling the use of key chemical substances.”

http://www.hitachigst.com/portal/site/en/menuitem.9dfc09befd639d1d92b86b31bac4f0a0/HP

HP

“HP has taken a proactive approach to evaluating materials and eliminating those that pose an environmental, health or safety risk. We may restrict or eliminate substances because of customer or legal requirements or because we believe it is appropriate based on a precautionary approach. We strive to replace legally permitted materials when scientific data has established a potential health or environmental risk and when less risky, commercially viable alternatives are available.”

“Brominated fire retardants (BFRs) and PVC […] Over the last ten years, HP has proactively eliminated most uses of these materials from our products, with limited exceptions.”

“HP supports the restriction of the substances proposed for the EU RoHS revision.”

http://www.hp.com/hpinfo/globalcitizenship/environment/productdesign/materialuse.html#BFR&PVC

JVC

"…we have initiated use of lead-free solder, discontinued use of PVC, and incorporated halogen-free circuit boards in order to reduce toxic chemical substances. And through our "Green Procurement" program, we have encouraged our many suppliers to also do their part in developing systems and materials that will reduce environmental impact."

http://www.jvc-victor.co.jp/english/company/environ/index.html

Lenovo

"Lenovo is committed to minimizing the environmental impact of its products. In order to implement this commitment, Lenovo's chemical and substance management policy supports a precautionary approach, ensuring Lenovo will take appropriate action even if some cause and effect relationships are not fully scientifically established.

Lenovo supports the definition of "BFR/PVC free" as defined in the "iNEMI Position Statement on the 'Definition of Low-Halogen' Electronics (BFR/CFR/PVC-Free)."

http://www.lenovo.com/social_responsibility/us/en/ThinkGreen_products.html#environment

LG Electronics

"LG Electronics recognizes that existing legal requirements are not always enough to protect human health and the environment.[…] If the impact on the environment and human health is not scientifically proven, but there is enough doubt that there might be an adverse effect, LG Electronics will follow the Precautionary Principle as referred to in the 1992 Rio Declaration (UN Earth Summit)."

"…substances that must be monitored or reduced. They are PVC, BFR, Phthalates, beryllium, antimony, selenium, VOC and so on."

http://www.lg.com/global/sustainability/environment/management-of-hazardous-substances.jsp

Microsoft

"Microsoft is committed to phasing out the use of substances in its consumer hardware electronic products that pose a risk or threatened risk to human health or the environment. We try to restrict the use of such substances and that is why our starting point is the precautionary principle. The pre cautionary principle was defined in the UN Rio declaration as "Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation." We believe acting preventatively to reach a sustainable use of natural resources and a sound environment creates better products."

http://download.microsoft.com/download/1/9/9/199b2229-c731-47b2-b420-a6806027d5d5/Restricted_Substances_for_Hardware_Products.docx

Motorola

“Motorola is working to reduce the amount of hazardous substances in our products and to find environmentally sound alternatives, while maintaining performance and quality.”

“We conduct research to identify alternative materials with reduced environmental impact.” “Our management of substances of concern is based principally on independent expert scientific reviews and regulatory requirements. Motorola’s experts are continually reviewing the evidence regarding chemicals and physical agents used in manufacturing. When scientific evidence about a chemical or physical agent is limited or conflicting, our experts and engineers assess potential adverse impacts, risks of substitutes, needs for precautionary measures, and technical and economic feasibility. This multi-disciplinary process may lead Motorola to take voluntary measures to reduce, phase out or eliminate substances that are not currently banned or controlled by regulatory agencies.”

http://responsibility.motorola.com/index.php/environment/products/materials/

NEC

“NEC carefully examines environmental impact and safety in handling chemical substance, from receipt and use to disposal. NEC takes all possible measures to reduce consumption of chemical substances and to replace harmful substances with safer ones.”

http://www.nec.co.jp/eco/en/issue/chemical/index.html

Nintendo

“Nintendo is currently working towards eliminating the use of Polyvinyl Chloride, which has been designated as a “Substance Subject to Early Withdrawal…”

“Substances Subject to Early Withdrawal: Substances expected to be classified as banned substance due to the enactment of future legislation. As part of our risk management and environmental protection efforts, Nintendo plans to switch over to alternative substances and remove these substances from our products as soon as possible: PVC”

“Substances under Application Control: Substance that with prolonged exposure pose a potential health risk and in Nintendo’s view, require continual monitoring for their content levels:[…]BFRs”

http://www.nintendo.co.jp/corporate/en/csr/pdf/nintendo_csr2009e.pdf

Nokia

“Nokia follow the precautionary principle. Where we have reasonable grounds for concern over the possibility of severe or irreversible damage to health or the environment, we believe that lack of full scientific certainty should not be an obstacle to triggering actions to gather and assess additional data. That may lead us to voluntarily take steps, e.g. to substitute substances of concern with safer alternatives, where feasible alternatives are available.”

http://www.nokia.com/environment/ourresponsibility/substance-and-material-management

Panasonic

"With regard to polyvinyl chloride (PVC) resin, there are concerns about the generation of hazardous substances through the inappropriate disposal of waste resin and the harmful effects of an additive (phthalate ester) used to soften the resin."

http://panasonic.net/eco/products/chemical_substance/case_study.html

"Panasonic has been manufacturing products in line with its basic policy, which is to minimize the use of chemical substances that might adversely affect human health and the environment throughout their life cycles."

http://panasonic.net/eco/products/chemical_substance/index.html

"Also, although halogenated fire retardants are currently essential to protect consumers and to minimize the risk of flammability in some electronic products, we are investigating ways to replace them wherever possible."

"In environmental impact assessment, impacts of hazardous substances which are emitted from components containing highly-concentrated brominated fire retardants in inappropriate treatment for collecting rare metals from disposed products such as burning off the field are concerned."

http://panasonic.net/eco/products/chemical_substance/action_plan.html

Philips

"Philips has decided to phase out the use of certain substances from a precautionary point of view, despite the fact that there is no regulation which requires us to do so."

"Examples of voluntary phase-out (based on the precautionary principle)" "Polyvinyl Chloride[…]"there are stakeholders that focus on potential environmental side effects for instance unsafe recycling, outside well equipped recycling systems."

"In 2008 we have started a pilot to replace BFR in certain consumer products aiming to have BFR free consumer product models on the market year in by year-end 2008."

http://www.philips.com/about/sustainability/environmentalresponsibility/chemicalmanagement.page

Ricoh

"Major Ideas in the Ricoh Group Mid- and Long-Term Environmental Impact Reduction Goals[…]Pollution Prevention: Reduce the impact of chemical substances on the environment […] from the fiscal 2000 level. […] Concept: Implement risk management that covers not only impact on the environment but also impact on human health. Carry out risk management taking information on consumption, emissions, hazards, and exposure of chemical substances into consideration. Give priority to the high-risk chemical substances in reduction and replacement in order to prevent possible pollution.“

http://www.ricoh.com/environment/management/vision.html

Samsung

“By acting above and beyond legal requirements, and considering cases where the scientific evidence is conflicting or not yet absolute, Samsung Electronics incorporates the Precautionary Principle into our approach for managing target substances.”

“Samsung Electronics believes that the enactment of legislation such as updated EU RoHS Directives will play an important role in addressing problems relating to the elimination of PVC and BFRs use. Through this legislation, the industry-wide replacement of PVC and BFRs could be expedited.

Samsung Electronics will comply if the EU decides to include PVC and BFRs as restricted substances in the RoHS amendment.”

http://www.samsung.com/us/aboutsamsung/sustainability/environment/chemicalmanagement/policyontargetsubstances.html

Sharp

“Sharp develops products in the spirit of the 1992 Rio Declaration’s Precautionary Principle.” “Sharp will proactively support revised EU’s RoHS directive for the ban of Polychlorinated biphenyls, Polychlorinated naphthalene (Only polychlorinated naphthalene with three chlorines and more), Short chain chlorinated paraffin, Polychlorinated Terphenyls, and Hexabromocyclododecane. In addition to substances whose harmful effects have been scientifically proven, Sharp gathers data on other hazardous substances that are suspected of having harmful environmental and health effects and, where necessary, bans or sets goals for the reduction of these.”

“It has been suggested that improper treatment of polyvinyl chloride (PVC) and phthalates after disposal can have harmful environmental and health effects.[…] Sharp makes its utmost efforts to reduce the use of PVC and phthalates according to the Precautionary Principle.”

“It has been suggested that improper treatment of brominated fire retardants (BFRs) and antimony compounds after disposal can have harmful environmental and health effects.

[…] Sharp is committed to eliminating BFRs from all products […] according to the Precautionary Principle.”

http://www.sharp-world.com/corporate/eco/data_list/chem.html

Sony

“Sony defines “Environment-related Substances to be Controlled” (called “Controlled Substances” hereafter) as certain chemicals that Sony has determined to have significant environmental impact on both humans and the global environment, including substances that may not be controlled by laws. Sony prohibits the use of these substances in products or phases them out wherever a viable substitute which meets all product quality and technical requirements is available."

"PVC may pose a risk to the environment if disposed of improperly. Another concern is that PVC might contain various other chemical substances, including plasticizers and stabilizers, which could pose risks to the environment and human health. While PVC currently is not regulated by any laws that apply to chemical substances used in electronics products, Sony has been promoting the use of its alternatives."

"Sony is promoting the use of alternatives to BFRs, which can generate harmful substances if treated improperly after disposal."

http://www.sony.net/SonyInfo/csr/environment/chemical/products/index.html

Sony Ericsson

"At Sony Ericsson[…] we decided to use alternatives for fire protection, mainly because of the risk that BFRs form dioxins in uncontrolled incineration. It is also important to note that 99% of the use of BFRs was in cables, casings and boards."

"At Sony Ericsson we have taken actions to remove Polyvinyl Chloride (PVC) from our products."

"Sony Ericsson is concerned about PVC because it releases hydrochloric acid and dioxins when it is burned. Dioxins are highly toxic and accumulate in the fatty tissues of animals, especially oily fish such as salmon. Dioxins are known mutagens and carcinogens and also cause serious skin diseases."

http://www.sonyericsson.com/cws/companyandpress/sustainability/consciousdesign?cc=se&lc

Toshiba

"Toshiba PC's basic policy regarding the reduction and / or elimination of hazardous substances is based on the "precautionary principle" and the "substitution principle". "We will replace hazardous substances with alternatives, whether those hazardous substances are restricted by the law or not."

"We will endeavor to replace the hazardous substances with alternatives, although the hazardous property has not yet been proved."

http://www.toshiba.co.jp/pc_env/eco/lca.html#comm5

Wipro

"The core mission of Wipro Green Computing is to provide to our customers, products that are safe for the environment. Preserving the environment for future generations is our foremost duty[…] Wipro vision is to avoid the use of substances in its products that could seriously harm the environment or human health."

“Wipro further believes that if reasonable scientific grounds indicate a substance (or group of substances) could pose significant environmental or human health risks, even if the full extent of harm has not yet been definitively established, precautionary measures should be taken to avoid use of the substance(s) in products unless there is convincing evidence that the risks are small and are outweighed by the benefits.

Wipro considers these to be substances of concern that need to be eliminated in the long term and substituted or gradually phased out in the short term. Wipro identifies substances for elimination after studying the harmful substances recommended by the Ministry of Environment and Forest, Government of India, international treaties and conventions, RoHS legislation etc. as applicable to its area of operations.”

http://www.wiprogreentech.com/chemicals_policy_and_management.html

“Wipro’s Chemical Precautionary Policy is focused on continually identifying the chemicals in components based on OSPAR list of chemicals.”

http://www.wiprogreentech.com/chemical_management.html