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LIFE-FLAREX PROJECT Deliverable

Deliverable A1 - Report of fabrics and flame retardant selection

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1. Introduction

This document contains the results of **Task A1.1 Selection of textile materials** and **Task A1.2 Selection if FR** within "*Action A1 - Selection of most representative textile materials and finishing technologies*" which objective was to collect information related to the use of Flame retardants (FR) products and their experience with different finishing processes and products.

The results of this task have contributed to the selection of current FR, alternatives and fabrics.

Action A1 has been developed from July 2017 to December 2017, coordinated by CTB and with the collaboration of AEI TEXTIL, LEITAT, ATEVAL, CLUTEX and CS-POINTEX.

Task A1.3 has been leaded by AEI TEXTIL with the collaboration of ATEVAL, CLUTEX, CS-POINTEX and CTB.

This action was extended to December 2017.

2. Selection purpose

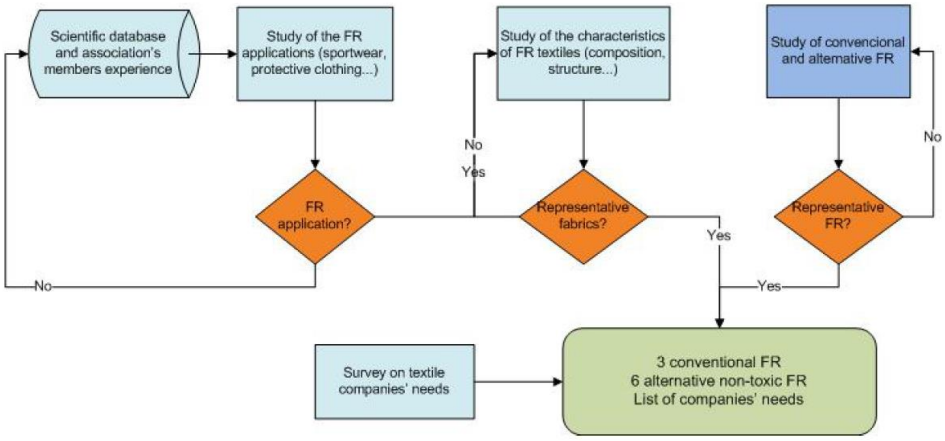
The overall purpose of the selection of both the fabrics and flame retardants is to determine the starting point of implementation actions (section B). The goal is to focus the project toward widely used fabrics for home textile sector and the flame retardants adequate for that purpose.

This report includes feedback from the parallel Task A1.3 – Survey to industry which feeds in and validates the textile selection and flame retardant selection.

3. Methodology

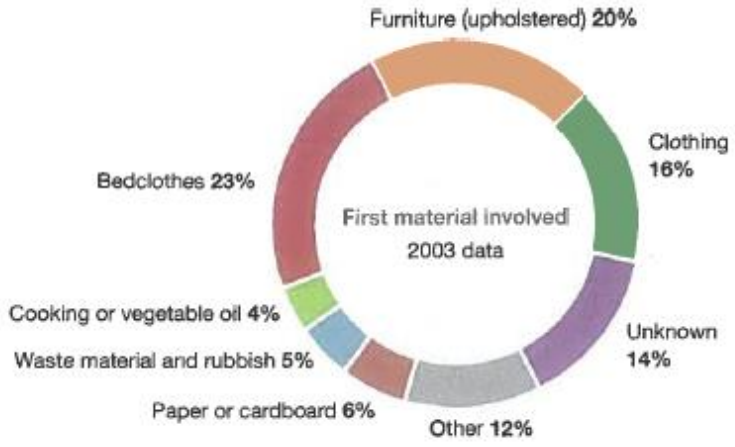
The methodology for preparing the information for this report has been based on iterations of feedback among technical clusters and research centres.

The following diagram describes the thinking process of the selection:



The first part, the determination of the FR applications, was conducted during the proposal preparation stage where home textiles were defined as the primary market for applications of FR.

Home textiles are the main cause of ignition for most household fires according to the 'Consumer fire safety report' by M. Kobes and K Groenewegen (2009) as in Figure 1. Bedlinen and upholstered furniture are the primary start point of fire, togetherh representing more than half of the fires where ignition is known.

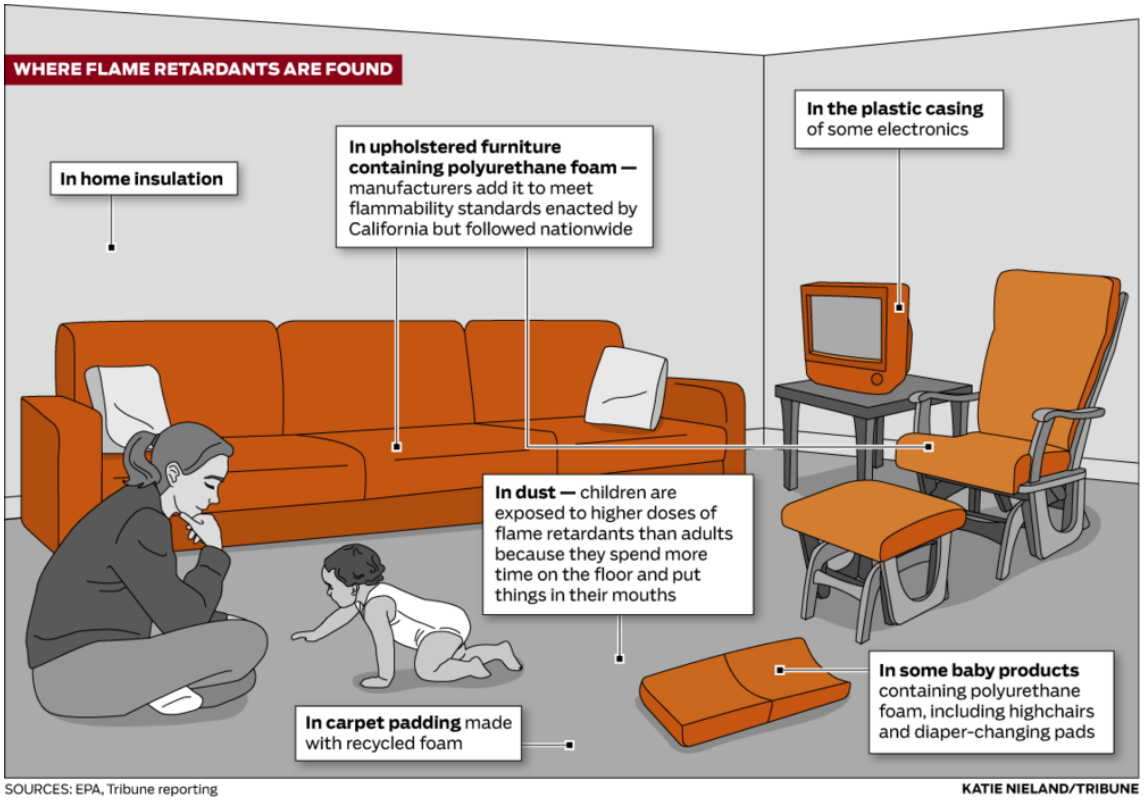


Source: M. Kobes, and K. Groenewegen - Ter Morsche, Consumer fire safety: European statistics and potential fire safety measures, Netherlands Institute for Safety Nibra, January 2009, p. 27.

Figure 1: First materials involved in fire

4. Textile selection

Within home textiles, flame retardants are found in several materials such as upholstered furniture (sofas, chairs…), bed clothing and beds, curtains/shades or carpets. Additionally, FR can also be found in other construction materials such as insulation, plastic casing for electronics or furniture foams.



After limiting the home textiles to four final applications, we can look into detailed compositions of those:

4.1 Upholstered furniture

Upholstery is usually made of a mixture of materials in order to provide comfy seating with the desired look and FR can be applied to all or some of those materials (covering material, interlining and filling material).

Upholstered furniture can come in a broad range of finishes of textiles and non-textiles (such as leather or synthetic leather/plastic). In case of synthetic leather the flame retardant will be added to the coating formulation.

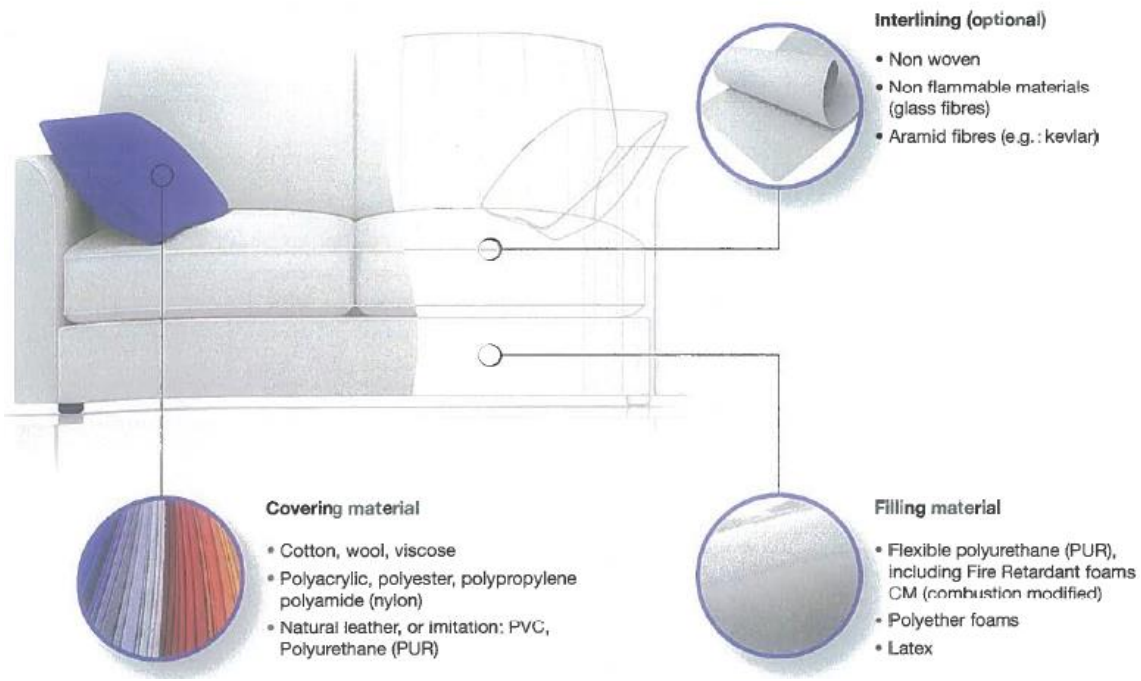


Figure 2: Source: EFRA, keeping fire in check,
An introduction to flame retardants used in upholstered furniture and textile applications

4.2 Bed clothing and mattress ticking

Bed clothing can come in multiple material compositions depending on the quality and the component (bed linen, bedding pack, cushions etc.). Mattress ticking can also be produced out of a variety of textiles, mostly blended to obtain the desired properties.

Most common textiles used are: cotton, polyester (PES), blends PES-CO, silk, linen, wool, lyocell, viscose, PP, PA or bamboo.

Bed clothing is made flame retardant via a padding procedure, while the mattress ticking is made flame retardant by either a padding treatment or a backcoating with an instable FR foam formulation. Another method to pass the flame retardant tests is to insert a non-flammable interlining (e.g. aramid) into the bed, thereby avoiding the application of flame retardant products on the ticking.

4.3 Curtains/shades

Curtains and shades, alike previous fabric applications, are produced out of different materials depending on the quality, look and usage. The desired light translucency also plays an important role in the choice of fabric.

Most common materials are: cotton, PES, wool, silk, viscose, linen, PA, PP, polyacrylic, jute, elasthane or even aramids.

In black-out curtains the flame retardant is incorporated into the applied coating, while the other FR curtains/shades underwent a flame retardant finish. Another option is the use of inherent flame retardant fibres like Trevira CS or aramids.

4.4 Carpets

Carpets, unlike previous described home textiles, are not made flame retardant via a padding treatment. Flame retardancy is obtained by adding flame retardants, mostly aluminium or magnesium hydroxide, in high loadings in the backing of the carpet. A latest trend is that manufacturers are investigating the possibility to produce flame retardants carpets by using pile materials which are made flame retardant during the extrusion process of PES, PP or PA.

Main materials used for carpets are PES, sisal, viscose, wool, PA, PP and flax.

4.5 Final selection of textile materials

The three textile fabrics selected, after detailed review in aforementioned sections, are:

- Polyester
- Cotton
- Blends PES-CO (polyester – cotton blends)

Those selections are based on the both literature review and as outcome of the deliverable A1.3 dealing with industry needs and practices survey.

Those three materials can be found on the targeted applications of bed clothing, mattress ticking, curtains/shades and upholstered furniture. Besides, while not relevant due to different flame retardant application method, a lot of carpets are also made of those materials.

Final characteristics of the fabrics such as end-use, density and finished knitted, woven or non-woven will be performed during activity B1 with inputs from companies involved in the demonstration phase in order to be able adapt to their industrial settings and facilitate their commitment.

5. Use of flame retardants

The last decades new, more combustible synthetic materials found their way in everyday life hence boosting the use of flame retardants (FRs). Regulation is also becoming more and more stringent, leading to an increase in their use. Textile can be given a FR finish via a foulard process, the FR can be added to a coating or can be incorporated into the yarn during the extrusion process.

Flame retardants can be found in diverse textile applications:

- Work clothing
- Firefighter and military apparel
- Institutional and commercial carpet, draperies and upholstery (contract market)
- Transportation (train, airplane, bus, boat: blankets, seatcovers, carpets)
- Bedding
- Professional racer's garment
- Sometimes children's nightwear (flame retardancy is generally met by choice of thermoplastic synthetic fabrics).

Flame retardants are also classified according to the durability of the flame retardant textile in 1) non-durable, 2) semi-durable and 3) durable. The desired durability will de depending of the final textile application.

1) Non-durable flame retardants are generally based on water-soluble salts such as ammonium phosphates, ammonium sulphate, boric acid and their combinations. They are only physically bonded to the fibre surface which makes the process relatively cheap and can be easily adjusted within the routine textile finishing sequence. These systems are generally applied to mattresses, draperies, theatre curtains which are rarely, if ever, washed, disposable goods such as disposable medical gowns, party costumes and sometimes wall covering.

2) Semi-durable flame retardants typically contain an acrylic binder and a melamine-formaldehyde resin and a curing step at high temperatures (130°C-160°C) is often introduced to allow the incorporation and interaction of the finish with the fibre, conferring some resistance to water soak and gentle laundering treatments such as dry cleaning. They are generally used for tents, carpets and curtains.

3) Durable flame retardants are a type of flame retardant materials that react covalently with the fibre or form cross-linked structures on the fibre. The flame retardant is incorporated into the polymer chain by co-polymerisation imparting washing, leaching and infant sucking durability. Among the durable flame retardants are organophosphorus and halogenated compounds.

6. Working principle of flame retardants

To understand the modes of action and classification of flame retardants it is essential to become familiar with the combustion process of polymer systems. This is schematically represented in Figure 1. The combustion process of polymeric substances takes place at four different stages: heating, volatilization or decomposition, combustion and propagation. Heating the organic material causes pyrolysis of the material (thermal break and disintegration). By this process, flammable substances (alkanes, hydrogen, CO, ...) are released. The composition and quantity of 'polymer fuel' is, of course, a function of the composition of the substrate and of the temperature of the pyrolysis process. These fuels start to burn in the presence of atmospheric oxygen and an ignition source. This process not only releases gases and particles (smoke, soot) in the environment, but also heat, acting in their turn on the non-affected material. Because of this formed heat, in principle, the combustion cycle can be further maintained until all combustible material is burned. The combustion reactions (reaction with oxygen) run mainly via a radical process.

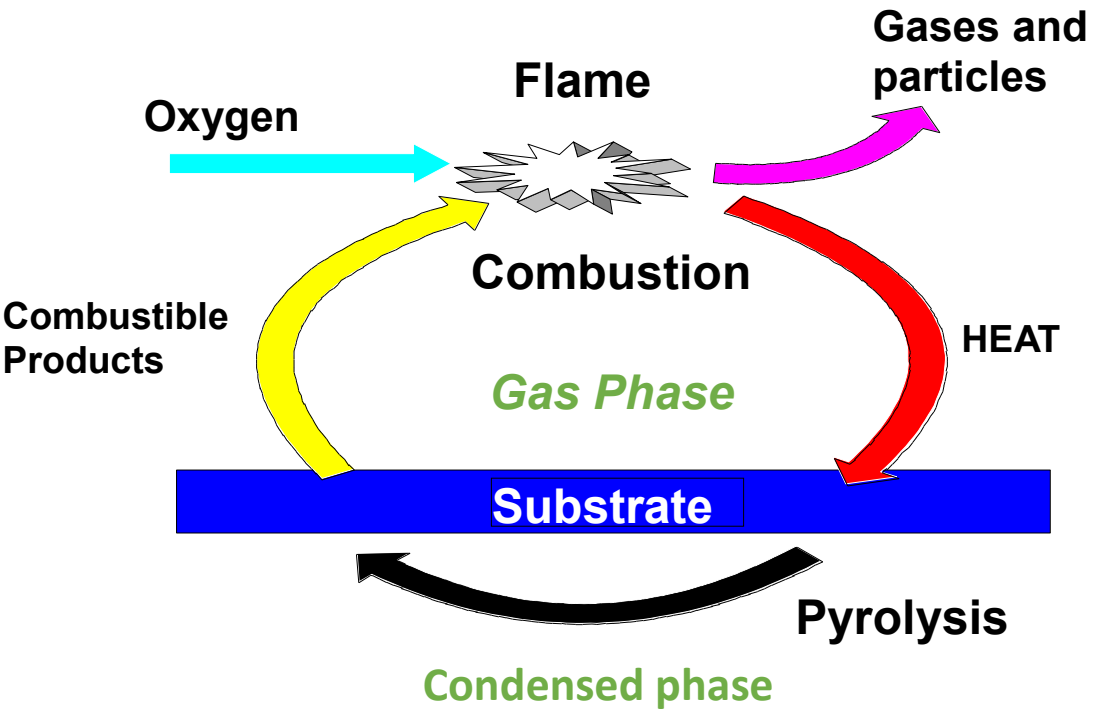


Figure 3. Combustion cycle (1).

Fire retardant products are applied to combustible materials to inhibit or suppress the combustion cycle. The FR-operation of the different systems can be reduced to their mode of action on 1) the gas phase (the top of the burning material) or on 2) the condensed phase (in the material and to the surface of the material) (2). However, most FR additives are not so selective as to act solely on the gas or condensed phase.

An effective FR-system should be functional at the correct moment (when the fire occurs) and in the right place (where the fire occurs). Depending on the fire test and the test material, an FR system may not act too early nor too late on the fire. In this context, an effective FR system includes a tailored formulation that takes the requirements of the fire safety standard into account and the composition of the material.

Flame retardants can be added to certain materials in order to meet the necessary fire safety standards, i.e. in order to withstand the relevant fire tests. Later the different burning behaviour tests will be discussed in more detail. A flame retardant is a material that prevents ignition, or once ignited, slows down the fire spread. The flame retardant should also minimise the smoke generation and prevent dripping of the matrix and should not lead to the formation of toxic gases.

The following processes are related to flame-retardants:

- removal of H and OH radicals,
- prevention of pyrolysis,
- formation of a protective layer on the material,
- formation of nitrogen or other non-combustible gases that expel the oxygen,
- production of water, allowing the burning or flammable object to be cooled and to remove heat (energy).

There are also flame retardants which synergistically combine these processes.

When the term "flame retardants" is used, people often do not realize that it is a large variety of substances with respect to physico-chemical properties, environmental fate, toxicology and legal status. Several products therefore require different solutions. Four different types of flame retardants can be distinguished: halogenated, phosphorous based, nitrogen based and others.

7. Classification of flame retardants

7.1. Halogenated flame retardants

The mechanism of halogenated flame retardants is based on the cleavage of the halogen atom as a radical that reacts with the free radicals which promote the fire in the combustion process.

Cleavage of the halogen atom

$$RX \rightarrow R^{\bullet} + X^{\bullet}$$

Formation of hydrogen halogenides

$$RH + X^{\bullet} \rightarrow HX + R^{\bullet}$$

Neutralisation of high energetic radicals

$$HX + H\bullet \rightarrow H_2 + X\bullet$$

$$HX + OH\bullet \rightarrow H_2O + X\bullet$$

During a fire, the halogenated flame retardant compounds (RX) decompose and release halogen radicals (R•, X•) which form hydrogen halogenides (HX) by abstracting hydrogen from the flame retardant or the polymer in the combustion zone. These halogen radicals react with the high-reactive radicals HO• and H• formed during the pyrolysis/decomposition of the polymer. The exothermic processes, which occur in the flame, are thereby stopped, the system cools down and the supply of flammable gases is reduced and eventually completely suppressed.

Two main classes of halogenated flame retardants can be distinguished, namely compounds with chlorine or bromine. The most efficient flame retardant is a compound with bromine, because it reacts faster than a compound with chlorine. The brominated FR compounds have a higher trapping efficiency and lower decomposing temperatures than their chlorinated counterparts.

Brominated flame retardants (BFRs) consist of five major classes: brominated bisphenols (not for skin contact), cyclododecanes, diphenyl ethers, phenols and phthalic acid derivatives. Especially, the first three classes represent the major production volumes, with the main representatives are respectively tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCDD, REACH annex XIV, not for textile) and polybrominated diphenyl ethers (PBDEs). The penta- and octa-BDE are already included in the annex XVII (REACH). The deca-BDE is registered as SVHC (Substances of Very High Concern) will be restricted from March 2019. Home textiles cannot contain more than 0.1 wt% deca-BDE.

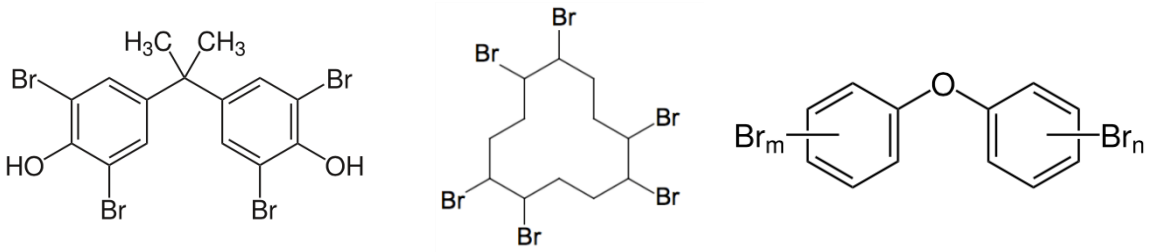


Figure 4: left) tetrabromobisphenol A; middle) hexabromocyclododecane; right) polybrominated diphenyl ethers

This group currently represents 50% of the total production volume of flame retardants. Because of their availability, high efficiency and attractive price/performance ratio, halogenated flame retardants are commonly used in textiles.

Compounds containing both halogens and phosphorus like tris(1,3-dichloro-2-propyl) phosphate are also on the market (PU foam, tents). Compounds like tris(2-chloroethyl)

phosphate (TCEP) were used in the past but are not allowed to be used in home textile since 2015 (Annex XIV).

Halogenated FRs are synergized by antimony trioxide Sb_2O_3 (ATO). Halogenated FRs in the presence of antimony trioxide gives rise to the formation of the flame-quenching antimony trichloride or tribromide which trap the high-energy radicals in the combustion zone which feed the flame phase of the fire (chemical gas phase mode of action), thus reinforcing the flame suppressing effect of the halogenated flame retardants. Because of this high synergetic effect it is also used for reducing the amount of additives and/or halogenated flame retardant agent to be used but it is costly and do not meet the criteria for PBT and or vPvB (very persistant and very bioaccumulative substances).

A low priced commodity FR additive is **decabromodiphenyl ether** (deca-DBE, Figure 5 left), which has a good overall performance and good thermal stability. The use of this product diminishes because it is registered on the SVHC list and will be restricted in 2019 (REACH, Annex XVII). A substitute which is more and more applied is the decabromodiphenyl ethane (DBDPE, Figure 5 right) which is an easy drop-in for deca-BDE.

Other largely used brominated FRs are tetrabromobisphenol A (TBBPA), tetrabromobisphenol A bis(2-hydroxyethyl ether) (TBBPA DHEE) and ethylene bis-(tetrabromophthalimide)

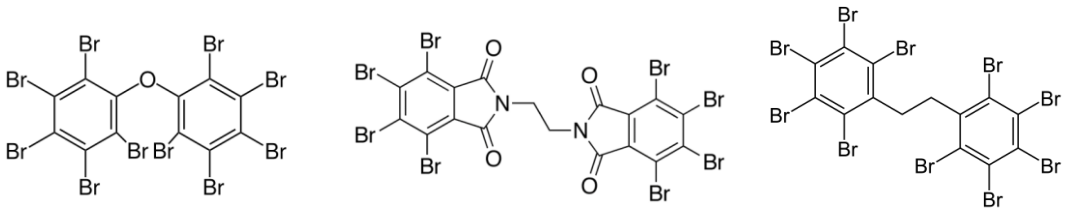


Figure 5: left) decabromodiphenyl ether; middle ethylene bis-(tetrabromophthalimide), right) decabromodiphenyl ethane

Halogenated flame retardants are inexpensive and provide high flame retardant properties and efficiency at low doses without decreasing mechanical properties. However they present health and environmental problems since most of them are not covalently bound to the products they are applied to and the potential for volatilization or leaching from products over time is significant. Furthermore, these flame retardants convert into dioxins and furans when burned which are long lived, toxic and build up in the body overtime. These substances were used for 30 years though most of them were phased out or banned worldwide in the last decade and others are under scrutiny. This has led to the development of new brominated-polymeric compounds with higher molecular weight and less environmental and health associated problems, increase on the production and use of organophosphorus and inorganic compounds (3), silicone based multi-elements materials, developments of new solutions based on amongst others nanomaterials.

Polymeric brominated compounds have been developed in the last years. Because of their polymeric structure and high molecular weight they do not leach to the environment, are washable and show good flame retardant properties. Dow developed and marketed a new polybrominated (PolyFR) flame retardant as a replacement of HBCDD through three licenses to Chemtura (Emerald Innovation 1000 and 3000), to Albemarle (Saytex HP-310 and GreenCrest®) and to ICL (FR-122P and TexFRon® series) (4).

Brominated FR products are more effective than **chlorinated paraffins**, the latter having the benefit of low cost, ease of processing and substantial lack of blooming. The high chain length paraffins (LCCPs) tend to be limited by their stability, up to about 230°C, which allows their use in polyolefins and rubber (elastomers). The use of short chain chlorinated paraffins (SCCPs) is forbidden due to their bio-accumulative, persistent and toxic behaviour.

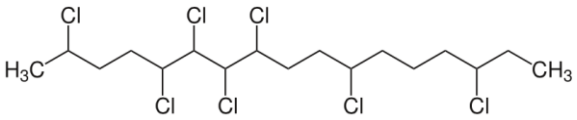


Figure 6: chlorinated paraffin

7.2. Phosphorous based flame retardants

During a fire phosphorus based flame retardants will form poly-phosphoric acids and meta-phosphoric acids (phosphoric acids ring-shaped), which form an oxygen-barrier layer. They are classified in phosphates, phosphonates, phosphinates, phosphazenes and phosphonium salts. They are most effective when they are in the highest oxidation state (P^{+5}, being phosphate (P^{+5}) > phosphonate (P^{+3}) > phosphinate (P^{+1}) > phosphonium salts (P^{-3}).

The characteristics of P-based flame retardants are:

- low water solubility
- low volatility
- often effective in low doses
- degradation to possibly hazardous substances
- danger of toxic emissions of monophosphate

Phosphorus compounds are quite commonly used. This group represents 20% of the total production of flame retardants.

7.2.1. (Poly)phosphates

Organophosphorus compounds are oxygen-containing char-forming products mainly used in polymers like PU, PA, PET or epoxies. During a fire the phosphorus component

breaks down to phosphorus acid, which can attack the oxygen functionality of the polymer, leading to char. Lots of products are commercially available based on organophosphorous compound, but mostly their structure is proprietary. Examples are isopropyl phosphate (IPP), isopropylated triphenyl phosphate (IPPP), triphenyl phosphate (TPP), resorcinol bis(diphenyl phosphate) (RDP), diphenyl phosphate (BADP), tricesyl phosphate (TCP) and tributyl phosphate (TBP).

A widespread FR is ammonium (poly)phosphate (APP). It is used for cotton in combination with urea or guanylurea salt of phosphoric acid. Ammonium polyphosphate, sometimes combined with pentaerythritol and/or melamine, is often used in backcoatings. A semi-durable finish for cotton is produced this way.

Other well-known compounds are melamine and guanidine phosphate (semi-durable finish of cellulose), cyanoguanidine salt of methylphosphonic acid, and ethylenediamine phosphate, which are self-intumescent. Also resorcinol diphosphate and bisfenol A diphosphate are often used in coatings.

7.2.2. Phosphonates

Phosphonates, mostly diphosphonates, are applied via the thermosol process (padding). After drying the fabric undergoes a high temperature treatment (190°C-210°C) which opens up the fibre so the FR can migrate into the fibre, which improves washability. They are mainly used for polyester fabrics.

PES is for example treated with the molecule below:

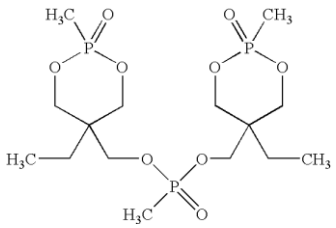


Figure 7: FR for PES

7.2.3. Phosphinates

The aluminium salt of diethylphosphinate is used as intumescent FR in latex and dispersions used in textile.

7.2.4. Proban

The Proban treatment is based on tetrakis(hydroxylmethyl)phosphonium salts (for example tetrakis(hydroxymethyl)phosphonium chloride salt, THPC, and

tetrakis(hydroxymethyl)phosphonium sulphate) which are reacted with urea and applied to the textile and dried. Then crosslinking of the flame retardant formulation on the cotton fibres is done via an ammonia treatment, which can be done in an ammonia chamber. Finally an oxidation is needed (e.g. hydrogen peroxide) which makes it resist up to 100 laundry cycles giving rise to a very durable flame retardant with suitability for cotton and cotton/polyester blends. In contact with a flame charring occurs and the fabric does not melt or spread the flame.

7.2.5. Red phosphorus

Red phosphorus is a thermodynamically stable high-polymer form of phosphorus and is the most effective (by weight) phosphorus flame retardant. It has a complex mode of action: most likely it depolymerises to white phosphorus, which partially evaporates and acts as a gas phase inhibitor. It also partially reacts with certain polymers like polyamide and enhances char formation. It is widely used as a synergistic agent in many kinds of polymer matrices such as cotton, polyesters, polyurethanes and polyamides. A drawback is the red-purple colour, which limits usage in certain applications. The problems with safety and stability (red phosphorus is flammable as a powder and its used in textiles was minimal due to irritability to the skin and the evolution of corrosive phosphoric acids) have been overcome by the commercially availability of masterbatches or coated red phosphorus powder.

7.3. Nitrogen based flame retardants

Nitrogen-based flame retardants have limited flame retardant effect by themselves and are often used in combination with other flame retardants, in particular, phosphorus based flame retardants. Due to the formation of molecular structures, the further decomposition of the material is prevented. In addition, N_2 is expelled that dilutes the fire gases.

Characteristics:

- high efficiency in polyamides
- in certain polymers strong P / N synergistic effect
- possible formaldehyde emissions

This group represents 10% of the total production of flame retardants.

7.3.1. Melamine and its derivates

Nitrogen containing FRs are mostly based on melamine, which has a melting point of 354°C. Far below this melting point, already at 200°C, melamine starts to vaporize or

sublimate, thereby diluting the fuel gases and oxygen in the combustion zone. This sublimation process, and later on the decomposition, is endothermic, which cools down the polymer.

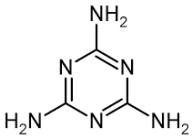


Figure 8: Chemical structure of Melamine

Several melamine derivatives are on the market:

Melamine cyanurate is more stable than the melamine on its own and has the property that it enhances dripping of the polymer. Thereby the polymer subtracts itself from the ignition source before catching fire.

Melamine (poly)phosphate. Melamine monophosphate is a salt of melamine and phosphoric acid which releases water at 200°C and 260°C, which results in heat sinks. During this dehydration process, polyphosphate is formed. Melamine polyphosphate undergoes endothermic decomposition at 350°C, thereby cooling the system. The released phosphoric acid acts to coat and thereby shield the condensed polymer. The phosphoric acid also interacts with the polymer to form a layer of char around the polymer. The released melamine also acts as a blowing agent. The formed carbonaceous material is blown up resulting in an intumescent behaviour.

7.3.2. Hindered amines

N-substituted hindered amines are mostly added in the polymer matrix as stabilizers in order to avoid light-induced polymer degradation. Some of these compounds also have a flame retardant activity; they dissociate to free radicals upon heating which leads to a gas phase mode of action. The melt flow of the polymer is also affected, benefiting the flame retardant action. They show a synergistic effect with many other kinds of flame retardants.

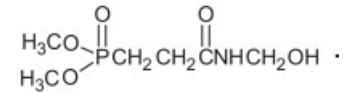
7.3.3. Thiourea-formaldehyde oligomers

The precondensate is applied to nylon under acidic conditions in a padding system. It stimulates melt flow and dripping and due to binding to the nylon it become fairly wash-durable.

7.4. Nitrogen/phosphorous based flame retardants

7.4.1. Pyrovatex

The main component of the Pyrovatex treatment is N-methylol dimethylphosphonopropionamide. To enhance the fixation onto cellulose tri(or tetra or penta)methylolmelamine is added. Low formaldehyde grades have been developed. The treatment is wash durable (up to 50 cycles).



N-Methylol dimethylphosphonopropionamide

Other examples of N/P compounds are ethylene diamine phosphate as intumescent char former or ammonium polyphosphate can also be categorised as N/P flame retardant.

7.5. Other types of flame retardants

7.5.1. Inorganic endothermic flame retardants (5)

Inorganic flame retardants are mostly metal hydroxides like aluminium hydroxide (ATH) or magnesium hydroxide (MDH). During fire, they are converted from metal hydroxides into metal oxides and water molecules. The water molecules ensure that the oxygen concentration around the burning material is lowered and flammable gases are diluted, diminishing the fire intensity. Moreover, the reaction is endothermic, resulting in heat extraction from the fire. The metal oxide forms a layer on the non-combustible material.

Example:

$2Al(OH)_3$ (heated at 300°C) → Al_2O_3 + 3 H_2O (formation oxide layer and water)

$Mg(OH)_2$ (heated at 200°C) → MgO + H_2O

Characteristics:

- Economically attractive: low price
- Ecologically attractive: low toxicity
- Because of the low efficiency, a high loading is required (± 60% or more) which results in poor mechanical properties, limited possibilities for yarn extrusion, incompatibility with the softness of textile.

This group represents 20% of the total production of flame retardants. They are approached as ‘minerals’ instead of ‘chemicals’ and they generate less smoke and no acidic gases.

7.5.1.1. ATH

Aluminium trihydroxide - $Al(OH)_3$ starts to decompose at a temperature just above 200°C and by reaching 300°C anhydrous alumina is formed. It is available in a wide range of particle sizes. In the textile industry ATH is mainly used in contract carpeting. ATH needs to be incorporated in high loading which can impair the mechanical and electrical properties of the polymer. ATH is for example employed in acrylic rubbers and moulding, thermosetting resins, thermoplastic cable sheathing and PVC flooring.

7.5.1.2. MDH

Magnesium dihydroxide - $Mg(OH)_2$ is comparable to ATH but is thermally more stable (up to 330°C). MDH is used in comparable applications as ATH.

7.5.1.3. Ultracarb

Ultracarb is a mixture of huntite and hydromagnesite. It releases both water and carbon dioxide when heated. It has the same physical properties as ATH but has a better thermal stability. It reacts at 230°C, with minor loss, while the majority of the reaction takes place at 420°C-550°C.

7.5.1.4. Talc

Talc is natural magnesium silicate. It has a lamellar structure and upon heating, it forms a mass transfer barrier, shielding the polymer. It is used to reinforce polymers, improve their stiffness, dimensional stability or processability.

7.5.1.5. Boron compounds

Boric containing (borax and its mixture with boric acid) compounds act by the stepwise release of water and by the formation of a glassy coating protecting the surface. The mixtures of boric acid and borax are used for cellulosic textiles.

7.5.2. Expandable graphite

Expandable graphite is granular graphite in which sulphuric acid has been introduced between the layers of the graphite structure with some oxidation of the carbon. The acid is tightly held and does not leach out. Grades are available with an acidic or neutral character. During a fire, the graphite expands very quickly to over 100 times its original volume, resulting in a heat and mass transfer barrier. This effect is visible in almost any thermoplastic, and is sometimes used in combination with other flame retardants like ammonium polyphospate (APP).

7.5.3. Nanocomposites

In addition to the conventional flame retardants mentioned above, nanotechnology is a growing market. Nanotechnology has the advantage that through the larger specific surface of the particles, lower concentrations may be dosed, which possibly could provide a solution to the limitations of the present additives. Some examples of nano-additives that exhibit flame retardant properties are nano-MgO, polyhedral oligomeric silsesquioxane (POSS), graphene, carbon nanotubes (CNT) (6) or nanoclay.

In this class, several types of **natural clays** are used, e.g. montmorillonite. They act as non-combustible fillers and are generally used in combination with other flame retardants, hence leading to a reduction of the overall amount of flame retardants added to the polymer which has a positive effect on the specific gravity of the polymer.

Materials like **carbon nanotubes** and **carbon nanofibres** favour the formation of a strong coherent char and thus can provide improved fire performance. They are used in combination with ATH or MDH.

7.5.4. Borates

Zinc borate, mostly used in combination with ATO, releases water with heat absorption at 325°C and forms a barrier. It can lead to the formation of the undesired boric acid, which can be avoided by the use of calcium or barium borate. Sodium borate (borax) is used to flame retard cellulose.

7.5.5. Zirpro treatment

Wool can be treated with hexafluorozirconate to improve the flame retardancy via intumescence. Synergy with tetrabromophthalic acid and salts is proven.

8. Selected Flame Retardants materials.

Three harmful and six non harmful flame retardant finishing materials have been selected for their application to Cotton, Cotton/Polyester blends and Polyester textile substrates that are found within the home textile sector and which comprises selected applications: 1) bed clothing, 2) curtains/shades and 3) upholstery for home furniture (sofas, chairs, beds, mattresses, stools, etc).

Table 5. *Three selected harmful Flame retardant materials.*

Selected Harmful Flame Retardant materials			
Chemical nature/structure	**Health and environmental comments**	**Textile applied to:**	**Application**
1) **Formaldehyde generation** **Dialkyl phosphono carboxylic acid amide**	-Products may release formaldehyde during processing.	-Cellulose fibers. -Cellulosic /Polyester fibre blends (up to 25%). -Polyester.	Depending on pyrovatex selected*: Decorative fabrics, curtains, upholstery and sun shades. -Pad application.
2) **Halogen based** **Hexabromo cyclododecane** (HBCDD) CAS 3194-55-6 **2´)** **or similar (priority FR within the Candidate list to be substituted)**	2) -Classified as PBT. -Included in Candidate list as SVHC and in the authorisation list (Annex XIV). -Production: 10.000-100.000 ton.	-Cotton.	-Backcoatings. -Polystyrene foam and textile adhesives and coatings.
3)	3) -Classified as PBT and SVHC.	-Cotton.	-Backcoatings.

Halogen based + ATO **Hexabromo cyclododecane + ATO** (HBCDD) CAS 3194-55-6 **3´)** **or similar**	-Included in Candidate list as SVHC and in the authorisation list (Annex XIV). -Production: 10.000-100.000 ton.		-Foam coatings and finishing of mattresses, upholstery, curtains and blinds.

Table 6. *Six selected non-harmful Flame retardant materials*.

Selected Non Harmful Flame Retardant materials			
Chemical nature	**Health and environmental comments**	**Textile applied to:**	**Application**
1) **Inorganic** **Aluminium tri-hydroxide** (ATH) CAS 21645-51-2	-Low toxicity.	-To be used in PVC, latex, or EVA back-coatings in polyamide or polyester carpets.	Carpet backing. To be used in PVC and latex back-coatings of polyamide or polyester carpets. Textile backcoatings of upholstered furniture (chairs and sofas).
2) **P-, N- based** **Ammonium polyphosphate** (water soluble, non water soluble)	-OEKO-TEX® label depending on grade.	-Cotton, -Cotton rich blends.	-Back-coatings for upholstery fabrics. -Curtains.

3) **Organic phosphorus and nitrogen compound** **Tetrakis (hydroxymethyl) phosphonium chloride (THPC) reacted with urea and crosslinked with ammonia.**	-OEKO-TEX® Standard 100 certified. -Meets EU ECO label.	-Cotton. -Cotton/ Polyester blends.	-Pad-dry-cure.
4) **Nitrogen and Sulfur based** **Ammonium sulfamate** & Cocamidopropyl betaine CAS 7773-06-0	-contains no REACH substances with Annex XVII restrictions, nor substance on the REACH candidate list, no REACH Annex XIV substances.	-Cellulosic textiles and blends.	-Backcoating or impregnation. -Mattress ticking and other textile applications that can be applied by foam coating.
5) **P- based** **Alkyl phosphonate**	-OEKO-TEX® Standard 100 certified.	-Polyester, - Polyester/ Polyamide blends.	-Decorative articles, upholstery, blinds, wall coverings, room dividers, bedding, workwear, automotive textiles. Pad process.
5´) **P- based** **Reactive organo phosphorus compound.**	-OEKO-TEX® Standard 100 certified. Product class I-IV.	-Cellulosic textiles. -Cellulosic/ synthetic blends (synthetic portion up to15 %).	-Workwear, children´s pyjamas, home textiles, military purposes. -Pad process.
6) **Under development:**	-	**1), 2), 3)** for -Cotton.	

1) Short tangled Multi-walled Carbon Nanotubes (MWCNTs) embedded in vynil silicone polymer (CAS 68083-19-2), **2)** Montmorillonite clay, **3)** POSS		-Polyester.	**1)** CNT silicone FR coatings for textile & foams. **2)** and **3)** Used with PU binder for textile coating.

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