Guidance on flame-retardant alternatives to pentabromodiphenylether (PentaBDE)

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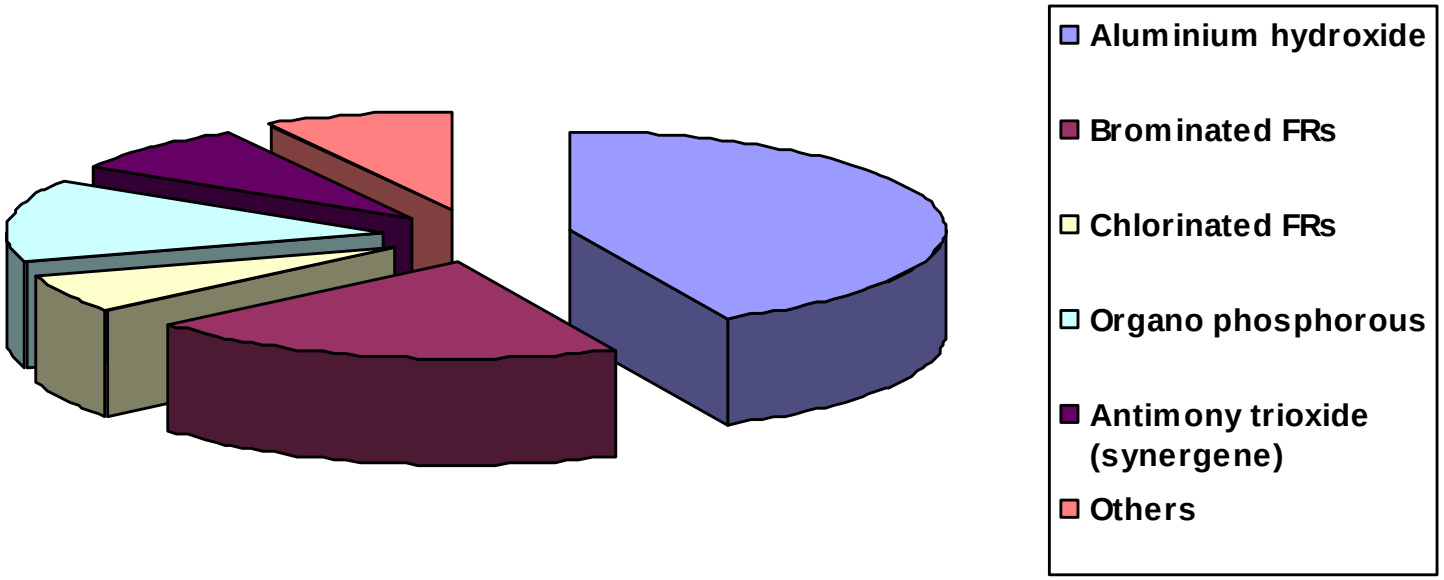
The global flame retardant market

With the increasing use of thermoplastics and thermo sets on a large scale for applications in buildings, transportation, electrical engineering and electronics, a variety of flame-retardant systems have been developed over the past 40 years.

Flame retardants mainly consist of inorganic and organic compounds based on bromine, chlorine, phosphorus, nitrogen, boron, and metallic oxides and hydroxides.



Background for the guidance document

- In 2005 Norway nominated the brominated flame retardant pentabromodiphenylether (PentaBDE) as a persistant organic pollutant (POP) to be evaluated for inclusion in the Stockholm convention.
- Based on the Risk Profile developed in 2006 and the Risk Management Evaluation Report developed in 2007 the POP Review Committee (POPRC) concluded that global action on PentaBDE is warranted.
- At the POPRC meeting in November 2007 Norway was commissioned to issue a guide of alternative flame retardants to PentaBDE.
- The Norwegian Pollution Control Authority (SFT) has therefore commissioned Swerea IVF (Sweden), to perform this guide that is presented here today.

Components of commercial PentaBDE (C-PentaBDE)

Categories of PBDEs	Tridiphenyl ethers		Tetradiphenyl ether	Pentadiphenyl ethers		Hexadiphenyl ether	Heptadiphenyl ether
Congeners	**BDE-17**	**BDE-28**	**BDE-47**	**BDE-99**	**BDE-100**	**BDE-153**	**BDE-154**
Content	Traces	Traces	Major	Major	Minor	Minor	Traces

Based on the information in the risk profile, PentaBDE, due to the characteristics of its components, is likely, as a result of long-range environmental transport and demonstrated toxicity in a range of non-human species, to cause significant adverse effects on human health or the environment, such that global action is warranted.

Historic use of C-PentaBDE

Materials/polymers/resins	Applications	Commercial commodities for the applications
Epoxy resins	Circuit boards, protective coatings	Computers, ship interiors, electronic parts.
Polyvinylchloride (PVC)	Cable sheets	Wires, cables, floor mats, industrial sheets.
Polyurethane (PUR)	Cushioning materials, packaging, padding	Furniture, sound insulation packaging, padding panels, wood imitations, transportation.
Unsaturated (Thermoset) polyesters (UPE)	Circuit boards, coatings	Electrical equipment, coatings coatings for chemical processing plants mouldings, military and marine applications: construction panels.
Rubber	Transportation	Conveyor belts, foamed pipes for insulation.
Paints/lacquers	Coatings	Marine and industry lacquers for protection of containers
Textiles	Coatings	Back coatings and impregnation for carpets, automotive seating, furniture in homes and official buildings, aircraft, underground.
Hydraulic oils	Drilling oils, hydraulic fluids	Off shore, coal mining

Note: PBDEs are used in different resins, polymers, and substrates at levels ranging from 5 up to 30% by weight

Selection criteria for flame retardants

Like any other additives, a flame retardant will be selected for the particular properties it imparts to make it satisfy the specifications for the final compound established by the customer;

- Fire retardant properties
- Mechanical properties
- Physical properties
- Health and environmental properties
- Commercial viability

The variety of alternative flame retardants

New flame retardant solutions are constantly introduced and some disappear from the market for a number of reasons.

Therefore the overview of alternative flame retardants to C--PentaBDE, presented on the next coming slides, is a on-the-spot account and cannot be complete.

The overview only act as a guide that illustrates the variety and optional chemical systems that are available and actually work as viable alternatives to C-PentaBDE.

It needs to be clearly understood that each flame retardant application is specific and unique, and there are no single universal solutions for fire protection of materials and applications.

Alternative flame retardants for epoxy resins

Materials/ polymers/ resins	Inorganic alternatives to PentaBDE	Phosphorous/ nitrogen organic alternatives to PentaBDE	Halogen organic alternatives to PentaBDE	Alternative flame inherent materials	Applications	Commercial commodities for the applications
Epoxy resins	Aluminium hydroxide (ATH) Magnesium hydroxide Ammonium poly phosphate Red phosphorous Zinc hydroxystannate (ZHS), Zinc stannate (ZS) & ZHS/ZS-coated ATH	Metallic phosphinates Reactive nitrogen anc phosphorous constituents (unspecified) DOPO[1]	Tetrabromobis phenol A (reactive) Etylenebis (tetrabromo) phtalimid	Polyethylene sulphide	Circuit boards, protective coatings	Computers, ship interiors, electronic parts.

N/A : not available or not applicable

[1] DOPO=Dihydrooxaphosphaphenanthrene oxide

Alternative flame retardants for PVC

Materials/ polymers/ resins	Inorganic alternatives to PentaBDE	Phosphorous/ nitrogen organic alternatives to PentaBDE	Halogen organic alternatives to PentaBDE	Alternative flame inherent materials	Applications	Commercial commodities for the applications
Polyvinylchloride (PVC)	Aluminium hydroxide (ATH) Zinc borate Zinc-molybdenum compounds (together with phosphate esters) Zinc hydroxystannate (ZHS), Zinc stannate (ZS) & ZHS/ZS-coated ATH	Tricresyl phosphate (also plasticizer)	Tris (dichloropropyl) phosphate Vinylbromide	Rigid PVC is flame inherent itself	Cable sheets	Wire end cables, floor mats, industrial sheets.

N/A : not available or not applicable

Alternative flame retardants for PUR

Materials/ polymers/ resins	Inorganic alternatives to PentaBDE	Phosphorous/ nitrogen organic alternatives to PentaBDE	Halogen organic alternatives to PentaBDE	Alternative flame inherent materials	Applications	Commercial commodities for the applications
Polyurethane (PUR)	Ammonium poly phosphate Red phosphorous Reofos (non-halogen flame retardant)	Melamine (nitrogen based) Dimethyl propane phosphonate (DMPP)	Bromoalkyl phosphates Tetrabromophtalic anhydride Tris(chloroethyl) phosphate (TCPP) (together with brominated polyols or red phosphorous)	Intumescent systems	Cushioning materials, packaging, padding	Furniture, sound insulation packaging, padding panels, wood imitations, transportation

N/A : not available or not applicable

Alternative flame retardants for UPE

Materials/ polymers/ resins	Inorganic alternatives to PentaBDE	Phosphorous/ nitrogen organic alternatives to PentaBDE	Halogen organic alternatives to PentaBDE	Alternative flame inherent materials	Applications	Commercial commodities for the applications
Unsaturated (Thermoset) polyesters (UPE)	Ammonium polyphosphate Aluminium hydroxide (ATH) Magnesium hydroxide Zinc hydroxystannate (ZHS), Zinc stannate (ZS) & ZHS/ZS-coated ATH	Triethyl Phosphate Dimethyl propane phosphonate (DMPP)	Dibromostyrene Tetrabromophtalic anhydride based diol, Tetrabromophtalic anhydride Bis (tribromophenoxy) ethane	Intumescent systems	Circuit boards, coatings	Electrical equipment, coatings coatings for chemical processing plants mouldings, military and marine applications: construction panels.

N/A : not available or not applicable

Alternative flame retardants for rubber, paints and lacquers

Materials/ polymers/ resins	Inorganic alternatives to PentaBDE	Phosphorous/ nitrogen organic alternatives to PentaBDE	Halogen organic alternatives to PentaBDE	Alternative flame inherent materials	Applications	Commercial commodities for the applications
Rubber	N/A	Alkyl diaryl phosphates (nitril rubber)	N/A	Intumescent systems	Transportation	Conveyor belts, foamed pipes for insulation.
Paints/lacquers	N/A	Triaryl phosphates (unspecified)	Tetrabromo phthalate diol Tetrabromophtalatic anhydride based diol Bis (tribromophenoxy) ethane	Intumescent systems Silicone rubber	Coatings	Marine and industry lacquers for protection of containers

N/A : not available or not applicable

Alternative flame retardants for textiles

Materials/ polymers/ resins	Inorganic alternatives to PentaBDE	Phosphorous/ nitrogen organic alternatives to PentaBDE	Halogen organic alternatives to PentaBDE	Alternative flame inherent materials	Applications	Commercial commodities for the applications
Textiles	Aluminium hydroxide Magnesium hydroxide Ammonium compounds (unspecified) Borax	Tetrakis hydroximethyl phosphonium salts such as chloride (THCP) or ammonium (THPX) Dimethyl phosphono (N-methylol) propionamide Diguanidine hydrogen phosphate	Trichloropropyl phosphate	Intumescent systems Aramide fibres (certain protective applications) Wool Modacrylic	Coatings	Back coatings and impregnation for carpets, automotive seating, furniture in homes and official buildings, aircraft, underground.

N/A : not available or not applicable

Alternative flame retardants for textiles (cont..) and hydrualic oils.

Materials/ polymers/ resins	Inorganic alternatives to PentaBDE	Phosphorous/nitrogen organic alternatives to PentaBDE	Halogen organic alternatives to PentaBDE	Alternative flame inherent materials	Applications	Commercial commodities for the applications
Textiles cont.		Aromatic phosphates (unspecified) Dimethyl hydrogen phosphite (DMHP) Melamine (nitrogen based) Phosphonitrilic chloride (PNC)				
Hydraulic oils	N/A	Butylated triphenyl phosphate esters	N/A	N/A	Drilling oils, hydraulic fluids	Off shore, coal mining

N/A : not available or not applicable

Health and environmental properties of alternative flame retardants to PentaBDE (1/3)

Since there is a lack of data on health and environmental properties, it is not always possible to perform a comprehensive comparison of all known flame retardant systems.

Chemical	Toxicological properties	Ecotoxicological properties	Comments
Inorganic flame retardants and synergists			
Aluminium hydroxide	Low concern	Low concern	Ecotox: Few data available
Magnesium hydroxide	Low concern	Low concern	Tox and ecotox: few data available
Red phosphorous	Non toxic in pure form Low concern	Very toxic to aquatic organisms	Highly flammable and May form toxic phosphine gas during combustion in combination with moisture.
Ammonium poly phosphate	Insufficient data for assessments	Insufficient data for assessments	May be slightly irritating to skin

Health and environmental properties of alternative flame retardants to PentaBDE, (2/3)

Chemical	Toxicological properties	Ecotoxicological properties	Comments
Inorganic flame retardants and synergists			
Zinc borate	High concern on zinc toxicity	High acute aquatic toxicity	Limited tox and ecotox data available
Boron compounds other than zinc borate, *(Borax and disodium tetra borate)*	Moderate concern due to 2-generation reproductive/developmental effects	Limited data available	Limited tox and ecotox data available
Antimony trioxide	Ranked as possible carcinogen by IARC[1] and EU	Low concern	May produce toxic or irritating vapours during combustion conditions
Zinc hydroxystannate & Zinc stannate	Low concern	Low concern	Very low acute toxicity. Very low aqueous solubility

[1]IARC – **I**nternational **A**gency for **R**esearch on **C**ancer

Health and environmental properties of alternative flame retardants to PentaBDE (3/3)

Chemical	Toxicological properties	Ecotoxicological properties	Comments
Organophosphorous flame-retardants			
Triethylphosphate	No data available	No data available	
Aryl phosphates	Low concern	A few compounds show high acute aquatic toxicity	
Halogen containing phosphorous compounds	A few compounds show moderate reproductive toxic properties	A few compounds show moderate or high persistence and acute aquatic toxicity	
Tris (2-chloro-1-methylethyl) phosphate (TCPP or TMCP)	Concern	Low concern	Subject to risk assessment in the EU under the 4th Priority List Will be transferred to REACH
Reactive phosphorous	No data available	No data available	
Nitrogen based organic flame-retardants			
Melamine	Low concern	Low concern	Allergic dermatitis has been reported among workers

Example of costs related to substitution of C-PentaBDE in flexible PUR foam

Not only the technical and environmental properties are important for feasibility of flame retardant systems, but also that they are commercially available and cost efficient.

The table below illustrates an example of a market cost comparison for flame retarded flexible PUR-foam that contain C-PentaBDE in combination with organophosphorous substances and another flexible PUR foam that contain tris (2-chloro-1-methylethyl) phosphate (TCPP).

Application	Content of FRs	Cost of flame retarded PUR per kg	Comments
Flexible PUR foam	10% PentaBDE in addition to approx 2% inexpensive organophosphorous substances	Approx 0,70 € per kg PUR	Price for PentaBDE was set to 6 € per kg, by 2005 when it was phased out in EU
Flexible PUR foam	20% TCPP	Approx 0,35 € per kg PUR	Present price of TCPP is 1,80 € per kg

Conclusions

- The objective of this report has been to review possible alternatives to PentaBDE.
- The available data illustrate that there are alternative flame retardants commercially available which are less hazardous than C-PentaBDE.
- It should be the overall target to replace harmful substances with safer options, but it is also important to point out that the alternative flame retardants presented need to be evaluated based on their range of application.
- A case by case assessment will be necessary to find the best suitable alternative for a specific use.
- The data presented in this report are just suggestive and not conclusive, and it is crucial to search for further health and environmental data to get a better understanding of toxicological and ecotoxicological effects of the alternatives presented.

Appendix

Some commercial flame retardant systems

Albemarle Corporation	**Ameribrom, Inc. (ICL Industrial Products)**	**Great Lakes Chemical Corporation (now Chemtura)**	**Supresta (Akzo Nobel)**
SAYTEX® RX-8500 *Proprietary reactive brominated flame retardant, proprietary aryl phosphate, triphenyl phosphate* *CAS 115-86-6*	FR 513 *Tribromoneopentyl alcohol* *CAS 36483-57-5*	Firemaster® 550 *Proprietary halogenated aryl esters, proprietary triaryl phosphate isopropylated, triphenyl phosphate*	Fyrol® FR-2 *Trs(1,3-dichloro-2-propyl) phosphate* *CAS 13674-87-8*
SAYTEX® RZ-243 *Proprietary tetrabromophthalate, proprietary aryl phosphate, triphenyl phosphate*		Firemaster® 552 *Proprietary halogenated aryl esters, proprietary triaryl phosphate isopropylated, triphenyl phosphate*	AB053 *Tris(1,3-dichloro-2-propyl) phosphate*
ANTIBLAZE® 195 *Tris(1,3-dichloro-2-propyl) phosphate* *CAS 13674-87-8*			AC003 *Proprietary organic phosphate ester, triphenyl phosphate*
ANTIBLAZE ® 205 *Proprietary chloroalkyl phosphate, aryl phosphate and triphenyl phosphate*			AC073 *Proprietary aryl phosphates, triphenyl phosphate*

Some commercial flame retardant systems cont…

Albemarle Corporation	**Ameribrom, Inc. (ICL Industrial Products)**	**Great Lakes Chemical Corporation (now Chemtura)**	**Supresta (Akzo Nobel)**
ANTIBLAZE® 180 *Tris(1,3-dichloro-propyl) phosphate* *CAS 13674-87-8*			Fyrquel 150, Fyrquel 220, and Fyrquel 300 *Butylated triphenyl phosphate esters*
ANTIBLAZE® V-500 *Proprietary chloroalkyl phosphate, aryl phosphate and triphenyl phosphate*			
ANTIBLAZE® 182 *Proprietary chloroalkyl phosphate, aryl phosphate and triphenyl phosphate*			
ANTIBLAZE®TL10ST (proprietary chlorophosphate) *CAS # propietary mixture*			

Principal mechanism for intumescent systems