Searching for safe Flame Retardants – an update on regulatory status and environmental assessments

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The Global Flame Retardants Market

- Worldwide consumption of FRs ca. 2 Million tons a year ~ 5 billion USD.
- Non-halogen products already have a large share and are growing.
- Will continue to grow at a global annualized rate of 4-5%.
- Use in plastics accounts for approximately 85% of all flame retardants used with textiles and rubber products accounting for most of the rest.
- North America consumed the largest volume of flame retardants in 2011 with a 28% share.
- Source: Townsend Solutions 2012
REACH is steaming ahead in Europe

Many flame retardants are already registered – dossiers are available on ECHA website
REACH and Flame Retardants

Annex 17 Restrictions lists these FRs:

- Pentabromodiphenyl ether* (PentaBDE, 0,1% w/w)
- Octabromodiphenyl ether* (OctaBDE, 0,1% w/w)
- Not allowed in articles for skin contact (e.g. textiles):
  - Tris(aziridinyl)phosphinoxide
  - Tris (2,3 dibromopropyl) phosphate (TRIS)
  - Polybromobiphenyls (PBB)

Annex 14 (Candidate) List of Substances of Very High Concern for Authorisation:

- Hexabromocyclododecane (HBCD) – PBT substance
- Tris(chloroethyl)phosphate (TCEP) – Reprotox Cat. 1b
- Alkanes, C10-13, chloro (Short Chain Chlorinated Paraffins) - PBT and vPvB
- Boric Acid – Reprotox

* as commercial formulations, i.e. including other congeners

Deca-BDE proposed as Annex 14 candidate (PBT, vPvB)
Ongoing regulatory activities: RoHS Recast

- EU Directive on the Restriction Of Hazardous Substances in electric and electronic equipment (RoHS, 2002/95/EC) was published in 2003
- Bans the heavy metals Cd, Pb, Cr (VI), Hg as well as PBBs and PBDEs, in E&E equipment since July 2006 (with exemptions for certain applications and duration)
- Directive “recast” in 2011 and published as 2011/65/EU
  - no new substance bans (Annex II), to be reviewed by 2014-07 (Art. 6)
  - recital (10) mentions certain phthalates and HBCD as priority substances
  - alignment with REACH foreseen (10, 16)
- WEEE Directive recast as 2012/19/EU
  - Higher recycling quotas and additional product groups covered
Market Drivers: NGOs, Ecolabels, Green Public Procurement

- Many ecolabels have restrictions for flame retardants
- Often detailed information on the flame retardants which are used is required
- EPEAT 2012: mandatory and optional requirements for halogen-free plastics
US-EPA: New Focus on Alternatives Assessment to BFRs

- Evaluation of environmental and health properties of alternatives to:
  - Tetrabromo bisphenol-A
  - Decabromo diphenylether
  - Hexabromo cyclododecane
- Hazard focused approach
- No black and white picture:
  - Alternatives (incl. halogen free) have chemical hazards, too, however,
  - Need to check relevance, e.g. by GreenScreen
  - Data gaps filled by read-across, computational methods or expert judgement
- [www.epa.gov/dfe](http://www.epa.gov/dfe)
GreenScreen

- Assessment scheme with 4 rating levels = “scores”
- pinfa has been running a pilot project to have some flame retardants evaluated
- Quick and simplified approach, however, the devil is in the detail - like data gaps, or ambiguous or contradictory data; review process; narrow classification boundaries
- GreenScreen does e.g. not take formation of dioxins by combustion into account
- http://www.cleanproduction.org/
ENFIRO: Life Cycle Assessment of Environmentally Compatible Flame Retardants

Impact assessment

Prioritization and selection

Risk assessment

Hazard Exposure Fire & Application performance

Chemical alternative cycle

The following slides are quoted from an ENFIRO presentation, courtesy of Pim Leonards, project coordinator.
Evaluation of HFFRs reveals many FRs with good environmental and health profile

| Generally safe, few issues of low concern identified | Aluminium diethylphosphinate (Alpi) | Inorganic and organic substances with low acute (eco-)toxicity and no bioaccumulation potential |
| - Aluminium hydroxide (ATH) | | - Chemical stability required for application results in limited degradation (persistence) |
| - Ammonium polyphosphate (APP) | | - Stannates: in vitro (neuro-)toxic effects were not confirmed in-vivo, probably due to low bioavailability |
| - Melamine polyphosphate (MPP) | | |
| - Dihydrooxaphosphaphenanthrene (DOPO) | | |
| - Zinc stannate (ZS) | | |
| - Zinc hydroxstannate (ZHS) | | |

| Low level of concern for potential environmental and health impact | Resorcinol bisphosphate (RDP) | RDP toxicity to aquatic organisms is main concern, may be linked to impurities (TPP). Low and high toxicity are found for same test species, which is may be due to batch differences |
| - Bisphenol-A bisphosphate (BDP) | | - BDP is persistent |

| Some issues of concern, risk assessment necessary | Triphenyl phosphate (TPP) | Toxicity of TPP to aquatic organisms is main concern, potential endocrine effects |
| - Nanoclay | | - Nanoclay showed strong in vitro neurotoxicity. May be due to the nanoparticle coating |
Assessment of FR/polymer material

- Leaching FR to air (off-gassing)
- Leaching FR to water (concentrations and toxicity)
- Fire performance (e.g., Toxic gasses)
- Applications

FR+polymer
Application performance

- All formulations (HFFR and BFR) showed equal or better performance for processability for injection moulding.
- Important aspect was input received from the Stakeholder forum.
- Printed circuit boards (PCBs) with HFFRs were as good as or better compared to the reference PCBs produced using BFRs.
Viable alternatives are available

**FR**

- Hazard
  - Some HFFRs are less toxic than BFRs
  - Suitable alternatives:
    - Alpi, DOPO, APP, MPP, ATH, ZHS, ZS

**Material**

- Technological assessment
  - HFFRs produce less smoke, except RDP, BDP
  - HFFRs leach as much as BFRs
  - Leaching is polymer dependent

**Product**

- Impact assessment studies
  - Improper treatment of products with BFRs can produce dioxins
  - HFFRs will not produce dioxins
The ENFIRO Consortium

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Who is pinfa?

- pinfa was established in 2009 as a Sector Group within Cefic, the European Chemical Industry Council
- pinfa North America was founded in 2012
- pinfa, the Phosphorus, Inorganic and Nitrogen Flame Retardants Association represents manufacturers and users of the three major technologies of non-halogenated flame retardants.
- pinfa members share the vision of continuously improving the environmental and health profile of their flame retardant products and offering innovative solutions for sustainable fire safety.
- Part of the mission of pinfa is to provide information on non-halogenated phosphorus, inorganic and nitrogen flame retardants
pinfa EU Members in 2013

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BASF The Chemical Company

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CATENA Additives

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DSM BRIGHT SCIENCE. BRIGHTER LIVING.

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www.pinfa.org
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- FRX Polymers
- Nabaltec AG
- Clariant Additives
- Huber Engineered Materials

- www.pinfa-na.org

- Polyone
- Network Polymers
- Applied Minerals
pinfa product selector

- List of more than 33 flame retardants
- Information on applications and regulatory status
- Applications range from
  - Thermoplastics
  - Foams
  - Textiles
  - Paints/Coatings
  - Adhesives
  - Thermosets
  - Wire and cables
- Actual REACH status for products is currently being implemented
- [www.pinfa.org](http://www.pinfa.org)
PIN FRs – what’s next

• Prediction of flame retardancy: “structure-activity relationships” are still difficult
• Oligomeric or polymeric vs. monomeric flame retardants
• Renewables: flame retardant solutions for “bio-plastics”
• Recycling of polymers with FRs
Summary

• Over the last 10 years the scientific and public debate on flame retardants has led to some regulatory restrictions on flame retardants (e.g. RoHS and WEEE directives, REACH in Europe).
• All these activities have led to a large pool of data on the environmental profile of flame retardants, REACH requires even more information on substance properties and uses.
• There is a strong trend towards more environmentally compatible FRs, driven by official assessments, NGOs, OEMs and legislation like RoHS, REACH.
• Flame retardants manufacturers in pinfa try to develop new and better products as well as supply their customers with all necessary information.
Thank you for your attention

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