pinfa

Phosphorus, Inorganic & Nitrogen Flame Retardants Association

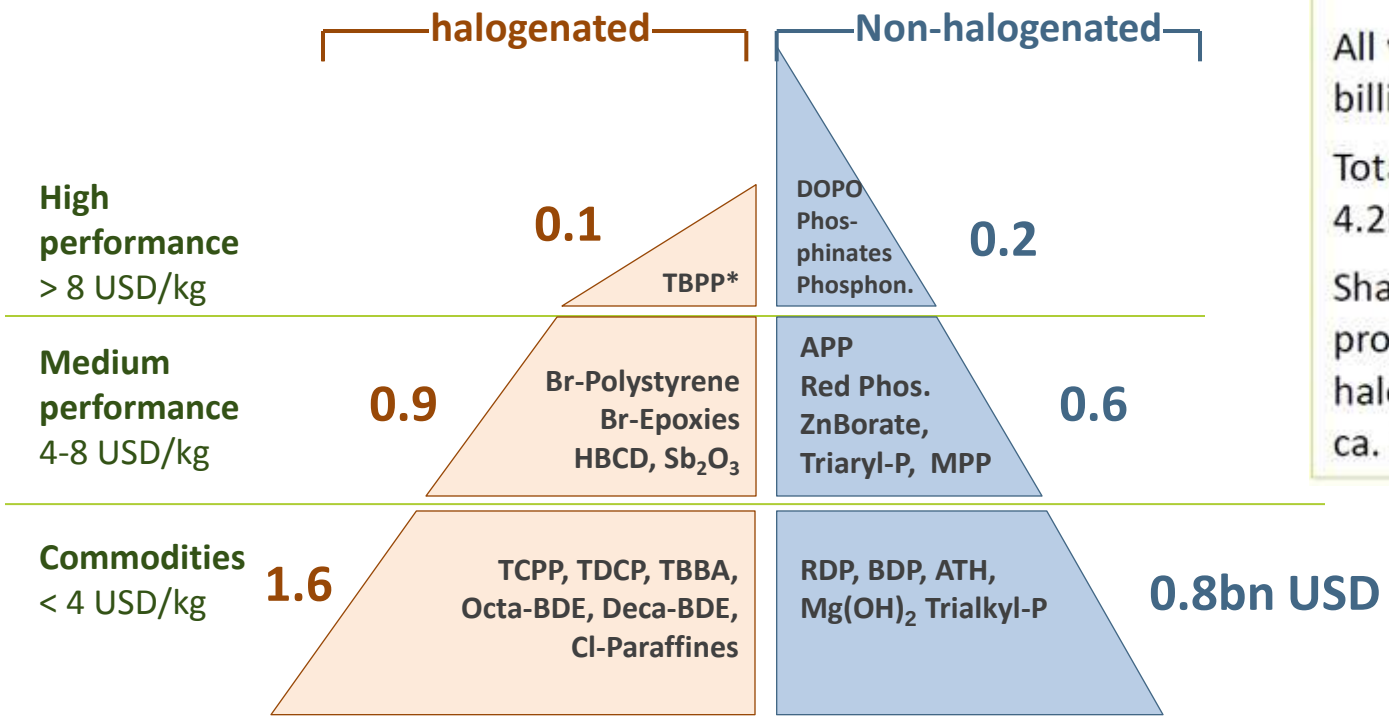
Flame retardants – an update on regulatory status and environmental assessments

ERA Technology - Electrical and Electronic Equipment and the Environment
14+15 Nov. 2012, Heathrow, London UK
Adrian Beard, Michael Klimes, Ulrich Wietschorke

cefic

Responsible Care®
Good Chemistry at Work

Global FR Market [value]



The area of a triangle represents the market share value.

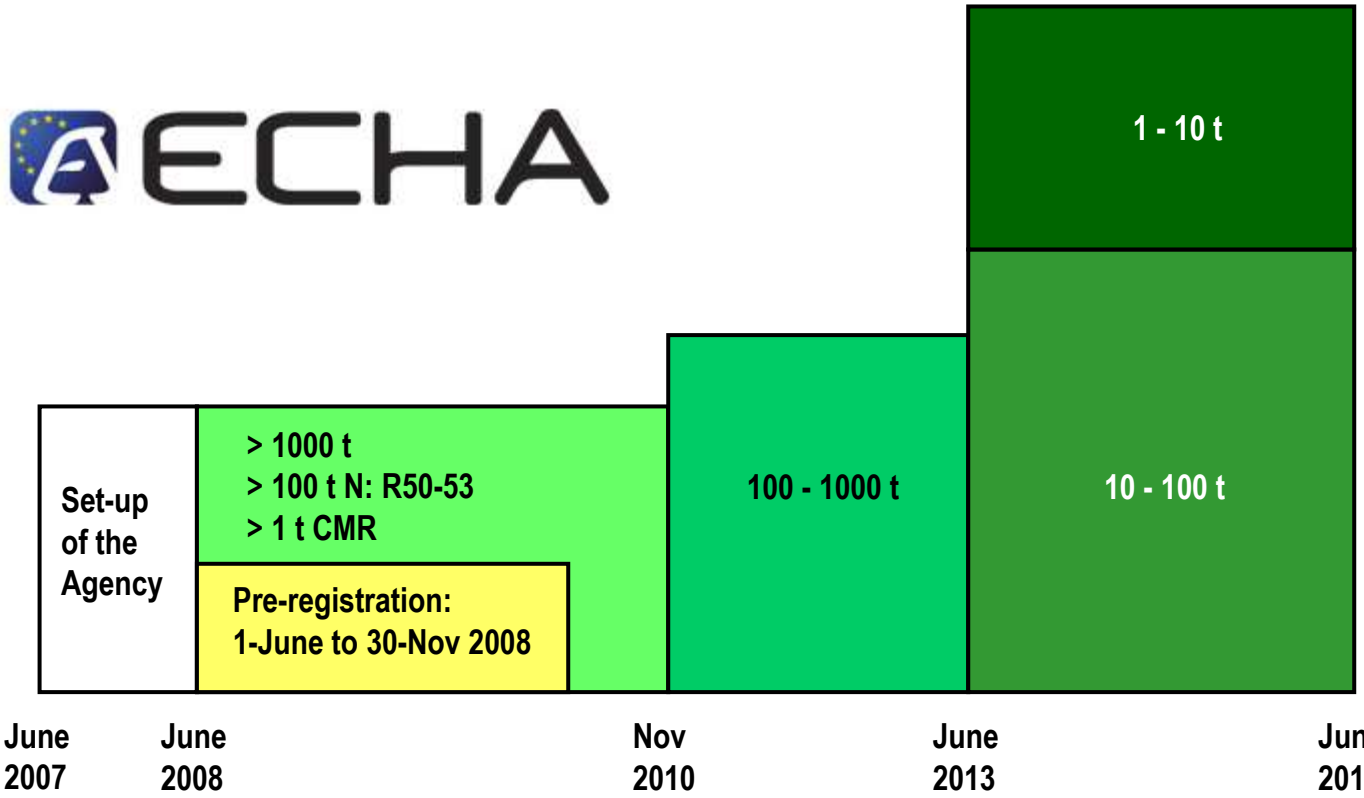
All values are in billion USD.

Total FR market size is 4.2bn USD (2007).

Share of brominated FR producers in non-halogenated FRs ca. 0.5 bn USD

Latest industry trends indicate a market shift towards non-halogenated products.
Global FR consumption for 2010 estimated at 3.9bn USD, 2012 at 4.3bn USD (Ceresana)

REACH is here



Many flame retardants are already registered – dossiers available on ECHA website

REACH and Flame Retardants

status 2012-10

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

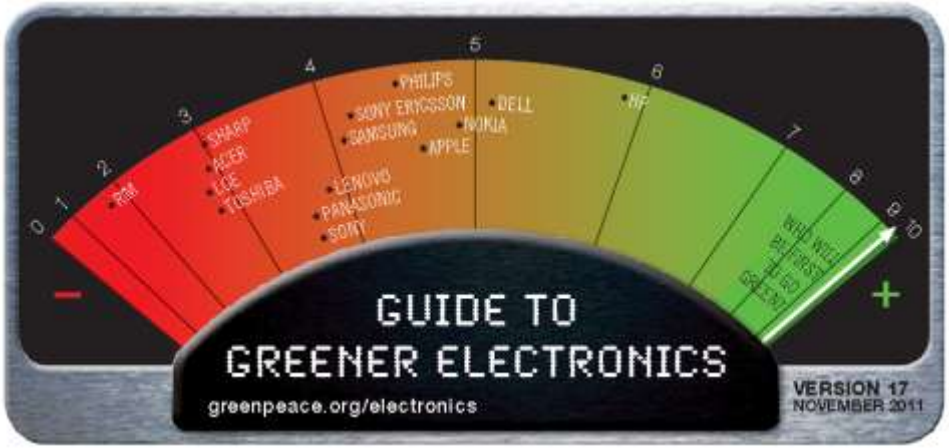
Deca-BDE proposed as Annex 14 candidate (PBT, vPvB)

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)
- Directive “recast” in 2011 and published as 2011/65/EU
  - no new substance bans (Annex II), to be reviewed 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 larger scope

picture: CT/tsa medien

Market Drivers: NGOs, Ecolabels, Green Public Procurement



- Many ecolables have restrictions for flame retardants
- Often detailed information on the flame retardants which are used is required
- EPEAT 2012: mandatory and optional require-ments for halogen-free plastics

Example: EU-Ecolabel Scheme and FR Restrictions

Product Group	Sub-Group	Valid until	Restrictions on Flame Retardants
Electronic Equipment	PCs & Laptops	MAY-31 2010 (OLD)	-PBBs & PBDEs excluded -Chloroparafin C10-17 FR excluded -FR excluded with R-phrases: R45, R46, R50, R50/53, R51/53, R60, R61
		JUNE 09 2014 (NEW)	-PBBs & PBDEs excluded -Chloroparafin C10-17 FR excluded - FR excluded with R-phrases: R23, R26, R24, R25, R27, R28, R40, R45, R46, R48, R49, R50, R51, R52, R53, R60, R61, R63, R64,R68 and relevant combinations thereof

EPEAT: Halogen Free Requirements

- IEEE 1680.2-2012: IEEE Standard for Environmental Assessment of Imaging Equipment *and* IEEE 1680.3-2012: Televisions
  - 4.1.6.1 Required—Reducing BFR/CFR/PVC content of external plastic casings
    - External plastic casings greater than 25 g shall contain no more than 0.1% weight (1000 ppm) bromine and 0.1% weight. (1000 ppm) chlorine attributable to brominated flame retardants (BFRs), chlorinated flame retardants (CFRs), and polyvinyl chloride (PVC) with the following exceptions …
  - 4.1.6.2 Optional—Eliminating or reducing BFR/CFR content of printed circuit board laminates
  - 4.1.6.3 Optional—Eliminating or reducing BFR/CFR/PVC content of product
- IEEE 1680.1-2009: Personal Computers and Displays – still needs revision

www.epeat.net

OEM Commitments and Roadmaps

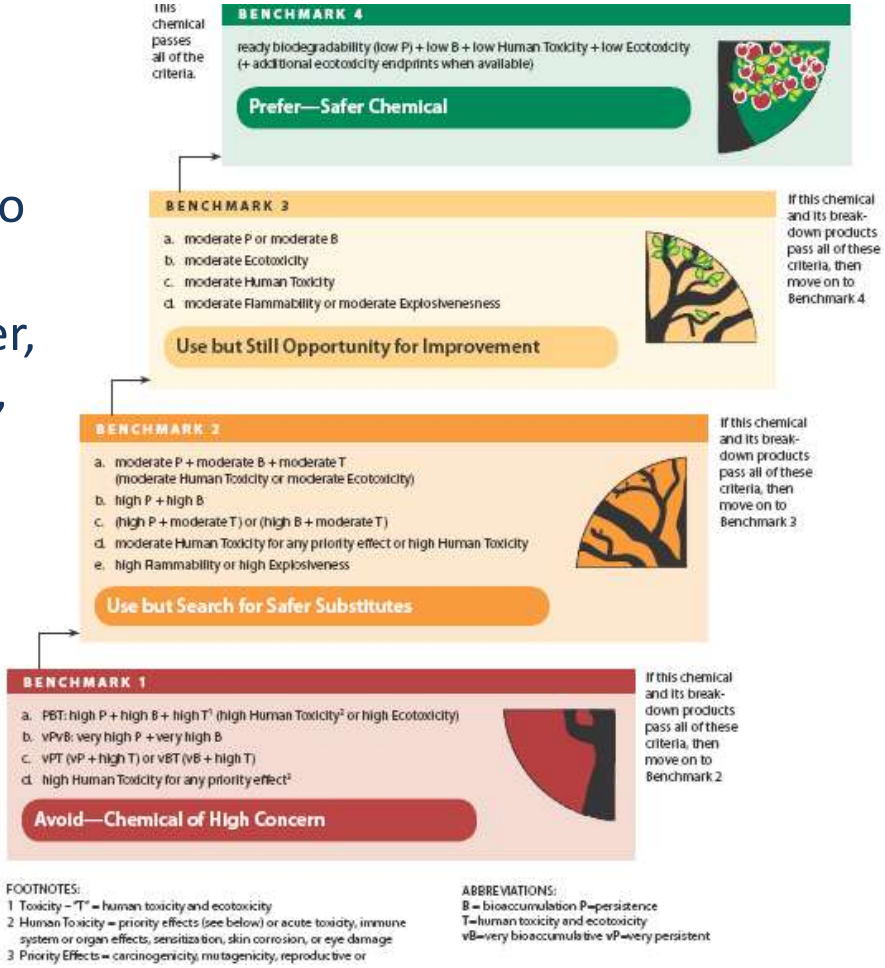
Examples of Original Equipment Manufacturers (OEMs) who have made commitments or defined roadmaps towards the use of non-halogenated flame retardants

US-EPA: Alternatives Assessment

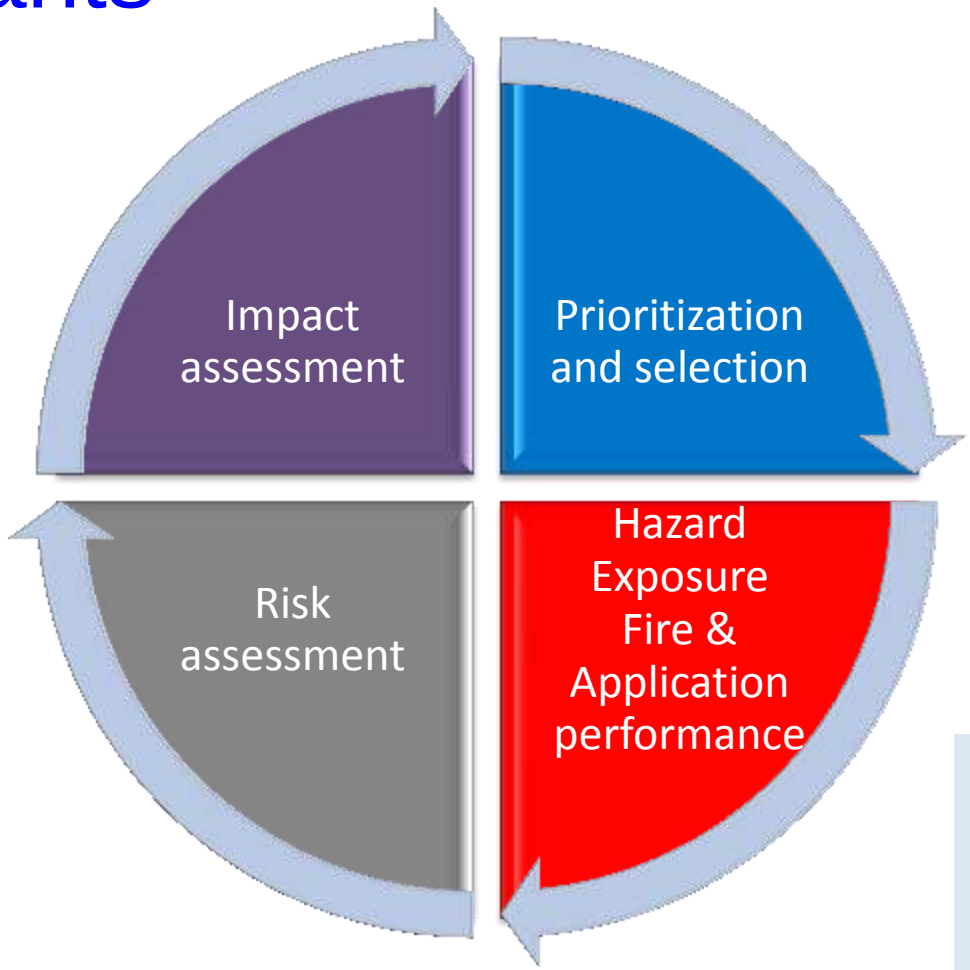
- Evaluation of environmental and health properties of alternatives to:
  - Tetrabromo bisphenol-A
  - Decabromo diphenylether
  - Hexabromo cyclododecane
- Hazard focused approach
- No black and white picture:
  - Alternatives have chemical hazards, too, however,
  - Need to check relevance
  - Data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

GreenScreen

- Assessment scheme with 4rating 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
- http://www.cleanproduction.org/



ENFIRO: Life Cycle Assessment of Environmentally Compatible Flame Retardants



Chemical alternative cycle

The following slides are quoted from an ENFIRO presentation, courtesy of Pim Leonards, project coordinator

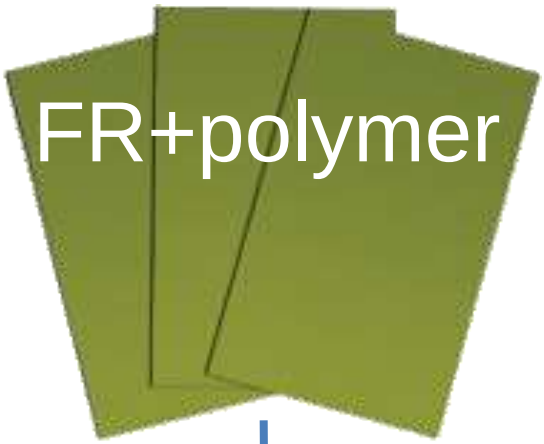
Evaluation of HFFRs

Generally safe, few issues of low concern identified	• **Aluminium diethylphosphinate (Alpi)** • **Aluminium hydroxide (ATH)** • **Ammonium polyphosphate (APP)** • **Melamine polyphosphate (MPP)** • **Dihydrooxaphosphaphenanthrene (DOPO)** • **Zinc stannate (ZS)** • **Zinc hydroxstannate (ZHS)**	• **Inorganic and organic substances with low acute (eco-)toxicity and no bioaccumulation potential** • **Chemical stability required for application results in limited degradation (persistence)** • **Stannates: in vitro (neuro-)tox effects were not confirmed in-vivo, probably due to low bioavailabillity**
Low level of concern for potential environmental and health impact	• Resorcinol bisphosphate (RDP) • Bisphenol-A bisphosphate (BDP)	• 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 • BDP is persistent
Some issues of concern, risk assessment necessary	• Triphenyl phosphate (TPP) • Nanoclay	• Toxicity of TPP to aquatic organisms is main concern, potential endocrine effects • 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)



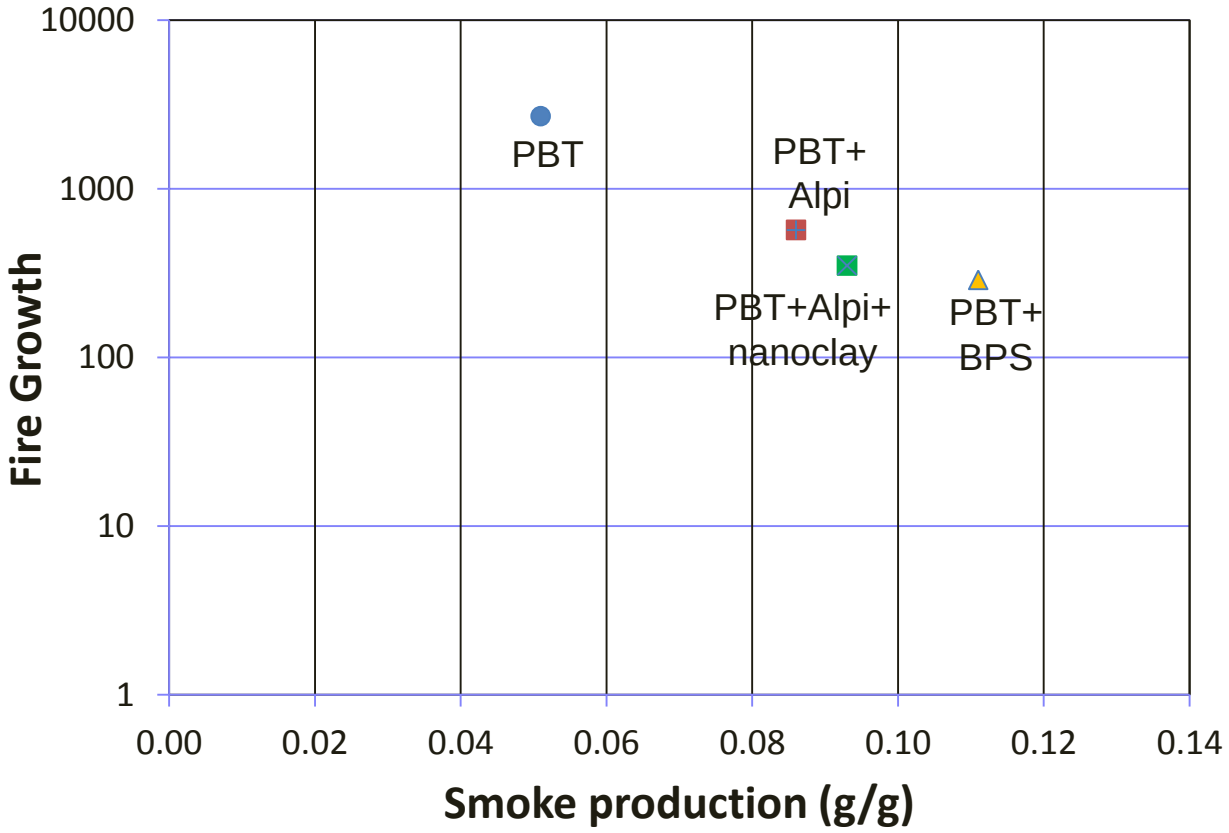
Fire
performance
(e.g. Toxic gasses)

Applications

Studied polymers/materials

- Epoxy resins
- High impact polystyrene (HIPS)
- Polystyrene blends: PC/ABS, HIPS/PPE
- Polyamide 6 and polyamide 6,6
- Polybutylene therephthalate (PBT)
- Polyethylene therephthalate (PET)
- Polyethylene/ethylene vinyl acetate (PE/EVA)
- Textile polymers (e.g. thermoplastics PUR)
- Intumescent Coatings (coating of HIPS)

Fire Performance BFRs - HFFRS



- In general, HFFRs had improved smoke suppression
- HFFRs had similar fire performance characteristics as BFRs in polymers, except for polymer blends

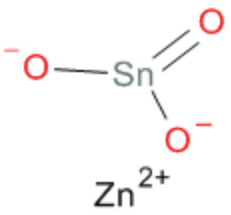
University of ULSTER
FireSERT

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 where as good as or better compared to the reference PCBs produced using BFRs

Viable alternatives are available

FR



Hazard

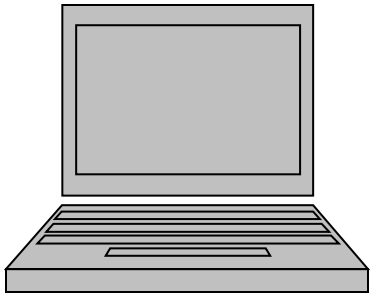
- Some HFFRs are less toxic than BFRs
- Suitable alternatives:
  - Alpi, DOPO, APP, MPP, ATH, ZHS, ZS

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

Highlights of ENFIRO (I)

- Viable alternative flame retardants are available
- All selected HFFRs do fulfil the regulatory fire tests
- HFFRs have similar fire performance and technical application capabilities as BFRs
- In general, halogen free systems produce less smoke and less toxic components in smoke
- For all polymer systems investigated a HFFR option was found

Highlights of ENFIRO (II)

- Some HFFRs showed:
  - Less risk for the environment and human health
  - Lower potency to bioaccumulate
- A lower human and environmental risk is expected due to the lower hazards of the HFFRs, but probably not due to a lower exposure
- The approach adopted by ENFIRO can be used for similar substitution studies

The ENFIRO Consortium

Acknowledgements

- ENFIRO consortium
- EU for funding ENFIRO (no. 226563)

www.enfiro.eu

pim.leonards@ivm.vu.nl

Who is pin*f*a?

pin*f*a Phosphorus, Inorganic & Nitrogen Flame Retardants Association

- pin*f*a was established in 2009 as a Sector Group within Cefic, the European Chemical Industry Council
- pin*f*a, the Phosphorus, Inorganic and Nitrogen Flame Retardants Association represents manufacturers and users of the three major technologies of non-halogenated flame retardants.
- pin*f*a 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 pin*f*a is to provide information on non-halogenated phosphorus, inorganic and nitrogen flame retardants

pinfa Members in 2012

ADEKA PALMAROLE

BASF The Chemical Company

Budenheim

CATENA Additives

Clariant

dartex coatings

delamin

DSM BRIGHT SCIENCE. BRIGHTER LIVING.

FRX polymers

Italmatch Chemicals

KREMS CHEMIE Chemical Services

LANXESS Energizing Chemistry

Nabaltec

Perstorp WINNING FORMULAS

Rhodia

ROCKWOOD ADDITIVES

THOR

williamblythe quality, chemistry, performance

iNEMI International Electronics Manufacturing Initiative

Schill+Seilacher

LUH GEORG H. LUH GMBH

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.eu

Product selector

‹ Back to list

Product identity

Chemical name	Ammonium Polyphosphate
CAS	68333-79-9
ECN°	269-789-9

Regulatory status

Current classification under directive 67 / 548 / EEC	none
Reach registered	2010
URL link	

Suppliers / trade names

Supplier	**Trade name**
Budenheim :	FR CROS 484
Clariant :	Exolit® AP 42x
Thor :	Afflamit® PCI 202

Application groups

Group	**Substrate**	**Application**
Solid Thermoplastics	Polypropylene (PP)	applicable
	Polyethylene (PE)	applicable

Advantages of PIN FRs

- **Smoke formation and composition**

– PIN FRs tend to release less smoke, because they function more by physical processes like release of water and formation of a charred layer at the product surface than by impeding the reactions in the flame zone

– PIN FRs do not release halogen acids (HBr, HCl) and have no potential for formation of halogenated dioxins and furans

– Therefore, PIN FRs are commonly used in aeroplanes, trains and public buildings because of strict smoke and smoke toxicity requirements

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 pin*f*a try to develop new and better products as well as supply their customers with all necessary information.

Picture: R. Baumgarten / Clariant

pinfa

Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Thank you for your attention

Electronics Goes Green Conference
12 Sep. 2012
Adrian Beard, Michael Klimes, Ulrich Wietschorke

cefic

Responsible Care®
Good Chemistry at Work