pinfa

Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Searching for safe Flame Retardants – what are producers of phosphorus, inorganic and nitrogen flame retardants doing?

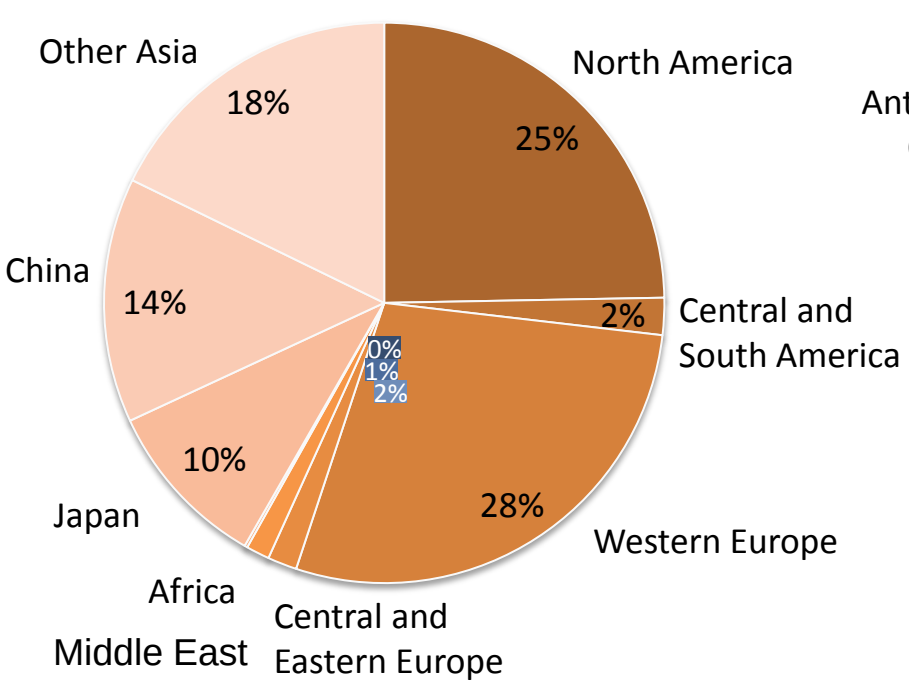
COST MP1105 WG 4 Standardisation Meeting
14 Oct 2013, Bolton, UK
Adrian Beard

cefic

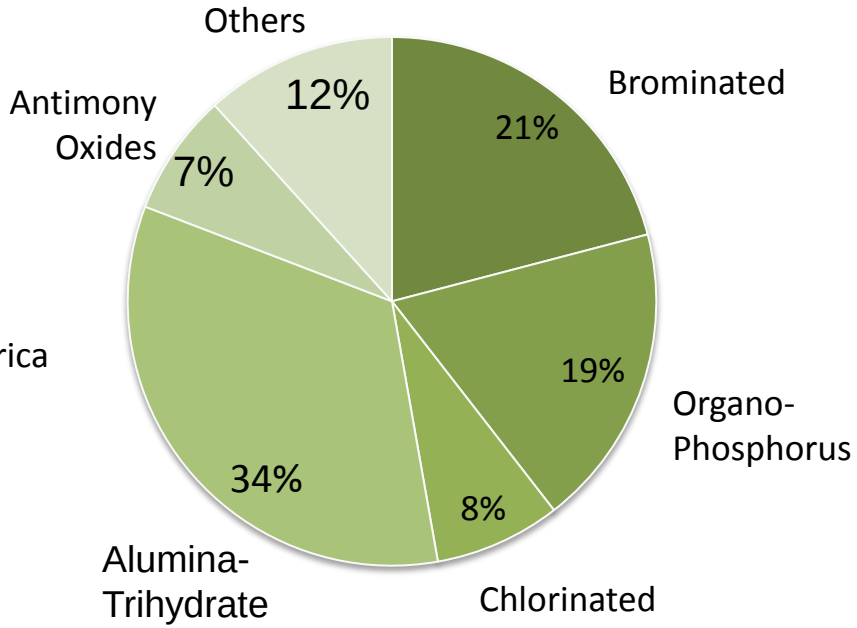
Responsible Care
Good Chemistry at Work

Global Consumption of Flame Retardants (2010)

5600 mio. USD FR Market by Region
Share in percent, 2010



1.8 mio. metric tons FR Market by Chemistry
Share in percent, 2010

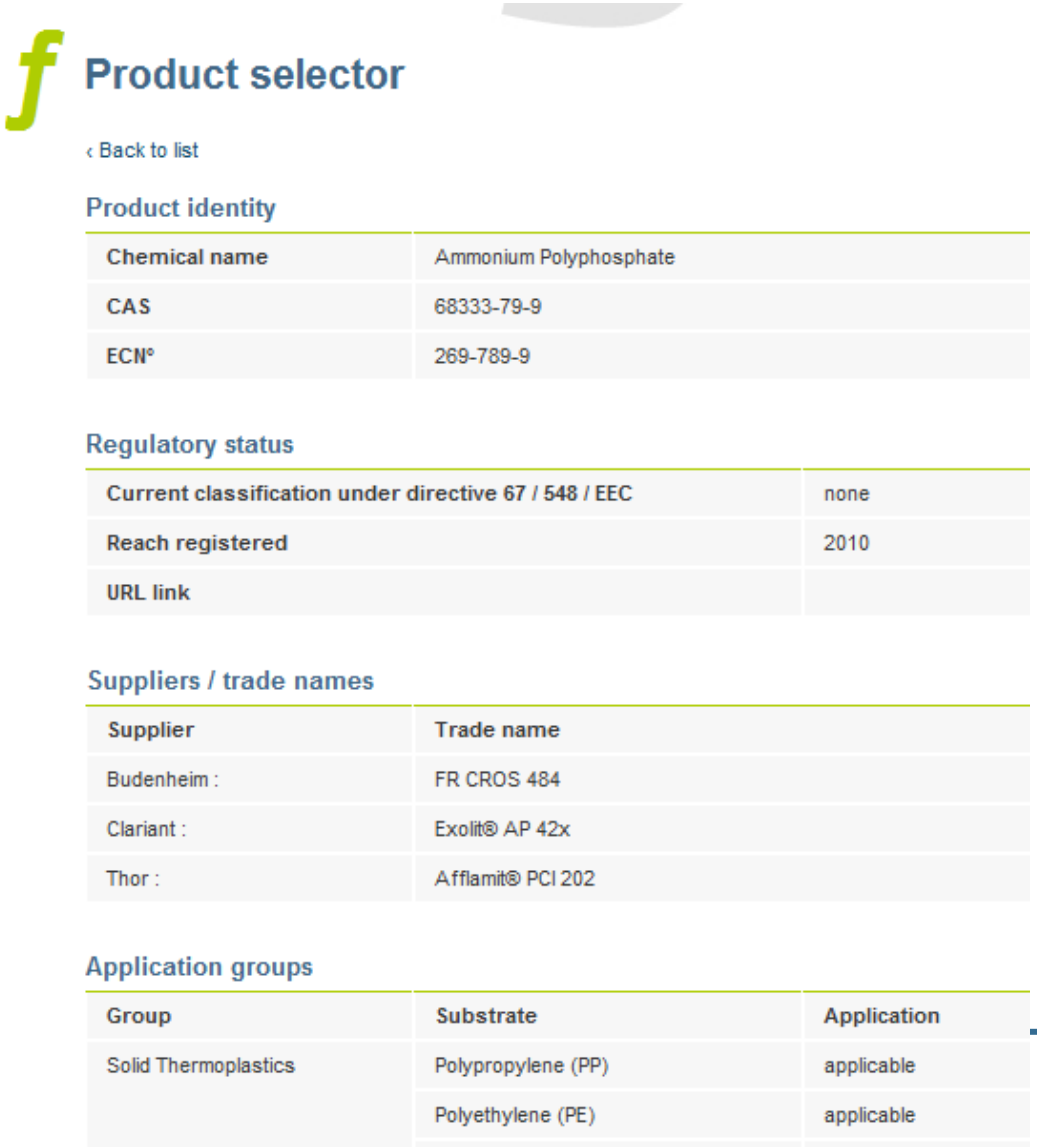


Source: SRI / IHS consulting 2011

pinfa EU Members in 2013

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



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

pinfa new brochure on construction

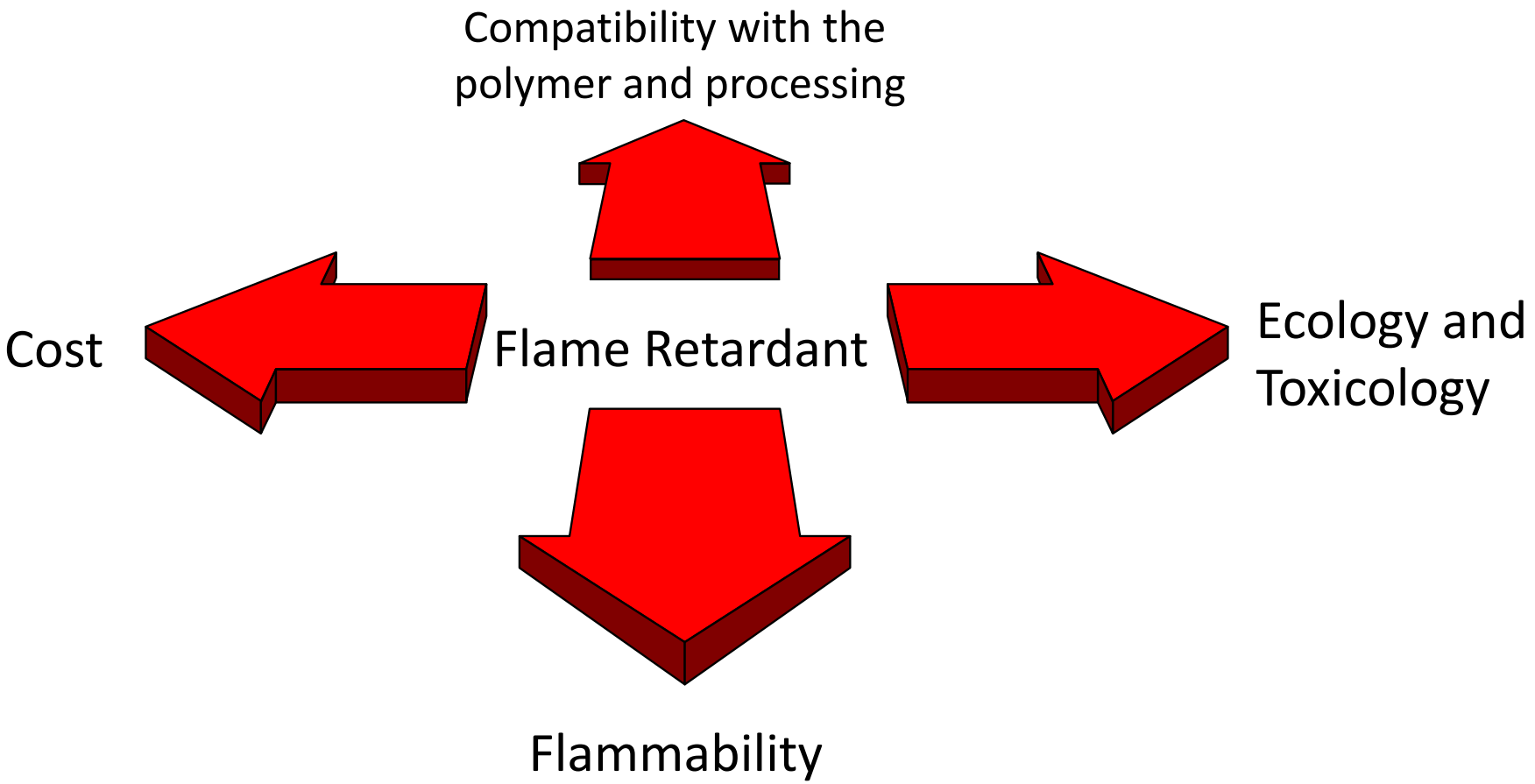
Available online at:
www.pinfa.eu/library/brochures.html

Flammability Standards and FR Producers

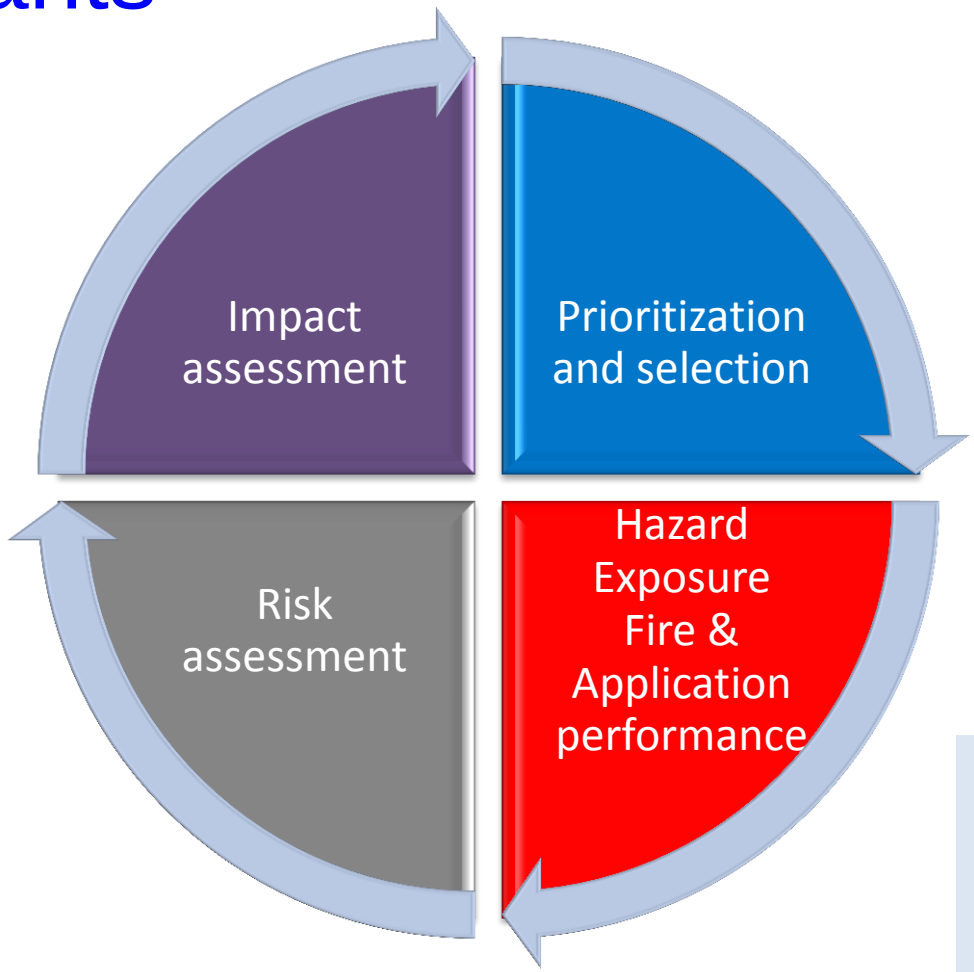
- All fire tests are scenario, NOT material tests

  ➔ properly define and state risk scenario
- Keep tests as simple as possible: sample size, equipment, …
- Do not mix other requirements into flammability standards (health, environment, …)
- Standards are the result of a consensus of different interests, often reflecting technical status quo (e.g. available materials)

Requirements on Flame Retardants



ENFIRO: Life Cycle Assessment of Environmentally Compatible Flame Retardants

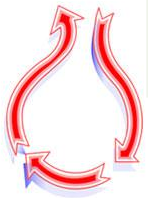


Chemical alternative cycle

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

Evaluation of HFFRs reveals many FRs with good environmental and health profile

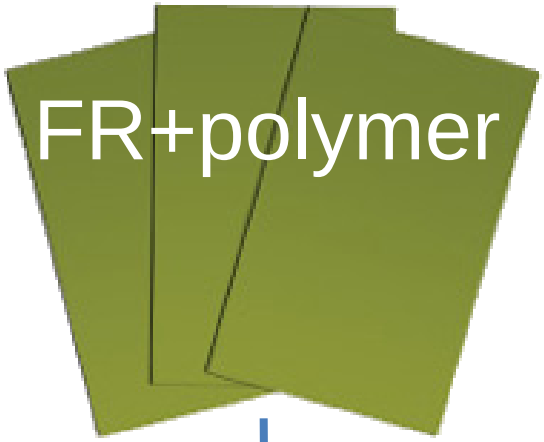
Generally safe, few issues of low concern identified	• **Aluminium diethylphosphinate (Alpi)** • **Aluminium hydroxide (ATH)** • **Ammonium polyphosphate (APP)** • **Melamine polyphosphate (MPP)** • **Dihydrooxaphosphaphenanthrene (DOPO)** • **Zinc stannate (ZS)** • **Zinc hydroxstannate (ZHS)**	• **Inorganic 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)

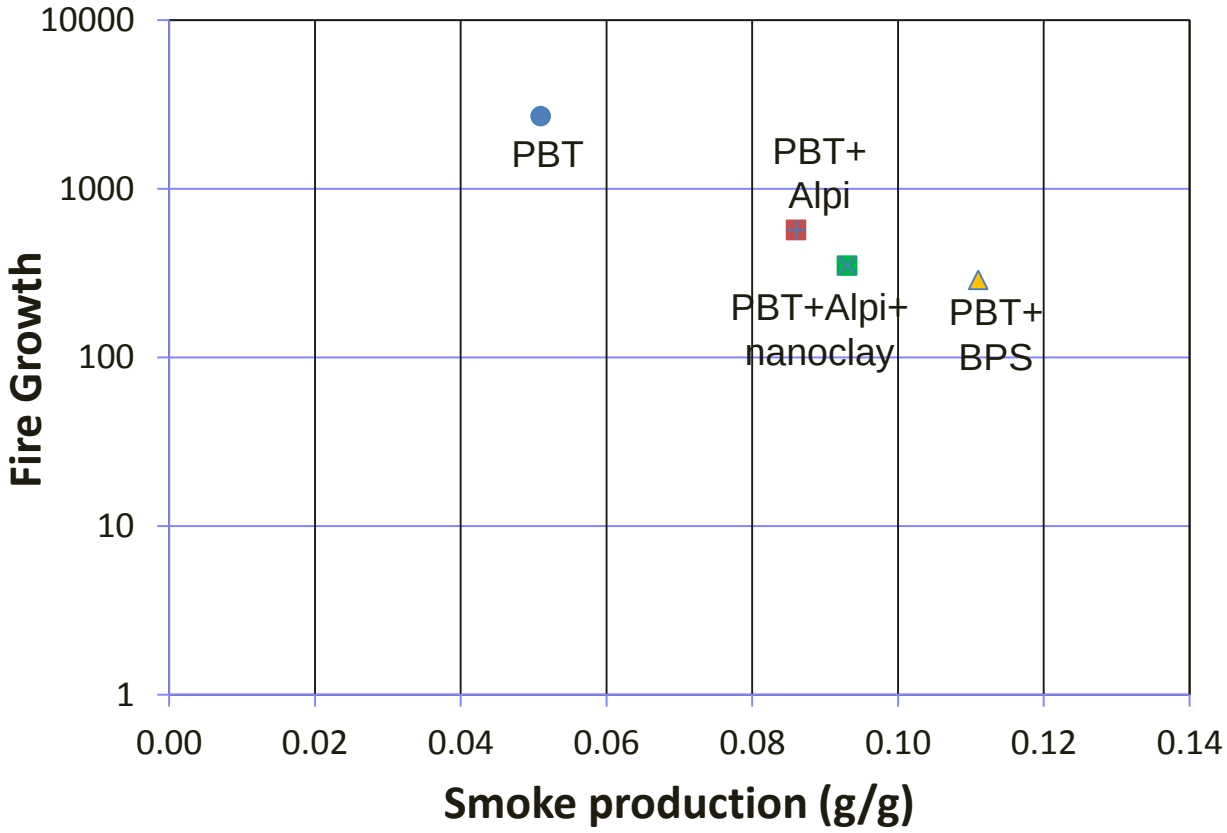
Leaching FR
to water
(concentrations and
toxicity)



Fire
performance
(e.g. Toxic gasses)

Applications

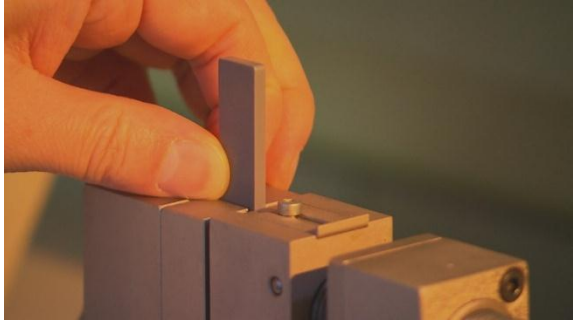
Fire Performance BFRs - HFFRS



- 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

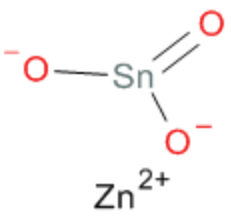
Application performance



- All formulations (HFFR and BFR) showed equal or better performance for processability for injection moulding
- Important input was 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

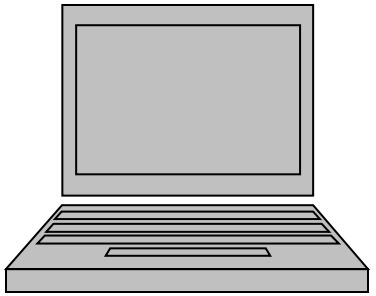
- Some HFFRs are less toxic than BFRs
- Suitable alternatives:
  - Alpi, DOPO, APP, MPP, ATH, ZHS, ZS

Material

Technological assessment

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

Product

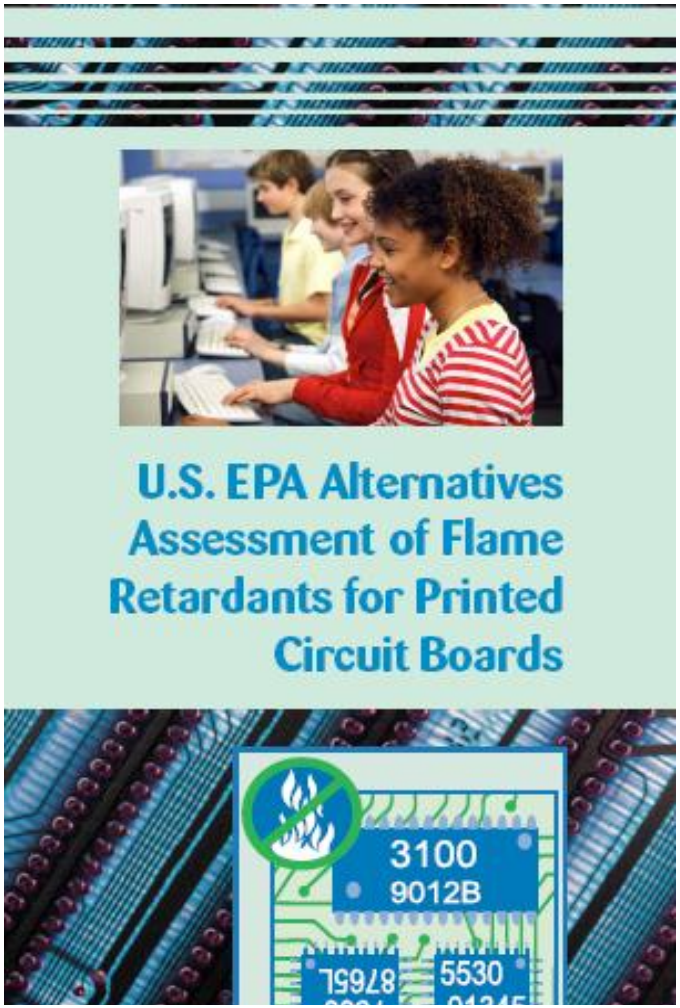


Impact assessment studies

- Improper treatment of products with BFRs can produce dioxins
- HFFRs will not produce dioxins

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:
  - Good alternatives available
  - Alternatives (incl. halogen free) have chemical hazards, too, however, need to consider relevance
  - Data gaps filled by read-across, computational methods or expert judgement
- www.epa.gov/dfe

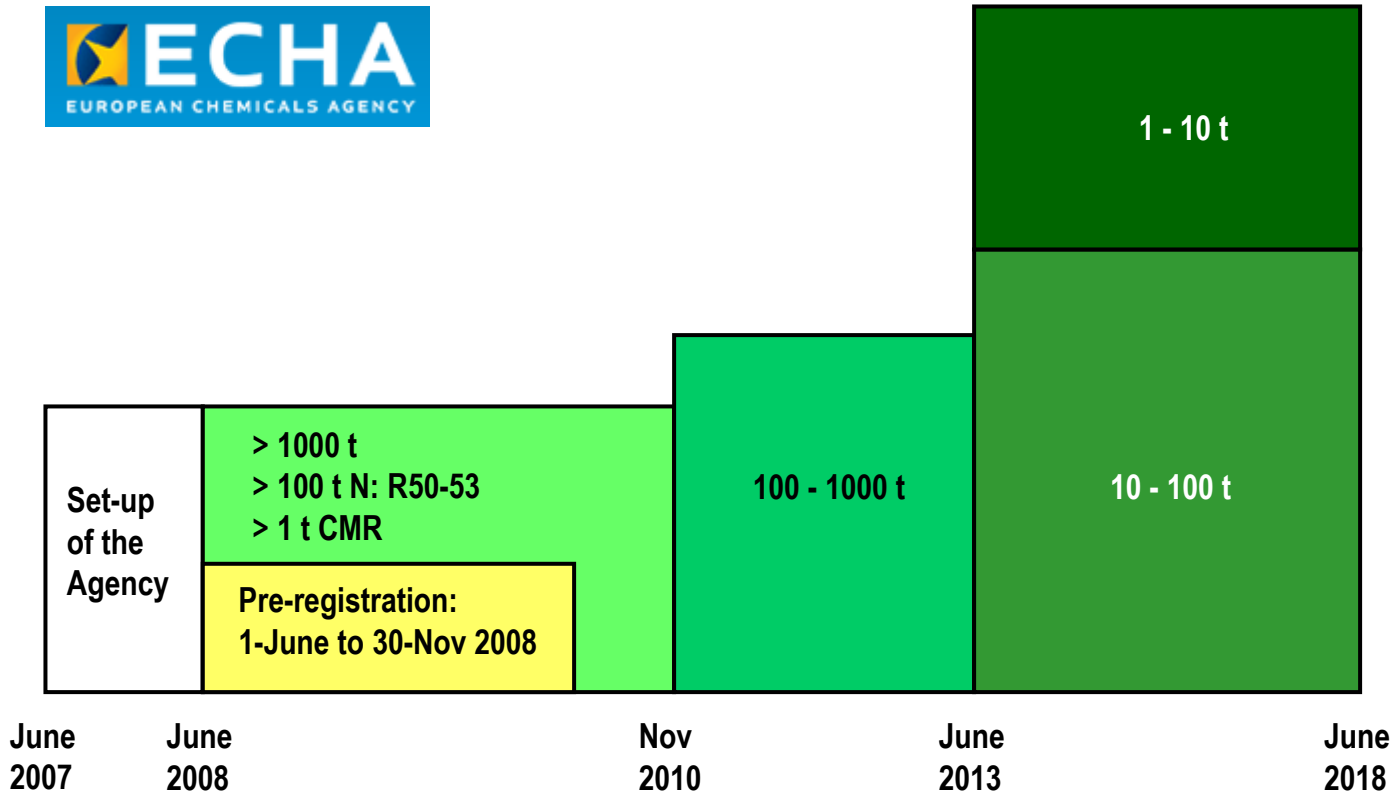


GreenScreen

- Assessment scheme with 4 rating levels = “scores”
- pinfa has run 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/

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)

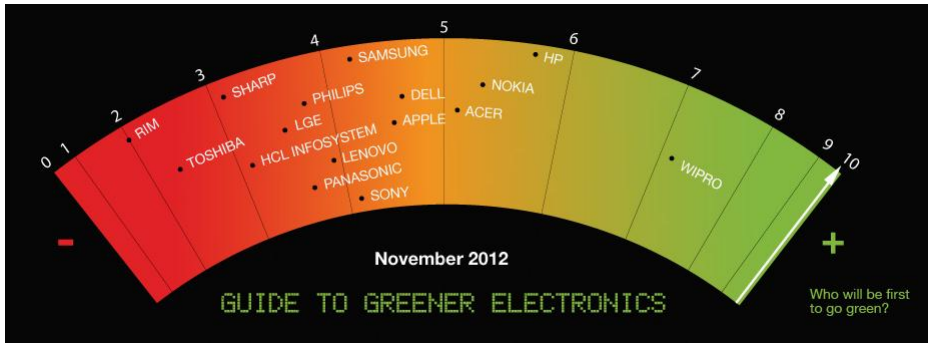
Deca-BDE: Norway has submitted a proposal to add the commercial mixture (c-decaBDE) to the Stockholm Convention on Persistent Organic Pollutants → ECHA to prepare Annex XV dossier

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

Market Drivers: NGOs, Ecolabels, Green Public Procurement



TCO Development

GPP

Umweltzeichen

EU Ecolabel
www.ecolabel.eu

epeat

- Many ecolabels 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

Summary

- 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) as well as the evaluation of alternatives.
- The EU ENFIRO project confirmed that viable alternative flame retardants are available, HFFRs have similar fire performance and technical application capabilities as BFRs
- Flammability standards should be reasonable, transparent and harmonized
- Flame retardants manufacturers in pin*fa* try to develop new and better products as well as supply their customers with all necessary information.

Picture: R. Baumgarten / Clariant

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Thank you for your attention

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Good Chemistry at Work