SCI Fire and Materials Group

OVERVIEW OF NON-HALOGEN FLAME RETARDANTS

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Public

Dr. Adrian Beard
Clariant Flame Retardants
pinfa.org
05.11.2015

what is precious to you?

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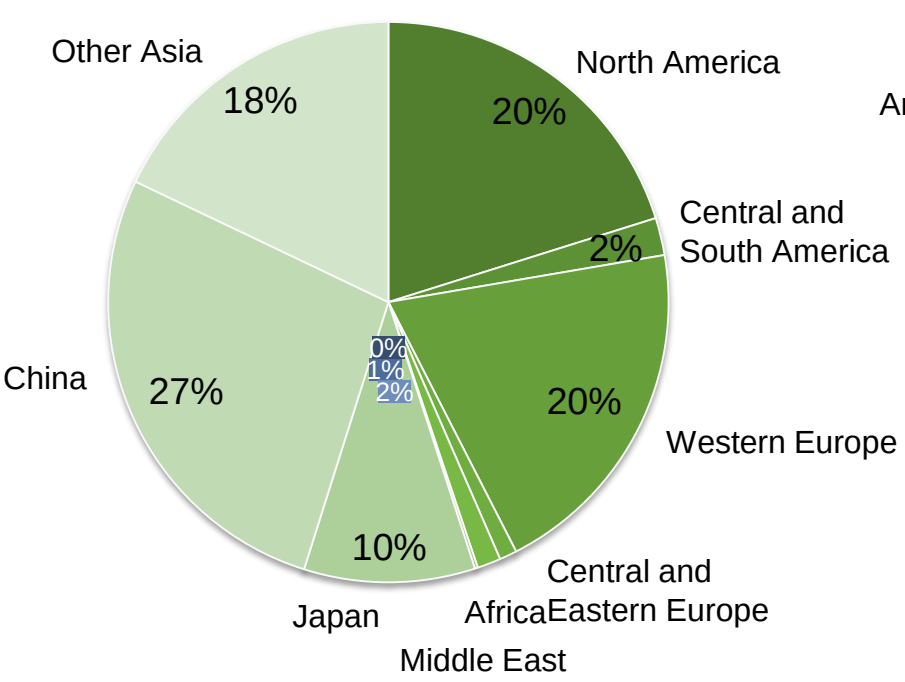
Global Consumption of Flame Retardants (2013)

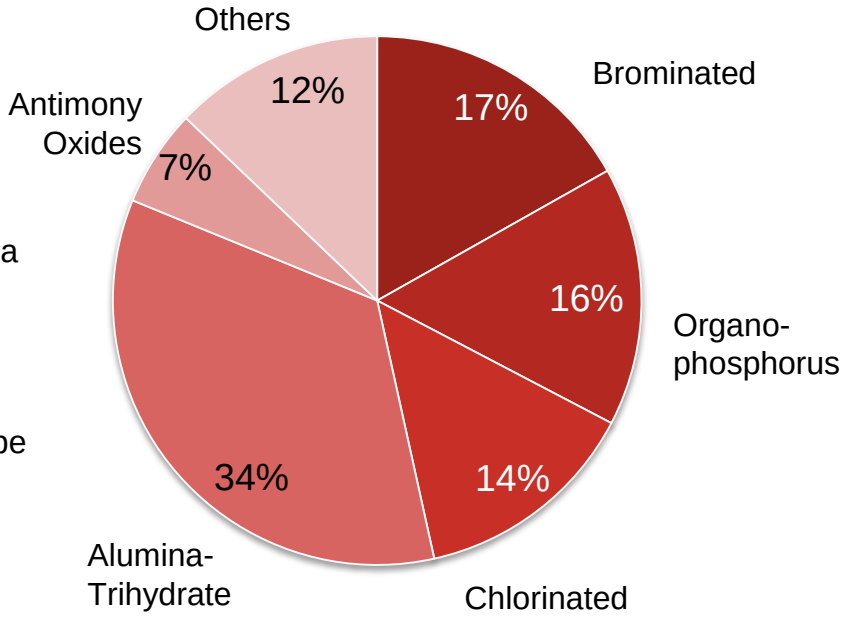
5622 Mio USD FR Market by Region

Share in percent, 2013



2.1 mio. MT FR Market by Chemistry

Share in percent, 2013



Estimated average growth 2013 to 2018 ca. 3.4% p.a.
Source: SRI/IHS consulting 2014

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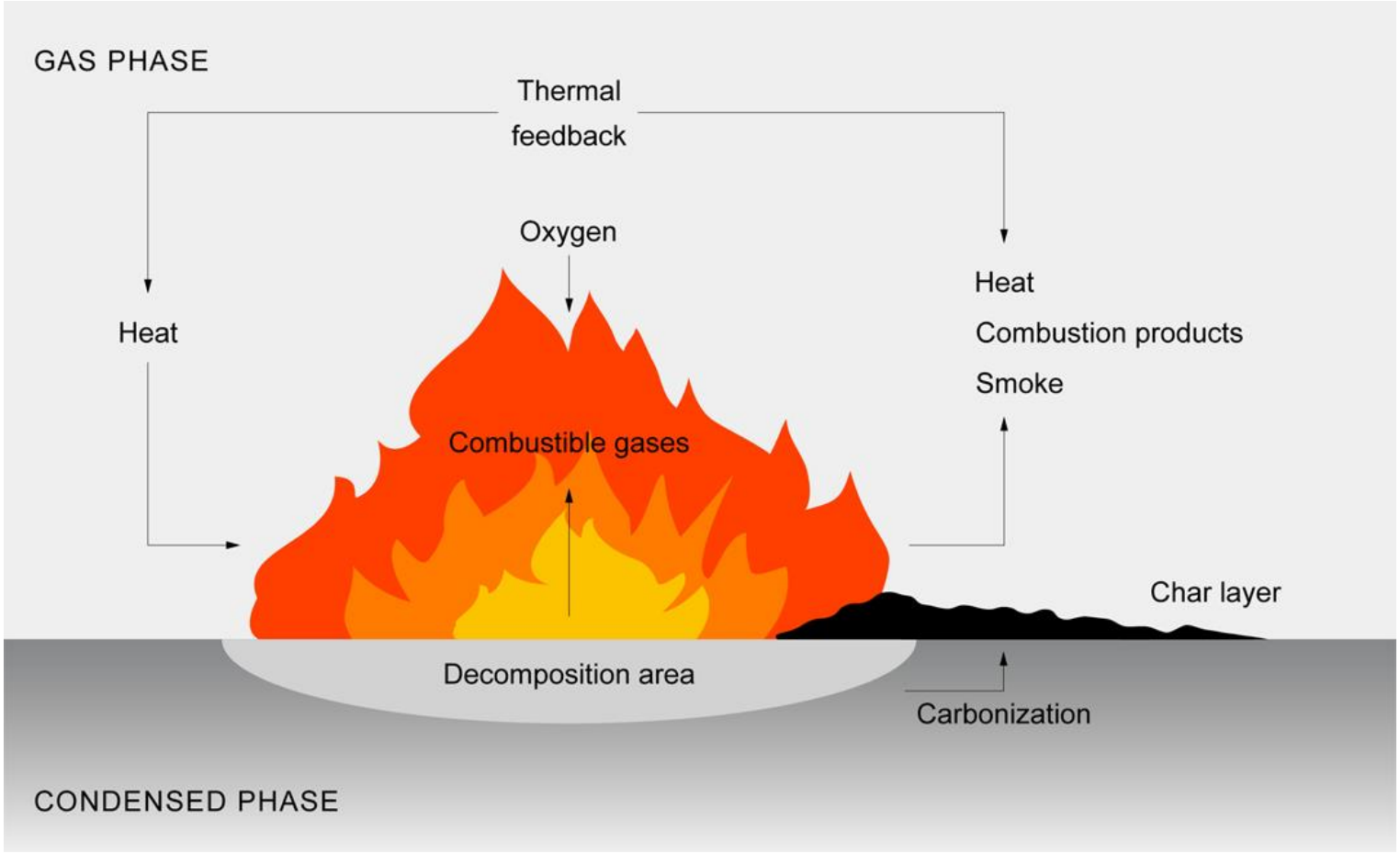
The Combustion Process



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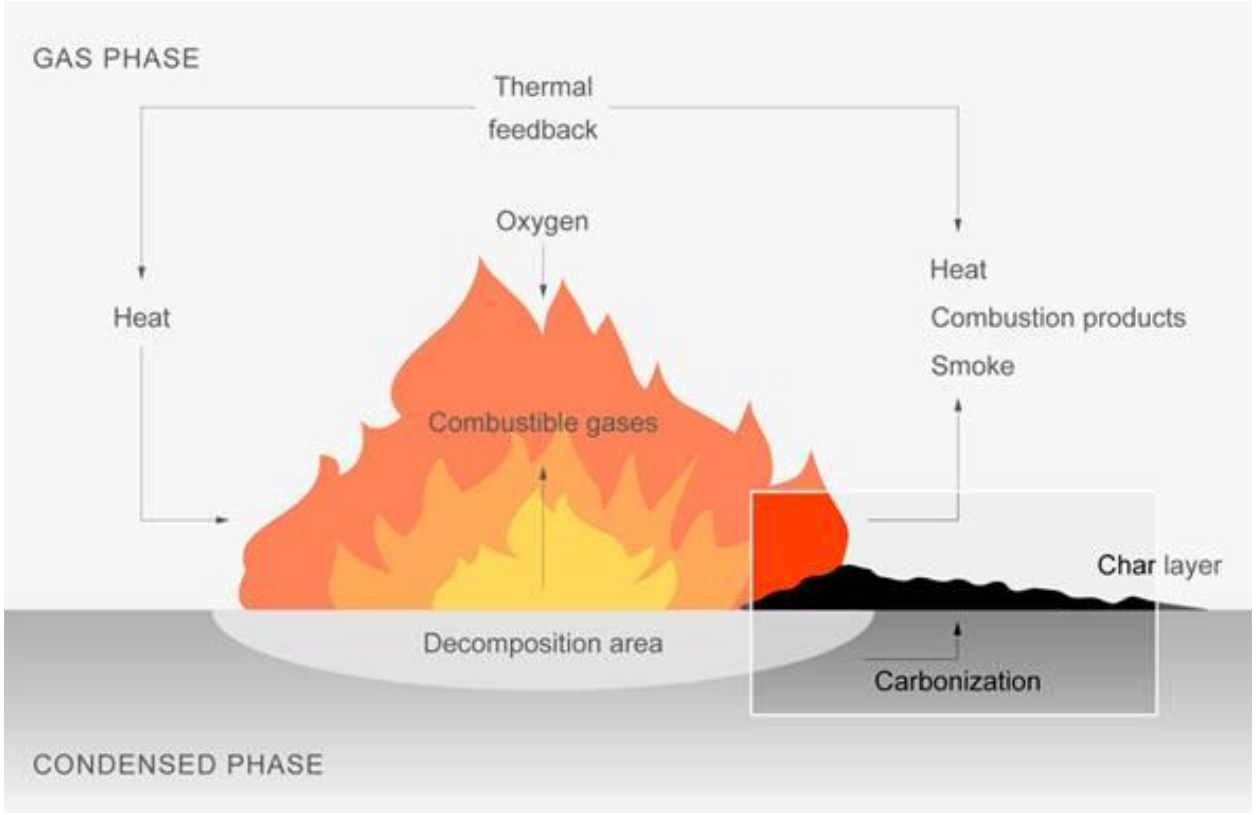
Phosphorus FRs - mechanism



- elemental (red) phosphorus, inorganic and organic phosphorus compounds are used
- main mechanism is by formation of a char layer at the surface, stopping the contact between fuel and air
- generally less smoke, because no forced incomplete combustion, less acidic gases

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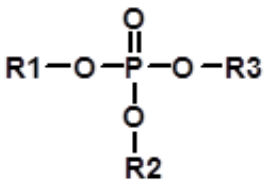
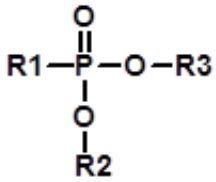
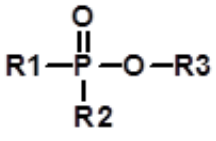
Phosphorus based Flame Retardants - examples



Phosphate ester

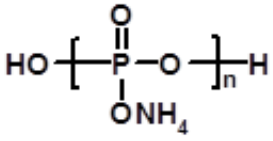


Phosphonate

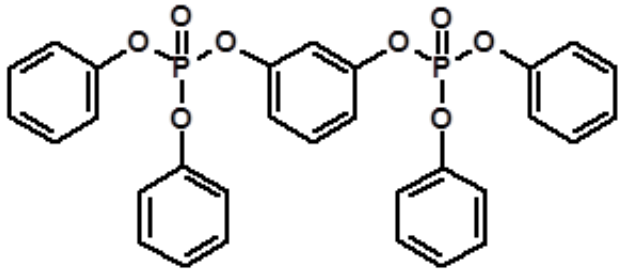


Phosphinate

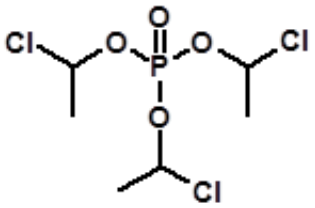
R1, R2, R3 are organic substituents, they can be the same or different



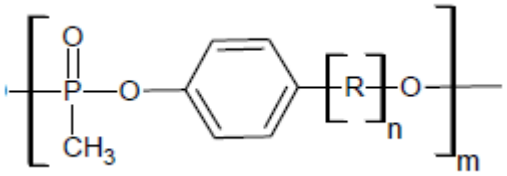
Ammonium polyphosphate



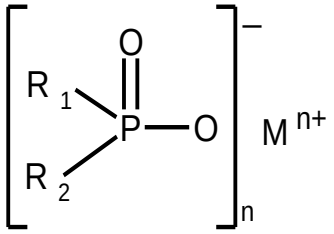
Resorcinoldiphosphoric acid tetraphenylester (RDP)



Tris-(chloroisoproyl) phosphoric acid ester (TCPP)



Polyphosphonate



phosphinic acid salts

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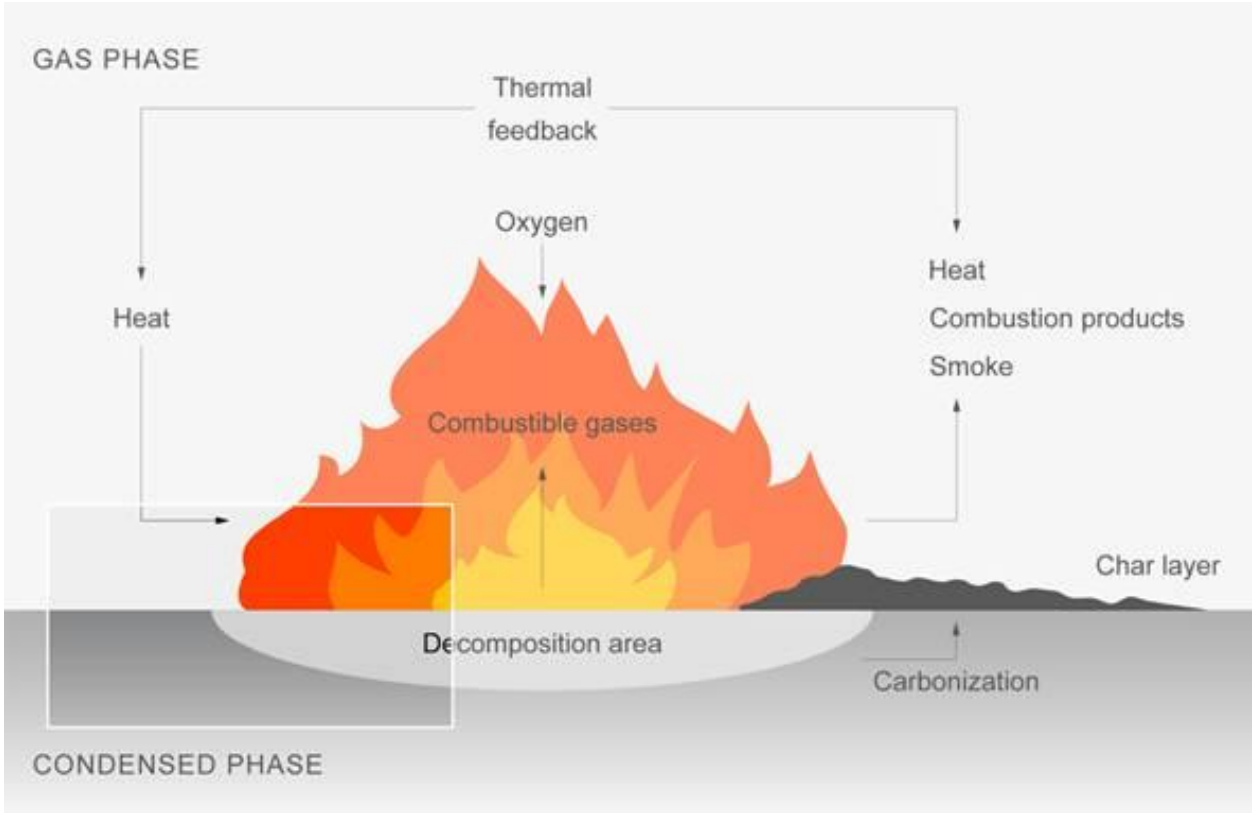
Inorganic hydroxide FRs - mechanism



- aluminium and magnesium hydroxides are the most common
- water is released upon heating, leading to a cooling of the combustion zone
- physical effect is less efficient ➔ high amounts are necessary
- less smoke, because no forced incomplete combustion, no acidic gases

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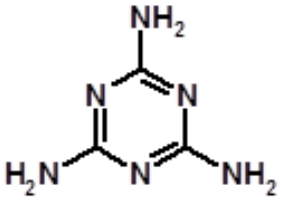
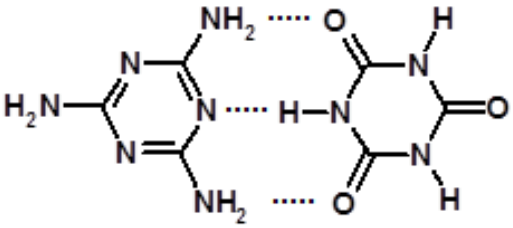
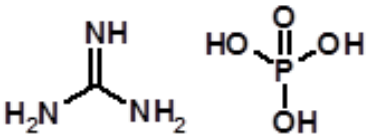
Nitrogen and Inorganic Flame Retardants - examples



Melamine



Melamine cyanurate (MC)



Guanidine phosphate

$$2\ Al(OH)_3 \xrightarrow[+\ 1050\ kJ\ /\ kg]{200\ °C} 3\ H_2O + Al_2O_3$$

$$Mg(OH)_2 \xrightarrow[+\ 1300\ kJ\ /\ kg]{300\ °C} H_2O + MgO$$

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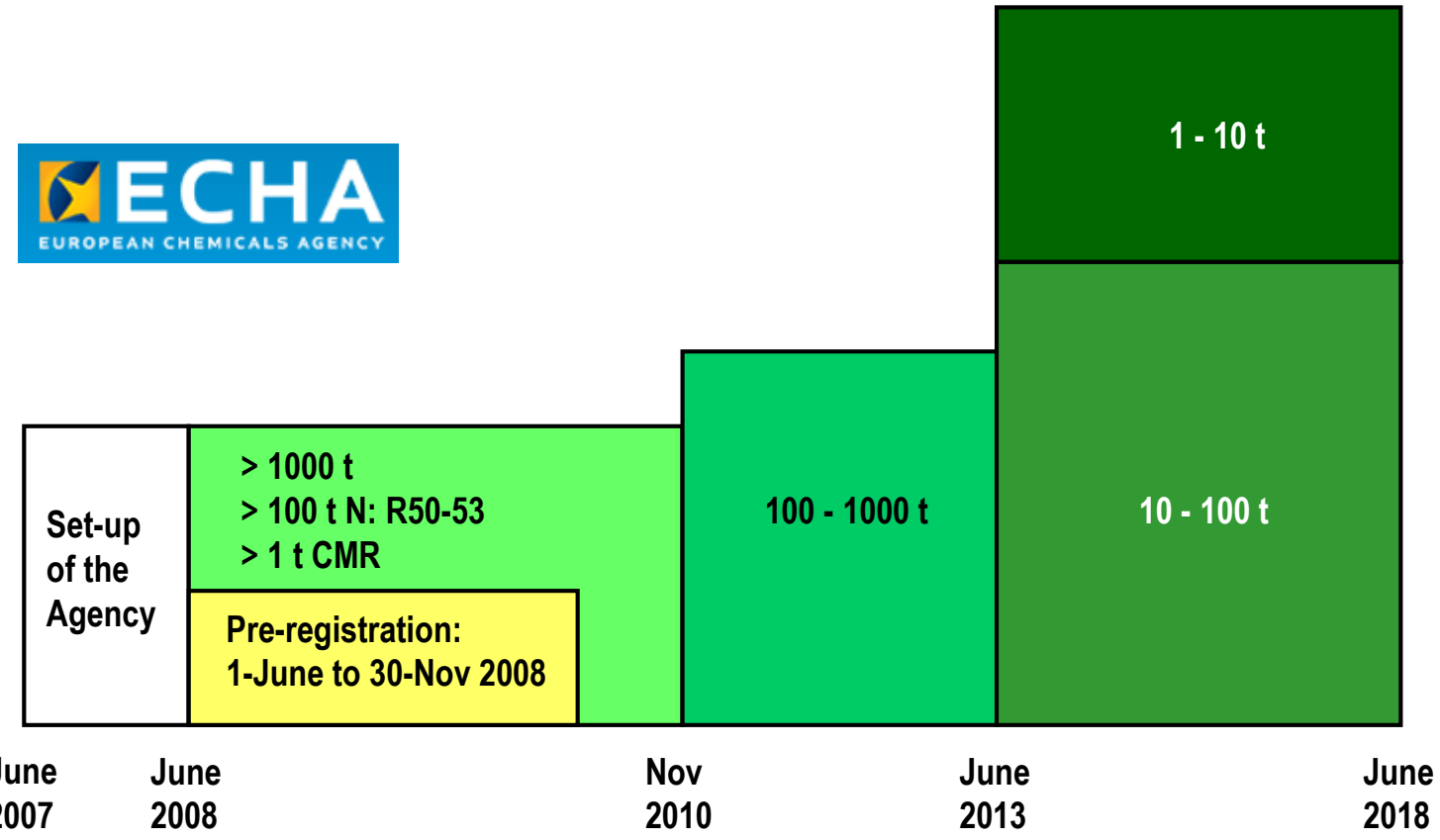
REACH is steaming ahead in Europe



Most flame retardants are already registered –
dossiers are available on ECHA website:
http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances

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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
  - Trixylylphosphate (TXP) – Reprotox Cat. 1b

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

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

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Europe RoHS and WEEE

- 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), but to be reviewed by 2014-07 (Art. 6): certain phthalates restricted by EU/2015/863
  - Restricted substances to be updated regularly; project by Austrian Umweltbundesamt produced priority list and methodology
- WEEE Directive recast as 2012/19/EU
  - Higher recycling quotas and additional product groups covered

picture: CT/tsa medien

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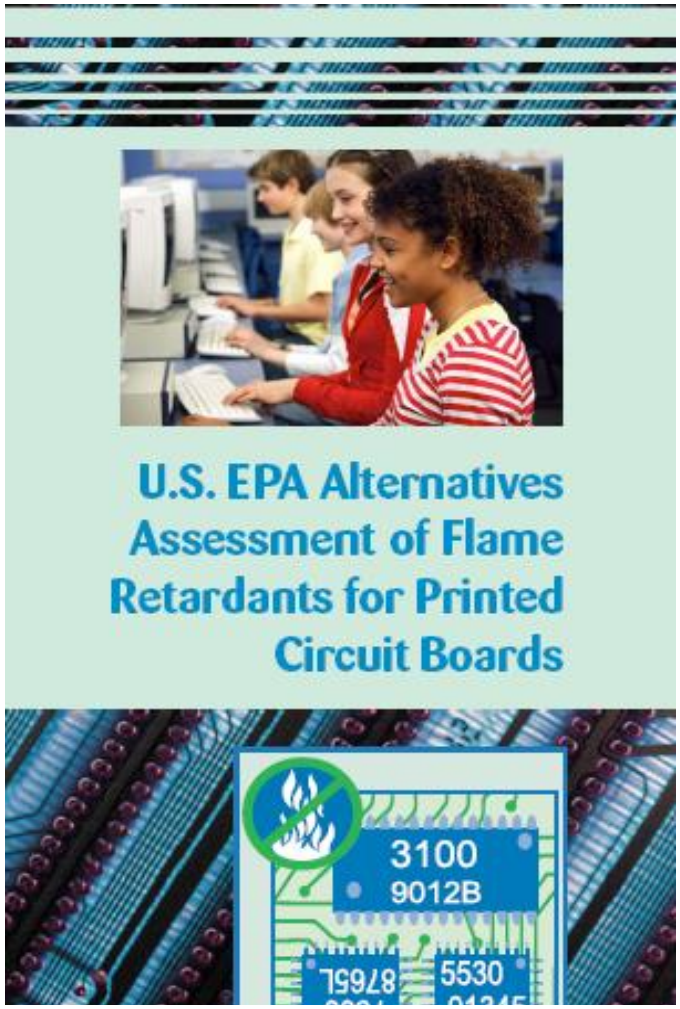
US-EPA: New Focus on Alternatives Assessment to BFRs

- Evaluation of environmental and health properties of alternatives to:
  - Tetrabromo bisphenol-A
  - Penta- and Decabromo diphenylether
  - Hexabromo cyclododecane
- Hazard focused approach
- Suitable alternatives to problematic products were identified
- 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

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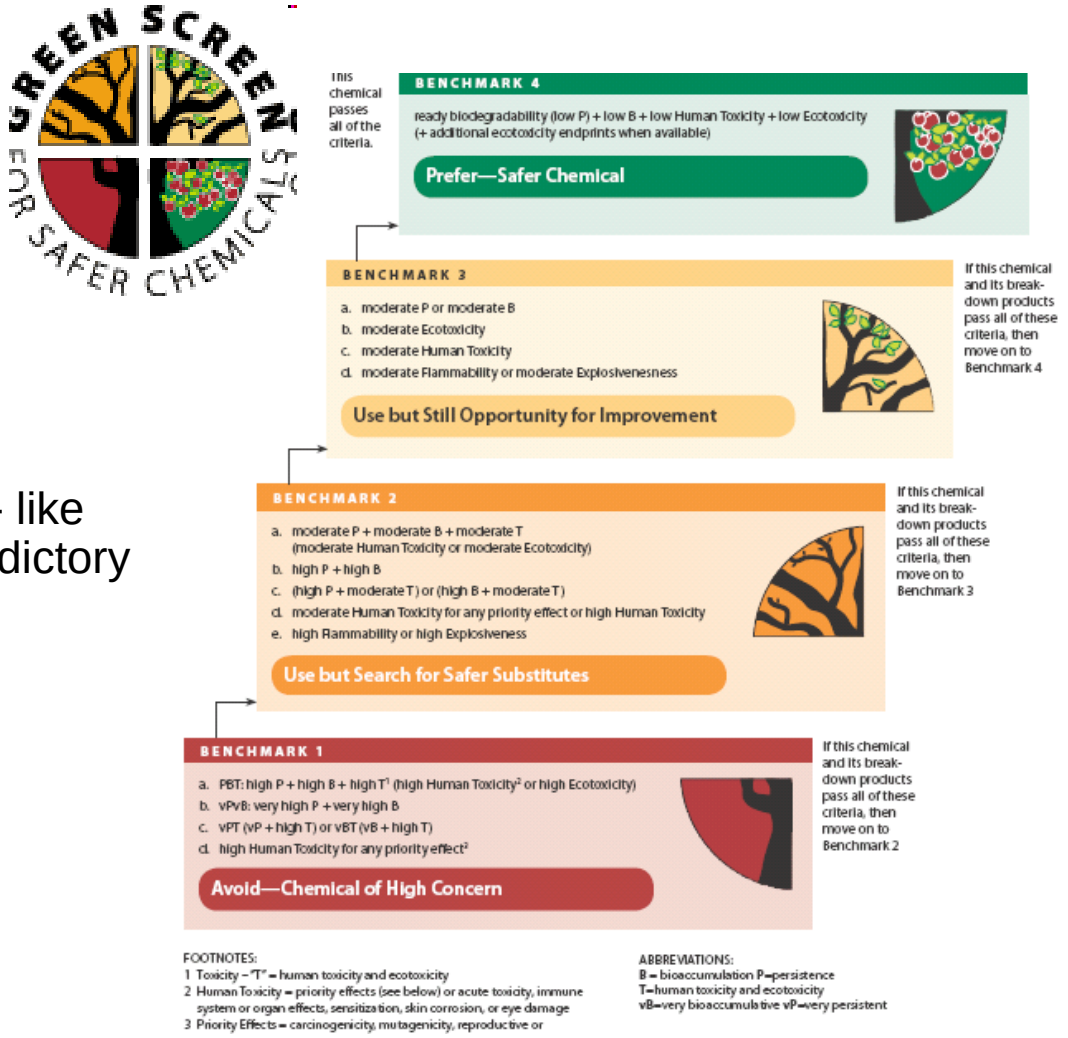
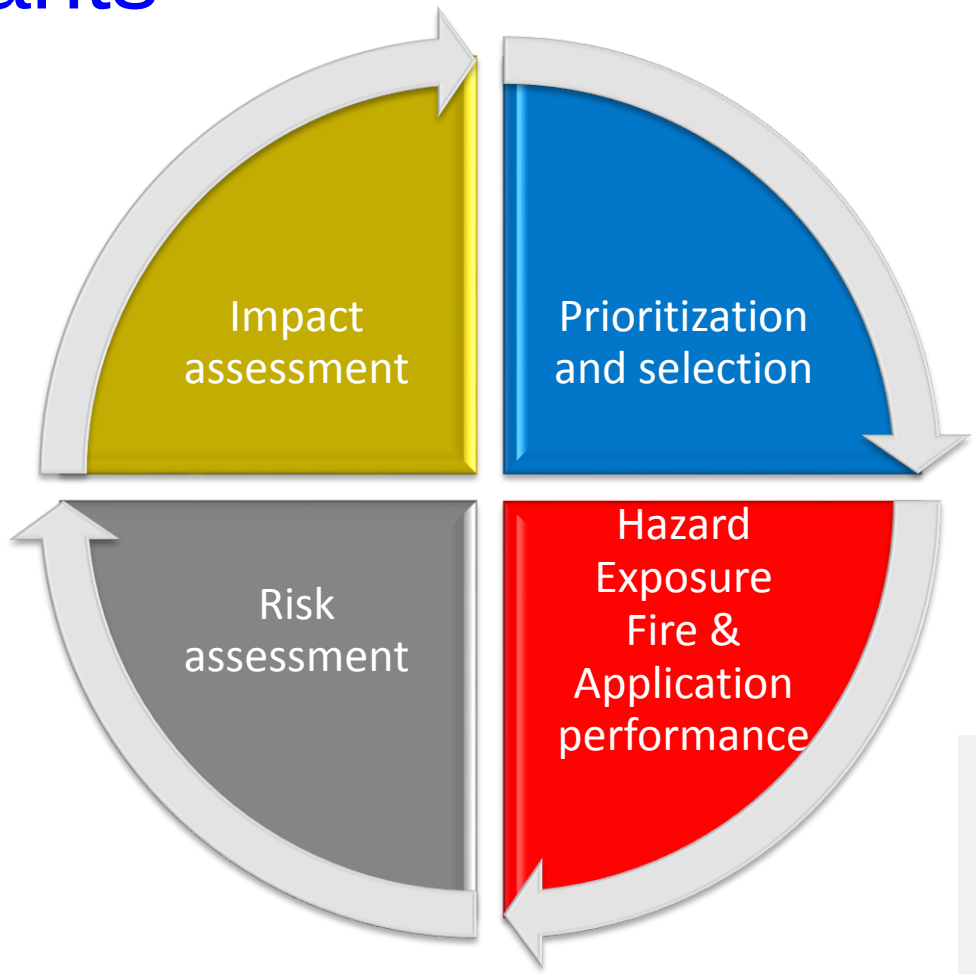
GreenScreen

- 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, ambiguous and 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

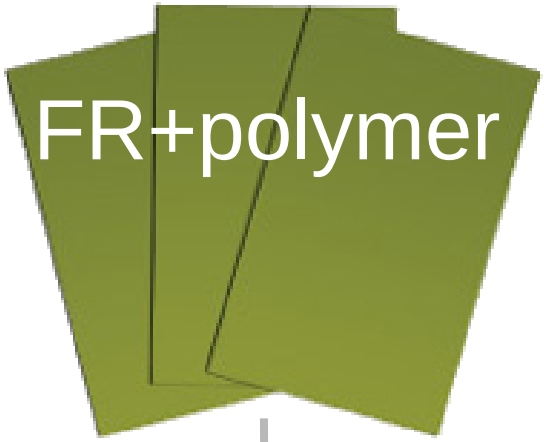
Evaluation of HFFRs reveals many FRs with good environmental and health profile

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)

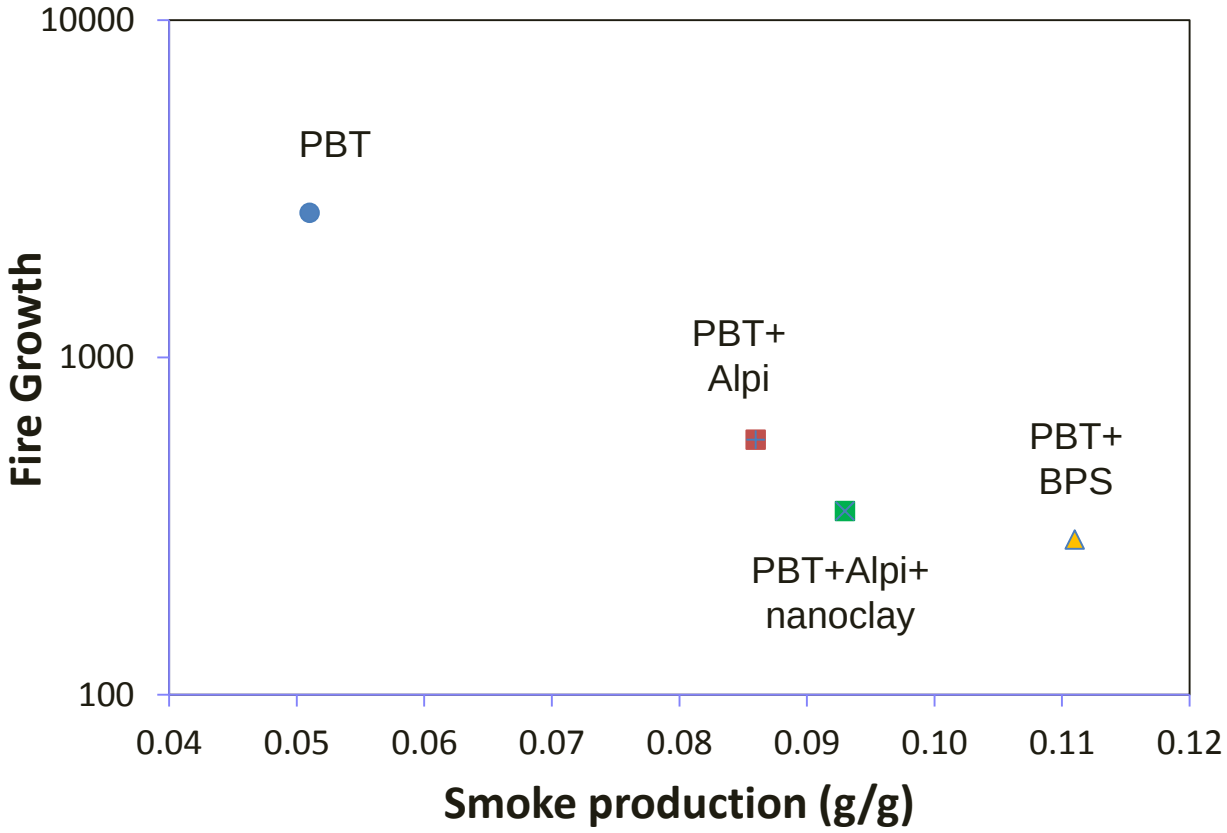
Leaching FR
to water
(concentrations and
toxicity)



Fire
performance
(e.g. Toxic gasses)

Applications

Fire Performance BFRs - HFFRS



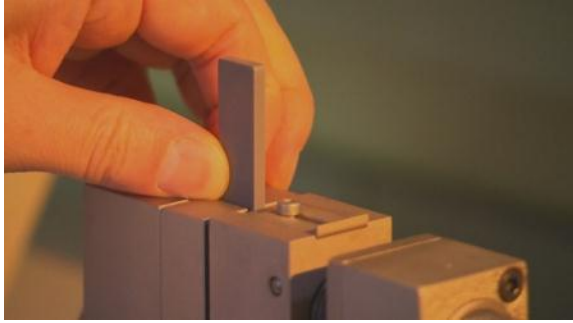
Zoomed view

- 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

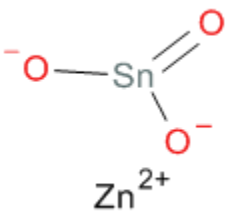
Application performance



- 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

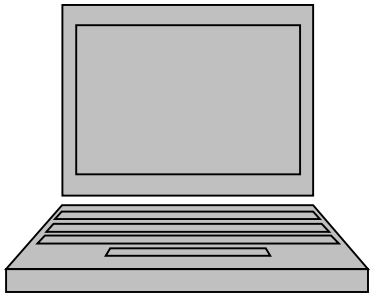
- Some HFFRs are less toxic than BFRs
- Suitable alternatives:
  - Alpi, DOPO, APP, MPP, ATH, ZHS, ZS

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

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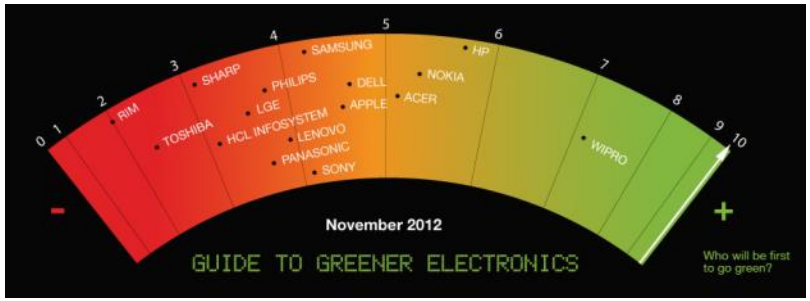
Market Drivers: NGOs, Ecolabels, Green Public Procurement

- Many ecolabels have restrictions for flame retardants
- Often detailed information on the flame retardants which are used is required
- EPEAT 2012: mandatory and optional require-ments for halogen-free plastics
- EU Ecolabels: task force on chemicals to revise simple hazard approach



TCO Development

GPP

Umweltzeichen weil Jury Umweltzeichen

EU Ecolabel www.ecolabel.eu

epeat

pinfa EU Members in 2015

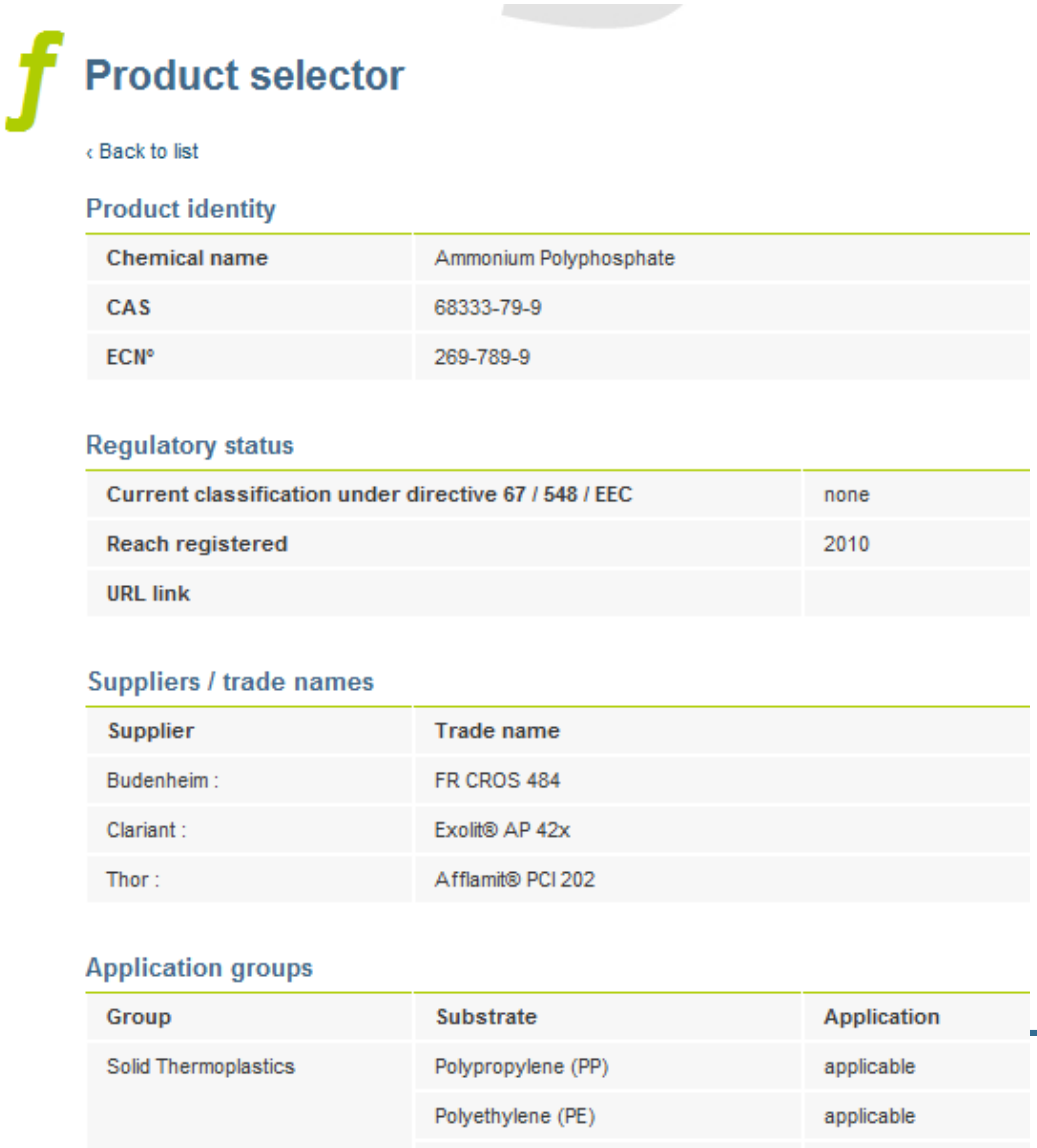
Who is pin*f*a?

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 North America was founded in 2012
- 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 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

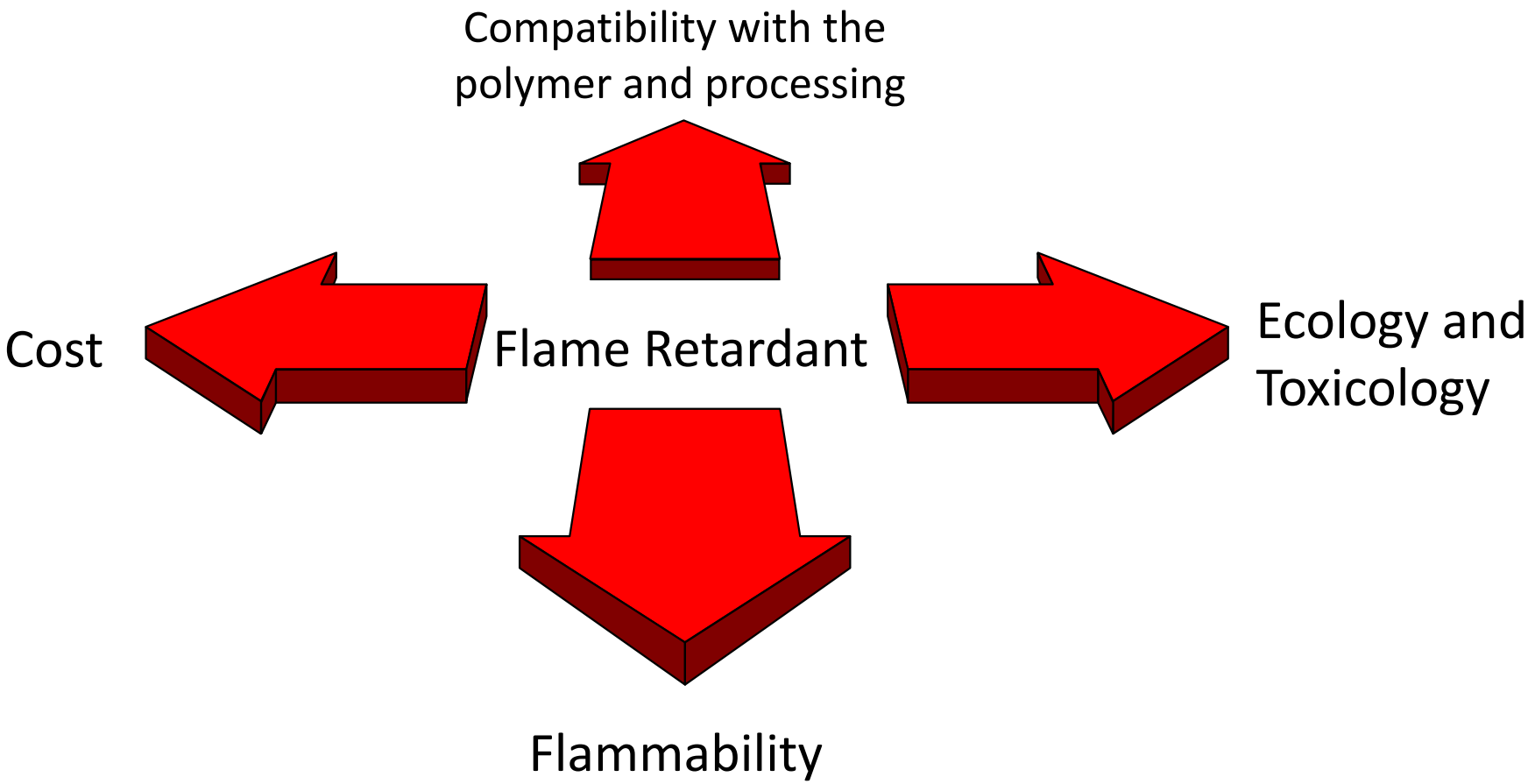
Application groups

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

Further Reading - brochures

- E&E applications
- Transportation
- Building & Construction
- Explain flame retardants by application
- www.pinfa.eu/library/brochures.html

Requirements on Flame Retardants



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Summary

- The scientific and public debate on flame retardants has led to some regulatory restrictions on mostly halogenated 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
  - In general, halogen free systems produce less smoke and less toxic components in smoke
- 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

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Thank you

FOR YOUR ATTENTION

what is precious to you?