An update on regulatory status and environmental assessments

SEARCHING FOR SAFE FLAME RETARDANTS

CLARIANT

Public

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Clariant Flame Retardants
pinfa North America
10.06.2014

what is precious to you?

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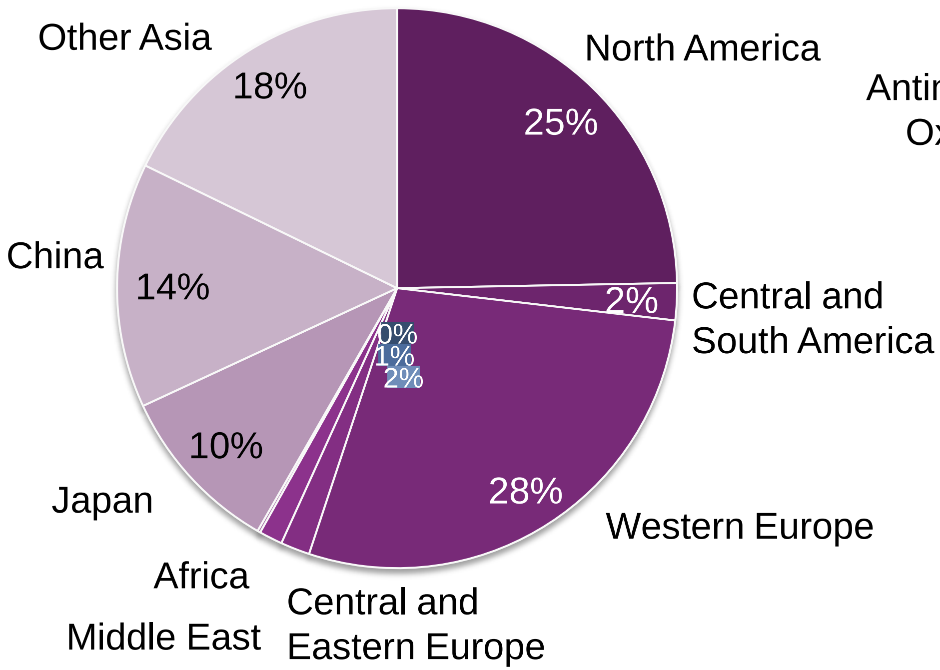
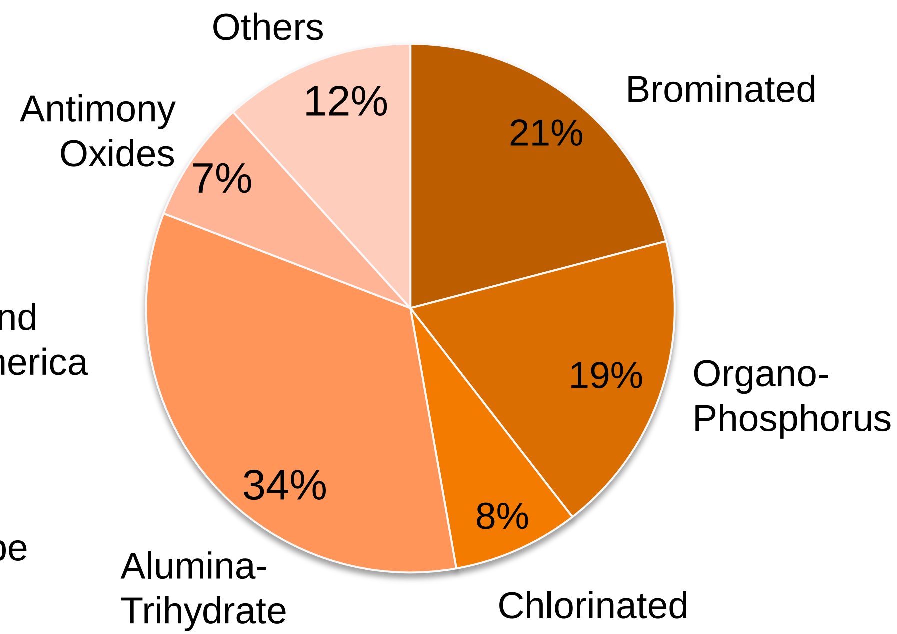
Global Consumption of Flame Retardants (2010)

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

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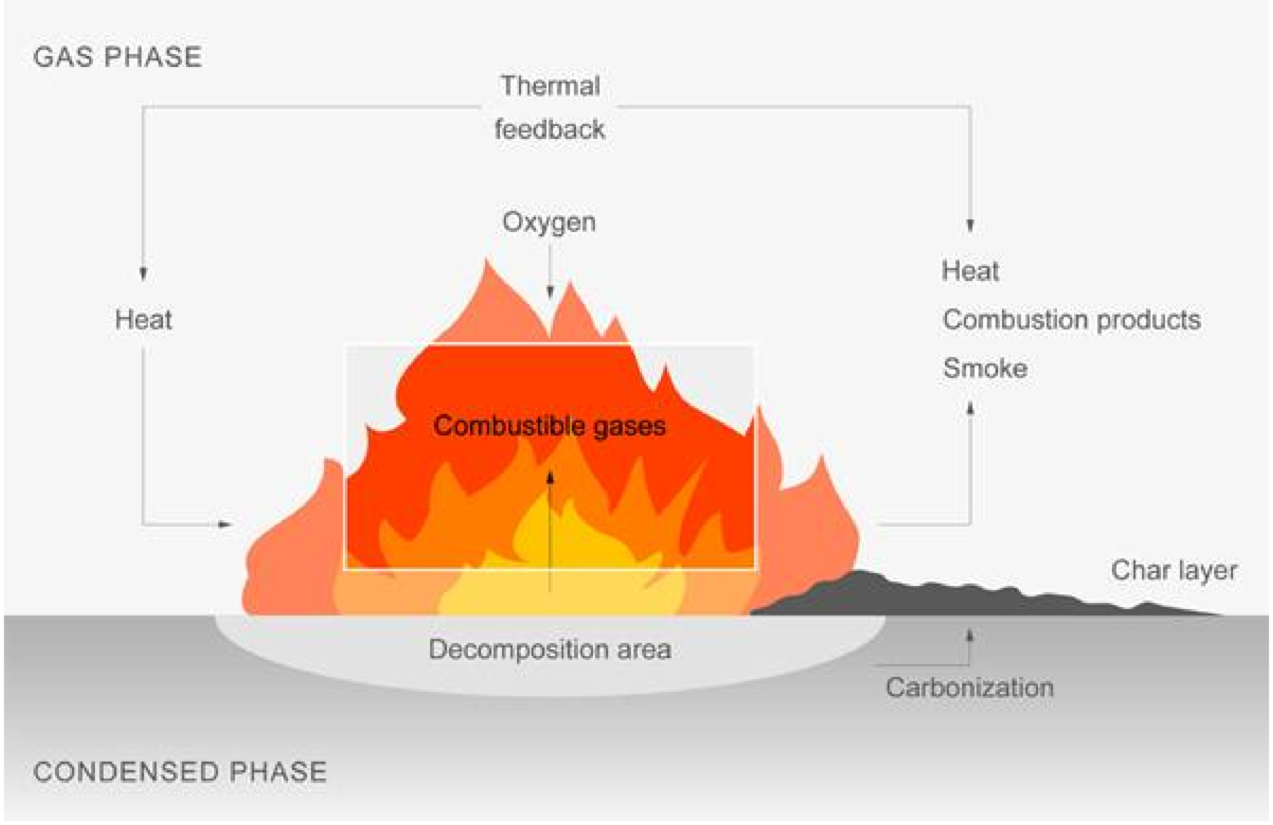
Halogenated FRs - mechanism



- brominated and chlorinated compounds are commonly used
- halogen radicals impede reactions in the flame zone
- forced imcomplete combustion leads to copious amounts of smoke
- halogen acids are also formed
- often used in combination with antimony trioxide

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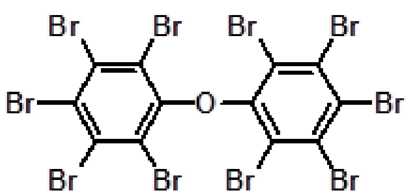
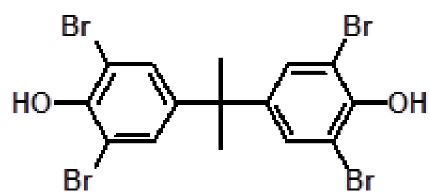
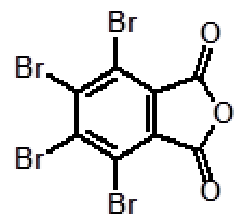
Brominated and chlorinated Flame Retardants - examples



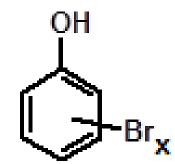
Deca-BDE



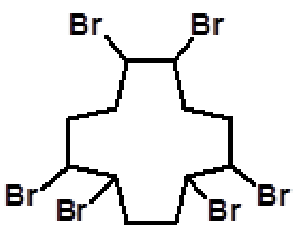
Tetrabromobisphenol-A



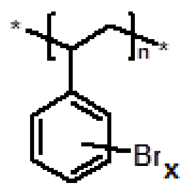
Tetrabromophthalic anhydride



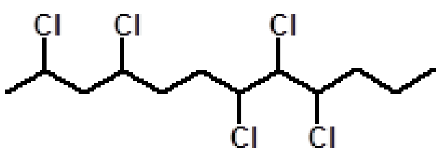
Brominated phenols



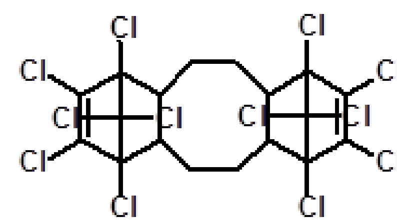
Hexabromocyclododecane (HBCD)



Brominated polystyrene

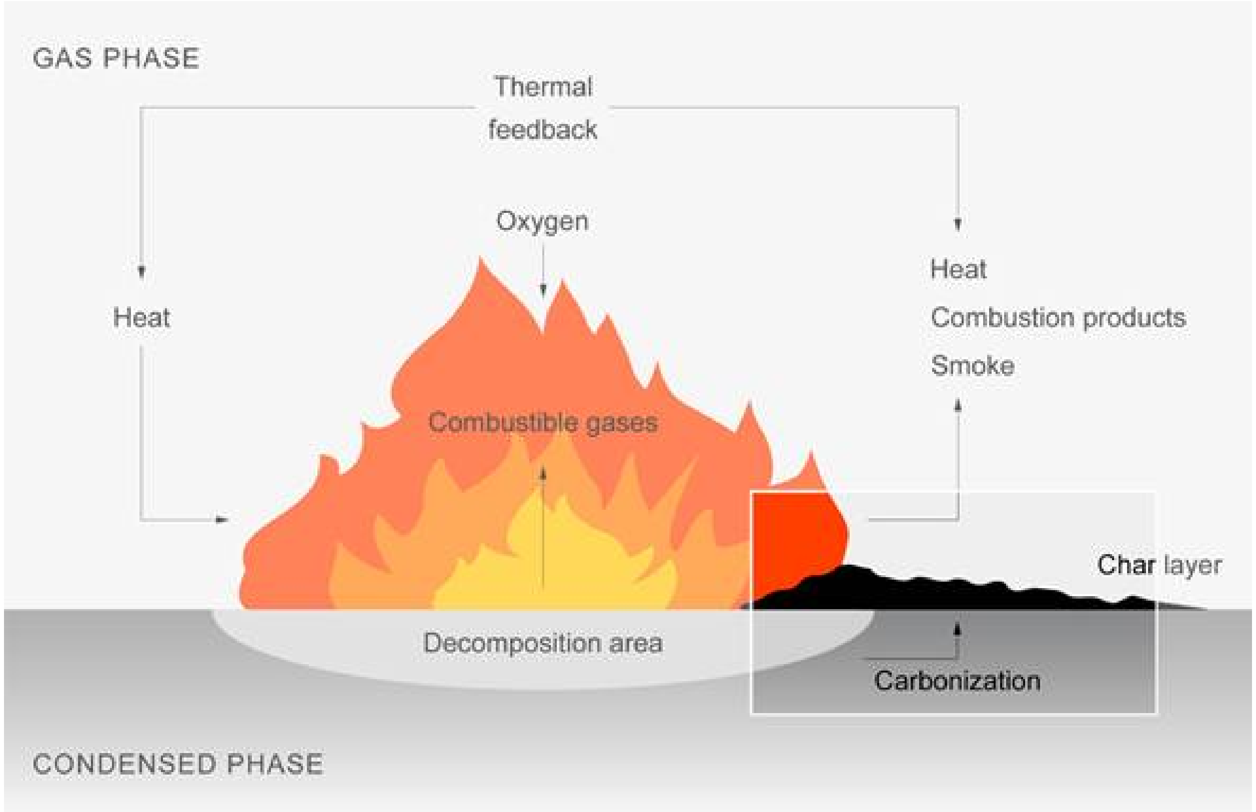


Chlorinated paraffins (example)



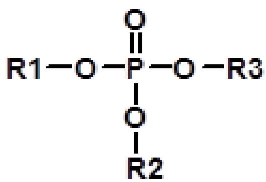
Dodecachlorpentacyclooctadecadien (Dechlorane)

Phosphorus FRs - mechanism

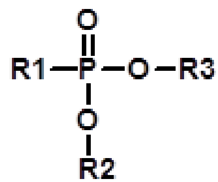


- elemental (red) phosphorus, inorganic and organic phosphorus compounds are used
- main mechanism is by formation of a char layer at the surface, stopping the contact between fuel and air
- generally less smoke, because no forced incomplete combustion, less acidic gases

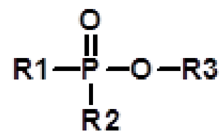
Phosphorus based Flame Retardants - examples



Phosphate ester

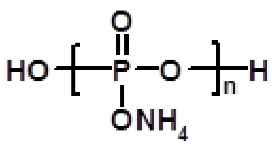


Phosphonate

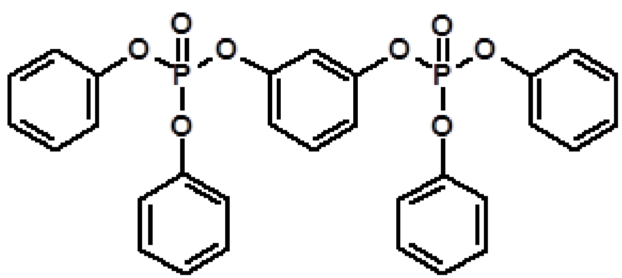


Phosphinate

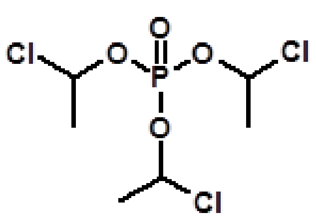
R1, R2, R3 are organic substituents, they can be the same or different



Ammonium polyphosphate

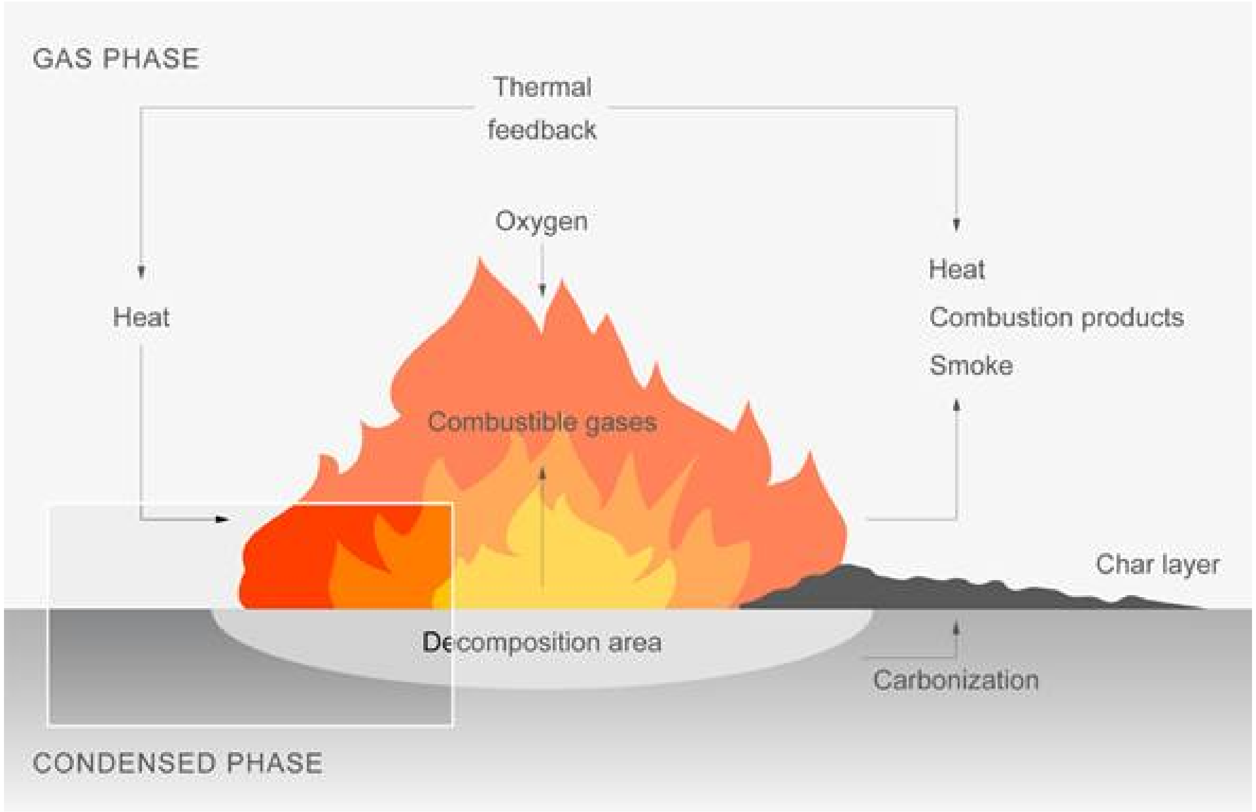


Resorcinoldiphosphoric acid tetraphenylester (RDP)



Tris-(chloroisoproyl) phosphoric acid ester (TCPP)

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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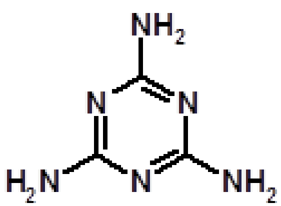
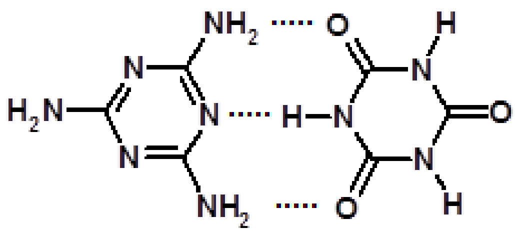
Nitrogen and Inorganic Flame Retardants - examples



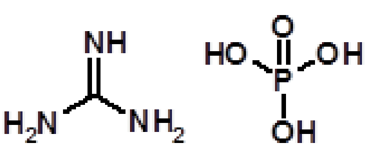
Melamine



Melamine cyanurate (MC)

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

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



Guanidine phosphate

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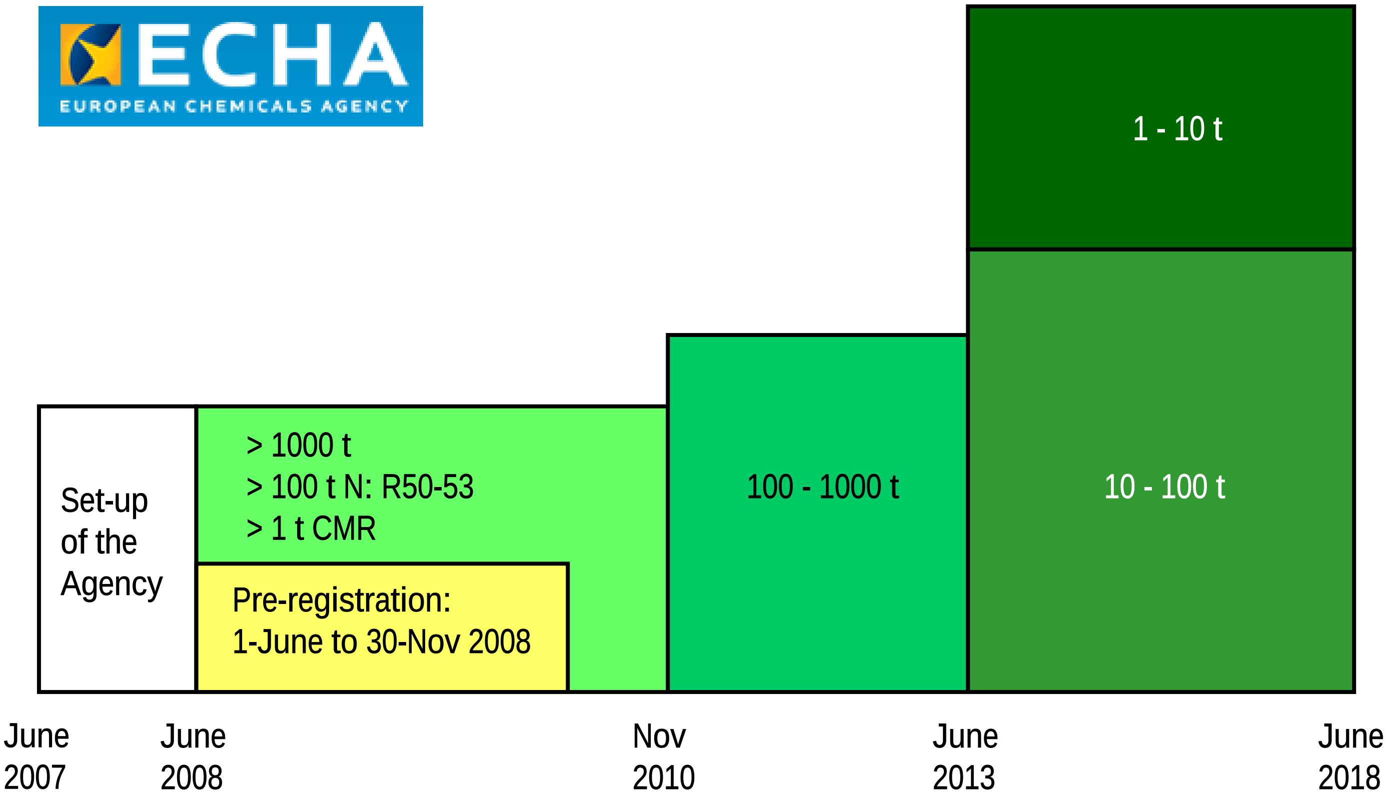
REACH is steaming ahead in Europe



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

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Europe: REACH – concept

- REACH is the European Community Regulation on chemicals and their safe use (EC 1907/2006).
  - **R**egistration: “no data, no market” → industry has to provide basic data and submit registration dossier, including target uses (→ requirements for downstream users)
  - **E**valuation: spot checks are done by authorities on dossiers
  - **A**uthorisation: “Substances of very high concern” (SVHC) need an authorisation from the authorities for being used
  - Restriction of **Ch**emical substances: for certain or all uses
- Sound and comprehensive concept, but the devil is in the detail, e.g.
  - Substance identification, substances in articles
  - Consortia of producers / importers (Substance Information Exchange Forums (SIEFs): data and cost sharing …

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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

- 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 and HBCD very likely
  - Restricted substances to be updated regularly
- WEEE Directive recast as 2012/19/EU
  - Higher recycling quotas and additional product groups covered

picture: CT/tsa medien

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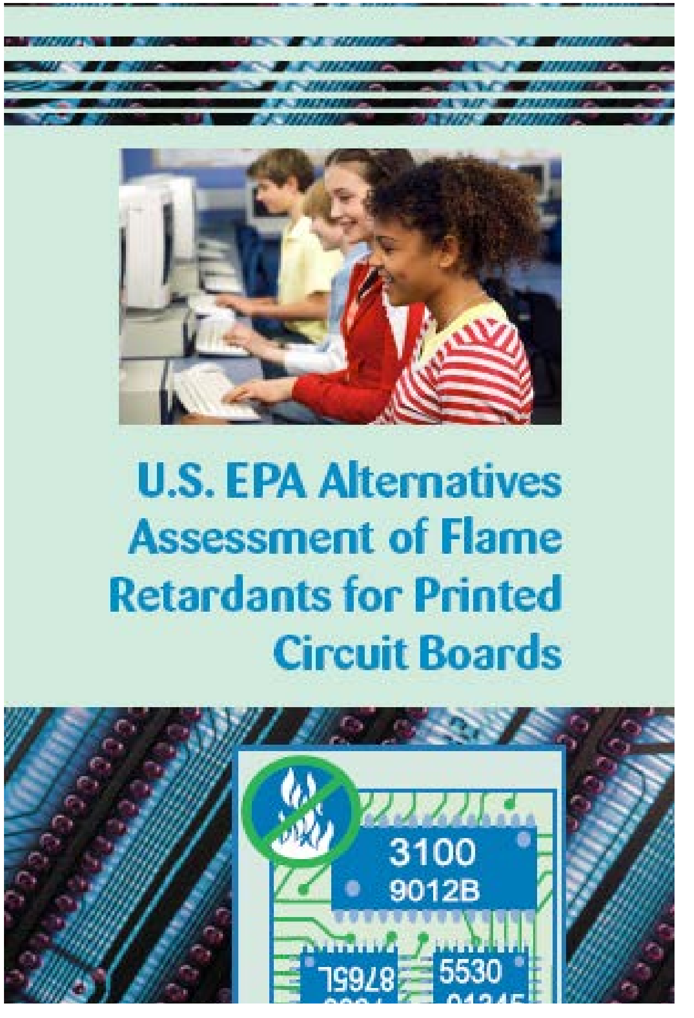
US-EPA: New Focus on Alternatives Assessment to BFRs

- Evaluation of environmental and health properties of alternatives to:
  - Tetrabromo bisphenol-A
  - Decabromo diphenylether
  - Hexabromo cyclododecane
- Hazard focused approach
- No black and white picture:
  - Good alternatives available
  - Alternatives (incl. halogen free) also have chemical hazards, however, need to consider relevance
  - Data gaps filled by read-across, computational methods or expert judgement
- Combustion testing confirmed formation of dioxins and higher smoke tox (CO) from BFRs (TBBPA)



www.epa.gov/dfe

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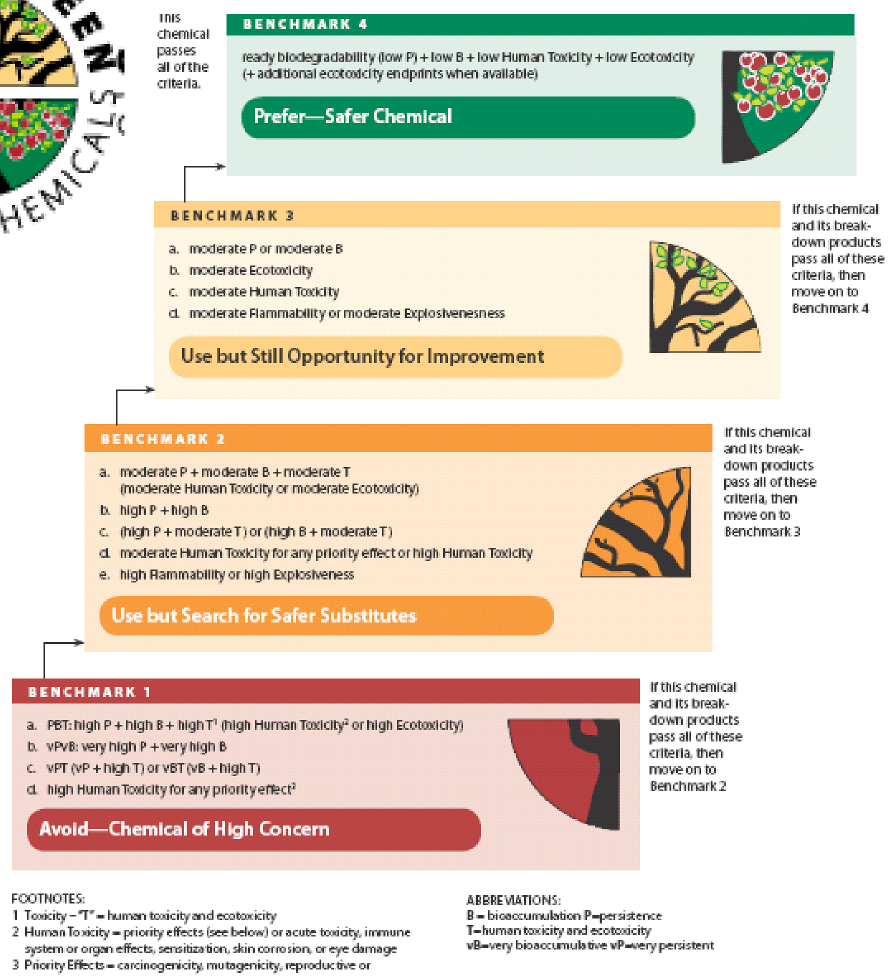
GreenScreen

- 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/

GREEN SCREEN FOR SAFER CHEMICALS



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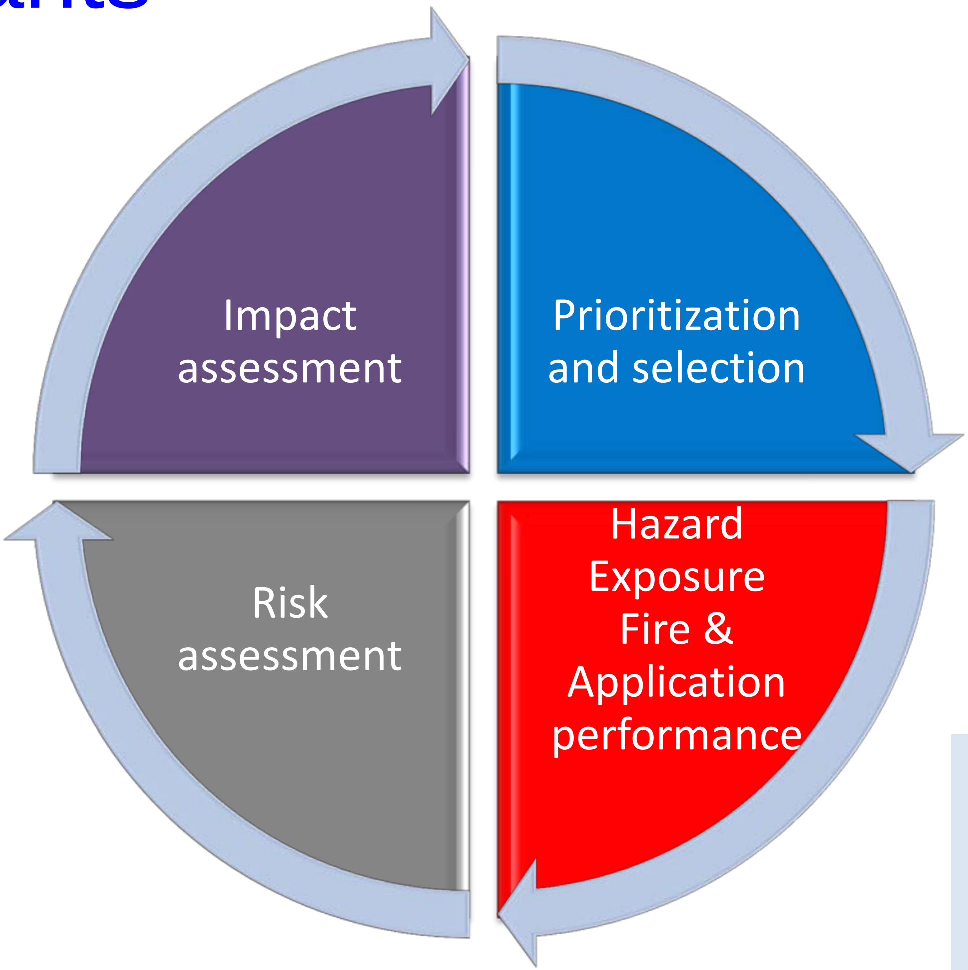
Translation of DfE data to GreenScreen Benchmarks for non-hal FRs in Deca-BDE report

DfE to GreenScreen Translations	Benchmark Scores
Antimony Trioxide (1309-64-4)	1
Melamine Cyanurate (CAS# 37640-57-6)]	1
N-alkoxy Hindered Amine Rx Products (CAS#191680-81-6)	1
Phosphonate Oligomer (CAS#68664-06-2)	1
Zinc Borate 1332-07-6, 138265-88-0	1
Aluminum diethylphosphinate (CAS#225789-38-8)	2
Aluminum Hydroxide (CAS#21645-51-2)	2
Melamine Polyphosphate (CAS#15541-60-3)	2
Poly[phosphonate-co-carbonate] (CAS# 77226-90-5)	2
Resorcinol Bis-Diphenylphosphate (CAS#125997-21-9)	2
Red Phosphorus (CAS# 7723-14-0)	2
Substituted Amine Phosphate mixture (CAS# 66034-17-1)	2
Triphenyl Phosphate (CAS#115-86-6)]	2
Ammonium Polyphosphate (CAS # 68333-79-9)]	3
Magnesium Hydroxide (CAS # 1309-42-8)]	3
Polyphosphonate (CAS#68664-06-2)	3
Bisphenol A Bis-(diphenyl phosphate) (CAS#181028-79-5 and 5945-33-5) (BAPP)	U
Phosphoric acid, mixed esters with [1,1'-bisphenyl-4,4'-diol] and phenol; BPBP (CAS#1003300-73-9)]	U
	4

- Some assessments may still be subject to change ("upgrade")
- To date, only water has been classified as benchmark 4

http://www.newmoa.org/prevention/ic2/projects/resource/hazassesstool.cfm

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

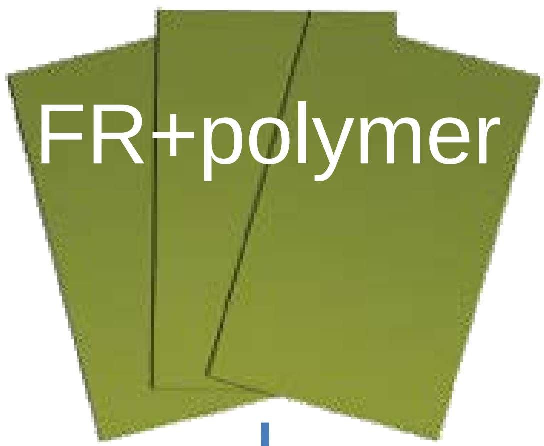
Evaluation of HFFRs reveals many FRs with good environmental and health profile

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)



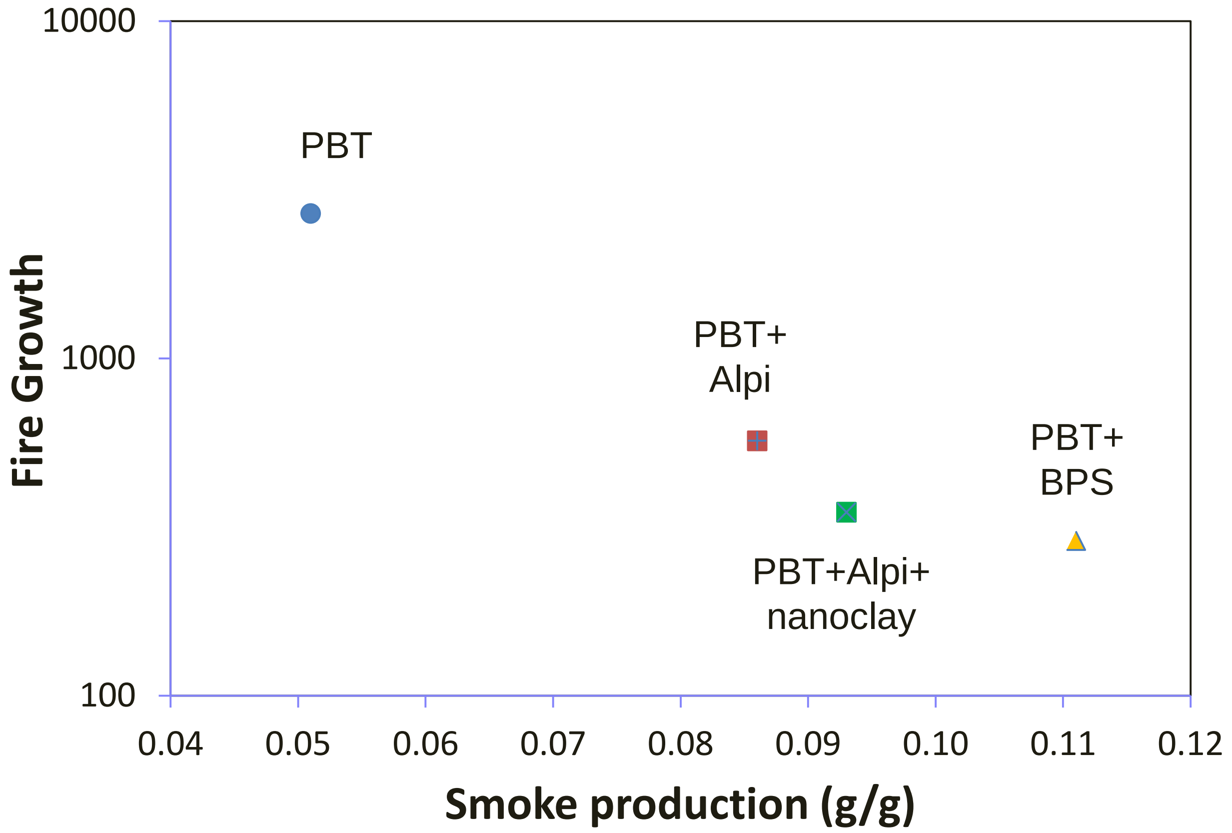
Fire
performance
(e.g. Toxic gasses)

Applications

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



Zoomed view

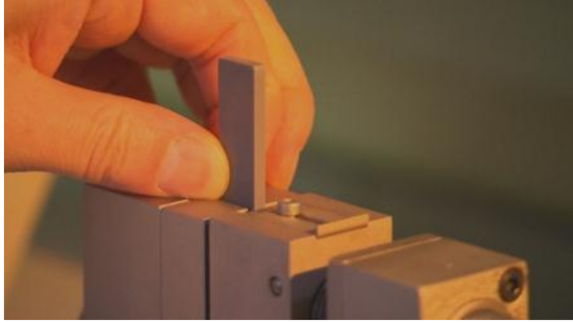
- In general, HFFRs had improved smoke suppression
- HFFRs had similar fire performance characteristics as BFRs in polymers, except for polymer blends

University of ULSTER

FireSERT

ENFIRO

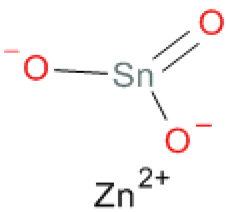
Application performance



- 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

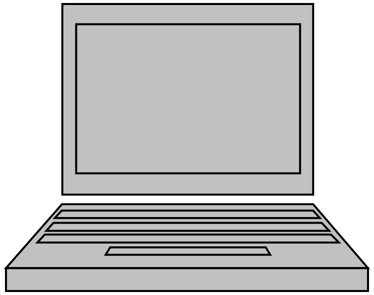
- Some HFFRs are less toxic than BFRs
- Suitable alternatives:
  - Alpi, DOPO, APP, MPP, ATH, ZHS, ZS

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

The ENFIRO Consortium

Acknowledgements

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

www.enfiro.eu

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Institute for Environmental Studies

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University of ULSTER

FireSERT

Clariant

Stockholm University

PROCOAT

IBED

Callisto Productions

callistoproductions.com

Universiteit Utrecht

Institute for Risk Assessment Sciences

SEVENTH FRAMEWORK PROGRAMME

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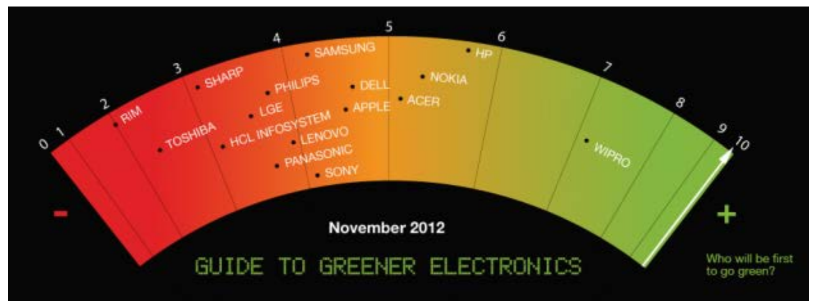
Market Drivers: NGOs, Ecolabels, Green Public Procurement

- 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



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dartex coatings

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DSM BRIGHT SCIENCE. BRIGHTER LIVING.

FRX polymers

Italmatch Chemicals

KREMS CHEMIE Chemical Services

LANXESS Energizing Chemistry

Nabaltec

Perstorp WINNING FORMULAS

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ROCKWOOD ADDITIVES

THOR

williamblythe quality, chemistry, performance

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pin*f*a North America Members 2014

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HUBER ENGINEERED MATERIALS

NETWORK POLYMERS
SOLID FLEXIBILITY

Nabaltec

FRX polymers

PolyOne

ADEKA

APPLIED MINERALS

A. Schulman

www.pinfa-na.org

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

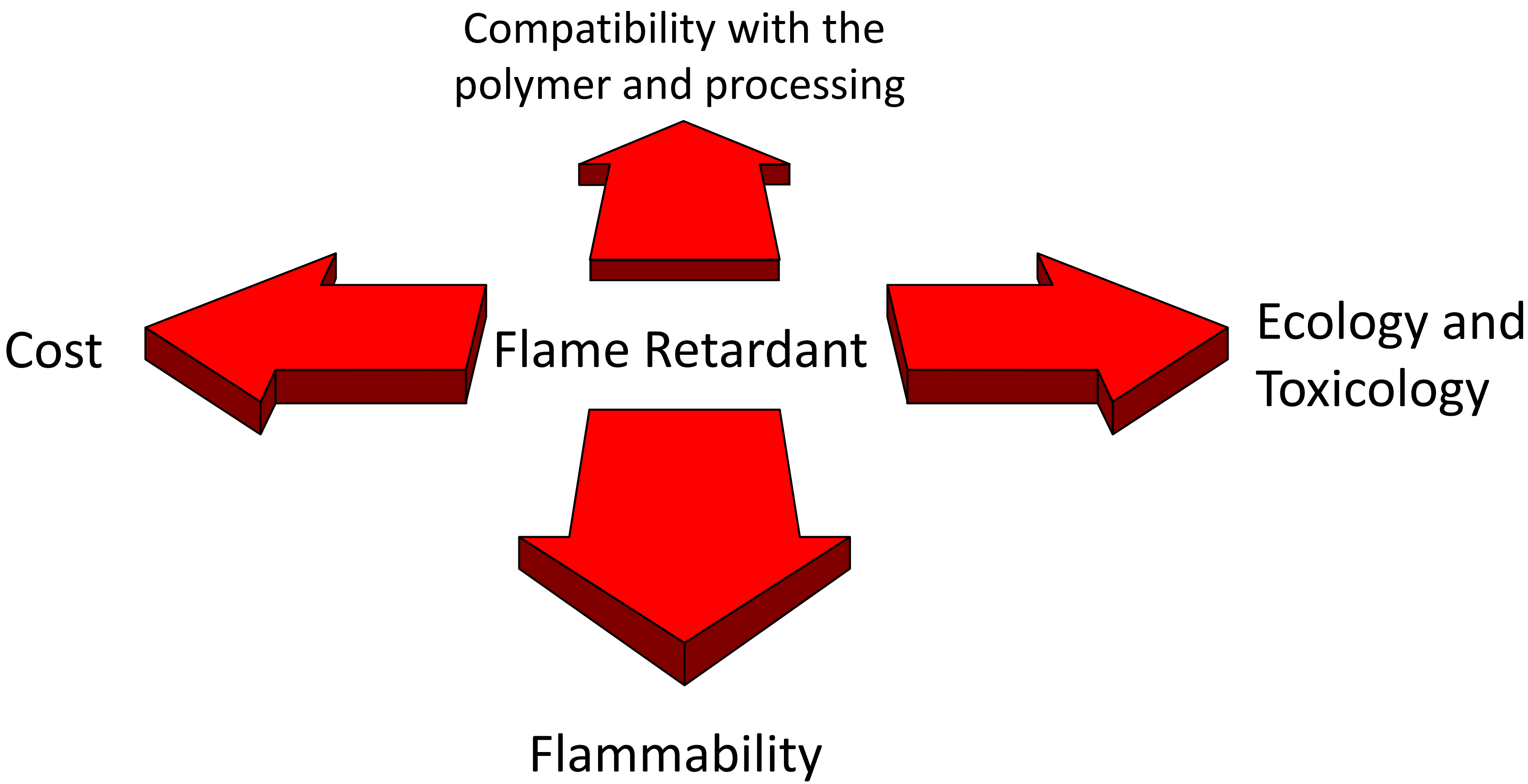
Application groups

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?