pinfa

Phosphorus, Inorganic & Nitrogen Flame Retardants Association

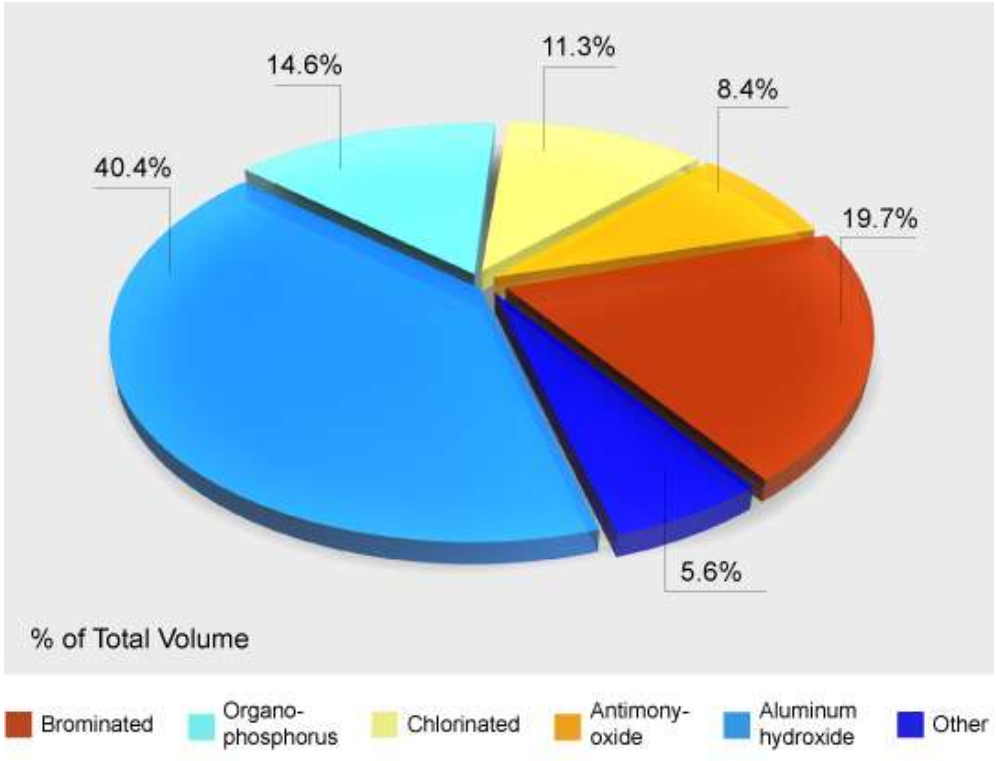
Searching for safe Flame Retardants – an update on regulatory status and environmental assessments

Safer Products Summit
3 April 2013, San Francisco, California, USA
Adrian Beard, Michael Klimes

cefic

Responsible Care®
Good Chemistry at Work

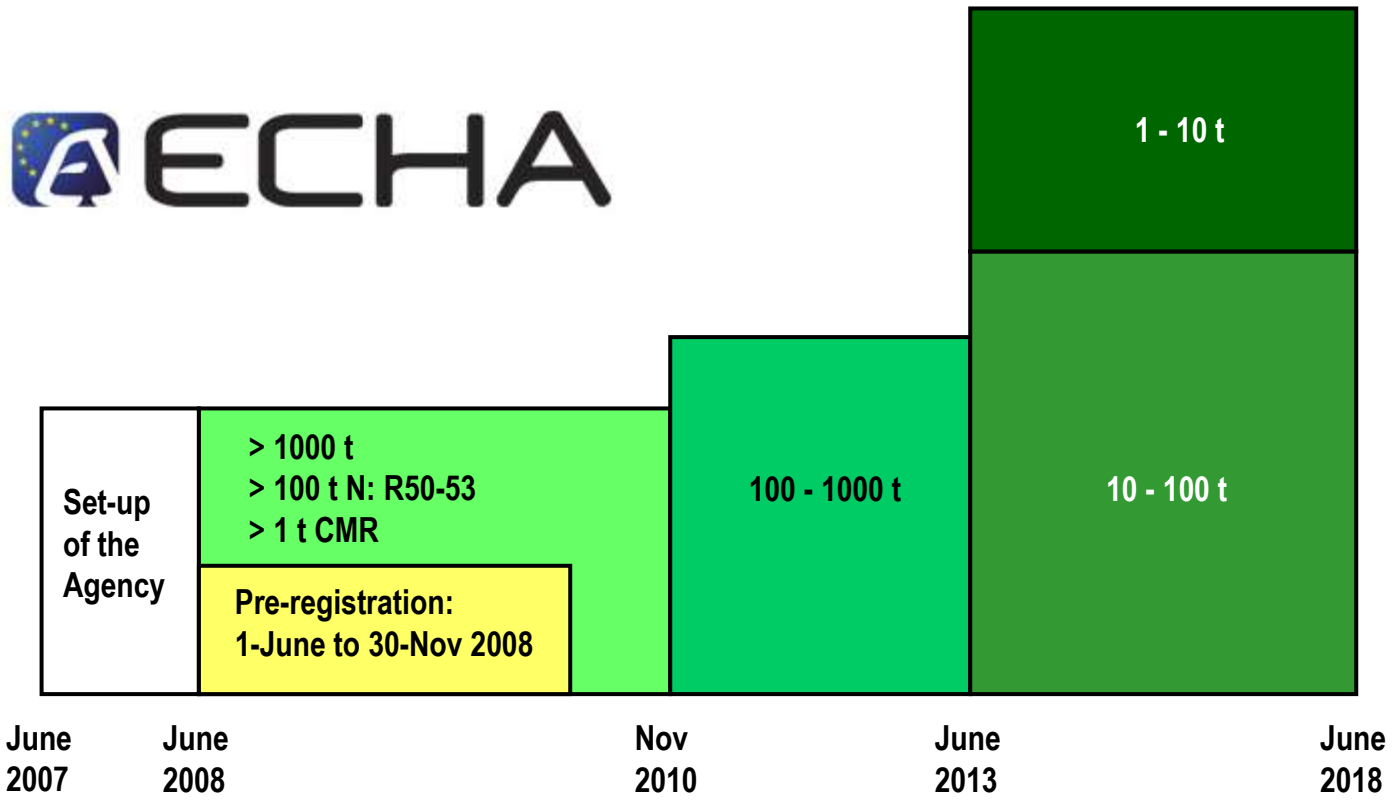
The Global Flame Retardants Market



Global Consumption of Flame Retardants in Plastics by Type, Tonnes – 2011:

- 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

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

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

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

picture: CT/tsa medien

Market Drivers: NGOs, Ecolabels, Green Public Procurement

TCO Development

GPP

Umweltzeichen weil ...

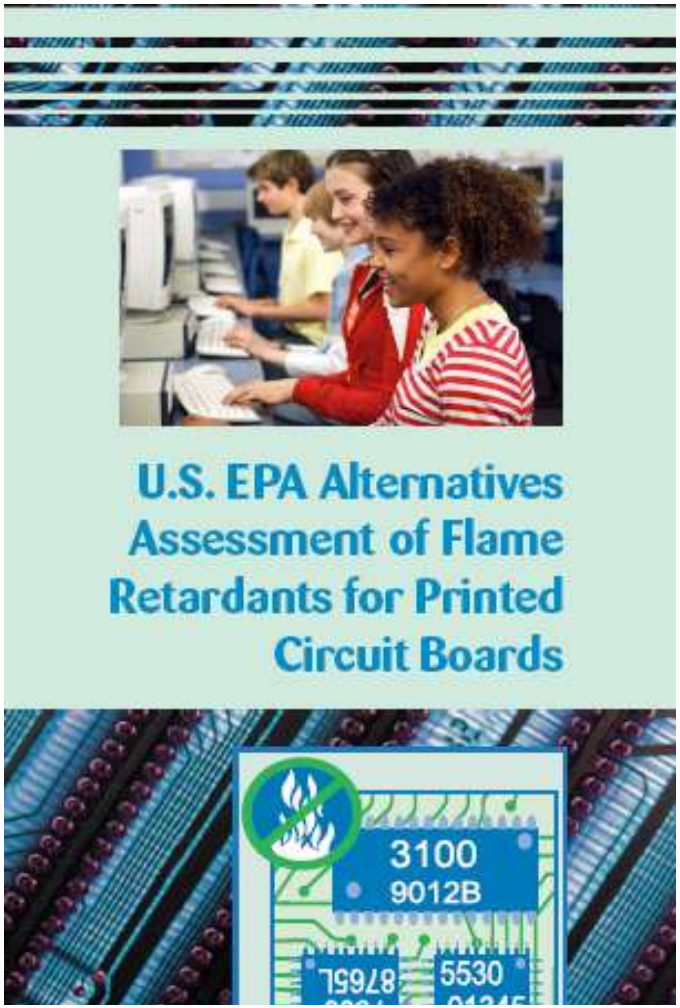
EU Ecolabel
www.ecolabel.eu

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

US-EPA: New Focus on Alternatives Assessment to BFRs

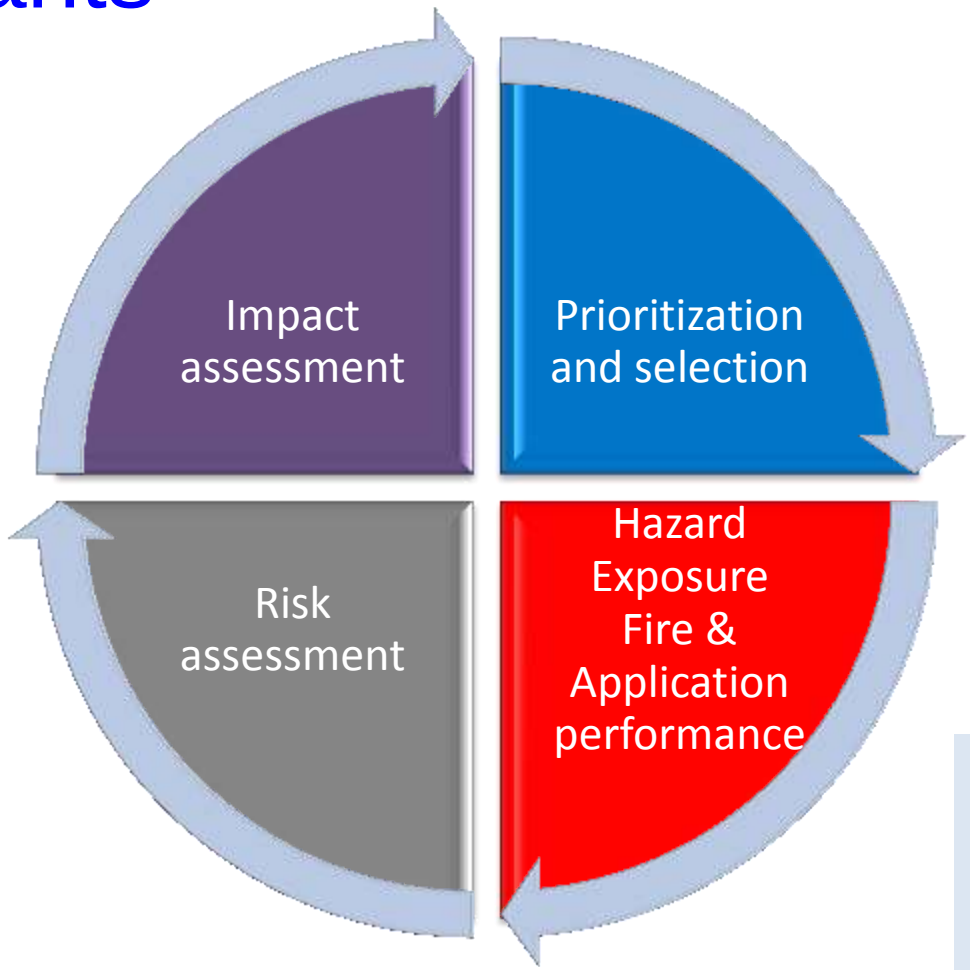
- Evaluation of environmental and health properties of alternatives to:
  - Tetrabromo bisphenol-A
  - Decabromo diphenylether
  - Hexabromo cyclododecane
- Hazard focused approach
- No black and white picture:
  - Alternatives (incl. halogen free) have chemical hazards, too, however,
  - Need to check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



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 for-mation of dioxins by combustion into account
- 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

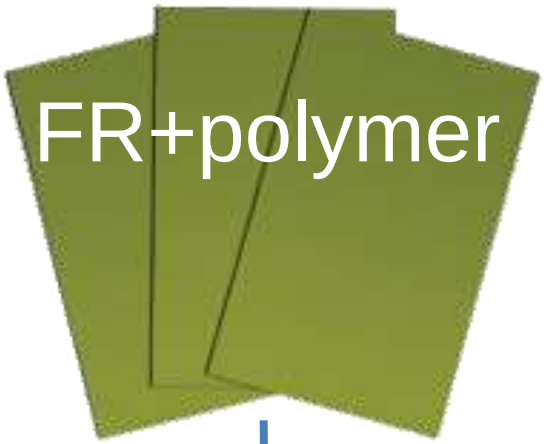
Evaluation of HFFRs reveals many FRs with good environmental and health profile

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)

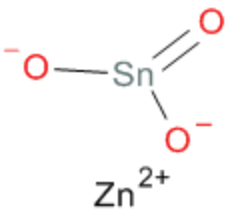
Applications

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

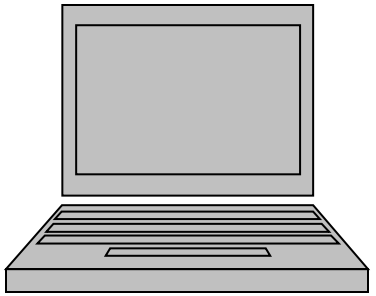
- Some HFFRs are less toxic than BFRs
- Suitable alternatives:
  - Alpi, DOPO, APP, MPP, ATH, ZHS, ZS

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

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 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 EU Members in 2013

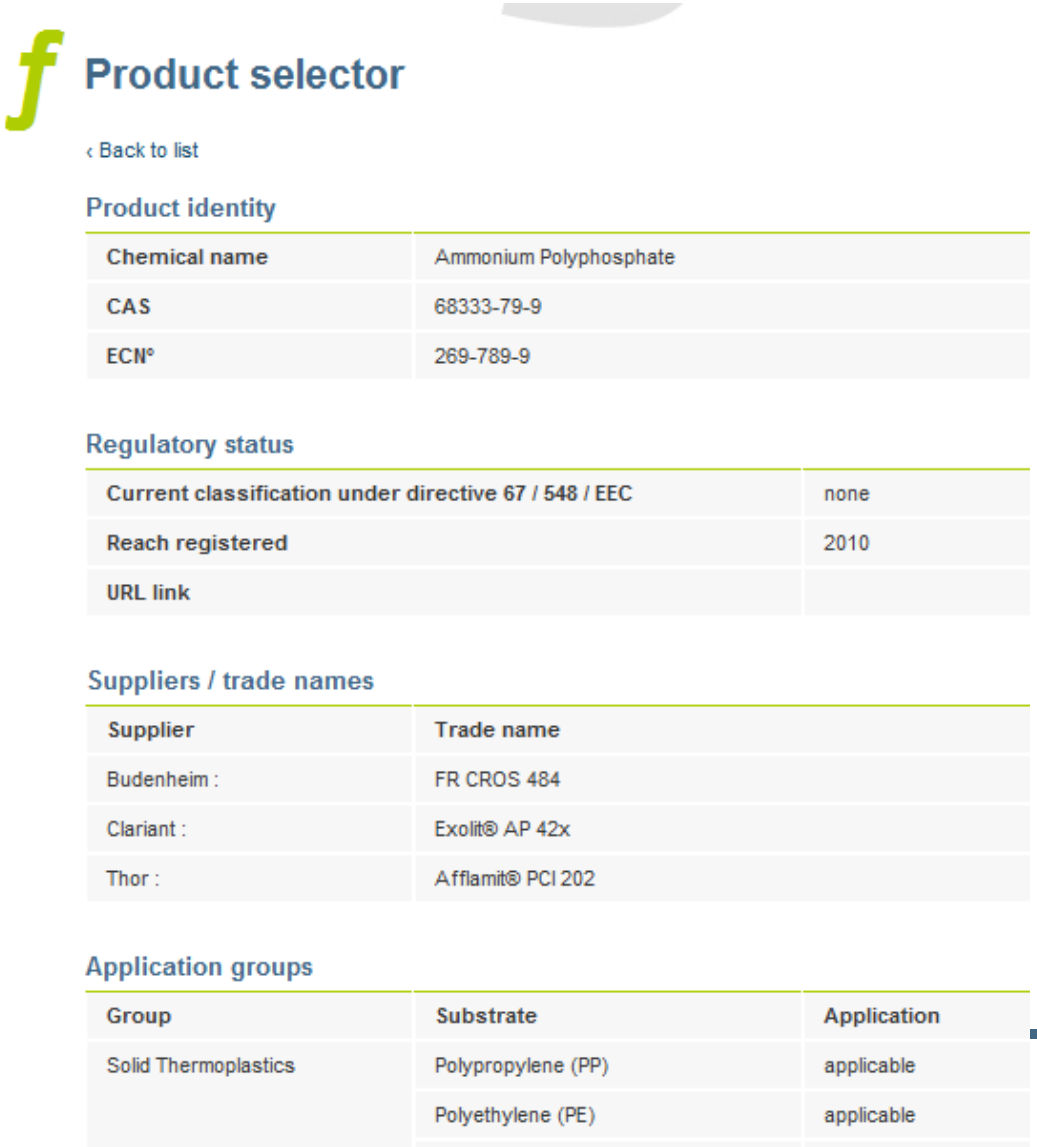
pinfa NA Members 2013

- FRX Polymers
- Nabaltec AG
- Clariant Additives
- Huber Engineered Materials
- Polyone
- Network Polymers
- Applied Minerals

- www.pinfa-na.org

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

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 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

Safer Products Summit
3 April 2013, San Francisco, California, USA
Adrian Beard, Michael Klimes

cefic

Responsible Care®
Good Chemistry at Work