Flame Retardants: Design for Environment and End-of-Life - is there a life after WEEE, RoHS and REACH?

Dr. Adrian Beard ©

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Author Biographical Note

Adrian Beard works for Clariant Corporation, Hurth near Cologne in Germany, where he is in charge of industrial relations and regulatory affairs for phosphorus based flame retardants in the division Pigments and Additives. Since 2001, he also is vice-president of the European Flame Retardants Association (EFRA), a sector group of the European Chemical Industry Council (Cefic), Brussels, Belgium. In addition, he gives lectures on fire safety at the University of Wuppertal, Germany. From 1991 to 1999, before joining Clariant, he was head of the environmental analytical laboratory at the Fraunhofer-Institute for Environmental, Safety, and Energy Technology in Oberhausen, Germany.

Abstract

Flame retardants are a key element of the safety of many products of daily life and in the workplace environment. Many plastics, textiles and natural materials are quite flammable and burn well. In a number of application areas this fire risk has to be reduced by measures like the use of flame retardants – the E&E sector being one of the most prominent areas. However, there are concerns about the environmental and health properties of some flame retardants, in particular brominated systems. The European WEEE and RoHS directives have responded to these concerns and declared the phase out of PBBs (polybrominated biphenyls) and PBDEs (polybrominated diphenylethers) as well demanding the separation of plastics containing brominated flame retardants before further recycling operations. In expectance of these directives and the growing pressure on halogenated flame retardants, the flame retardants market has responded with an increasing demand for non-halogenated flame retardants. Phosphorus and nitrogen based as well as mineral flame retardants have experienced above average growth rates over the last years. Material recycling of flame retarded plastics is usually technically feasible – the major problem is how to obtain a continuous supply of input material which is well defined in its composition. Otherwise, only feedstock recycling or energy recovery are sensible options.

A way to assess the environmental profile of flame retardants is to examine the release of the flame retardant and its degradation products over key stages of the life cycle of plastics like the processing by extrusion, the use phase, accidental fires, incineration and end-of-life disposal. These tests were carried out with a new class of phosphinate based flame retardants and compared to currently used brominated systems in polyamide (PA) 6, polyamide 6.6, high temperature nylon (HTN) and polybutylene terephthalate (PBT). The methodology presented can be applied to other flame retardants and plastics additives in order to evaluate the environmental profile of these products, especially within the context of upcoming European chemicals regulations (REACH).

For further information see:

www.flameretardants-online.com
www.flameretardants-online.com/news/frame_news_downloads.htm
www.exolit.com
www.cefic-efra.com

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Adrian Beard
Clariant GmbH, Hürth-Knapsack

ERA Designing and Recycling of Electrical and Electronic Equipment 2005
22-23 November 2005, London Gatwick

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Outline

- Issues and concerns about flame retardants
- Flame retardants in WEEE, RoHS and other legislation
- Recycling options for plastics containing flame retardants
- Measuring the environmental performance of flame retardants by eco-profiles
- The trend towards halogen-free flame retardants

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Fire Casualties and Damage (Europe 25)

- About 15 casualties in Europe per day
  - ~ 75 % of victims in private homes
  - intoxication by smoke is main cause of death
- Costs of 30 billion EUR per annum
  - ~ 0.3 % of gross domestic product

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Trends in fire safety requirements

- International standards (ISO, IEC, CEN)
- Sophisticated fire test methods
  - from fail / pass towards numerical data: RHR, FIGRA, MAHRE, …
  - example: EN 45545 railway rolling stock
- Audio-/Video Equipment: External ignition
- Europe: enhanced producer liability and de-regulation
  - Harmonized Standards – „New Approach“
  - General Product Safety Directive
  - Construction Products Directive
  - Low Voltage Directive

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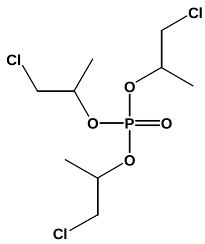
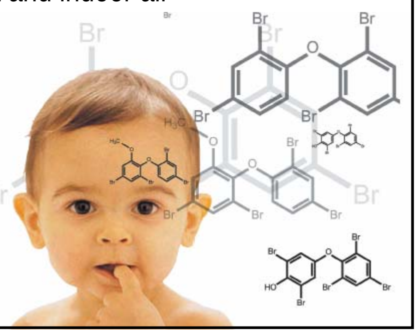
Concerns against flame retardants

- Concerns voiced in Europe on environmental impact, fate and toxicology of certain flame retardants
- Studies and publications on FRs presented in Germany, Sweden, Denmark, the UK and Switzerland
- Topics: Persistence, Bioaccumulation, Toxicity (PBT)
- FRs found in environment, biota and indoor air



TCPP



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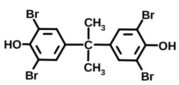
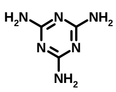
The Variety of Flame Retardants

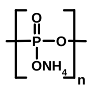
- diversity in terms of physical / chemical properties, environmental fate, toxicology, and regulatory status



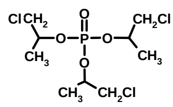
^{35}Cl ^{31}P ^{27}Al

$Al(OH)_3$

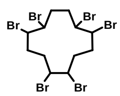




^{80}Br



^{14}N



^{24}Mg

^{11}B

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WEEE + RoHS Directives

- European Directives on
  - waste electric and electronic equipment (2002/96/EC)
  - restriction of hazardous substances in E&E (2002/95/EC)
  - published Feb-2003
- ban of polybrominated biphenyls and penta-BDE and octa-BDE as of August 2004
  - 2003/11/EC
- deca-BDE has been exempted from RoHS
  - 2005/717/EC published 15-Oct-2005
- separation requirement of plastics containing brominated flame retardants

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EU Risk Assessments – status of FRs for E+E

- Deca-BDE: Completed May 2004: No risks identified for human health or environment. Industry continuing long term studies and product stewardship initiative
- HBCD: Additional degradation studies in progress – completion 2006
- TBBPA: Human Health completed - No risk identified. Further studies in progress for Environmental – Completion early 2006

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EU Risik Assessments

Substance		Rapporteur	Priority List no. (year)	Status
Antimony trioxide	ATO	Sweden	4 (2000)	Under way
Short-chain Chlorinated Paraffins	SCCP	UK	1 (1994)	Published
Medium-chain Chlorinated Paraffins	MCCP	UK	3 (1997)	Draft circulated
Pentabromodiphenyl ether	PBDE	UK	2 (1995)	Published
Octabromodiphenyl ether	OBDE	UK/France	1 (1994)	Published
Decabromodiphenyl ether	DBDE	UK/France	1 (1994)	Published
Hexabromocyclododecane	HBCD	Sweden	2 (1995)	Draft circulated
Tris(2-chloroethyl) phosphate	TCEP	Germany	2 (1995)	Draft circulated
Tetrabromobisphenol A	TBBPA	UK	4 (2000)	Under way
Tris(2-chloroisopropyl) phosphate	TCPP	Eire/UK	4 (2000)	Under way
Tris(1,3-dichloroisopropyl)phosphate	TDCPP	Eire/UK	4 (2000)	Under way
2,2-bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate)	V6	Eire/UK	4 (2000)	Under way

- PEC = Predicted Environmental Concentration
- PNEC = Predicted No Effect Concentration
- MOS = Margin of Safety
- http://ecb.jrc.it/existing-chemicals/

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REACH – New European Chemicals Regulation (as of 2006 ?)

- under discussion:
  - substitution principal (“safer” chemicals)
  - authorisation based on “priority lists” as well as volumes?
  - chemicals in “articles” – WTO issues
  - existing risk assessments?
- ecoprofile will help:
  - chemical safety assessment
  - exposure scenarios

http://europa.eu.int/comm/environment/chemicals/reach.htm
http://europa.eu.int/comm/enterprise/reach/
http://www.cefic.org/ [REACH in the left menu]

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Ecolabels and Green procurement

- various national schemes
  - since the late 1970ies, e.g.
- Blue Angel in Germany:
  - restricts halogenated FRs in a number of products, some exceptions for parts < 25 g and recycling
- EU Flower
  - uses risk phrases from classification of chemicals
  - only few FRs are explicitly blacklisted (e.g. PBDEs)

TCO Development

  - wide-spread acceptance in the business electronics sector
  - restricts halogenated FRs
  - manufacturers have to submit environmental and tox data

EG-Umweltzeichen

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Current EOL situation for WEEE plastics

- Printed Circuit Boards go to copper smelters (or China, India)
- Largest volume goes to landfill
- 10% to incineration for energy recovery
- After dismantling, still 60% to landfill
- Hardly any feedstock recycling or re-use is taking place
- Mechanical recycling mainly for closed loop

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Mechanical Recycling of FR Polymers

- Mechanical recycling requires separation of different …
  - types of plastics
  - colours
  - flame retardants and other additives;
- variety of techniques under commercial development:
  - Cost?
  - Robustness? Easy to handle?
- Stability of flame retardants favours recycling without loss of physical properties

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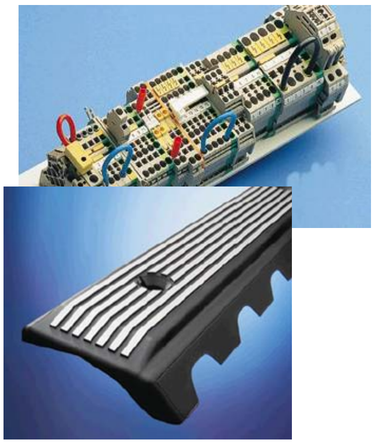
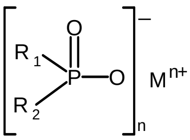
New flame retardants based on organic phosphinic acid salts

- especially effective in polyamides and polyesters
- synergism with selected nitrogen containing organic substances
  - Exolit® OP





Structure of phosphinic acid salts

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Mechanical Recycling of Flame Retardants

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- Example: Exolit OP (phosphinate) and brominated FR in Polyamide 66, glass fiber reinforced
- Test procedure
  - Injection molding of compounds (1. pass)
  - Grinding of the test bars
  - Mix 50% of grinded material with 50 % of neat compound
  - Injection molding
  - etc.
- Comparison of 1st , 3rd and 6th pass

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Mechanical Recycling PA

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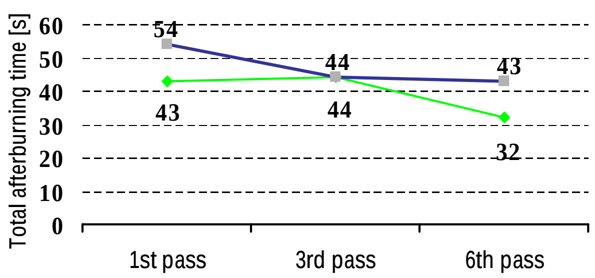
- UL 94 Performance at 0.8 mm

	PA 66 GF	OP 1312	brom. PS
1st pass	n.c.	V-0	V-2
3rd pass	n.c.	V-0	V-2
6th pass	n.c.	V-0	V-2

- Total afterburning time



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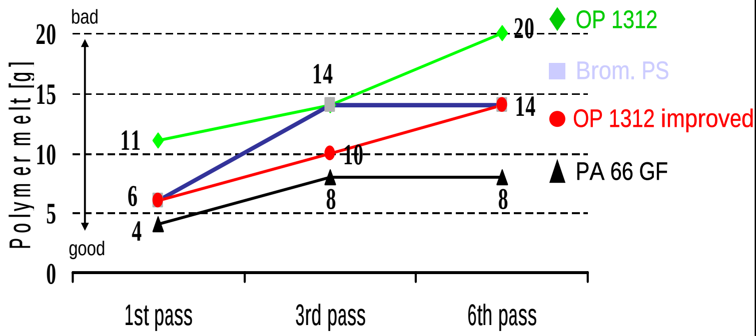
Mechanical Recycling PA

- Stability of Polymer melt during injection molding (Internal test)
  - g of Polymer melt flowing out of the die



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FRs and Mechanical Recycling

- Main conclusion of various extrusion and injection molding tests: Majority of the mechanical properties were maintained during 3 or 5 recycle steps and also fulfilling the German chemical banning ordinance
- These plastics can be recycled for same applications due to maintenance of physical properties of polymer and flame retardant (e.g. UL tests V-0 and 5VB)
- Main issue is historical plastics containing Penta- and OctaBDE plus PBBs which needs to be sorted out. Also for these old plastics the issue of dioxin/furans related to the German chemical banning ordinance can be difficult to meet

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E&E plastic waste: current trends and possible options

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- Other than mechanical recycling:
  - Metal smelters (mainly PWBoards)
  - Incineration co-combustion
  - Landfill
  - Cement kilns – fuel replacement
- New possible options
  - Feedstock recycling: Haloclean etc.
  - Dehalogenation with blast furnaces
  - Creosolv, solvolysis, super critical CO_2 extraction
  - Smelter (copper and precious) as reducing agent as during the Umicore trial with 250 ton WEEE plastic

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Available technical solutions for WEEE Plastics

Process-installation	Definition: Energy Recovery/material recycling or disposal	Cost Euro/ ton	Issues
Mechanical recycling	Material recycling	?	Sorting, quality, economics, end market
Feedstock recycling (FS)	Material recycling /Energy Rec	150-400	Economics, reliability new technique
FS: Dehalogenation	Material recycling	?	Economics, new technique
FS: Haloclean	Material recycling	?	Pilot scale
Solvolyse process	Material recycling	High	
Super Critical Water Oxidation	Material recycling	High	Economics, pilot scale
Metal smelter	Energy recovery with material recycling (metals)	Low?	Definition of energy recovery/ type of smelter
Cement kiln-fuel replacement	Energy recovery or after EU hearing material recycling as option	Low?	Corrosion / energy recovery
Plastics with BFR's as additive	Energy recovery or after EU hearing material recycling as option	Low?	Definition of energy recovery?
House hold waste incinerators co-combustion	Energy recovery	50-130	Political acceptance, max 3% WEEE plastics
Landfill	Disposal	50-130	Politically not accepted

from: "What are processing alternatives and market opportunities for mixed plastic fractions? " L.Tange, D.Drohmann, Presentation to workshop Where are "WEEE"going? October 2004 Antwerp

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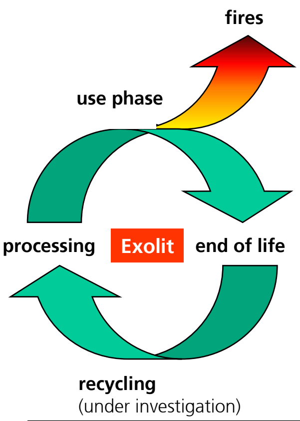
EcoProfile of Exolit flame retardants
including the life cycle of polymers

Flame Retardants in Product Life Cylces



- Concerns because of potential environmental effects of flame retardants
- Halogenated flame retardants have been in the focus of public scrutiny
- Alternatives to halogenated flame retardants have to prove their environmental benefits
- Market introduction of phosphinates as a new class of flame retardants for polyamides and polyesters by Clariant
- This study compares these new flame retardants with currently used brominated systems in polyamide (PA) 6, polyamide 6.6, high temperature nylon (HTN) and polybutylene terephthalate (PBT)

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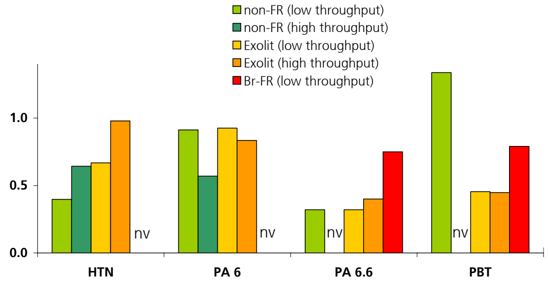
Exactly your chemistry.

EcoProfile of Exolit flame retardants
including the life cycle of polymers

Extrusion – emissions to gas phase

Total Organic Carbon (FID-C)
mg / kg compound

- all samples (incl. non-FR) do release organic substances to air
- no apparent dependence on polymer type and throughput



* = limit of detection for this sample
nv = no value, not measured

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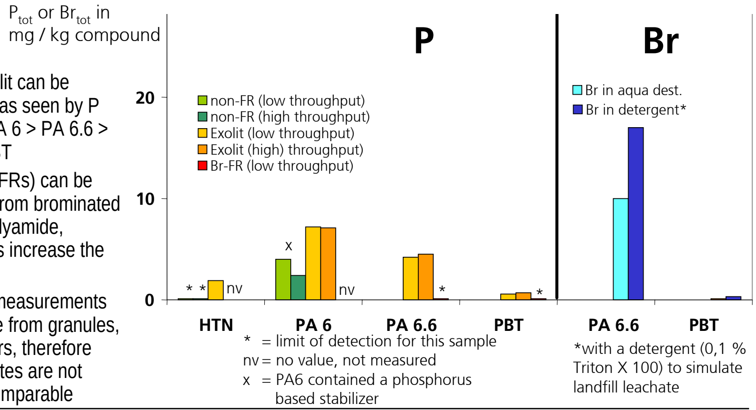
EcoProfile of Exolit flame retardants
including the life cycle of polymers

Migration into water – Phosphorus and Bromine

- some Exolit can be released, as seen by P results: PA 6 > PA 6.6 > HTN > PBT
- Bromine (FRs) can be released from brominated FRs in Polyamide, detergents increase the release
- Bromine measurements were done from granules, P from bars, therefore release rates are not directly comparable



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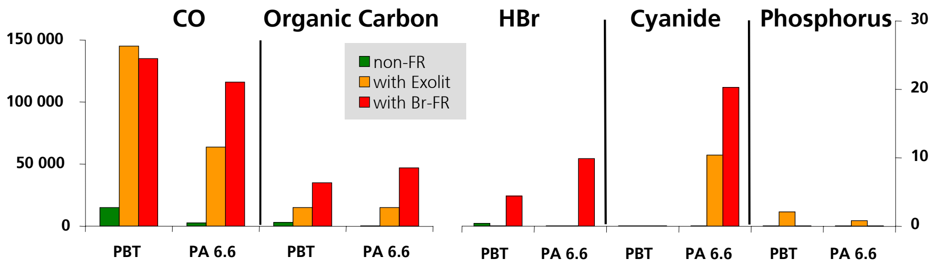
Combustion products with acute toxicity

yields in mg / kg sample



- by their very nature, adding flame retardants to polymers causes an impeded combustion, seen by the low CO_2 / CO ratio, the production of low molecular weight organic substances and the increased release of HCN by polyamides
- Nota bene: the DIN-oven scenario which was used is a forced thermal degradation and combustion where FRs cannot act in their usual role of preventing or slowing the fire

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EcoProfile of Exolit flame retardants
including the life cycle of polymers

Conclusions

- The environmental behaviour of Exolit OP 930 / 1230 is characterised by:
  - the flame retardant itself is non-toxic, does not bioaccumulate (Clariant data)
  - no release of volatiles from finished products
  - some release of flame retardant in contact with water (based on salt nature of Exolit)
  - lower smoke toxicity in case of accidental fire compared to brominated flame retardants

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New halogen free raw materials

- Halogen free FRs for engineering thermoplastics and thermosets
  - Clariant Exolit OP range
  - Chemtura (former Great Lakes CC)
  - Supresta (former Akzo Nobel)
  - Inorganic fillers: Martinswerke, Nabaltec, …
- New halogen free FR resins
  - Huntsman
  - Dow
  - Bakelite
  - Tohto Kasei
  - Nan Ya
  - Japan Epoxy Resin
  - …

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Halogen free capacities are expanding

- Matsushita Electric Works will double its halogen-free production from 10 to 20% in 2006.
- Tohto Kasei (Japan) increasing its capacity of halogen-free epoxy resin (phosphorus type) for CCL to 3 000 tons per year
- Park Electrochemical Corp.
  - introduction of its new N4000-7 EF halogen-free, 165 degrees C Tg substrate
  - lead-free compatible, excellent thermal and moisture resistance
  - CAF resistance and UL 94 V-0
  - exceeds the electrical attributes of a brominated FR-4 system

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Halogen free FRs: perspectives

- “Halogen free” is no longer simply a marketing term, it has become a market.
- Halogen free PWB should represent a market share of 3-4 % in 2005 vs. 0 % in 2001 (Clariant estimate)
- Further growth driven by market demand
- End market: Consumer electronics
  - Possibly automotive applications, too

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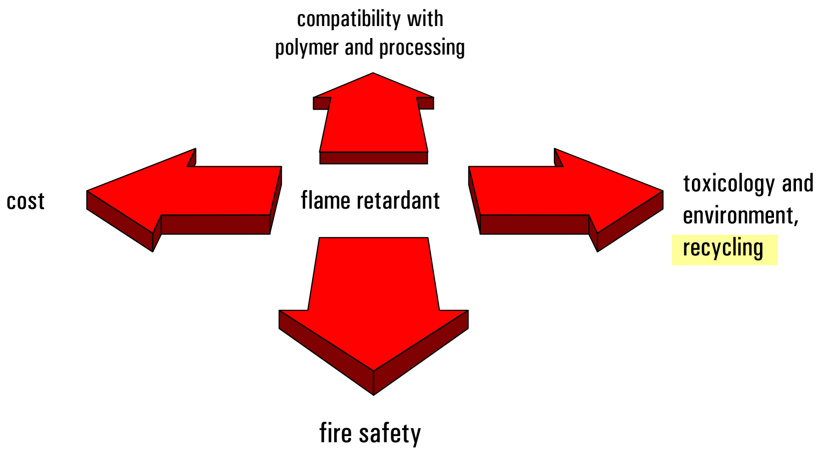
Requirements for Flame Retardants



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Conclusions

- Flame retardants are important for achieving fire safety in E&E products
- There are several recycling options for FR-plastics, however, challenges remain:
  - Technology
  - Logistics
  - Economics / costs
- There is a growing demand for non-halogenated flame retardants in E&E
  - Proven environmental profile
  - Existing systems are improved
  - New flame retardants developed

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