New Phosphorus based Flame Retardants for E&E Applications: A case study on their environmental profile in view of European legislation on chemicals and end-of-life (REACH, WEEE, RoHS)

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BIOGRAPHICAL NOTES

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 business unit Plastic Industries. 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. He holds a doctorate in analytical chemistry from the University of Waterloo, Ontario, Canada and a diploma in geo-ecology from the University of Bayreuth, Germany.

Since 1999, Thomas Marzi has been head of the environmental analytical laboratory at the Fraunhofer-Institute for Environmental, Safety, and Energy Technology (UMSICHT) in Oberhausen, Germany. He joined UMSICHT in 1990 has since then carried out numerous research projects in the area of waste treatment and management as well as environmental and process analytics. He holds a doctorate and a diploma in chemistry from the University of Duisburg, Germany.

ABSTRACT

On the one hand, flame retardants save many lives and property because they prevent accidental fires. On the other hand, there are concerns related to chemical release into the environment and potential health effects. Since halogenated flame retardants have been in the focus of public scrutiny, flame retardants based on other chemistries like phosphorus and nitrogen have been developed and need to prove their environmental benefits.

Therefore, the release of flame retardant and degradation products over key stages of the life cycle of flame retarded plastics was investigated: processing by extrusion, use phase, accidental fires, incineration and end-of-life disposal. The new class of phosphinate based flame retardants from Clariant Corporation (Exolit OP) was compared to currently used brominated systems in polyamide (PA) 6, polyamide 6.6, high temperature nylon (HTN) and polybutylene terephthalate (PBT). The authors believe that 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). The status of flame retardants within European end-of-life directives like WEEE and RoHS will also be discussed.

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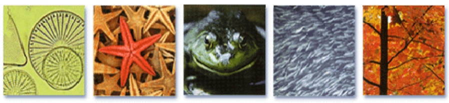

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Dr. Thomas Marzi

Dr. Adrian Beard

Addcon World 2005, 22 Sep. 2005, Hamburg, Germany

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WEEE – Electronic Waste

- European Directive 2002/95/EC on the Waste of Electrical and Electronic Equipment, published on 13-Feb-2003
- Objective: shift responsibility for the collection, recycling and re-use of end-of-life E&E products to E&E producers
- Impact on brominated flame retardants:
  - Annex II: separation of brominated FRs before recycling, energy recovery or disposal
  - Costly separation requirements on dismantlers/ recyclers and costs borne by E&E manufacturers?

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RoHS – Restriction of Hazardous Substances

- European Directive 2002/96/EC on the Restrictions on the use of certain Hazardous Substances in Electrical and Electronic Equipment published on 13-Feb-2003
- 4 brominated flame retardants concerned:
  - Ban of Polybrominated Biphenyls (PBB), Penta-BDE and Octa-BDE: August 2004 (2003/11/EC), they need to be sorted out and handled in thermal processes
  - Deca-BDE: after positive risk assessment, decision on exemption from ban (to become effective July 2006) still pending

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Ecolabels and Green procurement

EG-Umweltzeichen

- 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

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REACH – New European Chemicals Regulation

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

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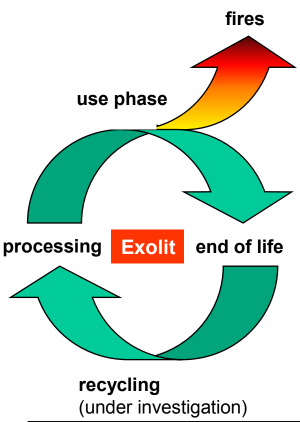
Starting Point



- 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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Processing: Extrusion – no phosphine (PH_3)

Photo: www.leistritz-extrusion.de

- **No emission of phosphine:**
  - measurement directly at the outlet of the extruder by Draeger tubes and gas sensor
  - all mesured values below detection limit (< 0.01 ppm PH_3)
- Conditions:
  - Extruder 40/36D (Leistritz AG), Nürnberg
    - polymer laboratory of Fraunhofer UMSICHT, Willich
  - Temperatures:
    - HTN 290 °C
    - PA 66 270 °C
    - PBT 230 °C
    - PA 6 210 °C
  - Throughput ca. 20 kg/h (low) and 40 kg/h (high)

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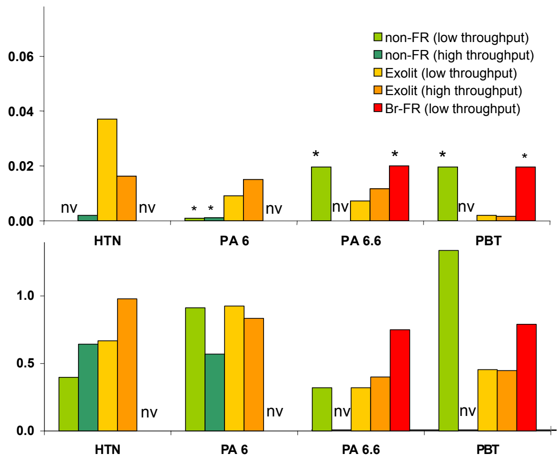
Extrusion – emissions to gas phase

Phosphorus, total
mg / kg compound

- low levels of phosphorus are released from Exolit samples: HTN > PA 6 ~ PA 6.6 > PBT

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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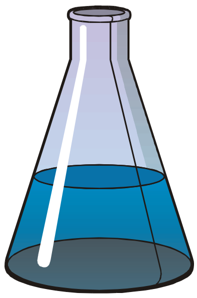
Use phase and disposal: contact with water - Elution



- What happens when FR-polymers come in contact with water (e.g. accidentally during use or landfill situation)?
- German standard method DEV S4 was used:
  - 100 g sample suspended in 1 Liter of water
  - shaken for 24 h, analysis of the water
- Polyamide is a „hydrophilic" polymer which can take up water (up to 30 g/kg at room temperature and 50 % relative humidity)
- therefore the encapsulation of flame retardants against aqueous media is limited

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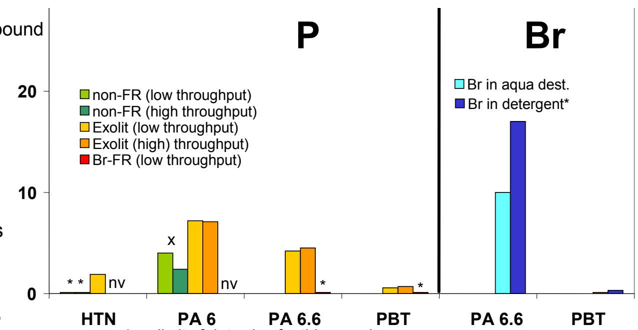
Elution – Phosphorus and Bromine

- 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

P_{tot} or Br_{tot} in mg / kg compound



* = limit of detection for this sample
nv = no value, not measured
x = PA6 contained a phosphorus based stabilizer

*with a detergent (0,1 % Triton X 100) to simulate landfill leachate

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Use phase: gaseous emissions / volatiles

- Daimler Chrysler Test PB VWI 709
  - = measures Volatile Organic Compounds (VOC), these can usually be found in automobile interior air
  - – result: very low VOC-values: target value < 100 mg/kg; measured: 0 - 5 mg/kg
- Fog-value
  - = sum of less volatile substances; condensation at room temperature, „fogging“ on windscreen
  - – result: no significant Fog-values: target value < 250 mg/kg; measured 0 - 6 mg/kg
  - – Polyamide 6.6 with brominated FR: indication of emission of brominated compounds

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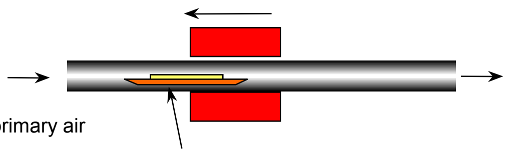
Use Phase: accidental fires - Combustion experiments according to DIN 53436



Test conditions chosen to simulate a well ventilated, developed fire:
- sample weight: 5 g
- air supply: 200 L / h
- temperature of sample: 700 °C

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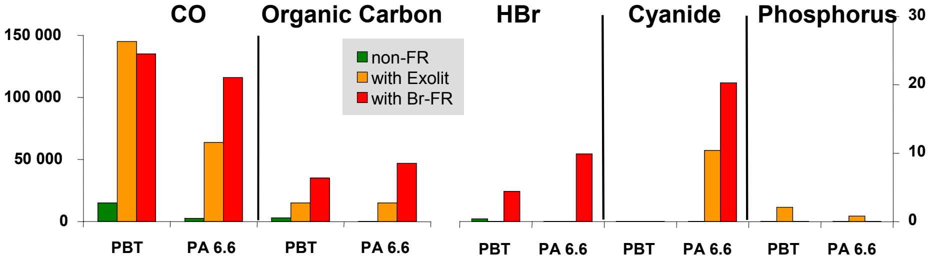
Combustion products with acute toxicity: yields in mg / kg sample



- 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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Combustion products with potential long-term effects: Toxicity of condensates from combustion flue gasses

Mutagenicity: Ames test with Salmonella typhimurium TA 98;
Cytotox: Cell culture of TK6-cells and larynx cancer cell line (to mimmick human respiratory effects);
- no effect
(-) ambiguous negative results
(+) weak positive effects
+ clearly positive effects

Toxicity testing done by Institute for Toxicology at the University of Würzburg

		Mutagenicity		Cytotox	
		ST 98	+activation	Proliferation	Cell death
PA 6,6	no FR	-	-	-	-
	P	(+)	(+)	-	-
	Br	(+)	+	+	+
PBT	no FR	-	-	-	-
	P	-	-	-	(-)
	Br	-	-	+	+

Combustion products identified by gas chromatography – mass spectrometry:
- non-FR compounds: aromatic compounds like benzene, naphthaline, phenol
- Exolit samples: benzene, xylenes, styrene, benzaldehyde, phenols
- Br-FR samples: brominated aliphatic and aromatic compounds like dibromo methane, bromo methanol, (mono- and di-) bromo benzene, brominated styrenes

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Summary:
accidental fires

- brominated flame retardants produce volatile brominated low molecular weight substances and largest amounts of carbon monoxide
- no organic phosphorus compounds could be identified by GC-MS in the combustion gases of polymers with Exolit OP types
- smoke condensates exhibited cytotoxic and mutagenic effects for PA and PBT with brominated flame retardants; for Exolit only weak effects in PA were seen

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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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Thank you for your attention!

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Annex I:

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including the life cycle of polymers

Materials

The FR compositions were chosen such that they pass UL 94 V0 at 0.8 mm thickness.
All polymers were commercial grades from major suppliers.

Polymer		Supplier / Type	GF	Flame Retardant	
PA 6	70 %	A	30 %	-	
PA 6	52 %	A	30 %	18 %	Exolit OP 1311
PA 6.6[1]	70 %	B	30 %	-	
PA 6.6[1]	55 %	B	30 %	15 %	Exolit OP 1311
PA 6.6	52 %	C	30 %	18 %	Exolit OP 1312 M1 [2,3]
PA 6.6[1]	42 %	B	30 %	20 % + 7,5 % + 0,4 %	Brominated polystyrene, 80 % Sb_2O_3 in PA 6.6 PTFE powder
PBT[1]	70 %	D	30 %	-	
PBT[1]	50 %	D	30 %	20 %	Exolit OP 1230
PBT	55 %	E	25%	20 %	Exolit OP 1200 [2]
PBT[1]	52 %	D	30 %	12 % + 6 %	Polypentabromo benzylacrylate 80 % Sb_2O_3 in PBT
HTN	65 %	F	35 %	-	
HTN	53 %	F	29 %	18 %	Exolit OP 1230

[1] measured in the 2002 campaign. Aqueous elutions were carried out with extrusion granules. For the other samples tensile strength test bars were used.
[2] contains a nitrogen based synergist
[3] contains zinc borate and is therefore labelled N R51/53 (toxic for aquatic organisms)

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Annex II:

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Physical and Chemical Properties of Exolit OP 930 / 1230
(Clariant data)

Property	Value
solubility in water	2,5 g / L
pH in aqueous suspension	~ 4,0
pKa (phosphinic acid)	3,3
log Pow	-0,44

- since Exolit OP is a salt, it behaves partly like an inorganic flame retardant
- Exolit OP has a low water solubility
- in water there is an equilibrium between the acid and its anion; this is also the reason for the low pH of an aqueous suspension
- the pKa shows that the corresponding phosphinic acid is quite strong (stronger than acetic acid, weaker than very strong acids like HCl, H_2SO_4)
- the negative log Pow indicates that Exolit OP tends to remain in the aqueous phase and not accumulate in hydrophobic phases like lipids

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Ecotoxicological and Environmental Properties of Exolit OP 930 / 1230

(Clariant data)

Property	Value
Daphnia toxicity	EC_0 = 100 mg/L ; EC_{50} > 100 mg/L
algae toxicity	no inhibition at 180 mg/L
fish toxicity	LC_0 = 100 mg/L ; LC_{50} > 100 mg/L
bacteria toxicity	EC_{20} = 480 mg/L ; EC_{50} = 1970 mg/L
biodegradability	not readily biodegradable
hydrolysis	stable (tier I of OECD 111)
photolysis	stable (no uv-vis absorption)

- the data show that Exolit OP has a very low aquatic toxicity and does not have to be labelled for ecotoxic effects (threshold LD_{50} = 100 mg/L)

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Toxicological Properties of Exolit OP 930 / 1230

(Clariant data)

Property	Value
28 days toxicity test (rat)	NOAEL = 1000 mg/kg, no neurotoxic effects observed
acute toxicity	LD_{50} > 2000 mg/kg (rat)
skin irritation	not irritating
eye irritation	weakly irritating
sensitization	not sensitizing
Ames-test	not mutagenic
cytogenetics in vitro	not mutagenic

- these data show that Exolit OP is non-toxic, there is no need for labelling it as a hazardous substance
- a 28 day feeding study on rats revealed that the small Exolit OP fraction which is resorbed (< 5 %) is excreted as the well water soluble phosphinic acid via urine and blood with a half life time of 5 hours which indicates **no potential for bioaccumulation**

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No Neurotoxicity of Exolit OP 930 / 1230

(Würzburg University)

- No adverse neurotoxic effects were found in rats while testing for subacute oral toxicity (28 days testing).

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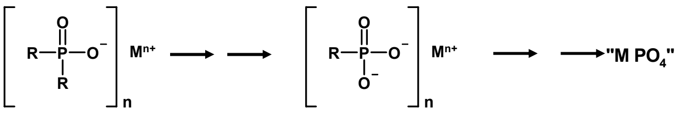
Thermal decomposition of neat Exolit OP 930 / 1230

(Clariant data)

- Experiments:
  - tube furnace with neat Exolit at temperatures of 320 to 800 °C in air
  - Differential Thermal Analysis (DTA) combined with Thermo-Gravimetry (TG)
- Results:
  - alkyl groups are removed by oxidation
  - major products are diethyl phosphinic acid, ethyl phosphonic acid and phosphoric acid and their respective salts



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