

THE ECOLOGICAL FOOTPRINT OF FLAME RETARDANTS OVER THEIR LIFE CYCLE – A CASE STUDY ON THE ENVIRONMENTAL PROFILE OF NEW PHOSPHORUS BASED FLAME RETARDANTS

Thomas Marzi⁽¹⁾ & Adrian Beard⁽²⁾

(1) Fraunhofer UMSICHT, D-46047 Oberhausen, thomas.marzi@umsicht.fraunhofer.de

(2) Clariant GmbH, D-50354 Hurth-Knapsack, Germany, adrian.beard@clariant.com

ABSTRACT

On the one hand, flame retardants (FRs) 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 promoted. However, halogen free flame retardants need to prove their environmental benefits.

Rather than using typical global life cycle assessment parameters like energy consumption or global warming potential, a benchmark approach was used: comparing the performance of new flame retardants versus currently employed FR systems and also to the non-flame retarded polymer. The polymers studied were polyamide (PA) 6, polyamide 6.6, high temperature nylon (HTN) and polybutylene terephthalate (PBT). 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. Other end-of-life options like feedstock recycling, incineration (energy recovery) or landfilling were studied and current waste streams assessed, in order to gain an estimate of the total material mass flows and balance over the life cycle of the flame retardants. In addition, experiments on mechanical recycling were carried out.

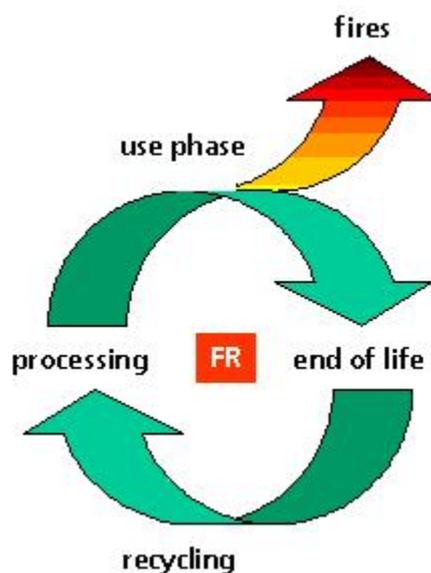
The authors believe that the methodology presented can be applied to other flame retardants and plastics additives in order to evaluate the environmental profile of these products, especially within the context of upcoming European chemicals regulations (REACH¹) and waste regulations for electronic equipment (WEEE² and RoHS³).

INTRODUCTION

Flame retardants prevent or at least impede the ignition of materials and can therefore save lives and protect property⁴. Despite of these benefits, there are concerns and reservations against potential environmental and health impacts of FRs, particularly in Europe. This discussion was caused by findings of brominated FRs in the environment^{5, 6}, biota and humans⁷, the possible formation of halogenated dioxins and furans by uncontrolled combustion⁸ as well as findings of phosphate FRs in indoor air^{9, 10}. These concerns have led to the inclusion of 12 high volume FRs (chlorinated, brominated and phosphorus based) in the European Risk Assessment process¹¹. On this basis, restrictions to marketing and use of certain FRs have been implemented in Europe, e.g. the ban on penta- and octa-brominated diphenyl ethers by Directive 2003/11/EC¹². Scandinavian countries like Norway and Sweden have been considering national bans of some brominated FRs, even restricting some which had a positive EU risk assessment.

Two studies from the Swedish research institute SP looked at the emissions of pollutants over the life cycle of TV sets¹³ and upholstered furniture¹⁴, comparing non-flame retarded items to flame retarded ones and taking into account fire statistics. They were able to show that due to much fewer fires in the flame retarded sofas and TVs, their emissions were less than those of the untreated products.

Figure 1: Life cycle of Flame Retardants



Brominated flame retardants have been in the focus of scientific and public attention which led to the search for alternatives by FR users and environmental regulators. E.g. in 2001 the German Federal Environmental Agency issued a report on “Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals”¹⁵. In the United States, alternatives to deca brominated diphenylether have been studied¹⁶ and the FRs used in upholstered furniture were evaluated by the Environmental Protection Agency¹⁷ in 2005. Alternatives to halogenated FRs have to prove their merits in the environmental and health profile, since they have not been studied in such detail as their brominated counterparts. This paper tries to contribute to the establishment of environmental profiles of FRs by looking at emissions over the life cycle of FRs: 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, recycling and end-of-life disposal. Rather than using typical global life cycle assessment parameters like energy consumption or global warming potential, a benchmark approach was used: comparing the performance of new flame retardants versus currently employed FR systems and also to the non-flame retarded polymer.

MATERIALS AND METHODS

Polymers and Flame Retardants

The polymers studied were polyamide (PA) 6, polyamide 6.6, high temperature nylon (HTN) and polybutylene terephthalate (PBT). 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 (see Table 1).

Polymer extrusion

Plastics reach temperatures > 200 °C during the extrusion and are also subjected to high shear forces. The experiments should answer the question whether there are emissions of flame retardants or degradation products under these conditions. A twin screw extruder type 40 / 36 D of Leistritz AG, Nuremberg, was used. It had separate side feeders for flame retardants and glass fibres. The throughput ranged from 16 to 40 kg / h and the maximum set temperatures were for HTN 290 °C, PA66 270 °C, PBT 230 °C, and PA6 210 °C. Emissions were captured at the extruder outlet by a specially fitted hood (1.5 L volume). Air was drawn from this hood and by separate sampling lines led to a flame ionization detector (FID, determination of total organic carbon), a gas analyzer for CO, CO₂, O₂ and NO_x, and wash bottles with 0.1 N NaOH (for HBr and HCN), 0.1 N HCl (for PH₃, total phosphorus and metals) and dichloro methane (determination of organic compounds). In addition, phosphine (PH₃)

was measured directly at the outlet of the extruder by Draeger tubes and a dedicated gas sensor (MST unit 4-20, type 9604-0202). Since the extruder does not produce gaseous emissions as such, but rather a “steaming” polymer stream, the air drawn in by the sampling system is mainly from the surroundings of the sample hood. The concentrations measured in the sampled air were calculated back to the polymer discharge rate of the extruder, so that they are presented as mass analyte per mass polymer produced.

Table 1: Polymers and flame retardants used in the study.

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% Brominated polystyrene + 7,5% 80% Sb ₂ O ₃ in PA6.6 + 0,4% 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% Polypentabromobenzylacrylate + 6% 80% Sb ₂ O 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)

Migration tests in aqueous media

The real behaviour and fate of a material in the environment, e.g. a landfill, can only be assessed by sophisticated simulation tests like lysimeters. However, a comparison of different materials can also be achieved with simple migration / elution tests like the German DEV S4 method. In this test, 100 g of material are added to 1 L of distilled water and shaken head over heels for 24 h. The suspension is then filtered and the water analysed. In order to simulate conditions in a landfill more realistically, in addition water with a detergent was used (0.5 % of Triton X 100 (O-[4-(1,1,3,3-tetramethylbutyl)phenyl]deca-oxy-ethylene)). The water was analysed for pH, electrical conductivity, total organic carbon (TOC), total phosphorus (P_{tot}), total aluminium (Al_{tot}), total bromine (Br_{tot}). The analytical methods used are listed in Table 2.

Table 2: Analytical methods used for elemental analysis and summary parameters.

Parameter	Method
pH	electrode DIN 38404
Electric conductivity	electrode EN 27888
Total organic carbon (TOC)	combustion and IR-detection, DIN EN 1484
Phosphorus, total (P _{tot})	ICP-OES, EN ISO 11885 DEV E22
Aluminium compounds (Al _{tot})	ICP-OES, EN ISO 11885 DEV E22
Bromine total (Br _{tot})	ICP-OES
Nitrogen total (N _{tot})	combustion with fluorescence detection EN 12260
Individual organic compounds	extraction of 250 mL sample with 25 mL dichloro methane, GC-MS-screening

ICP-OES = Inductively coupled plasma with optical emission spectroscopy

GC-MS = gas chromatography with mass spectrometry

Evaporation testing

The emissions of flame retardants from the plastic materials were measured with the Daimler-Chrysler test PB VWI 709. This test simulates the conditions in a hot car interior and therefore represents a worst case scenario for gaseous emissions. Two values are determined by thermodesorption and subsequent GC-MS:

- at 90 °C a VOC-value (volatile organic compounds): it covers substances in the boiling range from pentane (C₅) to eicosane (C₂₀)
- at 120 °C a Fog-value (for “fogging”): these compounds are supposed to condensate at room temperature; they cause the “fogging” film on the inside of car windows

Accidental fires

The combustion products were determined by using the DIN 53 436 apparatus as fire model and chemical analysis of the effluents. The sample of ca. 5 g is inserted in a quartz tube and an electric oven of 10 cm length passes over the sample at a speed of 1 cm / min. The continuously formed combustion gasses are diluted with secondary air before analysis. The fire conditions of 200 L/min air supply and 700 °C were representative of a well ventilated fire. The effluents were analysed for the components given in Table 3.

Table 3: Analytes measured in combustion experiments according to DIN 53 436.

Component	Method	
Permanent gasses CO, CO ₂ , O ₂ , NO _x	gas analyzer	continuously measured with Testo 360
Organic substances	FID-C	continuously measured with flame ionization detector
organische Stoffe	absorption in Dichlor-methan ¹	GC-MS screening
HBr	absorption in 0.1 N NaOH	bromide by ion chromatography DIN EN ISO 10304-1
HCN	absorption in 0.1 N NaOH	total cyanide by photometry DIN 38405 D13
PH ₃	absorption in 0.1 N HCl	total phosphorus by ICP OES EN ISO 11885 DEV E22

In order to evaluate the toxic potential of flue gasses, condensates were produced by leading the gasses through 3 impingers with air, water at 0 °C, and acetone / dry ice (- 80 °C). The first two impingers were meant to capture soot and water vapour and prevent clogging to the cold trap. The three fractions were dissolved in methanol and sent to the University of Würzburg where they were tested by Prof. Wolfgang Dekant's group for mutagenicity by Ames test with *Salmonella typhimurium* TA 98 as well as for cell toxicity by exposure of a cell culture of TK6-cells and a larynx cancer cell line (to mimic human respiratory effects).

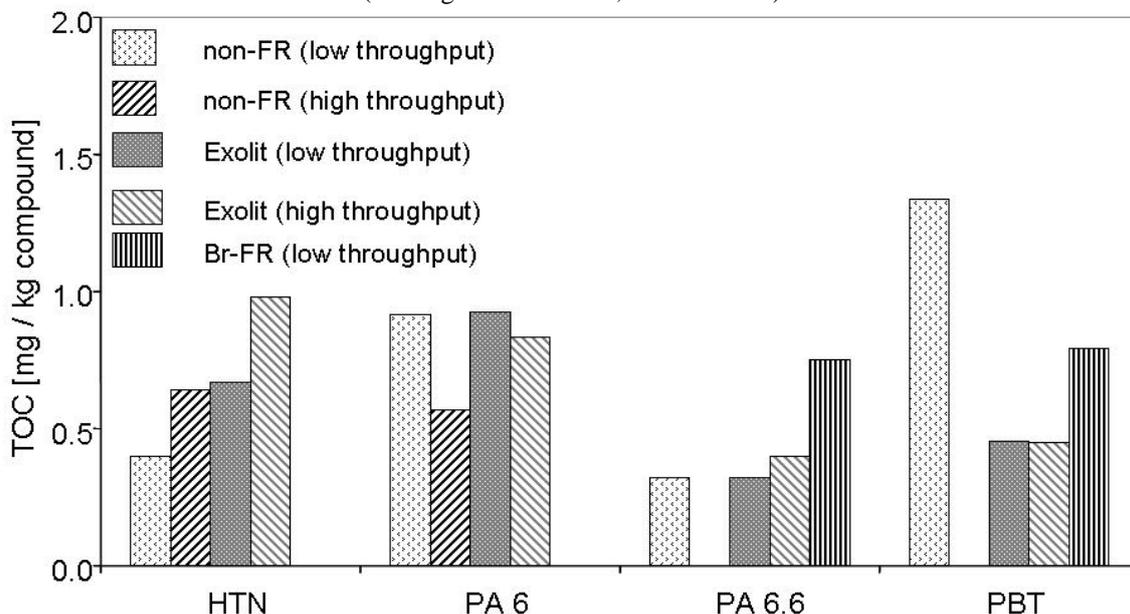
RESULTS and DISCUSSION

Polymer extrusion

Due to the mechanical and thermal stress which polymers experience during extrusion processes, there is some degradation of the polymer and additives. This is reflected in the measurable values for total organic carbon in all samples, including the neat polymers (see

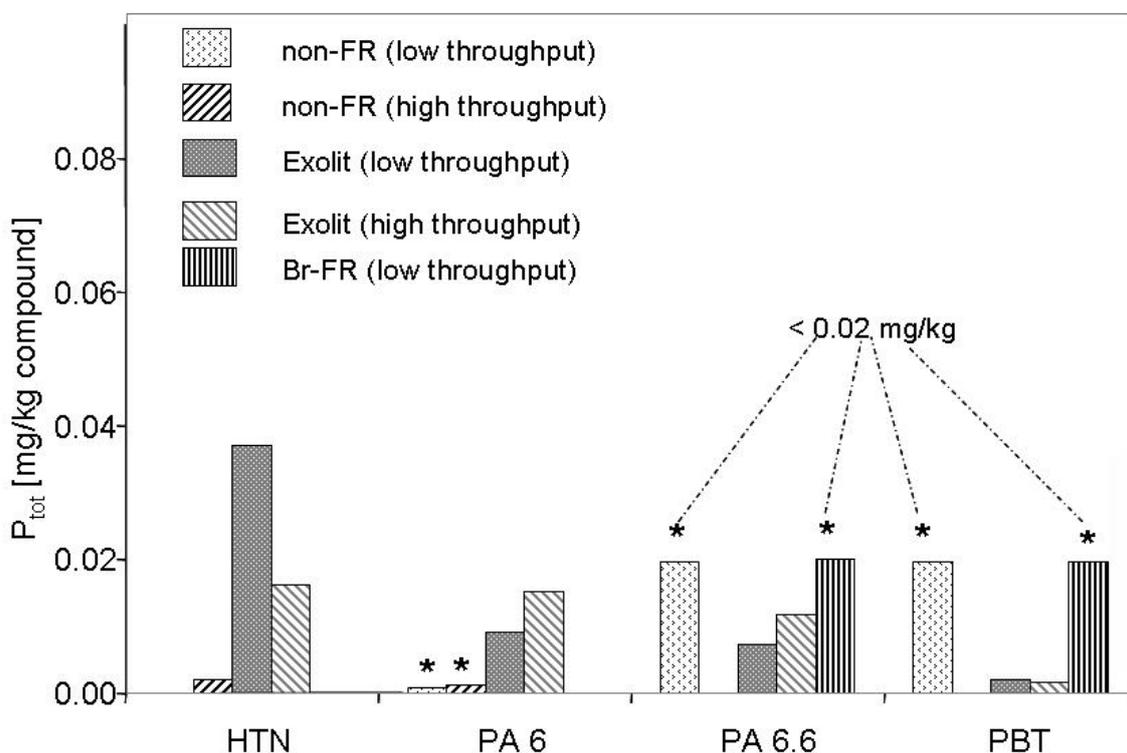
Figure 2). All measured values are quite low and in the range of 1 mg / kg finished polymer (compound) or below. In some instances the TOC is somewhat higher when the polymer contains flame retardants (HTN, PA 6.6 with brominated FR). In the HTN system with Exolit at higher throughput, also particulate emissions were observed.

Figure 2: TOC (total organic carbon) measured in emissions of the extrusion process.
(missing bar = no value, not measured)



A common question for phosphorus based FRs is whether there are any phosphine (PH_3) emissions, which is known phenomenon from red phosphorus. However, the phosphinate salts employed here did not release any measurable quantities with a detection limit of 0.01 ppm PH_3 (determined by two independent techniques) nor was there any specific odour (PH_3 strongly smells of garlic). The total emission of phosphorus compounds was also analyzed (see Figure 3). The figure shows that all phosphorus containing samples emit low levels of phosphorus compounds, below 0.04 mg/kg, in the order HTN > PA 6, PA 6.6 > PBT. The measured total phosphorus value can include particles of the flame retardant or its degradation products.

Figure 3: Emissions of phosphorus compounds during extrusion, measured as total phosphorus (missing bar = no value, not measured; the samples marked with * and <0.02 mg/kg had this limit of detection).



Migration tests in aqueous media

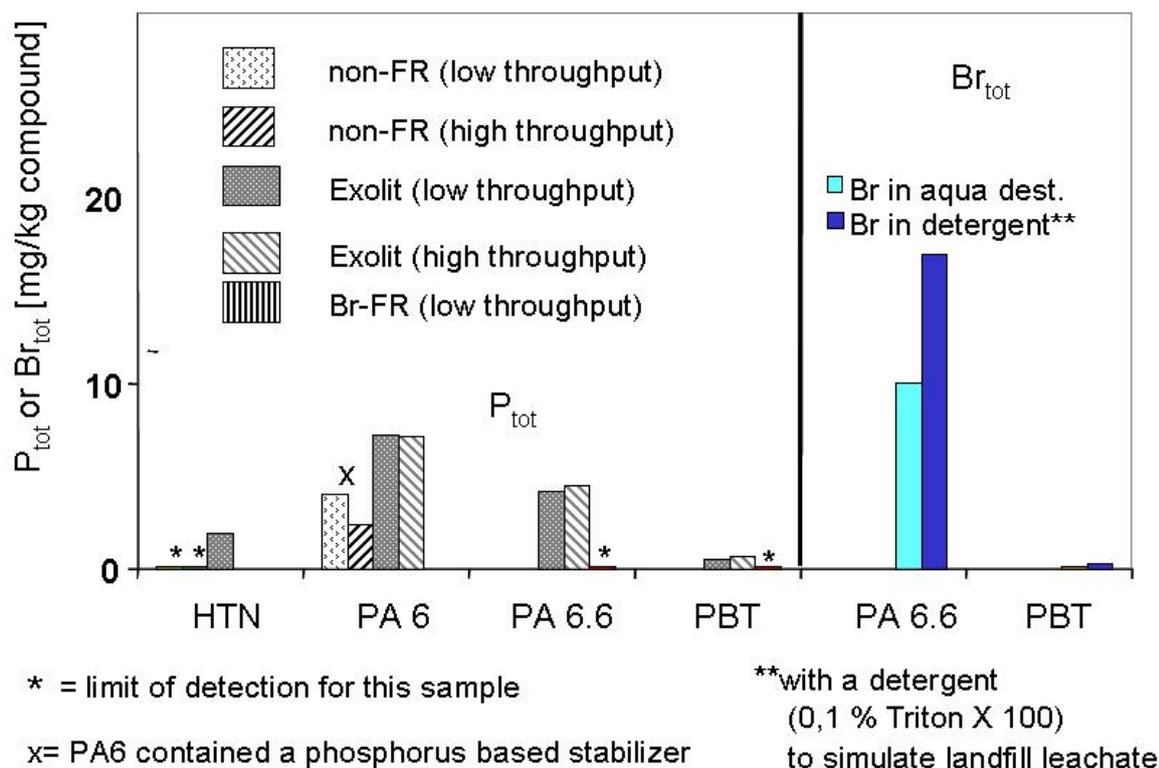
The migration respectively elution tests were carried out to evaluate the release of flame retardants from plastics in contact with water, either – accidentally - in the use phase or if they are disposed off into a landfill. The results of the elution tests by the German DEV S4 method are presented in Figure 4. The Exolit containing samples do release some phosphorus, in the order of PA 6 > PA 6.6 > HTN > PBT. These results can be explained by the fact that polyamide is a „hydrophilic“ polymer which can take up a considerable amount of water - up to 30 g/kg at room temperature and 50 % relative humidity. Therefore, the encapsulation of flame retardants against aqueous media is limited for polyamide, especially for flame retardants with a water solubility (which may be very small as for the Exolit types). Further analysis revealed that it is mainly the neat flame retardant which is released from the polymer. This is probably different for the bromine measured, because the brominated flame retardants used have an very low water solubility. However, during the extrusion process there is some degradation of the flame retardant leading to more water soluble degradation products or even bromide ions. In order to simulate the behaviour of the lipophilic brominated flame retardants under landfill leachate conditions, an additional extraction with a detergent solution was carried out. Not surprisingly, markedly more brominated compounds are mobilized with this detergent solution (see Figure 4).

Evaporation testing

Since the publication of findings of flame retardants in indoor and automobile air as well as dust, the evaporation (“outgassing”) of flame retardants has become a topic of public interest. The flame retardants found in indoor air have been mainly phosphate esters which have a low but still considerable vapour pressure. This is particularly important at higher temperatures like they are found e.g. in automobile interiors which can reach around 80 °C in hot summer conditions. Therefore, specific test which simulate these extreme car interior conditions were chosen as a worst case scenario to study the potential gaseous release of flame retardants from polymers. For all samples the tests found very low

values for volatile organic compounds (VOC) of 0 ... 5 mg / kg, the applicable target value is < 100 mg / kg. The measured “Fog-values” which reflect the sum of less volatile substances were also very low at 0 ... 6 mg / kg versus a target value of < 250 mg / kg. However, the sample of polyamide 6.6 with brominated FR indicated the emission of brominated compounds.

Figure 4: Migration of phosphorus and bromine compounds into the water phase. Bromine measurements were done from granules, phosphorus from bars: therefore the release rates are not directly comparable (missing bar = no value, not measured).



Accidental fires

By their very nature, adding flame retardants to polymers causes an impeded combustion. In the combustion experiments, this is reflected in the measured low CO₂ / CO ratios, the production of low molecular weight organic substances and the increased release of HCN by polyamides (see Figure 5). However, 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. In a real world situation one has to combine the emission rates with data on the spread of the fire to estimate the effects of fire effluents.

GC-MS analysis of the effluents revealed the formation of volatile brominated low molecular weight substances like brominated aliphatic and aromatic compounds like dibromo methane, bromo methanol, (mono- and di-) bromo benzene, and brominated styrenes from brominated flame retardants. These FRs also produced the largest amounts of carbon monoxide. For the phosphorus based flame retardants, no organic phosphorus compounds could be identified by GC-MS in the combustion gases of the polymers. Similar to the non-flame retarded polymers, aromatic compounds like benzene, naphthaline, xylenes, styrene, benzaldehyde, and phenol were found.

The smoke condensates were also checked for cytotoxic and mutagenic effects (see Table 3). For the brominated flame retardants, cytotoxic effects were detected in PA and PBT and mutagenic effects in PA only. For the phosphorus flame retardants, only weak mutagenic effects in PA were found.

Figure 5: Combustion products with acute toxicity as measured with the DIN oven.

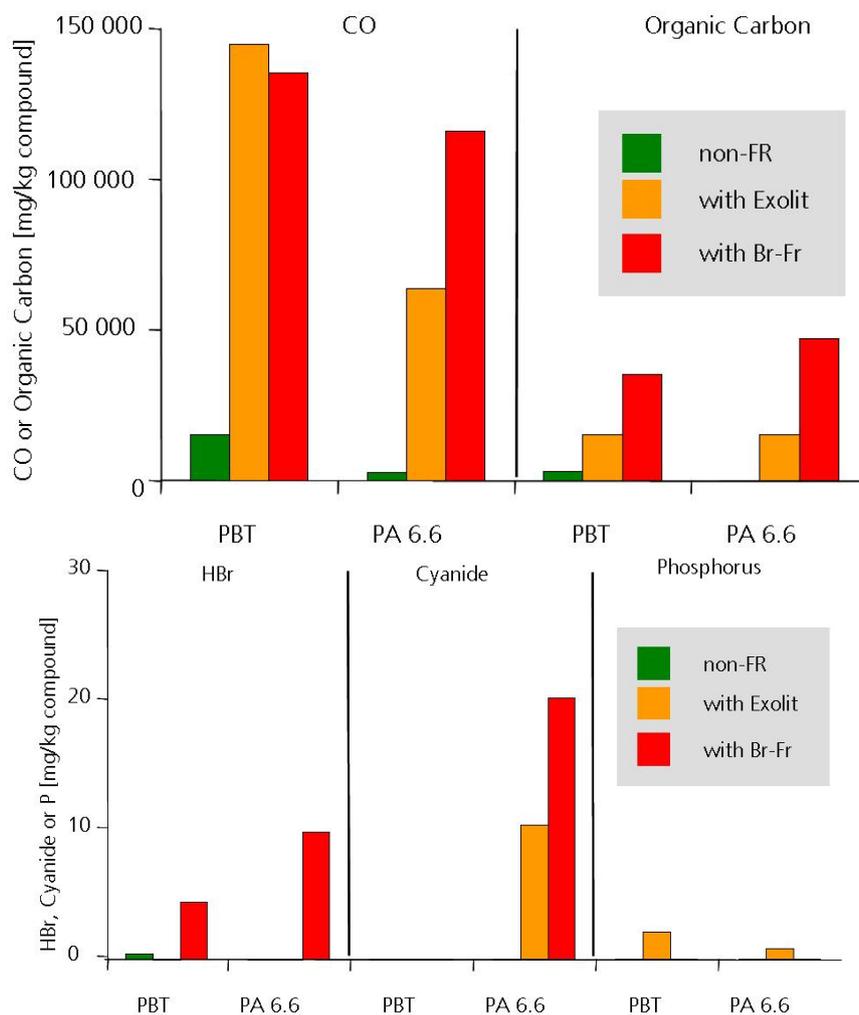


Table 4: Combustion products with potential long-term effects: mutagenicity (Ames test) and cytotoxicity of condensates from combustion flue gasses; - no effect, (-) ambiguous negative results, (+) weak positive effects, + clearly positive effects; measured by Institute for Toxicology at the University of Würzburg.

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

PROPERTIES OF ELECTRICAL AND ELECTRONIC EQUIPMENT WITH EXOLIT DURING WASTE TREATMENT

The results described above were supplemented by a study of the properties of Exolit products related to an existing waste management system. The research was done for electric and electronic components containing polyamide 6.6 with Exolit OP 1312 and polybutylene terephthalate with Exolit OP 1230. Also printed circuit boards based on epoxy resins containing Exolit OP 930 were examined. The research was done under consideration of the general conditions of the German waste management system.

The considered scenario is based on the total amount of electrical and electronic equipment which is disposed of each year. The stream of flame retardants coming from used electronic equipment is calculated from the contribution of different polymers in the electrical and electronic industry and the market share of the flame retardants under consideration. One fraction of the polymers used in electronic equipment is captured by the recycling of electrical and electronic equipment. Another fraction becomes a part of domestic waste.

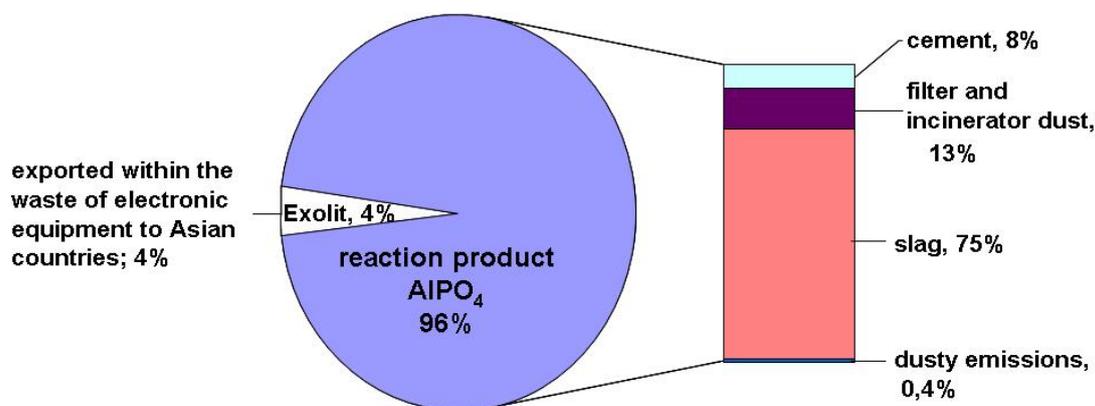
Since June 2005, carbon containing waste must not be deposited on German landfills anymore, so that an elution of the flame retardants from the polymers is implausible. Exolit which comes from electrical or electronic waste as part of the domestic waste will mainly end up in waste incineration plants or plants for mechanical and biological treatment. During the mechanical and biological treatment Exolit is captured in the so called "high caloric fraction". This fraction is incinerated in a waste incineration plant or utilised as a secondary fuel in a cement oven. In both cases Exolit reacts to aluminium phosphate, which is fixed in ashes, slags and cement.

A small fraction of electro and electronic equipment is separated and exported to Asian countries, e.g. China. This part of the equipment corresponds to approximately 4 % of the total German Exolit load in electro and electronic waste. The electric and electronic equipment is "recycled" there by thermal and chemical treatment, often under dubious conditions.

During the recycling process for electric and electronic equipment a fraction of Exolit will end up in the so called "shredder fraction" which contains polymers and metal parts. It can be used in the production process for copper. Depending on economic conditions, a more sophisticated recycling process for electro and electronic equipment will be used. In this case Exolit is collected in a fraction of mixed polymers, which is incinerated by waste incineration or used for a gasification process. In both cases Exolit is oxidised to aluminium phosphate and fixed in ashes or slags.

From this result it becomes clear that there is no release of flame retardants based on Exolit, within the limits of a modern waste management, particularly, if landfilling at low standards can be excluded. Only the export of electric and electronic equipment to Asia must be assessed negatively.

Figure 6: Waste from electric and electronic equipment: the distribution of Exolit 1312 and its reaction product aluminium phosphate to different matrices.



CONCLUSION

This study looked at the release of phosphorus based and brominated flame retardants and their degradation products over key stages of the life cycle of flame retarded thermoplastics: extrusion processing, use phase, accidental fires, incineration, recycling and disposal. The release of volatiles from finished products was negligible. However, there are differences in the release of flame retardants in contact with water, emission of by-products during processing, the toxicity of smoke in the case of an accidental fire and the properties for waste disposal. The methodology presented is of particular relevance in view of the upcoming European chemical regulations (REACH), where detailed knowledge of emissions forms the basis for accurate exposure scenarios. 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
- no release during waste treatment within the limits of a modern waste management system (without a low standard landfilling)

BIOGRAPHICAL NOTES



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 1992 and has 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.



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.

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