SUSTAINABLE PHOSPHORUS BASED FLAME RETARDANTS: A CASE STUDY ON THE ENVIRONMENTAL PROFILE IN VIEW OF EUROPEAN LEGISLATION ON CHEMICALS AND END-OF-LIFE (REACH, WEEE, ROHS)

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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, degradation products or 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 employed brominated systems in engineering thermoplastics like polyamides and polyesters. 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.

1. INTRODUCTION

Flame retardants (FRs) prevent or at least impede the ignition of materials and can therefore save lives and protect property [1]. 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 [2, 3], biota and humans [4], the possible formation of halogenated dioxins and furans by uncontrolled thermal stress or combustion [5] as well as findings of phosphate FRs in indoor air [6, 7]. These concerns have led to the inclusion of 12 high volume FRs (chlorinated, brominated and phosphorus based) in the European Risk Assessment process [8]. On this basis, restrictions to marketing and use of certain FRs have been implemented in Europe, e.g. the ban on penta- and octabrominated diphenyl ethers by Directive 2003/11/EC [9]. 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 sets [10] and upholstered furniture [11], comparing non-flame retarded items to flame retarded ones and taking into account the emissions from fires and the frequency of fires from 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.

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. For example, in 2001 the German Federal Environmental Agency issued a report on “Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals” [12]. In the United States, alternatives to deca brominated diphenylether have been studied [13] and the FRs used in upholstered furniture were evaluated by the Environmental Protection Agency in 2005 [14]. 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 (Figure 1). 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). 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. The procedural details have been published elsewhere [15].

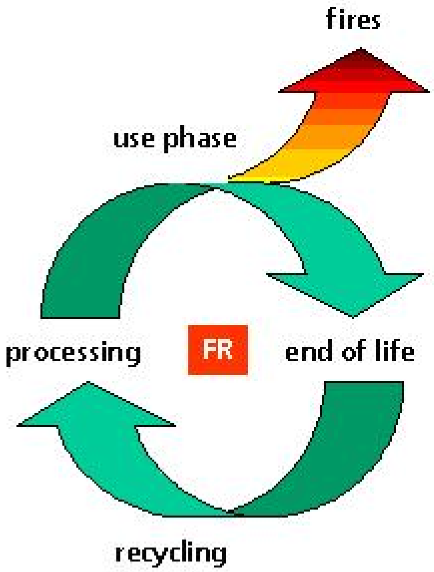


Figure 1: Life cycle of Flame Retarded Polymers

2. WEEE, RoHS AND REACH

The growing amount of waste electric and electronic equipment has led to concern amongst European regulators that this waste stream should be handled in a more controlled way and that valuable materials should be recovered. In addition, the content of heavy metals and some flame retardants was perceived as problematic.

Therefore, the European Commission issued the Directive on Waste of Electrical and Electronic Equipment (2002/96/EC), published on 13-Feb-2003. Its main objective is to shift responsibility for the collection, recycling and re-use of end-of-life E&E products to producers. Flame retardants are only referred to in Annex II which requires the separation of plastics containing brominated FRs before recycling, energy recovery or disposal. The rationale for this requirement is that certain hazardous brominated FRs should not re-enter the material cycle via mechanical or feedstock recycling of old equipment. Because it is very difficult to determine which FR exactly is contained in a polymer sample, whereas detecting the presence of bromine is less difficult, this requirement was extended to plastics containing any brominated FR. How this separation requirement will be dealt with in practice, is still an open question. There are proposals to allow waste handling processes which are known to destroy any organic FRs, like e.g. metal smelters or incineration.

Whereas the WEEE Directive covers the end of life of E&E products, the Directive on the Restriction of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS, 2002/95/EC) addresses new equipment and as of July 2006 restricts the heavy metals cadmium, mercury, lead and hexavalent chromium as well as some brominated FRs: polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE). Some of them, namely the PBBs, penta-BDE and octa-BDE have been banned in Europe already as of August 2004 by directive 2003/11/EC as a result of their European risk assessments. The major PBDE product, deca-BDE, has been exempted from RoHS by directive 2005/717/EC published 15-Oct-2005. However, Denmark and the European Parliament have taken legal action against the exemption. All exemptions shall be reviewed every four years.

A major topic for the whole chemical industry and even beyond, since the whole value chain will be involved, is REACH, the new European legislation on chemicals which will probably come into force in 2007/2008. REACH stands for Registration, Evaluation and Authorisation of Chemicals. It introduces a total paradigm shift in that producers and importers of chemicals have to demonstrate the safety of their products before they can be marketed. Under the current system (at least for “existing chemicals”), the authorities have to prove that a product is not safe before any restrictions can be issued.

Under REACH, the manufacturers have to carry out risk assessments for their products, taking into account not only the toxicological properties of the chemicals, but also possible exposure situations and circumstances. At this point the methodology described below comes into play: we look at emissions of FRs during different stages of the polymer life cycle. The emissions can be used for estimating worker and consumer exposure to FRs or their degradation products.

Besides the European regulations, ecolabels and green procurement play an increasing role in the choice of sustainable FRs. Since the late 1970ies various national schemes were developed, e.g. the Nordic Swan or the Blue Angel in Germany. They often restrict halogenated FRs and only have exceptions for small parts (< 10 or 25 g) – since RoHS does not have this size limit, the ecolabels may reconsider their position. The European Flower ecolabel has turned to risk phrases from the classification of chemicals for limiting certain substances. In the E&E sector, the TCO label from Sweden has gained wide acceptance. Their criteria also restrict halogenated FRs. In addition, manufacturers have to submit environmental and toxicity data of the FRs that are employed.

3. POLYMER EXTRUSION

Plastics reach temperatures > 200 °C during the extrusion and are also subjected to high shear forces. The experiments carried out in this project should answer the question whether there are emissions of flame retardants or degradation products under these conditions. A twin screw extruder with separate side feeders for flame retardants and glass fibres was used. 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). 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.

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.

A common question for phosphorus based FRs is whether there are any phosphine (PH3) emissions, which is a 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 (PH3 strongly smells of garlic). The total emission of phosphorus compounds was also analyzed: 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.

4. MIGRATION TESTS IN AQUEOUS MEDIA

The real behaviour and fate of a material in the environment, e.g. in 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, water with 0.5 % of a detergent was used in an additional experiment.

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 3. 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 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 3).

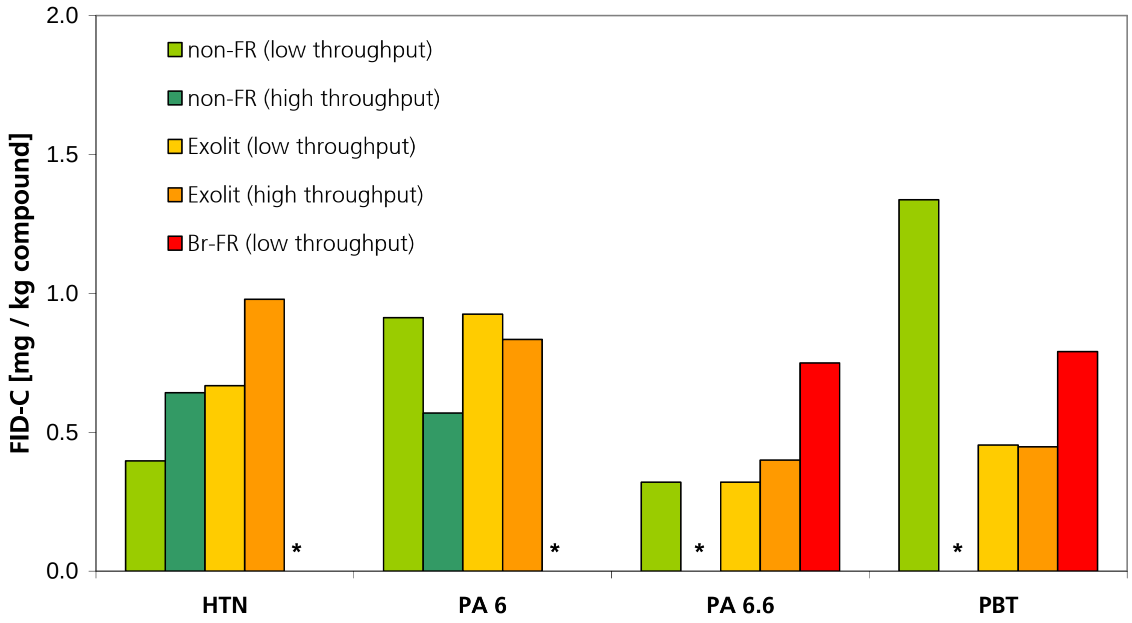


Figure 2: TOC (total organic carbon) measured in emissions of the extrusion process.
(* missing bar = no value, not measured)

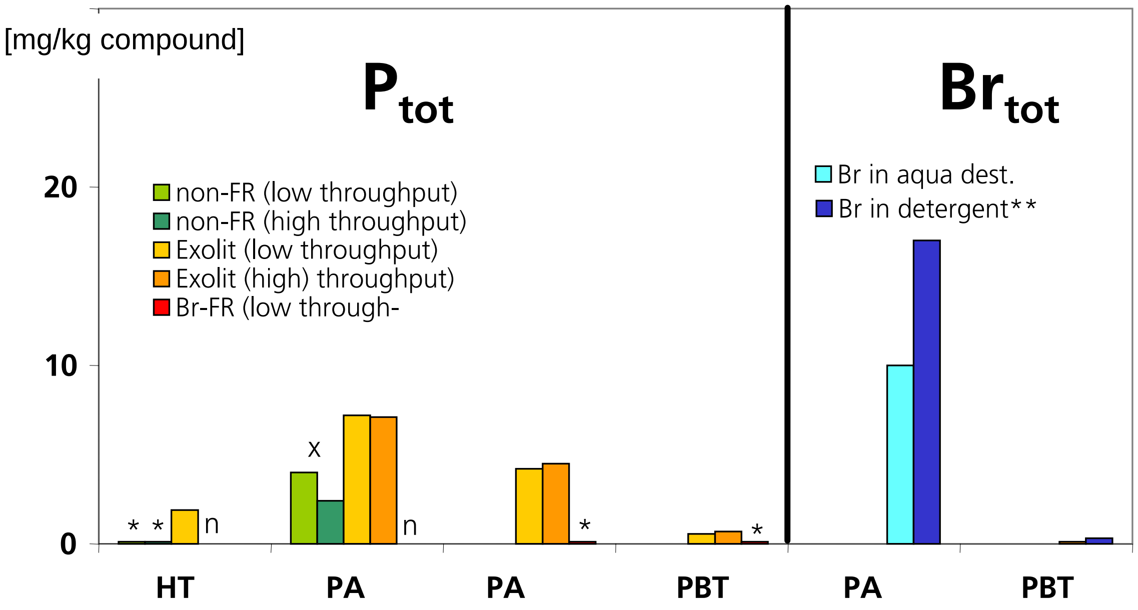


Figure 3: Migration of phosphorus and bromine compounds into the water phase. Bromine measurements were done from granules, phosphorus from bars: therefore, the release rates are not directly comparable.
* = limit of detection for this sample
** = with a detergent (0,1 % Triton X100) to simulate land fill leachate
n = no value, not measured
X = PA6 contained a phosphorus based stabilizer

5. EVAPORATION TESTING

The emissions of flame retardants from the plastic materials were measured with the Daimler-Chrysler test PB VWl 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 will condensate at room temperature; they cause the “fogging” film on the inside of car windows.

Since the publication of findings of flame retardants in indoor and automobile air as well as dust, the evaporation (“out gassing”) 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 tests 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.

6. 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 into a quartz tube. 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.

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 4). 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.

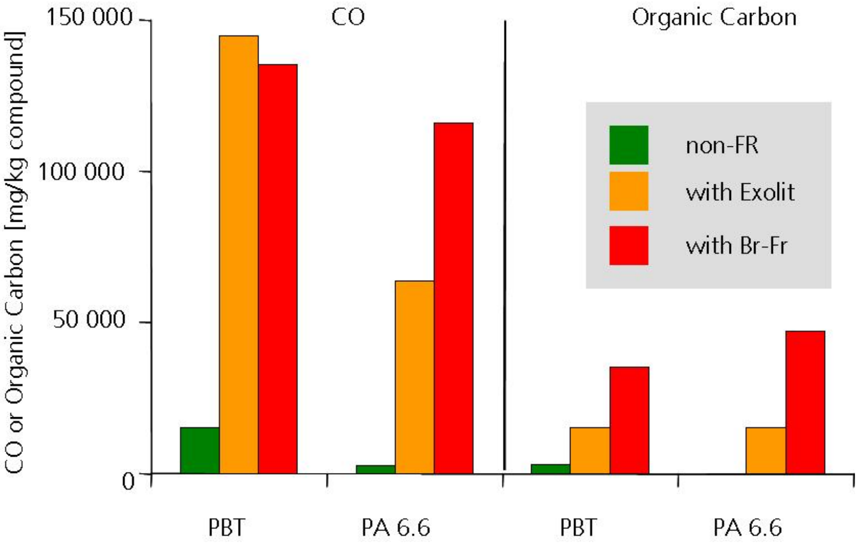
GC-MS analysis of the effluents revealed the formation of small amounts of volatile brominated low molecular weight substances like brominated aliphatic and aromatic compounds like dibromo methane, bromo methanol, (mono- and di-) bromo benzene, and brominated styrenes from brominated flame retardants. 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.

In order to evaluate the toxic potential of flue gasses, condensates were produced in cold traps. At the University of Würzburg 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). 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.

7. ELECTRONIC WASTE ISSUES

The results described above were supplemented by a theoretical study of the properties of the phosphinate FRs 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 current German waste management system served as a reference for the considered scenario that 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.



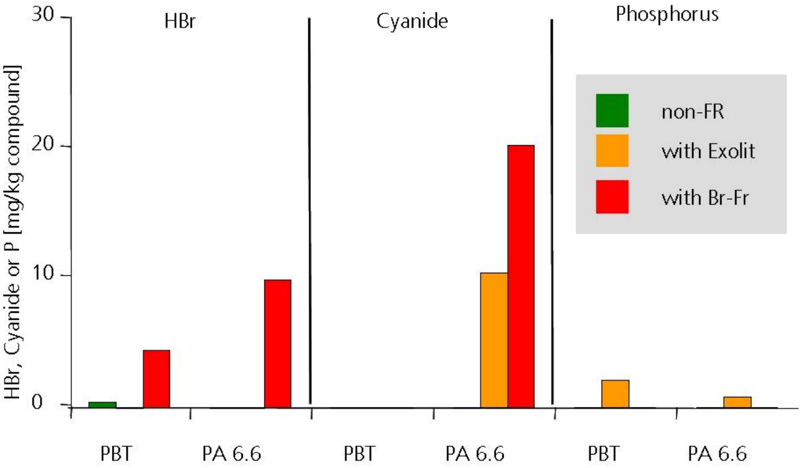


Figure 4: Combustion products with acute toxicity as measured with the DIN oven.

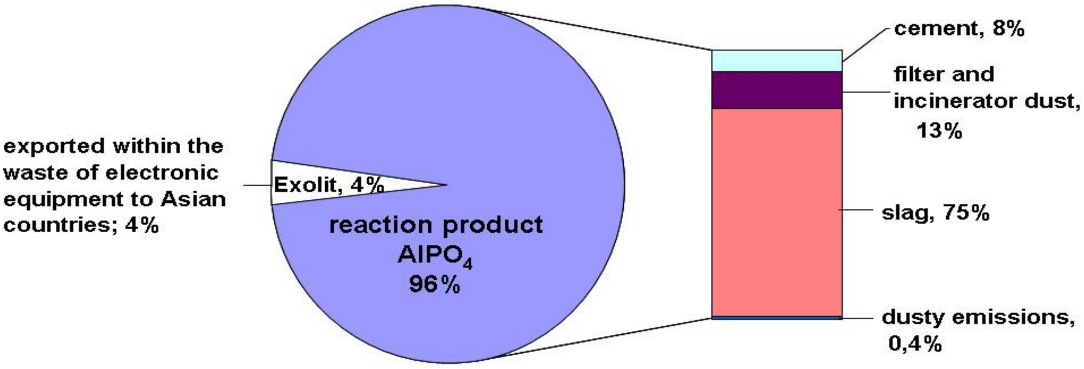


Figure 5: Waste from electric and electronic equipment: the distribution of the phosphinate flame retardant Exolit 1312 and its reaction product aluminium phosphate to different matrices.

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. FRs which come 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 FRs are 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 kiln. In both cases Exolit reacts to aluminium phosphate, which is fixed in ashes, slags and cement. Aluminium phosphate is commonly found in slags and ashes, from the other sources of these elements than flame retardants.

A small fraction of electric and electronic equipment is separated and exported to Asian countries, e.g. China. This fraction is estimated to amount to approximately 4 % of the total German electric and electronic waste. The electric and electronic equipment is "recycled" in Asia by thermal and chemical treatment, but often under hazardous conditions for the workers.

During the recycling process for electric and electronic equipment a fraction of the FRs will end up in the so called "shredder fraction" which contains polymers and metal parts. It can be used in metal reclaiming processes, e.g. copper smelters. Depending on economic conditions, a more sophisticated recycling process for electro and electronic equipment will be used. In this case the FRs are 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 land filling at low standards can be excluded. Only the export of electric and electronic equipment to Asia must be assessed negatively.

8. CONCLUSIONS

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. For the environmental behaviour of the examined phosphinate flame retardants it can be stated that:

- the flame retardant itself is non-toxic, does not bioaccumulate (Clariant data)
- there is no release of volatiles from finished products
- there is some release of flame retardant in contact with water (based on salt nature of the flame retardant)
- the smoke toxicity is lower in case of accidental fire compared to brominated flame retardants
- the flame retardant is not released during waste treatment within the limits of a modern waste management system (without a low standard land filling).

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