

Fire safety and environmental aspects of flame retardants. Current status and future developments

Juergen Troitzsch

Fire Protection Service, Wiesbaden, Germany. juergen.troitzsch@t-online.de

Introduction

The Moscow Ostankino TV-tower fire on August 28th, 2000 was caused by the overload of the numerous cable systems used, which led to overheating and eventually to ignition. It is assumed that one of the reasons for the extent of the fire was the use of non flame retarded polyethylene cable sheathing, which had therefore a very low fire safety level. The use of flame retarded cables would have reduced the impact of the fire or possibly even prevented it. This shows that there is an imperative need for products containing flame retardants to ensure high fire safety levels. However, today, for flame retardants, the focus is rather on environmental and toxicological than on fire safety considerations.

Flame retardants, environmental and fire safety considerations

Since many years, concerns on the environmental impact, fate and toxicology of certain flame retardants have been voiced particularly in Europe. Besides Germany and the European Union, which will be covered in some more detail in the following, flame retardants are a major topic in countries like Sweden, Denmark, the UK and Switzerland. Particularly in the Scandinavian countries, many studies and publications were made and mostly recommend discontinuing the use of halogenated and phosphorous-containing flame retardants.

The situation in Germany

It all started in Germany, where in the mid-Eighties concerns arose that halogenated flame retardants may not only be detrimental to health and the environment for possibly releasing halogenated dibenzodioxins/furans from plastics in case of fire, but also in their lifetime use as consumer goods and after when recycled, disposed or incinerated. This led to various mandatory and voluntary measures: Limit values for halogenated dibenzodioxins and -furans in the German Chemicals Banning Ordinance, ecolabels banning the use of halogenated plastics and flame retardants in consumer and office electronic equipment housings, and downgrading of products containing brominated and more recently phosphorous flame retardants in German consumer magazines [1].

The problem we have today is that these voluntary measures do not address the initial concerns against single flame retardants, but involve whole families like the halogenated or the phosphorous flame retardants without any differentiation. The consequence is that not only the general public, but specialists, users and regulators very often consider flame retardants to be substances with virtually identical physical, chemical, environmental and toxicological properties. In reality however, flame retardants are a

large group of substances based on organic and inorganic halogen, phosphorous, nitrogen and mineral containing compounds with strongly differing individual sets of properties.

The banning of whole families of flame retardants can create fire safety problems:

Fire safety levels of consumer goods

The fire safety level of TV-sets available in Europe has dropped because TV-sets producers, who voluntarily had used halogenated flame retardants in housings for achieving a high fire safety level (UL 94 V0) in the past, fear downgrading in consumer magazines and have since generally stopped using flame retardants in housings. Studies made with such lower fire safety (UL 94 HB) TV-sets on the market in Europe have shown that external fire sources easily set them on fire and quickly lead to room flashover, while the UL 94 V0 high fire safety level TV-sets available on the US and Japanese markets did not burn.

Flame retardants in the European Union: Risk assessments and planned directives

The problems connected with just banning whole families of flame retardants because one or a few members are suspected of potential impacts on human health and the environment have been identified. Experts and scientists therefore favour the risk assessment of single substances.

On European Commission level, since 1994, four Priority Lists for assessing the risks of twelve flame retardants in the context of the Council Regulation on the Evaluation and Control of the Risks of Existing Substances have been published. The flame retardants contained in the Priority Lists are summarised in Table 1:

Table 1: Ongoing risk assessments for flame retardants contained in the priority lists

First Priority List of 25.5.1994	Third Priority List of 27.1.1997
Decabromodiphenyl ether Octabromodiphenyl ether Chloroparaffins C ₁₀ – C ₁₃	Chloroparaffins C ₁₄ – C ₁₇
Second Priority List of 27.9.1995	Fourth Priority List of 25.10.2000
Pentabromodiphenyl ether Hexabromocyclododecane Tris(2-chlorethyl)phosphate	Tetrabromobisphenol A Antimony trioxide Tris(2-chloro-isopropyl)phosphate Tris(1,2-dichloro-isopropyl)phosphate 2,2-bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate)

Two substances of the polybrominated diphenyl ethers, which were under high pressure, deca- and octabromodiphenyl ether, will not require risk reducing measures

according to the findings of the not yet officially published respective risk assessments. For two other substances, pentabromodiphenyl ether and short-chain Chloroparaffins C₁₀ – C₁₃, risk reduction measures were recommended and draft guidelines for banning their use are under preparation. The ongoing risk assessments of the other flame retardants will create a scientific basis for evaluation opposed to the current “family” banning activities without comprehensive factual background.

In parallel, the European Commission Environment Directorate-General DG XI published proposals for directives on waste electrical and electronic equipment (WEEE) and on the restriction of the use of certain hazardous substances in electrical and electronic equipment (ROHS). In the WEEE, waste plastics containing brominated flame retardants would require a selective treatment in 2004 and in the ROHS, polybrominated biphenyls (PBB) and diphenylethers (PBDEs) would be banned in E&E equipment in 2006.

This is in contradiction with the findings of the EU risk assessments regarding deca- and octabromodiphenyl ether and ignores the approach of assessing the risk of single substances. These different approaches are problematic and need to be resolved.

Flame retardants and waste recovery

Another important topic in the use of flame retardants is their role in waste recovery, particularly in waste incineration, mechanical and feedstock recycling. In this context, some basic work on a life cycle assessment model on flame retardants has been carried out and first illustrated for TV-sets housings with or without flame retardants

Fire LCA study

Comprehensive work has been done for better understanding the effects of flame retardants on the environment and waste recovery. A life cycle assessment model has been developed for flame retardants used in TV-set housings. It shows that in case of fire the environmental impact of pollutants from TV-sets with housings containing brominated flame retardants is lower than that of TV-sets without flame retardants. In addition, TV- sets containing flame retardants help to dramatically reduce the number of fires [2].

Flame retarded plastics in waste incineration

The question whether waste containing PVC or plastics treated with brominated flame retardants lead to the formation of appreciable amounts of polyhalogenated dibenzodioxins and –furans has been a major point of discussion in recent years.

In order to find out the effects of varying amounts of waste electrical and electronic equipment (WEEE) containing brominated flame retardants on the formation of polybrominated dibenzodioxins and –furans during the incineration process, several studies were conducted and have shown that flame retarded plastics waste can be used

together with municipal waste for energy recovery without exceeding the 0.1 ng (TE¹)/m³ limit value required in the German waste incineration ordinance.

This was shown in comprehensive test programmes of the Karlsruhe Research Centre, Germany, mainly performed in the TAMARA pilot plant for waste combustion [3]:

The typical bromine content in municipal solid waste is very low (30-200 mg Br/kg) compared to the chlorine content (5000-8000 mg Cl/kg). Therefore, the presence of polybrominated dibenzodioxins and -furans (PBDD/PBDF) in the flue gas of waste incinerators is very low.

With raising bromine input by co-feeding flame retarded plastics, the formation of PBDD and particularly PBDF slightly increases and stabilises at bromine loads of approx. 500-1000 mg/kg. The prevailing homologues analysed contain one bromine atom and are not TE-relevant. In the test programme, it could be demonstrated that the total load of halogenated dioxins and furans stayed almost constant in spite of the increased load of brominated and chlorinated materials.

During the tests, samples taken after the flue gas had passed a charcoal filter resulted in residual PCDD/F concentrations of <0.001 ng (TE)/m³ which is a factor of 100 lower than the internationally accepted emission standard of 0.1 ng (TE)/m³. Bromine containing homologues could not be detected. This supports the conclusion that the contribution of bromine-containing species is of no concern to the emission of Municipal Solid Waste (MSW) incineration plants.

Mechanical recycling of plastics containing flame retardants

Studies on mechanical recycling of ABS containing brominated flame retardants and polypropylene containing ammonium polyphosphate (APP) based flame retarded systems have shown good recyclability.

The mechanical recycling of ABS containing a brominated epoxy oligomer flame retardant showed that the main properties like thermal and hydrolysis stability as well as the designed fire safety level (UL94 5VB) were maintained after extruding the material four times. The good results of the study have led to putting into practice the production of high quality recycled FR-ABS. The recycled material can be used for the same application as an alternative to the primary resin (so-called closed-loop recycling), by using FR-ABS recovered from discarded business machines [4].

Polypropylene reinforced with talc or glass fibres and flame retarded with APP can be recycled up to eight times and maintains its fire safety level (UL94 V0), melt flow properties and colour stability [5].

¹ TE = 2,3,7,8 tetrachlorodibenzodioxin Toxic Equivalent

Feedstock recycling of flame retardants

Feedstock recycling studies demonstrate that polyurethanes containing APP can be chemically transformed into polyols suitable for reuse in flame retarded polyurethane production. A feasibility study has shown that bromine recovery from waste electrical and electronic equipment is possible.

Rigid polyurethane foams containing APP as a flame retardant can be chemically recycled by glycolysis into a polyol, which can be reused as a polyol component. With the exception of a slightly enhanced acid number, no disadvantages occur during glycolysis in the presence of APP [6].

Bromine recovery from waste electrical and electronic equipment incinerated in a pilot plant for waste combustion was performed as follows:

The flue gases were quenched in water. The hydrogen bromide (HBr) was collected in a bypass system as HBr solution and the main flue gas stream was quenched in a caustic solution for recovery of the HBr as sodium bromide. For these streams a programme was set up to test the obtained bromine products for technical and economical evaluation of bromine recovery.

These experimental results were partly verified by experiences gained from full-scale experiments and are in line with results reported in the relevant scientific literature. This means that combustion combined with bromine recovery is an ecologically and economically feasible disposal route for halogen-containing plastic waste at least up to levels of 10% of municipal solid waste [7].

Conclusions and outlook

In Europe, there is an ongoing intensive discussion on flame retardants, currently rather focussing on environmental and toxicological aspects than on fire safety considerations. In many cases, voluntary activities like ecolabels ban the use of halogenated flame retardants and consumer magazines downgrade products containing brominated and more recently phosphorous flame retardants. The procedure to ban all flame retardants belonging to one group of substances is not based on facts and therefore unscientific.

In the meantime, there is a shift to assess the risk of single substances. On European Commission level, twelve flame retardants are currently risk assessed. Not yet officially published results show that two heavily suspected substances, deca- and octabromodiphenyl ether, will not require risk reducing measures, while others like pentabromodiphenyl ether and short-chain paraffins will be banned. The ongoing risk assessments of the other flame retardants will create a scientific basis for evaluation opposed to the current “family” banning activities without comprehensive factual background.

Waste recovery studies have shown that the use of products containing flame retardants is possible and allows mechanical and chemical recycling as well as energy recovery without adversely affecting the environment.

These findings have led to a more pragmatic and balanced approach regarding the use of flame retardants. Modern commercial flame retardant systems meet environmental and at the same time high fire safety requirements.

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