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Analysis for Bromine in Electronic Parts

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The reports are, however, published because the Danish EPA finds that the studies represent a valuable contribution to the debate on environmental policy in Denmark.

Contents

Summary

In 8 out of 16 purchased household appliances plastic parts containing brominated flame retardants were found.

The bromine content of the various types of plastics differs considerably, varying from 0.02 weight% to 9.6 weight%.

The detection limit for bromine and antimony is 0.01 weight%.

The 3 fan heaters analysed showed bromine and antimony in all the plastic parts used for the constructions.

In the other appliances it was small units with a content of flame retardants. In most cases it was electric components or units close to hot surfaces.

1 Background and Purpose

Brominated flame retardants are used as fire retardants in a large number of different products such as textiles, computer screens and household appliances. The brominated flame retardants primarily contain carbon, hydrogen and bromine. Some of the substances are concentrated in the food chain and are suspected of causing cancer and hormone disturbances.

The analysis shows the content of bromine and antimony in the products. However, it has not been examined which fire retardants the substances come from.

The National Agency of Environmental Protection has requested an analysis of a number of electronic parts and household appliances for content of brominated flame retardants. Mr. Jacob Maag, Cowi, has assisted in choosing the appliances on behalf of the National Agency of Environmental Protection. The appliances chosen were purchased by the Danish Technological Institute, Chemical Technology, Aarhus, where the analysis for content of bromine was carried out by X-ray technique. Prior to this analysis Mr. Nils Nilsson, Danish Technological Institute, Environmental and Waste Technology, had prepared a memo on bromine in electronic parts, concluding that a considerable content of bromine in plastics from household appliances came from components added to the plastics with the aim of having a fire retarding effect.

2 Bromine Content in Plastics and Electronic Parts

Prior to the practical analysis for content of bromine in the purchased appliances, an analysis of brominated compounds in plastics and electronic parts was carried out. The analysis was based on the collected knowledge on plastics at the Danish Technological Institute and on literature studies.

The conclusion of this analysis was that brominated compounds were merely added to the plastics to reduce the combustibility of the plastics. The brominated compounds can be divided into two types: 1) Compounds added to the plastics and 2) Compounds built into the plastic polymer.

The analysis is described in encl. C.

3 Results of Material Analyses

The appliances analysed comprise two irons, two coffee machines, three fan heaters, two deep fryers, two boiling pots, two food processors, two toasters and one heating blanket.

A list of the appliances analysed appears from encl. B.

As can be seen from the table of results, individual parts of the appliances have been analysed for content of bromine and antimony.

In about half of the appliances bromine was found in the plastic materials.

Encl. A, pages 1-16, show photos of all appliances with pictures of separated parts and indication of some of the elements.

As could be expected, brominated flame retardants were found in the parts of the appliances with the highest temperatures.

The table overleaf states the results of the analyses. The detection limit for bromine and antimony is 0.01 weight%.

table of results

Sample name and mark	Analysed parts	Content of bromine weight%	Content of antimony weight%
1. Idé-Line iron	Outer cabinet	< 0.01	< 0.01
	Adjusting handle	< 0.01	< 0.01
	Wire clamp on heating sole	0.1	1.5
2. Braun Proglide iron	Outer cabinet	< 0.01	< 0.01
	Plastics near heating sole	< 0.01	< 0.01
3. Melitta Look Fun coffee mach.	Blue outer plastics	< 0.01	< 0.01
	Black inner plastics	< 0.01	< 0.01
	Switch socket	9.6	3.7
	Cover over socket	< 0.01	< 0.01
4. Braun coffee machine	White outer plastics	< 0.01	< 0.01
	Outer switch, black	< 0.01	< 0.01
	Inner switch	< 0.01	< 0.01
5. Galax fan heater	Front and back of fan heater	1.3	< 0.01
	Main switch, greyish white	7.7	4.7
	Distribution unit for electricity	0.3	1.4
	Base	1.3	< 0.01
	Holder for main switch	< 0.01	< 0.01
6. OBH fan heater	Outer cabinet, light	8.3	2.6
	Outer cabinet, dark	0.6	0.3
	Fan blade	6.1	1.9
	Grey regulator	6.4	4.2
	Handle	8.5	2.6
7. Idé-Line fan heater	Outer cabinet	4.0	1.3
	Main switch	0.02	0.01

Sample name and mark	Analysed parts	Content of bromine weight%	Content of antimony weight%
	Distribution unit	5.2	2.9
	White cover plate	3.4	1.2
8. Moulinex Olea deep fryer	Outer cabinet	< 0.01	< 0.01
	Bottom near heating element	< 0.01	< 0.01
	Main switch	< 0.01	< 0.01
	Yellow handle	< 0.01	< 0.01
9. OBH deep fryer	Outer cabinet	< 0.01	< 0.01
	Light grey lid	< 0.01	< 0.01
	Wide grey ring	< 0.01	< 0.01
	Narrow grey intermediate ring	6.3	2.8
10. OBH boiling pot	Outer cabinet	< 0.01	< 0.01
	Internal switch	< 0.01	< 0.01
	Switch connection to heating element	< 0.01	< 0.01
11. Tefal boiling pot	Outer cabinet	< 0.01	< 0.01
	Grey contact switch	< 0.01	< 0.01
	Plastics with contact to heating element	< 0.01	< 0.01
12. Phlips Facilio food processor	Plastics around motor	< 0.01	< 0.01
	Yellowish plastics	< 0.01	< 0.01
	Brown top	< 0.01	< 0.01
	Adjusting unit in top	< 0.01	< 0.01
	Printed circuit board at motor, large	1.8	0.05
	Printed circuit board at motor, small	2.3	0.05

Sample name and mark	Analysed parts	Content of bromine weight%	Content of antimony weight%
13. Moulinex Masterchef 350	Outer cabinet	< 0.01	< 0.01
	Printed circuit board	< 0.01	< 0.01
	Plastic parts on print	< 0.01	< 0.01
	Switch	< 0.01	< 0.01
14. OBH toaster	Outer cabinet	< 0.01	< 0.01
	Grey bottom	< 0.01	< 0.01
	Printed circuit boards	< 0.01	< 0.01
	Switch handle	< 0.01	< 0.01
	Brown distance piece	6.6	2.5
	Light grey plastics	2.2	2.2
	Dark grey plastics	4.0	2.6
15. Moulinex toaster	Outer cabinet	< 0.01	< 0.01
	Printed circuit board	< 0.01	< 0.01
	Plastics around spring mechanism	< 0.01	< 0.01
16. OBH heating blanket	Textile wadding	< 0.01	< 0.01
	Switch unit	< 0.01	< 0.01

4 Analytical Methods

The chosen household appliances were separated and the materials selected from outer cabinets, printed circuit boards, where available, switches and other electric parts as well as plastics with direct contact to heating surfaces.

By the first screening of the selected parts some large and small plastic components containing bromine and antimony were found. For this screening a Philips EDAX PV9100/9500 energy dispersive X-ray fluorescence spectrofotometer was used.

By this relatively fast screening it was possible to sort out plastic parts containing brominated flame retardants for further quantitative analysis by the use of elementary analysis and analysis on plane surfaces with Philips PV2400 wavelength dispersive X-ray fluorescence spectrofotometer.

On the basis of these results the EDAX equipment was calibrated. In this way it became possible to carry out a quantitative analysis for bromine and antimony of samples not being shaped as plane surfaces.

As a consequence of the shape of the samples and for instance content of calcium (Ca) in the plastics, overlapping the analysis for antimony by EDAX, there is a deviation in the results for antimony of up to 25% rel. The accuracy of the bromine value is 10-15% rel.

The following pages, which make encl. A, show photos of the examined products.

Project: Bromine in Electronic Parts
Encl. A-1 Ide-Line Flex Steam Iron

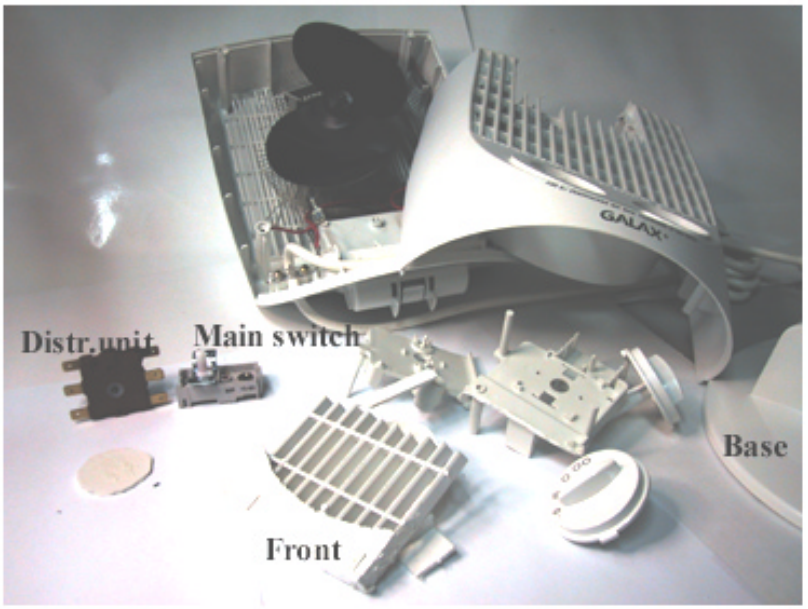
Project: Bromine in Electronoc Parts
Encl. A-2 Braun Proglide Jet Iron

Project: Bromine in Electronic Parts
Encl. A-1a Melitta Look Fun coffee machine

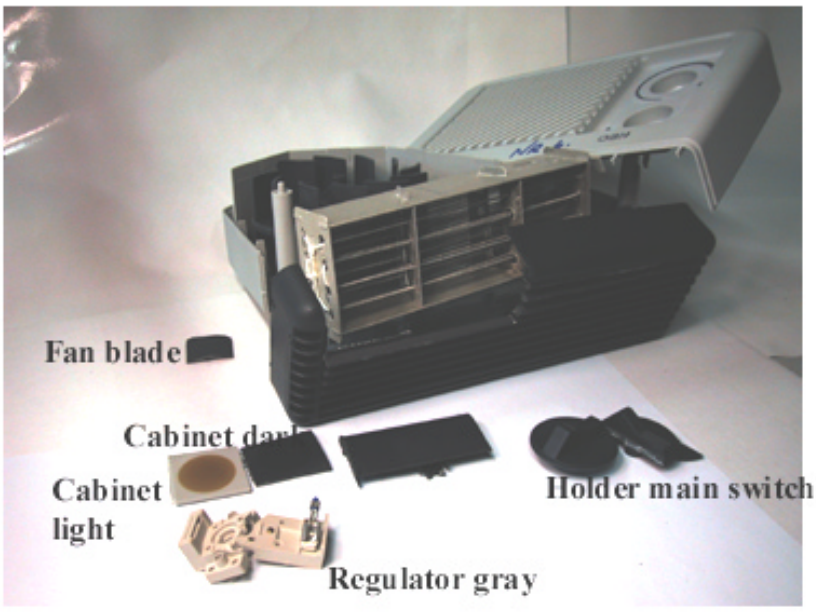
Project: Bromine in Electronic Parts
Encl. A-1b Melitta Look Fun coffee machine

Project: Bromine in Electronic Parts
Encl. A-4 Braun coffee machine

Project: Bromine in Electronic Parts
Encl. A-5 Galax Fan heather



Project: Bromine in Electronic Parts
Encl. A-6 OBH Fan heater

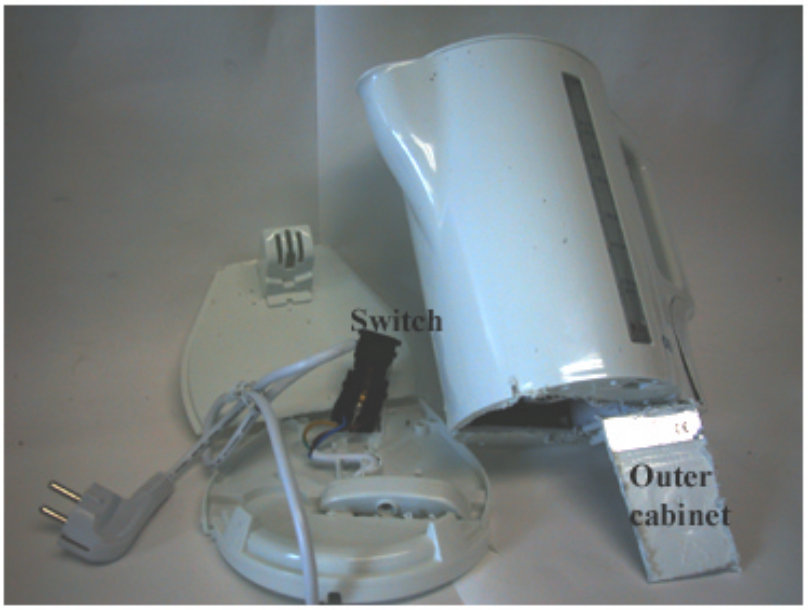


Project: Bromine in Elrctronic Parts
Encl. A-7 Ide-Line Fan heater

Project: Bromine in Electronic Parts
Encl. A-8 Moulinex Olea Deep Fryer

Project: Bomine in Electronic Parts
Encl. A-9 OBH Deep fryer

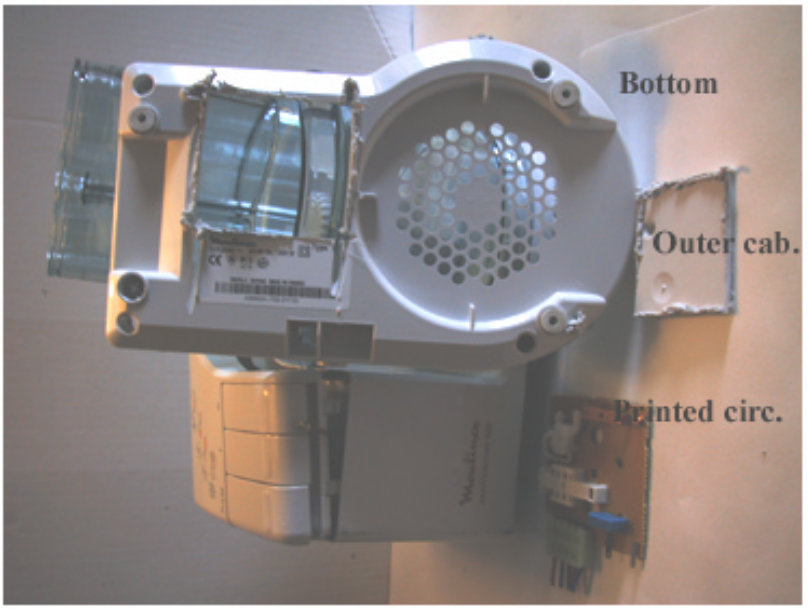
Project: Bromine in Electronic Parts
Encl. A10 OBH Boiling Pot



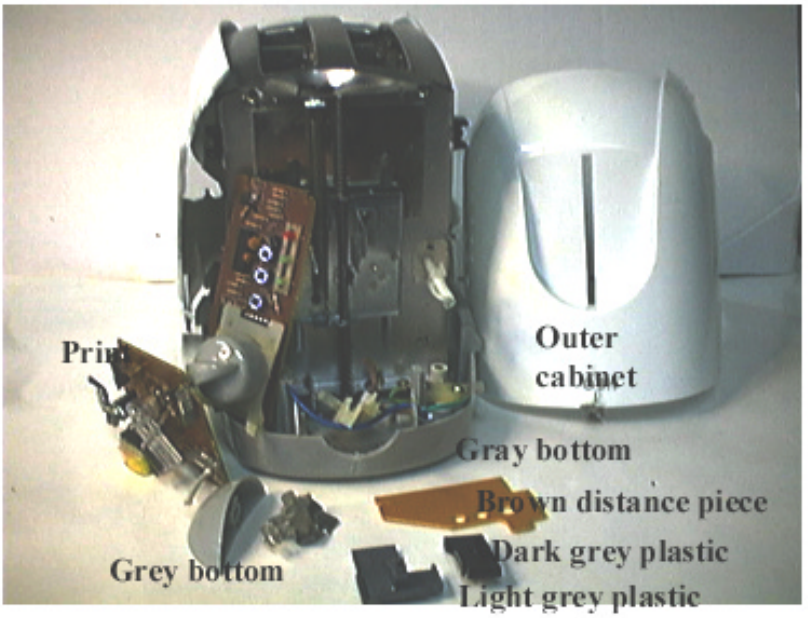
Project: Bromine in Electronic Parts
Encl. A-11 Tefal Boiling Pot

Project: Bromine in Electronic Parts
Encl. A-12 Philips Facilio food processor

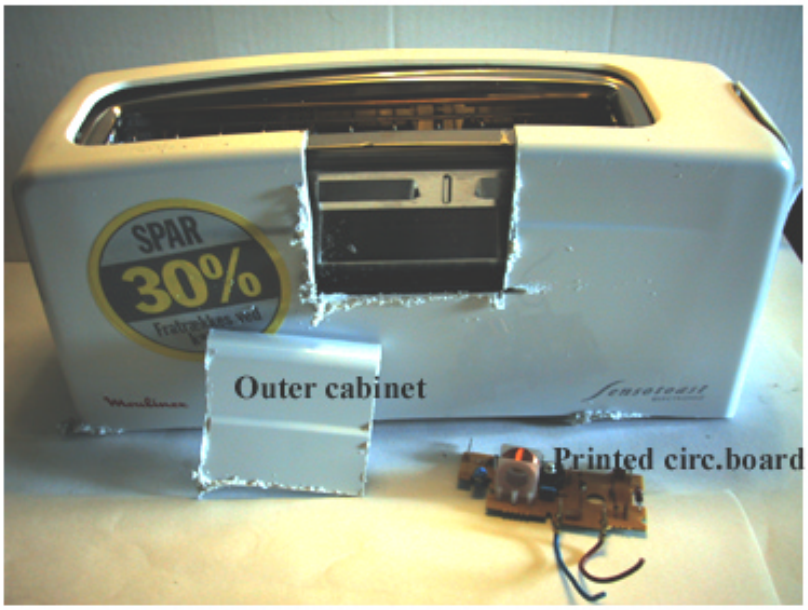
Project: Bromine in Electronic Parts
Encl. A-13 Moulinex Masterchef 350



Project: Bromine in Electronic Parts
Encl. A-14 OBII Toaster



Project: Bromine in Electronic Parts
Encl. A-15 Moulinex Toaster



Project: Bromine in Electronic Parts
Encl. A-16 OBH Heating Blanket

Encl. B

List of purchased products

Prod.name	Prod. descrip.	Name & address of prod. and/or importer	Date of purchase	Bar code	Article/ order No. Batch No.	Sample No.
Idé-Line, Flex Steam	Iron	?	21/8-01	5709121 410280	JP 8100C	1
Braun Proglide	Iron	Spain	21/8-01	4210201 150824	PV 3210	2
Melitta Look Fun	Coffee machine	?	21/8-01	4006508 160297	M 620-1/107 Art. nr. 4-0006-8D	3
Braun Aromaster	Coffee machine	?	21/8-01	4210201 124450	KF 32	4
Galax	Fan heater	Dankram A/S, Denmark	23/8-01	5709375 131313	1313, 100-F80-3	5
OBH	Fan heater	Denmark	21/8-01	5708642 061209	Type 6120	6
Idé-Line Oscillating	Fan heater	?	21/8-01	5709121 700305	FH 202	7
Moulinex Olea	Deep fryer	France	21/8-01	3016661 090257	CP2-51	8
OBH	Deep fryer	Denmark	21/8-01	5708642 063302	6330	9
OBH	Boiling pot, 1.7 L	Denmark	21/8-01	5708642 068116	6811	10
Tefal Delfina	Boiling pot, 1.7 L	France	21/8-01	3168439 144010	91440	11
Philips Facilio	Food processor	Philips, Hungary	23/8-01	-	HR 7720	12
Moulinex Master-chef 350	Food processor	France	21/8-01	3016661012860	AB 6624 F B6624	13
OBH Design 2001	Toaster	OG Bødker Hansen A/S, Denmark	21/8-01	5708642 022491	Type 2249	14
Moulinex Sensotoast	Toaster	Spain	21/8-01	3016661 072130	AF 1 48	15
OBH	Heating blanket	Denmark	21/8-01	5708642 045308	Type 4530	16

Memo on the Project: Analysis for Bromine in Electronic Parts

Prepared by Nils H. Nilsson, Environmental and Waste Technology, Danish Technological Institute, for Ivan Christensen, Chemical Technology, Danish Technological Institute

introduction

The primary aim of the project was to determine to what extent brominated flame retardants are found in household appliances on the Danish market.

The present memo assesses the possibility of other bromine compounds than brominated flame retardants being present in the plastic parts of the household appliances than the brominated additives added to the plastics to have a fire retardant effect.

overall conclusion

On the basis of the Institute's collected knowledge on plastic materials and a brief literary survey of additives for plastics it seems to be extremely unlikely that other brominated compounds have been added to the plastics of the household appliances than the bromine-based flame retardants and under no circumstances in concentrations of an order corresponding to that of the fire retardants. In the first place, the bromine compounds are rather expensive as compared to the corresponding chlorinated compounds, secondly, no examples of commercially offered or otherwise used additives in the form of bromine compounds for plastics other than the brominated flame retardants have been found in the handbooks and literature studied.

The reason why the bromine-based flame retardants are used to such an extent is that by addition of a comparatively small amount of the bromine-based flame retardants a fire retardant effect is achieved so that the plastics can fulfil the so-called UL-requirements or other standardized fire classifications. However, it must be added that the bromine-based flame retardants in large concentrations may function as plasticizers in the plastics if the solubility parameters make it possible. Otherwise the flame retardant must be regarded as a filler.

Furthermore, it should be mentioned that in principle it is possible to build bromine-substituted monomers into the plastic polymer with the same purpose, viz. to reduce the combustibility of the plastics. It depends entirely on the type of plastics if this is a realistic possibility. Another possibility is to brominate the polymer after the polymerization process. This is hardly very realistic. Reactive flame retardants are primarily used in connection with thermoset, for instance polyurethane polymers and epoxy polymers. These

plastic types are not assessed to be used in household appliances to any appreciable extent. However, thermoplastic polyurethane types may form part of household appliances.

It should be added that reference1 states the possibility of building hologen-containing monomers into ABS (acrylonitril-butadiene-styrene plastics). Both chlorine and bromine belong to the halogens.

Basis of assessment

The references state the literature that has been used as the basis for the conclusion. At the same time it can be mentioned that through almost 20 years' work with the chemistry, physics and technology of plastics the undersigned has not come across literature dealing with other bromine compounds added to plastics in relation to the plastic types used commercially in electric and electronic appliances, including household appliances, than bromine compounds with fire retardant properties.

household appliances

Household appliances comprise first and foremost electric articles such as vacuum cleaners, hair dryers, curling irons, toasters, coffee machines, hot water boilers, mixers, blenders and other electric types of mixing equipment as well as shavers and massage apparatuses.

types of plastics used for household appliances

A number of different types of plastics are used in electric household appliances. Whether the plastics is fire retardant or not depends on the location of the plastics in relation to the electric parts of the appliance, how high and critical the temperature is at maximum load, and the legislative requirements applying to electric articles /electronics.

The most frequently used plastic types for household appliances are polyethylene, polypropylene, acrylonitril butadiene styrene (ABS), polyester types (PBT, PET), polycarbonate (PC), polyamides (PA 6, PA 66), polysulfone (PSU), polyphenylene oxide (PPO), polyether sulfone (PES) and phenol plastics. The last type is a thermoset as compared to the rest which are all thermoplastic types. The choice of plastic type depends on the kind of mechanical properties essential to the perfect functioning of the household appliance, the temperature to which it is exposed, electric properties (insulating, antistatic), possible demands in relation to food contact, etc.

Fibres or fillers may often be added to the plastics. These may both contribute to strengthening the plastics, but also to reducing the combustibility of the plastics. Polyethylene (HDPE) and polypropylene (PP) are the less expensive of the plastic types. However, they are also those of the above-mentioned plastic types with the lowest melting interval/softening point, and therefore, there is a limit to the temperature to which they can be exposed. PBT and PET are much used in electric household appliances, among other things because of their high softening temperature and a relatively favour-

able price of the raw material.

fire retardants

There are brominated fire retardants reacting with the plastics and therefore chemically bound in the plastics as well as fire retardants not chemically bound. Antimony trioxide, which appears on the National Agency of Environmental Protection's list of undesired substances, is often used together with brominated flame retardants as there is a synergistic effect.

The reactive types of brominated flame retardants are used in the thermoset types unsaturated polyester, polyurethane and epoxy. These plastic types are not considered of great use in household appliances. However, epoxy is applied for printed circuit boards.

The table overleaf shows examples of the concentrations of flame retardants used in the different types of thermoplastics in order to be able to fulfil the UL 94 fire klassification (UL = Underwriters' Laboratories). The information comes from reference 7. Owing to their chemical lay-up and very high melting temperature, the polysulfone types have low ignition properties and flame spread in the case of fire. Therefore, there is little or no need for adding flame retardants to these types.

concentration of flame retardants in thermoplastic types

Plastic type	Flame retardant system	Concentration of flame retardant in plastics in per cent
HDPE	TBBA-bis(2,3-dibromine-propylether) Antimony trioxide	7 –10 3 –4
PP	TBBA-bis(2,3-dibromine-propylether) Antimony trioxide Ethylene-bis-(dibromine-norbornan-dicarboximid) Antimony trioxide	6-20 3-10 2-4 1-2
ABS	Octabromine-diphenylether Antimony trioxide TBBA Antimony trioxide Bis(tribromine-phenoxy)-ethane Antimony trioxide	18- 22 4-8 18-22 4-8 20-24 4-8
PA 6 og PA 66	Polybromine-diphenylether Antimony trioxide Ethylene-bis-(tetrabromine-phthalimid) Antimony trioxide	17-20 4-5 7-10 4-5
PBT	Ethylene-bis-(tetrabromine-phthalimid) Antimony trioxide	7-10 4-5
PS impact-proof	Decabromine-diphenylether Antimony trioxide	10-12 3-4

It can be seen that a combination of antimony trioxide and brominated flame retardant is used. Thus, the quantity of brominated flame retardant can be limited, reducing the risk of changing the mechanical properties of the plastics in a negative direction. Many of the plastic types are also available with glass fibre reinforcement or addition of small glass balls, which enables a change of the rigidity of the material and reduces the quantity of plastics in the construction, making it less expensive.

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