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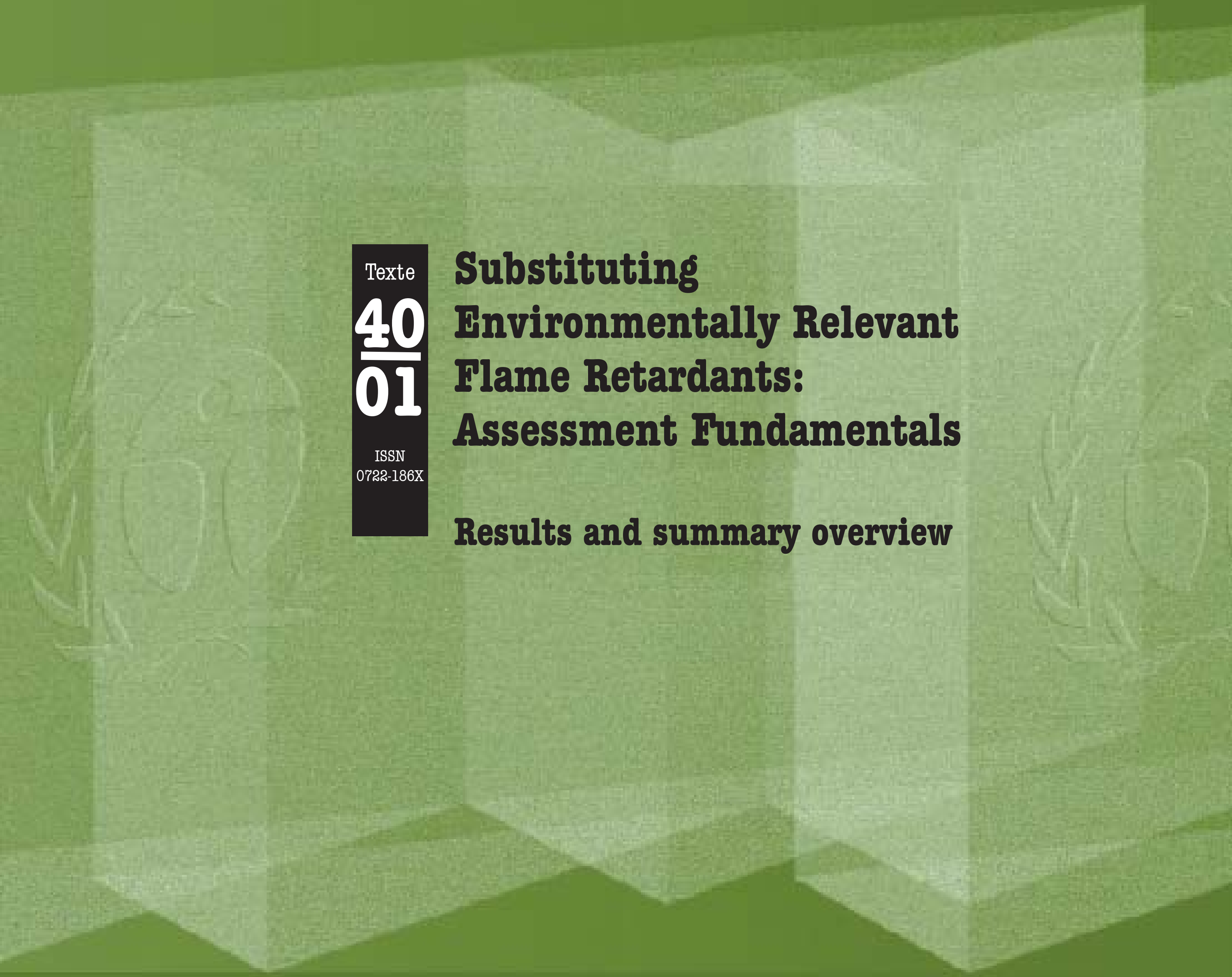

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Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals

Results and summary overview

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Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals

Results and summary overview

by

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Öko-Recherche
Büro für Umweltforschung und –beratung GmbH,
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Vol. III: Toxicological and ecotoxicological substance profiles of selected flame retardants

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16. Abstract

The study examines the status, trends and alternatives (substitution and reduction potentials) in the use of flame retardants in selected product sectors: construction; electronics and electrical engineering; rail vehicles; textiles/upholstery. In addition, the study characterises thirteen flame retardants in terms of material flows, applications and toxicology/ecotoxicology.

Vol. I: Summary overview of flame retardant applications in Germany in 1999/2000; characterisation of 13 flame retardants in terms of substance properties and application-specific characteristics, range of applications and quantities; derivation of assessment fundamentals for flame retardants, focussing on toxicology/ecotoxicology, suitability for closed-loop substance management, and potential for substitution and reduction; summary assessment of 13 flame retardants; summary overview of flame retardant applications.

Vol. II: Analysis of flame retardant applications (state of the art, trends, alternatives) in: unsaturated polyester (UP) resins (rail vehicles); polyurethane (PU) insulating foams and one component foams (OCF) (construction sector); plastics for generic uses in electronic and electrical equipment, in casings for electronic and electrical equipment and in printed circuit boards (electronics/electrical engineering); and in upholstery and mattresses (textile applications).

Vol. III: Toxicological/ecotoxicological profiles of substances: Decabromodiphenyl oxide; Tetrabromobisphenol A; Bis[pentabromophenyl]ethane; Hexabromocyclododecane, Tris[chloropropyl] phosphate, Resorcinol-bis-diphenylphosphate; N-Hydroxymethyl-3-dimethylphosphonopropionamide, Red phosphorus, Ammonium polyphosphate, Melamin cyanurate, Aluminiumtrihydroxide, Sodium borate decahydrate, Antimony trioxide.

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Flame retardants; fire protection; substance assessment; substance substitution; substance reduction; Decabromodiphenyl oxide; Tetrabromobisphenol A; Bis[pentabromophenyl]ethane; Hexabromocyclododecane,Tris[chloropropyl]phosphate, Resorcinol-bis-diphenylphosphate; N-Hydroxymethyl-3-dimethylphosphonopropionamide, Red phosphorus, Ammonium polyphosphate, Melamin cyanurate, Aluminiumtrihydroxide, Sodium borate decahydrate, Antimony trioxide; unsaturated polyester resins; polyurethane insulating foam; polyurethane one component foam; electronic/electrical casings; printed circuit boards; upholstery, mattresses

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Band I: Ergebnisse und zusammenfassende Übersicht;
Band II: Flammhemmende Ausrüstung ausgewählter Produkte – anwendungsbezogene Betrachtung: Stand der Technik, Trend, Alternativen
Band III:Toxikologisch-ökotoxikologische Stoffprofile ausgewählter Flammschutzmittel

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14. Abbildungen

15. Zusätzliche Angaben

16. Kurzfassung

Untersucht werden Stand, Trends und Alternativen (Substitutions- und Minderungspotentiale) beim Einsatz von Flammschutzmitteln (FSM) in ausgewählten Produkten aus: Baubereich, Elektrotechnik/Elektronik, Schienenfahrzeugbereich, Textil-/Polstermöbelindustrie. Parallel dazu werden dreizehn Flammschutzmittel hinsichtlich Mengenstrom, Anwendungen und Toxikologie/Ökotoxikologie charakterisiert.
Bd.I: Ergebniszusammenfassung zu Flammschutzmitteleinsatz in Deutschland 1999/2000; Charakterisierung von 13 FSM nach Stoff- und Anwendungseigenschaften, Einsatzspektrum, Mengen; Ableitung von Bewertungsgrundlagen für FSM mit Schwergewicht auf Toxikologie/Ökotoxikologie, Kreislauffähigkeit, Substitutions- und Minderungspotentialen; zusammenfassende Stoffbewertung zu 13 FSM; zusammenfassende Übersicht zu FSM-Anwendungen.
Bd.II: Anwendungsuntersuchungen (Stand der Technik, Trend, Alternativen) zu FSM bei UP-Harzen (Schienenfahrzeuge), bei PU-Dämm- und Montageschäumen (Baubereich); bei Kunststoffen für E+E-Geräte insgesamt, Außengehäusen für E+E-Geräte und Leiterplatten (Elektro/Elektronikindustrie); bei Polstermöbeln/Matratzen (Textilanwendungen).
Bd.III: Toxikologisch/ökotoxikologische Stoffprofile Decabromdiphenylether; Tetrabrombisphenol A; Bis[pentabromphenyl]ethan; Hexabromcyclododecan,Tris[chlorpropyl]phosphat, Resorcinol-bis-diphenyl-phosphat; N-Hydroxymethyl-3-dimethylphosphonpropionamid, roter Phosphor, Ammoniumpolyphosphat, Melamincyanurat, Aluminiumtrihydroxid, Borax, Antimontrioxid.

17. Schlagwörter

Flammschutzmittel; Brandschutz; Stoffbewertung; Stoffsubstitution; Stoffminderung; Decabromdiphenylether; Tetrabrombisphenol A; Bis[pentabromphenyl]ethan; Hexabromcyclododecan,Tris[chlorpropyl]phosphat, Resorcinol-bis-diphenyl-phosphat; N-Hydroxymethyl-3-dimethylphosphonpropionamid, roter Phosphor, Ammoniumpolyphosphat, Melamincyanurat, Aluminiumtrihydroxid, Borax, Antimontrioxid; Ungesättigte Polyesterharze; Polyurethan-Dämmschaum; Polyurethan-Montageschaum; Außengehäuse E+E-Geräte; Leiterplatten; Polstermöbel, Matratzen

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Abbreviations

A1, A2	construction material classes according to DIN 4102 standard
ABS	acrylonitrile-butadine-styrene
ADI	acceptable daily intake
AG	Aktiengesellschaft (Joint-Stock Company)
AP	ammonium phosphate
APME	Association of Plastic Manufacturers in Europe
APP	ammonium polyphosphate
ATH	aluminium trihydroxide, aluminium trihydrate
ATO	antimony trioxide
B1, B2, B3	construction material classes according to DIN 4102
BADP	bisphenol A diphenyl phosphate
BAT	Biologischer Arbeitsplatztoleranzwert/bological value for occupational tolerability
BMC	bulk moulding compounds
BMBF	Federal Ministry for Education and Research (Bundesministerium für Bildung und Forschung)
BS	British Standard
BSEF	Bromine Science and Environmental Forum
BT	bismaleinimid-triazin
CAS	Chemical Abstract System
CEM1, CEM3	printed circuit board types
CEN	European Committee for Standardization
Co	Company
CSD	UN Commission on Sustainable Development
D	Germany
DBPNG	dibromoneopentylglycol
DDT	dichloro-diphenyl-trichloroethane
DE	diphenyl ether
DeBDE	decabromodiphenyl ether/oxide
Deca	decabromodiphenyl ether/oxide
DEEP	diethylethylphosphonate
DIN	German Standards Institute (Deutsches Institut für Normung)
DM	Deutschmark
DMMP	dimethyl methyl phosphonate
DPK	diphenylcresylphosphate
EACEM	European Association of Consumer Electronics Manufacturers
Ed	Editor
E+E	electronic and electrical
EEG	electroencephalogram
EFRA	European Flame Retardants Association
EN	European Standard
EPS	expanded polystyrene
Etc.	et cetera
EU	European Union

EVA	ethylene vinylacetate copolymer
F0-F5	smoke development classes according to NFF16-101
F30 – F120	smoke resistance classes according to DIN 4102
FGRP	fibre-glass reinforced plastic
FR	flame retardant
FR 1 – FR 4	flame retardant printed board types
g	gramme
GefStoffVO	Gefahrstoff-Verordnung (Hazardous Substance Ordinance)
GmbH	Ltd.
HB	horizontal burning, flame-resistance level according to UL
HBCD	hexabromocyclododecane
HET acid	hexachloroendomethylenetetrahydrophthalic acid
Hg.	Herausgeber (Editor)
HIPS	high-impact polystyrene
hPa	hectopascal
IARC	International Agency for Research on Cancer
IT	Information Technology
ibid.	in the same place
k.A.	keine Angabe/no data
kg	kilogramme
kV	kilovolt
l	litre
LC_{50}	lethal concentration 50
LD_{50}	lethal dose 50
log	logarithm
LOAEL	lowest observable adverse effect level
LOEL	lowest observable effect level
LOI	limiting oxygen index
m	metre
MAK	Maximale Arbeitsplatz-Konzentration
M0-M4	flammability classes according to NFF 16-101
Mbar	millibar
MC	melamin cyanurate
MDI	methane diphenyl diisocyanate
mil.	million
MMA	methylmetacrylate
NEMA	National Electronics Manufacturers Association
ng	nanogramme
n.k.	nicht kennzeichnungspflichtig/no classification required
NL	Netherlands
Nm	nanometre
NOAEL	no observable adverse effect level

NOEL	no observable effect level
OECD	Organization for Economic Cooperation and Development
OEM	Original Equipment Manufacturer
PA	polyamide
Pa	Pascal
PBB	polybrominated biphenyl
PBDD/F	polybrominated dibenzo dioxin/furan
PBDE, PBDO	polybrominated diphenyl ether, polybrominated diphenyl oxide
PBDF	polybrominated dibenzo furan
PBT	polybutylene terephthalate
PC	a) personal computer; b) polycarbonate
PCDD/F	polychlorinated dibenzo dioxin/furan
PE	polyethylene
P-ester	phosphoric acid ester
pg	picogramme
phr	per hundred of resin
PIR	polyisocyanurate
PMMA	polymethylmetacrylate
pmol	picomol
POP	persistent organic pollutant
P_{OW}	octanol-water partition coefficient
PP	polypropylene
Ppb	parts per billion
PPE	polyphenyl ether
PPE, PPO	polypropylene oxide
ppm	parts per million
PS	polystyrene
PTFE	polytetrafluoroethylene
PUR	polyurethane
PVC	polyvinylchloride
RA	risk assessment
RDP	resorcinol-bis-diphenylphosphate
RP	red phosphorus
R-phrases	Classification according to GefStoffVO
RTM	resin transfer moulding
S1-S5	combustibility classes according to DIN 5510
SB	styrene-butadiene
SBI	single burning item
SE	Selbsteinstufung/self classification
SMC	sheet moulding compound
S-phrases	Classification according to GefStoffVO
SR1, 2	smoke development classes according to DIN 5510
ST1, 2	drip-capacity classes according to DIN 5510
t	tonne
TA	Technische Anleitung/technical guidelines
TBBA	tetrabromobisphenol A

TBPA	tetrabromophtalic acid anhydride
TCP	tricresyl phosphate
TCEP	tris(chloroethyl) phosphate
TCPP	tris(chloropropyl) phosphate
TDA, TDI	tolerable daily intake
TDI	toluene diiso cyanate
TE	toxicity equivalent
TEGEWA	German association of textile auxiliary, leather auxiliary, tanning agent and detergent feedstock industries (Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoff-Industrie e.V.)
TEP	triethylphosphate
TFI	German carpet research institute (Deutsches Teppich-Forschungsinstitut e.V.)
THPC	tetrakis(hydroxymethyl)phosphonium chloride
TPP	triphenylphosphate
TRK	Technische Richtkonzentration
TV	television
UBA	German Federal Environmental Agency (Umweltbundesamt)
UL	Underwriters Laboratories
UP	unsaturated polyester
UV	ultraviolet
V0,V1	flammability resistance according to UL
VCI	German chemical industry association (Verband der Chemischen Industrie e.V.)
VKE	German Association of Plastics Manufacturers (Verband der Kunststofferzeugenden Industrie)
Vol.	Volume
W	Watt
WEEE	waste electrical and electronic equipment
WGK	water hazard class (Wassergefährdungsklasse)
XPS	extruded polystyrene
ZVEI	German electrical and electronic manufacturers’ association (Zentralverband der Elektrotechnik- und Elektronik-Industrie e.V.)
µg	microgramme

Preface

The present study, "Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals", was commissioned by the German Federal Environmental Agency (Umweltbundesamt, UBA) and prepared during the period from September 1998 to December 2000.

The present status, as well as trends and alternatives, with regard to the application of flame retardants in selected products of the construction sector, the electrotechnical and electronics industry, the rail vehicle sector, and the textile industry, are examined. In parallel, 13 flame retardants which are important in terms of their substance streams and toxicology/ecotoxicology are characterized and evaluated in detail with regard to their substance properties.

Approximately 100,000 tonnes of flame retardants were utilized in Germany during 1999. Of this approximately 50 percent were mineral-based, approx. 30 percent based on halogenated or antimony-halogen systems, and about 20 percent based on halogen-free phosphorus and other compounds. To have the required fire protection properties, the individual flame retardants must be dosed in varying amounts. A breakdown in terms of materials and plastics in which flame retardants are incorporated thus yields a different distribution among flame retardant groups. Approximately 15-20 percent of materials and plastics contain mineral flame retardants, more than 50 percent are flame-retarded with halogenated or antimony-halogen systems, and just under 30 percent incorporate other halogen-free flame retardants.

Overall, evaluation of the selected flame retarding systems shows that both the brominated and the organic phosphorus flame retardants present toxicological and ecotoxicological problems to varying degrees, and that for some of them a need for their substitution exists. At the same time, applications-oriented examination of flame retardant use shows that, in almost all areas of application, potentials for reducing the consumption of flame retardants and for using environmentally less harmful substances exist, while retaining the required fire safety properties. These potentials are at the present time and for various reasons not completely utilized. In contrast, most of the other flame retardants prove to be environmentally less relevant.

This study was prepared as a cooperative project of Öko-Recherche GmbH (Frankfurt/M.), in connection with the Institute for Toxicology of the University of Kiel, and Institut für sozial-ökologische Forschung (ISOE) GmbH (Frankfurt/M., Institute for Social-Ecological Research).

Volume I contains an overview of the research task, of flame retardants and their use in Germany, and of the specifically examined flame retardants (Öko-Recherche GmbH) and assessment bases (ISOE GmbH). Furthermore, this volume contains a summary of the main results with regard to substance evaluation (Institute for Toxicology of the University of Kiel), and an applications-oriented examination of the status of and trends in flame retardant usage in selected products (Öko-Recherche GmbH).

Volume II contains the research with regard to flame retardant use in selected products: structural and cladding elements for rail vehicles, made of unsaturated polyester (UP) resins; insulation and assembly (one-component) foams, made of polyurethane, with a discussion of polystyrene insulation foams; an overview of plastics and flame retardants used in E+E appliances; duroplastic base materials for printed boards/printed circuit modules; thermoplastic materials for casings of IT and TV appliances; textiles and covering materials for mattresses and upholstered furniture. Volume II was prepared by Öko-Recherche GmbH.

Volume III documents the substance profiles of the thirteen flame retardants assembled by the Institute for Toxicology/Kiel. Among these were four brominated compounds (decabromodiphenyl ether; tetrabromo-bisphenol A; bis[pentabromophenyl]ethane; hexabromocyclododecane), two inorganic phosphorus compounds (red phosphorus, ammonium polyphosphate), one nitrogen-based flame retardant (melamin cyanurate), aluminium trihydroxide as a mineral flame retardant, as well as sodium borate decahydrate and synergistic antimony trioxide. Besides this, the opinions of the manufacturers of flame retardants with regard to the draft substance profiles are documented in the Annex to Volume III.

Two workshops with manufacturers of flame retardants, users and experts in the field took place within the framework of the project.

We would like to thank the manufacturers of the above flame retardants, as well as a number of other companies and experts in the industries using these substances, for providing data and information relevant to the questions raised by this project.

Frankfurt am Main and Kiel, December 2000

Amendment of the publisher:

This publication covers only volume I of the full report. Volume II and III (see report cover sheet) are available only in German language. They are published as UBA-Text 26/01 and 27/01.

Chapter I: Task definition and methodology

Chapter contents

1. Task definition

The task of the present study is to develop evaluation criteria for the substitution of environmentally relevant flame retardants. For this purpose a selection of thirteen flame retardants (including synergistic antimony trioxide) is examined with regard to their environmentally relevant properties (essentially: toxicity, ecotoxicity, and suitability for closed-loop substance management). It is examined how these flame retardants are currently utilized in important areas of application, and on what conditions the utilization of flame retardants depends.

Characterization and evaluation of the 'pure flame retardants', that is the trade products, is based on the substance profiles developed within the framework of this study, in which the relevant toxicological and ecotoxicological data are compiled. These substance profiles are documented in Volume III of the study.

The applications-oriented analysis (Volume II of the study) seeks to ascertain what possibilities for action are available for replacing environmentally harmful with less problematic flame retardants. The point of departure for defining a basis for evaluation is that the fire safety standards must be met for each of the application areas of the products examined, but that, at the same time, the environmental impacts of flame retardants and their decomposition products are reduced in quantitative or qualitative terms.

2. Flame retardance and fire safety – the issues

Incorporating a flame retardant in combustible materials and plastics is a common procedure in preventive fire safety measures, and is applied to reduce the risk of fires. Flame retardants reduce the flammability of plastics. They are active during the starting phase of a fire, in that they prevent the spread of an inner (e.g. short-circuit) or exterior source of ignition to the flame-retarded material, and thereby prevent, delay, or inhibit the spread of a fire. One of the properties that are demanded of flame-resistant materials in many application areas is that they be self-extinguishing once the source of ignition has been removed. In the event of a sufficient and continuous supply of energy and oxygen, it is nevertheless possible that flame-resistant materials will not prevent the spread of ignition into a full-scale fire and their subsequent complete destruction by fire. Flame retardants are therefore just one element among many in a concept for preventive fire safety.

With the rapidly growing use of plastics, which are usually quite flammable, the use of flame retardants has also increased strongly. Like all additives, flame retardants are in principle environmentally relevant, since they – and their converted forms and decomposition products – can be released during manufacturing, during incorporation into polymers, and during the entire lifecycle of flame-retarded products, and thereby enter the environment. To what degree this happens, and to what extent this is associated with environmental damage, depends largely on the substance properties of the flame retardants, as well as the substrates to which they are applied.

Discovery of toxicologically and ecotoxicologically problematic or hazardous flame retardants, as well as their decomposition products, in the various compartments of the biosphere (e.g. sediments, water, indoor air, biota) have in the past led to public debate and to regulations requiring the decreased use of such substances. A number of flame retardants have been banned for this reason, whereas for others voluntary phase-out declarations have been made. Currently a number of flame retardants are being reviewed within the context of the 1993 EU Regulation (793/93) on the evaluation and control of the risks of existing substances. In some instances, proposals for further substance and application bans have been made within the framework of European chemicals policy and regulations.

In this context, it must be taken into account that all flame retardants, or their active ingredients and decomposition products, become environmentally relevant at the latest during the waste disposal phase, because, depending on the disposal pathway and technology, they are either released from the polymer (incineration) or are transported into the environment together with the material in which they are incorporated (landfill). Whether this leads to damaging effects depends on the substance and product properties, as well as the waste disposal methods used.

In the case of recycling, too, this aspect is of fundamental importance. Recycling at the level of materials (as distinguished from feedstock recycling) is, for instance, associated with mechanical or thermal material processing, during which flame retardants that are a part of the material/plastic can be released and/or react with other components. Consequently, flame retardants must be appraised with regard to the closed-loop substance management characteristics of products and the ease with which they can be disposed of.

The toxicological and ecotoxicological reservations vis-à-vis flame retardants concern not only the persistent, bioaccumulating, toxic or ecotoxic substances, but also, for instance, agents with allergenic properties in cases where their range of use makes them relevant to indoor air quality, despite such flame-retarded products being used in accordance with regulations. In general it needs to be taken into account in this context how and in what way the flame retardant or its decomposition products are environmentally available. After incorporation in the material – *additively,* as an only physically incorporated additive, or *reactively,* as a component of the matrix that has been bound by a chemical reaction – the flame retardant occurs together with the material or end product. Its availability in the environment cannot be derived simply from the properties of the 'pure substance' or trade product, but rather depends on the type of bonding in the matrix, the material properties, and the utilization conditions of the product, as well as the combined behaviour of the matrix and flame retardants, for instance under thermal load and similar factors.

Within the context of harmonization of fire safety standards and tests within the EU, more attention is being paid to combustion products. This includes the toxicity and density of fumes which occur in the event of fire (e.g. during the utilization phase of flame-retarded products, or during their disposal, such as in incineration or landfill fires), which are influenced by flame retardants to varying degrees, as has been shown in comparative tests. Besides the aspect of personal protection (fume toxicity and acidity, and especially fume density, because of visibility hindrance in the case of evacuation), property protection also plays a role in this (corrosiveness of fumes, disposal costs in connection with toxic by-products). The importance of the (uncontrolled) fire aspect in any such assessment must however be weighed in each concrete instance, as it depends strongly on the application and utilization conditions of the respective products (for instance in closed rooms, as against use in the open air).

The harmonization of standards and test procedures at the European level (construction products, rail vehicles) refers back to the relationship between the fire scenario and combustion behaviour of the flame-proofed materials and plastics on which the corresponding tests are based, as well as their classification for the purposes of the test. As the tests, depending upon the assumed fire scenario in each instance (energy supply, oxygen supply, position of the test product, etc.), are always only a partial reflection of a real fire, flame retardants are usually formulated 'in the direction of' the applicable test conditions. Future changes in fire safety standards and tests can therefore also require changes in flame-resistant additions to materials if test requirements are to be met successfully.

The increasing utilization of flame retardants is not only a consequence of the growing use of plastics, but must also be seen in connection with the development of fire safety standards, as well as the standards that are consequently required with regard to flame-retardant additives in materials and plastics. This definition of standards is a result of social aims and preferences, as is also true for environmental standards, and therefore is subject to varying viewpoints, risk perceptions, social needs and interests. This can be seen in the discussions about the required and sufficient level of flame retardance in diverse products (for instance TV casings, upholstered furniture, printed circuit boards, small accessories and components for electric and electronic appliances), as well as in the different definition of standards in various countries. This aspect of varying social risk perceptions and risk evaluation must be taken into account when developing assessment criteria.

3. Methodology

3.1 Flame retardants and substance profiles

In consultation with the German Federal Environmental Agency (Umweltbundesamt, UBA), which commissioned the present study, a group of 13 flame retardants was selected to examine their toxicological and ecotoxicological properties. This group included antimony trioxide (ATO), which does not itself have flame-retarding properties but is used as an effect-intensifying synergist in halogenated flame retardants. The corresponding basic information is contained in the substance profiles. The substance profiles refer in the first instance to the 'pure flame retardants' (trade products), but in part also cover the applied flame retardants, that is the properties of flame retardants in a composite material (flame retardant/matrix), and in part the properties of the active agent of the flame retardants.

On the basis of these substance profiles, individual flame retardants can be evaluated in toxicological and ecotoxicological terms (see Chapter V of this volume).

Overview I/1: Selected flame retardants

Flame retardant	Abbreviation	CAS No.
Halogen-based flame retardants		
Decabromodiphenyl ether	Deca	1163-19-5
Tetrabromo-bisphenol A	TBBA	79-94-7
Bis(pentabromophenyl)ethane	Saytex 8010	84852-53-9
Hexabromocyclododecane	HBCD	3194-55-6
Organic phosphorus-based flame retardants		
Tris(chloropropyl)phosphate	TCPP	13674-84-5
Resorcinol-bis-diphenyl-phosphate	RDP	57583-54-7
N-hydroxymethyl-3-dimethylphosphonopropionamide	Pyrovatex CP new	20120-33-6
Inorganic phosphorus-based flame retardants		
Red phosphorus	RP	7723-14-0
Ammonium polyphosphate	APP	68333-79-9
Nitrogen-based flame retardants		
Melamin cyanurate	MC	37640-57-6
Mineral-based flame retardants		
Aluminium trihydroxide	ATH	21645-51-2
Other flame retardants		
Sodium borate decahydrate	Borax	1303-96-4
Synergists		
Antimony trioxide	ATO	1309-64-4

The selected flame retardants (see Overview I/1) belong to all relevant groups of flame retardants, so that, with their examination, the entire range of flame retardants can at least be covered in a qualitative manner (see Chapter II.2). The selected substances comprise four brominated flame retardants, including polybrominated diphenyl ether, three organic phosphorus-based flame retardants (halogenated and not halogenated), of which one substance is specifically used for textiles, and furthermore two inorganic phosphorus compounds, one nitrogen-based flame retardant, and sodium borate decahydrate. Aluminium trihydroxide is selected as the most important mineral-based flame retardant, and antimony trioxide as a halogen synergist. Depending on the flame retardant group, the examined flame retardants represent between 50 and more than 90% of the corresponding volume (see Chapter III.2).

The above flame retardants compete in part with other flame retardants in various application areas. For a number of flame retardants relevant in this regard, the ratings of the German Hazardous Substances Ordinance (Gefahrstoffverordnung, GefStoffVO) are utilized to compare their substance properties with the 13 flame retardants examined in detail in the study.

3.2 Applications-oriented analysis

A main focus of the study is the applications-oriented examination of flame retardants, and in this regard the status, trends and alternatives with regard to the incorporation of flame retardants in selected products.

The products selected in consultation with UBA come from the two largest application areas of flame retardants – the construction sector and the electrical and electronic appliance sector – as well as track vehicles, with their fire safety requirements determined by transport conditions, and the textile industry, where textile finishing with flame retardant agents is controversial. The selection takes into account products with and without relevance for indoor air quality, various plastics and materials (duroplastics, thermoplastics, textiles), as well as products that are manufactured and traded under very diverse conditions, subject in part to national, regional, or globalized production and development conditions and fire safety standards.

Overview I/2: Selected products by application areas and materials

Application area	Products	Materials
Rail vehicles	Structural and cladding elements for interior surfaces and exterior parts	Fibre-glass reinforced plastics on the basis of unsaturated polyester resins, furthermore phenolic resins
Construction products	Insulation materials and one-component foams	Polyurethane rigid foam (plus discussion of polystyrene insulation foams)
Electrical and electronic appliances	Duroplastic printed circuit boards	Epoxy resins; furthermore phenolic resins
Electrical and electronic appliances	Casings for IT and TV components	Various thermoplastics (ABS, PC/ABS, HIPS, etc.)
Textiles	Cover materials for mattresses and upholstered furniture, upholstery composites	Diverse textiles; PUR flexible foam

Since the utilization and behaviour of flame retardants are highly dependent on the respective plastic/material and its processing properties, the applications-focused analysis examines the plastics with their material-specific flame-protection formulations, and collates data – where available – on emissions, combustion properties and combustion behaviour, as well as the possibilities for recycling and disposing of products containing flame retardants. In addition, the study present alternatives – in terms of feedstocks, materials and product design – to the presently practised incorporation of flame retardants.

The selected products (see Overview I/2) come from various areas with different fire safety requirements. Included are:

- Insulation materials and one-component foams composed of polyurethane rigid foam (construction sector),
- structural and cladding elements made of unsaturated, fibre-glass reinforced polyester resins (rail vehicle sector),
- printed circuit boards (largely manufactured from epoxy resins) and
- casings for computers, printers and similar IT components, as well as TV appliances in the electrical and electronic sector, and also
- textiles for mattresses and upholstered furniture.

The product specific fire safety standards are explained in the specific application chapters.

During the course of the applications-focused analyses it became apparent that the consideration of some additional products and application areas is both necessary and expedient; this concerns, in the case of insulation materials, polystyrene insulation materials, which are discussed separately. Within the group of electrical and electronic products, we have also considered complete printed circuit modules. With regard to casings, it became necessary to examine a whole range of products more closely (casings for PCs, printers, monitors, servers/mainframes, as well as TV appliances) because of a very diverse status of flame retardant incorporation and varying fire safety standards in the information and entertainment electronics industry. Because the variety of flame retardants is very wide, corresponding to the different plastics used in E+E appliances, we have included a separate chapter on plastics and flame-protection in E+E appliances, in order to assess the meaningfulness of the results derived from the specific application cases of casings and printed circuit boards.

3.3 Evaluation criteria

We approach the evaluation of flame retardants and their applications mainly from the perspective of their toxicity, ecotoxicity, and closed-loop substance management characteristics. These criteria represent only a part of the whole range of relevant evaluation dimensions. The derivation, pragmatic selection and supporting evidence for these evaluation criteria is covered in a separate section (see Chapter IV).

Our point of departure is that to evaluate flame retardants in terms of environmental relevance, it is essential to combine the assessment of substances and applications. Toxicological and ecotoxicological statements with regard to the pure flame retardants cover essential aspects of the environmental properties of flame retardants themselves. However, the possibility of equipping or constructing products in accordance with the required fire safety standards and in an environmentally least harmful manner must be approached from the applications-oriented ‘product side’, not purely from the flame retardant side. Since the flame retardant and the substrate must be consistent with one another – i.e. they must be compatible, the required material characteristics must remain guaranteed, etc. – ‘drop-in’ substitution of flame retardants is, in any case, only rarely possible. Similarly, statements with regard to the recyclability of flame retardants under semi-experimental conditions are not very meaningful, if the reality of plastics disposal and recycling is not taken into account.

Furthermore, we proceed from the assumption that in the combination of substance and application evaluations differential weighting must be applied to the product-specific and application-specific factors. This is, for instance, applicable to fires and their by-products, which are of much greater importance with regard to indoor applications than in open-air applications. Furthermore, in contrast to the presently practised evaluation of chemicals, it is taken into account that intrinsic substance properties such as persistence and bioaccumulation will be given more weight in future substance evaluations, and therefore must be considered now as a precautionary measure.

The applications-oriented evaluation of the status and trends in equipping materials with flame retardants proceeds not only from the substance properties of the utilized flame retardants, or those that could be used as an alternative, but also considers individual or combined measures to reduce the environmental impacts of flame retardant incorporation and product design – such as substance substitution, polymer modification, alternative materials and product construction. This consideration takes place within the scope of the required fire protection properties of the products. In this regard, the examination of applications must test whether appropriate possibilities for action exist, and whether these should or could be supported.

4. Forms of cooperation within the framework of the project

Within the framework of this project two workshops were held at the German Federal Environmental Agency (UBA), together with representatives of the flame retardant manufacturers, industrial users, and specialists. During the first workshop (14 June 1999)

- the selection of flame retardants and products,
- the matrix for the substance profiles,
- and the basic elements of the evaluation method

were presented, substantiated and discussed.

The second workshop (6 April 2000) concentrated on interim results for

- flame retardant applications,
- substance profiles and substance evaluations, and
- applications-oriented evaluation of flame retardants.

At the second workshop it was agreed that the manufacturers of flame retardants should provide comments on the substance profiles. The final form of the substance profiles and evaluations are the sole responsibility of the authors of this study.

The acquisition of data and information, both for the preparation of the substance profiles and the examinations-oriented analyses, relied to a high degree on cooperation with the manufacturers of the examined flame retardants and the utilizing industry.

Chapter II: Flame retardant types and their consumption

Chapter contents

1. Flame retardants: Functions, modes of action, groups

In this section we give a short overview of the functions, modes of action, main groups, consumption volumes and trends with regard to flame retardants.

1.1 Functions of flame retardants

It is the task of flame retardants to impede the ignition of materials and to slow down the spread of flames. They become effective during the ignition phase of a fire, in that they slow down or prevent those processes that can lead to a fully developed fire: namely the heating of the flammable material, its thermal decomposition, the ignition of the flammable decomposition products, and the spread of flames. The incorporation of flame retardants in materials (plastics, textiles, etc.) can reduce both the flammability and the spreading of flames. Flame-retarded materials can nonetheless be ignited, if they are exposed long enough to sufficiently high ignition energies. Flame retardants are furthermore only active during the ignition phase of a fire. Once a fire has developed fully, they can not prevent the further spread of a fire, as the temperatures are so high that material incorporating flame retardants will decompose and burn unhindered. Flame retardants are therefore only one element among many in fighting fires, as well as in concepts for preventive fire safety, which are designed to prevent or limit the occurrence and spread of a fire.

1.2 Modes of action

Flame retardants are active in various chemical and/or physical ways during the ignition phase of a fire (see ANZON no year; Sutker 1988; Troitzsch 1990). Their effect is normally triggered by the thermal heating of the material in which they have been incorporated. They decompose and absorb energy, and they may release fire-retarding products or react in a fire-retardant manner with the polymer. The decomposition temperatures of flame retardants and materials must be harmonized with one another.

The physical effect of a flame-retarding agent may consist of a *cooling effect*, through which the ignition temperature is not reached; it can consist of the *formation of a protective layer*, which can be hard or gaseous, and prevents oxygen from continuing to reach the decomposing, flammable material, or prevents the supply of flammable decomposition gases to the polymer surface; it can also consist of a *dilution effect*, by which the flammable material or the air is diluted by non-flammable decomposition gases in such a manner that it does not ignite. The flame-retarding effect of mineral-based flame retardants resides, for instance, in a decrease in the mass of flammable substance, as well as in the cooling of the matrix and dilution of the flammable gases by means of released water vapour.

Flame retardants that act chemically can achieve this effect both in the solid and the gas phase. The most important effect in this instance is the *prevention of the forming of free radicals*. The free radicals that are released during the combustion of the decomposition products of hydrocarbons is strongly exothermic, that is, it provides additional heat to the combustion process and therefore supports the spread of a fire. Halogens (chlorine, bromine) formed through the decomposition of halogenated flame retardants act as an interceptor of radicals in the gas phase, in that they bind .H- and OH.-radicals. In this way they interrupt the radical chain mechanism, cool the combustion process, and slow it down. Antimony trioxide, which by itself has no flame-retarding effect, has a synergistic action with halogenated flame retardants mainly by leading to a stepwise release of halogen over a wide temperature range.

In the solid phase, the chemical effect of flame retardants can consist of *promoting decomposition* and consequently a ‘flowing-away’ of the flammable material from the flame, or in the *formation of a charred protective layer* with a very high melting point (carbonization) that inserts itself between the flammable material and the oxygen/flame. Carbonization is an effect especially of those flame retardants that contain phosphorus and release phosphoric acid.

1.3 Reactive and additive flame retardants

To be able to act in the described flame-retarding manner, flame retardants must be inserted in the matrix (polymer) or layered on the substrate (for instance textile fibres). The flame-retarding agent can be built into the polymer itself (added by reaction), or the flame-retarding agent and the polymer can be mixed. In the first case one speaks of *reactive* and in the second case of *additive* flame retardants. In both cases the matrix and the flame retardants must be harmonized or must be compatible with one another.

The main advantage of the *reactive* systems is their chemical bond, by which the flame-retarding agent is firmly integrated in the matrix and, in principle, cannot migrate. The effects on the properties of the polymer are rather small; reactive flame retardants do not have a plasticizing effect, and they do not influence the thermal stability of the polymer. Reactive flame retardants are usually more expensive than additive components. They are used mainly in duroplastics (polyester resins, epoxy resins, polyurethane, polycarbonate), for which additive flame retardants are also available.

In contrast, *additive* flame retardants are used mainly in thermoplastics, and are added during the manufacture of the polymer or introduced thereafter. Processing temperatures must be observed when selecting flame retardants for thermoplastics. Additive flame retardants can be released (‘by bleeding’ or evaporation) during or after use *more easily* from the matrix than reactively bound flame retardants, since they are not in a chemically bound form. This undoubtedly is a systematic disadvantage for additive flame retardants from an environmental viewpoint, insofar as they are environmentally relevant.

The substitution of flame retardants is limited from the outset by the required compatibility between the matrix and the flame retardants. This includes the following aspects: incorporation and processing qualities; effects on the thermal and mechanical stability of the polymer; and desired material properties. Practical experience shows that, as a rule, the ‘drop-in’ introduction of flame retardants is not possible; rather, adaptations of the flame retardants and the polymer are required.

2. The most important flame retardant groups

In the following, we characterize the most important groups of flame retardants. Grouping is based upon the chemical constitution of the flame retardant and its respective modes of action. The substances drawn together in these groups have common properties in many respects. However, as groups encompass a broad range of related compounds, the individual substance properties also exhibit a considerable range with regard to toxicity and ecotoxicity, so that their membership in a group can give an indication of possible problems, but their classification requires specific substance tests (see Chapter V).

Halogenated flame retardants: Bromine and chlorine compounds can be considered as flame retardants with a gas phase mechanism, whereby bromine compounds are released more easily (earlier) and are more effective, because of their weak bond to the hydrocarbons. The latter is also supported by the fact that they are released within a narrow temperature range as radical interceptors, that is, they occur in a concentrated form. Antimony-halogen systems can also make a contribution to carbonization during the solid phase. A disadvantage of those halogen compounds that are active in the gas phase is that they release corrosive gases (HBr, HCl), and that they at the same time promote the density of fumes, as well as contribute (to a highly varying degree; see Hutzinger 1990) the formation of dioxins/furans.

In the series of aliphatic, cycloaliphatic, and aromatic halogen compounds, the strength of the bond between the halogen and the basic structure of the molecule increases, which means that the temperature stability also rises, but the effectiveness may also decrease. Polybrominated diphenyl ethers (for instance decabromodiphenyl ether), as aromatic compounds, have more temperature stability than cycloaliphatic bromine compounds (such as for instance hexabromocyclododecane, HBCD), and can therefore be utilized with plastics that must be processed at relatively high temperatures, but they do require antimony trioxide as a synergist for raising their effectiveness.

From the viewpoint of volume, the most important compounds (see Table II/1) are the chlorinated chloroparaffins as aliphatic compounds and HET acid as a cycloaliphatic compound, and the brominated fire retardants HBCD (cycloaliphatic), tetrabromobisphenol A (TBBA) and derivatives, as well as the polybrominated diphenyl ethers, especially decabromodiphenyl ethers as aromatic compounds.

A second large group is represented by the *organic flame retardants containing phosphorus*. They have an effect primarily in the solid (condensed) phase, in that they release phosphoric acid during thermal decomposition, which leads to a carbonization of the substrate. The carbon layer that is formed on the surface of the polymers impedes the further supply of oxygen, or the oxidation at the ignition source, and thereby makes the progress of decomposition through oxidation more difficult. This mechanism is especially effective in oxygen-rich polymers.

The range of organic flame retardants containing phosphorus is large (see Table II/1). Phosphoric acid esters, aryl phosphates and alkyl-substituted derivatives are by volume most important, whereby halogenated and halogen-free phosphoric acid esters are to be differentiated. The most important phosphoric acid ester is currently

TCPP (tris[chloropropyl]phosphate) that, as a trade product, represents a mixture of various isomers.

Inorganic phosphorus compounds (red phosphorus, ammonium polyphosphate) also have an effect by means of the solid-phase mechanism that is characteristic for phosphorus compounds (carbonization).

Inorganic metal hydroxides represent a third large group, among which aluminium trihydroxide (ATH) dominates. ATH is by far the most important flame-retarding agent in terms of volume, which is due to the large application quantities that are required for achieving a flame-retarding effect. They therefore also have the characteristic of a filler, and thereby reduce the mass of flammable material in the polymer. The inorganic compounds, which are thermally relatively unstable (which limits their use, as do the large filling quantities), decompose in the solid phase, during which they form non-flammable gases. The effective mechanisms for flame retardance are cooling (as a consequence of endothermic decomposition), the formation of a protective layer, and dilution of the combustion gases through the release of water vapour. A substantial advantage of the inorganic flame retardants is that they release only small quantities of smoke and soot (see Schmidt/Toedt 1996), which is in contrast to the halogenated flame retardants, that are active in the gas phase and lead to an incomplete combustion.

Boron compounds (boric acid, Borax) are, as a rule, applied in combination with materials containing cellulose and are active both in the gas and solid phase (release of water vapour; carbonization).

The effect of *nitrogen compounds* (melamin, melamin cyanurate, and other melamine derivatives) is explained by cooling effects, formation of a covering layer, and dilution in the gas phase with inert gases.

3. Flame retardants – quantity estimation

Table II/1 gives an overview of the consumption of flame retardants in Germany in 1997.[1] The table displays the order of magnitude of the applied flame retardants for groups, in some instances also for single substances. Under consumption we understand that quantity which has been used or processed in Germany.[2]

3.1 Total consumption

Table II/1 shows approx. 95,000 tonnes of flame retardants for 1997. With an increase in turnover of 2–3% per year, one can count with a consumption of approx. 100,000 tonnes of flame retardants in Germany in 1999/2000.

Table II/1: Consumption of flame retardants, Germany in 1997 (estimation)		
Type of flame retardant	**Tonnes**	**Percent**
Halogen-based flame retardants	**14,500 – 18,500**	**18**
PBDO (polybrominated diphenyl ether)	1,000 – 1,500	
TBBA (tetrabromobisphenol A)	3.500 – 4,500	
HBCD (hexabromocyclododecane)	2,000 – 2,500	
Other bromine compounds (brominated polyolefins, TBBA derivatives, tetrabromophthalate compounds, brominated polystyrene, etc.)	4,000 – 5,000	
Chlorine compounds (chloroparaffins, dechlorane, HET acid)	4,000 – 5,000	
Organic phosphorus-based flame retardants	**13,500 – 16,000**	**15**
Halogenated organic phosphorus compounds	**5,500 – 7,000**	**6**
TCPP (tris-chloropropyl-phosphate)	5,000 – 6,000	
TCEP (tris-chloroethyl-phosphate);TDCP (tris dichloropropyl phosphate)	500 – 1,000	
Halogen-free organic phosphorus compounds - trialkylphosphate (DMMP, DEEP, triethylphosphate [TEP]) - triarylphosphates (triarylphosphate, triphenylphosphate [TPP], tricresylphosphate [TCP], diphenylcresylphosphate [DPK] etc.) - resorcinol-bis-diphenyl-phosphate (RDP)	**8,000 – 9,000**	**9**
Inorganic phosphorus compounds	**2,000 – 3,000**	**3**
Red phosphorus	1,000 – 1,500	
AP/APP (ammonium phosphate / ammonium polyphosphate)	1,000 – 1,500	
Other flame retardants	**57,500 – 63,500**	**65**
Melamin/melamin derivatives	1,000 – 2,000	
ATH (aluminium trihydroxide) $Mg(OH)_2$ (magnesium hydroxide)	45,000 – 47,000 1,000 – 1,500	**49**
Boron compounds (boric acid, Borax, etc.)	3,000 – 4,000	
Zinc compounds	500 – 1,000	
Antimony oxide	7,000 – 8,000	**8**
Total	**87,500–101,000**	**100**

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[1] The overview is based on a survey of manufacturers and dealers of flame retardants, as well as an analysis and evaluation of the various market studies. This estimation was presented during the first workshop held within the framework of the project as the point of departure for the selection of the flame retardants to be examined. Individual consumption quantities were corrected on the basis of more exact data.

[2] That is to say not the quantities of flame retardants that were contained in final products consumed in the home market (without export, incl. imported products), or were utilized in their manufacture. This is substantially larger in regard to products with high surplus imports (for instance electric and electronic appliances, such as TVs), which is of course relevant with regard to waste arisings and waste disposal. The corresponding quantity estimations of flame retardants in post-consumer waste is carried out for several flame retardants or active agents (e.g. halogens) in the chapter on applications.

3.2 Consumption according to flame retardant groups

The quantitatively largest group, with a share of almost 50%, is that of the *mineral* flame retardants. The *purely halogenated* flame retardants (without chlorinated phosphoric ester) amount to approx. 18% of consumption, and the organic and inorganic *phosphorus compounds* also to approx. 18%. The remainder is divided among *antimony trioxide* (8% share), which actually belongs to the group of antimony-halogen flame retardants, and various *other* flame retardants (nitrogen, boron and zinc compounds, and others).

If the purely halogenated flame retardants are added to the halogenated phosphoric esters, then the resulting share amounts to 23%, and together with antimony trioxide to a good 30% (group of antimony-halogen flame retardants).

Accordingly, the total consumption, when viewed from the side of the use of flame retardants, can be subdivided into

- 50% mineral-based agents,
- 30% antimony-halogen compounds and
- approx. 20% halogen-free phosphorus-based and other compounds,

these being the three main flame retardant systems.

3.3 Flame-retarded plastics according to flame retardant groups

However, the picture looks a little different if one views the flame-retarded plastics or materials.

Because of the very high filling ratio in the case of mineral-based flame retardants (on average approx. 50-60% of the product, as against an approx. 15-20% with antimony-halogen or phosphor-organic application, see Chapter III), the share of the plastics protected by mineral flame retardants is substantially lower than the share of mineral flame retardants. Similarly, the share of the other halogen-free or halogenated flame-retarding plastics is greater than the share of the respective group of flame retardants.

We therefore estimate that

- 15-20% of the plastics are *minerally* flame protected,
- more than 50% contain *antimony-halogen compounds,* and
- approx. 30% incorporate *other halogen-free* flame retardants.

Halogenated systems of flame retardants therefore continue to dominate in the area of plastics, as against halogen-free organic phosphorus compounds and mineral flame retardants.[3]

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[3] Calculations based on the Frost&Sullivan data show in the European market for polymers approx. 60% for antimony-halogen, less than 20% for phosphorus compounds, under 20% for mineral flame retardants, and approx. 5% for other flame retardants.

4. An international comparison of flame retardant consumption

A comparison of the estimated data for flame retardant consumption in the ‘triad’ of regions – Europe, USA, and Asia – is relevant because of the important role that imported products containing flame-retarded components (especially in the E+E area) plays, and the differing trends in flame retardant regulations (voluntary phase-out of PBDE in Germany), as well as fire safety philosophies and standards.[4]

With an estimated world-wide market of more than 800,000 tonnes of flame retardants, approx. 38% where accounted for by the American market in 1996, while the European and Asian markets accounted each for approx. 30%.

Table II/2: Flame retardant consumption by type of flame retardant, USA, Europe, and Asia, 1996 (estimated, in 1,000 t and percent)

Type of flame retardant	**USA**		**Europe**		**Asia**	
	1,000 t	**%**	**1,000 t**	**%**	**1,000 t**	**%**
Brominated flame retardants	67	21	53	21	97	38
Chlorinated flame retardants	17	5	16	6	11	4
Phosphoric acid ester	48	15	65	25	35	14
Antimony oxide	20	6	8	7	30	12
Aluminium hydroxide	150	48	90	36	75	29
Others	5	5	13	5	7	3
Totals	**316**	**100**	**255**	**100**	**255**	**100**

Compiled after Townsend 1997

Antimony-halogen flame retardants accounted for one third of flame retardant consumption in America and Europe, and for more than half of the consumption in Asia. In Germany the share is lower, at approx. 25% (without chlorinated phosphoric acid esters; see Table II/1.). Relative phosphoric acid ester consumption is substantially larger in Europe than in other markets. As concerns mineral-based flame retardants, the USA market is not only the largest in relative terms, but also in absolute terms.

The absolute data published recently by manufacturers on the international consumption of brominated flame retardants diverge widely from the brominated flame retardant figures in Table II/2. The absolute data make it probable that the

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[4] The reference is to global estimated data from market studies, which can be used as a rough orientation with regard to the actual consumption, but that will certainly vary in detail, as the comparison of Tables II/2 and II/3 for brominated flame retardants shows. However, no better data is available. Subordinate markets (Africa, Russia, etc.) have been included in the information for the triad centres, in accordance with the classification of the flame retardant manufacturers. Comparison of the studies of the different market research companies reveals distinct disparities. Townsend (1997) for instance estimates the European market at 255,000 tonnes, while Frost&Sullivan arrives at 295,000 tonnes (F&S 1997). This difference can be explained, among other things, by the fact that Townsend does not cover flame retardant consumption beyond plastics. For ATH, for instance, Townsend does not count 35,000 tonnes for non-plastic applications and 3000 tonnes of melamin compounds for intumescent laminations, which "are not a part of the study". Ammonium polyphosphate for rubber, laminations (coatings) and textiles, borates for cellulose insulation materials and phosphate esters for textiles and lubricants are also not reflected. An additional factor is the different evaluation of the function of flame retardants, which also serve as plasticizers. Chloroparaffins and phosphate esters for PVC are regarded by Townsend throughout as flame retardants, whereas they also function as secondary plasticizers. KIrschbaum (1997) proceeds from a 35–40,000 tonnes lower volume for phosphorus compounds, because of their plasticizing function. These are only some of the disparities.

European consumption of bromine compounds shown in Table II/2 (Townsend estimates) has probably been overestimated.

Table II/3: Brominated flame retardants by markets, 1999

Flame-retarding agent	America	Europe	Asia	Total
Tetrabromobisphenol A	21,600	13,800	85,900	121,300
Hexabromocyclododecane	3,100	8,900	3,900	15,900
Decabromodiphenyl ether	24,300	7,500	23,000	54,800
Octabromodiphenyl ether	1,375	450	2,000	3,825
Pentabromodiphenyl ether	8,290	210	-	8,500
Total	**58,665**	**30,860**	**114,800**	**204,325**

Source: BSEF 2000

The overall dimensions of the data, however, do fit. The centre of the international market for brominated flame retardants clearly lies in Asia, and in this it comes before the American market, which is the main consumer of flame retardants in general. If one looks at the flame retardants individually, then the picture that is presented is more differentiated:

While in the USA the share of polybrominated diphenyl ethers is approx. 58% of all brominated flame retardants, this share is 26% in Europe and 22% in Asia. The share of PBDO among brominated flame retardants is in our estimation much lower in Germany and amounts to a maximum of 10% (see Table II/1). Such strong differences indicate that the high consumption of PBDO is not based on any compelling technical reason, but that it is connected with regional habits, differences in environmental awareness, and possibly different standards. This therefore also indicates possibilities for substitution and action beyond the realm of technological constraints.

The high share of tetrabromobisphenol A in the Asiatic flame retardant market (75%), when compared to Europe (45%) and the USA (37%), probably is connected to the strong role of electronics and printed circuit board production among Asian components-supplying industries.

The HBCD share of the market for brominated flame retardants in Asia and the USA lies between 3% and 5%, while this is 29% in Europe. The cause for this is probably the proportionally much higher consumption share of polystyrene insulation materials in Europe, which is the main application area for HBCD, and furthermore PBDO substitution, in which HBCD plays a role.

5. Trends in flame retardant consumption and development

The growth expectations of flame retardant manufacturers are reflected in the data of Table II/4. At a European level, a distinct decline of the sales of brominated flame retardants and a continuation of weak sales of chlorinated flame retardants (apart from chlorinated phosphoric acid esters) are anticipated. In contrast, phosphorus compounds show a comparatively stable trend within the general growth trend. Among the mineral-based flame retardants, no disproportionate expansion is expected for ATH anymore. ATH, at the present, has conquered its sales areas and develops within the general growth trend. Otherwise, smaller (niche) products, such as magnesium hydroxide or nitrogen compounds, may show disproportionate growth at the expense of the other flame retardants. The long-term trend data for Germany correlate roughly with this picture.

Table II/4: Flame retardant consumption in Europe and Germany, trends and forecast data (estimated annual growth rates in percent)

Type of flame retardant	**Europe 1995-2000[1] Annual growth %**	**Europe 1998-2003[2] Annual growth %**	**Germany 1993-2003[3] Annual growth %**
Halogenated flame retardants			0.9
- Brominated flame retardants	3.0	1.5	
- Chlorinated flame retardants (without phosphorus-halogen)	-3.0	-3.4	
Phosphorus compounds			2.0
- Organic phosphorus compounds	2.6	2.2	
- Inorganic phosphorus compounds	2.0	2.2	
Aluminium hydroxide	4.5	2.5	2.3
Magnesium hydroxide	15.0	10.0	7.6
Antimony oxide	2.5	2.6	2.2
Melamin compounds	3.5	3.5	2.8
Average	**3.1**	**2.3**	**1.9**

Compiled after: [1]SRI 1996; [2]F&S 1998; [3]F&S 1997

Manufacturers and traders of flame retardants confirm the trend that is visible in the market expectations. The manufacturer Clariant sees a clear trend towards products with low vapour pressure that are migration-stable and halogen-free (Walz 1998). A large flame retardant trading firm declared in the mid-1990s that: “The controversy surrounding brominated diphenyl ethers, chloroparaffins, and antimony trioxide, has had a lasting influence on the market in the last years. For instance, the trend is clearly going in the direction of a quick and complete substitution of halogen-containing compounds to halogen-free systems.” At the same time it is stated that, besides an effective flame-protection, the toxicological harmlessness of not only flame retardants, but also their decomposition products in the event of fire, the reduction of smoke and the reusability of products incorporating flame retardants are gaining importance (Schilling 1995). This last tendency could increase in importance through the greater weight accorded to by-products of fires in the course of the harmonization of European fire safety standards and tests (see Mitzlaff 1997, Ebenau 1998, Antonatus 2000).

These trends also find their expression in a change of industry structure. The manufacturers of brominated flame retardants are entering the markets for phosphoric acid esters and other non-halogenated flame retardants. Great Lakes

Corp. has in 1998, for instance, taken over the flame retardant business of the British FMC Corp. (Manchester), a company that was specialized in phosphorus compounds, and now considers itself the world-wide No. 1 both for brominated flame retardants and for phosphoric acid esters. Albemarle has introduced organic phosphorus flame retardants for casing materials with its product line ‘NeendX’ 2000 (RDP substitutes, BADP), an area in which brominated flame protection is decreasing, and is cooperating with the Borax Flame Retardant Group with regard to zinc borate (see NN 2000, Widmer 2000).

The driving factors behind this restructuring are environmental aspects, such as re-classification in terms of the importance of flame retardant types, marketing aspects, such as the wish of many end-users to have ‘single sourcing’ of various flame retardant systems for different polymers (where cost-driven changes in polymer usage are of importance, for instance in casing materials), and aspects relating to the supply of raw materials.

With a view to the environmental discussions, the bromine industry has pooled its interests as of 1997 in the Bromine Science and Environmental Forum (BSEF).[5] With regard to substance regulations on the European level, the debate surrounding the EU Electroscrap Directive[6] is current the most prominent arena, followed in importance by the evaluation of existing commercial substances (risk assessments of decabromodiphenyl ether and hexabromocyclododecane).

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[5] Founding members: Albemarle Corp., Dead Sea Bromine, Great Lakes Chemical Corp., Elf Atochem, TOSOH Corp. (see CheManager 3/1998, p. 23).

[6] The European Commission’s draft Directive on Waste Electrical and Electronic Equipment and proposal for a Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (see CEC 2000), requires in the first Directive (Annex II) the removal of plastics with brominated flame retardants from separately collected electroscrap. In the draft for the second Directive, a ban on polybrominated biphenyls (PBB) and polybrominated diphenyl ether (PBDE) is proposed as of 2008.

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Chapter III: The flame retardants examined – general characteristics

Chapter contents

1. Individual substances

In the following overview, the flame retardants whose substance properties are examined in this study are presented with a short characterization of their application properties and areas. This information serves the general classification of these substances. The toxicologically and ecotoxicologically relevant substance properties are not a part of the presentation in this overview; they are documented in detail in the substance profiles (see Volume III of this study) and are summarized, discussed and evaluated in Chapter V of this volume.[7]

The following short descriptions contain a general characterization of the flame retardants and their modes of action, information with regard to their application area by polymer/substrate and end products, as well as volume data (polymer and substrate-specific dosing volumes, production, and consumption data) and state the trade products that were taken into consideration in this study. Furthermore, the chemical policy regulations for substances are listed; these include the tests pursuant to EU Regulation 793/93/EEC on the evaluation and control of existing substances (risk assessments), voluntary reductions and risk minimization measures etc., which limit or regulate the application and sale of flame retardants.

The information with regard to volumes consists of estimates of the consumption in the German market. The data are based on information and documents supplied by the manufacturers and trading companies of fire retardants. The overview that was published by EFRA in 1996 (EFRA 1996) still provides a very useful summary of the flame retardants sold in Europe.

The data with regard to application areas and volumes is summarized in tabular form in the two Overviews III/1.

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[7] A series of flame retardants that were identified as substitutes or as qualitatively important flame retardants in the applications-focused analyses (Volume II), and which do not belong to the list of the 13 flame retardants examined in detail, and for which consequently no substance profiles were created, can be included in the comparison on the basis of their ratings (see Tables V/14 and V/15 as well as Section 2 of this Chapter) under the German Hazardous Substances Ordinance (Gefahrstoffverordnung, GefStoffVO).

Overview III/1-1: Examined flame retardants by applications in plastics, end-products, and volume relevance
Halogen-based flame retardants and organic phosphorus compounds

Flame retardants	Potential plastics/substrates	Potential end-products	Volume relevance/tonnes (use)
Halogen-based flame retardants			
Decabromodiphenyl oxide (Deca)	HIPS; PBT/PET; polyester resins; polyethylene; polypropylene; ABS; polyamide; polycarbonate; styrene-butadine-rubber (SBR); textiles	Casings; electric/electronic components; textile back coating	D: 1000 t (application limitation)
Tetrabromobisphenol A (TBBA)	Epoxy resins; polycarbonate and phenolic resins; HIPS; ABS; PBT/PET, etc.	Printed circuit boards; materials for casings; elec. components; etc.	D: 3500 – 4500 t
Bis(pentabromophenyl)ethane	HIPS, incl. styrene polymers; ABS; PA; thermoplastic polyolefins, etc.	Casings; elec. components; cables; etc.	D: < 1000 t
Hexabromocyclododecane (HBCD)	Polystyrene (EPS, XPS); HIPS; acrylic and latex dispersions	Insulation materials (EPS; XPS); textile back coatings; casings	D: > 2500 t
Organic phosphorus-based flame retardants			
Tris(chloropropyl)phosphate (TCPP)	PUR rigid and flexible foams; unsaturated polyester resins, phenolic resins; thermoplastics; textiles	PUR insulation foam; one-component foam; Flexible foam (seats, mattresses); textile back coatings	D: 5000 – 6000 t
Resorcinol-bis-diphenylphosphate (RDP)	PC/ABS, PPO-HIPS; technical thermoplastics, thermoplastic PUR, PUR foams	Materials for casings; special cables	D: approx. 1000 t
Pyrovatex CP new	Cellulose fibres (with the exception of jute)	Textiles: Protective clothing; home textiles (for export)	D: Production > 1000 t, Consumption < 100 t

Overview III/1-2: Examined flame retardants by applications in plastics, end-products, and volume relevance
Inorganic phosphorus compounds, nitrogen compounds, mineral-based flame retardants and ATO as synergist

Flame retardants	Plastics/substrates	End-products	Volume relevance (use)
Inorganic phosphorus-based flame retardants			
Red phosphorus	Thermoplastic and duroplastic condensed polymers (polyamide, polyester, polyurethane, epoxy resins, etc.)	Components for electrical and electronic applications, cables, casting resins, glues, dispersions for automobile textiles	D: 1000 -1500 t
Ammonium polyphosphate (APP)	Polyurethane foams (rigid and flexible); polypropylene; epoxy and polyester resins; cellulose-containing materials; lattices for textile back coatings	Intumescent laminations; PUR flexible and rigid foam; glues; insulation materials; casting resins and components for electronic applications; textile back coatings	D: 1000 -1500 t
Nitrogen compounds			
Melamin cyanurate	Polyamides; thermoplastic polyurethane	Injection moulding parts (sockets, casing parts); special cables	D: 500 -1000 t
Mineral-based flame retardants			
Aluminium trihydroxide (ATH)	Duroplastics (polyester, epoxy, acrylate, melamin, phenolic resins, polyurethane); thermoplastics (polypropylene, polyethylene, ethylene-vinylacetate-copolymers, PVC); lattices; aqueous dispersions	Glass-fibre reinforced composite materials (laminates, construction materials); PUR flexible and rigid foam, coatings; cables; injection-moulded parts; carpet and textile back coatings; dispersion paints	D: 45,000 – 47,000
Other flame retardants			
Sodiumborate-decahydrate (Borax)	Cellulose-containing materials	Cellulose-based insulating materials	D: 1000 -1500 t
Synergists			
Antimony trioxide (ATO)	Thermoplastics and several duroplastics (with the exception of polystyrene, PUR foam); flexible PVC; natural and synthetic rubber; textile back coatings	PVC cables and foils; thermoplastic components for electrical and electronic devices; textile laminations, etc.	D: 7000 -8000 t

1.1 Decabromodiphenyl ether [CAS: 1163-19-5]

General characterization: Decabromodiphenyl ether has been manufactured since the end of the 1970s and is by far the most important representative of the polybrominated diphenyl ethers (global consumption 1999: 55,000 tonnes). Deca is available in the trade as a crystalline powder and is used as an additive flame retardant. Like all PBDEs, deca is solely used as a flame retardant. Deca is available at a relatively low cost in comparison to other flame retardants. A voluntary phase-out of its use by the associations VKE and TEGEWA (1986) has led to a marked decrease in the consumption of PBDO in Germany, and also for deca. Deca is nevertheless not prohibited and remains available through the trade.

Mode of action: Deca, like all brominated flame retardants, is active in the gas phase. It is thermally very stable (melting point approx. 300°C) and because of its high bromine content (83%) a very effective flame retardant.

Synergism, additivity: As a rule it is used as a synergist in combination with antimony trioxide (ratio 2:1 to 3:1).

Application areas with regard to polymers and materials: Deca is a ‘general-purpose’ flame retardant that can be used in almost all polymers. It has high thermal stability and is therefore especially useful in plastics that will be processed at higher temperatures. Application, among others, in high impact polystyrene (HIPS), polycarbonates, thermoplastic polyesters (PET, PBT), polyester resins, sheet moulding compounds (SMC), polyethylene, polypropylene, ABS, polyamide, and textiles (polypropylene materials and upholstered furniture). (The application areas of deca, HBCD, and bis[pentabromophenyl]ethane partially overlap.)

Application areas by end-products: Materials for casings and technical thermoplastics for E+E and TV appliances, cables, textile back coatings, etc.

For the early 1990s, the following application structure is reported: Approximately 30% for HIPS (casings among other things); 20% thermoplastic polyester for electrical/electronic components, switches, etc.; 15% for polyamide (injection moulding materials, electrical/electronic components); 10% styrene-butadine-rubber (SBR) for latex, textile back coatings; approximately 5% for polycarbonate (casing materials among other things); 15% for other polymers. Albemarle Corp. (2000) in contrast declares that 85% of deca use is in HIPS, in casings for E+E appliances.

Occurrence in the examined application areas: Materials for casings, technical thermoplastics for E+E appliances (components, externally bought parts); textile back coatings.

Filling level: 5-30%

Production: Until 1999 < 1000 t were produced in Europe. Current production sites of the three manufacturers Albemarle Corp, Great Lakes Chemical Corp. and Dead Sea Bromine Group are in the USA and in Israel (one site in each).

Consumption volumes: Sales in Europe are cited by BSEF as amounting to 7500 tonnes in 1999. Because of the voluntary phase-out by VKE and TEGEWA (1986) the consumption in Germany is relatively small and is estimated at approx. 1000 tonnes. The occurrence in products and thus in electroscrap materials can be higher, because of the high import rates of E+E appliances. Consumption trend: declining.

Products (trade names):
- FR-1210 (Dead Sea Bromine Group)
- Saytex 102 E (Albemarle Corp.)
- Great Lakes DE-83 R (Great Lakes Chemical Europe Ltd.)

Substance regulations: Deca is subject to a risk assessment in accordance with Regulation 793/93/EEC. In Germany TEGEWA and the association of plastics manufacturing industries (Verband der Kunststofferzeugenden Industrie – VKE) announced a voluntary phase-out of the use of polybrominated diphenyl ethers in 1986, including decabromodiphenyl ether. Within the framework of the OECD, a voluntary agreement on risk reduction with regard to brominated flame retardants was concluded in 1995, including PBDO (increase in product purity, reduction in emissions at the manufacturers). Indirect regulation via the 1994 German Dioxin Ordinance (Dioxin-Verordnung).

Information provided by: Albemarle Corp.1999a and b, 2000a; BSEF 2000; CMA 1999; Dead Sea Bromine 1997; DEPA 1999; Dioxin-Verordnung 1994; Great Lakes Chemical Corporation 2000; KEMI 1999; Kunststoffe 1997; OECD 1994; RA Deca 2000

1.2 Tetrabromobisphenol A [CAS: 79-94-7]

General characterization: Tetrabromobisphenol A (TBBA) is in volume by far the most important flame retardant (121,000 tonnes world-wide consumption in 1999 according to BSEF). TBBA is only produced for use as a flame retardant or as a flame retardant precursor for TBBA derivatives, is applied for the greater part reactively, and to a smaller extent (approx. 15 to 20%) also additively.

Mode of action: TBBA, like all brominated flame retardants, is active in the gas phase. TBBA has medium-level thermal stability (melting point approx. 180°C). The active substance content (bromine content) is 59% of weight.

Synergism, additivity: Besides its main application area (epoxy resins for FR4 printed circuit boards) TBBA is mostly used in combination with antimony trioxide as a synergist.

Application areas with regard to polymers and materials: With sales of approx. 13,800 tonnes in Europe (1999), the following use was made according to Dead Sea Bromine Group (2000): approx. 70% for epoxy resins in printed circuit boards (reactive); 15% in HIPS (mainly for casing materials, additive); 10% for processing into TBBA derivatives; 5% as additives to other polymers, such as for instance ABS and thermoplastic polyester (PBT, PET). TBBA is used reactively in polycarbonates, phenolic resins, and unsaturated polyester resins.

Application areas by end-products: Base material for printed circuit boards and epoxy-based moulding compounds for component casings; casings for E+E appliances; components for E+E appliances, etc.

Occurrence in the examined application areas: Base material for printed circuit boards; moulding compounds for components; materials for casings; components for E+E appliances; rail vehicles.

Filling level: 11% to 20%, depending on the polymer.

Production: One site in Europe (Broomchemie, Terneuzen/NL), otherwise production in the USA (Albemarle Corp; Great Lakes Chemical Corp.) and in Israel (Bromine Compounds Ltd (= Dead Sea Bromine Group) and Tetrabrom Chem. Ltd. (= Dead Sea Bromine Group/Great Lakes Chemical Corp.).

Consumption volumes (Germany): According to BSEF (2000), the European market for TBBA was approx. 13,800 tonnes in 1999. In this study, the consumption in Germany for printed circuit boards is estimated to be 2700 tonnes, with a total consumption of approx. 3800 tonnes. (The use of TBBA derivatives is estimated at between 500 and 1000 tonnes.) Because of the high import share of E+E appliances, the bromine content attributable to TBBA in printed circuit board scrap is larger, and represents an estimated application volume of between 4200 and 5100 tonnes of TBBA. Stable consumption trend.

Products (trade names):
- Saytex 100 E (Albemarle Corp.)
- FR-1524 (Dead Sea Bromine Group)
- Great Lakes BA-59P (Great Lakes Chemical Corp.)

Substance regulation: Within the framework of the OECD, a voluntary agreement for risk reduction with regard to brominated flame retardants was concluded in 1995, including TBBA. Indirect regulation via the 1994 German Dioxin Ordinance.

Information provided by: Albemarle Corp. 1997; BSEF 2000; CMA 1999; Dead Sea Bromine no year; 2000; DEPA 1999; Dioxin-Verordnung 1994; IPCS 1995; NRC 2000; OECD 1994.

1.3 Bis(pentabromophenyl)ethane [CAS: 84852-53-9]

General characterization: Bis(pentabromophenyl)ethane (product name: Saytex 8010) is an additive flame retardant with high thermal stability, which has a similar but more limited application spectrum than that of decabromodiphenyl ether, but is substantially more expensive than the latter. Saytex 8010 is supplied as a substitute for deca. It is available on the market since the mid-1980s.

Mode of action: Bis(pentabromophenyl)ethane, like all brominated flame retardants, is active in the gas phase. It has high thermal stability (melting point approx. 350°C) and a bromine content of 82%, which is similar to that of deca.

Synergism, additivity: Used as a synergist in combination with antimony trioxide (ratio 2:1 to 3:1).

Application areas with regard to polymers and materials: The main application areas are HIPS, and furthermore ABS and styrene polymers, polyamide, polypropylene, polyethylene. Technical resins, cables, and elastomers are cited in general.

Application areas by end-products: Casing materials made of HIPS; components for E+E appliances; insulation foams; cables; textiles; etc.

Occurrence in the examined application areas: Casing materials, textiles

Filling level: 12% (plus 4% ATO)

Production: Manufactured at Albemarle Corp. in the USA.

Consumption volumes: Germany: Sales statistics are not known; European sales are estimated at 2500 tonnes/year, consumption in Germany is estimated at < 1000 tonnes/year. Consumption trend increasing.

Products (trade names):
- Saytex 8010 E (Albemarle Corp.)

Substance regulations: Indirect regulation via the 1994 German Dioxin Ordinance.

Information provided by: Albemarle Corp. 1999c, 2000b; DEPA 1999; Dioxin-Verordnung 1994.

1.4 Hexabromocyclododecane (HBCD) [CAS: 3194-55-6]

General characterization: In terms of volume, this is the third most important brominated flame retardant (global turnover according to BSEF 1999 approx. 16,000 tonnes). Powdery, additive flame retardant. HBCD has partially been substituted by decabromodiphenyl ether in Germany.

Mode of action: HBCD, like all brominated flame retardants, is active in the gas phase. Medium-level thermal stability (melting point at 175 to 195°C, depending on product purity and temperature stabilization). Bromine content 73% to 75% (depending on product purity and temperature stabilization).

Synergism, additivity: For textile back coatings HBCD is used in combination with antimony trioxide, and in the case of polystyrene in combination with dicumylperoxide (ratio 5:3).

Application areas with regard to polymers and materials: Polystyrene (EPS, XPS); HIPS; SAN resins; polypropylene; textiles and carpet back coatings.

Application areas by end-products: Approx. 85% in polystyrene insulation foams; 10% in textile back coatings; 5% in HIPS, etc.

Occurrence in the examined application areas: Polystyrene insulation foams; materials for casings

Filling level: Expanded polystyrene, mostly about 1%, partially 2-3%; HIPS 1-4% of weight.

Production: Manufacture was discontinued in Germany in 1996. Produced in Europe in Hamlock/Great Britain (Great Lakes Chemical Corp.) and in Terneuzen/NL (Broomchemie/Dead Sea Bromine Group). Albemarle Corp. produces HBCD in the USA.

Consumption volumes (Germany): According to BSEF, sales in Europe were 8900 tonnes in 1999. Sales in Germany are estimated at > 2500 tonnes, of which > 2000 tonnes were used for polystyrene insulation foam and approx. 500 tonnes for textile and carpet back coatings. Consumption trend static.

Products (trade names):
- FR 1206 (Bromine Compounds Ltd. [Dead Sea Bromine Group])
- Saytex HBCD (Albemarle Corp.)
- Great Lakes CD-75P (Great Lakes Chemical Corp.)
- Great Lakes SP-75 (Great Lakes Chemical Corp.)

Substance regulation: HBCD is subject to a Risk Assessment in accordance with 793/93/EEC. Indirect regulation via the 1994 German Dioxin Ordinance.

Information provided by: Albemarle Corp. 1999a; BASF 2000; Broomchemie 2000; BSEF 2000; DEPA 1999; Dioxin-Verordnung 1994; RA HBCD 1999.

1.5 Tris(chloropropyl)phosphate (TCPP) [CAS: 13674-84-5]

General characterization: TCPP, as a trade product, consists of a mixture of four organic halogenated phosphoric acid esters that is used in a liquid form as an additive flame retardant, but also finds use as a flame-retarding plasticizer. Main components are approx. 75% tris(1-chloro-2-propyl)phosphate and 15-30% bis(1-chloro-2-propyl)-2-chloropropyl-phosphate. TCPP represents approx. 80% of the chlorinated organic phosphorus flame retardants in Europe and is by volume and on the whole the most important organic phosphoric acid ester flame retardant.

Mode of action: With chlorinated phosphoric acid esters, both the halogen and the phosphorus components have a flame retarding action (solid phase and gas phase mechanisms). The active substance content is 9-10% of weight phosphorus and approx. 32% of weight chlorine. TCCP decomposes thermally from 150°C upwards, i.e. it is less stable than the abovementioned brominated flame retardants.

Synergism, additivity: TCPP is used alone or in combination with other flame retardants, for instance brominated polyols or other organic phosphoric acid esters, in polyurethane insulation and one-component foams.

Application areas with regard to polymers and materials: Mainly polyurethane foam; furthermore unsaturated polyester resins and phenolic resins, in thermoplastics and for textiles.

Application areas by end-products: Mainly polyurethane insulation and one-component foams (rigid foam) and polyurethane flexible foams for furniture, upholstery, car seats, mattresses, and similar products, furthermore for textile back coatings.

Occurrence in the examined application areas: Polyurethane insulation and one-component foams; flexible foams for mattresses, upholstery, and similar products.

Filling levels: With insulation foams, approx. 5% of weight, with one-component foams, approx. 14% of weight (depending on the type of foam and the combination with other flame retardants); in flexible foams 3 to 5% of weight.

Production: BASF AG, Ludwigshafen; Bayer AG, Leverkusen; Akzo Nobel, Bitterfeld. Otherwise an import product.

Consumption volumes (Germany): Approximately 5000 tonnes TCPP for polyurethane insulation and one-component foams; < 1000 tonnes for upholstered furniture and chairs, mattresses, and similar applications (flexible foams). Consumption trend static.

Products (trade names):
- Levagard PP (Bayer AG)
- Fyrol PCF (Akzo Nobel Chemicals B.V.)
- TCPP (BASF AG)
- Antiblaze TMCP (Albright & Wilson GmbH)
- Tris(2-chlorisopropyl)phosphate (Clariant GmbH)

Substance regulation: none

Information provided by: AKZO Nobel 1998a, 2000; Albright & Wilson (no date); Bayer AG 2000a; Clariant 2000a; Eurofoam 1999; IPCS 1998; KEMI 1996; Stevens/Mann 1999; Troitzsch 1990

1.6 Resorcinol-bis-diphenylphosphate (RDP) [CAS:57583-54-7]

General characterization: RDP is a cross-linked arylphosphate that is used as an additive flame retardant, as well as a plasticizer. The trade products are preparations with a content of between <6% and <5% triphenylphosphate (TPP). RDP is offered as a substitute for halogenated flame retardants in casing materials and for TPP (advantages are a lower volatility, a higher thermal stability, and a higher P-content in comparison to TPP).

Mode of action: RDP is thermally stable; it decomposes above 300°C. RDP is active primarily by means of a solid phase mechanism, through dehydration and carbonization of the surface of the polymers, by which the re-supply of flammable material for the gas phase and the introduction of oxygen to the ignition source is inhibited. Besides this, a (weaker) gas phase mechanism is also assumed. The active substance content lies between 10 and 11% of phosphorus weight, depending on the product.

Synergism, additivity: RDP, which already contains triphenylphosphate as a trade product, is sometimes utilized in a mixture with TPP; since RDP has a lesser volatility than TPP, it is used without the addition of TPP to the mixture in those instances where emission of TPP during processing (coating in the tool) must be avoided. One supplier has stated that the addition of small quantities of halogen compounds acts synergistically. With PC/ABS, 0.5% of polytetrafluoroethylene (PTFE) is added to increase the viscosity of the molten mass and to prevent the dripping of burning product.

Application areas with regard to polymers and materials: Mostly PC-ABS blends and for PPO-HIPS. Furthermore it is being offered for technical thermoplastics in general, and for polyurethane systems (thermoplastic PU and PUR foams). RDP also serves as an auxiliary agent for processing thin-walled parts, by improving the flow of the fused mass.

Application areas by end-products: Materials for casings; special cables

Occurrence in the examined application areas: Casings for E+E appliances; printed circuit boards; PUR insulation foams.

Filling level: 4-9% in PC-ABS (depending on the mixing ratio); 10-13% in PPO-HIPS.

Production: Manufactured in Germany by Akzo Nobel (Bitterfeld), otherwise in Great Britain (Great Lakes Chemical Corp.) and in Japan (Daihachi Chemical Industry).

Consumption volumes (Germany): approx. 1000 tonnes. Consumption trend increasing.

Products (trade names):
- Fyrolflex RDP from Akzo Nobel
- Reofos RDP from Great Lakes Chemical Corp. UK
- CR-733-S from Nordmann, Rassmann & Co, Mfg. Daihachi Chemical Industry, Japan

Substance regulations: none

Information provided by: Akzo Nobel 1998b; Bayer AG 1997, 2000b; Great Lakes (no date); Jabs 2000; NRC 1993; NRC 2000

1.7 N-hydroxymethyl-3-dimethylphosphonopropionamide [CAS:20120-33-6]

General characterization: Quantitatively an important flame retardant for the permanent finishing of cotton textiles in civilian applications. ‘Fibre-reactive’, that is, a flame retardant that is bound to the fibre by a cross-linking reaction. The trade product (Pyrovatex CP neu) is fluid.

Mode of action: Pyrovatex CP acts as a Lewis acid: The cellulose is dehydrated at approx. 250°C and a stable carbon layer is formed, which prevents the release of flammable material. The active substance content is 14.1% of phosphorus weight and approx. 6.4% of chlorine weight.

Synergism, additivity: Auxiliary substances are required for its application (for instance melamin resins and orthophosphoric acid).

Application areas with regard to polymers and materials: Cellulose fibres, with the exception of jute.

Application areas by end-products: Home textiles; protective clothing made of cotton; cotton, polyester, and cotton/aramide (in Germany only for protective clothing, in other countries for children's nightwear and for furniture textiles made from cotton).

Occurrence in the examined application areas: Furniture textiles for export.

Filling level: Minimum coating, dependent on the applicable standard, 13-18% of weight.

Production: Manufactured in Germany mainly for export by Ciba Spezialitätenchemie Pfersee GmbH, Langweid, Thor GmbH, Speyer, Schill & Seilacher GmbH & Co, Böblingen (production volume > 1000 tonnes).

Consumption volumes (Germany): < 100 tonnes. Stable consumption trend.

Products (trade names):

- Pyrovatex CP neu from CIBA Pfersee
- Aflammit KWB from Thor GmbH
- Flacavon WO from Schill & Seilacher
- Amgard TFR1 from Albright & Wilson

Substance regulations: German water hazard class WGK 1 (as rated by industry)

Information provided by: Albright & Wilson (no date); CIBA 1998, 1999; Schill & Seilacher 1999

1.8 Red phosphorus [CAS:7723-14-0]

General characterization: Red phosphorus is used as an additive flame retardant. The trade product is stabilized by wetting it with additives, or by micro-encapsulation (for instance with phenol formaldehyde resins). The share of total consumption of red phosphorus (globally about 7500 tonnes) used for flame retardants is approx. 18%. Use restriction for visible applications, due to the red colour.

Mode of action: Red phosphorus decomposes thermally above 400°C. It acts as a flame retardant by means of a solid phase mechanism. It forms a rigid, glassy carbonized layer on the polymer that consists mainly of polyphosphoric acid, which prevents the re-supply of flammable material in the gas phase. The oxygen required for the formation of the polyphosphoric acid is derived preferentially from the matrix (polymer or other material). That is why red phosphorus is most effective as a flame retardant in materials with a high oxygen content (such as cellulose, oxygen-containing plastics). In polyolefins and polystyrene (oxygen-free), in contrast, synergists are required.

Synergism, additivity: Depending on the application, flame retardants are recommended that contain nitrogen or halogen.

Application areas with regard to polymers and materials: Condensation polymers (especially polyamide, polyester, polyurethane, polyisocyanurate, epoxy resins). With polyolefins and polystyrene, only in combination with synergists. Dispersions for textile finishing.

Application areas by end-products: Components made of polyamide for electrical and electronic appliances; glass-fibre reinforced plastics for electrical applications; cables; moulding resins (epoxy resins); synthetic glues; closed-cell foams; automobile textiles.

Occurrence in the examined application areas: Epoxy resins for printed circuit boards; PUR insulation foams; printed circuit boards (E+E appliances sector: for components made from PA, on offer and reported as existing, but not individually examined.)

Filling level: 2-10%.

Production: Manufactured Germany by Clariant GmbH, Sulzbach.

Consumption volumes (Germany): 1000 – 1500 tonnes; consumption trend static.

Products (trade names):
- Exolit RP series from Clariant GmbH

Substance regulations: none

Information provided by: Clariant 1998, 2000b,c; EFRA 1996; NRC 2000; Troitzsch 1990

1.9 Ammonium polyphosphate (APP) [CAS: 68333-79-9]

General characterization: Additive nitrogen and phosphorus-containing flame retardant, in a crystalline form or as a liquor. In contrast to other applications of ammonium phosphate (for instance for fertilizers), use as a flame retardant is quantitatively marginal.

Mode of action: APP begins to decompose above 275°C. As with phosphorus-containing systems in general, the flame-retarding action consists of the release of polyphosphoric acid and carbonization. In intumescent systems, AP is active in combination with dispensers of carbonic compounds and blowing agents as acid dispensers. At the same time a gas phase mechanism is postulated (release of non-flammable gases, which prevents the supply of oxygen to the flammable substrate).

The content of active ingredients for the individual products varies; APP 422 from Clariant GmbH for instance contains 31.5% phosphorus and 14.5% nitrogen.

Synergism, additivity: APP is used in intumescent systems together with polyalcohol (pentaerythrite) as dispenser of carbonic compounds and blowing agents (e.g. melamin) in the ratio 3:1:1; in UP resins in combination with aluminium trihydrate (ATH) in the ratio 1:5.

Application areas with regard to polymers and materials: Polyurethane foams (rigid and flexible); polypropylene; epoxy and polyester resins; cellulose-containing systems; washfast textile back coatings (combination of APP with, for instance, vinylacetate dispersions).

Application areas by end-products: Intumescent laminations (especially steel girders); PUR flexible and rigid foams; furthermore, moulding resins and components made of PP for E+E appliances; sealants, glues.

Occurrence in the examined application areas: Unsaturated polyester resins for rail vehicles; PUR insulation foams; textile back coatings

Filling level: For PUR flexible foam 4-10 parts/100 parts polyol; for PUR rigid foam B2 20-45 parts/100 parts polyol, depending on the blowing agent and volume weight; thermoplastics, glues, and sealants 10-20% of weight. In intumescent laminations, the APP content is 9-15% of weight.

Production: Manufactured in Germany by Clariant GmbH, Sulzbach.

Consumption volumes (Germany): approx. 1000-1500 tonnes. Consumption trend increasing.

Products (trade names):
- Exolit APP 422 from Clariant GmbH
- FR cros 484 Budenheim Iberica
- Antiblaze CL, Antiblaze TR from Albright & Wilson

Substance regulations: none

Information provided by: Albright & Wilson (no date); Chemische Fabrik Budenheim 1999; Clariant 1997, 1999, 2000d; Witte 1999.

1.10 Melamin cyanurate (MC) [CAS:37640-57-6]

General characterization: Additive nitrogen-containing flame retardant, crystalline. Until now a niche product with little quantitative importance, only manufactured as a flame retardant.

Mode of action: It is assumed that MC acts as flame-retarding through a cooling effect, and by diluting the oxygen atmosphere with non-flammable gases. The active substance content (nitrogen) is 48-49%. MC has high thermal stability (decomposition at 350°C).

Synergism, additivity: Used as the sole flame retardant in polyamides, otherwise in combination with other flame retardants.

Application areas with regard to polymers and materials: Polyamide (essentially PA 6 and PA66) and thermoplastic polyurethane. Because of its high thermal stability, MC is suitable for plastics with higher processing temperatures, such as technical thermoplastics; carpet back coatings.

Application areas by end-products: Injection moulding parts such as connectors, casing parts; automobile cables made of thermoplastic PUR (corrosion-resistant); carpet back coatings.

Occurrence in the examined application areas: Textiles; E+E appliances sector: on offer and reported as existing, but not individually examined (components made of PA); printed circuit boards, test material.

Filling level: 6.5-15%.

Production: Manufacture in the EU (not in Germany) among others by DSM Melapur (NL-Geleen) and CFB Chemische Fabrik Budenheim (Spain).

Consumption volumes (Germany): approx. 500-1,000 tonnes. Consumption trend increasing.

Products (trade names):

- Fyrol MC from Akzo Nobel N.V.
- Budit 314, 315 from CFB Chemische Fabrik Budenheim
- Melapur MC from DSM Melapur

Substance regulations: none

Information provided by: Akzo Nobel 1998c; Chemische Fabrik Budenheim 1999b; DSM Melapur 1998/1999/2000; Grabner 1998.

1.11 Aluminium trihydroxide (ATH) [CAS 21645-51-2]

General characterization: Additive mineral flame retardant, filler, and an additive for fume reduction. ATH is a relatively weak-acting flame retardant and must therefore be utilized in large fill quantities, which limits its application area, because of the associated influence on the properties of the polymer and materials. Since ATH decomposes at 200°C, its application is further limited and it cannot be used in plastics with higher processing and high operating temperatures.

Mode of action: Endothermic phase conversion with water separation takes place at 200°C, which leads to a cooling of the matrix and a dilution of the oxygen atmosphere. The formation of a protective layer from carbonization products also has a flame-retarding effect. ATH reduces the density of fumes through an absorption of soot particles by the protective layer.

Synergism, additivity: In many cases coatings with organic carboxyl or amino compounds (0.1 – 2% of the trade product) as a formulation auxiliary in order to insert large filling quantities into the matrix. Combination with flow enhancers and dispergent additives.

Application areas with regard to polymers and materials: ATH is used mainly in duroplastics, such as unsaturated polyester resins, epoxy, acrylic, melamin, and phenolic resins, and furthermore in polyurethanes, in thermoplastics and thermoplastic elastomers (PP, PE, EVA, PVC). Furthermore in lattices and aqueous dispersions.

Application areas by end-products: Glass-fibre reinforced plastics (laminations, construction materials); polyurethane flexible and rigid foam; polyurethane enamels and paints; conveyor belts; cables; injection-moulded parts; carpet and textile back coatings; dispersion paints.

Occurrence in the examined application areas: Unsaturated polyester resins for rail vehicles; printed circuit boards (CEM 3); polyurethane insulation foam.

Filling level: 30-600% (duroplastics: 100-150% of weight; thermoplastics 50-60% of weight; carpet backs up to 600% of weight in relation to latex dry substance; dispersion paints 100-400% of weight)

Production: Manufactured in Germany by Alusuisse Martinswerk GmbH (Bergheim) and Nabalwerke Aluminumhydroxid GmbH (Schwandorf)

Consumption volumes (Germany): approx. 45000 – 47000 tonnes. Stable consumption trend.

Products (trade names):
- Martinal series from Alusuisse Martinswerk GmbH;
- Apyral series from Nabalwerke Aluminumhydroxid GmbH
- Securoc A from Incemin AG

Substance regulations: none

Information provided by: Byk Chemie 1998; Incemin (no date), 1998; Martinswerk 1997,1998,1999; Nabaltec (no date)

1.12 Sodium borate decahydrate (Borax) [CAS: 1303-96-4]

General characterization: Borax is available in the trade as a crystalline powder. It serves as an additive flame retardant for cellulose applications. The application of Borax as a flame retardant is, with a maximum of 1%, a niche application, in contrast to the other consumption of Borax for detergents and in the enamel and ceramic industries.

Mode of action: Borax is active mainly in the solid phase (carbonization, release of chemically bound water). It shows little effectiveness with smouldering fires and afterglow.

Synergism, additivity: As a rule it is applied in combination with boric acid as an agent against smouldering fires, and, if necessary, with ammonium sulphate.

Application areas with regard to polymers and materials: Used with cellulose-containing materials.

Application areas by end-products: B2 insulation plates for thermal and acoustic insulation on a cellulose base.

Occurrence in the examined application areas: Insulation material sector (however, insulation materials on a cellulose base were not examined.)

Filling level: 10 (-40) percent of weight

Production: For the European market in Coudekerque, France (US Borax), and in Turkey (Etimine GmbH).

Consumption volumes (Germany): 1500 tonnes. Consumption trend static.

Products (trade names):
- Borax Decahydrate (Borax Consolidated Ltd.)
- Borax Decahydrat (Enichem Deutschland Chemie Handels GmbH)

Substance regulations: none

Information provided by: Deutsche Borax GmbH, no date; Enichem 1998; Etimine 1999; Homann 1999; NRC 2000

1.13 Antimony trioxide (ATO) [CAS: 1309-64-4]

General characterization: Antimony trioxide is a flame-retardant synergist, not a flame retardant, for halogenated flame retardants or halogen-containing polymers, which increases the effectiveness of the halogenated flame retardants or acts in a flame-retarding manner in combination with halogen from halogenated polymers. ATO is available in the trade in a moistened or pasted form (because of hazards from dust and the suspicion of carcinogenic properties), as well as encapsulated, or as part of a master batch. ATO is furthermore used in the enamel industry (opacifier) and in the glass industry (refining agent), and also in the manufacture of glass fibres.

Mode of action: ATO is thermally very stable (melting point 656 °C). The reactions that lie at the basis of the synergy between antimony trioxide and halogen have not been fully clarified. The general opinion is that the synergy during flame retardance rests on a gas phase mechanism, in the first instance, but also on promoting carbonization in the solid phase, and the inhibition of oxygen access to the fire zone, by covering it with heavy vapours, as well as a cooling of the burning material by means of a stepwise formation of antimony-halogen products.

Synergism, additivity: As a rule, ATO is used together with halogenated flame retardants, while halogenated flame retardants can also be utilized without ATO as a synergist. Conversely, there are application areas of ATO as a flame inhibitor (in halogen-containing polymers), where no flame retardants are added.

Application areas with regard to polymers and materials: ATO is a flame-retarding synergist for halogenated flame retardants in thermoplastics, to a lesser extent in duroplastics, and not in polystyrene and polyurethane foam. It is furthermore applied in flexible PVC compounds. According to information supplied by manufacturers for 1998, and with a total sale of approx. 22,000 tonnes, the European ATO market for flame-retardant applications is structured as follows: Thermoplastics: 50%; PVC (cables, foils) 32%; rubber 11%; unsaturated polyester and epoxy resins (duroplastics) 2%; textiles 5%.

Application areas by end-products: Thermoplastic products for E+E appliances; cables; paints; paper; textiles; etc. (mid-1990s approx. 60% for construction products, 30% for E+E appliances, and 10% for other applications).

Occurrence in the examined application areas: Rail vehicles; printed circuit boards; casings; and textiles.

Filling level: The combination ratio of halogenated flame retardants to antimony trioxide is as a rule 2:1 to 3:1.

Production: The largest manufacturers are Great Lakes Chemical (AZ) Ltd. (formerly Anzon) in Wallsend/UK, Campine N.V. in Diegem/Belgium, Mine de la Lucette, Paris. Raw materials are supplied from China and South Africa.

Consumption volumes (Germany): 6000-7000 tonnes. Consumption trend static/declining.

Products (trade names):
- Timonox series from Great Lakes Chemical (AZ) Ltd.
- Antiox series from Campine N.V.
- Plastriox-, Polytriox-, Triox series from Mine de la Lucette (Paris)
- Borax Decahydrate (Enichem Deutschland Chemie Handels GmbH)

Substance regulations: none

Information provided by: Campine 1994, 1998; Berstermann 1986; Enichem 1998; NRC 1998; Troitzsch 1990; Great Lakes 1998, 1999; Van Velzen 1998

2. Representativeness of the volumes of selected flame retardants

To what extent are the 13 examined flame retardants representative of the consumption of flame retardants in Germany (Table III/1)?

The selection of flame retardants took all relevant groups into account. Quantitatively, however, it needs to be ascertained how large the volume of the selected flame retardants is. Table III/1 compares the examined flame retardants with the estimated total consumption of flame retardants, organized in the three main groups: 'antimony-halogen flame retardants', 'mineral flame retardants' and 'other halogen-free flame retardants'.

Table III/1: Representativeness of the volume of the examined flame retardants by flame retardant groups

Flame retardant group	**Examined flame retardant [t] (average estimated volume)[1]**	**Total group volume [t] (average estimated volume)[2]**	**Share of the examined flame retardants in total volume [%]**
Antimony-halogen group	21,500	30,000	72
Mineral-based flame retardants	46,000	47,000	98
Other halogen-free flame retardants	8,500	16,750	51
Total	76,000	93,750	81

[1] See overview III/1; [2] see Table II/1

In the antimony-halogen group, four brominated flame retardants were taken into account (decabromodiphenyl ether, TBBA, bis[pentabromophenyl]ethane, and HBCD), TCPP as a chlorinated flame retardant, and antimony trioxide as a synergist. The share of these flame retardants in the total of the group is above 70%. Quantitatively important flame retardants not taken into account here are chloroparaffins and brominated polyols.[8]

With ATH, the quantitatively dominating flame retardant (98%), the whole group of mineral-based flame retardants is for all intents and purposes covered. [9]

Among the other flame retardants, the share of those flame retardants examined for their substance properties amounts to approximately half (51%) of the total group. The halogen-free organic phosphorus compounds (Pyrovatex CP; RDP) are not as well represented here as the inorganic phosphorus compounds (red phosphorus, ammonium polyphosphate). Since the halogen-free aryl-, alkyl-, and bis-phosphates are becoming increasingly important as substitutes for halogenated compounds, a number of them were included in Table V/15.[10] Melamin cyanurate is a smaller

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[8] In Table V/15 the following substances from the group of antimony-halogen systems are additionally listed: Brominated polyols, brominated polystyrene, dibromoneopentylglycol, tetrabromophthal acid anhydride (TBPA), as well as tetrakis(hydroxymethyl)phosphonium chloride (THCP). The HBCD synergist dicumylperoxide also belongs to this group.

[9] Table V/15 also contains magnesium hydroxide.

[10] Table V/15 contains the following substances from the group of halogen-free organic phosphorus compounds: Diethylethylphosphonate (DEEP), triethylphosphate (TEP), tri(2-ethylhexyl)phosphate (TEHP), diphenylcresylphosphate (DPK), tricresylphosphate (TCP) and triphenylphosphate, as well as

product[11] among the nitrogen compounds, while among the boron compounds approximately half of the sales for the group are accounted for by Borax. Additionally, Table V/15 also takes into account zinc borate and expanded graphite.

In summary, the substance stream of the 13 flame retardants that were examined more closely (incl. ATO) accounts for approx. 80% of the quantity of flame retardants in use.

"Struktol" as a reactive organic phosphorus compound for epoxy resin, and furthermore ammonium phosphate.

[11] In Table V/15 melamin is additionally taken into account as the main representative of the group.

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Chapter IV: Preparating assessment bases for environmental relevance of materials and products

Chapter contents

Preface

In this chapter we present some considerations which relate to the development of evaluation criteria for industrial chemicals in general and flame retardants in particular – out of necessity some are general and exceed the pragmatic access to the assessment problems possible within the scope of this project.

The following is to be taken into consideration:

- The controversial discussion about chemical risks in society;
- The necessity to increase the consideration of „intrinsic“ material properties (such as persistence or the ability for bio-accumulation) and the viewpoint of material reduction with substance assessment as a result of global environmental problems.
- The implementation of general objectives of environmental policy such as material intensity and re-cyclability for assessment criteria.

Section 1 serves to clarify what is understood by „environmental relevance“ within the scope of this study. Background considerations, which are decisive for the development of the general assessment criteria suggested in the following are presented in *Section 2.* These general criteria are the subject matter of *Section 3*. A major result of the material and application considerations is the realisation that the current information deficit is simply too large for a substance assessment on the basis of the general assessment grid, as it is sketched in Section 3. To manage this knowledge and information deficite in a pragmatic way requires recoursing on information basis available today regarding flame retardants and its applications – as they are described in Vol. II (Application considerations) and Vol. III (Substance profiles) It is exposed in more detail in *Section 4.*

1. Environmental relevance and ecotoxicity of chemical substances and products

A societal material flow management as well as material stream management on the business level requires more than considering the damage potentials defined by the EU chemicals directive and national law. Nowaday the focus is changing to the potential impacts which the chemical (used or intended for use) may have for the physical and social environment. Focussing this environmental relevace of chemical substances is facilitating the realization of the precautionary principle of environmental policy as well as a promotion of sustainable development. Equally the consideration of the environmental relevance of a chemical substance or product faciliates a comprehensive product liability (or product stewardship) of a manufacturer or a commercial applicant

Fundamentally, no chemical is environmentally neutral or environmentally friendly in all environmental aspects (when looking at it from a quantity-independent aspect). However, it has not yet been clarified how chemical substances and products can be differentiated with regard to their environmental relevance.

The term of environmental relevance

The term e*nvironmental relevance* is currently hardly used in the trade literature and has not been introduced systematically. However, there are relevant initial works available (cf. Umweltbundesamt 1999). Nevertheless, the term „Environmental relevance“ is self-explanatory in a certain way. As has been shown during the two workshops conducted during the project, one can bring about agreement that the assessment of an environmental relevance needs to be conducted on a broader basis than those for (eco-)toxicity, but on the other hand, must contain the concepts for the eco-toxicity: Environmental orientated (eco-)toxicity is focusing manifest environmental hazard potentials and latent hazard and critical potentials for the employed, the environment and the consumers. Additionally environmental relevance includes, in particular, the aspects of a *more environmentally appropriate management of the material flows*, as well as the *„critical pollution” of the environmental media*.

According to current understanding, in particular the following concepts and dimensions could be taken into consideration for an assessment, respectively evaluation of the environmental relevance:

- Protection against damage to organisms,
- Protection against a negative influence on nature‘s economy potentials,
- Upkeep of bio-diversity,
- Upkeep of the atmospheric system,
- No „stocking up“ of environmental media,
- Lessening of the persistent chemicals pollution load,
- Workers protection,
- Consumer protection,
- Resources protection (material intensity, capacity for recycling).

These dimensions are part of a comprehensive concept of environmental relevance (and will be explained further along, where necessary). This multi-dimensional concept of environmental relevance was presented as a general framework during the workshops conducted during the project. The experts from industry and environmental research who participated in these workshops, have agreed to them with regard to the flame retardant-problems to be researched.

Flame retardants and flame retarded product in the lifecycle

During these discussions it was confirmed that the environmental relevance of flame retardants cannot be determined simply on the level of the retail products and their formulations. Flame retardants, as most special chemicals, do not occur on their own – if we disregard the production phase –, but are combined in a product (which needs to be protected under fire protection aspects). This product contains, besides the material (e.g. polymer) flame proofing agents, and possibly other chemicals such as softeners, colour pigments and synergists. In practise, flame retardants do not unfold their flame retarding effects in isolation from the other chemicals in the product, but rather in combination with them.

The flame retardants are almost always incorporated in the matrix to be protected; this incorporation is effected by diffusion processes (e.g. via impregnating baths for textiles or wood) by addition to the (thermo)plastics or by chemical interaction during polymerization (e.g. duroplasts) Depending on the type of application and the stage in the lifecycle, the flame proofing agent and matrix, respectively the other chemicals in the product, can interact in different ways: Reaction products and an excess of chemicals emit into the atmosphere in particular during the *production stage* (production/formulation of the flame retardant and its incorporation into the product), respectively more currently during the *utilization stage*. Similar rules apply for additive flame retardants (here, the flame retardants can escape in gaseous form or fog out). Even during the *post-use stage*, e.g. during dismantling and material recycling, emissions can emit into environment. In certain cases compounds in products determined by flame retardants, interfere with material recycling (re-processing of the products). As a result, material recycling is replaced by the thermal utilization of the products, a solution not desirable from the perspective of a (more) sustainable resource management. By uncontrolled burning and depositing at landfills or dumps hazardous substances can also be emitted into environment.

A specific case is the *combustion stage*: Different fire conditions lead to chemical reactions of the matrix material, flame retardants and other substances (e.g. other additives, atmospheric oxygen, salts) and therefore to the generation of highly problematic by-products of fire.

The assessment or evaluation of the environmental relevance of chemicals with flame proofing effect is made even more complex by the fact that the same flame retardant is often incorporated into different polymers. According to the distinct ways of incorporation (reactive, additive), very different emissions of the fire retardant, respectively its decomposition products are to be expected. Depending on the application case and its corresponding fire protection, different fire protection requirements are resulting and thus different levels of equipment with flame retardants are to be expected. For the assessment or evaluation of the environmental relevance it is not sufficient to restrict the issue solely to the intrinsic material properties of the flame proofing agents. In addition, environmentally relevant aspects resulting from the application must be taken into appropriate consideration, too. In reasoning, not only the physical properties of the flame proofing agents need to be considered, but also the products equipped with them and their properties in all stages of their lifecycle.

2. Background considerations for the preparation of assessment bases for the substitution of environmentally relevant chemicals

The considerations which follow in this section are of a general nature. As they were leading in the preparation of possible assessment bases, they are presented here. It is however not absolutely necessary to attempt a mental follow-through process to appreciate the results which were worked out with their aid and which are presented in the following (cf. sections 3 and 4 of this chapter).

2.1. Combination of concepts for chemicals assessment and product evaluation

Methods for evaluating the physical properties of chemicals were already developed in the 19th century (cf. Hien 1994, Miles 1997, Büschenfeld 1998). To force back partial interests, toxicology already oriented itself along a scientifically controllable procedure for the assessment of chemical substances in those days. Correspondingly, until to present considering physical properties starts from the premise that an adequate assessment process should

- be based on a model which is as accurate as possible and scientifically correct,
- relate to a defined objective or value system as accurately as possible ,
- possess a formally consistent evaluation structure and
- lead to an action related order of the classified (evaluated) alternatives (Bechmann afterFränzle 1998, Kluge et al. 1995).

These considerations do apply in their beginnings for product evaluation procedures as well. However, the models and value systems used therein are strongly dependent on the corresponding application context and its specifics. Contrary to the methods used for chemical substance assessment many objectives, value systems, and indicators in product evaluation are limited to very narrow and specific application areas. (In respect of the chemical assessment in (environmental) toxicology, a few underlying causality models and also the indicator systems are broadly accepted within the scientific and practical fields and can be applied universally for many different application areas (e.g. the OECD criteria for the assessement and classification of chemicals according to European chemical law.) Due to the partly resultant complexity and the therefore necessary pragmatic orientation in product assessment, models need to be simplified strongly here; therefore they are frequently only remotely adequate for the subject. For example, smoke-gas experiments are executed with samples from one material instead of the real, complex composite systems, e.g. the passenger cell of a vehicle. Specific room conditions of fire-testing (amount of atmospheric oxygen, temperature) which can spread across a very wide spectrum in reality, can only be taken into consideration in a very narrow bandwidth.

While the standardising level of the chemical substance assessment was also characterised heavily by legislation, the objectives, resp. value systems of product assessment are definined mainly by sections of the applying practice (in technical standards).[1]

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[1] Here, partial interests can predominate and the standards oriented so that certain materials come off favourably or unfavourably. Historically, the plastic materials were initially disadvantaged by the fire-proofing standardisation as building materials – cf. Schramm et al. 1996.

The methods for assessing physical properties of chemical substances diverge considerably from the methods for product assessment. Until recently therefore, in industrial practise *methods of substance assessment* and *methods of product assessment* were not related to each other systematically, but at best pragmatically. Correspondingly, the assessment of substances and that of products were separated mentally from each other in the context of environmental or technological policies. In the meantime though, there are at least first starting points for an integrative combination of product and substance dimensions (cf. Gensch et al. 1995, UBA 1999), which could give valuable orientation for continuing work.

Fundamentally, the following aspects should be accepted for the combination of product and material assessments as requirement for assessment or evaluation procedures: They should

- be based on a factual model,
- be oriented towards a defined
- objective, resp. value system,
- have a formally consistent evaluation structure and
- contain action related orders of classified (evaluated) alternatives.

Reasoning, the assessment of environmental relevance should be based on an innovative, factual model which integrates the environmental relevance of physical properties of the chemicals and the adequate consideration of relevant application conditions (e.g. fire protection. Such a model – like the value, respectively objective system – cannot be worked out independent of practise. The participative working out of these systematic foundations of the integrated substance and product assessment represents a social, political and scientific challenge.

2.2. Excursus to the societal acceptance of the scientific model of chemicals assessment

Changes in the objective and value system

It is fair to assume that, under the perspective of sustainable development[2], the (legal) objectives resp. the (toxicological) value system of chemicals assessment will change and transform itself on its own.[3] Upt to now this scientific model determines the model and the pragmatic assessment for environmental relevance. With an intentional transformation of the objective, resp. value system one should not forget, that the current substance assessment and the scientific model on which it is based,

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[2] Sustainable development is not simply an inner-social orientation, it is at the same time a objective perspective which was determined with an internationally binding effect with Agenda 21 during the UN conference in Rio, which is implemented internationally by means of the UN commission on Sustainable Development (CSD) with the CSD-Process. This "Post-Rio"-process emphasises not just the nature based property of future development, but at the same time the equality between the North and South and between generations as well as the thought of participation.

[3] As the focus of sustainable development not only lies on the dimension of the environment, a major extension of the objective and value system on which the evaluation is based is necessary (cf. Enquete Commission 1994, 1997, Umweltbundesamt 1999): Resource-economical aspects must be taken up for this; on the other hand, such a value system should also be open towards aspects such as distribution equality, „accountability“ and the social negotiation process on sustainable development (cf Becker/Jahn 1999).

is only accepted without reservations by one part of the population. One may even speak of a social acceptance crisis of the scientific substance assessment. This acceptance crisis of the substance assessment is most likely based on the fact that the population and parts of the media do not generally share the background assumption of the substance assessment, which faced complete non-comprehension in some population groups. The largely unsuccessful PR campaigns of, for example the German Association of the Chemical Industry, to raise the acceptance of the scientific model show that it will probably not suffice simply to advertise for understanding for the scientific substance assessment model. Instead, in the mid- and long term it will depend on developing an improved objective, respectively value system in a way that it will find broad acceptance in society.

Different view towards risks

It must therefore be considered whether the value system on which the evaluation is based, should remain exclusively inner-scientific as before. If the causes for the acceptance problems are taken into account, a changed objective could be considered: The differentiated, sociological risk research, which followed as a result of the acceptance problems of major technologies such as atomic power and gene technology, has, e.g. elucidated that the exclusive orientation along scientific, resp. actuarially oriented handling of risks and hazard potentials is not sufficient for a social backing. The societal discourse distinguishes less between risks and hazard potentials than a scientific technical risk discourse would (Bechmann 1993, Wiedemann 1999). On the other hand it has also been shown that there are major knowledge limitaitons with the scientific assessment/dealing of hazards and risks. Long term there is also the chemical policy problem that certain risks cannot be excluded because they are not known: unintended effects of chemicals on the environment (and in part also on the human health) are only recognised after long-term used of these chemicals (e.g. Seveso-Dioxin, DDT, FCHC).

Handling knowledge deficits

Despite every assessment of effects and (eco)toxicological research, non-intended effects remain outside the sphere of consideration when evaluating risks and dangers in the developmental stage of a chemical substance, because they cannot (yet) be known. Undesired effects of chemicals on the environment and partly also on human health, which are not identifiable by the „analytical window“ of the tests executed on very few selected indicator species, will frequently be recognised only after long term use of these substances. New hazards and risks will also occur, which have not played a role previously in the background philosophy used for the substance assessment.

To be able to handle the considerable knowledge limitations with the scientific assessment/acquisition of hazards and risks in a socially appropriate manner, a strict orientation along the principles of precaution in environmental policy and an extensive product responsibility (consumer policy) is necessary. In light of the non-knowledge problem, there should be, e.g. even the tendency to consider the hypothetical, not yet empirically secured risk observations (cf. Schramm 1998). The problem of „non-konwledge“ must be considered systematically with the development of an improved objective and value system for the material and product assessment.

Consideration of public value and objective perspectives

The conclusion which are drawn within the public when dealing with chemical substances in the light of insecurities andignorance, should however be included now in the debate about environmental relevance of chemicals: on the one hand we need to mention the *minimisation order* at this point which has already been implemented for certain areas of environmental policy (e.g. drinking water supply). On the other hand, more or less diffuse perceptions of a „de-chemicalisation“ or „detoxification“ build a background perception for a general demand for products which are, e.g. free of halogenorganic combinations, or for the exclusive use of natural substances instead of xenobiotica .

Only when these value and objective perceptions existing in the public, are taken into consideration with innovations in flame retardant systems and material flow management, will any acceptance problems be reduced.

2.3. Conclusions for the substitution of environmentally relevant flame retardants

The assumption that a comprehensive screening of the substitutes and their supra-industry application scope is always carried out in the chemical and flame retardants applying industry for the substitution processes is unrealistic. Due to the utilization conditions in the companies, such a screening is replaced by simplified consideration methods along the lines of a value-adding chain, which calculates at best in the mean and long term. The additional orientation along non-scientific value scales which are however shared by the consumers (e.g. „de-chemicalisation“) often offers sufficient directional security. It follows that it is not necessary for the substitution of environmentally relevant flame proofing agents, to develop a new value and objective system for the integrated consideration of chemicals and product under inclusion of all interested parties as mandatory prerequisite.[4]

We have, in part, different innovation dynamics in the various areas in which flame are used. They are dependent on specific socio-economic conditions and mechanisms, but also on different material prerequisites, as the application relevant consideration in the project clarified (cf. Vol. II).

The following can be said in a generalised fashion about the forces regarding a substitution of environmentally relevant flame retardants (cf. also Schramm et al. 1996):

The economic driving forces in regard to the substitution of environmentally relevant flame are founded mainly in cost savings. The following act in the same direction: Order policy initiatives and voluntary agreements for the set-up of recycling systems, which forestall government regulations, respectively are intended to make them superfluous and by which the power over material flows remains within the

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[4] This allows to reduce the expectations placed on the preparation of evaluation bases for the substitution of environment relevant flame retardants. It is not the issue to prepare operationalised criteria for the innovation led by individual interests and a fundamental screening (e.g on the basis of the OECD criteria for material evaluation), but rather criteria, which reflect the chemicals and material flow policy – fields of environmental activity and thereby allow the upkeep of the material flow management on an overall social level.

companies. For these reasons, environmentally relevant flame retardants (e.g. halogens with the potential of forming dioxins) are being replaced by other agents.[5] In some areas (e.g. in the electro- or electronics sector) it is possible to refer to the scope of a constructive fire protection, if there is no other need for a chemical equipment with flame proofing agents.

Apart from these forces which favour the substitution of environmentally relevant flame retardants, hindering forces can generally also be identified. Here too, costs must be quoted as a prime point. Decisive is however the co-operation along the value-adding chain. When there is no focused co-operation with plastics or flame retardant manufacturers, the polymer processing industry usually handles its product innovations, or product optimisations for products with inflamation requirements without being conscious of which flame retardants are part of the corresponding compound.[6] In such cases, the innovation direction is primarily determined by cost aspects and from the compliance with required inflamation tests, and only on a secondary level by material and environmental aspects. The will alone for redesigning is however not sufficient to operate a chemical or operating substance substitution of particular environmental relevant flame retardants on behalf of the users. Moreover it is necessary that the involved companies can access the innovation process. Usually, the polymer processing industry can usually develop innovations, with which environmentally relevant flame proofing agents can be substituted, only in co-operation with plastics material suppliers or flame retardant manufacturers because of their comparably weaker economic situation. Very often therefore, the focused material substitutions of environmentally relevant flame retardants are dependant on economical interests of flame retardant manufacturers, resp. the plastics material suppliers[7] and, sometimes from the intermediate chemical trade.

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[5] Only a very small part is the substitution of just the flame proofing agent; in most cases the raw material is exchanged, so that the new matrix contains a less environmentally relevant flame proofing system.

[6] When alternative flame retardants for the application are on the market, specifications (e.g. antimony free) can be made.

[7] System houses have proven to be more of a hindering element as soon as market saturation has been reached, as has been shown by the development in the sector of PUR foams. It is obviously easier for self-formulators to replace environmentally relevant flame retardants.

3. Assessment dimensions

3.1. Requirements placed on criteria and assessment aspects

The development of criteria and assessment aspects for environmental relevance of flame retardants must orient itself along the following assignment of duties:

- On the one hand they are, on a national level, to serve the preparation of a uniform assessment of the environmental relevance of flame proofing agents in products which are used for certain application areas, and to simplify the synopsis of material properties and application aspects with the aim of its societal and also international material flow management (EU chemicals regulation, labelling);

- On the other hand, they should represent orientational guides for company internal innovations (resp. innovation expanding between industry sectors), to present an improved directional security under the fast changing socio-economic framework conditions.

- The consideration of only conventional assessment methods, as they have been determined upon the basis of the OECD criteria for the chemicals assessment (operationalisation of the chemical regulation), no longer suffices for the company and supra-company material flow management, as further environmental aspects as well as application aspects need to be integrated. Further criteria should therefore be developed supplementary to the OECD criteria, to enable concrete and measurable predicates about the environmental relevance of materials, respectively products.

First operationalisation attempts for the evaluation of flame proofing agents in their application contexts, which are aimed directly at feasible test and classification methods, were already identified in an earlier study for the Federal Environment Office and presented to the experts (cf. Schramm et al. 1996).

In this project the working hypothesis is that individual assessment aspects can be derived on the basis of a criteria grid for environmental relevance. Customary criteria for environmental relevance should be taken into consideration as far as possible (e.g. water hazard classes according to German water framework act). A different weighting of the individual lifecycles of flame retardants, respectively their applications, can be adequate. The set-up of a corresponding criteria grid with generally divided weighting factors for the various cycles will only be feasible in the medium to long term.

For this reason, *pragmatic* fundamental criteria and principles of action were identified for the relevant environmental to material policy fields of action, for which assessment aspects can be derived. Such comparatively general assessment aspects enable rough objectives for the substitution of environmentally relevant flame retardants due to their guiding function.

The comparative assessment of material properties of the flame retardants in the different application products presents a problem. Here, it was only possible to take a pragmatic approach and indicate the open questions. The weighting of the different states in the lifecycle of the products (manufacture, application/fire, post-usage stage) also represents a problem requiring a pragmatic solution. With the *concrete* consideration of materials in specific applications/products in individual case considerations, general material specific aspects are often relativised.[8]

3.2. Indications for components of a new objective and value system

In the light of the damage to the ozone layer and the anthropogenic climatic change, the understanding of the environmental hazard potential of materials has increased in society and politics over the last years.

The threat to earth‘s atmosphere has made it clear that the assessment of environmental hazard potentials of chemicals and products by means of just the conventional toxicological and ecotoxicological test methods is no longer adequate (cf. Kluge, Schramm, Hien 1995). In relation to the environmental media of water, earth and air, „critical loads” must be estimated (also with regard to their dynamics in time); it is possible here to orient oneself amongst other things, along additive assessment methods, such as for example, the Federal-State-Committee (Bund-Länder-Arbeitskreis Qualitätsziele für Oberflächengewässer) has worked out for the assessment of emission in flowing surface waters. In future the international convention for the protection of bio-diversity could possibly lead to the fact that, apart from the material effects on a few exemplary indicator organisms created in toxicological and ecotoxicological experiments, effects on associations of organisms (e.g. “living community” of an ecological system) need to be considered as well (cf. Kluge, Schramm, Hien 1995).

A definition of environmental relevance which remains appropriate over the next years must also consider aspects of material flow management, which are built upon the understanding of sustainable development. The internationally binding principle, that the current generation should act in a manner which is responsible for the following generations, is new in the history of mankind. Corresponding economical instruments, which help to secure the „Principle of Responsibility“ (Jonas 1979) laid down in Agenda 21, (e.g. internationalisation of external effects acting in the future) have up to now not been operationalised, resp. implemented.

There is no mutual, operationalisable understanding about sustainable development available for overall society, up to now. Based on initial work by the Enquête Commission „Protection of mankind and the environment“ of the German Bundestag in particular its resource-management rules it can generally be stated – that for the following generations the economical and social capacity to act should be maintained. For this purpose, the economical, social and environmental dimensions must be considered equally. In particular those resources which cannot be renewed must be used extremely sparingly. To enable this to happen without a qualitative lowering of the level of consumption, the use of materials presumably needs to be minimised and the material intensity increased (factor 4 resp. factor 10 discussion

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[8] Such a pragmatic consideration, which takes the concrete application conditions into account (e.g.: polymerization of the flame retardant; application relevance for internal rooms) cannot relativize fundamental toxicological/ecotoxicological criteria such as, for example, the occurrence of a material in food chains (e.g. flame retardants in breast milk); not even then, when e.g. there is doubt about the entrance paths, or other application forms of the material (e.g as softener) are known.

„ecological back-pack”). It will therefore also be necessary to lead the material flows in a cycle. The guiding principles of the German recycling act should be taken into consideration and implemented in operational practise (recyclability of products, disposal compatibility).

3.3. Criteria of a precautionary and sustainable material policy

For a further concretising of these thoughts, one can turn to the work by the Umweltbundesamt for a precautionary and sustainable material policy (1999) which were presented during the second workshop (lecture Eggers; cf. Overview IV/1).

Reduction of material volume for products and services without serious utilization sacrifices. The Umweltbundesamt (1999) suggested the following criterion for the material volume: Material intensity of products and services in the complete lifecycle.

Reduction of the consumption of natural material resources. The consumption of resources was defined as follows: scope and type of resource consumption for products and services in the complete lifecycle.

Reduction of energy volume when extracting, processing, utilizing, recycling and disposing of materials. The following criterion was recommended for the use of energy: Energy consumption in the lifecycle of products.

Increasing the long-term usability of products. The durability of products, as well as repair-friendliness and adaptability of products was defined as criterion for a long-term usability.

*Improvement of an environmentally compatible utilization*t. The criteria recommended for an environmentally compatible utilization are as follows: Utilization of products; environmental compatibility of utilization methods.

Minimisation of emissions to the technically unavoidable level. The amount and toxicity of the emissions was recommended as assessment aspects in this case.

Reduction of the complexity of material flows. The following criteria apply for the complexity of material flows: multi-step technical processes and their networking; scope of control measures required with technical processes to minimise accident risks; hazard potential of intermediate products.

Development of materials with environmentally and health compatible properties, as far as they are introduced into the environment during production, processing or use. (In particular for chemicals with environmentally open application). An ecological and health related profile must be developed for this purpose.

Risk reduction to avoid overloading the environment through ecotoxic and toxic substances. During the lecture at the 2nd workshop, an orientation along intrinsic material properties with the following action objectives were suggested as criteria: "The irreversible introduction of persistent and/or bioaccumulating xenobiotica into the environment is to be avoided completely, independent of their toxicity. This also applies to metabolites with such properties " (Umweltbundesamt 1999: 21; cf. Overview IV/1).

Overview IV/1: Umweltbundesamt, material policy criteria

Material group	**Properties**			
	Persistent and/or bioaccumulative	**Carcinogenic, mutagenic, reproduction toxic**	**Toxic/ecotoxic in other regards**	**Non-reclaimable**
Xenobiotica	Irreversible introduction is to be avoided completely	Introduction is to be avoided completely	Reduction of emissions into environment to technically unavoidable level	Increase of material introduction is to be avoided
Natural substances	No increase of geogenic/biogenic background load	No increase of geogenic/ biogenic background load	Reduction of emissions into environment to technically unavoidable level	Increase of material introduction is to be avoided

Source: H.-H. Eggers, Umweltbundesamt, Lecture 2nd workshop, 6.4.2000; UBA 1999

The introduction of xenobiotica with carcinogenic, mutagenic or reproductively toxic effects into the environment must be completely avoided. This applies correspondingly for metabolites with such properties. Not only xenobiotica, but also natural substances must be assessed critically: an anthropogenic release of natural substances with persistent and/or bioaccumulative properties or carcinogenic, mutagenic or reproductively toxic effects into the environment must not lead to an increase of the geogenic or biogenic background load. An increase of material introductions into the environmental media is to be avoided, independent of currently known effects and other intrinsic properties, if the reclaimability of the material from the environment is practically impossible due to the high distribution and/or the low exchange (UBA 1999: 22f).

The weighting of the criteria, which can be derived from the above stated fields of action, are different for the various substances and applications to be considered. Competitive relations between the material policy fields of action identified by the Umweltbundesamt (1999) cannot be excluded. For the purpose of simplification however, and in view of the present project for the development of assessment criteria for the substitution of environmentally relevant flame retardants, they can be summarized into two general principles of action, namely the *reduction order* and the *optimisation order*. These two orders for action are not independent of each other, rather they are in close connection and are complementary.

The reduction order mainly requires an active modulation (substitution respectively reduction) of

- Problem substances (POPs, persistent/bioaccumulative combinations),
- mutagenic/carcinogenic/reproductively toxic materials.

The *reduction order* also aims at a reduction

- of all emissions to a technically unavoidable level,
- of resource consumption,

- in the ecological backpack,
- when using energy (extraction/manufacture/application/recycling)
- of the amounts of waste

The *optimisation order* must be seen complementary to this. The optimisation order aims at an improvement of

- toxic/ecotoxic clearance,
- atmospheric clearance,
- ecosystematic clearance,
- care with resources.

When orienting along the optimisation order, the innovation processes will lead to an increase of

- environmentally contained applications,
- recyclability of the products,
- the material intensity,
- the suitability for disposal,
- the utilisation of regenerating raw materials.

The objective is the reduction of the use of particularly environmentally relevant materials, where the guarantee of the corresponding fire protection level relevant to the application fields is a fundamental prerequisite.

3.4. Data situation

The basic data required for such a comprehensive assessment procedure as has been sketched in the present section, are currently available in a very incomplete state. The development of assessment criteria encompasses the determination of information and knowledge deficits, which need to be closed for future proceedings. In particular the „links“ between

- hazard potentials of substances,
- matrix dependencies (polymer etc.), and
- exposures,

which vary depending on the use pattern and lifecycle, are – apart from some very minor exceptions – not known with sufficient accuracy. That the knowable is still not known, underlines the problem of non-knowledge. From our point of view the lack of data and knowledge is one important (however not unexpected) result of this study.

Therefore, within the scope of the present study – proceeding from the presented general assessment criteria (Section 3.3) – and on the basis of the available standard of knowledge (and within the limited scope of the project) a simplified access was selected, by using toxicology, ecotoxicology and recyclability as evenly weighted consideration levels (cf. Section 4).

Within each of the different application fields it is only ever possible to compare, at starting levels, the various flame retardants with regard to their environmental relevance for the same or similar applications.

Material reduction and environmental optimisation by means of chemical, polymeric and/or constructive substitution in direction to less problematic substances/applications would therefore be the major reference points for a future environmentally more appropriate handling of environmentally relevant flame proofing agents.

4. Assessment bases

4.1. Derivation of the assessment bases

A part of the data from which an environmental relevance can be derived (e.g. eco-balances, product line considerations, material intensity considerations) is currently not (yet) available for almost all of the considered flame retardants and their applications.[9]

For pragmatic reasons, the project, when considering the environmental relevance, concentrates on those ecological and health assessment dimensions which have played a particular role in the material policy discussions. Besides the conventionally considered toxicological and ecotoxicological criteria, these are in particular the *internal room air load* (during the production stage, during application – e.g. by fogging out or in house dust, as well as in the case of fire), *water protection* and *recyclability (the ability to be used more than one lifecycle)*.[10]

In relation to the above (chapter 3) emphasised minimisation and optimisation order, this means that currently the objectives

- the reduction of toxicity/ecotoxicity of the used active ingredients,
- the reduction of the amounts of flame proofing agents used and
- the increase of the recyclability through chemical, polymeric or constructive substitution of problematic flame retardants

are regarded as priorities.

A first access for a differentiated consideration of the reference points of material data, interaction with the matrix, behaviour in the post-use stage, can be achieved with the aid of the substance profiles prepared during the project and the specific application considerations. Such an integrating combination of chemical substance and application/process related consideration requires that the quantity aspects are taken into consideration for the assessment of the environmental relevance. These are, in particular, the informations and data about the total quantity of the substancess and the estimated emission into the environment (total load) gained within the scope of the application considerations.

For the preparation of the substance profiles and the application consideration, very different reference points need to taken into consideration, respectively corresponding data employed where possible:

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[9] Different from the dimensions of material intensity, resource and energy utilization, as well as the disposal compatibility covered by these methods, some reliable information is available for the recyclability.

[10] The behaviour in the recycling process is also an idicator for other environmental criteria which are not directly able to be considered due to the data situation: depending on whether a product is easy to recycle or whether the employed active ingredients or their conversion products in the matrix interfere (e.g. halogens from flame retardants), the material intensity in the product chain is different and thereby the environmentnal relevance of the flame proofing agent which cannot be maintained in the cycle indirectly. The disposal compatibility also improves with some recyclable materials.

- Trade products: In trade products, which form the starting point of the research, the chemicals used as flame retardants are generally not present in their pure form, but rather in isomer mixtures and with technical impurities.[11]

- Substances and decomposition products: the materials used as flame retardants are by no means stable in time. As a rule, the flame proofing agents do not only react under certain environmental changes (e.g. manufacture of the product, leaching) but rather – under long time observation – also under stable conditions by decomposition. Therefore, the different decomposition processes and the potential decomposition products of the chemical substances themselves need to be taken into consideration, too.

- Flame retardants interacting with the matrix: not only additive flame retardants, but also by-products resulting from the incorporation of flame retardants into the matrix, can emit into environment. In the case of fire, different decomposition products are resulting which are often quite problematic and need to be taken into consideration.

- Use-pattern of flame retardant: Fire protection philosophy in the corresponding application fields and technical requirements of inflamation protection; possibly informations in regard to the substitutionability by means of other less environmentally relevant flame retardants.

- Lifecycle of the products: in the various stages of the lifecycle (production, application, fire, post-consuming stage), environmentally relevant materials are emitting from the products (in different ways).

- Recyclability: Information whether the employed chemical substances interfere with recycling, or possibly prevent recycling under practical conditions – mainly that of really used material (and not primarily waste from the production).

- Quantities of formulas and total load: the identified effects are always dependent on the dose. It is therefore necessary to estimate both the quantities used and the quantities released. Besides the production quantities, resp. consumed quantities, the quantities already accumulated in the products must be estimated, as far as this is possible and allowed by the data situation, as these can be emitted earlier or later in the post-utilization stage. Besides these aspects – and where it is possible on the basis of individual data (e.g. findings in the sediments) statements on emissions and immissions are desirable.

The following assessment bases were identified on the background of these considerations (cf. Overview IV/2).

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[11] However, a partial risk minimisation has taken place with trade products by an improvement of the cleanliness, e.g. by using practically dioxine-free HBCDs in polystyrols (Dr. Werther, BASF, personal communication 1999).

Overview IV/2: Assessment bases for objectives when dealing with environmentally relevant flame retardants

Objective	Assessment bases	Lifecycle
Reduction of toxicity (ecotoxicity) of used flame retardants	1. Substance profiles and assessment of trade products 2. Information on the behaviour of flame retardant/Matrix (application considerations)	All stations
Increase of recyclability through substitution of flame retardants	Information/Data on recyclability (application considerations, material profile)	Post-consuming stage
Reduction of material uses	Information on the scope of minimising flame retardants; handling scope (application considerations)	Utilization stage (partly production stage as well)

4.2 Comparative assessment aspects

The assessment criteria listed in overviews IV/1 and 2 refer to the level of material properties as well as the level of applications. The following must be emphasised:

Assessment criteria (materials)

- Persistence
- Bioaccumulation
- Toxicity
- Ecotoxicity

Assessment criteria (Applications)

- Recycling impediment
- Emission tendency, in particular in internal rooms, resp. in waters (application specific use, on the waste dump, in the manufacturing stage)
- By-products of fire (smoke gas density, smoke gas toxicity and corrosiveness, fire extinguishing water loads etc).

Considerable *weighting problems* are given with the application of these assessment criteria. First of all, it must be weighted when competitive flame retardants become „conspicuous“ with different criteria. Secondly, the different lifecycle stages must be weighted against each other (cf. 4.3.); depending on each application case, one can obtain very different weightings.[12]

With the current state of knowledge and the lack of conventions on value and objective systems (cf. section 2) no „standardised“ weighting factors can be used here. Instead, the weighting must be defined pragmatically in each case.

The application conditions and their effects on emission need to be considered for these weighting problems: for example, lipophilic flame retardants, which are used in textiles, can be absorbed by the human body through accidental skin contact. Additive, volatile flame retardants can lead to internal room loads when the

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[12] For example, the smoke gas density for tunnel applications has essentially more weighting than for real external applications.

incorporation into the matrix is inadequate; dust can also be loaded permanently. Here, special attention must be paid to the toxicity of the gas/fog emission resp. the dust forms

In individual cases and from the user point of view, there is interest in relativising measured emissions. For example, the appearance of a flame retardant in breast milk or in house dust, can only be explained to some extent by the application as a flame retardant, when the chemical is, or was, used for other applications. The question, whether the emissions from the flame proofing agent equipment are causally rather major or rather negligible in comparison to other applications and sources of emission, is certainly academic from the perspective of the chemical's environmental relevance[13]. In principle, the minimisation order applies to *all* applications, which could lead to a corresponding environmental load.

4.3. Excursus: Weighting of the different stages

It is mandatory that, where possible, emissions are not released during the *production stage.* Where production integrated environmental protection and work protection (industrial safety) are not possible, the scope of additive workers and environmental protection meassures must be utilized to the full.

The *consumer stage* is characterised by application-dependant environmental loads of varying levels. The emission into the internal room air must be prevented; without complete and durable incorporation into the matrix, all flame retardants are initially to be evaluated as internal room relevant.

One can generally proceed from the assumption that the *fire* will be a rare special case in the application stage. Based on the low probability of occurrence of a fire and the predominance of the „normal“ application cases, it has been suggested by representatives of the plastics manufactures and the chemical industry under indication of pragmatic reasons, to exclude the case of a fire and the possible resultant toxic substances (e.g. dioxins from products which are enriched by halogen-organic flame retardants) from the consideration of an environmental relevance and instead to concentrate on the normal applications for created problem materials. This viewpoint however cannot be sustained and is not supported in the practise of flame retarding applications. The fire by-products that are resulting from combustion always play a major role for the assessment of flame retardants, both under the viewpoint of fire fighting and of protection of persons and material. In specific applications (e.g. fires in closed rooms such as vehicles or fires in large buildings such as airports or tunnels) a different weighting must be used: Due to the major air pollution through byproducts of fire and the damage caused as a result, e.g. to building parts, the consideration of problem substances occurring with fires and their comparison with the problem substance occurring with substitutions will be extremely practise relevant.

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[13] Here it must be proven first, that the observed emissions cannot be due to the flame retarding applications (e.g because of their encapsulation in the matrix). A – speculative – plausibility of this train of thought without empirical substantiation is inadequate here; measurements should be presented („reversal of burden of proof“) where the corresponding material is not substituted by a less environmentally relevant one immediately.

In addition the consideration of *smoke gas density* is important for certain applications (e.g. buildings) as a high density of smoke gas in the case of fires can sometimes make impossible the attack to the site of the fire by fire fighting personnel, and thereby in particular the rescue of endangered persons. Similar problems exist with regard to the *corrosiveness* and *toxicity* of the resulting smoke gases (besides halogen hydrogenes the focus must be directed towards hydrocyanic acid being produced by combustion of nitrogenated flame retardants).

With applications where extensive fire fighting measures need to be undertaken in the case of a fire, attention should be paid to any pollution of the *fire fighting water,* a subject on which practically no information has been published. Due to the potential loads of the fire fighting water, corresponding applications should be kept away from important drinking water catchment areas as a precautionary measure to prevent contamination of resources.

The significance of the *post-consuming stage* is considerable, e.g. the electronic scrap waste, due to the regulations of the German recycling act which still needs to be set in concrete for most application areas. Under the viewpoint of the reduction order, the further processing of flame retarded materials (e.g. by decomposition of the polymer) should not be considered, instead one should try re-using them. A thermal utilisation and the filtering out (and reclaiming) of basic materials such as e.g. bromine or chlorine cannot be seen as a broadly applicable solution - despite contrary views (cf. Drohmann & Tange 2000). At best it is a short to medium term aid in technological dead ends (until the substitution of the environmentally relevant flame retardants). Generally, German law leads to the following sequence: Recycling before dismantling before thermal utilisation before dumping. The incineration is gaining significance (due to the TA Siedlungsabfall [Technical guidelines municipal waste management]). In certain application cases (e.g. building rubble fractions), waste dumping will remain relevant; in these cases the risk of leaching into ground water and the guarantee of soil protection need special attention.

The recyclability has a correspondingly high weighting factor in light of the above considerations. With disassembly-type applications, the work place conditions (air pollution at work place) and in second place, the water protection, must be taken into consideration.

When comparing the defined factors it should be possible, to compare different substances/applications with regard to their environmental relevance within *one* application area.

The procedure with substance profiles and the application considerations is based on these initial considerations; they were used for the resultant assessment of the considered flame proofing agents and statements for substitution directions.

5. Final comments

We regard the „Criteria for a precautionary and sustainable material policy“ presented in section 3.3. as general base, on which a further discussion about the assessment of chemicals (here flame retardants) is to be oriented. Their application and practical „operationalisation“ does however prerequisite a far broader material and application knowledge, as available to us at this point of time. As the substance profiles (Vol III) and the summarising *substancel-related* assessments in Chapter V of this volume show, even important data for their toxicity and ecotoxicity are missing. They must therefore be sorted into the material-related assessment summary in Chap. V/14 under the heading „no recommendation possible due to knowledge deficits“.

The assessment in the scope of this study is limited therefore to the aspects of toxicology/ecotoxicology and recyclability emphasised in section 4. Important material-related criteria are materiel properties such as persistence, ability for bio-accumulation, toxicity and ecotoxicity. With the application related criteria, the recycling behaviour, amongst other things, the application dependant migration/emission tendency and effects on byproducts of fire must be mentioned.

The application related research (Vol II) on status and trend of flame proofing equipment with different products and raw materials should, amongst other things, determine the quantity relevance and check whether there are substitution and reduction potentials in the individual product areas. Resultant *application related* assessments can be found at the end of each application chapter in Vol. II and in summarized form in Chap. VI of this volume.

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Chapter V: Summarized Substance Evaluation

Chapter contents

Preface

In order to provide a toxicological evaluation of industrially produced, unnatural substances or anthropogenically conditioned accumulation of natural compounds and elements, it is first important to question their occurrence in water, soil, air as well as in enclosed spaces and food; after all it is the hazardous concentration that is responsible for health problems and ecosystemic damage. It is therefore important to carry out reliable measurements with the help of protected analytical methods in order to safely exclude random results.

This is followed by examining the human being himself (Humanbiomonitoring). Besides the proof of already existing substances in the environment it is necessary to predict the occurrence of new substances in order to be able to justify an authorisation. The basis of such experimental calculations are physicochemical and biochemical data such as boiling point, melting point, vapour pressure, water volatility, atmospheric breakdown, in water and soil as well as biochemical degradation. Water solubility and fat solubility are important factors with regard to processes in food chains. It is also necessary to thoroughly analyse the p-H content of substances on the test bed.

Data on toxicokinetics and toxicodynamics have to be ascertained for subsequent toxicological evaluation. Animal experiments (if possible various animal species) have to be analysed firstly for the resorption of inhaled, orally and dermally ingested substances. Then questions concerning the metabolism of the organism are to be elucidated as it is not uncommon for metabolites to release higher toxicity than source compounds. In connection with an assessment of metabolites it is necessary to determine the half-lives of the various organs in order to make a clear statement concerning the accumulation of substances in the organism.

Based on this, toxic effects have to be analysed. Acute effects are less useful for a toxicological evaluation. Thus, a LD_{50} value can not be used for the detection of chronic toxicity. It is necessary to carry out extremely complicated long-term studies to demonstrate the dose-effect-curve that should enable the detection of damage to humans on a low-dose-level. Evidently, the most sensitive organ in humans and potentially the most affected in animal and plant species should be taken into account.

Besides effects on the respiratory organs, skin, nerval and immune system as well as allergic reactions, cancer-inducing properties have the highest place value. When a substance is considered cancerous then it has no place value, that means, minimisation is absolutely essential which eventually leads to a non-authorisation of that substance.

The evaluation criteria mentioned thus far have to be supplemented by observations and application of the substance. Risks during production and processing have to be examined as much as reactions in cases of fire, waste disposal or recycling. After all, it is necessary to examine official substance regulations to ensure they comply with the latest level of knowledge with respect to substances in need of evaluation.

For 12 flame retardants and one synergist the main chemical properties put forward in the preface were questioned. The provided data was firstly thoroughly researched and compiled into substance profiles. The results were substantially supplemented with information provided by the manufacturers.

Systematic recording of data, however, immediately shows how incomplete the substance profiles are. The incompleteness of data was taken into consideration when the following brief evaluations were made. They elucidate critical properties in each flame retardant but also insufficient examination. It is often shown that decisive evaluation criteria such as hazard data concerning the environment or examinations of cancer-inducing properties are missing so that a risk evaluation as well as an assessment of tolerance levels cannot be made.

After all, an evaluation of flame retardant groups can only be possible if these can be differentiated from risks to the health of humans and damages to the ecosystem.

These short evaluations should be read together with the substance profiles compiled in Volume III. General information with respect to examined substances (e.g. effect mechanism, use areas, use volume) can be found in Chapter III of this volume. A final summary is offered following the observation of each substance.[1]

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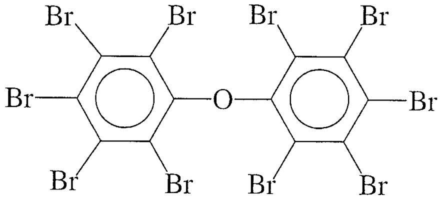
[1] Substance profiles documented in Volume III of this study serve as a basis for the following evaluation of single substances. The evaluated literature and other sources are listed together with the substance profiles. Comments made by the producers of flame retardants on the drafts of substance profiles are documented in the appendix of Vol.III. This commenting had been agreed upon during the second workshop within the framework of this project.

1. Decabromodiphenyl oxide (DeBDE)[2]

1.1 Substance properties

Decabromodiphenyl oxide is solid at room temperature and melts at 300°C. It is used as an additional flame retardant in a large range of polymers including High Impact Polystyrene, engineering thermoplastics, textile coating. The substance[3] has the chemical formula $C_{12}Br_{10}O$ (molecular weight: 959,22 Dalton) and the Cas-No. 1163-19-5. Thermal degradation starts at ca. 300°C. There is insufficient information as to the degradation products.



Bis(pentabromophenyl)ether (IUPAC-name)

Vapour pressure of 4.6×10^{-6} Pa at 21°C is relatively low. With respect to its behaviour in eco-systems, water solubility of only 0.1 µg/l water at 25°C is of significance. The octanol-water partition coefficient (stated as a logarithm) of > 5 indicates a tendency to bioaccumulation. While microbiotic degradation of DeBDE is not stated in the literature there is a report about photodegradation. DeBDE transforms into low brominated diphenyl oxides in the presence of UV- radiation.

Before 1970, technical DeBDE contained ca. 20% of Nonabromodiphenyl ether and a low percentage of low brominated diphenyl oxides. DeBDE currently used has a degree of purity of > 97%. Brominated dioxins and furans were not found in technical products.

1.2 Environmental effects

The sources of environmental effects can mainly be found on DeBDE production and processing sites. Further risks are created by the release of DeBDE and its degradation products from plastic consumer goods such as computer monitors, TV sets, instruments produced by the electronic industry during the application and recycling phase as well as the recycling of electronic and synthetic waste.

The analysis of DeBDE is very complicated. The analysis via a capillary gas chromatography coupled to a mass spectrometry has proven to be reliable after careful extraction from the matrix and the combination of various chromatographic steps of purification. The detection limits for environmental samples are at around 0.1 µg/kg material as well as 0.9 pg/m³ air.

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[2] See substance profile Decabromodiphenyl oxide, Vol.III, pp. 4-47.

[3] In Germany, Deca is not used on a voluntary basis anymore by association-bound companies in the plastics and textile industry.

Overview V/1: Decabromodiphenylether (DeBDE), CAS No. 1163-19-5 (additive)	
1. Physicochemical data	
1.1 Vapour pressure	4.6×10^{-6} Pa (21°C): low
1.2 Log $_{KOW}$	> 5: Bioaccumulation probable
1.3 Water solubility	0.1 µg/l: bad water solubility
2. Toxicology in humans	
2.1 Toxicokinetics	Concentrations in liver, kidney, spleen and fat
2.2 Acute toxicity	Oral: LD_{50} (Rat) > 2000 to > 5000 mg/kg Inhalative: LD_{50} (Rat) > 50 mg/l Dermal: LD_{50} (Rabbit) > 2000 mg/kg body weight DecaBDE is in acute form not toxic
2.3 Long-term toxicity (organs)	There is no data on long-term toxicity
2.3 Teratogenicity	No teratogenic effects up to 100 mg/kg body weight
2.4 Mutagenicity	Contradictory
2.5 Carcinogenicity	Cancer suspicion
3. Ecotoxicology	
3.1 Environmental occurrence	High concentration of sediments in rivers. Found in enclosed spaces.
3.2 Degradability	Persistent. There is evidence with regard to the breakdown of low brominated, more problematic BDE such as PentaBDE.
3.3 Accumulation	Accumulation in food chains not determined
3.4 Others	Distinct potential for dioxin and furan formation during combustion and recycling
4. Data situation	Relatively good, however, carcinogenicity equivocal
5. Balance	Application rejected

With respect to the occurrences of DeBDE in indoor air there are provisional estimates which are of little use in terms of risk evaluation. According to experimental calculations air pollution lies at around 0.5 µg/m^3 whereby ca. 50 % should be bound to particles. Oriented measurements show that these assumptions are unrealistically high. In rooms with TV screens and computers whose electrical parts are thermically contaminated, 0.5 to 3 µg DeBDE/g dust was found. In indoor air, BERGMANN et al. detected 0.08 ng DeBDE/m^3. On the contrary, KEMMLEIN did not find any DeBDE at a detection limit of 0.9 pg/m^3 in a computer training centre. Whether different DeDBE contents in the computer housings are responsible for these differences in concentrations was not examined. BALL indicated the total concentration of polybrominated diphenyl oxide with ca. 1 ng/m^3. Polybrominated dibenzofurans could be analysed in the average picogram area/m^3 directly on the TV. There is, in general, no reliable data with respect to occurrences in the air. Estimates start at around 4 ng DeBDE/m^3 in air. Between 20 ng and 25 µg DeBDE/m^3 outdoor air were measured in the vicinity of a production site. Air samples taken around Berlin did not show any DeBDE.

There are analyses of occurrences of DeBDE in sediment. While 200 to 1700 µg/kg solid weight were found in European river mouths, the background concentrations of the river sediment lies clearly below 5 µg/kg solid substance.

It is remarkable that there is a stronger accumulation of DeBDE in comparison to other polybrominated DE in the sediment. This can be explained with the high affinity of DeBDE to particles.

Swedish scientists found 160 to 260 µg/kg solid substance in sewage sludge.

No DeBDE concentrations > 1 µg/kg wet weight (detection limit) have so far been detected in food chains. DeBDE concentration slightly above the detection limit (shells) can only be found close to the DeBDE sources. To complete the picture one should refer to analyses carried out on mother's milk which merely confirm concentrations of low brominated diphenyl oxides in the lower µg area/kg of the fat in mother's milk. These results lead to the conclusion that the bioconcentration of lower brominated DE is higher than that of DeBDE.

1.3 Toxicology

The resorption of DeBDE was tested on rats indicating a resorption rate of around 6% after oral ingestion. Data concerning inhalative resorption was not found in the literature. Resorbed DeBDE is, as experiments with radiolabelled DeBDE show, accumulated in the liver, suprarenal gland, spleen and fat.

There is no reliable data concerning half-life values in the indicated tissue. It is, however, reported that fat accumulation "perseveres for over 90 days".

The metabolism of DeBDE is not elucidated.

There are results from animal experiments concerning the toxicity of DeBDE. Organs that are affected are the liver (increase of liver weight at a dosage of 800mg/kg body weight over a period of 14 days) and kidneys (degeneration of the kidney tissue at a dosage of 800 mg/kg body weight over a period of 30 days). Data concerning the effects on mucous membranes and skin is contradictory. While animal experiments do not show eye irritation and skin sensitisation, affected workers do complain of skin irritation and dermatitis when exposed to the solvents. It is not clear whether DeBDE has an endocrine effect or whether it attacks the immune system.

With regard to the toxicological evaluation, the analysis of carcinogenicity will be of decisive importance.

Feeding of 3500 to 7000 mg DeBD/kg body weight to mice and 1200 to 2400 mgDeBDE/kg body weight to rats suggests an elevated risk of cancer in the liver, pancreas, thyroid gland as well as a risk of leukaemia. The results are not clear. This could have to do with cancerogenic impurities of the DeBDE. As numerous mutagenic tests were negative, DeBDE is not classified as genotoxic. Examinations on BASF-workers were carried out. However, due to the small collective of people a statistical analysis cannot be carried out. Remarkable, however, is the higher occurrence of gullet cancer, rectum carcinoma- and duodenal cancer in a small group of exposed workers. Due to contradictory results no classification of NTP and IARC for carcinogenicity was made.

As a result of the existing suspicion of cancer, any deduction of an acceptable daily dosages for humans can only be possible with great reservation. Details as to cancer risks with the help of unit risk-values also can not be given due to the unsafe data situation.

With regard to non-cancerogenic organ damages the lowest NOEL dosage of 8mg/kg body weight day is indicated in the literature. From this it is possible to calculate a TDI value of 8 µg/kg body weight day with a safety factor of 1000. This dosage does not protect from cancerogenic risk.

1.4 Ecotoxicology

Concentrations which do not affect invertebrates, fish and seaweed can be found under 2 µg DeBDE/l water in the literature.

1.5 Fire case

In a case of fire, carbon oxides and hydrobromic acids are released which are irritable to the mucous membranes and lead to corrosion of metal devices. The formation of dioxins and furans during thermal use of DeBDE-containing plastics in fires has been recorded in numerous examinations. In wiping samples after fires Tetra-, Penta-, Hexa-, Hepta- und Octabromodibenzofurans are detected in concentrations of up to 120ng/m^2.

1.6 Post-application phase

Attempts of leaching of DeBDE-containing plastics under various circumstances indicate a low depletion such that the risks for ground water can be evaluated as low.

Several examinations of incineration plants confirm the formation of significant amounts of dioxins/furans in DeBDE-contaminated combustion products. In connection with DeBDE-containing plastics during combustion it is necessary to question the effectiveness of filter technologies in cleaning fumes from dioxins and furans.

The release of Deca during the recycling process should be seen as problematic. Air pollution of 11.5 to 70 ng/m^3 was measured during the dismantling of electronic devices in a recycling plant for electronic waste. 5 µg DeBDE/kg blood fat (median value) was detected in the blood of the workers.

To complete the picture one ought to refer to occurrences of Bromodibenzodioxins and -furans in recycled material. Occurrences of highly toxic 2,3,7,8 - polybrominated Dibenzodioxins and -furans in products after recycling DeBDE-contaminated plastics are particularly problematic. From these observations it can be concluded that DeBDE is a particularly dioxin laden compound.

1.7 Substance regulations

Limit values for DeBDE-contaminated products recorded in the German Ordinance for Dioxins are 1 µg (sum of four 2,3,7,8 substituted Tetra - and Pentabromodibenzodioxins and -furans) and 5 µg (sum of eight 2,3,7,8- substituted Tetra-, Penta- and Hexabromodibenzodioxins and -furans).

1.8 Conclusion

DeBDE, which is used as an additive flame retardant, belongs to the group of brominated diphenyl oxides. Accumulations of DeBDE have, contrary to low brominated diphenyl oxides, not been detected in food chains up until now.

As expected, DeBDE contamination was detected in indoor and outdoor air as well as in the sediment of river estuaries, the latter showing a significant degree of concentration in the proximity of DeBDE manufacturing and processing plants. Together with the occurrence of DeBDE in indoor air there is an occurrence of brominated furans, as measurements taken in the proximity of computers show.

Experiments conducted to determine the toxicity of DeBDE show an accumulation in the fat tissue of guinea pigs and effects on the liver and kidneys. The effects on eyes and skin are contradictory. Whilst animal experiments show negative results, occupational medicine makes references to skin and eye irritation.

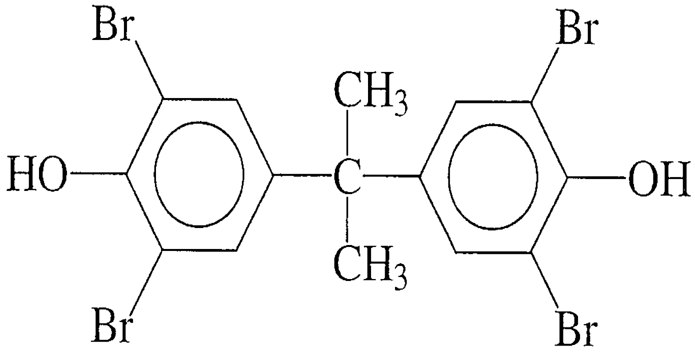
Particularly alarming are references to the cancerogenic effects of DeBDE in animal experiments as well as in exposed workers.

A considerable amount of brominated dioxins and furans is formed during outbreaks of fire, incineration of incineration plants and recycling processes. It is particularly important to highlight the high potential for furan formation during thermic processes. The results available lead to the conclusion that DeBDE, as a flame retardant, should be substituted due to its occurrence in sediment, in enclosed and open spaces, although its accumulation in food chains is comparably lower than that of lower brominated diphenyl oxides.

2. Tetrabromobisphenol A (TBBA)[4]

2.1 Substance properties

Tetrabromobisphenol A (official name: 2,2',6,6'-tetrabromo-4,4'-isopropylidene-diphenol) is a crystalline solid which melts at 182°C as pure compound and has a boiling point of 316°C. There is no data concerning the temperature in thermic degradation. TBBA is mainly applied as reactive flame retardant (ca. 80%) in epoxide resins and additionally applied in various, foremost technical thermoplastics. TBBA has the chemical formula $C_{15}H_{12}Br_4O_2$ (molecular weight: 543.9 Dalton), the Cas-No.79-94-7 and the chemical structure



Due to the aromatic bridging with carbon, the potential for furan and dioxin formation is reduced. The technical product is polluted with small amounts (< 1%) of low brominated phenol and with bromine. Toxicologically relevant are brominated dibenzofuranes and -dioxins detected in the region between 10 and 30 µg/kg TBBA in 1986. Whether there are occurrences of 2,3,7,8 substituted dioxins and furan that are particularly toxic for humans, is dealt with in a contradictory way in the literature.

TBBA's vapour pressure should not to be neglected for its ~ 1.3 mbar at 20°C. A transition to indoor air can not be ruled out.

There is no data concerning the evapouration of additive TBBA in connection with water (vapour volatility). However, it is assumed due to its phenolic structure.

Water solubility is recorded at 25°C with 4.16 mg/l. Despite its striking water solubility, the octanol-water partition coefficient (indicated as logarithm) is at ca. 5, so that accumulations in aquatic food chains can be assumed. Additionally, a high persistence (half-life ranging from 7 to 80 days - depending on season - in water) favours the bioconcentration.

Half-life in air is calculated between 5 and 6 days. 8 degradation products were identified in core chambers under UV irradiation (254nm).

With regard to bioaccumulation it should be added that a methylation of phenolic OH groups into mono and dimethyl oxides takes place in the sediment that are more

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[4] See substance profile Tetrabromobisphenol A, Vol. III, pp. 48-75.

lipophilic than the source compounds. Thus, one should assume a bioaccumulation of oxide in aquatic food chains.

Overview V/2:Tetrabromobisphenol A (TBBA), Cas-No. 79-94-7 [reactive/additive]	
1. Physicochemical data	
1.1 Vapour pressure	Ca. 130 Pa: modest; a transition to indoor air can not be excluded.
1.2 Log $_{KOW}$	5; Bioaccumulation probable
1.3 Water solubility	4.16 mg/l (25^{o}C): average
2. Toxicology in humans	
2.1 Toxicokinetics	Accumulation in liver and gonads
2.2 Acute toxicity	Animal experiments showed that skin and mucous membranes were affected first.
2.3 Long-term toxicity (organs)	Inhalative toxic LOAEL for damages on organs (rat): > 100mg/kg body weight Weak oestrogenic effects
2.3 Teratogenicity	No signs of teratogenic effects in animal experiments
2.4 Mutagenicity	No signs of mutagenic effects in animal experiments
2.5 Carcinogenicity	There are no studies on cancerogenicity
3. Ecotoxicology	
3.1 Environmental occurrence	Detected in enclosed spaces, mother's milk and sewage sludge. Accumulation in food chains. High concentration in sediments close to point sources.
3.2 Degradability	Persistent.
3.3 Accumulation	Detected in food chains (particularly in aquatic)
3.4 Others	High toxicity for water organisms. Potential for the formation of dioxins and furans reduced by carbonisation.
4. Data situation	Generally good. Analysis for cancerogenicity is missing.
5. Balance	Application of additive TBBA rejected, substitution for reactive TBBA desirable

2.2.Environmental risks

The analysis of TBBA and its methylated oxides is complicated. After careful separation of the matrix via extraction, the identification and quantification is most successful with the help of a capillary gas chromatography coupled with a mass spectrometry.

Measurements taken in outdoor air were without result (detection limit is not indicated). 1.8 µg TBBA/m^3 were analysed in the region of TBBA manufacturing sites.

There is equally no systematic examination with regard to TBBA occurrences in enclosed rooms. However, occasional single measurements taken from samples in air dust and home dust show occurrences of TBBA. We are familiarised with the fact that 2 laboratories were able to analyse several milligrams TBBA/kg dust in house dust aliquots.

Due to its tight bond to particles, an elevated TBBA concentration was, as expected, found in water close to TBBA manufacturing sites: Downstream from a factory up to 330g TBBA/kg sediment was measured.

Background concentrations of rivers into which sewage is released are at round 20 µg/kg dry substance for river sediment in Germany. Similar values were reported from the USA and Japan. With respect to occurrences in the water only Japanese data is available. A background load of ca 50 ng/l water is reported. Further analyses concerning background loads are absolutely necessary.

Soil was only examined for TBBA in exceptional cases. A TBBA content of ca. 200 ng TBBA/kg dry substance was for measured close to a production site. Swedish sewage sludge contained 3 to 75 µg TBPA/kg dry substance in 1998. If this contaminated sludge is regularly applied on cultivated land it is no surprise that TBBA concentrations of some ng/kg soil-dry substance can be found.

TBBA and methylated derivatives are accumulated in food chains as the octanol-water partition coefficient suggested. This is particularly valid for the aquatic food chain. While KEMMLEIN (2000) was able to detect 0.5 to 1 µg TBBA/kg in samples of fish fat, Japanese found 1-5 µg methylated TBBA /kg wet weight in shell fish in 1985.

It is, with respect to a toxicological evaluation, particularly important to point out that TBBA was recently analysed in samples of mother's milk: KEMMLEIN finds up to 1 µg TBBA/kg fat in mother's milk in samples of mother's milk taken in Berlin; 11 µg TBBA/fat in mother's milk were even measured in Danish samples of mother's milk. Further analyses of mother's milk will be unavoidable thanks to these indications.

2.3 Toxicology

There are neither results stemming from sound animal experiments nor any conclusions drawn from humans with regard to resorption rates after inhalative and oral exposure. Rat experiments only show that a single, orally fed dose of TBBA accumulates after resorption in the liver and gonads. The half-life of the substance in various organs in rats ranges between one day (liver) and three days (fat tissue). Excretion is made entirely unmetabolised via faeces. Half-life in blood is indicated with 20 hours.

There are no findings of TBBA toxicity in humans. Animal experiments show that targeted organs for first effects are mucous membranes (nose bleeding), skin (slight formation of erythem after application on sore skin), eye (rash of the connective tissue) and the enzymes system (microsomic induction). Furthermore, a weak oestrogenic effect of TBBA is reported. Effect-triggering doses are high.

It is alarming that there are no studies on cancerogenicity of TBBA. Animal experiments do not show any indication of mutagenic or teratogenic effects of TBBA.

Details given by a NOAEL are only possible under reservation as no information on cancerogenic risks exists. The lowest dose causing organ damage (LOAEL) is indicated in the literature with > 100 mg/kg body weight (rat). With regard to the transference to humans, the environmental office suggests an increase of the common factor, valid for non-cancerogenic substances, from 100 to 1000. This results in a *TDI* value (daily tolerable ingestion) of 0.1 mg/kg body weight. This value should, however, only be used for an approximate risk evaluation. Under caution, the risk evaluation results in the statement that TBBA concentrations detected in indoor air are neglectably low.

2.4 Ecotoxicology

TBBA concentrations in water of 1 to 10 µg/l cause effects in 50 % of invertebrates according to laboratory experiments. Even fish react to TBBA at a concentration between 150 and 300 µg/l. With regard to TBBA effects on microorganisms in the soil, plants and animals there is no information found in the literature.

2.5 Fire

In case of fire, as discovered during a major fire in which considerable amounts of TBBA were burnt, 2,3,7,8 - substituted tetra-, penta, and hexabrominated dibenzofurans and dioxins were produced. The concentrations are in the average nanogram area/kg fire dust. The relatively low concentrations correspond well with predictions made from the TBBA structure.

2.6 Post-application phase

During the combustion of TBBA-containing polymers in waste incinerators, polybrominated dibenzofurans and dibenzodioxins are formed. A complicated cleaning of fumes is necessary in order to ensure tolerable emission concentrations.

There is no information concerning the possible gradual loss of TBBA on landfills. New studies conducted by RIESS (1999), however, show that TBBA of *ABS* can be mobilised of up to 98.4 % in connection with lipophilicity of the solvent. It is particularly interesting for the behaviour of TBBA-containing plastics on disposal sites that the mobilising part of TBBA can increase when the temperature rises.

The recovery of copper and synthetic material from circuit boards containing TBBA flame retardant was not harmless: Dioxin and furan concentrations of 30 ng to 1 µg/kg material were detected In shredded circuit boards. The concentration rose by 4.5 µg/kg under thermic influence of up to 300^{o}C. Dioxin and furan formation is favoured in warmth through the catalytic effect of copper on circuit boards. Concentrations measured are below the detection limits of the dioxin ordinance.

2.7 Substance regulation

TBBA is considered harmful to the environment (classification N). It is also labelled as poisonous for water organisms (R50-53). The release of TBBA into the environment should be avoided (S61). There are special conditions concerning its disposal. (S60).

Detection limits for TBBA-containing products, subject to the values of 1 µg (sum of four 2,3,7,8 - substituted Tetra- and Pentabromodibenzodioxins and furans) and 5 µg (sum of eight 2,3,7,8 - substituted Tetra-, Penta- and Hexabromodibenzodioxins and furans) per kg product according to the dioxin ordinance, are to be referred to.

2.8 Conclusion

TBBA is a four times brominated, carbon reconciled diphenol, which is applied as reactive flame retardant on e.g. epoxide resins. While its release into the environment is not disturbing, emissions can be given off when it is used as additive flame retardant in casing materials and technical thermoplastics. The potential for the formation of dioxins is low due to aromatic bridging. An average water solubility in correlation with the persistence and the octanol/water-coefficient of 5, leads to an accumulation in the sediment (background concentration ~ 20 µg/kg sediment) of aquatic systems. It also leads to an accumulation of between 0.5 and 1 µg TBBA/kg samples of fish fat in inshore waters with undefined hazards. The current detection of TBBA in samples of mother’s milk is alarming.

As expected, TBBA can be found both in home dust and indoor air.

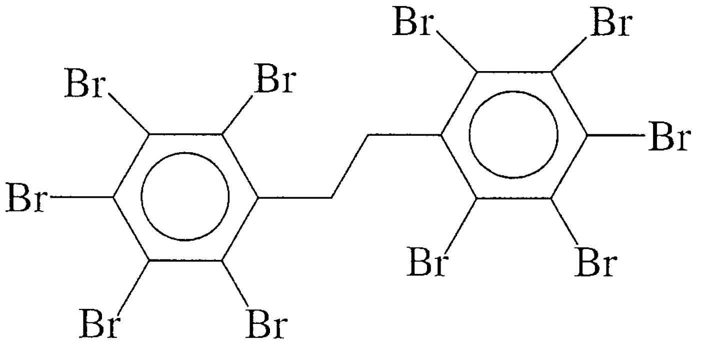
There are experiments on rats with regard to toxicokinetics. TBBA is excreted mostly unmetabolised after a half life of 20 hours in the blood. Accumulation in organs is unknown. Organ damage come down to effects on mucous membranes and eye irritations under intense concentrations. There is no data on cancerogenicity. With respect to ecosystems it is striking that water concentrations of 1-10 µg/l damage invertebrates by 50 %. While levels of dioxin and furan formations remain low in fire, 4.5 µg were detected in shredded circuit boards for the sum of the dioxins and furans per kg shredded goods.

In summary, further use of TBBA cannot be recommended due to the fact that TBBA has found a way into the food chain. This statement is based on a considerable level of toxicity and the lack of studies conducted on cancerogenicity.

3. 1 Bis (pentabromophenyl) ethane (Saytex 8010) [5]

3.1 Substance properties

1,2 - Bis - (pentabromophenyl) ethane is a crystalline substance which melts in its pure form at 361°C. The substance composition is $C_{14}H_4Br_{10}$ and thus has a molecular weight of 971,2 Dalton. Its Cas-No. is 84852-53-9. The structure formula of Saytex 8010 shows that the compound has, due to its aromatic bridging by two carbons, a reduced potential to form dioxins.



The product which is mainly used as additive flame retardant for electric parts (Polystyrene, Polyamide, Polyolefin) is, at a minimum of 98,5 % 1,2- bis (pentabromophenyl)ethane, relatively pure. The principal impurity is Nonabromodiphenylethan. In synthetic material, treated with flame retardant made of 1,2- bis (pentabromophenyl)ethane, the sum of toxicologically relevant impurities (eight 2,3,7,8- substituted congener of brominated dioxins and furans) was below detection limit (0.02-0.03 µg/kg). They contained a maximum of 64 µg Tetra - Octabrominated dioxins and furans.

Vapour pressure of Saytex 8010 is very low at $< 1 \times 10^{-4}$ Pa at 20°C. No significant concentrations in indoor air of enclosed spaces containing plastics with Saytex 8010 are assumed. Water solubility is very low at 0.72 µg/l. The octanol/water-coefficient (decade logarithm) is 3.2. Accumulation in food chains are assumed.

The compound is thermically stable up to 300°C. Data on light stability can not be found in the literature. Decomposition observed under the effect of xenon light can not be transferred to the real breakdown. However, it is assumed that bromine separates under the influence of light. Brominated diphenyl ethanes are formed as a result of that. There is no data available concerning acid and base stability.

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[5] See substance profile of 1,2 - Bis - (pentabromophenyl) ethane, Vol.III, pp 76-90.

Overview V/3: 1,2- Bis (pentabromophenyl)ethane, Cas-No. 84852-53-9 [additive]	
1. Physicochemical data	
1.1 Vapour pressure	<1 x 10^{-4} Pa (20°C): very low
1.2 Log $_{KOW}$	3.2: bioaccumulation possible
1.3 Water solubility	0.72 µg/l: very low water solubility
2. Toxicology in humans	
2.1 Toxicokinetics	There is no data concerning resorption and metabolism
2.2 Acute toxicity	Oral: LD_{50} (rat) > 5000 mg/kg Dermal: LD50 (rabbit) > 2000 mg/kg body weight
2.3 Long-term toxicity (organs)	NOEL 1000 mg/kg body weight
2.3 Teratogenicity	Not specified
2.4 Mutagenicity	Not specified
2.5 Carcinogenicity	There are no studies on cancerogenicity
3. Ecotoxicology	
3.1 Environmental occurrence	Not specified
3.2 Degradability	Moderate
3.3 Accumulation	No detection of accumulation in food chains
3.4 Others	Low potential for the formation of dioxins and furans during combustion and recycling
4. Data situation	Unsatisfying, study on cancerogenicity not available
5. Balance	Due to the data situation recommendation impossible

3.2 Environmental risks

There is no data concerning the occurrence of Saytex 8010 in indoor air, domestic dust, outdoor air, soil and water. It could be difficult to find evidence in aforementioned media due to the complicated analysis and moderate hazards. It is all the more important to use improved analytical methods to search for 1,2- bis -(pentabromophenyl) ethane on the end points of food chains and sewage sludge at an early stage. Fish and sediment downstream from manufacturing and processing sites provide good samples. Blood and fat tissue of affected workers should also be analysed.

3.3 Toxicology

No data concerning inhalative, orally and dermally ingested substances could be found despite feeding attempts (rats) with Decabromodiphenyl oxide in order to detect damaging effects. The authors report that absorption is “not significant”. There is also no data available on metabolism and half-life values. Accumulation in fat tissue is ruled out although the structure and the octanol/water-coefficient offer reason to believe the opposite.

Experiments on rats confirm toxic effects: Rats were fed 100, 320 and 1000 mg Saytex 8010/kg animal feed over a period of 90 days. At a dosage of > 320 mg/kg feed, changes in the lungs were detected. At a dosage of > 1000mg/kg animal feed cellular life changes were detected. No changes on kidneys, heart, hormones and immune system could be observed at the highest dose of 1000 mg Saytex 8010/kg feed. The substance has no irritating effect on mucous membranes. Possible allergic reactions were not analysed. Mutagenicity tests were negative. A long-term observation on cancerogenicity was dispensed of. The manufacturer indicates a NOEL of 1000 mg/kg body weight day. As cancerogenicity was not examined, a safety factor of 100 x 10 = 1000 (additional factor 10 if no analyses to carcenogenicity are available) should be taken into account when transferred to the TDI value for humans. From this results a TDI value of 1000 µg/kg body weight. Accumulation in the fat tissue of humans at this dosage should not be excluded.

3.4 Ecotoxicology

There are no examination results available with regard to the accumulation of Decabromodiphenyl oxide. With respect to fish toxicity, manufacturers indicate concentrations which can not dissolve in water.

3.5 Fire

In case of fire or during thermic influence > 320°C hydrobromic acid, bromine and carbon oxides are formed from Decabromodiphenyl oxide. Data that was collected during combustion attempts confirm the assumption of a strongly reduced potential for dioxin and furan formation.

3.6 Post-application phase

The manufacturer has not excluded the release of Saytex 8010 from plastics on disposal sites.

Various results concerning formation of dioxins and furans during combustion of HIPS armed with Saytex 8010 are provided. Whilst on one hand 2,3,7,8 - substituted dioxins and furans lay below their respective detection limit of 0.1 - 100 ppb, other examinations illustrated a furan concentration of up to 47.5 µg 2,3,4,7,8, - PBDF/kg. To what extent it is possible to remove concentrations from the fumes depends on how effective cleaning techniques at the respective incineration sites are.

Recycling of Saytex-containing plastics is possible: Even after recycling five times, dioxin and furan concentrations lay below maximum amount indicated in the dioxin ordinance.

3.7 Substance regulation

No data available.

3.8 Conclusion

The flame retardant Saytex 8010 is an entirely, at the aromatic structure brominated Diphenyl ethane. This structure has the effect that the potential for dioxin and furan formation under acute thermic influence is strongly reduced. Traces of brominated dioxins and furans can nevertheless be found in end products. No significant environmental concentrations have to be expected due to low vapour pressure and an octanol/water-coefficient of 3.2. Environmental supervision is necessary in order to anticipate possible environmental hazards in case of increased use of Saytex 8010.

The toxicology of Saytex 8010 has not been sufficiently analysed. This is true for both toxicokinetics and cancerogenic effects. The compound continues to be suspicious unless reliable results from animal experiments regarding cancerogenicity are provided.

Hydrobromic acid and bromine are formed in fire. Concentrations of dioxins and furans are, according to combustion experiments, moderate in comparison to PBDE. While the manufacturer cannot rule out a gradual loss of Saytex 8010 on disposal sites, examinations show that combustion at incineration sites is less problematic.

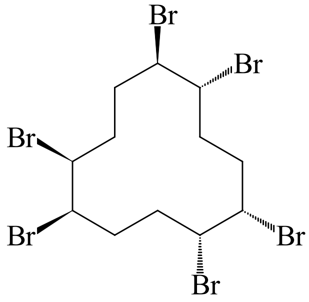
Dioxin and furan concentrations in products, that were recycled five times, were still below the legal maximum amount during recycling.

In summary, it is, seen from a toxicological point of view, necessary to undertake further analyses before it is possible to pass a final verdict on the use of Saytex 8010.

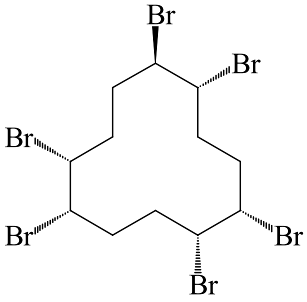
4. Hexabromocyclododecane (HBCD)[6]

4.1 Substance properties

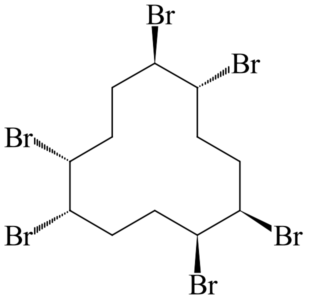
Hexabromocyclododecane is a colourless solid that melts at 195°C. This substance which is used as flame retardant has the chemical formula $C_{12}H_{18}Br_6$ (molecular weight: 641,7 Dalton) and the Cas-No. 3194-55-6. Thermic decomposition of HBCD starts at 230°C. A technical product containing 3 isomeric forms of the HBCD is used as flame retardant.



α Isomer



ß Isomer



γ Isomer

Additives, which are not laid open, are used in order to stabilise the technical product. HBCD is used as an additive flame retardant in combination with Antimony trioxide or Dicumylperoxide. Whether Dicumylperoxide is released from the product treated with the flame retardant is unknown. HBCD has impurities caused by Cyclododecane which are substituted with less than 6 bromine atoms. Vapour pressure of HBCD is very low at 6×10^{-5} Pa room temperature. With regard to the evaluation of its behaviour in ecosystems, the low level of water solubility of only 3.4 µg/l water at 25°C has to be mentioned. An accumulation in the food chain is assumed due to the octanol/water- partition coefficient (stated as logarithm) of ca. 6 and the persistence of HBCD. HBCD is not biologically degraded within 28 days and so the conclusion is drawn that HBCD is badly biodegradable under aerobic circumstances.

4.2 Environmental risks

The use of HBCD as additive flame retardant in Polystyrene (it is mainly used for this) and textile coating has already lead to environmental hazards. This is particularly true for manufacturers using HBCD in the textile production who, with their sewage, cause hazards in aquatic systems around the site.

The analysis of HBCD in environmental samples has proven to be difficult. Reliable data after a careful sample preparation depends on the capillary gas chromatography coupled with a mass spectrometry. Data on concentration results is not at all representative so far. It merely serves as orientation: too little data has been elaborated with barely ripened analytical methods.

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[6] See substance profile of Hexabromocyclododecane, Vol.III, pp. 91-122.

Swedish scientist found HBCD at a concentration level of approximately 6 pg/m^3 in outdoor air. Particle-bound HBCD subsides in outdoor air.

No HBCD has been detected in indoor air so far.

Overview V/4: Hexabromocyclododecane (HBCD), Cas-No. 3194-55-6 [additive]	
1. Physicochemical data	
1.1 Vapour pressure	6 x 10^{-5} Pa (room temperature): very low
1.2 Log $_{KOW}$	Ca. 6: bioaccumulation probable
1.3 Water solubility	3.4 µg/l (25°C): very low water solubility
2. Toxicology in humans	
2.1 Toxicokinetics	Evidence of accumulation in fat tissue
2.2 Acute toxicity	Oral: LD$_{50}$ (rat) > 1000 to > 10000 mg/kg Inhalative: LD$_{50}$ (rat) > 200 mg/m^3 Dermal: LD$_{50}$ (rabbit) > 8000 to > 20000 mg/kg body weight
2.3 Long-term toxicity (organs)	LOEL (mouse) 13 mg/kg body weight
2.3 Teratogenicity	Not specified
2.4 Mutagenicity	Not specified
2.5 Carcinogenicity	Not specified
3. Ecotoxicology	
3.1 Environmental occurrence	Partly high accumulation in sediment (point sources of the textile industry)
3.2 Degradability	Moderate
3.3 Accumulation	Persistent, no detection in food chains
3.4 Others	Low potential for the formation of dioxins and furans
4. Data situation	relatively good
5. Balance	Reduction sensible

Reliable data on hazards for water and sediment is also missing. Due to a reduced water solubility of HBCD and due to its striking ability to bind itself to particles, water should be less contaminated. Sediment, on the other hand, should be more contaminated. The background value for superficial water is indicated with 5-29 ng HBCD/l in the literature. Due to point sources (e.g. textile industry), concentration in sediment can be extremely variable. In Japanese sediment, 20 - 90 µg HBCD/kg sediment were found as general background concentration in 1986/87. Swedish scientist found ca. 1.600 µg/kg sediment (dry substance) in polluted river regions in 1999.

No data on HBCD measurements on soil can be found in the literature. The estimated levels of concentration between 5 and 1.630 µg/kg soil, based on models, should be unrealistically high as hazard levels in the air are minor. Data on contaminated sewage sludge could exist. Swedish scientist found evidence of ca. 50 µg HBCD/kg sewage sludge - dry substance. Whether these concentrations are toxicologically relevant depends on the degradability of HBCD in soil and the transfer factors soil/plants. Unfortunately, there is no data available for both factors.

The occurrence of lipophilic HBCD in food chains is of interest, as humans are primarily reached by HBCD concentrations via food. Estimations according to which

7 – 3600 µg/kg could be contained in food (theoretically deduced value for fish) and amounts of HBCD taken in at 39 µg/kg body weight via all routes, depart from emission levels which are clearly too high, according to new measuring levels.

HBCD could neither be detected in samples of human milk taken in the new German states nor in samples of cow milk taken in the region of Brandenburg and Westphalia (detection limit ca. 0.1 µg/kg fat). In one case a high level of HBCD concentration was found in fish (Sweden, in the region of textile suppliers, 8 mg/kg muscle fat).

4.3 Toxicology

Examinations on rats in order to elucidate toxicokinetics show that there is a deployment into liver, kidneys, gonads and fat tissue after the almost complete resorption of a single, orally fed dose. Elimination from the blood occurs in two phases with half-lives ranging between 4 and 17 hours. Breakdown in the fat phase takes significantly longer. Figures on half-life are, however, not available. A moderate part of HBCD seems to metabolise at an increased dosage. The source substance and 4 metabolites formed during degradation, of which the structure is undetermined, are excreted via faeces (72%) and urine (16%).

A toxicological evaluation of HBCD taken in via inhalation and food on a daily basis is insecure as findings with regard to toxicity in humans are insufficient. Reliable data of the effect of low doses in animals during chronical exposure is also unsatisfying. HBCD doses of 90 mg/kg body weight day in rats result in changes of liver weight. Skin contact causes inflammation and skin irritability.

Data on inhalative toxicity is contradictory. Indications range from ‘no effects’ to ‘irritation of the respiratory tract’.

Animal experiments do not offer any hints as to teratogenic and mutagenic effects. It is possible to deduce a tolerance value for daily intake via food and air with the help of a LOEL (lowest observed effect level). This is based on a long-term experiment on cancerogenicity in HBCD, carefully carried out on mice. This experiment offered no sign of a cancer-inducing effect.

A 18 month long feeding experiment for mice shows a LOEL of 13 mg/kg body weight day with regard to liver modifications. By starting at this value and by taking a safety factor of 100 into account it is possible to obtain a daily tolerable HBCD intake of ca. 130 µg/kg body weight and day.

As the aforementioned toxicological evaluation does not take any combinatory effect into account and is based on a few animal tests, the obtained tolerance value should be handled carefully. Further animal tests are necessary. Moreover, real exposure is largely unrecorded.

4.4 Ecotoxicology

A significant level of accumulation in fatty compartments of living organisms is feared due to the high octanol/water coefficient. The consequences of an accumulation of

HBCD in the single living organism are not elucidated. There is only a EC_{50} - data for invertebrates and a LC_{50} - data for fish which shows that HBCD can be toxic for these organisms.

4.5 Fire

In case of fire, HBCD produces, among other substances, hydrobromic acid, carbon monoxide, bromine and in traces dioxins and furans with bromine substitutes. Studies carried out on the formation of dioxins in fires, however, indicate that no significant dioxin increase in fly ash can be detected as a result of occurrences of HBCD in fires

4.6 Post-application phase

The disposal of HBCD-containing synthetic materials on disposal sites is not without risks as eluate experiments show that synthetic materials release HBCD. Whether eluent concentrations can reach the ground water or remain tightly bound to disposed materials has not been examined.

Examinations carried out on fumes at incineration sites have shown that concentrations of brominated dioxins and furans in exhaust fumes are not elevated when HBCD is added to the products of combustion.

4.7 Substance regulation

According to the criteria of the Ordinance for Hazardous Substances, the Umweltbundesamt suggests a classification into Class N (dangerous to the environment) and a labelling of R 53 (can be hazardous to water). The Risk-Assessment recommends a classification according to R 50/53 due its negative biodegradability, its high lipophilic and its effects on water organisms. A classification according to R 43 should be made as a result of such sensibilizing effects.

4.8 Conclusion

HBCD, as additive flame retardant, can be transmitted to environmental media. There is at the moment no incriminating evidence. HBCD has not been detected in indoor air. HBCD discharge in river sediment close to textile manufacturing sites, however, is problematic. With the exception of a single finding (fish in the region of a textile supplier) it was not possible to detect HBCD in the food chains despite a high octanol/water coefficient.

As the results of the food analysis do not correspond with the estimates made in relation to the daily HBCD intake of 39 µg/kg body weight, a systematic analysis of the end points of the food chains needs to be carried out. Alternatively, provisional estimates need to be revised.

Toxicological examinations only indicate striking features for eyes: Sensibilization and inflamation are reported. On the contrary, long-term tests on mice show neither teratogenic nor cancerogenic effects. It is possible to toxicologically support a TDI value at the level of 139 µg/kg body weight based on this results.

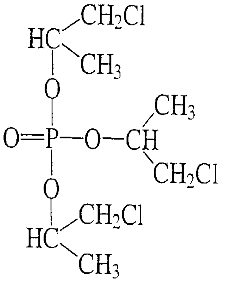
It is not possible to detect elevated concentrations of brominated dioxins and furans during waste combustion and during a case of fire. A gradual loss on disposal sites is likely.

Despite the small amount of incriminating results, a significant residual risk remains. It is based on analytical examinations of occurrences in food chains that are still due.

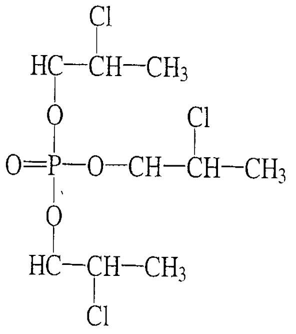
5. Tris (1-chloro-2-propyl) phosphate [7]

5.1 Substance properties

Tris (1-chloro-2-propyl) phosphate is liquid at room temperature and has a boiling point of about 342°C (melting point: approximately - 40°C). Its molecular weight amounts to 327 Dalton ($C_9H_{18}Cl_3O_4P$). The al-iso-Form is registered under Cas-No. 13674-84-5. As technical product (mainly as additive flame retardant in polyurethane foams), a mixture of the following isomers is put on trade



iso-Form



There are two other forms. A mixture of both structures, as shown above, dominate (sum approximately 90%) in most of the products. The incineration point of the isomer mixture is 200°C. The compound starts to disintegrate at 150°C. Phosphorus acid and chloropropanole are formed in the presence of acids and bases. These are suspected of inducing cancer, as tests on animals indicate.

Vapour pressure of this mixture of isomer is ca. 100 Pa at 20°C. Moderate transmissions of TCPP from open sources into indoor air can thus not be excluded. TCPP is, with ca. 1g/l, well-soluble in water. The octanol/water coefficient is approximately 3. If you take into account that TCPP is difficult to break down, it has to be assumed that the isomer compound might accumulate in food chains.

5.2 Environmental risks

Isomers, which can be analysed with the help of a gas chromatography (electronic entrance detector), are widely spread in the environment. While no hazard data is available for outdoor air, there are results which document the occurrence of TCPP in aquatic systems. Detectable concentrations range between 0,05 and 10 µg/l. water. In view of the accumulation potential of TCPP, tolerable concentrations in water should clearly lie below 0.1 µg/l. River sediment shows an accumulation of up to 165 µg/kg dry substance. There is no data with respect to occurrences in sewage sludge and soil.

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[7] See substance characterisation Tris (1-chloro-2-propyl) phosphat, Vol.III, pp.124-150.

Overview V/5: Tris(1-chloro-2-propyl) phosphate, Cas-No. 13674-84-5 [additive]	
1. Physicochemical data	
1.1 Vapour pressure	100 Pa (20°C): moderate
1.2 Log $_{KOW}$	Ca. 3: Bioaccumulation can not be excluded
1.3 Water solubility	Ca. 1g/l: good solubility
2. Toxicology in humans	
2.1 Toxicokinetics	Accumulation in liver and kidney
2.2 Acute toxicity	Oral: LD_{50} (rat) 500 - 4200 mg/kg body weight mg/kg Inhalative: LD_{50} (rat) > 4.6 mg/l to > 17.8 mg/l Dermal: LD_{50} (rabbit) 1230 to 5000 mg/kg body weight TCPP is not acutely toxic
2.3 Long-term toxicity (organs)	There is little data on long-term Tox., NOEL: 36 mg/kg body weight
2.3 Teratogenicity	No data on teratogenic effects
2.4 Mutagenicity	Data on mutagenicity
2.5 Carcinogenicity	There are no analyses. Suspicion of cancerogenicity.
3. Ecotoxicology	
3.1 Environmental occurrence	Detection in water, sediment and house dust
3.2 Degradability	Moderate
3.3 Accumulation	No detection of accumulation in food chain.
3.4 Others	WGK 2
4. Data situation	unsatisfying
5. Balance	Substitution desirable

Occurrences of TCPP in house dust are indicative. There are numerous examination results which manifest a concentration in dust of 1-14 mg/kg. While there is (still) no data on analysis of human material, basket-of-goods-studies exist. Concentrations can be detected in the region of a few µg/kg food.

5.3 Toxicology

Resorption of TCPP after oral, inhalative and dermal intake is not known. There is an acute need for further research. Experiments on animals show an accumulation in the liver and kidneys after feeding. Hydroxides of phosphorous acid are identified as metabolites in experiments on animals. Half-life in plasma is around 2-3 days. Ca. 90 % of the dose given to rats is excreted after 72 hours.

Toxic effects are observed in animal experiments on the liver (from 300 mg/kg body weight and day change in the liver weight) and kidneys (degeneration of the renal tubes in male rats from 7.500 mg/kg animal feed and day as well as from 50 mg/kg and day changes of the kidney function).

Differing data on irritations of skin and the mucous membranes in humans can be found in the literature. Skin and eye irritations in animals are unquestioned. Results obtained from various experiments on mutagenic effects need to be taken seriously: lymphoma test, DNA test, two cell transformation test and yeast gene mutation test are positive. It is thus incomprehensible and inacceptable that no examinations on cancerogenicity have been submitted. Due to the lack of information on cancerogenicity, a NOEL can only be brought in for a risk assessment under reservation. A NOEL value of 36 mg/kg body weight, obtained in animal experiments, does not take cancer risks into account. A tolerable daily dosage of 36 µg/kg body weight is obtained for humans, with a safety value of 1000 (1000 is necessary as cancerogenicity was not examined). Babies can reach this critical dose when exposed to a high level of hazardous substance in house dust (see above).

5.4 Ecotoxicology

Numerous analyses concerning the effects of TCPP on water organisms have been carried out. Ineffective doses are indicated with 6 mg/l water. These concentrations are clearly above the concentrations measured in water.

5.5 Fire

Carbon monoxide, carbon dioxide, phosphorous compound (phosphorous oxide such as *phosphorpentoxid*e and hydrochloric acid are formed during a fire. It is particularly important to point out the strong irritability phosphorous oxide and hydrochloric acid have on the mucous membranes: besides the eyes, particularly the upper respiratory tracts are affected.

5.6 Recycling

It is not known how TCPP behaves during recycling of plastics treated with TCPP.

5.7 Post-application phase

Combustion on incineration plants is unproblematic. Oxides of carbon monoxide and phosphorus as well as hydrochloric acid can be filtered by standard filter techniques.

5.8 Substance regulation

The labelling of TCPP is in compliance with the regulation of hazardous substances. The substance is considered hazardous to health (X_n) and is labelled with the R-numbers 22, 52 and 53. These numbers identify TCPP as hazardous to water organisms (not all trade products are labelled with R 52/53). Consequently, TCPP is listed in WGK 2 (category 2 of water damaging substances). Additionally, S-number 13, 21 and 36/37 are assumed to protect the worker from heath damage.

5.9 Conclusion

TCPP belongs to the chloroalkyl-phosphoric esters. A high environmental persistence coupled with an average lipophilicity leads to concentrations in aquatic and terrestrial food chains. House dust loads in enclosed spaces can be detected in the lower mg- region/kg. These loads can be traced back to the application of TCPP as additive flame retardant (or softener) in PUR, wallpaper, wall paint and other materials.

Examinations of samples taken from humans and indoor air are insufficient. There is a significant need to catch up.

Analyses upon toxicokinetics show that the blood half-life in rats is around 2-3 days. The consequence is an accumulation in the liver and kidneys. As expected, the kidney and the liver are the first organs targeted by the first effects. Irritation of the mucous membranes and the skin are well-known. The NOEL for organ damage is indicated at 30 mg/kg body weight and day. It is extremely problematic to deduce a daily tolerable intake amount. There is information on cancerogenic effects that needs to be taken seriously.

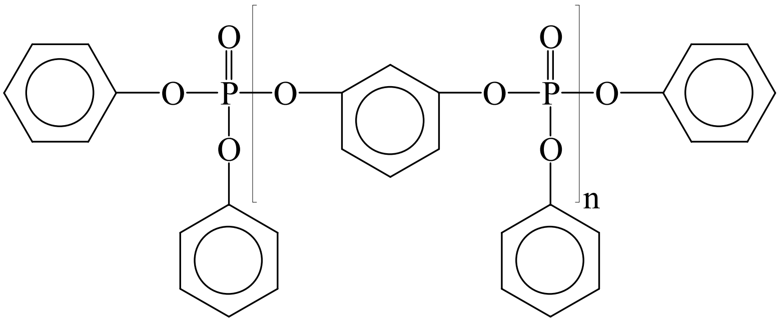
Combustion on incineration plants is unproblematic.

In summary, we believe that due to the occurrence of TCPP in environmental samples and the uncertainty of possible cancerogenic effects a substitution of TCPP should be envisaged. The reduction of the application of the substance is in any case sensible.

6. Resorcinol bis (diphenylphosphate) (RDP)[8]

6.1 Substance properties

The flame retardant Resorcinol bis (diphenylphosphate) (RDP; Cas-No.Cas-No.57583-54-7) is liquid at room temperature and boils at approximately 300°C. It is used as a congeneric combination*:*



n = 1-7

There is a chemical formula of $C_{30}H_{24}O_8P_2$ (molecular weight: 574,5 Dalton) for n = 1. There is no exact data on water solubility ('in water insoluble' and 'can not mix well with water'). The octanol/water coefficient is not indicated.

Depending on the producer, differently compound technical mixings for technical thermoplastics (PC/ABS) are put on the market. Trade products are preparations with a content of < 5 to < 6 percent triphenyl phosphate. Detailed information on the combination is not available.

Data on the light stability of RDP can not be found in the literature. With regard to the acid/basis-stability occurring reactions are only reported in the presence of acids and bases. Hydrolyses products are not mentioned. An ester separation is assumed due to the chemical structure. Phenol, resorcinol and phosphorous acids are formed. Yet, a further going polymerisation is possible.

Vapour pressure is moderate with 138 Pa at 38°C.

6.2 Environmental risks

There is no data available on RDP occurrences in the environment as well as degradation products. Analyses in the vicinity of manufacturing and processing plants are as necessary as analyses on house dust in flats, in which consumer goods such as electronic devices containing RDP are found. There is, after all, the evidence that RDP containing fumes and aerosol are released during the application of RDP on production sites.

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[8] See substance profile of Resorcinol bis (diphenylphosphate), Vol.III, pp.151-162.

Accumulation in organisms is unlikely due to the observed metabolism in relation to polar degradation products (see 6.3).

Overview V/6: Resorcinol bis (diphenylphosphate) (RDP, Cas-No. 57583-54-7 [additive]	
1. Physicochemical data	
1.1 Vapour pressure	< 130 Pa: moderate; transition into indoor air can not be excluded
1.2 Log $_{KOW}$	No data available
1.3 Water solubility	No data available
2. Toxicology in humans	
2.1 Toxicokinetics	Accumulation in the organism does not take place
2.2 Acute toxicity	
2.3 Long-term toxicity (organs)	NO(A)L (rat): 0.1 mg/l (inhalative)
2.3 Teratogenicity	No data on teratogenicity
2.4 Mutagenicity	No data on mutagenicity
2.5 Carcinogenicity	There are no analyses.
3. Ecotoxicology	
3.1 Environmental occurrence	There are no analyses
3.2 Degradability	'Inherent'
3.3 Accumulation	No detection of accumulation in food chains
3.4 Others	Disposal is unproblematic. There is no data on its behaviour during recycling.
4. Data situation	Unsatisfying. Study on cancerogenicity is missing.
5. Balance	Due to a lack of data no recommendation possible.

6.3 Toxicology

The toxicological evaluation of RDP assumes combinations with triphenyl phosphate. These combinations were used in animal experiments. This fact needs to be taken into account. In spite of an initial moderate accumulation in lungs and bones, no bioaccumulation was observed; not even with the help of a C-14 preparation. And this despite resorption data not being determined after inhalative, dermal and oral application. Excreted products were identified as Resorcinol bis (diphenylphosphate) (half-ester) and its hydroxy compound, Resorcinol and Hydroxy RDP.

Oral (no data on concentration) and inhalative (0.5 mg/l) application resulted in liver weight gain, liver amplification and *periportal* hypertrophy in rats. A significant finding perhaps is that technical products do not result in cholinesterase inhibition. This is possibly caused by Triphenyl phosphate. No examinations have been carried out on cancerogenicity.

Statements concerning effects on the eye, irritations on the mucous membranes and skin are contradictory. On the one hand we are warned against eye contact, on the other hand it is reported that no effects on eyes, mucous membranes and skin were observed. Only Akzo Nobel admits eye irritations. With respect to NOEL in relation to inhalative effects, 100 mg/l air are indicated for rats. This value is far above the concentrations that can possibly occur in indoor air.

6.4 Ecotoxicology

There is no data concerning the effects on ecosystems. It needs to be acknowledged that Triphenyl phosphate (TPP), as part of RDP trade products, is acutely toxic to water organisms.

6.5 Fire

Carbon oxides and phosphorus oxides are released during combustion. Whether organic particles of molecules are emitted during incomplete combustion is unknown. It is possible that compounds, which strongly irritate mucous membranes, are formed (Phosphorus oxides transform into acids when in direct contact with humid mucous membranes).

6.6 Post-application phase

Disposal on landfills is seen as permissible but the breakdown into phosphorus acid and phenol should be taken into account as these substances are soil permeable and could reach the ground water. Combustion of RPD-treated blends of *PC/ABS* at waste incineration sites is seen as unproblematic by the manufacturer. We are unfamiliar with the analyses on which this statement is based.

6.7 Substance regulation

The Gefahrstoffverordnung (Ordinance for Hazardous Substances) classifies RDP as R 52/53 (hazardous to water organisms) and S61 (avoid release into the environment). Manufacturers categorise RDP into Water Risk Class 1 and 2. It is also pointed out that RDP should not reach ground water.

6.8 Conclusion

RDP is a halogen-free phenol phosphate which, due to its varying numbers of Resorcinol bridges, appears as congeneric combination. This technical product which is mainly used for casing material (such as PC/ABS, PPO-HIPs) is blended with Triphenyl phosphate.

It cannot be said whether the release of RDP from plastics treated with flame retardant is relevant, as no analytical results are available.

If RDP reaches the organisms, an accumulation is improbable as a rapid metabolisation into phenol and phosphorus acids takes place. Toxic effects during experiments on rats were observed in an increase of the lung weight, amplification of the liver and eye irritation. No data is available as to the dose. It is striking that technical products which were treated with Triphenyl phosphate did not show any acetylcholinesterase inhibition.

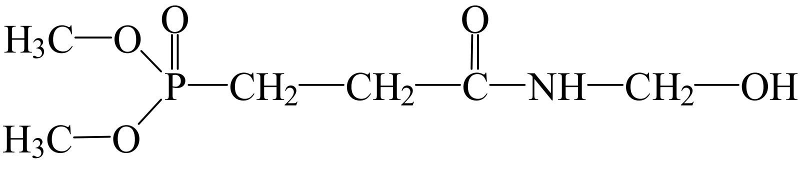
Its behaviour during disposal is unproblematic. There is no information regarding its behaviour during recycling.

As a whole, RDP is a flame retardant that has not been sufficiently researched. Its application can only be judged if analyses on occurrences in environmental media and cancerogenicity are carried out.

7. N-Hydroxymethyl-3-dimethylphosphonpropionamide (Pyrovatex CP new)[9]

7.1 Substance propertied

N-Hydroxymethyl-3-dimethylphosphonpropionamide is liquid at room temperature and boils in pure form at 290°C. The substance has the chemical formula $C_6H_{14}NO_5P$ (molecular weight: 211.2 Dalton) and is registered in CAS as 20120-33-6. Physicochemical stability is provided by the structural formula



A rapid formaldehyde separation takes place in an alkaline environment. A slow ester separation takes place during release of methanol on the phosphoric ester part under acid circumstances. The compound is persistent in sodium chloride. Up to 3 % of ethylene carbamide is added to the flame retardant Pyrovatex in order to obtain stability. The product contains 1% formaldehyde and 3% methanol.

There is no data on the water solubility of Pyrovatex. The structure assumes a good water solubility. The octanol/water coefficient of - 1.7 shows that an accumulation in the food chains does not need to be feared. Vapour pressure of 23 hPa at 20°C is surprisingly good. Formaldehyde emissions from the product have not been published.

7.2 Environmental risks

N-Hydroxymethyl-3-dimethylphosphonproprionamide is a fibre-bound flame retardant used for cotton. In Germany, it is only being used for working clothes. Abroad it is also used for home textiles (upholstery material, children's nightwear). There is no data on occurrences of the flame retardant in indoor air, house dust, outdoor air, water, soil and sewage sludge. Data on formaldehyde emissions released from the flame retardant, in which N-Hydroxymethyl-3-dimethylphosphonpropionamide is contained in consumer goods made of cotton would be desirable.

There is data on concentrations in sewage and fumes during manufacturing and processing provided by the producer: apparently a mere 20 kg of the product during production of 10 t of Pyrovatex CP new are release into water.

Investigations on the product and preliminary stages of the product in the vicinity of production sites (water, air, sediment) should be carried out. This is equally valid for processing sites.

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[9] See substance profile N-Hydroxymethyl-3-dimethylphosphonproprionamide, Vol. III, pp.163-173.

Overview V/7: N-Hydroxymethyl-3-dimethylphosphonproprionamide (Pyrovatex CP new), Cas-No: 20120-33-6 [fibre active]	
1. Physicochemical data	
1.1 Vapour pressure	2300 Pa (20°C):high
1.2 Log $_{KOW}$	-1.68 (25°C): accumulation is unlikely
1.3 Water solubility	No data (probably good solubility)
2. Toxicology in humans	
2.1 Toxicokinetics	No data available
2.2 Acute toxicity	References to irritation of skin and mucous membranes
2.3 Long-term toxicity (organs)	NO(A)EL (rat): > 1000 mg/kg
2.3 Teratogenicity	No analyses
2.4 Mutagenicity	No evidence of mutagenicity
2.5 Carcinogenicity	No analyses
3. Ecotoxicology	
3.1 Environmental occurrence	No analyses
3.2 Degradability	Average
3.3 Accumulation	Accumulation in food chains not proven
3.4 Others	Toxity in algae relatively high
4. Data situation	Insufficient
5. Balance	No recommendation possible due to the data situation

7.3 Toxicology

A toxicological evaluation is without substance due to a lack of data on concentrations in environmental media. Only experiences made during animal tests with Pyrovatex can be interpreted.

There is no data with regard to the toxicokinetics of the substance. In terms of toxic effects, there are references of irritations of skin and mucous membranes. The failure to examine the cancerogenicity during a long-term trial has to be reprimanded. The Ames-test does not show effects.

As expected, N-Hydroxymethyl-3-dimethylphosphonproprionamide causes skin damage. The release of formaldehyde is ultimately responsible for this. Consequently, substances were extracted from Pyrovatex CP-containing textiles via saliva and sweat . These extracts were subsequently tested on eyes and skin of tested animals. A slight irritation on the eye was reported as a result of high doses. A sensibilizing of the skin of a guinea pig entirely depends on the amount of formaldehyde injected into the flame retardant. A sensibilization of the skin in humans is not excluded.

With respect to deductions of daily tolerable doses there is a NOEL value (1000 mg/kg body weight rat and day) which does not contain any data on toxicodynamic end points so that a deduction of a TDI value can not be taken seriously. In order to provide a toxicological risk evaluation, examinations on concentrations with respect to the NOEL and to cancerogenicity during a long-term test phase need to be carried out first.

7.4 Ecotoxicology

Due to the physicochemical behaviour (octanol/water coefficient and water solubility), neither accumulations nor chronic effects need to be feared. Damage to water organisms can not be ruled out in rivers close manufacturing and processing sites, considering a low NOEL value for algae with 22 mg N-Hydroxymethyl-3-dimethylphosphonproprionamide/l.

7.5 Fire

In a case of fire, the release of hydrocyanic acid, nitric gases, phosphorus oxide and carbon monoxide have to be expected in the presence of Pyrovatex-treated cotton. To what extent these toxic gases, resulting from the decomposition of Pyrovatex, have a significance in terms of amount depends on the respective fire situation.

7.6 Post-application phase

No data is available. However, it is assumed that products decompose on disposal sites and that they release emissions or reach the ground water. The product itself can leach and reach the ground water.

There are no analyses with regard to combustion on incineration sites.

7.7 Substance regulation

The German Ordinance for Hazardous Substances (Gefahrstoffverordnung) recommends a careful handling of the product due to skin senibilization (R 43). R43 points out possible irreversible damages. S-terms 23, 24 and 37 indicate allergic reactions produced by N-Hydroxymethyl-3-dimethylphosphonproprionamide. The substance has to be labelled with Xi in order to stress irritating effects. The substance is allocated in Water Hazards Class 1 (hazardous effects on water are weak).

7.8 Conclusion

Pyrovatex CP new is a halogen-free dimethylester of phosphonopropionicacidamide which is substituted with a hydroxymethylene-group on nitrogen. Pyrovatex CP new is used in flame retardant cotton. The structural formula suggests that Pyrovatex CP new, preferred in alkaline environment, separates formaldehyde and decomposes into methanol and phosphorus acids under acidity. Pyrovatex CP new does not accumulate in food chains due to the negative octanol/water coefficient.

The product is enhanced with ethylen carbamide as formaldehyde trap, due to the fact that formaldehyde separates easily.

There is no data on occurrences of Pyrovatex CP new in environmental samples.

The toxicokinetics of the substance is undetermined. Toxic effects are shown in skin and mucous membrane irritations. Dose/effect data is missing. Tests on cancerogenicity were not carried out. There are only extraction via sweat and saliva from cotton. Targeted investigations with respect to the transmission of the flame retardant via skin into the organism do not exist.

In case of fire hydrocyanic gases and nitric gases are formed from Pyrovatex CP new. There is no data on its behaviour on disposal sites and of the influence of fume gases on incineration plants.

On the whole, Pyrovatex CP new has been little researched. Skin and mucous membrane irritations are reported as the effect of the separation of formaldehyde and phosphorus acid.

There are many knowledge gaps with respect to the toxicity of Pyrovatex CP new and its transmission potential from clothes into the human organism.

8. Red Phosphorus[10]

8.1 Substance properties

Red phosphorus is, next to white phosphorus, a stable transformation form of the element phosphorus. It can be found in the fifth core group of the periodical system and has the order number 15. Its atom weight amounts to 31 Dalton. Red phosphorus turns volatile at 400°C. Red phosphorus has an amorphous structure.

Red phosphorus, which is micro-encapsulated (e.g. with phenol-formaldehyde resin) or integrated into a thermoplastic polymer, is mainly handled as flame retardant for condensation polymers. Impurities found in this technical product mainly stem from white phosphorus which ignites in the presence of air (up to 200 mg/kg red phosphorus). It is interesting for an ecotoxicological evaluation that red phosphorus does not dissolve easily in water; it reacts slowly on the water's surface whereby phosphine (phosphorus on oxidation level - 3) and hypophosphorous acid (phosphorus on oxidation level + 1) are formed by disproportionating.

Hypophosphorous acid can further be oxidated into phosphoric (III+) and phosphorous acid (V+). The reaction is accelerated in an alkaline environment. The same reaction into phosphine and phosphoric acid takes place in the presence of air.

8.2 Environmental risks

No data on concentrations in indoor and outdoor air, soil (via sewage sludge), water, sediment as a consequence of the use of red phosphorus as flame retardant can be found in the literature. If at all, minor amounts of phosphorus accumulation can be detected in house dust when phosphorus, encapsulated by synthetic material, is rubbed off. There are no measurements with regard to this. Risks of the environment being contaminated with phosphorus as a result of the use of RP as flame retardant is very unlikely. Inertial and micro-encapsulated RP does not pose a threat to the environment.

8.3 Toxicology

Oral ingestion of free red phosphorus is unlikely due to its degradability in the environment.

The possibility is being discussed whether phosphine is formed on sections of synthetic material from red phosphorus when it comes into direct contact with air and water, being highly toxic when inhaled.

Due to a moderate release of elementary phosphorus from plastics in enclosed spaces, it is possible to rule out a toxicologically critical formation of phosphine.

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[10] See substance profile for Red phosphorus, Vol. III, pp.174-187.

8.3 Toxicology

Oral ingestion of free-flowing red phosphorus is unlikely due to its degradability in the environment (see above). Whether resorption takes place when micro-encapsulated RP is orally ingested has not been examined so far.

Overview V/8: Red Phosphorus (RP), Cas-No: 7723-14-0 [additive]	
1. Physicochemical data	
1.1 Vapour pressure	< 10 Pa (20°C):low
1.2 Log $_{KOW}$	Ecosystemic accumulation is unlikely
1.3 Water solubility	Does not dilute in water
2. Toxicology in humans	
2.1 Toxicokinetics	No data available upon resorption and metabolism
2.2 Acute toxicity	Inhalative: LD_{50} (rat): 4.3 mg/l Acute toxicity moderate as metabolism is rapid; irritation of eyes and mucous membranes (due to the formation of acid)
2.3 Long-term toxicity (organs)	No data available
2.3 Teratogenicity	Weak results
2.4 Mutagenicity	No data available
2.5 Carcinogenicity	No data avilable
3. Ecotoxicology	
3.1 Environmental occurrence	No data available
3.2 Degradability	RP can be eliminated in sewage plants via adsorption in sewage sludge
3.3 Accumulation	
3.4 Others	Release of phosphorus oxides and phosphorus acids in case of fire
4. Data situation	Sufficient
5. Balance	Use unproblematic

It is equally undetermined how large the RP amounts could be under most unfavourable circumstances. While health risks should remain very moderate when RP-loaded synthetic dust is orally ingested, irritating effects on contact with skin and mucous membranes are likely due to the formation of acids. The eye and respiratory tracts are particularly affected by direct contact with RP. Depending on the duration of exposure and dose, slight irritation to destruction of tissue can be expected. LD_{50} can not be brought in for a toxicological evaluation as phosphorus acid can be formed thanks to a high reactivity of phosphorus in its derivative phosphine.

8.4 Ecotoxicology

Ecosystemic accumulation and effects are unlikely to be a consequence of the flame retardant RP, used in plastics as reactions in relation to phosphine and phosphorus acid unfold rapidly.

8.5 Fire

In a case of fire, RP produces phosphorus acids and polyphosphorous acids with differing levels of oxidation of the phosphorus and various polymerisation levels depending on the oxygen content. The acids remain mainly in the ash. In case of a high oxygen provision volatile phosphorus oxides are formed. Its occurrence in fumes can lead to irritations of skin and mucous membranes of the person directly affected by it. Lack of oxygen results in the formation of white phosphorus that ignites in the presence of air. During combustion of RP-containing plastics on waste incineration plants, both polymer phosphorus acids, which stay in the clinker, and phosphorus oxides are formed in fumes. These gases can be retained by conventional flue gas treatment systems.

8.6 Recycling

Information concerning recycling provided by the manufacturer is unsatisfying.

8.7 Substance regulation

Pure red phosphorus is considered dangerous for water organisms and has therefore been classified as N and R50. A re-classification of the trade products (preparation with red phosphorus) to R52 (hazardous to water organisms) has been applied for by the manufacturer. Due to its flammability in air and explosiveness with oxygen, R11 and R16 apply. RP must not be kept in closed receptacles due to the risks of phosphine formation (S 7).

8.8 Conclusion

RP used for condensation polymers or micro-encapsulated RP can only be released into the environment via synthetic segments. On the surface, phosphorus reacts with water into phosphine and hypophosphorous acid. This is followed by oxidation in air to phosphoric oxides and phosporic acids. The occurrence of phosphorus compounds in environmental samples as a result of the use of RP as flame retardant can not be dealt with separately from natural occurrences of phosphorus compounds. Health risks resulting from the release of toxic phosphine on synthetic segments could be neglected in view of the modest doses.

Although the resorption of the micro-encapsulated RP has not been analysed, a neglectably low resorption is most likely. Effects on organs are unlikely. The contact of RP with skin and mucous membranes could lead to irritations on humid organs due to the formation of acids.

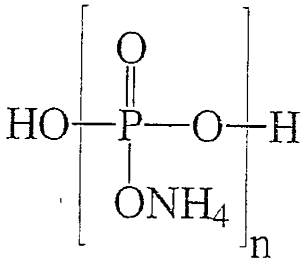
Negative effects on aquatic systems are not feared as concentrations of phosphorus are low when compared with natural occurrences.

Phosphorus oxides and acids released in a fire, however, should not be ignored as they result in irritation of skin mucous membranes of the person affected. Despite the favourable properties of RP used as flame retardant, questions concerning the recycling of PR-containing plastics remain unanswered.

9. Ammonium polyphosphate (APP)[11]

9.1 Substance properties

Ammonium polyphosphate is a crystalline, inorganic salt that melts at ca. 275°C and decomposes at 300°C under release of ammonia. At a polymerisation level of approximately = 1000, a molecular weight of ca. 100.000 Dalton is reached. Its Cas-No. is 68333-79-9. Its structure formula is



$$HO-[P(=O)(ONH_4)-O]_n-H$$

n > 1.000,

which results in the chemical formula of (NH_4PO_3).

This flame retardant, primarily used for polyurethane and intumescent coatings, is currently applied as liquid solution, mixed with some % of carbamide.

With regard to its toxicological and ecotoxicological evaluation, it has been recognised that the vapour pressure of Ammonium polyphosphate (solid substance) is very low at room temperature. At a higher temperature its decomposition under release of ammonia plays a more important role (see above). The octanol/water-coefficient is at approximately 10g/l water.

9.2 Environmental risks

Environmental hazards for aquatic systems caused by Ammonium polyphosphate are, at the most, thinkable in the direct vicinity of production and processing sites. Hazards caused by APP as flame retardant and found in the ground water below landfills will, in relation to phosphate, not be detectable thanks to the high background concentrations. Contamination of air caused by APP is unlikely due to its physicochemical properties. Whether it accumulates in house dust when APP-containing products are used is unknown.

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[11] See substance profile of Ammonium Polyphosphate. Vol.III, pp.188-198.

Overview V/9: Ammonium polyphosphate (APP), Cas-No. 68333-79-9[additive]	
1. Physicochemical data	
1.1 Vapour pressure	< 10 Pa (20oC):low
1.2 Log $_{KOW}$	no indication
1.3 Water solubility	10g/l: very good
2. Toxicology in humans	
2.1 Toxicokinetics	No analysis
2.2 Acute toxicity	No toxicological effects expected
	Irritation of the mucous membranes possible
2.3 Long-term toxicity (organs)	No analyses
2.3 Teratogenicity	No analyses
2.4 Mutagenicity	No data on mutagenicity
2.5 Carcinogenicity	No analyses
3. Ecotoxicology	
3.1 Environmental occurrence	No analyses
3.2 Degradability	Break down in soil and sewage sludge fast
3.3 Accumulation	Accumulation in food chains undetected
3.4 Others	In case of fire formation of nitrogen oxides and ammonia
4. Data situation	Sufficient
5. Balance	Use unproblematic

9.3 Toxicology

Although no data as to the resorption of APP after oral ingestion is available, a high resorption rate can be assumed as a result of experiences made with comparable compounds. APP is metabolised into ammonia and phosphate. These substances become integrated into the general nitrogen and phosphate cycle, which, with regard to background concentrations, are insignificant. Neither considerable concentrations in the organism nor toxic effects are to be feared when APP is implemented in plastics as an additive flame retardant. Sensitivizing effects on skin and the mucous membranes can be expected when APP comes into contact with skin either as solid substance or liquid solvent, as a hydrolysis into acid and ammonia salts takes place in an aqueous medium. No data on the dose-effect-relationship can be found in the literature. No conclusion can be drawn from the LD_{50} (>2000 mg/kg) data on chronic toxicity.

9.4 Ecotoxicology

No measurable hazards on ecosystems have to be feared from APP amounts used in Polyurethane - this does not apply to the immediate surroundings of manufacturing and processing plants. Breakdown in soil and sewage sludge into ammonia and phosphate happens rapidly.

Although no exact data on volume relevance exists, the problem regarding eutrophication of waters has to be mentioned here for the sake of completeness.

9.5 Fire

Nitrogen oxide and ammonia in various concentration relationships as well as phosphorous oxide are formed from APP-containing plastics in case of fire and during waste combustion. This depends on the combustion circumstances. Effects on health can not be ruled out in fire cases due to these aggressive gases.

9.6 Recycling

APP does not have a negative impact on the recycling of PUR according to data provided by the manufacturer.

9.7 Substance regulation

Ammonium polyphosphate does, according to the German Gefahrstoffverordnung (Ordinance of Hazardous Substances), not need to be classified. Manufacturers allocate it in WGK 1 as eutrophication of water is possible as result of a great load of APP released to the hydrosphere.

9.8 Conclusion

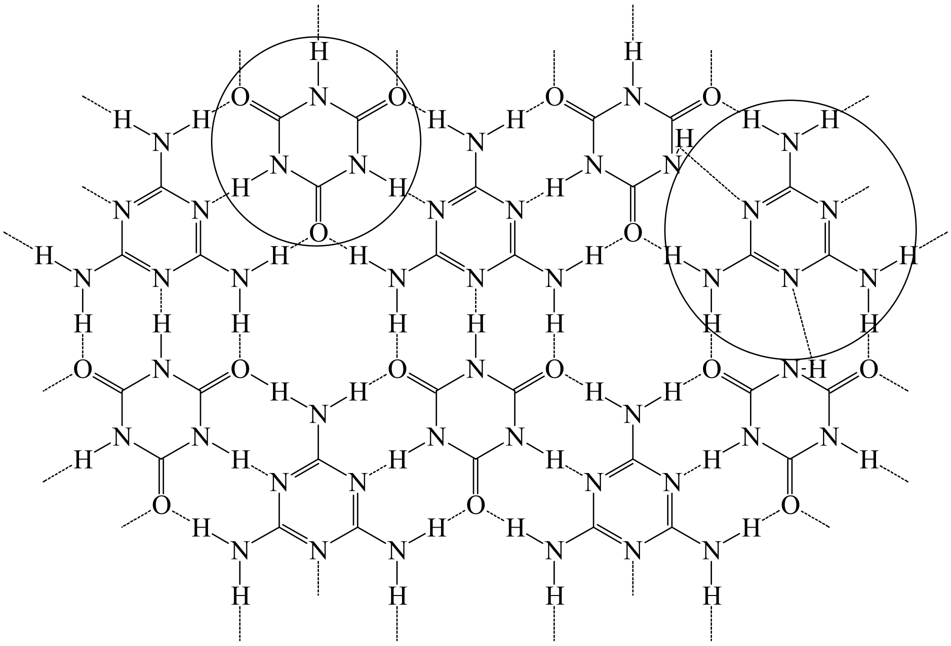
Ammonium polyphosphate (APP) is mainly used as additive flame retardant for Polyurethane and intumescent coating. Release into the environment is thus possible. No critical additional hazards to water, groundwater and house dust (except for manufacturing and processing sites) result from moderate emissions. There are no hazardous effects. Irritations of the skin and the mucous membranes are mentioned at direct contact with skin as phosphorous acids are formed on humid organ segments due to hydrolysis.

In case of fire, nitric oxides and ammonia are formed. APP's behaviour during recycling is favourable. As a whole, seen from a toxicological viewpoint, APP is an unproblematic flame retardant.

10. Melamine cyanurate (MC)[12]

10.1 Substance properties

Melamine cyanurate (Cas-No. 37640-57-6) is a crystalline, colourless substance. The molecular weight amounts to 255.2 Dalton. The official name is 1,3,5 - triazine - 2,4,6 - (1H,3H,SH) trione/ 1,3,5 - triazine - 2,4,6, - triamin (1:1), which results in the chemical formula $C_6H_9N_9O_3$.



MC which is mainly used for polyamide has a purity degree of > 99%. Thes technical product shows impurities. 0.5 % are caused by melamine and a maximum of 0.2 % by isocyanur acid.

MC disintegrates into carbon monoxide, carbon dioxide, ammonia, nitrogen oxide and, moderately, into hydrocyanic acid and isocyanates at a temperature of 350°C. An accumulation of MC in octanol in comparison to water does not take place so that a bioaccumulation in the food chain need not be feared. Solubility in water is good: it is approximately 2.8 g/l (25°C).

10.2 Environmental risks

Hazards in the workplace with dust-bound MC are well-known. Environmental concentrations in the direct vicinity of MC production sites and the general surrounding are not known. Polluted groundwater below landfills is likely due to MC's water solubility.

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[12] See substance profile of Melamine cyanurate, Vol. III, pp.199-206.

Overview V/10: Melamine cyanurate (MC), Cas-No. 37640-57-6 [additive]	
1. Physicochemical data	
1.1 Vapour pressure	Not available
1.2 Log $_{KOW}$	< 0: no accumulation in food chains likely
1.3 Water solubility	ca. 2.8 g/l (25^{o}C): very good
2. Toxicology in humans	
2.1 Toxicokinetics	no analyses
2.2 Acute toxicity	High L_{50} and LC_{50} values, however, no statement can be made due to a lack of data.
2.3 Long-term toxicity (organs)	s.a.
2.3 Teratogenicity	No analyses
2.4 Mutagenicity	No data on mutagenicity
2.5 Carcinogenicity	Contradictory data
3. Ecotoxicology	
3.1 Environmental occurrence	No analyses
3.2 Degradability	In principle biodegradable (no exact data)
3.3 Accumulation	Accumulation in food chains undetected
3.4 Others	In case of fire formation of HCN
4. Data situation	Unsatisfying
5. Balance	Recommendation impossible due to the data situation.

10.3 Toxicology

There is no data available on the toxicity of MC as no useful information with regard to both toxicokinetics and dose-effect-relationship can be found in the literature. It is also not provided by the manufacturing companies. A classification in ‘a little toxic’, simply based on the high value of LD_{50} (>2000mg/kg) and LD_{50} (> 100mg/l) is impermissible. A mutagenicity test was carried out with negative result. Data upon cancerogenicity are contradictory. Only skin irritation, eye irritation and breathing problems during inhalation are mentioned as effects. A dose of ca. 10 g that had been ingested in the course of an accident led to lower abdominal pain. A well-founded toxicological evaluation can only be successful if a dose-effect-relationship for chronic diseases exists.

10.4 Ecotoxicology

It is generally reported that MC is, in principle, biodegradable. However, there is no data concerning degradation products and half-life values. No details are given as to the effects on micro-organisms, animals and plants.

10.5 Fire

Ammonia, carbon monoxide, carbon dioxide, nitrogen oxides, hydrocyanic acid and isocyanates are formed during fire at a temperature of 350^{o}C. As hydrocyanic acid and isocyanates are formed from MC in rather significant amounts during fires, application of MC as flame retardant is problematic.

10.6 Substance regulation

No information on this is available.

10.7 Conclusion

MC, which is mainly used for polyamide, is a polymer product consisting of Triamin and Triazin. It shows a good water solubility and does not tend to accumulate in food chains. No data informs us of occurrences of MC in environmental media such as air, soil and water.

MC's toxixology has not been examined yet. An evaluation based on the manufacture's classification ' little toxic' and the reference to weak effects of irritation on mucous membranes is impossible.

With regard to the ecotoxicology, we have one statement that indicates that MC is 'basically biodegradable'.

Ammonia, carbon monoxide, carbon dioxide, nitrogen oxides, hydrocyanic acid and isocyanates are built during a fire. Due to the two last fume gases, one has to assume very toxic fume gases in MC-treated enclosed spaces during fires.

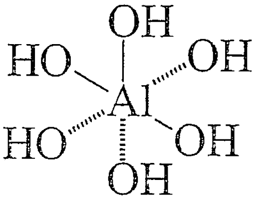
A gradual fading of MC on disposal sites can not be ruled out.

At the moment it is impossible to provide a toxicological evaluation of MC based on existing data.

11. Aluminium trihydroxide (ATH)[13]

11.1 Substance properties

The molecular weight of the crystalline compound Aluminium trihydroxide (ATH) amounts to 78 Dalton and corresponds to the chemical formula $Al(OH)_3$. The structure of crystalline ATH can be described as a monoclinic elemental cell with octohydronical surrounding of one Al-atom with six OH-groups, where each Al-atom belongs to two Al-atoms:



The compound does not fuse without decomposing: as an inorganic compound, ATH is not combustible. When heated to temperatures up to > 200°C, water is separated while hydrated Aluminium oxides are built.

In neutral water, ATH is with ca. 1.5 mg/l not readily soluble. In acids and bases, Aluminium Trihydroxide dissolves more readily due to the formation of complex ions. Crystalline, difficult to dissolve γ-$Al(OH)_3$ is used as a flame-retardant which is extracted via precipitation of sodium-aluminium-solutions. ATH is traded in different particle sizes (1 μm to > 5 μm [ground ATH-types]), but the particles are often covered with carboxyl- or amino-compounds (0.1-2% proportion of weight of the flame-retardant).

11.2 Environmental pollution

Because of the ubiquity of aluminium oxide hydrates in soil, plants and the air, it does not make much sense to determine the environmental pollution resulting from the application of flame retardant. Additionally, the analysis of small amounts of aluminium is very easily disrupted by ubiquitous aluminium.

11.3 Toxicology

Effects on humans (oral, dermal, and inhalative) resulting from the use of flame retardants should not be toxicologically relevant. Inhalative intake of small particles containing aluminium possibly has to be tested for potential carcinogenic effects.

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[13] See substance profil of Aluminium trihydoxid, Vol. III, pp. 207-230.

Overview V/11: Aluminium trihydroxide (ATH), CAS-No. 21645-51-2 [additive]	
1. Physicochemical data	
1.1 Vapour pressure	At 20ºC not measurable.
1.2 Log_{kow}	
1.3 Water solubility	Low.
2. Toxicology in humans	
2.1 Toxicokinetics	No investigations available.
2.2 Acute toxicity	Target organs are nervous system and immune system (high doses).
2.3 Long-term toxicity (organs)	Altogether, toxicologically not relevant.
2.3 Teratogenicity	Teratogenic effects only in combination with aluminium-lactate or lactic acid
2.4 Mutagenicity	Mitogenic, cytotoxic
2.5 Carcinogenicity	No indication for carcinogenicity.
3. Ecotoxicology	
3.1 Environmental occurrence	Hardly any difference from geogenic content.
3.2 Degradability	No investigations available.
3.3 Accumulation	Accumulation in food chains not detectable.
3.4 Others	
4. Data situation	Sufficient.
5. Balance	Use unproblematic.

Nevertheless, toxicokinetics and effects from high doses of aluminium should be - as far as known - shortly introduced. The oral resorption of ATH mainly depends on the presence of complex-building organic acids (e.g. citric acid). ATH accumulates in rats' brains. The half-life of absorbed aluminium is not known. High doses of ATH induce disturbance of the nervous system and the immune system (200 mg/kg body weight and day). Besides, a reduced increase in foetuses' weight is observed when mother animals are contaminated via food.

11.4 Ecotoxicology

When water is polluted with more than 1.5 mg aluminium (bound as hydroxide)/l, first behavioural disturbances like reduction of locomotion of water organisms, can be observed. Knowledge about effects on plants is available. E.g. accumulation of aluminium in the roots with decreasing pH-level of the ground (acid rain) is discussed as a factor for the death of forests.

11.5 Fire

Here it is of certain interest, whether in case of fire or other thermal influences carcinogenically reacting aluminium particles can be formed. This is not the case, because the hexagonal little tiles of the ATH are preserved depending on temperature (up to 600ºC). According to the manufacturer, no needle-shaped Aluminium trihydroxide is formed, because bigger flat structures or spherical particles are formed by sintering of the edges of the little tiles.

11.6 Recycling

ATH does not generally interfere with recycling. However, data on health and environmental concentrations that might result from this is not available.

11.7 Substance regulations

According to EU-directives and the German Ordinance of Hazardous Substances (Gefahrstoffverordnung), ATH does not need to be labelled. The limit value for aluminium in drinking water is 0.2 mg aluminium/l. The BAT-value for aluminium in urine is given at 200 µg aluminium/l. The maximum workplace concentration MAK is 1.5 mg/m^3 for aluminium. Aluminium-compounds shaped as fibrous dust are classified carcinogenic in the category II. R- and S-terms have not been determined for aluminium.

11.8 Conclusion

ATH is used as a mineral flame-retardant either directly or with a plastic covering on a wide range of duro- and thermoplastics, latices. In spite of vast amounts, the environmental intakes resulting from the use as flame-retardant are, when commonly used (that does not apply to the surroundings of production and processing sites) so low that it does not result in a measurably higher content of geogenic aluminium in the environment. But even small emissions of ATH from plastics - formation of dusts resulting from corrosion as well as gradual loss on disposal sites - is, from a toxicological point of view, not really hazardous to humans and the environment.

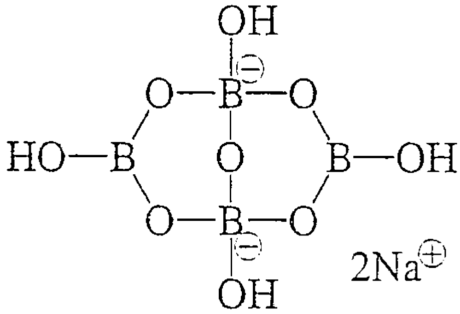
In case of fire, no toxic particles are formed. Recycling of plastics containing ATH is possible.

From a toxicological and ecotoxicological point of view, there is no objection against using ATH as a flame-retardant.

12. Sodium borate decahydrate (Borax)[14]

12.1 Substance properties

Sodium borate decahydrate is a crystalline salt which melts together under loss of water at temperatures from 62°C. The molecular weight is 381 Dalton. Sodium borate decahydrate is registered in CAS under 1303-96-4. The chemical is $Na_2B_4O_7 \bullet 10\ H_2O$ and has the following structure:



Sodium borate decahydrate, which is used as a flame-retardant in ca. 1% of the industrial production mainly for insulation material based on cellulose, is very pure (99%). Determination of a water/octanol-coefficient for the estimation of a possible food chain-accumulation does not make much sense, because Sodium borate decahydrate does nor dissolve easily in organic solvents. It is, however, readily soluble in water (approximately 5% in water at 20°C). With acids or bases, boronhydroxy-oxo-compounds are formed with different boron/oxygen-ratios.

12.2 Environmental risks

A measurable increase of geogenically caused occurrence of boron in the environment as a result of emissions from flame retardants is unlikely. This does not apply to the region around manufacturing and disposal sites.

16 ng boron/m^3 have been detected in outdoor air in Germany. Up to 44 mg Borax/l seawater can be found in water. Values between 10 and 210 µg/l have been detected in German drinking water, The soil shows concentrations between 88 and 177 mg Borax/kg soil dry substance.

There is no information about boron in indoor air. It would be important to know which concentrations of boron occur in apartments equipped with boron-containing insulation material.

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[14] See substance profile of Sodium borate decahydrate, Vol. III, pp. 231-259.

Overview V/12: sodium borate decahydrate (Borax), CAS-No. 1303-96-4 [additive]	
1. Physicochemical data	
1.1 Vapour pressure	Low.
1.2 Log$_{kow}$	Can not be determined
1.3 Water solubility	Very good.
2. Toxicology in humans	
2.1 Toxicokinetics	At high, chronic boron pollution, accumulation in bones, scalp, hair, fingernails and teeth.
2.2 Acute toxicity	Oral: LD$_{50}$ 2000 to > 6000 mg/kg bodyweight Inhalative: LD$_{50}$ (rat) >2 mg/l Dermal: LD$_{50}$ (rabbit) > 10000 mg/kg bodyweight Can irritate eyes, respiratory organs and skin.
2.3 Long-term toxicity (organs)	According to animal NOEL-values from 7.4 to 154 mg Borax/kg bodyweight and day.
2.3 Teratogenicity	Indication for teratogenicity.
2.4 Mutagenicity	Contradictory data.
2.5 Carcinogenicity	No indication.
3. Ecotoxicology	
3.1 Environmental occurrence	High geogenic background contamination.
3.2 Degradability	Formation of naturally existing boron-compounds.
3.3 Accumulation	Contrasting of geogenic occurrences not possible.
3.4 Others	
4. Data situation	Sufficient
5. Result	Minimising sensible.

12.3 Toxicology

The organism is mainly polluted with boron via food. Average intake in Germany is 1.6 to 4.5 mg/person and day. At a half-life of approx. 21 hours, boron is removed via urine. There is no data on inhalative intake. Resorbed boron is evenly distributed in soft body tissue and usually rapidly degraded. High, chronic boron pollution (e.g. at the workplace) leads to accumulation of boron in bones, scalp, hair, fingernails, and teeth.

There are many observations on humans and results from animal experiments with regard to effects caused by boron.

High doses (2820 mg boron/day) lead to stomach problems with the risk of subsequent anorexia after a few months. The use of aqueous Borax solutions in eye-wash-solutions has led to the experience of eye-irritations after contact with Borax. Direct skin contact (e.g. Borax in cleaning agents) can lead to inflammation of skin. Irritations of the mucous membranes are possible at air concentrations > 21 mg Borax/m^3 .

With regard to effects on the hormone system, it is known that already 3 mg boron/day can lead to an increase of the plasma-concentration of testosterone for post-menopausal women. These results are important in so far as the background concentrations of the population caused by boron range from 1.6 to 4.5 mg boron/day. The nervous system is damaged at daily doses > 152 mg Borax/kg bodyweight: cramps and vomiting occur.

The reproductively toxic effect of Borax is very important. Experimental observations on animals reach from atrophy of testicles (776 mg Borax/kg bodyweight and day), reduction of spermatogenesis (418 mg Borax/kg bodyweight and day) to sterility in the third generation (rats received 516 mg Borax/kg bodyweight and day in their the food for 2 years).

Teratogenic effects were also observed through oral ingestion of Borax during animal experiments. Pregnant rats fed with 25 mg boron/kg body weight and day in form of boric acid, gave birth to babies showing changes in birth weight and bones.

Results of mutagenicity are inconsistent. There is no indication on carcinogenic effects.

2.5 mg boron (corresponds to 22 mg Borax)/kg bodyweight and day is discussed as NOEL for humans. Considering the daily pre-intake of 1.6-4.5 mg/person with the food, an additional boron concentration is not tolerable e.g. by using it as a flame-retardant. In any case, it needs to be proven whether the use of Borax in insulation material significantly increases the daily intake of Borax.

12.4 Ecotoxicology

The ubiquitous boron is already effective in small doses in water: 476 mg Borax/l water are lethal for rainbow trouts and after 32 days for 50% of the fish.

12.5 Fire

In case of fire, boron oxides, which are bound to particles, are released..

12.6 Recycling

If boron-containing material reaches a disposal site, Borax is released into ground water through leaching.

There is no information on recycling of boron-containing insulation material.

12.7 Substance regulations

Borax is regarded as hazardous to health (X_n). It is suspected to be damaging to fertility (R 63) and can affect reproduction (R62). Furthermore, Borax can irritate eyes, breathing organs and skin (R36/37/39).

12.8 Conclusion

Borax belongs to the mineral flame retardants and is used mainly with cellulose-containing insulation material. (Max. 1% of the total consumption of Borax is used during application of the flame retardant).

It is important for its evaluation, that it is hardly volatile and does not accumulate in the food chain. However, emissions from flame retardants applied on soil (sewage sludge-findings) and water are likely. It is normally not possible to detect this due to a significant geogenic occurrence of boron.

Because the daily intake of boron via food (1.6-4.5 mg/person and day) is already close to the NOEL, additional boron expositions from flame retardants should be low.

The toxicology of Borax is well-researched: in animal experiments, very high doses cause stomach problems, irritation of the eyes, nerve damage, reduction of spermatogenesis and teratogenicity. Carcinogenic effects have not been observed. Only 3 mg boron per person and day can lead to an increase of the plasma concentration of testosterone for post-menopausal women. This dose is only slightly higher than the daily intake.

In view of the comparably small amounts of Borax used as flame-retardant, it is not assumed that the daily intake of boron will, as a result, significantly rise.

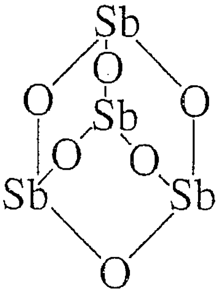
In summary, the use of Borax as flame-retardant is acceptable. As background concentration via food is already so high that the daily tolerable amount of intake is reached, it needs to be ensured that the application of boron as flame retardant will not result in additional concentrations for humans.

13. Antimony trioxide (ATO)[15]

13.1 Substance properties

Antimony trioxide is a colourless, crystalline compound, which turns yellow while heated. The compound melts at 656°C and boils at 1556°C under normal pressure. The molecular weight of the compound registered under CAS-No. 1309-64-4 is 291.5 Dalton.

ATO has, in its cubic appearance, the following structure:



ATO kubisch

Powdery ATO, a synergist used for bromo- and chloro-containing flame retardants (in the heat of fire, fire-resistant antimony-halogens are formed with a halogen-containing flame-retardant) - is mixed with softeners, mineral oils or pastes from water in order to reduce dust formation, or dispersions in PVC or PE are produced.

The vapour pressure of ATO is very low at room temperature. Solubility in water depends on pH. 20 mg ATO/l water are soluble at pH = 5 whereas ca. 30 mg at pH = 9. An octanol/water coefficient is not given in the literature. Antimony trioxide reacts with acids and bases to Sb^{3+} compounds (acid) and to antimony $[Sb(OH)_4]^-$ (base).

13.2 Environmental risks

Diantimony in outdoor air is being investigated worldwide. Traced concentrations of diantimony are between 0.5 pg and 170 ng antimony/m3. Measurements taken from flying dust in Schleswig-Holstein show air pollution of 1 - 5.2 ng antimony/m^3. The main pollution sources for the amounts of diantimony existing in air are thermical sites such as waste incineration sites, melting huts, carbon combustion, and cement rotary furnaces. The part of outdoor air pollution produced by ATO as flame-retardant is not known. There is a different situation in the workplace where diantimony has been detected in the lower microgram area per m^3 air. In seawater and rivers, diantimony values between 0.05 and 0.4 µg/l are being analysed. The ATO-producing industry is contributing only a little to this pollution, unless it is detected in the vicinity of these production sites in water and sediment.

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[15] See substance profile of diantimony trioxide, Vol. III, pp. 231-259.

Overview V/13: Antimony trioxide (ATO), CAS-No.1309-64-4 [synergist, additive]	
1. Physicochemical data	
1.1 Vapour pressure	
1.2 Log_{kow}	No investigations available.
1.3 Water solubility	20 mg ATO/l (pH 5), 30 mg (pH 9): low solubility
2. Toxicology in humans	
2.1 Toxicokinetics	Accumulation in thyroid glands, liver, spleen, kidneys, heart, and bones.
2.2 Acute toxicity	Depending on oxidation level, whereas compounds with three-valent antimony are about one order more toxic than the five-valent. Organic antimony compounds are less toxic than inorganic bonded antimony.
2.3 Long-term toxicity (organs)	NOEL 70 µg/m3
2.3 Teratogenicity	No indication.
2.4 Mutagenicity	Suspected.
2.5 Carcinogenicity	Suspected with inhalative intake.
3. Ecotoxicology	
3.1 Environmental occurrence	Ubiquitous.
3.2 Degradability	
3.3 Accumulation	Accumulation in food chains not detected.
3.4 Others	Catalyst for dioxin/furan-formation in case of fire
4. Data situation	Unsatisfying.
5. Result	Reduction desirable.

The concentration in soil is geogenically caused and has in 0 -10 cm soil depth a value between 0.2 and 0.5 mg/kg dry substance. The transfer of diantimony from the soil into plants is low with ca. 3%. There are investigations about the daily intake of diantimony in humans via drinking water and food. About 5 µg diantimony per day and person are ingested.

Diantimony concentrations in humans resulting from the use of ATO as flame-retardant cannot be indicated. A minor contamination from ATO-“rub off” of domestic consumer goods or through direct object-mouth contact for children can be assumed.

In 1994, some scientists expressed the suspicion, that sudden child mortality could be connected to the flame-retardant ATO used in mattresses whereby highly toxic, volatile stibine (SbH_3) would be formed through microbial conversion. Targeted investigations with regard to this could not confirm this suspicion.

Evaluations of exposition make little sense because e.g. information on concentration of diantimony in house dust is missing.

13.3 Toxicology

Especially for ATO, there is no information on oral resorption. Values of ca. 3% are indicated for antimony salts. Inhalative resorption is decisively dependant on the size of airborne particles as antimony is bound to particles. Dermal resorption of antimony from dust was detected in experiments on animals.

Resorbed antimony is rapidly eliminated from blood and accumulates in the thyroid gland, liver, spleen, kidney, heart, and bones. There is no precise information as to the half-life in these organs. Only a half-life value for the entire body is stated in the literature with a duration of 4 days. Five-valent antimony is mostly converted to three-valent antimony in the organism. Detoxification through methylation, as with arsenic, does not occur with antimony.

There are animal experiments and observations on humans with regard to the toxicity of antimony. Organs that are mainly targeted by antimony effects are lung, heart, eyes, and skin. For rats, inhalation of 1.6-4.2 mg ATO/m^3 leads to fibrosis, adenoma, hyperplasia and hyperplasia of pneumocytes. Damages on the myocard have been observed in rats, dogs, and rabbits that were exposed to 3-6 mg ATO/m^3 for one year. EEG-changes were found on workers dealing with antimony; five-valent antimony was in this case less effective than the three-valent one. Reports are available on antimony-air-pollution causing doses-related cataract. Observations of skin-effects are contradictory. Evidence of contact-dermatitis caused by antimony, antimony-dermatosis and papuler damages. These effects have all got in common that they cure within 14 days after exposure stops.

While the results on reproductive damages are uniform both in rats and humans (increase of miscarriages and premature births), investigation about mutagenicity and carcinogenicity is contradictory and polemic. While experiments on rats and mice do not confirm chromosome aberrations, these, on the other hand, were observed during tests carried out on hamsters. Chromosome-aberrations with ATO-exposure have also been observed in humans. Concerning cancerogenicity, there are reliable indications, that high pollution (antimony-workers) increases lung-cancer-mortality significantly. Results obtained from experiments on animals are not as clear.

No observed effect level with inhalative intake of 70 µg ATO/m3 (hyperplasia in peribronchial lymph nodes) and 6.4 mg/kg bodyweight and day (loss of weight and muscular atrophy) is indicated. It is, however, difficult to calculate a tolerable daily intake value from that because of grave indications of carcinogenicity.

13.4 Ecotoxicology

Investigations on ecotoxicology – effects on fish, invertebrates, bacteria, plants, and animals – confirm that no effects can be triggered by antimony oxide which is soluble in water.

13.5 Fire

In case of fire, not only ATO itself but also antimony halides (s. a.) are released. Antimony halides can be detected in soot in concentrations of 0.1 - 500 mg/kg. In connection with fire, it is to point out that ATO has the catalytic ability to accelerate the de novo-synthesises of chlorinated and brominated dioxins and furans. In this case there is a special risk when the synergist ATO is used.

13.6 Recycling

According to several estimates, the major part of ATO used in consumer goods reaches disposal sites. ATO incinerated with plastic material reaches the clinker to

50% and to an additional 50% the E-filter of the incineration sites. 5 µg antimony/m3 were detected in fume gas. It has not been investigated to what extend the antimony fume gas concentration is influenced by the antimony-input during waste combustion.

Recycling: no information.

13.7 Substance regulations

In 1991, the US-EPA derived a limit value for water of 5 µg/l by taking into account the accumulation in fish. The ADI-value of 0.4 µg/kg bodyweight and day offers the base of such reasoning. The ADI-value was derived from the unobserved effect level with a security factor of 1000. The limit value for antimony in the Ordinance for Drinking Water is 10 µg antimony/l. According to TA-air, the emission dust-shaped inorganic compounds (antimony, lead, chrome, copper, manganese, platinum, palladium, rhodium, vanadium, tin) must not exceed 5 mg/m3 at a mass flow of 25 g/h. No MAK-value for Antimony trioxide is fixed in the workplace. A TRK-value of 0.3 mg diantimony trioxide/m3 is valid. The carcinogenic effect of inhalatively ingested antimony is sufficiently proven according to the IARC. The suspicion of a carcinogenic effect in humans is sufficient. According to the Ordinance of Hazardous Substances, ATO is labelled with Xn, R40, S22, and S36. ATO is allocated in Class 2 of Water Hazards.

13.8 Conclusion

ATO is no flame-retardant. It is, as an inorganic powder, used together with bromine and chlorine-containing flame retardants as synergist which, in a case of fire, reacts into fire-inhibiting antimony-halides. Because of its use in large volumes, the toxicological significance of antimony as synergist has to be specially put to test.

Antimony exists naturally in the environment. Concentrations in air depend on the incineration sites in the region, as confirmed by air-surveillance. Natural occurrence dominates in soil and water. Only in enclosed spaces with antimony-containing consumer goods, an increase of antimony in house-dust can be possible. There is no analysis on the possible transmission of dust-bound antimony to humans.

It is known, that on average ca. 5 µg antimony/day is taken up via food and drinking water.

With regard to toxicology it is known, that high doses lead to effects on lung, heart, eyes, and skin. It needs to be pointed out in particular that there are very serious indications that inhalatively ingested antimony is carcinogenic. Discussion has not been completed.

Toxic antimonyhalide is formed in fire. Furthermore, antimony works in thermic processes as a catalyst for the formation of dioxin.

It needs to be proven, to what extend input of antimony-containing plastic waste on incineration sites or cement rotary furnaces leads to a higher emission of antimony.

As a whole, ATO as synergist used for flame retardants, does not cause any toxicologically relevant concentrations for humans and the ecosystems during normal use. A release of toxic antimonyhalides and antimony dusts is assumed in case of fire and when thermically disposed of.

14. Summary

14.1 Bases and categories of evaluation

Recommendations concerning the application of these 12 selected flame retardants and of the synergist antimony trioxide are based on a *toxicological comparison*. Relevant to the decision-making are accumulation potential in environmental media, factually proven occurrences in the immediate surroundings of humans and in humans themselves, chronic toxicity – cancerogenicity is top priority – acute toxicity in contact with skin and the post-application phase during disposal and recycling. As these properties remain unknown for some flame retardants, a classification will continue to result in a negative evaluation until evidence proves the opposite. With regard to the release of flame retardants from consumer goods it is of utmost important whether the flame retardant was bound in reactively or added to the plastics, thus enabling emission. It is often the case that questions concerning the importance of impurities in flame retardants – in this case halogenated dioxins and furans play an important role – and added components to improve technical properties can not be answered. And finally, a division into five categories of all 12 flame retardants and synergists is possible:

- rejection of application necessary
- to aim at substitutions in order to prevent environmental pollution
- problematic properties, therefore modification sensible
- due to a knowledge deficit no classification possible
- application is unproblematic seen from a toxicological viewpoint

14.2 Summarized substance characterisation

The most decisive properties to each flame retardant as shown in the summaries are as follows:

Decabromodiphenyl ether: High concentration in river sediment. Decabromodiphenylether and brominated furans are detectable in inner room air. The substance is persistent. Occupational medicine and animal tests show indications for a cancerogenic potential. Significant amounts of brominated furans are built in thermic processes.

Tetrabromobisphenol A: Moderate remission during application of reactive flame retardant. The use of additive flame retardant results in occurrences in environmental media and food chains. TBBA is persistent. High sediment contamination in the immediate region of textile factories; detectable both in fish and samples of mother's milk. High concentrations in house dust and inner room air. Cancerogenicity has not been examined. Acute effects on mucous membranes were observed. Water toxicity is high. The potential concerning furan and dioxin formation is reduced thanks to carbon-bridging.

1,2 - bis (pentabromophenyl)ethane: High accumulation in food chains are not to be expected. Environmental contamination, however, needs to be surveyed. There are no examinations as to the toxicokinetics and cancerogenicity. The potential regarding dioxin and furan formation is moderate as shown in examinations carried out on recycled products and during combustion experiments.

Hexabromocyclododecane (HBCD): Transmission into the environment is possible due to additive application. Significant accumulation in river sediments with discharge from the textile industry is proven; so far no evidence in food chains. No systematic analysis has been carried out on this though. Analyses upon toxicity show no significant toxic effects. The potential concerning dioxin and furan formation is modest.

Tris (1-chloro-2-propyl) phosphate (TCPP): High environmental persistence. Detected in food. Occurrence in samples taken from house dust. Reliable analyses on exposure in humans are missing. There are some references concerning cancerogenic effects. No data on behaviour during recycling.

Resorcinol bis (diphenylphosphate) (RDP): No data concerning occurrences in environmental samples. Analyses based on animal experiments are incomplete. Studies on cancerogenicity are missing. Disposal is unproblematic. Data on behaviour during recycling is missing.

N-Hydroxymethyl-3-dimethylphosphonpropionamide: As the flame retardant is fibre-bound, a release into environmental media is limited. Accumulation in food chains is unlikely. No data available on occurrence and toxicokinetics of Pyrovatex CP new. Acute effects are represented by skin irritation. Cancerogenicity has not been examined.

Red Phosphorus: Additional hazards caused by red phosphorus used as flame retardant play a minor role considering natural occurrences of phosphorus. Toxicity is low except for skin irritation caused by direct contact with red phosphorus. Phosphor oxide and phosphorous acid are released in a case of fire. Data on recycling of phosphorous-containing plastics is missing.

Ammonium polyphosphate (APP): Due to the application as additive flame retardant in polyurethane, release into environmental media is possible. However, no relevant hazards are caused. Toxic effects are not mentioned. Merely irritations of the skin and the mucous membrane are reported. Nitrogen oxide and ammonia are formed in fire. Its behaviour during recycling is favourable.

Melamine cyanurate (MC): This flame retardant is used additively. Release into environmental agents is possible. Environmental agents have not been analysed. Toxicology of melamine cyanurate has not been examined. Toxic fumes such as hydrocyanic acid and isocyanate are formed in a case of fire.

Aluminium trihydroxide (ATH): There is no measurable increase with regard to the aluminium content in environmental samples as a consequence of the application as flame retardant. No indication of human- or ecotoxicological problems.

Sodium borate decahydrate (Borax): Due to its additive use for insulation material, release into environmental media is possible. Soil and ground water are likewise affected. Toxicology is well-researched with the result that daily consumption is in the order of tolerance values. Further borax-exposure is undesired. What needs to be determined is whether Borax can lead to additional exposure when used as flame retardant.

Diantimony trioxide: is no flame retardant but a synergist for halogen-containing flame retardants. In a case of fire it reacts into antimonyhalides, which have an anti-flammable effect. Release of antimony trioxide from plastics is moderate. Release of Antimony compounds is problematic with regard to waste-combustion. Inhaled Antimony is probably cancerogenic.

Based on this substance characterisation the following evaluation as seen in the overview V/14 is made.

Overview V/14: Evaluation summary on flame retardants	
I Application rejected	- Decabromodiphenyl oxide - Tetrabromobisphenol A, additive
II Reduction sensible, substitution desired	- Tetrabromobisphenol A, reactive - Tris(1-chloro-2-propyl) phosphate
III Problematic properties; reduction sensible	- Hexabromocyclododecane - Sodium borate decahydrate - Antimony trioxide
IV Recommendation impossible due to a data deficit	- Decabromodiphenyl oxide - Resorcinol bis (diphenyl phosphate) - Pyrovatex CP new - Melamine cyanurate
V Application unproblematic	- Red Phosphorus - Ammonium polyphosphate - Aluminium trioxide

15. Appendix: Overview on flame retardants according to the classifications made by GefStoffVO

In the overviews V/15-1 and V/15-2, an additional 14 flame retardants are introduced next to the 13 already examined and their classification according to R- and S- terms in compliance with the German GefahrstoffVerordnung (Ordinance of Hazardous Substances, under the regulations of Appendix III of the EU-directives 67/548/EWG]). These are additional substances which were often found during application analyses (comp. Chapt. VI and Vol. II of this study) or recommended as substitutes.

This listed substances could be found in the following fields of application (comp. application-related analyses in Vol. II):

- *Rail vehicles*: brominated polystyrene, tetrabromophthalic anhydride and melamine resin.

- *PUR - rigid foams*: dibromoneopentyl glycol, brominated polyols, diethyl ethylphosphonate (DEEP), diphenylcresyl phosphate (DPK), triethyl phosphate (TEP), tricresyl phosphate (TCP), triphenyl phosphate (TPP), expandable graphite and melamine; dicumyl peroxide as synergist in expandable polysterene.

- *Outer casings for electronic devices*: diphenylcresyl phosphate (DPK), triphenyl phosphate (TPP)

- *Printed cuircuit boards*: diphenylcresyl phosphate (DPK), Struktol, tricresyl phosphate (TCP), triphenyl phosphate (TPP), and melamine.

Textile/upholstery composites: THPC (Proban), ammonium phosphate and melamine (the two latter substances in flexible foam).

These additional flame retardants can be divided into brominated alkanols, brominated glycols, phosphoric esters (organophosphates) and inorganic compounds. It has to be said emphatically that a classification with R- and S- terms does not permit a toxicological/ecotoxicological evaluation and subsequent recommendation for application. It is necessary to have a closer look at substance data available in order to obtain evidence of chronical toxicity, dose-dependant organ damages, accumulation potential, persistence and occurrence in environmental media.

We consider a data clarification upon halogen-free phosphoric esters to be of utmost importance as their effects are repeatedly brought into connection with neurotoxic damages. It is important to carefully evaluate the cancerogenic potential of brominated polyols. Melamine on which there is no data in overview V/15-2 is badly biodegradable and occurs in environmental samples. Evidence on cancerogenicity as a consequence of moderate organ toxicity is provided by experiments on animals. It should be viewed as problematic substance. Merely zinc borate, magnesium hydroxide and expandable graphite should not cause any problems when used.

Classification of relevant flame retardants

Compilation of classifications in compliance with the Ordinance of Hazardous Substances according to the appendix III of EU-directives (67/548/EWG). The following data is product-related and was taken out of the safety data sheet provided by manufactures and chemical retail.

Overview V/15-1: Classification of relevant flame retardants - 13 Flame retardants investigated in this study

Flame retardant	Hazard Symbol	R-Terms	S-Terms	WGK	CAS Nr.	Product/Manufacturer
Decabromodiphenyl oxide (DeBDE)	k.A	k.A	k.A	k.A	1163-19-5	Saytex 102E (ALBEMARLE, 1999) DE-83 and DE-83R (GREAT LAKES, 1997)
Tetrabromobisphenol A (TBBA)	N	R 50/53	S 60, 61	k.A.	79-94-7	Saytex CP-2000, Saytex RB-100 (ALBEMARLE, 1999 + 1997) BA-59P and BA-59PC (GREAT LAKES, 1998) FR-1524 (BROMINE COMPOUNDS, 1998)
1,2-Bis (pentabromophenyl) ethane	k.A.	k.A.	k.A.	k.A.	84852-53-9	Saytex 8010 (ALBEMARLE, 1999)
Hexabromocyclododecane (HBCD)	k.A.	k.A.	k.A.	k.A.	25637-99-4 (mixture of isomers) 3194-55-6 (HBCD))	FR-1206 (DEAD SEA BROMINE COMPOUNDS, 1995) Saytex HBCD (ALBEMARLE, 1995) Micronized CD-75P (GREAT LAKES, 1998)
Tris (1-chloro-2-propyl) phosphate (TCPP)	Xn	22,52,53	13 21 36/37	2 (SE)	13674-84-5	Fyrol PCF (AKZO NOBEL, 1995) Antiblaze TMCP (ALBRIGHT & WILSON, 1998) Levagard (BAYER, 1999) TCPP (CLARIANT, 1999)
Resorcinol bis (diphenylphosphate) (RDP)	k.A.	52/53	61	1 (SE) 2	57583-54-7	Fyrolflex (AKZO NOBEL, 1999) CR-733-S (NRC, 1997) Reofos (GREAT LAKES, 2000)
N-Hydroxymethyl-3-dimethylphosphonpropionamide	Xi	40, 43	23 24 37	1 (SE)	20120-33-6	Pyrovatex CP new (CIBA, 2000)

Flame retardant	**Hazard Symbol**	**R-Terrns**	**S-Terms**	**WGK**	**CAS Nr.**	**Product/Manufacturer**
Red Phosphorus (RP)	N	11, 16 50, 52	2 7 43.1	1 (SE) 0 (SE)	7723-14-0	Exolit RP 614 (CLARIANT, 2000) RP (SIGMA ALDRICH, 1999)
Ammonium polyphosphate (APP)	n.k.	n.k.	n.k.	1 (SE)	68333-79-9	Antiblaze CL/TR (ALBRIGHT & WILSON, 1998) Exolit AP 422 (HOECHST, 1982) FR CROS 484 (BUDENHEIM IBERICA, 1996)
Melamine cyanurate (MC)	k.A.	k.A.	k.A.	k.A.	37640-57-6	Fyrol MC (AKZO NOBEL, 1994) Budit 315 (BUDENHEIM IBERICA, 1997) Melapur (DSM, 1999)
Aluminium trihydroxide (ATH)	n.k.	n.k.	n.k.	n.k.	21645-51-2	(ALUSUISSE MARTINSWERK GmbH, 1998) (ALCAN CHEMICALS EUROPE, 1998)
Sodium borate decahydrate (Borax)	Xn	R 22 36/37/38, 62, 63	S 22, 26, 36/37/39, 45	1	1303-96-4	Sodium Borate Decahydrate (SIGMA-ALDRICH, 1999)
Antimony trioxide (ATO)	Xn	40	22, 36	2	1309-64-4	(Timonox, GREAT LAKES CHEMICAL [AZ] Ltd., 1993) (White, Blue Star, CAMPINE N.V.)

Comp. substance profiles Vol. III and Chapt. V1-13

Overview V/15-2: Classification of relevant flame retardants - Additional Substances

Flame retardants	**Hazard Symbol**	**R-Terrns**	**S-Terms**	**WGK**	**CAS Nr.**	**Product/Manufacturer**
1. Halogen-based flame retardants						
Brominated polystyrene (BrPS)	k.A.	k.A.	k.A.	k.A.	88497-56-7	Saytex HP-7010P / -HP-7010G (ALBEMARLE, 1997b) Pyro-Chek 60PB, -60PBC, -68PB, -68PBC, -68PBG, -77B, -LM (FERRO CORPORATION, o.J)
Dibromoneopentyl glycol	k.A.	22, 36, 40	36/37/39	k.A.	3296-90-0	Saytex FR-2000 (ALBEMARLE, 1999) FR-521, FR-522, (DEAD SEA BROMINE GROUP, 1991 AND 1999)
Tetrabromophthalic anhydride (TBPA)	Xi	k.A.	k.A.	k.A.	632-79-1	Great Lakes PHT4 ™, Saytex RB-49 (GREAT LAKES, 1997)
Tri(2-ethylhexyl)phosphate (TEHP)	Xi	26/27/28, 36/37/38, 45	23, 24/25, 45	2	78-42-2	99 %-ig (SIGMA-ALDRICH, 1999, ALBRIGHT & WILSON, 1989, BAYER AG, 1999)
Brominated polyols						
- Polyol Ixol B251	Xn	22, 36	26	k.A.	68441-62-3	(Solvay Fluor und Derivate GmbH, 1998)
- Polyol Ixol M125	Xn	22		k.A.	86675-46-9	(Solvay Fluor und Derivate GmbH, 1998)
- Saytex RB 79/	n.k.	52/53	k.A.	k.A.	20566-35-2	Saytex RB 79 (Solvay Fluor und Derivate GmbH)
PHT4-DIOL	Xn	22				PHT4-DIOL (Great Lakes Chemical (Europe) Ltd.)
- FoxOPolVD280					k.A.	FoxOPol VD280 (Resina Chemie B.V., 1995)
2.1 Halogen-free organophosphates.						
Diethyl ethyl phosphonate (DEEP)	Xi, N	38, 41, 51, 53	24/25, 26	1	78-38-6	Levagard VP AC 4048 (Bayer AG, 1999)
Diphenylcresyl phosphate (DPK)	k.A.	k.A.	k.A.	1	247-693-8	Reomol CDP (Ciba-Geigy) Disflamoll DPK (Bayer AG)
Struktol (PD 3730)	Xi	43			35948255	(Schill & Seilacher GmbH, 1997)
Struktol (PD 3710, 3720)	n.k.	n.k.	n.k.		35948255 35948255	(Schill & Seilacher GmbH, 1997)
Triethyl phosphate (TEP)	Xn	22	25	1	78-40-0	99 %-ig (SIGMA-ALDRICH, 1999)
Tricresyl phosphate (TCP)	Xn	21/22, 51/53	20-21, 28	2	1330-78-5	Tritolyl phosphoate (SIGMA-ALDRICH, 1999) Lindol (AKZO NOBEL, 1996) Disflamoll TKP (BAYER AG, 1999)

Flame Retardants	**Hazard Symbol**	**R-Terms**	**S-Terms**	**WGK**	**CAS Nr.**	**Product/Manufacturer**
Tetrakis (hydroxymethyl) Phosphoniumchloride (THPC)	k.A.	23/24/25, 34, 45, 46	23, 26, 36/37/39, 45	k.A.	124-64-1 (THPC) 27104-30-9 (THPCU)	THPC (SIGMA-ALDRICH, 1997)
Triphenyl phosphate (TPP)	N	20/21/22, 50/53	36, 61	2	115-86-6	Disflamoll TP (BAYER AG, 1999) 99 %-ig (SIGMA-ALDRICH, 1999)
2.2 Inorganic Phosphate						
Ammonium phosphate (AP)	k.A.	36/37/38	26, 36	k.A.	7722-76-1 (Mono-AP) 7783-28-0 (Di-AP)	(SIGMA-ALDRICH, 1999)
3. Other inorganic substances						
Expandable graphite	n.k.	n.k.	n.k.	1 (SE)	12777-87-6	(NORDMANN, RASSMANN GMBH & CO, 1998)
Magnesium hydroxide	k.A.	k.A.	k.A.	1 (SE)	1309-42-8 (anhyd.)	Magnifin (ALUSUISSE MARTINSWERK, 1999) 99 %-ig (SIGMA-ALDRICH, 1999)
Zinc borate	n.k.	n.k.	n.k.	n.k.	1332-07-6 149749-62-2 138265-88-0	Firebrake 500 (Enichem (Deutschland) Chemie Firebrake 415 Handels GmbH, 1998) Firebrake ZB
4. Nitrogen compounds						
Melamine	k.A.	k.A.	k.A.	k.A.	108-78-1	> 99.8 %-ig (DSM MELAPUR, 1996)
5. Synergists						
Peroxan DC	Xi, O, N	7, 36/38, 51/53	3/7, 14, 36/37/39, 50, 61	2	80-43-3	Dicumylperoxid (PERGAN GMBH, 2000)

Source: Safety data sheet of the manufacturer

Explanation of classifications (R- and S-phrases according to Annex III EU 67/548)

Xi:	irritant
Xn:	harmfull
N:	dangerous to environment
O:	oxidizing

R 7:	May cause fire
R 22:	Harmful if swallowed
R23/24/25	Toxic by inhalation, in contact with the skin and if swallowed
R 26/27/28	Very toxic by inhalation, in contact with the skin and ig swallowed
R 34	Causes burns
R 36:	Irritating to eyes
R 37	Irritating to respiratory system
R 38:	Irritating to skin
R 40:	Possible risk of irreversible effects
R 41:	Risk of serious damage to eyes
R 43:	May cause sensitisation by skin contact
R 45	May cause cancer
R 46:	May cause heritable geneticdamage
R 50:	Very toxic to aquatic organisms
R 51:	Toxic to aquatic organisms
R 52:	Harmful to aquatic organisms
R 53:	May cause long-term adverse effects in the aquatic environment
R 62	Possible risk of impaired fertility
R 63	Possible risk of harm to the unborn child

S 2:	Keep out of reach of children
S 3:	Keep in a cool place
S 7:	Keep container tightly closed
S 13:	Keep away from food, drink and animal feedstuffs
S 14:	Keep away from ... (incompatible material to be indicated by the manufacturer)
S 20/21:	When using do not eat, drink or smoke
S 23	Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer)
S 24:	Avoid contact with the skin
S 25:	Avoid contact with eyes
S 24/25:	Avoid contact with skin and eyes
S 26:	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S 28:	After contact with skin, wash immediately with plenty of ... (to be specified by the manufacturer)
S 36:	Wear suitable protective clothing
S 37:	Wear suitable gloves
S 39:	Wear eye/face protection
S 43.1:	In case of fire use water
S 45:	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)
S 50:	Do not mix with ... (to be specified by the manufacturer)
S 53:	Avoid exposure – obtain special instructions before use
S 60:	This material and/or ist container must be disposed of as hazardous waste
S 61:	Avoid release to the environment. Refer to special instructions/material safety data sheet

WGK 0:	nicht wassergefährdend/non hazardous to waters
WGK 1:	Schwach wassergefährdend/low hazard to waters
WGK 2:	Wassergefährdend/hazard to waters
(SE):	Selbsteinstufung/self classification
n.k.	nicht kennzeichnungspflichtig/no classification required
k.A.	keine Angaben/no data

Chapter VI: Flame retardant use in selected products – state-of-the-art, trends, alternatives

Chapter contents

Preface

This chapter summarizes the main results of the applications-oriented analyses of the use of flame retardants in various products. The following Overview VI/1 lists the

Overview VI/1: Flame retardants – quantitative overview by application areas examined (1999)

Application area	**Flame retardants used**	**Percentages of total flame retardant consumption** [1]
Rail vehicles - interior fittings and exterior parts made of UP resins	- Approx. 850 t aluminium trihydroxide - Small amounts of HET acid	< 1% of total flame retardant quantity < 2% of total mineral-based flame retardant quantity
Construction products – insulation and one-component foams	Approx. 12000 t flame retardant (brom. polyols, halogenated and halogen-free phosphoric acid ester in PUR; HBCD in polystyrene)	approx. 12% of total flame retardant quantity
Of this: - Polyurethane	of this in polyurethane: approx. 10,000 t total quantity - 4500 – 5000 t brominated polyols - 4000 – 5000 t TCPP + 500 t halogen-free organic phosphoric acid ester	- 10% of total flame retardant quantity - approx. 40% of brominated flame retardants - approx. 35% of organic phosphoric acid esters
- Polystyrene	of this in polystyrene: - 2000 t HBCD (without synergist dicumylperoxide)	- approx. 2% of total flame retardant quantity - approx. 17% of brominated flame retardants
Electrical and electronic applications – duroplastic printed circuit boards	- 3200 t TBBA (manufacture of base material) + small amounts of phosphoric acid compounds and ATH - Printed circuit boards in electronic scrap: represent approx. 4200 – 5100 t TBBA consumption	approx. 3% of total flame retardant quantity; - approx. 27% of brominated flame retardants
Electrical and electronic applications – outer casings for IT and TV appliances	Used for products sold in Germany approx. 4200 – 4600 t flame retardants - 1750 t brominated flame retardants + 460 t ATO; - Approx. 2200 t organic phosphoric acid compounds	4-5% of total flame retardant quantity - approx. 15% of brominated flame retardants - approx. 15% of the organic phosphoric acid compounds
Textile applications: Mattresses and covers for upholstered furniture	- Approx. 150 t flame retardants (home market and export) (antimony-halogen compounds; APP compounds; P-N compounds)	0.2% of total flame retardant quantity
All application areas	- Approx. 20500 t flame retardants in total - Approx. 11500 – 12500 brominated flame retardants (incl. import surplus contained in products) - Approx. 6700 – 7700 t phosphoric acid compounds - Approx. 1000 t mineral-based flame retardants	Approx. 22% of total flame retardant quantity

[1] The statement of percentages of total consumption of flame retardants (see Chapter 2, Table II/1) is only possible with qualifications, as the total consumption of flame retardants refers to production quantities, while the examined flame retardant content in the applications-focused analyses also takes into account the content in imported products. This share is particularly high with E+E appliances.

application areas, the main categories of flame retardants and their volumes.

The 13 flame retardants that were examined more closely in this study cover approximately four-fifths of total flame retardant consumption in Germany (all application areas; see Chapter III). The size of this proportion has, among other things, something to do with the fact that the selection contains a number of ‘prime products’; aluminium trihydrate (ATH) alone already covers approx. 50% of the total volume of flame retardants. If we proceed from the estimations that were made for the use of flame retardants in the application areas and for products, then this has a magnitude of 20 to 25% of the total flame retardant consumption.

The examined application areas represent highly diverse quantities of flame retardants. With reference to the total consumption in Germany (for 1999/2000 estimated at approx. 100,000 t; see Chapter II, Table A 1/1) [1] the magnitude is below 1% for UP resins for rail vehicles, approx. 12% for insulation and one-component foams in the construction sector, approx. 8% for printed circuit boards and the selected casings for E+E appliances (the share of the electrical and electronics sector as a whole is substantially higher). For covers of mattresses and upholstered furniture (also foam) this amounts to approx. 0.2%.

In the case of the brominated and the organic phosphorus flame retardants, the quantity of flame retardants identified in the applications-focused analyses is relatively high in comparison to total consumption. With mineral-based flame retardants this however is only approx. 2%, since the examined application area, in which they play a quantitatively important role (UP resins for rail vehicles) is small in absolute terms. However, the advantages and limits of mineral-based flame retardants are clearly seen in this example. From an overall perspective, the flame retardant groups that present problems from a toxicological and ecotoxicological viewpoint are well represented.

The applications-focused analysis of flame retardants shows that with regard to most of the examined products, a trend has started towards the substitution of halogenated flame retardants, or new formulations of flame retardant systems have been and are being developed that refrain from using halogenated flame retardants. Organic phosphorus flame retardants are gaining importance on the one hand, as are on the other hand design and material solutions in flame protection that are able to do without flame retardants. The evaluation views this trend as positive; however, the environmental relevance and especially the emissions behaviour of the organic phosphorus additives will demand greater attention in future. Overall, the various application areas show a substantial potential for the substitution and reduction of the use of environmentally relevant flame retardants.

In the following, only the most important results are presented; detailed information, as well as all sources and supporting documentation, is given in Volume II of this study.

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[1] Strictly seen, the consumption quantities of flame retardants estimated in Chapter II and the quantities identified in the applications-focused analyses cannot be related directly to each other, as the latter partially take into account the flame retardant contents of imported products, for instance of appliance casings, which are, for all intents and purposes, no longer produced in Germany.

1. Rail vehicles – interior fittings and exterior parts made of UP resins

In this chapter[2] we examine the flame retardance of components made of fibre-glass reinforced unsaturated polyester resins, which accounts for approximately three-quarters of the plastics that are utilized in modern rail vehicles. By way of comparison, we also look at fibre-glass reinforced components manufactured on the basis of phenolic resins.

Overview VI/2: Rail vehicles – interior fittings and exterior parts made of UP resins	
Examined products	Components made of fibre-glass reinforced unsaturated polyester resins for the interior fittings of rail vehicles (interior ceilings, side walls and cabinet panelling) and exterior parts (exterior aprons, roof panelling, vehicle heads, etc.)
Fire safety requirements	DIN 5510; comparison with BS 6853 [Great Britain] and NFF 16-101 [France]
Utilized plastics	Fibre-glass reinforced plastic on the basis of unsaturated polyester resins; comparison with phenolic resins
Plastics by quantity and representativeness	1999 approx. 1700-1800 tonnes UP resin; approx. 75% of the plastics utilized in rail vehicles
Recommended/ utilized flame retardants	• Previously brominated (and chlorinated) flame retardants • Today up to 90% aluminium trihydroxide (ATH); also HET acid
Use status and trends	Far-reaching substitution of halogenated flame retardants by ATH.
Flame retardant quantities and totals	• 1990 approx. 100 tonnes halogen/ATO flame retardants + 750 tonnes filler (chalk or ATH) • 1999 approx. 850 tonnes ATH + formulation auxiliary additives
Emissions; by-products of fires	Fume density and toxicity for UP resins with ATH systems (and for phenolic resins) substantially lower than for UP resins incorporating halogenated flame retardants.
Recyclability	Recycling of fibre-glass reinforced plastics from rail vehicles does not occur at this time. This will probably be facilitated by a change to ATH flame protection.
Substitution and reduction potential	Largely exhausted.
Evaluation	Sensible trend

Rail vehicles for passenger traffic (railroads, urban railroads, trams) demand special technical requirements for fire safety. They are closed vehicles that offer limited escape possibilities and partly travel underground or in tunnels, which further limits the escape and rescue possibilities, while increasing the hazards associated with fire and the by-products of fires.

The halogenated flame protection that was usual until the end of the 1980s for fibre-glass reinforced UP resins in rail vehicles has been largely replaced by the development of UP resin systems that contain a high percentage of filler incorporating the flame-retarding aluminium trihydrate (ATH). The development of such systems made an adaptation of the resins and the ATH types necessary, including the introduction of special additives, without which the corresponding filling level could not be reached. The information provided refers to Germany. This trend, however, is determined by developments in fire safety requirements, which are

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[2] Summary of Chapter I: Rail vehicles - interior fittings and exterior parts made of UP resins, Volume II, pp. 1-35.

higher in some foreign countries (Great Britain, France) and will be higher within the framework of the upcoming EU harmonization.

1.1 Plastics in rail vehicles

Plastics are mainly used in rail vehicles for the interior fittings of the trains (interior ceilings, side wall and cabinet panelling, tables, seating shells, etc.), but are in part also utilized for exterior components (exterior aprons, roof panelling, vehicle heads, etc.). The share of plastic in the carriages of rail vehicles operating in public passenger transport is currently approx. 4-5% of weight. The share of three-dimensional pre-formed components made of fibre-glass reinforced plastic (FGRP) has increased distinctly in the past. This amounted to approx. 20% in the 1970s and is presently reaching a share of over 50% for interior fitting components in comparable train types.

Among the utilized plastics, duroplastics clearly dominate with approx. 90%. Thermoplastics (especially PVC) amount to approx. 10%. Of the duroplastics, 80% (or three-quarters of the total application of plastics) are unsaturated polyester resins (UP resins). The remainder (20% of the duroplastics) are phenolic, melamin, and epoxy resins, as well as acrylates, etc.

The order of magnitude of the UP resins utilized at the end of the 1990s in Germany is between 1700 and 1800 tonnes. From a viewpoint of volume, we are therefore dealing with a comparatively small area.

1.2 Fire safety requirements

DIN 5510 documents the fire safety requirements for rail vehicles that are valid in *Germany*. This standard assigns rail vehicles to four fire classes, in accordance with the type of traffic operation (above ground/underground/distance between stops), and establishes flammability classes (S1-S5), smoke development classes (SR1, SR2), and ‘non-dripping on combustion’ classes (ST1, ST2) for construction components. As a rule, the higher fire safety classes S3 or S4, as well as the smoke development class SR2, must be met in rail vehicles for public passenger traffic.

The fire safety requirements in France and Great Britain are a good deal stricter than in Germany. Those materials that are assigned to the highest protection levels in Germany, in accordance with DIN 5510, do not reach the level of the strictest fire safety classes of these two countries.

In *Great Britain*, the fire in the London Underground, at King's Cross station in 1987, has led to an increase in the requirements for fire safety in rail vehicles, with regard to toxicity and fume density. Flammability, fume density, and toxicity are in fact equally important in the British standard BS 6853. This is similarly valid for the *French* standard NFF 16-101, with it's flammability classes M0 – M4 (classification according to inflammability, speed of fire spreading, dripping properties of burning materials) and fume development classes F0 – F5 (classification according to fume density and toxicity).

Within the EU, efforts have been underway since 1991 for a harmonization of the fire safety requirements for rail vehicles. Here greater importance is also being attached to the by-products of fires. Harmonization of the applicable standards is not to be expected before 2002.

1.3 UP resins: Formulation, processing, combustion behaviour

Unsaturated polyester (UP) resins are polycondensation products that are hardened into irreversible, three-dimensional, cross-linked moulding compounds (composites) in two steps. In the first step a half finished product is manufactured (a resin that has not finished reacting and is 'filled' with glass fibres and filling substances), which is given form and precipitation-hardened in the second step. The glass fibres provide a high tensile strength and bending rigidity, while the fill and aggregate materials guarantee crushing strength, and the duroplastic reactive resins ensure the cohesion and form stability. The formulation of the resins (composition of the resins, filler content, fibre-glass share) is dependent on various factors, such as the material requirements, including fire safety requirements, compatibility of the components, processing methods, etc.

40–50% of fibre composite materials are manufactured by the hot pressing method (mainly sheet moulding compounds [SMC], furthermore bulk moulding compounds [BMC]), and 50–60% in more work intensive processes, such as a hand lay-up process (40% share), resin transfer moulding (RTM), pultrusion, etc.

UP resins without flame-protection burn well. Decomposition starts at 120–140°C. Because of their aromatic structure content, UP resins that have been hardened with polystyrene exhibit strong smoke development in the event of fire, while the utilization of non-aromatic hardeners (ethyl-acetate, methylmetacrylate) lessens the development of smoke.

in the 1980s halogenated flame retardants were incorporated in UP resins so as to be able to reach the highest fire safety classes. Because of increasing fire safety requirements with a view to the by-products of fires (fume density and toxicity), this method fell into disuse after 1987 (King's Cross). This development at first favoured phenolic resins.

Phenolic resins require high ignition energy and burn slowly. Depending on their formulation, they are temperature-resistant up to 120-175°C and decompose at approx. 300°C. They extinguish once the source of ignition is removed, but do have a tendency to afterglow. In the event of fire, phenolic resins develop little smoke and, in comparison with duroplastics (UP resins) containing halogenated flame retardants, the fumes are less toxic.

In the meantime though, modern glass-fibre reinforced UP resins containing non-halogenated flame retardants have at least the same if not better flame-protecting properties than phenolic resins. The other advantages in comparison with phenolic resins, for instance in processing technology and costs (phenolic resins are 10-20% more expensive in comparison to polyester resins), may be the reason why they largely have replaced not only halogenated UP resins, but also phenolic resins.

However, halogenated flame retardants for UP resins and halogenated UP resin systems continue to be offered for sale.

1.4 Flame-retardant systems for UP resins – status, trends, quantities used

Halogenated flame retardance

Halogenated flame retardance was a standard with UP resins for a long time and can be achieved both reactively (using e.g. HET acid [Hexachloro-endo-methylenetetrahydrophthalic acid], tetrabromophthalic acid anhydride, dibromoneopentylglycol) and additively (diphenyl ether, chloroparaffins, brominated polystyrene or polypentabromo benzyl acrylate) in connection with antimony trioxide as a synergist.

The quantity of halogenated or brominated flame retardants, which must be added to UP resins, is dependent on the required fire safety class and the filler, among other things. If ATH (filler share in the composite material approx. 50%) is used as a filler, which is more expensive than chalk and has a flame-retarding action on its own, then the share of the halogenated flame retardant in the composite (fire safety according to DIN 5510, highest level: S4, SR2, ST2) is 3-4%, plus 1.5% antimony trioxide. An average share of 5% halogenated flame retardant in the composite is presumably the upper limit.

The share of UP resins that are protected with halogenated flame retardants is currently estimated at approx. 10% (flame retardant: HET acid). Such resins are used especially where the mechanical requirements are high, for instance the exterior parts of locomotive noses that are produced by a hand lay-up process, where the requirements cannot be met using a high filler content, but where the requirements with regard to smoke development are lower than for interior parts.

Halogen-free flame retardance

Use of ATH in pre-formed components made of UP resins is today both possible and usual, even for the highest fire safety requirements.

If ATH is used as the sole flame retardant, then it must be added in larger proportions. The required filling levels can in the meantime be reached, due to the further development of UP resins, modified flow and fill behaviour of ATH, as well as the application of additives as flow-enhancing agents.

For SMC pre-formed parts made of UP resins, the maximum fill proportion of ATH was around 150-200 phr[3] in the beginning of the 1990s. With this, the highest German standard for SMC materials in interior fittings for rail vehicles is achieved (flammability class S4, smoke development class SR2, and ‘non-dripping on combustion’ class ST2, in accordance with DIN 5510,T.2). This fill level is however not sufficient for the highest British or French standards (for instance, according to NFF 16-101 it only warrants the category M3/F2).

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[3] phr: per hundred of resin.

In comparison to this, UP resin formulations with ATH were ready for mass production by the mid-1990s, with an ATH fill-level of 250 – 350 phr with a fibre-glass content of 25%. These UP resins reach an M2/F1 or M1/F0 classification according to NFF 16-101 (French standard). They therefore conform to the classifications for phenolic resins and receive a higher classification than halogenated UP resins, with regard to the by-products of fires.

Pure ATH flame retardance first gained acceptance with SMC pre-formed parts that contained a high share of resins and a comparatively low share of glass fibres. For pre-formed parts produced by the hand lay-up process or another closed process, in part with a high glass fibre content and a lesser resin and filler content (pultrusion, resin transfer moulding/injection process), and which together account for approx. 50-60% of UP resin processing, the preconditions for non-halogenated flame retardance through formulations with a high ATH content have also been realized since the mid-1990s.

For processes with a reduced resin content, and therefore more difficulties with introducing larger quantities of ATH into the system (pultrusion and RTM processes), phosphorus compounds (ammonium polyphosphate, with an intumescent action, and red phosphorus) are being offered as a flame retardant, besides or in combination with ATH. Through the comparatively low filler quantities, the viscosity (flow characteristics) and density of the resin, and with this the processing properties, can be influenced to advantage.

Flame retardant quantities used

With a halogenated flame retardance of UP resins, the quantity balance sheet would have to show the use of approx. 75 tonnes of halogenated flame retardants, 23 tonnes of antimony trioxide, besides approx. 750 tonnes of filler, based on the current annual production in rail carriages (3300 in 1999). The switch that took place in the 1990s to ATH flame-retarded UP resin systems has replaced approx. 100 tonnes of halogen and antimony trioxide flame retardants with approx. 850 tonnes of aluminium trihydrate that, in this instance, fulfils the function of both flame retardant and filler.

1.5 Comparison of combustion behaviour and the by-products of fire in halogenated and halogen-free flame-retarded UP resins

In a smouldering or combustion condition, the fume density of UP resins filled with ATH is substantially less than that of halogenated UP resins (up to a factor of 10) and is similar (smouldering) or less than (combustion) that of phenolic resins. The comparatively high fume density and toxicity of halogenated flame-retarded UP resins was the most important reason that spoke against their further utilization.

The following is remarkable: Those UP resins which contain a high level of filler fare better in the classification according to NFF 16-101 (combined index for fume and toxicity of the French standard) and in the cone calorimeter test, than the phenolic resins that were permitted for use in the London Underground. But they do less well in the fire test, which is required by the British BS 6853 standard and therefore for the utilization permit in the London Underground (3 m³ test), than phenolic resins, and they therefore do not meet the corresponding permit requirements. The differing test requirements and the weaker fire source in the 3 m³ test can explain this at first sight surprising and contradictory result. At lower ignition energies, the phenolic resin does not ignite as quickly as UP resins, and under these conditions its fire properties are more advantageous. But if it starts to burn at a higher ignition energy, then its combustion properties (by-products of fire) are worse.

Such contradictory test results highlight the need for a uniform testing procedure within the framework of the European harmonization of fire safety requirements. In the newly developed SBI fire test[4] and after a preliminary test series, highly filled SMC UP resins show somewhat better results than phenolic resins.

1.6 Material properties, costs

With an increasing ATH content, the density and weight of the systems rise with highly filled UP resins; the density can reach a value of 2.2, as against 1.4 – 1.5 for halogenated flame-retarded systems. The increase in the density can be partially cushioned by a combination of ATH with ammonium phosphate, or through the substitution of styrene, as hardening monomer, by the more expensive methylmetacrylate (MMA). The increase in density, and the associated deterioration of mechanical properties, is at this time viewed as a limiting factor for the future utilization of ATH as a flame retardant in high-performance structures manufactured from fibre-glass reinforced plastics for weight-reduced rail vehicles.

Systems filled with ATH are, as a rule, cheaper than UP resins that are flame-retarded by halogenation.

1.7 Design and material alternatives

Duroplastic synthetics compete primarily with the classic materials, such as steel and aluminium, in the construction of rail vehicles. For the selection of materials, the material properties, such as rigidity, impact strength, density (weight), durability (corrosion resistance), fire safety, as well as costs are the deciding factors. With otherwise comparable material properties, the competitive advantage of composite materials containing fibres lies mainly in their potential for reducing weight, which has contributed to the growth of their share in the market during the past years. This potential is estimated at approx. 10%, in comparison to metallic materials. One of the limitations of duroplastics, in comparison to metallic materials, results from the physical-mechanical properties that are especially observable in ‘crash tests’, which they do not survive as well as metallic materials.

Among the duroplastics, the main competitors are *UP and phenolic resins*, whereby the advantages that phenolic resins enjoyed, because of their fire properties, have been cancelled out in the last few years by the developments in UP resins. In comparison to polyester resins, phenolic resins are 10-20% more expensive. *Melamin laminates* have technological processing disadvantages compared to other duroplastics, because they cannot easily be formed three-dimensionally.

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[4] SBI test: A new testing method, developed within the framework of the harmonization of the European fire safety standards, in which the combustion behaviour of a single burning object, located in a corner of a room, is examined.

Thermoplastic composites, which are lighter than duroplastics, have good pigmentation properties, and are easier to recycle, nevertheless are competitive only with limitations, because of their mechanical properties and their combustion behaviour.

1.8 Recycling/disposal

While fibre-glass reinforced plastics incorporating flame retardants, including UP resins from the automobile industry, are collected by a company that is supported by the duroplastic manufacturers, are recycled as ground stock, and added to new products in limited quantities, halogen-free flame-retarded UP resins from rail vehicles have so far not been recycled. In contrast to halogenated UP resins, the recycling company does not see any basic problems in a comparable re-use of ATH filled UP resins. This is also the view of the manufacturers of rail vehicles, who assume that, in view of a service life of between 20 and 30 years for rail vehicles, relevant quantities of halogen-free flame-retarded UP resins will only arise in two decades. This is why incineration and landfill are the usual disposal methods.

1.9 Trends

With regard to UP resins for use in rail vehicles, the previously common flame-protection with halogenated or brominated flame retardants (reactive and additive), in combination with antimony trioxide, has been almost completely replaced by ATH.

The most important innovations in the 1990s were:

- Resin formulation (combination of UP resins with thermoplastics; reduction of viscosity and a resulting improvement in flow behaviour);
- The development of ‘adapted’ ATH types, with a reduced average particle size and a broad range of size, which results in an advantageous flow behaviour, a reduced tendency to sedimentation, and improved flame-retarding properties;
- The application of additives, which serve to lower the viscosity by reducing the attraction between solid particles, giving them better flow properties in the resin.

Through the development of corresponding resin, ATH and additive systems, filling levels of between 400-450 phr can currently be attained.

The decisive impetus for this development came from rising requirements with regard to by-products of fires (fume density and toxicity in the event of fire) that were implemented outside of Germany. Ultimately, the fact that ATH flame-retarded UP resins are cheaper than halogenated UP or phenolic resins encouraged this substitution. Deutsche Bahn AG (the German rail operator), as a major client, demands non-halogenated flame retardance as a matter of principle. Besides personal safety, the protection of property (corrosion, damage to electronic components by fire gases) as well as the cleanup and disposal costs associated with the formation of dioxins/furans in the event of fire are also decisive factors.

1.10 Evaluation

Aluminium trihydroxide (ATH), which is used as a substitute for halogenated flame retardants, is – both as a pure substance (trade product) and as an applied flame retardant – largely unproblematic[5] from a toxicological and ecotoxicological viewpoint. In the event of fire and in comparison to halogenated flame-retardance, it has favourable effects on the by-products of the fire (fume density; fume toxicity). The material recycling of flame-retarded composite materials made of UP resins is, in principle, possible. The increase in material density and weight must, in contrast, be evaluated negatively. In comparison to halogenated UP resins, this is not important, as they do not conform to the higher fire safety requirements. It could, however, be a factor that limits utilization in the future.

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[5] See Chapter V. 11 and Volume III, substance profile ATH, pp. 207-230.

2. Construction products – polyurethane insulation and one-component foams (with a discussion of polystyrene insulation foam)

We examine insulation and one-component foams made of polyurethane (PUR) rigid foam with regard to flame-retardant status and trends. Because of their different formulation and flame-retardant incorporation, insulation and one-component foams must be considered separately. For the purpose of comparison, the flame-retardant composition of polystyrene insulation materials is also discussed.[6]

Overview VI/3: Polyurethane insulation and one-component foams in the construction sector	
Examined products	PUR insulation and one-component foams (block foam and slabstock, sandwich elements, in-situ PUR foam, one-component foam); for comparison: insulation foams made of polystyrene
Fire safety requirements	DIN 4102
Utilized plastics	Polyurethane (PUR) and polyisocyanurate (PIR) rigid foam
Plastics by quantity and representative-ness	• PUR insulation and one-component foams 1998/1999: approx. 80,000 tonnes. PUR insulation foam: approx. 6% of total insulated surface area • PS insulation foam: approx. 170,000 t, around 40% of total insulated surface area
Recommended/ utilized flame retardants	Brominated polyols; TCPP; halogen-free organic phosphoric acid ester (DEEP, TEP, DPK, etc.). Solid flame retardants (ammonium polyphosphate)
Use status and trends	• Block and slabstock foam: Classic flame-retardant composition (flame retardant content: Approx. 10% of weight) using brominated polyols and halogenated phosphoric acid esters (previously: TCEP + TCPP, currently: TCPP). On switch from PUR to PIR-modified PUR foams (polymer modification) phase-out of use of brominated polyols, partial substitution of TCPP by halogen-free triaryl-/trialkyl phosphate acid ester (largely realized with block foam, 60% realized with slabstock) • Sandwich elements: until now, classic flame-retardant composition; switch to PIR modified PUR foam is expected. • In-situ PUR foam: Classic formulation. PIR foam not possible. • One-component foam: Classic flame-retardant composition (flame retardant content: Approx. 20% of weight); new formulations without brominated polyols and with reduced flame retardant content (approx. 10% of weight) substituting TCPP by halogen-free P-ester.
Flame retardant quantities and totals	Utilization 1999 approx. 4500 – 5000 t brominated polyols, 4000 – 5000 t TCPP; 500 t halogen-free phosphoric acid ester. Total approx. 10,400 t flame retardants (of which 6600 t in insulation foams and 3800 t in one-component foams)
Emissions; by-products of fires	TCEP/TCPP relevant in terms of indoor air quality and water resources protection. Fume density with PIR foam is less than with PUR foam.
Recyclability	Recycling of PUR insulation foams does not occur (minor exceptions: production waste).
Substitution and reduction potential	In the case of polymer modification (from PUR to PIR foam; new formulation of one-component foam) a substitution and reduction potential becomes possible with coninuous-process foam and sandwich elements, with a maximum of 4000 t flame retardants, and in the case of one component foams a maximum of 50% of the utilized flame retardants (approx. 1900 t).
Evaluation	Full use of the substitution and reduction potential is expedient; halogen-free phosphoric acid esters must be tested with regard to their emissions potential.

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[6] Summary of Chapter II, Construction products - insulation and one-component foams made of polyurethane, Volume II, pp. 37-116.

From the viewpoint of flame-retardance, construction products made of plastic must conform to the prescribed construction material classes that are required in accordance with building regulations. This usually presupposes incorporation of flame retardants. The testing and classification of construction materials are at present still disparate across Europe, but will be harmonized in future in accordance with the European construction products directive.

The quantitatively important flame retardant types, among the flame-retarded PUR insulation materials, are on the one hand the reactive brominated polyols, and on the other hand additive halogenated or halogen-free organic phosphorus compounds, which are added in a fluid form. Ammonium polyphosphate (APP) is marketed as a solid flame-retarding additive. In polystyrene insulation foams hexabromocyclododecane (HBCD) is used as a flame retardant exclusively.

The flame-retardant composition of PUR insulation materials depends greatly upon the formulation of the PUR foam. While maintaining an equivalent fire safety classification, the amount of the halogenated reactive flame retardant can be reduced or a part of the halogenated phosphoric acid ester can be replaced by halogen-free phosphorus compounds, when a high share of isocyanurate structures is present in the foam (so-called PIR foam). This developing trend presents an important substitution and reduction potential with regard to flame retardants for PUR insulation and one-component foams.

2.1 Insulation foams in the construction sector

Among the three quantitatively important insulation materials, namely mineral wool, polystyrene (expandable polystyrene, EPS, and extruded polystyrene rigid foam, XPS), and polyurethane, PUR is clearly positioned in third place. PUR insulation materials, with approx. 6%, represent only a small share of the total insulated surface area in the construction sector. With regard to surface area, the share of mineral-based insulation materials (without flame retardants) is approx. 50%, and that of (flame-retarded) polystyrene approx. 40%. Despite the small share in total surface, PUR insulation materials nevertheless account for two-thirds of total flame retardant consumption.

Important application areas of PUR insulation foams are roof, wall, and floor insulation, composite elements (sandwich elements) for the construction of industrial buildings, halls and cold-storage houses, fillers for joints and cavities (one-component foam), as well as surface-adapted technical insulation materials for roofs, interior spaces and technical applications (moulding and spray foam). The two last-mentioned application areas are a result of the fact that PUR foams, in contrast to all other insulation foams, can be foamed directly at the site. PUR insulation foam, while providing the best insulation performance, is substantially more expensive than mineral wool and EPS at the same performance level.

More than 80,000 tonnes of flame-retarded PUR rigid foam is sold annually in Germany, for insulation and assembly purposes in the construction sector and for technical applications (reference years 1998/1999). The single most important market segment is the manufacture of *sandwich elements* for the construction of industrial halls and buildings (34,000 tonnes, 40% of the total volume). The second most important segment of the market is the production of *slabstock products* (23,000 tonnes, 28%), followed by *one-component foams* (17,000 tonnes, approx. 20%), *block foam* (approx. 7%), and *in-situ foam* with just under 4% market share.

2.2 Fire safety requirements

Polyurethane insulation materials in the construction sector are considered as construction products (permanently placed building materials in built structures) and are subject to the fire safety requirements of the applicable construction regulations, which vary among the regional states (Länder) of Germany. Their fire safety testing and classification is regulated in the DIN 4102 standard on the combustion behaviour of building materials and components.

As organic materials and in contrast to mineral wool, PUR insulation and one-component foams are classified, like polystyrene insulation foam, in the building material class B (flammable building materials), not as building material class A (non-flammable building materials). Flame-retarded PUR insulation foam is available almost exclusively (more than 95%) in the B2 class (‘normally flammable’ building materials).

The European directive on construction products provides for uniform testing and classification of building materials throughout Europe in the future. The building materials classified as B1 and B2 in DIN 4102 will fall within the European classifications B, C, D, and E. A new testing method, the Single Burning Item (SBI) test, will be introduced for classifications in the European classes C, D, and E. Fume toxicity and smoke density will increase in importance in these tests. It is possible that this will bring about changes in the classification of PUR insulation foams and have an effect on their flame-retardant composition. A transition period of 5 to 10 years can be expected for implementation of this EU directive.

2.3 PUR insulation and one-component foams: Formulation, processing, combustion behaviour

Polyurethane rigid foams consist of cross-linked macromolecules with a closed cell structure. Polyurethanes (PUR) are *organic flammable duroplastics* that are derived from a reaction between isocyanates and polyols.

One important innovation of the last years in polyurethane chemistry was the transition from PUR foams to so-called PUR-modified PIR (polyisocyanurate) foams, or isocyanurate-modified PUR foam. PUR and PIR formulations are differentiated with regard to their polyol base and the quantity of isocyanate, as well as according to the quantity and type of flame retardants utilized. PIR foam with a higher share of isocyanate is cross-linked more strongly. PUR foam contains mainly polyether as a polyol component, while PIR foam contains mostly polyester. Polyester polyols have, because of the somewhat higher thermal stability of the ester bond, a better combustion behaviour than polyether polyols and they contribute to a quicker formation of a carbonized surface.

In order to be able to obtain a B2 classification, the polyether polyols in PUR foams are combined with halogenated polyols (as a reactive flame retardant component) and flame-retardant additives. The better combustion behaviour of PIR foams can be traced to the polyester-polyol base, the higher isocyanate proportion and therefore higher share of aromatic compounds, as well as the isocyanurate ring structures. With B2 classified PIR foams, the reactive flame retardant component is no longer necessary and, at the same time, the quantity of additive flame retardants can be reduced substantially, whereby, under certain circumstances, halogen-free products can be substituted for halogenated products.

This transformation in foam formulations from PUR to PIR, which is promising from a fire safety perspective, so far only concerns block and slabstock foam. The PIR share in this is around 65%. In total, more than three-quarters of polyurethane insulation and one-component foams are today still formulated as PUR. The expected switch to PIR foam for sandwich elements would involve a substantial change in the quantity ratios, which would also affect flame retardant usage. The in-situ and one-component foam products used at construction sites have up to now been exclusively formulated as PUR foams.

Combustion behaviour

PIR/PUR rigid foam materials are, like all organic materials, flammable. Their combustion behaviour is largely influenced by the combustion behaviour of the original products (especially the polyols), by the degree of cross-linking of the rigid foam, that is the formation of the polyisocyanurate (PIR) structures in the macromolecule, and by the incorporation of flame retardants in the polymer.

Polyurethane foams are thermally stable up to and above 120°C. They begin to decompose into their component substances (isocyanate and polyol) at approx. 200-220°C; the structure of the foam material begins to carbonize. A strong production of smoke occurs in the event of fire. Pure PUR continues to burn, even after the removal of the ignition source, which is not true for foam containing flame retardants.

PIR foam does not decompose easily, because of the stronger spatial cross-linking. This reduces the release of gaseous products and the production of smoke, and provides an all-round greater thermal stability. PIR foam produces a carbonized protective layer more quickly than PUR, which impedes further combustion. Isocyanurate-modified PUR foams attain a building material class B2 with the addition of less flame retardants than PUR insulation materials.

2.4 Flame-retardant systems for PUR insulation and one-component foams – status, trends, quantities used

PUR insulation foams (block foam, slabstock foam, sandwich elements, in-situ and one-component foams) today have a flame-retardant system consisting of reactive brominated/chlorinated polyols and of halogenated (and/or halogen-free) phosphoric acid esters. In the case of insulation foams, the average flame retardant share lies above 10% of weight, of which a little less than 5% are additive and more than 5% are reactive flame retardants.

Flame retardants used

In the case of PUR foams, brominated-chlorinated polyether polyols (mainly Solvay Ixol B 251 and M 125 with a bromine content of 31.5 and a chlorine contents of 6.9% of weight), tetrabromophthalate diols (Great Lakes PHT4-Diol, bromine content 46% of weight; Saytex RB 79 and 7980 from Albemarle, bromine content 45 or 36% of weight) and other brominated polyether polyols that have not been defined more closely are fixed in the matrix as reactive flame retardants. Other reactive bromine compounds (dibromoneopentylglycol; tribromoneopenty alcohol; tetrabromophthalic acid anhydride, etc.) are quantitatively unimportant. The share of brominated polyols can amount to as much as 30% of the polyol component. The reactive flame retardants also include several phosphorus polyols. However,their application area is small.

While brominated (polyether-) polyols are utilized for traditional PUR formulations and are, in contrast, rarely used in PIR foams, additive flame retardants are utilized with both types of foam. Here chlorinated phosphate esters dominate.

Until the mid-1990s, a mixture of tris(2-chloroethyl)phosphate (TCEP) and tris(chloropropyl)phosphate (TCPP) in a ratio of 1:1 was most usual. TCEP, which has the higher chlorine and phosphorus content (36.7% chlorine, 10.8% phosphorus) and is more effective in contrast to TCPP, has been replaced during the last few years by TCPP in Germany for occupational health and safety reasons (R40 classification, "possible risks of irreversible effects"). The two German manufacturers have discontinued production. For this reason, 90% of the additive flame retardants are currently accounted for by TCPP. TCPP, like TCEP, is classified as a ‘water polluting substance’, but it is not classified as ‘environmentally dangerous’ and R40. TCPP is the cheapest of all additive flame retardants. Other halogenated organic phosphorus compounds are of no importance with regard to PUR rigid foam.

Halogen-free organic phosphorus compounds are utilized only in small quantities. Worthy of mention are diethyl ethane phosphonate (DEEP), which is classified as environmentally dangerous and toxic to aquatic organisms; triethylphosphate (TEP); diphenylcresylphosphate (DPK); diethyl-N,N’-bis(2-hydroxyethyl)aminomethyl-phosphonate. Other halogen-free organic P-compounds do not play any quantitative role.

Solid phosphorus-based flame retardants currently only have marginal importance in PUR rigid foams. Between 1000 and 1200 tonnes/year of long-chained ammonium phosphate (APP) are utilized in Europe in PUR rigid foam, but this has only marginal importance in Germany, in contrast to flexible foam. Red phosphorus is used in small amounts in rigid foam blocks (the quantity is estimated to be less than 10 tonnes/year).

Flame retardant quantities and trends

On the basis of the starting formulations and foam quantities stated by the processors of PUR and PIR foams, consumption quantities in the two main groups, namely halogenated (brominated) polyols and organic phosphoric acid esters, are as follows:

- Halogenated polyols: annual consumption in the order of 4500 – 5000 tonnes.

- The share of TCPP is estimated at 4000 – 5000 tonnes in PUR rigid foam.
- Halogen-free P-esters amount to approx. 10% of flame retardant consumption for additive components, i.e. approx. 500 tonnes.
- Solid flame retardants are quantitatively unimportant in Germany at this time.
- In 1998/1999 the total quantity of flame retardants for PUR insulation foams was 6600 tonnes, 3800 tonnes for one-component foams – together a total of 10,400 tonnes.

In view of the changes in the formulation of foams that are beginning to emerge, in the direction of PIR foam for quantitatively important mass products (sandwich elements; continuous-process foam), the consumption of halogenated polyols can be expected to decline significantly. At the same time, the consumption of additive flame retardants, per unit of weight, need not be increased and can rather be decreased, because of the better thermal properties of PIR foam. Moreover, both with PIR foams, which have already been tested in practice and are quantitatively relevant, and with one-component foams, which is a high-volume consumption segment that is in the early stages of development or introduction, a trend to the substitution of chlorinated P-esters by non-halogenated organic phosphorus compounds can be observed, without an increase in the utilization quantity per unit product.

An important determining factor in this trend is the cost of formulation. Standard systems currently have the advantage of the low TCPP price. In the transition to PIR foams for sandwich elements, the processors expect cost neutrality or a reduction of costs, because of savings on flame retardant use.

Mainly those processors that are able to formulate the basic components on their own are currently manufacturing PIR. This is not possible in the case of in-situ and one-component foams; they, and the manufacturers of sandwich elements, work with pre-formulated systems from the so-called ‘system suppliers’. If the market for PUR rigid foam is viewed as a whole, then more than 70% of the base products are delivered by ‘system suppliers’. This means that the ‘system suppliers’ also deliver the flame retardance of the foam for 70% of the market. The ‘system suppliers’ must pay special attention to the storage stability and the uncomplicated processing of their systems, which is why they are sceptical with regard to an expansion of the PIR foam share.

Newly developed products are available for one-component foams, where a change in the overall formulation (polymer modification) and a phase-out of halogenated flame retardants are also expected. Typical are: Switch from polyether to polyester polyols, phase-out of brominated polyols and halogenated phosphoric acid esters and, if required, a change in the isocyanate component, as well as a general reduction of the flame retardant content (a reduction by half from approx. 20% to approx. 10% of weight).

The manufacturers of canned foam products see the cost question as the most important barrier in the adaptation of foam formulations, since canned foam would become more expensive with the new formulations.

2.5 Emissions, by-products of fire

Halogenated (TCEP, TCPP) and halogen-free (triethylphosphate, triphenyl phosphate) organic phosphoric acid esters, which, among other things, also find application as flame retardants in polyurethane insulation and one-component foams, are being detected in surface waters and samples of house dust (here also tricresyl phosphate). While a direct link to the utilization of flame retardants in PUR foams is not possible, because of the variety of applications of organic phosphoric acid esters (also as a plasticizer), such a link also cannot be excluded. According to information provided by the manufacturers, studies on the release of flame retardants from PUR insulation and one-component foams are not available.

Individual data are available for by-products of fires which indicate that PIR foam has lower smoke density than PUR foam, and that the utilization of halogenated flame retardants through APP in PUR foams also leads to a reduction of smoke density and toxic by-products of fires (CO, HCN, HCl). When PUR insulation foams are burned along with other products in modern waste incinerators, the bromine and chlorine content in the incineration gases increase and a small concentration of brominated PBDD/F is produced, which should however be retained by flue gas purification systems. During normal fires and in co-incineration without appropriate flue gas purification, contamination must be expected.

2.6 Material properties, costs

The case of polyurethane illustrates clearly that changes in the formulation of foams, including changes in the utilization of flame retardants and a modification of polymers (PUR - PIR), impact upon material properties. Securing these properties has been one of the main tasks of PUR foam development. Besides the quality of the foam, such factors as the bonding of the covering layer (especially for sandwich elements, where possible problems are seen in connection with PIR foams), storage stability (especially the ‘system suppliers’ draw attention to this), and the processing properties are of importance. Processing problems (among other things an abrasive effect) is used as an argument against the application of solid flame retardants, such as ammonium polyphosphate, whereby the flame retardant manufacturers and plant constructors refer to available application experience. With in-situ foams, foamed at a construction site, a transition from PUR to PIR cannot be realized because of processing problems. With regard to one-component foams, the higher cost for canned foam is an important obstacle to a transition to halogen-free formulations with lower flame retardant contents.

2.7 Design and material alternatives

2.7.1 PUR and other insulation materials

As a B2 construction material, the application area of polyurethane insulation foams is limited in comparison to mineral-based (A1, A2) and polystyrene (B1) insulation materials. PUR is, for engineering reasons, the unquestioned No. 1 among the B1 composite elements (sandwich elements). PUR foams are not very suitable wherever humidity is an enduring problem. PUR insulation materials will be used whenever other insulation materials do not meet the specific properties that are required. The advantages of PUR, in comparison to other insulation materials, is its very good insulation performance (the same thermal insulation with a comparatively thinner and space-saving material), more advantageous mechanical properties in comparison to other plastics (EPS, XPS), a lower weight, and a lower sensitivity to humidity than mineral wool, as well as the exclusive possibility of being foamed directly on location (this is especially applicable to one-component and in-situ foams). An important application limitation results from the comparatively high costs of PUR (per unit surface for the same insulation performance).

Insulation materials therefore do not compete interchangeably, but rather serve specific application segments, for which they provide substance specific advantages. The substitution of one for the other is either not possible, or only possible under certain circumstances.

2.7.2 Polystyrene insulation foam

Insulation materials made on the basis of polystyrene account for approx. 40% of the insulated surface area and around one-third of the volume of the insulation material market in Germany. Foamed polystyrene (expandable polystyrene, EPS) accounts for approx. 90% of this volume, while compact polystyrene (extruded polystyrene rigid foam, XPS) accounts for approx. 10%. The total annual German market for polystyrene insulation materials can be estimated at approx. 170,000 tonnes.

Polystyrene is flammable and must be composed with flame retardants, so as to be able to reach the B1 classification that is required for sale as a building material. The B1 composition of polystyrene foams for the construction sector is largely limited to German-speaking regions.

Polystyrene (PS) ignites when exposed to a flame and, because of the release of aromatic compounds, burns with a strongly sooty flame, and it continues to burn even after the removal of the ignition source. Polystyrene is the plastic with the highest smoke or soot density. PS foam treated with flame retardants normally shrinks away from the ignition source without igniting, but it will nevertheless burn under the influence of other ignited materials.

EPS is flame-retarded by means of approx. 1% of weight hexabromocyclododecane (HBCD; additive flame retardant), with the addition of dicumyl peroxyde as a synergist. In the case of XPS foams, the HBCD dose is approx. 2-3% of the foam. Dicumyl peroxyde is classified as environmentally dangerous. In the view of the ‘system suppliers’, there is, in the case of polystyrene (EPS, XPS), no suitable competitor to HBCD as a flame retardant. Approximately 85% of the total consumption of HBCD is used for the flame retardance of polystyrene. Estimated total consumption in Germany: 2000 tonnes HBCD and 1200 tonnes dicumyl peroxyde.

Data on emissions is available for wastewater at sewage treatment plants, and for emissions to air at the manufacturers of EPS and XPS (in the µg/l range), while no information is available at the foam processors with regard to contamination of wastewater treatment sludge and liquid effluents. Only very small amounts of more highly brominated PBDD/F occur during the incineration of polystyrene containing HBCD as a flame retardant.

Polystyrene insulation materials are currently disposed of as construction waste and are mainly landfilled. The total sale of polystyrene insulation materials between 1960 and 2000 (German market) is not known; we estimate these sales at approx. 3.4 million tonnes of insulation material, containing around 34,000 tonnes of HBCD or 25,500 tonnes bromines. Here too, as in the case of the PUR insulation foams, most of these insulation materials have not been disposed of yet, but will arise as wastes in the future and will have to be incinerated as organic waste (under the German technical regulations on municipal waste – TA Siedlungsabfall).

2.8 Recycling/disposal

Little is known in detail about the fate of PUR insulation and one-component foams. Recycling of these products does not take place, with the exception of production scrap, and to a limited extent of stock remainders in the case of one-component foams.

Polyurethane insulation materials from the construction sector arise from the demolition or repair of buildings as mixed construction waste. A separation of these materials by different types is not considered possible; a system for the return of these materials is, in the view of the manufacturers, not feasible because of the small quantities. It is assumed that PUR construction waste is mainly landfilled. In the case of sandwich elements, the sheet metal layer is removed and melted down. The rigid foam core is either treated like PUR construction waste or, in the case of smaller quantities, can be recycled (filling material for gymnasium mats; aggregate in the production of chipboard). The order of magnitude of PUR insulation foam that has been used in the construction sector between 1967 and 1997 (excluding one-component foams) is estimated at approx. 1 million tonnes, of which it is assumed that approx. 15% have already been disposed of. 1 million tonnes of PUR insulation foam contain approx. 47,000 tonnes of additives and 55,000 tonnes of reactive flame retardants (chlorine content ca. 19,000 tonnes, bromine content ca. 17,000 tonnes).

The one-component foam that has been used in construction becomes part of the construction waste. Used pressure containers, including remainders of prepolymers, are disposed of to at least 70% together with normal municipal waste (landfill and incineration). Approximately 30% are stated to be taken back, whereby the remainder of the prepolymer can be regenerated for use in the manufacture of one-component foam.

2.9 Trends

With polyurethane insulation and one-component foams, which ‘classically’ incorporate brominated polyols and halogenated phosphoric acid esters, a trend towards the substitution of brominated polyols, by a transition to PUR modified PIR foams, is becoming apparent (polymer modification through the insertion of isocyanurate structures), and a reduction or complete substitution of halogenated phosphoric acid esters, in the direction of non-halogenated organic phosphorus products. Furthermore, the application of solid flame retardants is under debate.

This trend has been widely accepted for block foam and has achieved substantial acceptance in slabstock foam products (up to approx. 60%), but has not established itself with sandwich elements, which represent more than 50% of PUR insulation foam and are thus its main application area. It is for technical reasons not realizable with in-situ foams. This trend shows a possible direction for decreasing environmental impacts. The reduction potential in the area of continuous-process foam and sandwich elements is estimated at more than 4000 tonnes of flame retardant, or up to 60% of the estimated flame retardant quantities presently being applied in PUR insulation foams. 80–90% of this assumed reduction volume is in sandwich elements, and furthermore continuous-process foam and slabstock products for other insulation works in buildings.

Newly developed formulations are available for one-component foams, which can lead to a reduction of more than half of the flame retardant content, from 20–25% to 8–11%, while simultaneously phasing out the use of halogen-containing components. At present levels, this would mean a theoretical reduction potential of approx. 1900 tonnes of flame retardants for one-component foams, which represents half of the currently utilized flame retardant quantity.

This possible reduction and substitution trend faces two obstacles. In sandwich elements, which represent the main consumption area for PUR insulation foams, there are technical problems that must be solved (bonding of the facing layer). And in one-component foams, which is quantitatively the second most important area, the primary concern is costs, as the manufacturers expect higher costs for halogen-free new products. Furthermore, the differing interests between ‘system suppliers’ and companies preparing their own formulations must be taken into account.

2.10 Evaluation

Full exploitation of the stated potential for substance reduction and substitution in insulation and one-component foams is in principle expedient.

Halogen-free trialkyl- and triaryl phosphates are being considered as a substitute for TCPP, while in insulation foams triethylphosphate (TEP) is generally being considered, and in addition, for one-component foams, diethylethylphosphonate (DEEP), triphenyl phosphate (TPP) and diphenylcresylphosphate (DPK) come into consideration.

According to their classification in the German Hazardous Substances Ordinance (Gefahrstoffverordnung, GefStoffVO)[7], TEP and DPK (mixture) are preferable over TCPP. DEEP and TPP are considered environmentally hazardous and therefore, in comparison with TCPP, are given a less positive classification. Furthermore, the volatility of these substances must be taken into account; triaryl phosphates are, like

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[7] TCPP: Xn (harmful), R 22 (harmful if swallowed), R 52/53 (harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment), WGK 2 (German water hazard class 2; voluntary classification of manufacturers); TEP: Xn, R 22, WKG 2; DEEP: Xi (irritating), N (environmentally dangerous), R 38 (irritating to skin), R 41 (risk of serious damage to eyes), R 51 (toxic to aquatic organisms), R 53 (may cause long-term adverse effects in the aquatic environment), WGK 1; TPP: N, R 20/21/22 (harmful by inhalation, in contact with skin and if swallowed), R50/53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment), WGK 2.

TCPP, relevant in indoor spaces. The substitutes are halogen-free, which is in principle advantageous from an environmental point of view (for instance by-products of combustion).

Toxicologically and ecotoxicologically, the substitution of TCPP with TEP or DPK does deliver a certain advantage in terms of the classifications of the German Hazardous Substances Ordinance (GefStoffVO). It nevertheless needs to be examined whether sufficient information is available for these two substances to be able to make a definitive statement in comparison to TCPP. A further need for research exists in this regard.

APP, as a solid flame retardant, and on the basis of its substance profile, proves to be largely harmless from a toxicological and ecotoxicological point of view.

According to manufacturer information, no alternative exists to the currently used flame retardant system for polystyrene that consists of HBCD and dicumyl peroxide. HBCD is only a weak precursor of dioxins/furans. The possibility of substituting the HBCD/dicumyl peroxide system should nevertheless be examined, particularly in view of the relatively large bromine quantities that are used in polystyrene, which will in future enter waste disposal systems (incineration), and the fact that dicumyl peroxide is, among other things, classified as environmentally dangerous (N). The discovery of HBCD in sediments can probably be traced back to its use in the coating of textile backs (production sites). A reduction of the halogen load in PUR insulation foams is fundamentally advantageous from an environmental point of view (by-products of incineration).

3. Flame-retarded plastics in electrical and electronic (E+E) appliances

In this chapter[8] we present an overview of flame-retarded plastics in the area of electrical and electronic appliances, according to quantities, application areas and flame retardant composition. This provides an orientative framework for categorizing, firstly, ‘printed circuit boards/printed circuit board modules’ and, secondly, ‘materials for casings’, which are examined in greater detail in the subsequent chapters.

Plastics for component and appliance casings have become very important in the electrotechnical and electronics areas, because of their favourable electrical properties (insulation properties, low electrical losses), as well as their engineering and cost advantages.

Since electrical and electronic appliances contain electricity-conducting components, in which thermal loads, leakage currents, short-circuits, and similar sources of ignition occur or can occur, the plastic flammable components require flame retardant additions. The corresponding fire safety regulations and tests in the electrotechnical area normally proceed from protection against an *inner* source of ignition.

The overview of the E+E sector is based on various surveys of the consumption of plastics and flame-retarded plastics in the E+E industry in Europe (APME) and Germany (ZVEI, VKE) in the 1990s, as well as information obtained from the Siemens Group, which accounts for approx. 20% of plastics consumption within the E+E sector in Germany.

Overview VI/4: Flame-retarded plastics in the electrical and electronics sector
Quantity estimation for Germany (1997/1998)

Plastics group	**Quantity [tonnes]**	**Share [percent]**	
Plastics (total)	500,000 – 600,000	100	
Including flame-retarded plastics	125,000 – 150,000	25	100
Including			
- Thermoplastics	83,000 – 100,000		66
for casings	*50,000 – 67,000*		44
for small accessories and bought-in parts	*28,000 – 33,000*		22
- Duroplastics	42,000 – 50,000		33
Including plastics			
- with halogenated flame retardance	78,000 – 94,000		60-65
- with halogen-free flame retardance	47,000 – 56,000		35-40

3.1 Flame-retarded plastics for E+E appliances – quantities

The share of flame-retarded plastics in total plastics consumption in the sector can be estimated at approx. 25%. At the Siemens Group, the share of plastics incorporating flame retardants is, at one-third, above average, which may be due to a larger share of ‘flame retardance intensive’ E+E appliances.

Under the assumption of a total consumption of 500,000 – 600,000 tonnes in the electrical and electronic industry in Germany, an annual volume of approx. 125,000 –

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[8] Summary of Chapter III: Flame retardants in plastics in E+E appliances (overview), Volume II, pp. 117-137

150,000 tonnes of flame-retarded plastic for electrical and electronic appliances follows.

3.2 Flame retardance according to plastics and appliance components

Among the flame-retarded plastics, thermoplastics containing additive flame retardants predominate for casings and small accessories (2/3), as against reactively flame-retarded duroplastics that are mainly used for printed circuit boards and appliance components (1/3). Thermoplastics are accordingly the main market for flame retardants in the E+E sector. These ratios are also interesting because additive flame retardants in thermoplastics are less firmly bound into the matrix than reactive flame retardants in duroplastics (migration and outgassing problems).

Categorized by *appliance components*, most of the quantity of flame-retarded plastics is accounted for by materials for casings, followed by materials for printed circuit boards and appliance components, as well as small accessories and components.

On the other hand, the *share of flame-retarded plastics* is the highest among the duroplastics. Among the thermoplastics the share of flame-retarded plastics is higher in small accessories and bought-in parts than in thermoplastic materials for casings. This reflects the level of thermal load and the problems with ignition sources, which are more pronounced with electrical and electronic operational parts than with the materials for exterior casings of E+E appliances.

3.3 Breakdown among flame retardant groups

Regarding the *breakdown among flame retardant types (groups)*, 60-65% of the flame-retarded plastics in the E+E sector are halogenated and in the first instance *brominated* flame retardants. Among the remaining 35-40% the share of *mineral-based* flame retardants (and nitrogen compounds that quantitatively only represent a small part) is greater than the share of plastics incorporating *phosphorus* compounds.

On the basis of these shares, the annual quantity of halogenated flame-retarded plastics in the electrical and electronic industry is in the order of 85,000 tonnes.

3.4 Major application areas for halogenated flame retardants

The main application areas for halogenated flame retardants are, firstly, printed circuit boards and appliance components and, secondly, small accessories/components. The relative share of halogenated compounds in plastics for casing materials is much lower and decreasing, but in absolute terms of a similar magnitude as the small accessories/components, since substantially more plastic is utilized for casings. *Polybrominated diphenyl ethers* (PBDE), which are regularly found in electroscrap, probably come mainly from the small accessories/components fraction.

3.5 Flame retardance by appliance type

When classified by *appliance type*, the share of flame-retarded plastics in overall plastics usage is especially high in office appliances and data processing components, followed by entertainment electronics. In other E+E appliances (for instance household appliances), a substantially smaller share of flame-retarded plastics is utilized. In the total utilized volume of flame-retarded plastics, entertainment electronics and data processing are clearly ahead of office appliances and other electric appliances.

3.6 Evaluation

The quantity estimations can only be considered orientative, because of the many insecurities in the calculation basis. Nevertheless they show that large annual volumes amounting to between 125,000 and 150,000 tonnes of flame-retarded plastics are utilized in the E+E sector in Germany, and will need to be disposed of as electroscrap. A high share of up to 85,000 tonnes of halogenated flame-retarded plastics can be expected.

It is further apparent that with the application areas ‘exterior casings for E+E appliances’ and ‘printed circuit boards/printed circuit modules’, which are examined in the following chapters, the quantitatively most important flame retardants applications in the E+E sector are covered.

In qualitative terms, the area of *small accessories and bought-in parts* is the second most important area for halogenated flame retardants in E+E appliances, and this is where the main volume of the polybrominated diphenyl ethers can be found that are still being utilized (estimated: 50% of the halogenated flame retardants of this sector). Special substitution problems will probably be encountered in this segment, which must be looked at separately, because of the higher thermal load of components and the large variety of industrial thermoplastics.

4. Electrical and electronic applications – duroplastic printed circuit boards

In the electrical and electronic (E+E) sector, one-third of the flame-retarded plastics are accounted for by duroplastics that are used most frequently for printed circuit boards and casting compounds for electronic components. Printed circuit boards contain flame retardants as a matter of principle. Among the E+E appliances, they are the main application area for halogenated (brominated) flame retardants, even leading the other small accessories and components made of technical thermoplastics. The status and trends in flame retardant usage in printed circuit boards is the subject of this chapter.[9]

Overview VI/5: Duroplastic printed circuit boards	
Examined products	Base material for printed circuit boards made of epoxy resin and fibreglass fabric (prepregs, laminates) as well as phenolic resin/laminated paper. For comparison: printed circuit board assemblies (flat modules)
Fire safety requirements	UL94-V0, as the internationally valid standard for FR4 materials
Utilized plastics	Epoxy resin; phenolic resin (with marginal importance: Triazine resins, polyimides, etc.)
Plastics by quantity and representativeness	• Manufacture of base material for printed circuit boards 1999 approx. 21,000 tonnes, >10,000 tonnes resin (50% of weight). • Estimated quantity of plastic (resin) in printed circuit boards scrap: 14,000 t.
Recommended/ utilized flame retardants	With FR4 printed circuit boards (> 90% of the total market): TBBA (bromine content: 18-20% of resin weight, 9-10% of laminate weight). Phosphoric acid ester (trialkyl compounds) with marginal importance for phenolic resin laminates, mineral-based flame retardants (ATH) in CEM composites.
Use status and trends	• Standard: TBBA • New developments: Halogen-free flame retardance, as a rule on the basis of reactive phosphoric acid compounds, in some cases in combination with nitrogen compounds, also in combination with ATH.
Flame retardant quantities and totals	• 1999: 3200 tonnes TBBA for laminates manufactured in Germany (1900 t bromine). • Bromine content in printed circuit board scrap approx. 2500-3000 tonnes (corresponds to a utilization of 4200-5100 tonnes of TBBA).
Emissions; by-products of fires	Bromine substitution avoids the occurrence of PBDD/F in the event of fire. Reduced toxicity/corrosiveness of the fire gases in the case of phosphoric or phosphorus-ATH systems.
Recyclability	Duroplastic printed circuit boards so far cannot be recycled, though the copper content can be recovered. Particle downcycling is in preparation on a limited scale. Bromine substitution makes the recovery of copper easier.
Substitution and reduction potential	• TBBA substitution by halogen-free flame retardants is in principle possible, while this does in part still present technical, processing, and especially cost obstacles. • Reduction potential: The UL94-V0 fire safety standard is considered as exaggerated for approx. 50% of the products, a reclassification to V1 would enable a reduction of TBBA by approx. 50% of the total quantity. • The reduction potential by means of material alternatives cannot yet be assessed fully.
Evaluation	A utilization of halogen-free flame retardants is sensible, but the public awareness with regard to new developments is inadequate. The reduction potentials should be examined in greater detail.

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[9] Summary of Chapter IV: Electrical and electronic applications - duroplastic printed circuit boards, Volume II, pp. 138-212

The standards for material and processing properties of printed circuit boards, including their flame retardance, are internationally uniform. Many efforts have been made during at least the last ten years to replace the presently prescribed brominated flame retardants, made on the basis of tetrabromobisphenol A (reactively inserted into the matrix), in the main types of printed circuit boards with halogen-free alternatives. Especially Japanese companies are pushing corresponding substitution efforts within the framework of the 'green electronics' trend. The introduced alternatives are based mainly on additive organic phosphorus flame retardants, or in combination with nitrogen carriers, while mineral-based flame protection has recently also entered the arena. As a rule, the substitution substances are not individually known with regard to the utilized flame retardants and their formulation.

4.1 Printed circuit boards and base material for printed circuit boards

Printed circuit boards serve as a 'wiring base' for electronic circuits (flat modules) and are today the most frequently used connection device for electronic components. As a globally traded and processed component of the IT industry they are standardized throughout. The various circuit board types, base materials, and requirements are differentiated in accordance with the American NEMA standard, which has gained world-wide acceptance.

Plates with a copper lamination made of electrically highly insulated laminated plastic serve as the main base material. The base material for these laminated plastics normally consists of reinforcing materials (paper; a fibreglass fabric, etc.) that are impregnated with duroplastic resins (phenolic resins, epoxy resins). By far the most frequently used base material today is fibreglass reinforced epoxy resin with tetrabromobisphenol A as a flame retardant (standard: FR 4-V0); besides this, printed circuit boards on the basis of phenolic resin laminated paper (FR 2-V0) play an important role. Epoxy resins are also the base material for the so-called composites (CEM 1, CEM 3). Other base materials (polyimides; bismaleinimide/triazine resins, etc.), and the printed circuit board types that are based on these materials, only have marginal importance.

The quantity of printed circuit board base material manufactured in Germany in 1999 (laminates and prepregs) amounted to approx. 21,000 tonnes, half consisting of resins and fibre-glass fabric. The quantity that is contained in the home-market equipment inventory is however substantially higher because of product imports, which must be kept in mind with regard to electroscrap.

Calculated on the basis of the overall surface area of laminates and prepregs, the share of base material for printed circuit boards incorporating brominated flame retardants was more than 95% in 1999.

Today the four most important application areas of FR 4 material are telecommunications, computers, industrial controls, and automobile electronics. The most important sales areas for paper laminates (FR 1, FR 2) are consumer electronics (TV, audio, video), simple automobile electronics (electronic regulation devices, instruments), and household appliances (fittings). The majority of printed circuit boards are sold in the telecommunications sector. The mobile radiotelephone sector is at this time the 'technological pacemaker' in the miniaturization and increasing integration density both of electronic components and printed circuit boards.

4.2 Fire safety requirements (V0-/V1 standard)

Internationally, the technical standard of NEMA (National Electronic Manufacturers Association, USA) has been generally accepted for laminates and printed circuit boards. With regard to the flammability of the base material of printed circuit boards, the NEMA standard requires the UL94 class V1 (self-extinguishing within 30 seconds) developed by Underwriters Laboratories as a minimum for FR types, and especially for the dominating FR-4 standard. In practice though, the market for printed circuit boards has agreed world-wide on the standard UL94 class V0 (self-extinguishing after 10 seconds) for FR4 materials. The cause for this increased level of fire safety are the applicable requirements of the USA market, which have become generally excepted in the world market. The V0 class, in contrast to the V1 classification, is up to the present realized in standard materials through the addition of brominated flame retardants. For CEM types, the NEMA standard also prescribes a V0 classification.

The universal employment of the UL94 V0 standard for base materials in printed circuit boards is viewed as exaggerated and ‘over-engineered’ by the manufacturers of base materials. In their view, the employment of V0 material in printed circuit boards for appliances (for instance in battery-powered devices, cellular phones, pocket calculators, large parts of automobile electronics, etc.) that are operated at a low voltage (1.5 – 12 volts) makes little sense from a technical point of view. In contrast to this, V0 is viewed as sensible with electronic components that operate at a higher voltage density, such as main circuit boards in television appliances, computers, or certain parts of automobile electronics, that is with applications that include approximately half of all printed circuit board material.

The reduction of the fire safety requirements from V0 to V1, in those areas where they are not considered as compelling, would have substantial effects on their fire retardant usage. On the one hand, one could dispense with brominated flame protection. And on the other hand, flame retardance with a smaller dose of phosphorus, or phosphorus/nitrogen systems, and/or mineral-based flame retardants would be possible. The discontinuance of the use of brominated flame retardants would lead to a number of easements in the disposal of electroscrap.

4.3 Impregnation resins for printed circuit board base materials: Processing, fire properties

The insulating base material is a composite material for 95% of the printed circuit boards, which consists of a reinforcing material (impregnated paper or fibreglass fabric) and duroplastic resins with which this reinforcing material is impregnated. In laminates, the share of resins and of reinforcing material usually amounts to approx. 50% of weight for each.

Phenolic and epoxy resins are most commonly used as impregnating resins. Epoxy resins (first utilized in 1960) have to a great extent overtaken the phenolic resins in importance, which were first used in the 1950s for hard paper that was laminated on one side with copper. Other duroplastics, such as triazine resins (bismaleinimide/triazine, so-called BT resins, available since 1970), polyimides, etc. have only marginal importance.

In a hardened condition, the duroplastic resins are three-dimensionally cross-linked and cannot be melted anymore. *Hard paper laminates* are produced by impregnating paper with resin lac (phenolic or epoxy resins) and drying it. The impregnated paper is then hot-pressed with a copper foil. *Fibreglass fabric laminates* are produced in a similar fashion. The fibreglass fabric is impregnated with gum lac and dried, during which the impregnating resin hardens into an intermediate state (B state), the so-called prepregs. The resin re-melts during the following hot-press process, and is irreversibly and completely hardened under pressure and temperature into a laminate. The epoxy resin also is the dielectric for *composites* that are made with a core of hard paper/epoxy resin (CEM 1), or of fibreglass with epoxy resin (CEM 3). In both cases, the outer layers consist of fibreglass fabric/epoxy.

Phenolic resins are duroplastics that burn with difficulty and are temperature-resistant up to 120–175°C, depending on the formulation. Decomposition occurs at approx. 300°C. Phenolic resins only burn as long as the ignition flame is not removed. They have a tendency to carbonization, through which the occurrence of volatile products is impeded. Their tendency to produce smoke is therefore weak. In contrast, epoxy resins, especially those produced on the basis of bisphenol A burn substantially better than phenolic resins. They have a lesser tendency to carbonization and continue to burn, even after the removal of the ignition source. They are thermally stable up to 120–130°C and begin to decompose at approx. 240–350°C, depending on their formulation. In the event of fire, epoxy resins have a tendency to strong smoke development.

Epoxy resins have been very widely accepted as the base material for printed circuit boards, because of the in some respects advantageous material and processing properties.

4.4 Flame retardant systems for printed circuit board base materials – status, trends, quantities used

Because the resin is the flame-retarded component of the base material, the type of flame retardance is oriented to the resin chemistry.

Phenolic resin paper laminates (FR1, FR2)

In *phenolic resin paper laminates,* brominated and bromine-free flame retardance coexist, whereby, in contrast to the world market, the halogen-free material dominates among German manufacturers. A V0 classification (*bromine-free*) is reached by a combination of phosphorus and nitrogen additives. The base material contains between 10 and 11% melamin resin and nitrogen, as well as approx. 8% arylphosphate (diphenylcresylphosphate [DPK] or a mixture of DPK and triphenylphosphate [TPP]) as a phosphorus source. FR 2 laminates with *halogenated flame retardance* contain brominated epoxy, as well as phosphorus and nitrogen compounds, without an antimony trioxide supplement.

FR4 printed circuit boards

FR4 printed circuit boards on the basis of fibreglass fabric/epoxy resin today account for more than 90% of the manufactured surface area of laminates and prepregs (the volume share is somewhat lower). Flame retardance is reactive throughout and is provided through a bromination of the epoxy resin, by way of tetrabromobisphenol A as initial component. Antimony trioxide, as a synergist, already fell into disuse in the mid-1990s (however, this is not necessarily the case with imported products). To be able to reach the UL94-V0 classification, the bromine content of the epoxy resin amounts to between 18 and 20%, whereby 18% is the lower limit. Since the resin accounts for approx. 50% of weight of the laminate, the bromine content of the laminate lies between 9 and 10%.

It remains to be observed that polybrominated diphenyl ethers, used as a flame retardant, have also been discovered when disassembled epoxy resin circuit boards were examined.

Halogen-free flame retardance

All of the manufacturers of resins and base materials that serve the German market are working on the development and introduction of halogen-free FR4 materials with a V0 quality. In 1999/2000, at least two of the four resin manufacturers were in a position to deliver halogen-free flame-retarded epoxy resin; two other manufacturers were preparing the market introduction of a corresponding resin. The laminators already have introduced corresponding materials, or these are in development.

The trend to halogen-free flame-retarded base material is being pushed especially in Japan. The manufacturers in the USA and Europe are following suit. The project undertaken by the Siemens Group and several of its cooperation partners ("Halogen-free flame-retarded duroplastic materials for electronics" [BMBF 1995]) in the beginning of the 1990s, and the developments that were connected with this project, had a pilot function in this regard.

The bromine-free FR4 material, which is in the meantime in development or has appeared on the market, is usually flame-retarded with reactive phosphorus compounds by the European manufacturers, or with phosphorus-nitrogen compounds. The phosphorus and nitrogen components can be inserted reactively in the epoxy resin and hardener. Another product that is in development combines phosphorus with temperature-stabilized ATH. Phosphorus-ATH or phosphorus-nitrogen-ATH systems are also reported from Japan. Additive flame-protection with microencapsulated red phosphorus has been tested, but has proven to be problematic. This path is therefore no longer being pursued.

Within the study, a number of examples of halogen-free flame-retarded base material (FR4) for printed circuit boards are presented, coming from European and Japanese manufacturers, and American manufacturers with European subsidiaries. The formulations of these products are generally not being revealed by manufacturers at this time.

Composites

Flame retardance in composites (*CEM quality, epoxy resin base)* is also guaranteed by reactively inserted TBBA. In most cases these products are free of antimony trioxide. With CEM 3 (glass fabric core), an additional flame-retarding effect is brought about by the mineral fillers (aluminium trihydrate, ATH). They are primarily intended for guaranteeing that the material can be processed by punching. Depending on the formulation, the bromine content of the resin lies between 4 and 7%. CEM 3 is in the meantime available in a bromine- and ATH-free version, which includes a reactive aromatic phosphorus compound as a flame retardant. Here too, the laminate contains ATH as a filler. For CEM 3, printed circuit board base material has been proposed with only a mineral-based flame-protection (ATH). Bromine-free CEM 1 is in development.

Flame retardant quantities used

We estimate the bromine content of the laminates manufactured in Germany in 1999 at just below 1900 tonnes. The respective turnover in TBBA amounts to approx. 3200 tonnes (without bromine-containing casting compounds for components). The bromine content that is caused by the flame-protection in printed circuit board scrap (incl. automobile electronics) is estimated at 2500 – 3000 tonnes bromine per year. This bromine quantity represents approx. 4200 – 5100 tonnes tetrabromobisphenol A, which must be utilized for the bromination of the epoxy resins. The difference between the utilized quantities and the bromine content of flame retardants present in printed circuit board scrap is a result of the high import surplus of IT appliances containing printed circuit boards (in 1999, the number of units of important IT appliances sold in Germany was three times German production).

4.5 Emissions, by-products of fire

Emissions

Almost no research has been done with regard to gas emissions from the printed circuit boards under normal operating conditions (normal operations of the corresponding appliances). Since the active flame-retarding substance of TBBA, that is the bromine, is reactively fixed in the resin matrix, no relevant migration is to be expected.

‘Heat nests’ with substantially higher temperatures form on and in printed circuit boards during normal operation (the measured temperature distribution for circuit boards in TVs varies between 20 and 70°C). As thermal gravimetric analysis has shown, the base material only begins to decompose quantitatively at much higher temperatures (above 300°C), so that the release of bromine can only be expected under such conditions and not under normal operations. Only a very small release of bromine and chlorine occurred in the emission gases from brominated and halogen-free flame-retarded printed circuit boards that were tested at 260°C (simulation of the temperature load during soldering). Also in long-term tests, with a temperature load of between 100°C and 230°C, the manufacturers reported no significant decomposition. Accordingly, no release of brominated compounds, including dioxins/furans, is to be expected from the printed circuit boards during normal and ‘stand by’ operations. Where this could be ascertained in individual cases, for instance in test chamber research on TV appliances, a relationship to an inner source in the appliances could not be established. A release is more likely, insofar as more highly volatile compounds were utilized as a flame retardant. This is also unlikely for reactively bound material, whereas this is more likely to be the case in additively produced materials.

Increased air concentrations of tetrabromobisphenol A and decabromodiphenyl ethers, which are used as a flame retardant in the base material of printed circuit boards and that also occur in components, were discovered at a company that disassembles electroscrap.

By-products of fire

Research into fume density has found strong smoke development in the event of fire with printed circuit boards protected by halogenated flame retardants, whereas base material protected by organic phosphorus flame retardants exhibited only weak smoke development. Bromine-free material exhibited hardly any corrosive effects, while with brominated flame-retarded material these effects were substantial. This is explained in both instances by the tendency of circuit boards, which are flame-retarded by organic phosphorus compounds, to form a fire- and emissions-reducing carbon layer.

Comparative combustion studies on decomposition products at 600°C with halogen-free and brominated flame-retarded printed circuit boards has found that PCDD/F can also occur in halogen-free flame-retarded printed circuit boards (chlorine contamination of the epoxy base material during the manufacturing process); PBDD/F, in contrast, only occurred in the case of brominated (TBBA) flame-protection.

If printed circuit boards flame-retarded by various systems are tested according to the French fire safety standard NFX 70-100 for the toxicity of the fire gases, then the toxicity index is distinctly lower for phosphoric ATH flame retardance and pure phosphorus-based flame retardance than it is for brominated flame retardance or phosphorus-nitrogen systems.

4.6 Material properties, costs

The base material will be influenced in its material and processing properties by new flame-retardant components. The guarantee of existing technical standards is named as a precondition for the acceptance of halogen-free flame-retarded base material. Besides the electrical properties, the most important criteria are especially water absorption, bonding properties, bonding between the laminate layers (or delamination time), and the glass transition temperature. The laminate manufacturers stress that certain material properties, especially the long-term stability and storage properties of the material, which stand in relationship to the water absorption (delamination under temperature load during processing), can only be tested in practice during a process taking one to two years.

At the same time and because of too strong changes in material properties, it will not be possible to completely replace conventional printed circuit boards on a one-to-one basis with new developments, so that adapted solutions may have to be looked for. In this regard, further steps in the development of epoxy resins and in the processing technologies will be required for guaranteeing the processing safety that is presently available, after decades of practical experience with the current FR4 standard.

At the present time, the manufacturers of the base material for halogen-free printed circuit boards (laminates) are still talking of additional costs of approx. 30%. However, a decline in marginal unit cost is already increasingly a subject of debate.

4.7 Design and material alternatives

Design and material alternatives to the existing types of duroplastic printed circuit boards have been developed within the framework of the ‘Green TV’ research project supported by the German Research Ministry (BMBF) (replacement of an FR2 board made of phenolic resin impregnated paper with halogen-free additive flame retardance [diphenylcresylphosphate]). These can be soldered without lead and do not use a flame retardant in the base material. One concept is based on a polysiloxan foil, and the other is based on various injection moulding thermoplastics.

4.8 Recycling/disposal

Duroplastic printed circuit boards are manufactured from composite materials that cannot be re-melted and are therefore fundamentally non-recyclable. The copper fraction of the boards can, however, be recovered during disposal in primary copper smelters. Because of the dioxins/furans that occur during the associated combustion process, and the therefore required flue gas purification, this procedure is not possible in secondary copper smelters, which limits the quantities that can be recycled. One company has proceeded to grind waste from laminate and printed circuit board production, and to separate this into metal and plastic fractions. The plastic fraction (including flame retardants) is intended for use as a supplement in the manufacture of products made of flame-retarded duroplastics (downcycling).

If one combines end-of-life printed circuit board scrap with the waste from base material and printed circuit board manufacture (annual quantity in Germany approx. 70,000 tonnes), then approx. 20,000 tonnes (28%) of this is subjected to metal recovery procedures. 90% of the total waste quantity is incinerated or deposited, including the plastic fraction of approx. 10,000 tonnes that results from mechanical separation. The remaining 10% represents recovered metal (copper).

Printed circuit boards with halogen-free flame retardance are, as a composite material, also non-recyclable. From a disposal perspective, they have the advantage that the base material does not contribute to the formation of brominated dioxins/furans. This would substantially ease the problems in the disposal of printed circuit boards (for instance through metal recovery in secondary copper smelters).

4.9 Trends

In the quantitatively absolutely dominating FR4 printed circuit boards, conventional flame retardance with TBBA continues to be state-of-the-art. The UL94-V0 standard, even though it is being discussed as questionable, similarly remains unquestioned in practice and is generally being maintained.

Bromine- and antimony-free duroplastic printed circuit boards with the required UL94-V0 fire properties have been introduced in marketable products, especially by Japanese OEMs, and are in development with other resin and laminate manufacturers. According to announcements, these shall be the standard material with several companies in a few years, and it is assumed that this will be the case in the long-term for the entire sector in Japan and the USA. The combination of the switch away from lead solder and the introduction of halogen-free base materials is, as a rule, seen as sensible, since both have an effect on the base material and the processing techniques.

The evaluation in and for Germany is more sceptical. The laminate manufacturers see a lengthy acceptance and introductory phase for halogen-free flame-retarded printed circuit boards, as the material that is presently available is normally 30% more expensive, can not simply be substituted for FR 4 standard material, and poses a number of technical problems. An increase in the market share of halogen-free FR 4 quality materials of 5% in the next 2 to 3 years would be seen as a great success.

The development problems that have been raised by the manufacturers (namely the guarantee of the current material standards, including the corresponding long-term tests; an adaptation of the processing methods for the laminates or printed circuit boards, similar to the impending substitution of lead solder; the impossibility of a one-to-one substitution of conventional printed circuit boards with halogen-free boards, including the necessity of developing adapted solutions) indicate that further steps are required in the development of resins and processing technologies, so as to be able to guarantee the processing safety that is available after decades of practical experience with the current FR 4 standard.

The survey however also indicates that it is not primarily the technical development problems that have stood in the way of a broader development and the introduction of halogen-free base materials, but that the problems lie with marketing and cost aspects, including the question as to who among the several manufacturers involved in the production of printed circuit boards would be responsible for which costs. In this regard, the aversion of the ultimate buyers (OEMs) against a dependency on monopolistic suppliers (‘single sourcing’) is also raised. A growing supply of halogen-free laminates from various suppliers would certainly promote an opening of the market.

4.10 Evaluation

Less know-how is generally available with regard to the presented alternatives than for the traditionally brominated flame-retarded printed circuit boards. The available information however shows that the substitution of brominated flame protection in printed circuit boards is both possible and sensible. This is supported by the available information about the substitutes and the by-products of fire that they produce.

Tetrabromobisphenol A, as the most important flame retardant for printed circuit boards, is persistent and is now being detected in sewage sludge and food webs, all the way to mothers' milk. TBBA is classified as environmentally dangerous and very toxic to aquatic organisms, and its toxicology with regard to carcinogenic properties has not been sufficiently researched. An additional point is its potential for forming dioxins and furans (which, however, because of its aromatic compound cross-linking, is lower than with PBDE). For these reasons, a decrease in utilization and a substitution in printed circuit boards, also in the case of the reactively bound TBBA, is environmentally desirable and therefore indicated.

Insofar as comparative examinations of products (printed circuit boards) have been presented, the halogen-free flame-retarded printed circuit boards fare distinctly better with regard to the by-products of fire. Insofar as the alternative flame-protection systems consist of reactively bound phosphoric and nitrogen compound flame retardants, it is to be expected that they, like brominated flame-retarded printed circuit boards, do not exhibit any relevant gas emission or migratory behaviour under normal operating conditions, but only in the event of fire. In contrast, the expected gas emission and migration behaviour must be critically examined in alternatives that are based on additive flame retardants. Abandoning the use of halogenated flame retardants could make the recovery of material (copper) as well as an intended particle recycling easier, despite the basic obstacles to recycling duroplastic printed circuit boards.

The reduction potential in flame retardant utilization through material and design alternatives, as well as through adaptation of fire safety requirements with regard to printed circuit board applications using low voltages (V0/V1 classifications), should be examined further. This should include the question of the preconditions for a corresponding supply of V1 printed circuit board material, which is desirable but not available according to the OEMs, and is possible but not demanded by the market according to the manufacturers of base materials.

5. Electrical and electronic applications – thermoplastic outer casings for IT and TV appliances

The outer casings of electrical and electronic appliances, for instance monitors, computers, printers, copying machines, or television receivers, are an important market for flame-retarded plastics, because the internal power sources represent a potential fire source. They account for more than 40% of the plastics incorporating flame retardants in E+E appliances and approximately two-thirds of the thermoplastics utilized in E+E appliances. The status and trends in flame retardant usage in such outer casings are the subject of this chapter.[10]

Overview VI/6: Exterior casings for IT and TV components	
Examined products	Large-surface exterior casings for monitors, computers, printers, copying machines, TV appliances
Fire safety requirements	IT devices: EN 60950; European and USA standards are similar TV appliances: EN 60065; USA with a stricter standard Possibilities: Internal fire-protection casings; flame retardant composition; design-based solutions
Utilized plastics	ABS; PC/ABS; SB/HIPS; PPE/HIPS
Plastics by quantity and representativeness	1999 approx. 70,000 tonnes casing materials for monitors, printers, copying machines, TV appliances Approx. 80% of total plastic content in these appliances
Recommended/ utilized flame retardants	• ABS: TBBA; Octa (declining) among other brominated flame retardants • PC/ABS: Bromine polycarbonate, among other brominated flame retardants; organic triaryl- and bisphosphate (DPK, TPP, RDP, BADP, etc.) • SB/HIPS: previously PBDE (Octa-, DecaBDE); various brominated flame retardants; halogen-free with organic triaryl- and bisphosphates (TPP; RDP, etc.) • PPE/HIPS: previously bromine aromatics, today triaryl- and bisphosphates
Use status and trends	• Plastics: Shift from ABS to PC/ABS and HIPS (especially for monitors and TV casings) • Growing importance of design-based solutions in fire safety with TV appliances, inkjet printers and, in part, monitors • Flame-retarding agents: Brominated flame retardants declining; PBDE only rarely; increasing importance for additive phosphoric organic compounds. Other flame retardants unimportant.
Flame retardant quantities and totals	• Brominated flame retardants: 1990 approx. 16,000 tonnes plastic with 2000 t bromine content (= approx. 2500 t brominated flame retardants) + approx. 640 t ATO; 1999 approx. 11,500 t plastic with 1400 t bromine content (= 1700 t brominated flame retardants) + approx. 460 t ATO. Totals: 1990 approx. 2500 t brominated flame retardants, 1999 approx. 1750 t. • Organic phosphoric acid ester: 1999 approx. 20,000 t plastic with 2000 – 2400 t flame retardants
Emissions; by-products of fires	Research level unsatisfying. Proven indoor air and water resources pollution for both flame retardant classes; phosphoric organic compounds with higher tendency to emissions
Recyclability	Industrial recycling of casing materials hardly occurs; main problems: type-specific materials recovery, dioxin/furan formation; release of PBDE; release of halogenated flame retardants.
Substitution and reduction potential	Possible through switch to low emission organic phosphorus flame retardants and design-based fire safety solutions.
Evaluation	Overall sensible trend with slow acceptance; review of the emission behaviour of organic phosphorus flame retardants is needed.

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[10] Summary of Chapter V: IT and TV appliances - thermoplastic exterior casings, Volume II, pp. 213-279

Fire safety can be ensured in IT and TV appliances through flame retardants or through design measures. A shift has occurred in the plastics used for exterior casings during the last ten years, from those which cannot use halogen-free flame retardants to casings that are compatible with halogen-free flame retardants (phosphoric organic compounds). This is also reflected in a changed consumption of flame retardants. At the same time, more casings are being manufactured from flame-retarded plastic. The development, however, is proceeding along different paths for the individual casing types.

5.1 Thermoplastic synthetic materials for exterior casings of IT and TV appliances

Manufacture and market turnover of exterior casings in Germany

In 1999 nearly 20 million larger electronic appliances (PC systems with a computer and monitor, printers, scanners, copying machines, fax machines) and nearly 6 million TV appliances were sold, whose exterior casing may incorporate flame retardants. German market sales of IT and TV appliances are three times larger than German production. One may therefore proceed from a high import surplus in this area. The environmentally relevant magnitude of the electroscrap issue results from market sales and not from production in Germany.

Altogether, the PCs, printers, copying machines, and TVs sold on the German market in 1999 contained almost 70,000 tonnes of casing materials (thermoplastics). This amounts to approx. 80% of the total synthetic material content of the above-mentioned appliances. In this, printers and copiers account for half as much casing plastic as monitors or TV casings.

As a rule, only the back walls of flame-retarded TV appliances, which account for approximately half of the plastic consumption for TV casings, contain flame retardants.

Materials for casings

For *large-surfaced exterior casings*, the manufacturers prefer styrene copolymers and blends (polystyrene [PS] or HIPS; ABS or PC/ABS) as materials, since these conform best to the technical and cost requirements applicable to such casing parts. Partially under cost aspects, a shift away from ABS and towards PC/ABS and HIPS has taken place in the 1990s. This shift concerns the quantitatively relevant application in monitors and TV receivers.

A whole range of requirements applies to the material and processing properties of the materials for exterior casings, which, besides compatibility with the flame retardants and the material, must be taken into account in the selection of flame retardant additives. Good flow characteristics are very important from a viewpoint of processing (injection moulding), because of the often very long flow paths for thin and large-surfaced casing walls; mineral-based flame retardants can be eliminated from consideration, for this reason alone.

The standard plastics being utilized for *new products* are to be found almost exclusively among the following styrene-copolymers and blends:

- ABS (styrene-acrylonitrile copolymers modified with unvulcanized rubber);
- PC/ABS (polycarbonate-ABS blends);
- SB or HIPS (styrene-butadine; high impact polystyrene; impact-resistant polystyrene modified with unvulcanized rubber);
- PPE/HIPS (a blend of polyphenylether with HIPS).

5.2 Fire safety requirements

The target of fire safety in IT appliances, according to the European standard EN 60950 (DIN VDE 0805), and TV appliances, according to EN 60065 (DIN VDE 0860), are the *inner* sources of fire, while *exterior* sources that could lead to the ignition of the appliances are not considered in the regulations for electrotechnical appliances.

On the basis of EN 60950, there are three main possibilities for controlling fires with regard to the exterior casings of IT devices: a) utilization of flame-retarded materials; b) utilization of interior flame-protection housings made of flame-retarded plastic or metal, which block the spread of potential fire sources to other device components; c) design measures, such as protective barriers or sufficiently large gaps, which effectively separate components with high temperatures that could act as a source of fire for inflammable materials (exterior casings). The usual practice that has developed out of these regulations is to use internal flame-protection casings, whereby the exterior casing must only correspond to the very low classification UL94-HB.

EN 60065 also presents the possibility for such a design-based flame retardance of TV appliances. Flame retardance of the material for casings is not required if a barrier or a sufficiently large gap (at least 13 mm) exists between a potential ignition source and the outer casing, or if (in case of no-load voltage over 4 kV) a potential source of ignition is surrounded by an interior flame-protection housing.

EN 60950 is valid for the American market. In contrast, the USA market has its own standard for TV receivers, which requires exterior casings made of V0 material, as a matter of principle.

5.3 Thermoplastics for exterior casings: Processing, burning behaviour

Plastics for exterior casings are available as completely formulated trade products from the plastic manufacturers or compounders, they can however also be formulated by the processors (injection moulding fabricators) themselves.

The combustion behaviour of plastics that are not flame-retarded can be characterized as follows:

ABS plastics, like polystyrene, burn with a strongly soot producing flame, even after the removal of the ignition source (classification as UL94-HB). Since they, like polystyrene, tend to decompose into aromatic compounds in the gas phase, they deliver large quantities of soot and dense fumes in the event of fire.

The *polymer blend PC/ABS* is produced by creating a mixture of ABS with polycarbonates. While PC, on its own, burns with a sooty flame and extinguishes once the ignition source is removed, PC/ABS, with flame retardance, corresponds to the classification UL94-HB. The plastic burns with a sooty flame and the melted material drips away.

For *high impact polystyrene (HIPS),* styrene-butadine (SB) with a content of 25% to 30% styrene is preferred. It burns when exposed to a flame and continues to burn, even after the removal of the ignition source.

Pure *PPE (polyphenylether)* has a pronounced tendency to carbonize and is generally accepted by most flammability tests as self-extinguishing. Blends of HIPS with PPE therefore show more favourable combustion behaviour than pure HIPS. PPE/HIPS burns with a sooty flame.

5.4 Flame-retardant systems for thermoplastics for exterior casings – status, trends, quantities used

Available flame retardant systems according to plastic type

Halogen-free flame retardance for *ABS* is presently not available. TBBA, or octabromo diphenyl ether, with antimony trioxide as an additive flame retardant, is utilized by preference for flame-retarded types. The utilization of PBDE has presumably declined lately in favour of bromine compounds, which present fewer problems with regard to dioxins/furans and are available in a substantial selection. In products that carry the German ‘Blue Angel’ ecolabel, ABS is free of flame retardants, since the Blue Angel scheme excludes brominated flame retardance and non-halogenated flame retardance is not available for ABS.

Flame-retardant systems for *PC/ABS* are available on a halogenated and on a halogen-free basis. Brominated polycarbonate (copolymer made of bisphenol A and tetrabromobisphenol A) is available for halogenated flame retardance in combination with organic phosphorus or phosphoric acid esters. As halogen-free flame retardance, organic triaryl and bisphosphate, as well as diphenylcresylphosphate (DPK), triphenyl phosphate (TPP), resorcinol-bis-diphenylphosphate (RDP), and BADP (bisphenol A diphenyl phosphate) come into question. Bayer AG and GE-Plastics have obtained patent protection on PC/ABS with an RDP flame retardance. BADP, as an alternative to RDP, is in an introductory phase.

Appliances carrying the ‘Blue Angel’ (printers, PCs) which have casings made of flame-retarded PC/ABS correspondingly contain triaryl and bisphosphate as a flame retardant.

HIPS used to be the domain of brominated flame retardants, especially of PBDE (one of the main application areas of decabromodiphenyl ethers). The flame retardants being offered today still consist mainly of brominated compounds. The bromine industry is offering compounds with a lower potential for the formation of dioxin/furan, such as 1,2-bis(pentabromophenylethane) (Saytex 8010) or ethylene-bis-tetrabromophthalimide, as PBDE substitutes. A widely used process with HIPS is flame-retarding composition on the basis of organic phosphorus (triaryl phosphate: TPP, RDP, butylated triaryl phosphate) without halogen compounds. Halogen-free impact-resistant polystyrene from BASF or Dow is based on such organic phosphorus flame retardance.

In the past, flame-retarded *PPE/HIPS* was halogenated (bromine aromatic compounds with higher thermal stability) or incorporated alkyl-substituted triaryl phosphates. In present practice, only triaryl- and bisphosphates (TPP, RDP, BADP) are being offered as flame retardants by the bromine manufacturers for PPE/HIPS.

Status and trends in flame retardant use according to appliance type

Information in this study with regard to the status and trends of flame retardant use in different types of casings is based on information obtained from the manufacturers, as well as on various qualitative studies of the flame retardant content of casings currently available on the market.

ABS and PC/ABS dominates in the area of *PC monitors and computers*, whereby the share of PC/ABS has increased to an estimated 80% in the second half of the 1990s, especially at the expense of ABS. HIPS, as an ABS substitute, is also gaining in importance. This reversal of the quantitative share in favour of PC/ABS is of substantial importance with regard to flame retardants, since, in contrast to ABS, the use of brominated flame retardants can be substituted by phosphorus compounds in PC/ABS. This corresponds to the information available from the casing and plastic manufacturers that in Europe plastic casings for PC monitors and computers are, as a rule, manufactured without flame retardants or with halogen-free flame retardance, which need not be the case for imported products (sector estimate: 80%). Research by Stiftung Warentest (German foundation for product research) on new appliances, for the period 1998 and 1999, show a share of exterior casings with bromine/antimony flame retardance between 30 and 10%, and for casings with organic phosphorus flame retardance a share of approx. 70% (1999).

For *printers,* a differentiation must be made between inkjet printers (approx. 70%) and laser printers (approx. 30%). *Inkjet printers* have only low power consumption and a minor internal thermal load. While these casings used to be made of ABS or PC/ABS, both incorporating flame retardants, they are presently being manufactured mostly from ABS, PC/ABS, or HIPS without flame retardants. The share of HIPS is increasing (approx. 60% share).

Laser printers have higher power consumption. Their heating elements reach an approximate temperature of 200°C. Design-based solutions are viewed as difficult in this case. Mostly flame-retarded ABS or PC/ABS is being utilized as a material for the exterior casings. Halogen-free (organic phosphorus flame retardance) PC/ABS is used in the case of ‘Blue Angel’ appliances. The same is true with regard to plastics and flame retardants used in *copiers*. (Copying machines and printers are the E+E appliances that most frequently carry the ‘Blue Angel’ label.)

In *TV appliances* (back walls), HIPS has generally been accepted world-wide as the material of choice. The utilization of recycled flame-retardant-free ABS material by one German manufacturer of TV appliances is an unusual development.

During the dioxin debate in the late 1980s, casings for TV appliances, which at that time used PBDE as a flame retardant in the casing, were viewed critically because of possible emissions. A number of manufacturers thereafter began with the substitution of PBDE by TBBA/antimony trioxide systems. As a rule, flame retardance in exterior casings is no longer being used for TV receivers that are manufactured in Europe or destined for the European market. According to research carried out by Stiftung Warentest, the share of halogenated flame-retarded TV casings amounted to approx. 60-70% in 1993/94, approx. 25% in 1995, and under 10% in 1996/97. Fire safety is being guaranteed through design-based measures in accordance with the EN 60065 standard. In contrast, non-European manufacturers still use flame retardants in the material for casings, or they utilize a combination of design solutions and flame retardants. Halogenated, flame-retarded HIPS (self-extinguishing according to UL94-V0) dominates the market outside of Europe and especially the USA market.

Flame retardant quantities and trends

The following can reported as the *trend* in exterior casings (German market): Decrease of brominated flame retardants, with an almost complete disappearance of PBDE, and a strong increase in halogen-free organic phosphorus flame retardant additives; a growing importance for design-based fire-protection with a discontinuance of flame retardant utilization in exterior casings. Other flame retardants (for instance mineral-based) are without significance in this regard.

The share of brominated flame-retarded casings for PC monitors, printers, copiers, and TV appliances was approx. 50% in 1990 (16,000 tonnes plastic), and 25% in 1999 (11,500 tonnes plastic). Seen in absolute numbers, the quantity of plastic with brominated flame retardance has only decreased by a quarter and was not halved. This is due to the increased total turnover. The bromine content of casings can be estimated at approx. 2000 tonnes for 1990 (plus 640 tonnes antimony trioxide), and is estimated at 1400 tonnes for 1999 (plus 460 tonnes ATO), which is less than in printed circuit board scrap (2500–3000 tonnes). The quantity of the brominated flame retardants that were used for this can be estimated to have been approx. 2500 (1990) or 1750 tonnes (1999). The share of organic phosphorus flame-retarded plastic for casings has increased in the past. This quantity however can only be determined for 1999 and is estimated at approx. 20,000 tonnes plastic, including 2000–2400 tonnes flame retardant. The total quantity of flame retardants that was consumed for the fire safety of the examined casings (which exclude, among other things, at least 20 million cellular phones) accordingly amounted to approx. 4500 tonnes in 1999, and it therefore is of the same order of magnitude as for printed circuit boards.

5.5 Emissions

Flame retardants, which are among other things also used in the materials for casings, are also to be found in indoor air and in aqueous media. Proof that they originate from the materials of the casings can only be provided in the rarest of cases, as this presupposes casing-specific examinations in a test chamber.

Minor concentrations of among other things DecaBDE, TBBA, and bis(2,4,6-tribromophenoxy)ethane can be identified in the indoor air of office rooms that are equipped with computers. Air concentrations of TBBA and Deca have been found to be higher by a factor of 3-4 in rooms where PCs and monitors are disassembled.

During test chamber examinations of brominated, flame-retarded casings from older TV appliances, monitors, and video recorders, which were carried out to simulate real operations, emissions of brominated and chlorinated compounds were found that do not represent flame retardants, but which are probably almost exclusively to be traced back to halogenated solvents used in the manufacture of flame retardants. Such solvents are no longer being utilized since 1990. Flame retardants (dibromomethyl dibromocyclohexane) or decomposition products of flame retardants (1,2-bis-[tribromophenoxy]ethane) were only found as an exception during this examination.

Additive organic phosphorus flame retardants have a higher volatility in contrast to bromine compounds. Test chamber examinations of TV appliances, monitors, and video recorders showed substantial TCEP and TCPP emissions. Triphenylphosphate (TPP) was also found. Resorcinol-bis-diphenylphosphate (RDP) is used as a somewhat less volatile substitute for TPP.

Brominated flame retardants (PBDE; TBBA; bis[tribromophenoxy]ethane) can be released from granulated casing materials into aqueous solutions, or better still into lipophile media.

5.6 Material properties, costs

Apparently the reported substitution trend (decrease of brominated flame retardants, increase of organic phosphorus flame retardants) has no relevant effect on the material and processing properties of the materials. The choice of plastics utilized for the manufacture of casings depends in high degree upon costs. The substitution of materials (increasing importance of PC/ABS and HIPS at the expense of ABS) is, at least in the case of HIPS, determined by costs.

5.7 Design and material alternatives

In case of a design-based solution to fire safety requirements in the exterior casings (back wall) of TV appliances, for instance through the maintenance of safety distances between high-voltage parts of the device (mains power area, line scanning unit) or the introduction of barriers, the use of flame retardants is dispensed with completely. This possibility is given by EN 60065 (minimum interval of 13 mm or insertion of a barrier). Internal and stricter regulations are being followed by some manufacturers.

BASF presented a design-based solution with regard to the utilization of flame-retardant-free plastic casings for monitors in 1998. The inner metal housing or ‘metal net', which is built into most monitors as an electromagnetic protection, is reworked by means of relatively small design adaptations (size of holes) into an inner flame-protection housing. In accordance with EN 60065, incorporation of flame retardants in exterior casings can then be discontinued. This design, while meeting the American fire safety regulations, has not been able to establish itself on the US market, which hems its further introduction.

5.8 Recycling/disposal

Materials made of thermoplastic synthetics can in principle be recycled. Flame retardants, however, can pose grave problems in this regard.

Recycling presupposes the recovery of clean material sorted according to type. In this regard, the flame retardants contained in older products must be taken into account. For manufacturers that are a member of an association which has agreed to the voluntary phase-out of PBDE in Germany, the recycling of PBDE-protected plastics is not possible. The recovery of other thermoplastics incorporating brominated flame retardants becomes more difficult because of the necessary separation of PBDE-containing material. A sure method of separating brominated plastics out of end-of-life products may be required so as to be able to recover halogen-free flame-retarded material. This is not possible at this time in an industrially automated manner. The current draft of the European electroscrap directive requires the removal of plastics with brominated flame retardants from the separately collected electroscrap.

The possibility of materials recycling of brominated flame-retarded casing plastics has been examined on various occasions from the viewpoint of observance of the limit values set by the German Dioxin Ordinance (Dioxin-Verordnung). This has shown that mixed electroscrap, including PBDE-containing thermoplastics, as well as type-specific separated PBDE-containing thermoplastics, are not recyclable from the electroscrap that arises in practice. In laboratory studies, HIPS, flame-retarded with Deca, could be recycled without overstepping the dioxin/furan limits. In the case of other brominated flame retardants with a low potential for forming dioxins/furans (TBBA; bis[pentabromophenyl]ethane), recycling of type-sorted material is possible in a manner compliant with the limit values set by the German Dioxin Ordinance.

In industrial practice, the recycling of materials for casings only occurs rarely. In one instance, flame-retarded PC/ABS is recovered, whereby contamination with bromine/antimony from brominated flame retardants cannot be prevented. The exclusion of PBDE from the return of PC/ABS requires logistic measures (only own products, and those that are known with regard to their additive flame retardant content, are accepted for return by the companies). In another instance, only flame-retardant-free ABS is utilized. The separation of brominated end-of-life products is achieved through material recognition on the basis of a manufacturing date identification and similar markings.

5.9 Trends

This overview shows that the use of flame retardants in exterior casings for IT and TV appliances has undergone marked changes in the German (and European) market over the past ten years.

Use of brominated flame retardants is declining substantially. PBDE, which was absolutely dominant in the early 1990s and is still being offered by the manufacturers of flame retardants for casing materials, is only rarely found in new appliances in the German market and can be done without from a technical point of view. Organic phosphorus flame retardants have strongly increased in importance. Other flame retardants (mineral-based flame retardants, nitrogen compounds) are without significance among the materials for casings. The use of flame retardants in exterior casings is increasingly being replaced by design solutions that meet the fire safety requirements. Material-based alternatives for exterior casings, such as casings made completely of metal (magnesium alloys for laptops), are a peripheral phenomenon.

The driving force behind these changes can be seen in the combination of a public debate about the harmful substance content in IT and TV appliances (dioxins; voluntary phase-out of PBDE), legislative measures (German Dioxin Ordinance; recycling obligation), public evaluation of new appliances (test magazines for products; Stiftung Warentest), labelling (‘Blue Angel’, etc.), and cost management by the companies (cost of changes in the utilization of plastics). The voluntary discontinuance of flame retardants in favour of design-based fire-protection solutions is, in part, viewed critically by the manufacturers of flame retardants.

The substitution trend has however not developed uniformly among the examined appliance types. This is shown especially by the absolute quantities. Between 1990 and 1999, the utilization of casing materials incorporating brominated flame retardants decreased for TV appliances by more than two-thirds of the quantity utilized in 1990, and by one-quarter for PC monitors. The absolute quantities of halogenated flame-retarded plastics used for other appliance types remained almost constant. The differences in the trend can be related to the different substitution paths (design-based for TV appliances, primarily substance-based for monitors) and technical hindrances (e.g. laser printers). The substitution trend is progressing rather slowly, in view of the strong growth of the IT and TV sectors.

5.10 Evaluation

From an environmental point of view, the trend that we have presented is to be evaluated positively and, as a matter of principle, to be promoted, especially where design-based (and substance-based) measures guarantee the required fire safety and reduce the utilization of chemicals. With the reduction of the utilization of brominated flame retardants, the risk of an emission of brominated dioxins/furans, as well as corrosive and toxic gases, is also diminished. At the same time, this helps to remove barriers to recycling. The emission behaviour, and the toxicity and ecotoxicity of the organic phosphorus substitutes, must be subjected to concrete tests.

In all cases where environmental monitoring of the brominated compounds examined in the present study has been carried out, a more or less pronounced presence in the environment has been found. At least in part, there are indications of bioaccumulation (generally high log P_{OW}; accumulation in food webs, all the way to mothers' milk in the case of TBBA, in fish for HBCD; Deca, in contrast, is not found in the food chain, but can be found in the blood of recycling personnel; bis[pentabromophenyl]ethane) was not examined). Furthermore, with the exception of HBCD, there is lacking clarity with regard to carcinogenicity (Deca: suspicion of carcinogenicity not resolved; TBBA and bis[pentabromophenyl]ethane: not examined). For these reasons, substance reduction and substitution in favour of environmentally less relevant substances is both sensible and recommended. Evaluation problems caused by insufficient data arise in the case of bis[pentabromophenyl]ethane. It is being offered as a substitute for casing materials, has a lower log P_{OW} in comparison to decabromodiphenyl ether and, because of the cross-linking of the aromatic compounds, a comparatively negligible dioxin/furan formation potential, but it has not been examined for its carcinogenic properties.

The increasing utilization of organic phosphorus flame retardants makes a differentiated analysis necessary. As additive flame retardants with high volatility, they show a greater tendency towards emission, which is seen in the corresponding environmental presence. Triphenylphosphate, for instance, which is not only used as a plasticizer and as a component of RDP formulations, but also as a flame retardant on its own, has a high vapour pressure, is relevant to indoor air quality and water resources quality, is classified as environmentally dangerous and very toxic to aquatic organisms, and furthermore as harmful by inhalation, in contact with skin and if swallowed. In the case of RDP, which belongs to the 13 flame retardants that have been examined, and which is used as a halogen substitute in materials for casings carrying a 'Blue Angel' label, accumulation in the food chain is not to be expected. The substance has a substantially better classification than for instance TPP (TPP is a component of RDP formulations), but is classified as harmful to aquatic organisms and hazardous to water resources (classified by manufacturers themselves in the German WGK 1 or 2 water hazard classes). The available data is insufficient for a conclusive evaluation of RDP (in part absent substance data, no examination of carcinogenic properties).

In view of the unsatisfactory state of the available information, a review of the emission behaviour and the toxicological and ecotoxicological substance properties of organic phosphorus substitutes is indicated (measurements). Low-emission products should, as a matter of principle, be preferred to such products that have a higher emissions potential.

6. Textile applications – materials for upholstered furniture and mattresses

Efforts have been under way for a long time within the EU to prescribe by legislation low flammability for upholstered furniture and mattresses used in the private sphere. At this time, this is only required by law in Great Britain and Ireland. A corresponding draft EU directive was withdrawn in 1995. At the present time and in spite of various initiatives and national legislative proposals, regulation at European level is not to be expected, although fire safety oriented initiatives within the framework of the EU directive on general product safety (92/59/EEC) are conceivable.

Where upholstered furniture and mattresses are flame-retarded, this concerns not only the textile covers but also the flexible foam cushions. An examination that limits itself to the textile cover is therefore not expedient. The combustion behaviour of mattresses and upholstered furniture is determined by both elements of the composite product and these are, as a rule, tested for flammability in a unified test procedure.

Overview VI/7: Textile applications – upholstered furniture and mattresses	
Examined products	Mattresses (covers and foam); upholstery composites for upholstered furniture (covers and foam)
Fire safety requirements	DIN 4102; BS 5852; DIN EN 1021 (cigarette/match test)
Utilized materials	Foam: Polyurethane flexible foam (standard, high resilience, and combustion-modified high resilience (CMHR) foam) Covers: various fibres/fabrics
Plastics by quantity and representativeness	Maximum 2% of upholstery composites for furniture contain flame retardants (of this max. 1% for German market demand in commercial/institutional buildings/facilities) and max. 1% of mattresses.
Recommended/ utilized flame retardants	Foam: TCPP; TDCP; melamin resin, expandable graphite. Covers for upholstered furniture: Antimony-halogen compounds or APP compounds for back cover lamination; N-P compounds for full bath finishing. Covers for mattresses: inherently/permanently flame-retarded fabric (Trevira CS, etc.); flame retardance with N-P compounds (in part wash-proof, and partially not wash-proof).
Use status and trends	Upholstered furniture: Foam 50% without, 50% CMHR with flame retardants; covers: 1/3 without, 2/3 with flame retardants; Mattresses: Foam 90% without, 10% with flame retardants; covers: 70% fibre-modified flame-retarded, 30% finished with N-P compounds.
Flame retardant quantities and totals	Upholstered furniture: Foam 126 t, textiles: 31 t Mattresses: Foam 5 t, textiles 8 t Total: 139 t. In the event of the expansion of flame-retardance to cover all upholstered furniture and mattresses, prospective flame retardant use is estimated at approx. 7500 t on the basis of the status of flame retardant composition in the year 2000.
Substitution and reduction potential	Small, since upholstered furniture and mattress manufacturers largely do not use flame retardants in foam (materials-based solution through higher volume weight of the foam) and are critical with regard to an expansion of flame retardance. Substitution proposal for TCPP in flexible foam: Phosphoric polyols.
Evaluation	Increased use of flame retardants in upholstered furniture and mattresses should definitely be avoided from a toxicological and environmental perspective.

In contrast to the other selected product areas, a detailed examination of individual products is not possible within the scope of the present study, because upholstered furniture and mattresses are in fact upholstery composites using a great array of highly disparate cover materials, with different combustion behaviour and material properties.

In the following, we provide a summary overview of the total utilization of flame retardants in textiles, followed by a description of the flame retardance of foam and textile coverings for upholstered furniture and mattresses, in terms of quantities and flame retardant application.[11]

6.1 Flame retardants for textiles – overview

Flammability of textile fibres

Textile fabrics can be manufactured from a large variety of natural and synthetic fibres that display highly diverse combustion behaviour. From the perspective of their flammability they can be differentiated as (in brackets: LOI value; in case of LOI < 21 easily inflammable)

– easily flammable and combustible, as well as melting fibre fabrics (acrylate, acetate and polypropylene fibres; LOI 17-20);
– easily flammable and combustible, non-melting fibres (cotton, linen, viscose; LOI 18-20);
– not easily flammable, combustible and melting fibres (polyamide, polyester; LOI 20-22);
– not easily flammable and combustible, fibres more likely to carbonize than melt (natural silk, wool, acrylate/PVC fibres; LOI 23-30);
– self-extinguishing, non-melting and non-carbonizing in fibres (flame-retardant cotton, flame-retardant viscose, flame-retardant wool, etc.; LOI > 27)
– inherently flame-retarding fibre materials, partially melting (for instance Trevira CS or Lenzing flame-retarding Viscose).

Flame retardants for textile fibres

Corresponding to the great diversity of fibres that must be finished and the material and utilization properties that must be taken into account, a large range of different flame-retardant formulations exist for textiles. The share of the active substance (flame-retarding substances plus auxiliary substances) in the formulations of flame retardants for the textile industry is approx. 50%, however this varies strongly in accordance with the application area. For instance, while formulations utilized for the permanent finishing of protective clothing contain 50-95% flame-retarding substances, the share in non-permanent finishings is 35-55%, and in compounds for the automobile and carpet industry (back laminations) 5-10%.

As with other finishing agents, the products are applied by the pass, dip, spray, or lamination method. The product layer on the fabric is decisive for the flame-retardant

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[11] Summary of Chapter VI: Textile applications - materials for upholstered furniture and mattresses, Volume II, pp. 281 - 322

effect. The recommended utilization quantities vary strongly, averaging 25-30% of product weight.

For flame retardants, five main formulation types can be differentiated, which differ strongly with regard to their composition and properties.

Organic and inorganic salt finishes. Compounds that are not resistant to soaking and are not temperature-resistant, on the basis of boric acid, sulphamic acid, or phosphoric asset; ammoniates, salts of organic amines, metallic salts, ammonium phosphates, ammonium sulphamates, etc. Temporary (non-permanent) finishing.

Products on the basis of metal oxides and chlorinated binding agents. Resistant to soaking and weather resistant, but not wash resistant. Mostly antimony oxide plus chloroparaffin, chlorine rubber or PVC. Mostly permanent finishing.

Compounds based on antimony and organic halogen compounds plus binder. These compounds are resistant to soaking, weather, as well as washing and dry cleaning. Permanent finishing.

Phosphorus- and nitrogen-containing products, often in combination with resins. Resistant to soaking and weather, as well as washing, dry cleaning, and boiling laundering. Permanent finishing.

'Fibre active' organic phosphorus-nitrogen compounds. Resistant to soaking and weather, as well as washing, dry cleaning, and boiling laundering. Permanent finishing.

With the exception of the 'fibre active' compounds, these are additive flame retardants that are layered on the fibres or fabric as part of a compound, without creating a chemical bond to the fibre material. From the application perspective, the most important distinction is between permanent and non-permanent finishing. In *non-permanent finishing* washout and migration of the flame retardants must be taken into account, while with permanent (wash-resistant) finishing the flame retardant remains bound in a more or less stable manner. *Permanent finishing* includes: 'Fibre active' flame retardants for cellulose; spun introduction of flame-protection in viscose; potassium hexafluorozirconate for wool; inherently flame-retarded fibres.

Flame retardant consumption, Germany 1997

A distinction must be made between the trade products ('tel quel products') and the flame retardant content (active substance content) in the flame retardants sold by the textile auxiliary agent industry. The flame retardant content in trade products sold by the textile auxiliary agent industry for textile finishing varies greatly depending on the application area. For instance, for the permanent finishing of protective clothing it amounts to between 50 and 90%, for non-permanent finishing approx. 35–55%, and in compounds for the automobile and carpet industry only 5–10%.

In Germany, the companies that are a member of the TEGEWA association reported a sale of approx. 7900 tonnes of flame-retarding formulations to the textile and fibre manufacturing industry for 1997. According to calculations of the TEGEWA association, the share of active flame-retarding substances in the trade products was approx. 1000 tonnes or 13% in 1997. That this share is so small is, according to this calculation, due to the relatively large share of carpet back laminations that have a very low flame retardant content (without the aluminium trihydroxide, which is counted as a filler here and is utilized for 80% of carpet back laminations).

Taking into account imports and those companies that are not a member of an association (together approx. 20% of the market volume), the sale of flame retardants for textiles in Germany in 1997 can be estimated at approx. 1250 tonnes, or at about 1.3% of the total flame retardant consumption.

6.2 Materials for mattresses and upholstery composites

When mattresses and upholstered furniture are to be flame-retarded, all the important elements of the composite must be taken into account, that is the cushion or foam core, as well as the cover.

The dominant material for cushions is polyurethane flexible foam. PUR foams of varying density, which are manufactured in the block foam process, are utilized almost exclusively for furniture and mattresses.

A large variety of different fabrics and knitted goods is utilized in covers for upholstered furniture, so that no generally valid statements about their behaviour and properties can be made. The fabric range for mattresses is not that large; the flame-retarded area includes additively flame-retarded cotton materials, as well as polyester/viscose, polyester/polypropylene, and polypropylene/viscose fabrics. Quantitatively however, the synthetic and inherently/permanently flame-retarded Trevira CS is the dominant fabric.

6.3 Fire safety requirements

A legal basis for flame retardance of mattresses and upholstered furniture follows in part from the relevant regulations for fire safety that are part of the special construction regulations (Sonderbauordnungen) for institutional/commercial buildings and facilities (meeting halls, high-rise buildings, hospitals, old age homes, prisons, psychiatric institutions, ships, hotels, etc.) and in connection with the DIN 4102 standard. In most instances though, pragmatic regulations and guidelines of the procurement authorities or the procuring administration, as well as the supervisory authorities for construction, including those authorities involved in construction supervision from a viewpoint of fire safety (fire brigades), are decisive. For these, the cigarette test in accordance with DIN EN 1021 is important.

There are no applicable fire safety regulations in Germany for upholstered furniture and mattresses in private use. Matters are handled effectively like this in all of Europe, with the important exception of Great Britain and Ireland, where flame retardance in accordance with BS 5852 (cigarette and match test, wooden crib test) is required in the private domain since 1988. As a consequence, upholstered furniture and mattresses for private use in Germany are, as a matter of principle, not flame-retarded.

Flame-retarded upholstered furniture and mattresses are produced in Germany only for a limited part of the institutional/commercial buildings/facilities sector (among others ships, hospitals, hotels). Quantitatively this represents a maximum of 1% of the mattresses and 2% of the upholstered furniture, of which 1% is flame-retarded for institutional/commercial buildings/facilities and 1% for export (Great Britain, USA, etc.).

6.4 Combustion behaviour of upholstery composites

PUR flexible foam is easily flammable; its ignition temperature is > 400°C, whereby a strong development of smoke must be expected in the event of fire. The highly diverse combustion behaviour of textile fibres is characterized in greater detail in section 6.1.

Of decisive importance is the combustion behaviour of the composite made of foam and textiles. Detailed examinations are available in this regard (among others from the TFI Institute in Aachen, Germany). These show that most of the upholstery composites meet the so-called ‘cigarette test’ without flame retardants. If a high-resilience (HR) foam, that has a volume weight of 35 (without flame retardants), is selected, then only an upholstery composite made with pure cotton does not pass the test. In contrast, if the ‘match test’ is applied, then out of 191 tested combinations of different foam cushions and textiles 90 (exposed to flame for 15 seconds) or, respectively, 121 (exposed to flame for 20 seconds) combinations fail. This is also valid for many upholstery composites with HR foam. All composite materials that were made of any textile cover in combination with a so-called combustion-modified high-resilience (CMHR) foam (volume weight 30, flame-retarded) and a flame-retarded interliner made of viscose passed the test (the only exception: an upholstery composite covered with a light cotton-viscose material).

The obligatory introduction of the cigarette test could in principle be handled without the utilization of flame retardants, by means of changes in the design with regard to materials and construction (selection of foam and textiles). However, in case of an obligatory introduction of the match test, a far-reaching utilization of CMHR foam and flame-retarded covers for upholstered furniture would be required.

6.5 Flame retardant usage

Flame-retarded mattresses

Approximately 90% of the flame-retarded mattresses are manufactured with high-resilience foam (volume weight > 40). By itself, HR foam passes the cigarette test without flame retardants from a volume weight of 25 upwards, and the match test from a volume weight of 35. 10% are manufactured from a cheaper flexible foam that has a lower volume weight and contains flame retardants. Halogenated (chlorinated) phosphoric acid esters serve as a flame retardant in the foam (tris[chloropropyl]phosphate [TCPP] and tris[1,3 dichloroisopropyl]phosphate [TDCP]; see Chapter V/5, TCPP substance evaluation).

Approximately 70% of the mattresses are covered with inherently/permanently flame-retarded drill (in nine cases out of ten Trevira CS) and 30% with fabrics finished with a flame retardant.

In Teviora CS, 3% of weight (in relation to the fabric) methylphospholane is actively inserted for flame retardance. The phosphorus content is approx. 0.6%. In accordance with DIN 4102, Trevira CS is classified as B1 and it melts away when exposed to flame. Nitrogen-containing phosphorus compounds are used as flame retardants in other fabrics for mattress covers, whereby both 'fibre active' substances for permanent finishing and salt products that are not wash-resistant are used (including Pyrovatex CP neu and THPC/Proban; see Chapter V/7 and Overviews V/14 and 15). In the case of drill, the flame retardant application is approx. 5% of weight.

Upholstered furniture

In the case of upholstered furniture for the home market that is not easily flammable, HR foam is used (in an estimated 2/3 of instances) in such a combination with a covering material, without the addition of flame retardants, that the cigarette test can be passed (see Section 6.4). A covering material for upholstered furniture that is finished with flame retardants is only used in a smaller number of cases (1/3, estimation) for the German market for insitutional/commercial buildings and facilities.

This is in contrast to export products for the English and other overseas markets with comparable fire safety requirements. Here CMHR foam is utilized, which for instance contains (>10% of foam weight) a mixture of melamin resin and expanded mineral carbon, as well as halogenated phosphoric acid ester (TCPP/TDCP). For the English market, the covering material is a mixed fabric, the back finish consists of state-of-the-art antimony-halogen compounds (halogen component in Germany: hexabromocyclododecane as a substitute for decabromodiphenyl ethers, which are otherwise state-of-the-art); dry application: 30-40 g/flame retardant per m^2 fabric. A compound made of ammonium polyphosphate and a binder can also be applied as a back finish. The dry application, with between 100 and 200 g/m^2, will then however be substantially higher. In the case of cellulose fibres, a full-bath finishing with nitrogen-phosphorus compounds is usual; in this instance the dry application is approx. 35 g/m^2.

6.6 Trends

The quantities show that flame retardance in upholstered furniture and mattresses has marginal importance in Germany.

An estimated 39 tonnes of flame retardant are accounted for by upholstered furniture and mattresses, which is barely 3% of the total utilization of flame retardants for textiles, that amounted to 1250 tonnes in 1997. It must further be taken into account that at least half of the upholstered furniture, which is the main application area, is manufactured for export.

Approximately 100 tonnes of flame retardant are required for the flame retardance of PUR flexible foams. These are used almost exclusively for upholstered furniture (export products). According to the manufacturers of upholstered furniture, because of the complicated upholstery composites the flame behaviour of these products demands flame retardant incorporation in the foam if compliance with BS 5852 is required, in contrast to products for the German market.

In relation to the total consumption of nearly 100,000 tonnes of flame retardants in Germany, the sector of upholstered furniture/mattresses is, with 0.2%, very small. However, in the event of complete flame-retardance of upholstered furniture and mattresses for private uses, as has been proposed on occasion, the consumption of flame retardants would increase substantially. Projection from the current status (2% of upholstered furniture with 125 tonnes, 1% of mattresses with 13 tonnes flame retardants in covering fabric and the foam) to full flame retardance, in accordance with the flame retardant mix described for Germany, results in a total volume of 6250 tonnes flame retardants for upholstered furniture and 1300 tonnes for mattresses (together 7500 tonnes) that would have to be consumed every year. The corresponding projection of flame retardant consumption for textiles (covering fabrics) would reach a magnitude of 2330 tonnes (flame retardants without solvents), and the flame retardant consumption for foam would exceed 5200 tonnes. That this estimate is rather towards the lower end is shown by the available information on flame retardant consumption for mattresses and upholstered furniture in Great Britain, which is reported to amount to a total of 14,000 tonnes (whereby it is not clear whether these are ‘tel quel’ compounds or pure flame retardants).

6.7 Evaluation

Chlorinated phosphoric acid esters, melamin, and expandable mineral carbon are mainly used as a flame retardant in foam, while antimony-halogen compounds, as well as phosphorus-nitrogen compounds, and furthermore ammonium polyphosphate compounds are utilized for covering fabrics. From a toxicological and ecotoxicological point of view, these flame retardants are in part evaluated critically (in declining order: TCPP; HBCD; melamin), or they raise questions (Pyrovatex CP) that stand in the way of a conclusive evaluation. Ammonium polyphosphate and expandable mineral carbon are unproblematic in this regard.[12] In view of the possibly large required utilization quantities of flame retardants in residential interior rooms, from a toxicological and environmental perspective an expansion of flame retardant use in upholstered furniture and mattresses should definitely be avoided.

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[12] See the summary substance evaluations in this volume in Chapter V/5 (TCPP) and V/7 (Pyrovatex CP), as well as the references in Chapter V/15 to melamin and graphite; similarly the substance profiles in Volume III (TCPP: pp. 124 ff, Pyrovatex CP pp. 163 ff.)

Tables

Overviews