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RISK REDUCTION MONOGRAPH NO.3:

SELECTED BROMINATED FLAME RETARDANTS

BACKGROUND AND NATIONAL EXPERIENCE WITH REDUCING RISK

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

Paris 1995

OECD Environment Monograph Series No. 102

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SELECTED BROMINATED FLAME RETARDANTS

Background and National Experience with Reducing Risk

Environment Directorate

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RISK REDUCTION MONOGRAPHS

Risk Reduction Monograph No. 3: Selected Brominated Flame Retardants – Background and National Experience with Reducing Risk is the third in a series of OECD documents concerned with risk reduction activities for specific chemicals or groups of chemicals. The Risk Reduction Monographs contain sections on: the commercial life cycle; the environmental life cycle, including sources of environmental releases, pathways, and estimations of exposure; risk reduction and control measures; and international and national positions on the perceived risk.

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FOREWORD

Background

In 1990, the Council of the OECD adopted a Decision-Recommendation on the Co-operative Investigation and Risk Reduction of Existing Chemicals [C(90) 163/Final]. This OECD Council Act is aimed at the reduction of risks from chemicals to the environment, and/or to the health of the general public or workers. It is based on the premise that international co-operation in risk reduction activities can enhance the technical and institutional aspects of risk management in Member countries through burden-sharing and a reduction of duplicative efforts. Furthermore, such activities can lead to a more effective use of the knowledge about risks that is being generated through, for example, national chemicals reviews and assessments; the OECD co-operative investigation of existing chemicals; and the work of other international organisations conducting hazard and risk evaluations, such as the United Nations' International Programme on Chemical Safety (IPCS).

International co-operation can provide a forum for the exchange of views on risk reduction strategies, thus increasing mutual understanding and facilitating the harmonization of programmes being undertaken at the national level. By means of this forum, technical barriers to trade can also be prevented.

The OECD's approach to risk reduction

The risk reduction process normally begins at the national level. However, the international character of the use and marketing of chemicals, and the mobility of certain chemicals in the environment, give risk reduction activities an international dimension.

The OECD's approach to risk reduction relies on the sharing and exchange of information on the management of specific chemicals. Readily available information concerning national risk reduction strategies can make comparative analyses possible. Where common interests emerge, the development and implementation of measured and consistent responses to unacceptable health and/or environmental risks can be facilitated.

In this context, risk reduction activities can take into account all stages of a chemical's commercial and environmental life cycles, beginning with the natural resources needed to produce it and extending through the chemical's uses to its eventual disposal. The chemical's health and environmental effects can be considered, together with exposure via all routes and media to different populations.

OECD work on brominated flame retardants risk reduction

OECD Member countries chose brominated flame retardants as one of the five chemicals (or groups of chemicals) to be included in an initial pilot project on co-operative risk reduction. An OECD Clearing House made up of the Netherlands, Sweden, Switzerland and the United Kingdom began collecting information in support of this Risk Reduction Monograph in 1993. Drafts of the document were developed with the support of Mr Pedro Arias, a consultant to the OECD.

The Joint Meeting of the Chemicals Group and the Management Committee of the Special Programme on the Control of Chemicals recommended that this document be derestricted. It is being made public under the authority of the Secretary-General.

EXECUTIVE SUMMARY

The main purposes of this document are:

- to provide a summary of information regarding releases of selected brominated flame retardants to the environment, and the ensuing environmental and human exposures; an international (IPCS) risk assessment; and a summary of the ways OECD Member countries perceive the risks associated with exposure to these flame retardants; and

- to describe the actions these countries and industry have taken, or contemplate taking, to reduce the perceived risks associated with exposure to selected brominated flame retardants.

This document reflects information provided in 1993-1994 and should be considered as a "snapshot" of the most recent thinking and activities during this time period. For countries considering risk reduction, or additional risk reduction measures, for selected brominated flame retardants, this document may assist in evaluating the effectiveness of national strategies by identifying common trends in the setting of criteria, standards or national policies. It may also suggest rationales, and possibilities, for concerted international actions, if necessary.

General information on brominated flame retardants is summarized in Chapter 1 and the appendices. However, the discussions of exposure and effects in Chapters 2 through 5 mainly address only polybrominated biphenyls (PBBs), polybrominated diphenyl oxides (PBDPOs) and tétrabromobisphenol A (TBBPA).

Where risk reduction activities for brominated flame retardants are in place or contemplated in Member countries, they are expected to continue to create information and technology conduits, and to promote the development and transfer of knowledge regarding the nature and efficacy of responses to situations in which countries believe the risk resulting from exposure to brominated flame retardants is unacceptable.

Chapter Summaries

1. Production and Use of Brominated Flame Retardants

The need for (and life cycle of) flame retardants:

Concern for safety has existed as long as there has been fire. Each year thousands of people die from burns or, more commonly, from the inhalation of toxic smoke produced by fires. Certain polymers such as synthetic fibres and plastics are combustible (like wood) and therefore are treated with flame retardants to meet fire safety standards if applied in critical applications (curtains, electrical and certain building applications). Brominated chemicals, along with chlorine, phosphorous, nitrogen, antimony, aluminium and magnesium based chemicals, are the most widely used flame retardants for these materials.

Bromine, the base chemical for brominated flame retardants, is extracted from sodium bromide solutions in brines, saline deposits or sea water. The bromination of chemical intermediates such as bisphenol A or diphenyl oxide produces brominated flame retardants.

Over 30 brominated chemicals are used as flame retardants. They are incorporated into polymers either by blending to form a mixture, or by reaction. In the latter case, they become a part of the polymer backbone.

Flame retardant compounds are transformed into parts of articles or semi-finished products in numerous industries, including construction (roofing, facing, interiors), transportation, and electrical/electronics (switches, sockets, lighting, office machines, radios, televisions, etc.).

Market demand:

OECD countries account for 55 per cent of world bromine production, estimated at 438,000 tonnes in 1990. Much of the remainder is produced in Israel and the ex-USSR.

Flame retardants make up the largest segment of bromine based chemicals, accounting for 20 per cent of world bromine demand. Other major bromine markets are pesticides, gasoline additives, drilling fluids and water treatment chemicals.

The amount of chemicals used as flame retardants for the polymer and textile markets is over half a million tonnes. The total demand for brominated flame retardant chemicals (which cost from US$ 3500 to over US$ 6000 per metric tonne) is estimated at 150,000 tonnes per year. Tétrabromobisphenol A and its derivatives account for 33 per cent of the total, and brominated diphenyl oxides for 27 per cent. Of all these chemicals, decabromodiphenyl oxide is the most economical in relation to bromine content and effectiveness, particularly in styrenic polymers.

Most of the worldwide demand for brominated flame retardants comes from three regions: North America (40 per cent), the Far East (30 per cent) and Europe (25 per cent). The type of consumption varies greatly from country to country. Some countries may only import such chemicals and incorporate them in products used domestically; others may produce the chemicals domestically, but compound them into polymers in another country. National fire safety standards appear to be responsible for some of the variation in consumption patterns.

Overall, the annual growth rate in the demand for flame retardant (FR) chemicals is expected to be far greater than that for polymers and textiles, based on forecasts of more national regulations requiring flame retarded end products and more harmonization of FR test procedures (particularly in the European Union). At the same time, the current geographic distribution of worldwide production is likely to undergo major changes as companies move the production of semi-finished or finished products to countries that are only limited consumers of such products.

2. Environmental Fate, Transport and Occurrence

There are a few studies of the environmental fate of brominated flame retardants. The three most studied groups of families are polybrominated biphenyls (PBBs), polybrominated diphenyl oxides (PBDPOs) and tétrabromobisphenol A (TBBPA).

Since these chemicals have low vapour pressure and low water solubility, it is estimated that once they are released to the environment they will be distributed principally to soil and sediment.

Photodegradation via debromination was observed in the case of some brominated flame retardants under laboratory conditions, but decomposition under environmental conditions still needs to be studied. Biodegradation in water, sediment and soil is not likely to occur easily. It is considered that PBBs and PBDPOs are persistent in the environment, although little information is available on hydrolysis.

Certain PBBs may be poorly metabolized and accumulate in lipid layers of biota. Ingestion of fish is considered to be a source of PBB transfer to mammals and birds. Higher BCF (bioconcentration factor), more than 10,000, was reported for pentabromodiphenyl oxide (PeBDPO). Some lower-brominated phenyl oxides (HxBDPO, PeBDPO and TeBDPO) have been detected in biota. Except for these substances, bioaccumulation of the brominated flame retardants has not been observed despite their suspected persistency and lipophilicity. This may be attributed to their relatively high molecular weight.

One major concern associated with these chemicals is the formation of PBDFs (furans) and PBDDs (dioxins) as thermal decomposition products. Numerous studies have been conducted. The results vary according to the products tested, temperatures applied, and other test conditions such as presence of oxygen and catalysts.

For example, thermal decomposition of PBBs depends on the temperature as well as the presence of oxygen. Without oxygen, no furans have been formed; with oxygen, small amounts of furans have been detected. When tested with polystyrene and polyethylene, even higher levels have been found. In combustion studies of PBDPOs, furans have generally been formed and dioxins have either not been formed, or have been formed at lower levels. Antimony trioxide appears to increase the formation of furans. Mono- and dibromofurans have been mainly formed by the pyrolysis of TBBPA. However, low levels of 2,3,7,8-substituted PBDFs/PBDDs have been detected in some cases.

3. Exposure

There are various sources of release and exposure to brominated flame retardants, but little information is available. It has been reported that consumer exposure is limited because these chemicals are unlikely to be leached from polymers. Little information is available on occupational exposure. Data on the detection of decabromodiphenyl oxide (DeBDPO) was only available for workroom environments. Production sites appear to be a source of environmental exposure.

Brominated flame retardants can be released into the atmosphere in the form of dust or particulates from production sites because of their low vapour pressure and high melting points. Several chemicals, such as DeBDPO, have been identified in air samples in the vicinity of manufacturing sites (25 $\mu g/m^3$). PBDDs and PBDFs have been found in solid material sampled from industrial and municipal waste incinerators. Accidental fire might be another source of emission.

It is estimated that effluents from manufacturing sites include these chemicals, even though no direct analysis has been reported. High concentrations of tétrabromodiphenyl oxide (TeBDPO) in fish (118 mg/kg fat) have been found in Sweden. PBBs have been detected in sediments and leachate from landfill sites. TBBPA has been detected in fish near an industrialized area in Japan.

Many kinds of brominated flame retardants have been found in the environment, although available information is geographically limited. While they are rarely found in water, DeBDPO, OBDPO, PeBDPO, TeBDPO, PBBs and TBBPA have been found in sediment. As for concentrations in wildlife, PBBs have been detected in fish, terrestrial and marine mammals, and birds in the United States and Europe. PeBDPO and TeBDPO have mainly been found in fish or shellfish in Japan and Northern Europe. They have also been found in pooled samples of terrestrial and marine mammals in Sweden.

As for human levels, PBBs and TeBDPO have been detected in breast milk in Europe. DeBDPO and OBDPO have been detected in adipose tissue in the United States.

4. International and National Positions on the Risks from Brominated Flame Retardants

This chapter presents evaluations from the International Programme on Chemical Safety (IPCS) of the risks from polybrominated diphenyl oxides, polybrominated biphenyls, and tétrabromobisphenol A.

Also presented in this chapter are statements, provided by Member countries, in regard to their perception of and concern for the risks associated with the continued production and use of certain brominated flame retardants, and the risks from exposure to the degradation products.

The risk assessments and risk characterizations that have led countries to take action have a national character. Countries develop positions on the need for risk reduction activities only after they have analysed the hazard and significance of certain exposures and have factored in local social, economic and political considerations. These positions are usually arrived at after considerable debate on the numerous factors involved, and thus are not consistent across Member countries.

5. Mechanisms for Risk Reduction

The brominated flame retardant risk management activities of 13 Member countries are described in this chapter. These descriptions, provided by each country, include information on steps taken in the past to reduce exposure to polybrominated biphenyls, and proposed steps to reduce exposure to polybrominated diphenyl oxides.

Countries' risk management activities with regard to PBBs are summarized in Annex A to this chapter. (Similar tables for the other brominated flame retardants are not included, since no country has taken final action on these chemicals.) Lack of information in this document on a particular Member country indicates either that no risk reduction activities have taken place in that country, or that the country has not responded to requests for information.

The following is a brief summary of the risk management actions described in this chapter:

Austria: Austria has banned the production, placing on the market, and use of PBBs for all applications.

Belgium: No risk reduction actions have been taken on brominated flame retardants, and further study is needed before a national statement on risk can be developed.

Denmark: Denmark has banned the use of PBBs in textiles.

Finland: Polybrominated biphenyls may not be used in textile articles, such as garments, undergarments and linen, intended to come into contact with the skin (in accordance with EC Directive 83/264).

France: France has implemented EC Directives concerning PBBs and their use on textiles.

Germany: The German government adopted in 1994 a second modification of the Chemicals Prohibition Ordinance which imposes limits on chlorinated dioxins and furans, as well as on brominated dioxins and furans. Prohibitions apply to products (which could include brominated flame retardants) if they contain these pollutants above certain levels. Similarly, a proposal has been made to limit worker exposure to 2,3,7,8-TCDD equivalents (TEQ).

Italy: No risk reduction actions have been taken on brominated flame retardants as a result of government requirements. However, some risk reduction measures have been taken on a voluntary basis by some public organisations and industries to exclude the use of halogenated flame retardants.

Japan: Industries continue to restrict voluntarily the production and use of PBBs, hexabromodiphenyl oxide (HxBDPO) and tétrabromodiphenyl oxide (TeBDPO).

The Netherlands: The Netherlands has proposed a resolution to prohibit having in stock biphenyls or diphenyl oxides containing bromine, or products or preparations containing these substances, or to make them available to third parties. The proposed resolution would not apply to products intended for export.

Sweden: Sweden has banned the use of PBBs in textiles intended to come in contact with the skin. A Government Bill, adopted by the Parliament, stated that the use of brominated flame retardants is to be restricted.

Switzerland: The manufacture, supply, import and use of PBBs and terphenyls (PBTs), and products containing these substances, have been prohibited. By the same ordinance, the supply and import of capacitors and transformers containing halogenated aromatic substances such as polychlorinated and polybrominated biphenyls, halogenated diarylalkanes or halogenated benzenes have been forbidden.

United Kingdom: The UK has implemented EC Directives restricting the use of tris(2,3-dibromopropyl) phosphate and PBBs in textiles. The UK and France have been jointly assigned DeBDPO and OBDPO for risk assessment under EC Council Regulation 793/93, which requires them to propose any risk reduction action required. Assessments are now in hand. These may also address risks from PeBDPO.

The UK controls dioxin and furan emissions from municipal solid waste (MSW) incinerators by ensuring efficient operating conditions under the Environmental Protection Act. Occupational exposures are subject to the Health and Safety at Work, etc. Act, and specifically the Control of Substances Hazardous to Health Regulations.

United States: Industry voluntarily discontinued use and production of PBBs in the late 1970s. The Environmental Protection Agency (US EPA) has issued a Significant New Use Rule that requires anyone intending to resume the manufacture of eight specified PBBs to notify EPA 90 days prior to manufacture.

EXPOSE DE SYNTHESE

Le présent document a pour principaux objectifs :

- de résumer les informations relatives aux rejets d’ignifugeants bromés dans l’environnement, à l’exposition de l’environnement et de l’être humain, ainsi qu’à la façon dont les pays Membres de l’OCDE perçoivent les risques associés à l’exposition aux ignifugeants bromés ; et

- de décrire les dispositions que ces pays et les industries concernées ont prises ou envisagent de prendre afin de réduire les risques qui leur paraissent être associés à l’exposition aux ignifugeants bromés.

Ce document s’inspire d’informations fournies de 1992 à 1993 et doit être considéré comme un «instantané» des réflexions les plus récentes et des activités de cette période. Il peut aider les pays qui envisagent de réduire les risques associés aux ignifugeants bromés ou d’adopter des mesures complémentaires pour réduire ces risques à évaluer l’efficacité des stratégies nationales en faisant ressortir les tendances communes dans l’établissement de critères, de normes ou de politiques nationales. Il peut également, le cas échéant, proposer des domaines où des actions internationales concertées se justifieraient et seraient possibles.

Ce document contient une information générale sur tous les ignifugeants bromés dans le premier chapitre et dans les appendices. Dans les chapitres 2, 3, 4 et 5, les discussions relatives à l’exposition et aux effets concernent principalement les biphényles polybromés (PBB), les oxydes de diphényle polybromés (OPBD) et le tétrabisphenol A (TBBPA).

Qu’elles soient en cours ou seulement envisagées, les activités visant à réduire les risques associés aux ignifugeants bromés devraient normalement continuer d’alimenter des flux d’informations et de technologies entre pays Membres, et encourager l’acquisition et l’échange de connaissances relatives à la nature et à l’efficacité des mesures prises pour remédier à des situations dans lesquelles, de l’avis de certains pays, les risques posés par l’exposition aux ignifugeants bromés sont inacceptables.

Résumé des différents chapitres

1. Production et utilisation des ignifugeants bromés

Nécessité et cycle de vie des ignifugeants :

Depuis la découverte du feu, on s'efforce de s'en protéger. Chaque année, des milliers de personnes meurent à cause de brûlures ou, plus communément, de l'inhalation de fumées toxiques produites lors d'incendies. Certaines matières synthétiques, telles que fibres de synthèse et matières plastiques, sont combustibles (comme le bois) et doivent donc être traitées avec des produits ignifugeants de façon à respecter les normes de sécurité incendie dans certaines utilisations critiques (rideaux, équipement électrique et certaines applications dans le bâtiment). Des produits chimiques bromés, ainsi que des produits chimiques à base de chlore, de phosphore, d'azote, d'antimoine, d'aluminium et de magnésium, sont les ignifugeants les plus largement utilisés pour de telles matières.

Le brome, substance chimique de base des ignifugeants bromés, est extrait du bromure de sodium en solution dans les eaux saumâtres, les dépots salins ou l'eau de mer. La bromation de produits chimiques intermédiaires, comme le bisphénol A ou l'oxyde de diphényle, aboutit à des ignifugeants bromés.

Plus de 30 produits chimiques bromés sont commercialisés en tant qu'ignifugeants qui sont incorporés à des matières polymérisées, soit par mélange, soit par réaction pour les intégrer au squelette du polymère.

Les composés ignifugeants sont transformés en constituants de produits finis ou semi-finis utilisés dans de nombreuses industries, notamment la construction (toiture, revêtements de parois extérieures et intérieures), les transports, l'industrie électrique et électronique (interrupteurs, prises de courant, éclairage, bureautique, radio, télévision, etc.).

Demande sur le marché :

Les pays de l'OCDE contribuent pour 55 pour cent à la production mondiale de brome, évaluée à 438 000 tonnes en 1990, le reste étant produit en grande partie en Israël et ex-URSS.

Les ignifugeants constituent le segment le plus important du marché des produits chimiques bromés et absorbent 20 pour cent de la demande mondiale de brome. Les autres grands débouchés du brome sont les pesticides, les additifs de l'essence, les fluides de forage et les produits chimiques pour le traitement de l'eau.

Plus d'un demi-million de tonnes de produits chimiques sont utilisées comme ignifugeants sur les marchés des polymères et des textiles. La demande totale d'ignifugeants bromés, qui coûtent de 3 500 $ à 6 000 $ et plus la tonne, est évaluée à 150 000 tonnes par an. Le tétrabromobisphénol A et ses dérivés représentent 33 pour cent du total et les oxydes de diphényle bromés 27 pour cent. De tous ces produits chimiques, l'oxyde de décabromodiphényle est le plus économique en termes de teneur en brome et d'efficacité, notamment dans les polymères du styrène.

L'essentiel de la demande mondiale d'ignifugeants bromés émane de trois régions : Amérique du Nord (40 pour cent), Extrême-Orient (30 pour cent) et Europe (25 pour cent). La façon dont ces produits chimiques sont utilisés varie considérablement d'un pays à l'autre. Certains pays peuvent se limiter à les importer et à les incorporer à des produits utilisés sur le marché intérieur ; d'autres peuvent produire ces substances sur place, mais celles-ci sont incorporées à des polymères dans d'autres pays. Les normes nationales de sécurité incendie sont apparemment à la base de certaines différences constatées dans les modes d'utilisation.

Dans l'ensemble, la demande annuelle d'ignifugeants devrait augmenter à un rythme bien plus rapide que la demande de polymères et de textiles si, comme on le prévoit, davantage de réglementations nationales exigent des produits finis ignifugés et si les protocoles d'essai des ignifugeants s'harmonisent davantage (notamment au sein de l'Union européenne). En outre, il est vraisemblable que l'actuelle répartition géographique de la production mondiale va aussi connaître des modifications majeures au fur et à mesure que les entreprises transfèrent la fabrication de produits finis ou semi-finis vers des pays où la consommation de tels articles reste limitée.

2. Devenir, transport et présence dans l'environnement

Il n'existe que peu d'études sur le devenir des produits chimiques bromés dans l'environnement. Les deux familles de produits les plus étudiées sont les biphényles polybromés (PBB), les oxydes de diphényle polybromés (OPBD) et le tétrabromobisphénol A (TBBPA), même si le présent chapitre contient des données relatives à quelques autres groupes de produits chimiques.

Puisque ces produits chimiques ont une faible pression de vapeur et sont peu solubles dans l'eau, on admet qu'une fois libérés dans l'environnement ils vont se répartir essentiellement dans les sols et dans les sédiments.

Dans les conditions du laboratoire, des phénomènes de photodégradation, comme la débromation, ont été observés, mais la décomposition en milieu naturel reste encore à étudier. Il est peu probable que ces substances soient facilement biodégradables dans l'eau, dans les sédiments et dans les sols, sauf dans le cas de l'oxyde de monobromodiphényle (OMBD). On estime donc que les produits chimiques bromés sont persistants dans l'environnement, bien qu'on ne dispose que de peu d'informations sur leur hydrolyse.

Les biphényles polybromés (PBB) sont peu susceptibles de métabolisation et s'accumulent dans les tissus adipeux des organismes vivants. Un facteur de bioconcentration élevé, supérieur à 10 000, a été signalé pour l'hexabromocyclododécane (HeBCD) et pour l'oxyde de pentabromodiphényle (OPeBD). A l'exception de ces catégories de substances, on n'a pas constaté de taux élevés de bioaccumulation des produits chimiques bromés, en dépit de leur persistence et de leur lipophilie. Ceci pourrait être attribué à leur poids moléculaire relativement élevé.

Ce qui rend ces produits chimiques particulièrement préoccupants, c'est la formation de dibenzofurannes polybromés (BPDF) et de dibenzodioxines polybromées (PBDD), en tant que produits de décomposition thermique. De nombreuses études ont été effectuées et leurs résultats varient en fonction des produits soumis à essai, des températures appliquées et d'autres conditions opératoires, comme la présence d'oxygène et de catalyseurs.

Par exemple, la décomposition thermique des PBB dépend aussi bien de la température que de la présence d'oxygène. Sans oxygène, il n'y a pas de formation de furannes, mais avec de l'oxygène, on en a détecté à de faibles quantités. Lors d'essais avec du polystyrène et du polyéthylène, on a mesuré des taux plus élevées. Au cours d'études de la combustion des OPBD, des furannes se sont généralement formés mais pas de dioxines, ou alors à des concentrations plus faibles. Le trioxyde d'antimoine semble accroître la formation de furannes.

3. Exposition

Ces produits chimiques sont émis par diverses sources et présentent différentes formes d'exposition, mais on dispose de peu d'informations en la matière. On a fait état d'une exposition limitée des consommateurs, car ces produits chimiques sont peu susceptibles d'être extraits des polymères par lixiviation. Les informations disponibles concernant l'exposition professionnelle sont peu nombreuses. On ne dispose, pour les lieux de travail, que de données sur la détection d'oxyde de décabromodiphényle (ODeBD). Les sites de production semblent constituer une source d'exposition de l'environnement.

Ces produits chimiques peuvent être émis dans l'atmosphère à partir des sites de production sous forme de poussières ou de particules, du fait de leur faible pression de vapeur et de leur point de fusion élevé. Plusieurs produits chimiques, comme l'ODeBD, ont été identifiés dans des échantillons d'air prélevés au voisinage de centres de production (25 $\mu g/m^3$). On a trouvé, en outre, des dibenzodioxines polybromées et des dibenzofurannes polybromés dans des échantillons de matières solides provenant d'incinérateurs de déchets industriels et urbains. Un incendie peut également constituer une source d'émission.

On suppose que les effluents des sites de fabrication contiennent ces substances, bien qu'aucune analyse directe n'ait été signalée. Des concentrations élevées d'oxyde de tétrabromodiphényle dans des poissons (118 mg/kg de tissu adipeux) ont été relevées en Suède. Des PBB ont été détectés dans des sédiments et des lixiviats de décharge. La présence de tétrabromobisphénol A dans des poissons prélevés dans une zone industrielle a été mise en évidence au Japon.

De l'oxyde de tétrabromodiphényle a été détecté dans des boues d'épuration (15 µg/kg) en Suède.

Des produits chimiques bromés de toutes sortes ont été trouvés dans l'environnement, bien que les informations disponibles soient géographiquement limitées. On les rencontre rarement dans l'eau, mais plutôt dans des sédiments et chez des espèces sauvages. Pratiquement tous les ignifugeants bromés étudiés ont été retrouvés dans des sédiments. Pour ce qui est des concentrations relevées chez des espèces sauvages, on a trouvé aux Etats-Unis des PBB dans des poissons, des mammifères marins et des oiseaux. L'ingestion de poisson est considérée comme un mode de transmission des PBB aux mammifères et aux oiseaux. Des oxydes de penta- et de tétrabromodiphényle ont principalement été retrouvés dans des poissons ou des crustacés au Japon et en Europe du Nord et localisés essentiellement dans les tissus adipeux. Les concentrations maximales d'oxyde de tétrabromodiphényle relevées atteignent 450 µg/kg chez le hareng et 1 800 µg/kg chez le balbuzard. Il a été signalé qu'en Suède, les concentrations dans les oeufs d'oiseaux de mer et dans les sédiments étaient en augmentation au cours de la présente décennie. Au Japon du TBBPA a été détecté dans les poissons à des taux de µg/kg et le dérivé dimethoxy a été trouvé dans les moules.

S'agissant des concentrations chez l'être humain, des PBB et de l'oxyde de tétrabromodiphényle ont été trouvés dans du lait maternel en Europe. De l'ODeBD et de l'oxyde d'octabromodiphényle (OOBD) ont été détectés dans du tissu adipeux aux Etats-Unis.

4. Positions adoptées au niveau international et national quant aux risques imputables aux ignifugeants bromés

Ce chapitre contient une évaluation acceptée au plan international, établie par le Programme international sur la sécurité des substances chimiques (PISSC), des risques liés aux oxydes de polybromodiphényle, aux PBB et au tétrabromobisphénol A.

Il contient aussi des déclarations des pays Membres, relatives à la façon dont ils perçoivent et surveillent les risques associés à la poursuite de la production et de l'utilisation de certains ignifugeants bromés, ainsi que les risques découlant de l'exposition aux produits de dégradation. Les évaluations et les caractérisations des risques qui ont amené les pays à prendre des mesures ont un caractère national. Les pays ne prennent position sur les mesures nécessaires pour réduire les risques qu'après avoir analysé le danger et la gravité de certaines expositions et pris en compte divers facteurs d'ordre social, économique et politique. Ces positions sont adoptées d'ordinaire après examen approfondi des nombreux facteurs en cause et diffèrent d'un pays Membre de l'OCDE à l'autre.

5. Dispositifs pour la réduction des risques

Ce chapitre passe en revue les activités que 15 pays Membres ont consacrées à la gestion des risques. Il comporte aussi un examen des mesures déjà prises pour réduire l'exposition aux biphényles polybromés, ainsi que des mesures envisagées pour réduire l'exposition aux oxydes de polybromodiphényle.

Les activités spécifiquement nationales de gestion de risque liés aux PBB sont résumées à l'Annexe A de ce chapitre. Dans le présent rapport, l'absence d'informations pour un pays Membre donné signifie soit que ce pays ne consacre pas d'activités à la réduction des risques, soit qu'il n'a pas répondu aux demandes d'informations.

Les paragraphes qui suivent résument succinctement les informations figurant dans ce chapitre :

Autriche : L'Autriche a inderdit la production, la mise sur le marché et l'utilisation des PBB pour toutes les applications.

Allemagne : Le Gouvernement allemand a adopté en 1994 une deuxième modification de l'Arrêté sur l'interdiction de produits chimiques qui impose des limitations aux dioxines et furannes chlorés et aussi aux dioxines et furannes bromés. Des interdictions pèsent sur des produits (qui pourraient renfermer des ignifugeants bromés) s'ils en contiennent au delà de certains plafonds. Il a été proposé, de façon similaire, de limiter l’exposition des travailleurs aux substances équivalentes à la tétrachloro-2,3,7,8 dibenzoparadioxine.

Belgique : Aucune mesure de réduction des risques n’a été prise pour les ignifugeants bromés et une étude approfondie est nécessaire avant qu’une déclaration nationale sur les risques puisse être élaborée.

Danemark : Le Danemark a interdit l’utilisation des PBB dans les textiles.

Etats-Unis : L’industrie a cessé de son plein gré d’utiliser et de produire des PBB vers la fin des années 70. L’Environmental Protection Agency (US EPA) a publié un règlement («Significant New Use Rule») qui stipule que quiconque ayant l’intention d’entreprendre la production de huit PBB spécifiques doit informer l’EPA 90 jours avant le début de cette production.

Finlande : Les PBB ne doivent pas être utilisés dans les articles en textile destinés à entrer en contact avec la peau humaine, tels que vêtements, sous-vêtements et linge (en accord avec la Directive européene 83/264).

France : La France interdit la production, l’importation, la vente ou la distribution à titre gracieux de PBB.

Italie : Aucune mesure de réduction des risques n’a été prise pour les ignifugeants bromés à la suite de prescriptions gouvernementales ; néanmoins, certaines dispositions en ce sens ont été adoptées volontairement par quelques organisations et industries publiques pour supprimer l’utilisation des ignifugeants halogénés.

Japon : L’industrie continue de limiter volontairement la production et l’utilisation des PBB, de l’oxyde d’hexabromodiphényl et de l’oxyde de tétrabromodiphényl.

Pays-Bas : Les Pays-Bas ont proposé une résolution interdisant d’avoir en stock des biphényles ou des oxydes de diphényle contenant du brome, ou des produits ou préparations contenant de tels produits chimiques, ou encore d’en fournir à des tiers. La résolution proposée ne s’appliquerait pas aux produits destinés à l’exportation.

Royaume-Uni : Le Royaume-Uni contrôle les émissions de dioxine et de furanne provenant des incinérateurs de déchets urbains solides en assurant des conditions de fonctionnement efficaces conformément à la Loi sur la protection de l’environnement.

Les expositions professionnelles sont soumises à la Loi sur l’hygiène et la sécurité sur les lieux de travail, etc., et notamment aux Réglementations sur le contrôle des substances dangereuses pour la santé.

Suède : La Suède a interdit l’utilisation de PBB dans les textiles destinés à entrer en contact avec la peau humaine. Un projet de loi, adopté par le Parlement, a précisé que l’utilisation des ignifugeants bromés allait être limité.

Suisse : La fabrication, la fourniture, l’importation et l’utilisation de PBB, de terphényles polybromés (PBT) et de produits en contenant ont été interdites. Le même arrêté a interdit la fourniture et l’importation de condensateurs et de transformateurs contenant des substances aromatiques halogénées comme les biphényles polychlorés et polybromés, les diarylalcanes halogénés ou les benzènes halogénés.

CHAPTER 1

PRODUCTION AND USE OF BROMINATED FLAME RETARDANTS

1.1 The need for, and use of, brominated flame retardants (BFRs)

As long as there has been fire, concern for safety has existed. Each year thousands of people die from burns or, more commonly, from the inhalation of toxic smoke produced by fires, which accounts for 70 per cent of fire deaths. In the United Kingdom alone, the inhalation of combustion products is estimated to be responsible for 1000 deaths and 63,000 disabling illnesses annually (Kirschbaum 1993).

Certain polymers, such as synthetic fibres and plastics, are combustible (like wood). They are therefore treated with flame retardants to meet fire safety standards if they are intended for critical applications (curtains, electrical and certain building applications). Brominated chemicals, along with chlorine, phosphorous, nitrogen, antimony, aluminium and magnesium based chemicals, are the most widely used flame retardants for these materials. Flame retardants act by reducing the amount of fuel supplied to the flame, reducing the amount of oxygen in the air, and/or changing the relative value of the diffusion and heat of combustion.

In the last two decades, as the use of polymers has increased, the use of flame retardants has also increased sharply on an international scale, although consumption varies among countries. The significant use of brominated flame retardants can be expected to continue. Brominated compounds are the type of flame retardants used predominantly in television sets, business machines, and electrical/electronic auxiliary equipment (such as housing, printed circuits and switching gears). The demand for flame retardant materials is increasing in this area.

Future growth in the use of brominated flame retardants will be affected by new flammability performance and toxicity standards, which will determine both the type and amount of retardant that need to be used. In addition, the demand for brominated flame retardants will be affected by the outcome of current efforts to develop low-flammability polymers which produce little smoke and only non-corrosive gas – and which do not therefore require the addition of flame retardants. However, it is more likely that future research will concentrate on the development of ways to minimize the undesirable effects (such as smoke production) of some of the more widely used brominated flame retardant polymers, perhaps through the use of new co-additives.

1.2 The production of BFR-containing articles

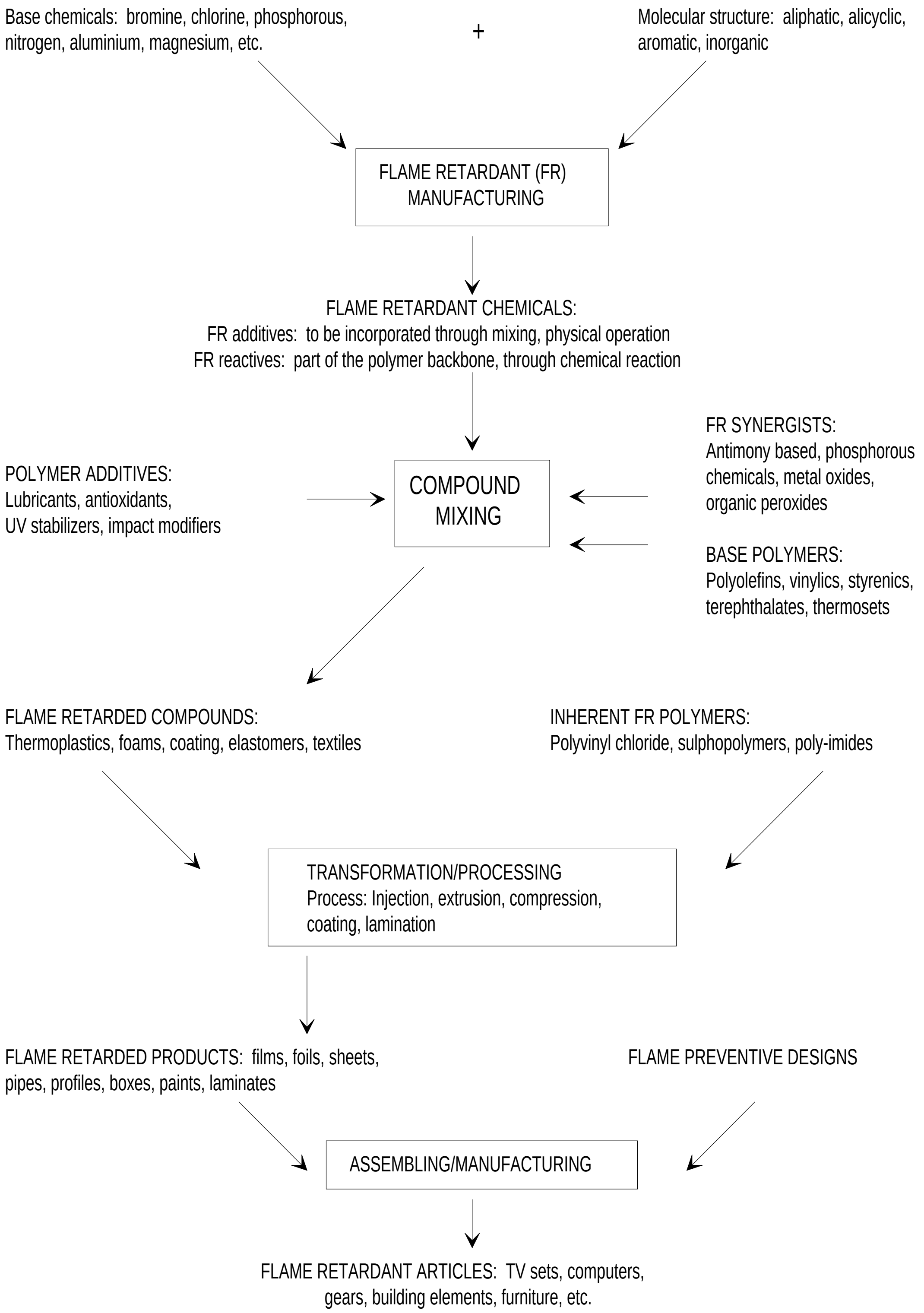
The production of brominated flame retardants begins with sodium bromide solution in brines, saline deposits or sea water. Processes for extracting bromine from these natural sources use chlorine as a reactant.

The bromination of inorganic and/or organic chemicals results in the full range of brominated flame retardant products – inorganics, aliphatics, alicyclics and aromatics. Brominated flame retardants can be incorporated into polymeric material by blending with the polymer, or by reacting with and chemically binding to the polymer and becoming part of the polymer chain. The incorporation of brominated flame retardant chemicals into polymers is generally complemented by the use of flame retardant synergists, most commonly antimony trioxide, as well as other plastic additives, impact modifiers, UV absorbers, stabilizers, lubricants, etc., depending on polymer and functional application requirements. The polymer mixtures are then manufactured into articles or semi-finished products for numerous industries including construction (e.g. roofing, facing, interiors), transportation, electrical/electronics (e.g. switches, sockets, lighting, office machines, radios, televisions), and mining.

Figure 1.1 presents an overview of the production of a flame retarded product from base chemical (e.g. bromine) through final assembly into an article (e.g. a computer). It should be noted that end products that inhibit flames or smoke need not be the result of intentional addition of a flame retardant chemical. As can be seen in the figure, some polymers like polyvinyl chloride are *inherently flame retardant* and need no additional chemicals to impart this desired quality. (It is possible, however, that some applications of the pure PVC polymer may require the use of plasticizers to impart the desired degree of flexibility. These plasticizers may increase flammability by diluting the high chlorine polymer with combustible material.) Similarly, articles can be assembled in such a way that they achieve the desired fire safety level, and yet contain no components treated with flame retardants. For instance, by allowing sufficient separation between a component and a heat source, the component may not require flame retardant chemicals to prevent ignition. This separation can be *designed* into certain equipment. It should be noted that while such an approach will provide protection from internal heat sources, it may not protect against external ones.

There is an overview of flame retardant chemicals and compounds (i.e. non-brominated flame retardants) in **Appendix 1**.

Figure 1.1 Production of Flame Retarded Articles



1.3 The industry and the products

1.3.1 Production and use of bromine

Bromine is widely distributed in the Earth's crust, but in small quantities. The oceans are by far the largest potential source of bromine. The concentration of bromine in sea water is quite low (only 65 parts per million), so that large amounts of water are required for processing to obtain bromine. Purified commercial grade bromine contains over 99.7 per cent elemental bromine, less than 0.1 per cent chorine, and no iodine. Technical grade is 99.5 per cent pure elemental bromine (Lyday 1992).

The United States and Israel account for over 70 per cent of worldwide production of bromine (**Table 1.1**). Bromine plants in the United States are located in Arkansas, where brines contain 5000 ppm bromine. In Israel, the Dead Sea contains 14,000 ppm bromine.

Table 1.1 World Production of Bromine
(thousands of tonnes)

Production (1990)		**Main production sources**
United States	177	well brines
Israel	135	bittern of potash
ex-USSR	60	well brines
United Kingdom	28	sea water
France	18	sea water and bittern
Japan	15	sea water
other countries*	5	
Total	**438**	

** including Germany, Italy, Spain, China, India*

In 1990, world production of bromine was estimated at 438,000 tonnes, valued at approximately US$ 0.5 billion. In that year, OECD countries accounted for 55 per cent of world production. Most of the remainder was produced in Israel (31 per cent) and in the ex-USSR (13 per cent).

In addition to the US, other OECD countries with bromine production capacity include, in order of importance, the UK, France, Japan, Germany, Italy and Spain. Israel has recently increased its bromine raw material production at Sodom, in the Dead Sea, to reach a bromine capacity of 180,000 tonnes per year. The ex-USSR bromine plants located in Turkmenistan, Azerbaijan, Crimea and Ukraine have a total capacity of more than 60,000 tonnes, limited by brine availability. China and India are other non-OECD bromine producing countries with, respectively, 12,000 and 2000 tonnes of production capacity.

In the United States, the average price of bromine is $US 980 a metric tonne (1990). The material costs of producing bromine include the cost of chlorine and brine, which account for 30 per cent and 20 per cent respectively of the total cost. Manufacturing costs are energy-related (around 14 per cent of the total cost). An average of 20 persons are employed for each million dollars of sales (Bromine Report 1990).

The demand for bromine based products has changed considerably in the last 20 years. Whereas in the past agrochemicals, gasoline additives and drilling fluids made up the most significant portions of the market, today flame retardants are the most significant, capturing 20 per cent of the entire market.

The increased demand for flame retardants and other products has offset, to some extent, the steadily decreasing use of ethylene dibromide (EDB) in gasoline, traditionally the major bromine chemical use, due to new restrictions on lead content in gasoline. Uncertainty regarding another regulatory development is also affecting demand: the US EPA has proposed a ban on methyl bromide that could affect over 60,000 tonnes of worldwide use of this soil fumigant (UNEP, Montreal 1992).

According to the 1992 Copenhagen Amendment to the Montreal Protocol on the Protection of the Ozone Layer, the consumption of methyl bromide in countries which are Parties to the Protocol must not, in 1995, exceed consumption in 1991.

The current market distribution of bromine-based chemicals is shown in **Table 1.2**.

1.3.2 Structure of the brominated flame retardant industry

During the last ten years, the brominated flame retardant industry has experienced major structural changes. Currently, around ten companies make up this industrial sector.

The brominated flame retardant industry produces some 50 different chemicals (aromatics, aliphatics and alicyclics), of which approximately 30 are in major commercial use (**Table 1.3**).

Of these 30 substances, tetrabromobisphenol A (TBBPA) and decabromodiphenyl oxide (DeBDPO) are the most significant. Other widely used products include octabromodiphenyl oxide and pentabromodiphenyl oxide (from the polybrominated diphenyl oxide family which includes deca-), and tetrabromobisphenol A derivatives. While the production and use of polybrominated biphenyls (PBBs) has all but ceased in some countries due to health and environmental concerns, decabromobiphenyl continues to be produced (< 2000 tonnes per year) in France. Other commercial brominated flame retardant groups of products are based on: phthalic anhydride, cycloaliphatic hydrocarbons, aliphatic alcohols, ethylene, phenol, and benzene and/or styrene.

The amount of chemicals applied as flame retardants for the polymer and textile markets is over half a million tonnes. The total demand for brominated flame retardant chemicals, which cost from US$ 3500 to over US$ 6000 a metric tonne, is estimated at

150,000 tonnes per year. Tetrabromobisphenol A and its derivatives are responsible for 33 per cent of the total, and brominated diphenyl oxides for 27 per cent. Of all the chemicals, decabromodiphenyl oxide is the most economical in relation to bromine content and effectiveness, particularly in styrenic polymers.

The bulk of worldwide demand for brominated flame retardants comes from three regions: North America (40 per cent), the Far East (30 per cent) and Europe (25 per cent). The type of consumption varies greatly from country to country. Some countries (e.g. Belgium, Canada, Germany, Italy, Spain, Switzerland and the Scandinavian countries) may only import such chemicals and incorporate them in products used domestically. Other countries (e.g. the Netherlands, the UK, the US, and Israel) may produce the chemicals domestically and compound them into polymers, or export them for compounding elsewhere. National fire safety standards appear to be responsible for some of the variation in consumption patterns.

Overall, the annual growth rate in the demand for FR chemicals is expected to be far greater than that for polymers and textiles. This is based on forecasts of more national regulations mandating flame retarded end products, and greater harmonization of FR test procedures (particularly in the EU). In addition, the current geographic distribution of worldwide production is likely to undergo major changes as companies move the production of semi-finished or finished products to countries that are only limited consumers of such products.

1.3.3 Incorporation of bromine compounds into polymers (compounding/mixing)

Brominated flame retardants can be incorporated into polymers in different amounts, or in different loadings. Loading depends on:

- the flame retardancy level required by regulations for the end product;
- the effectiveness of the bromine and flame retardant synergist with the polymer;
- the qualities desired for the end product, e.g. colour, density, stability; and
- the uses to which the flame retarded polymer will be put.

The incorporation of brominated compounds into polymers is generally accompanied by the addition of a synergist to increase the flame retardant efficiency. This also decreases the amount of flame retardant needed in the final product. The most common synergist, antimony trioxide, is used at a ratio of one part Sb_2O_3 to two to three parts bromine chemicals (Borms 1993). Phosphorus and organic peroxide are also used as synergists.

Examples of brominated flame retardant/synergist loading (by per cent) in polymers are shown in **Table 1.4**.

Flame retardant formulations of polymers contain other additives, such as impact modifiers, stabilizers, UV absorbers, etc., to improve those of the polymers' properties affected by the introduction of flame retardants.

Table 1.2 Uses of Bromine Based Chemicals

Bromine demand (% of total)	Main brominated chemicals concerned
20% – Flame retardants	
aromatic	tetrabromobisphenol A (TBBPA), polybrominated diphenyl oxides (PBDPOs)
aliphatics	hexabromocyclododecane (HBCD), vinyl bromide (VBr)
inorganics	bromine (Br_2), ammonium bromide (NH_4Br)
15% – Agrochemicals and sanitary	
fumigants	methyl bromide, ethylene dibromide, halacrinate
Cl insecticides	bromo-DDT, bromocyclen (C56 Br), bromodichloroimidazoles
P insecticides	bromophos, naled, bromophos ethyl, profenofos
herbicides	bromacil, metobromuron, bromoxynil, bromofenoxim
rodenticides and acaricides	brodifacoum, bromopropylate
biocides	bromonitropropane diol (bronopol), brominated benzonitriles
disinfectants	quaternary ammonium polybromo compounds
14% – Gasoline additives	ethylene dibromide (EDB)
10% – Drilling fluids	calcium bromide, sodium bromide, zinc bromide
8% – Dyes	bromoanthraquinones, bromodinitroaniline, bromobenzanthrones
6% – Water chemicals	bromo chloride, bromohydantoins, bromocyanobutanes
4% – Photographic	potassium bromide, ammonium bromide, sodium bromide
3% – Pharmaceuticals	
intermediates	bromoacetic acid, bromoform, tribromophenol
products	neostigmine, bromocriptine, bromovinyldeoxyuridine (BVDU)
20% – Other uses	
electrolytes and electronic	zinc bromide, quaternary ammonium bromides, bromosilanes
fire extinguishers	chlorodifluorobromomethane, trifluorobromomethane
synthetic rubbers	bromobutyl rubber
intermediates and catalyst	tetrabromoethane, cobalt bromide, octyl bromide
minerals separation	bromoform, tetrabromoethane
toiletries	bromosuccinimides, tribromosalicylanilide (TBS)2
radio detection and control	radioactive bromine (bromine isotopes 74 to 90)
air conditioning	lithium bromide

Table 1.3 Brominated Flame Retardants

Brominated FR chemicals (most widely used)	**Bromine content (%)**	**Melting point (°C)**	**Wt. loss (%) at temp. (°C) -TGA-**	**Main applications** **R = FR reactive** **A = FR additive**
Tetrabromobisphenol A (TBBPA)	59	180	95%-500°C	R. epoxy, PC, UPE
TBBPA carbonate oligomer	55	230	25%-475°C	A. ABS, eng. thermoplast.
TBBPA-bis(2,3-dibromopropyl ether)	68	95	50%-337°C	A. polyolefin
TBBPA-bis(allyl ether)	51	120	50%-332°C	R. PS foams
TBBPA epoxy oligomer	52	NA	NA	A. styrenics, PBT
TBBPA-bis(2-hydroxyethyl ether)	51	115	95%-501°C	A. eng.plastics, coatings
Decabromodiphenyl oxide (DeBDPO)	83	310	95%-447°C	A. general purpose
Octabromodiphenyl oxide (OBDPO)	79	110	95%-296°C	A. ABS, PC, thermosets
Pentabromodiphenyl oxide (PeBDPO)	71	liquid	95%-340°C	A. textile, PUR
Decabromobiphenyl (DeBB)	84	370	90%-450°C	A. general purpose
Tetrabromophthalic anhydride (TBPA)	69	275	95%-325°C	R. UPE, coating
TBPA diester/ether diol	45	liquid	90%-400°C	R. rigid PUR foams
Ethylene bis(tetrabromophthalimide)	67	450	90%-750°C	A. similar to DeBDPO
Tetrabromophthalimide	69	NA	NA	A. eng. thermoplast.
Disodium salt of tetrabromophthalate	15	solution	50%-700°C	A. textile, coatings
Hexabromocyclododecane (HBCD)	75	190	50%-280°C	A. (w/o Sb_2O_3) in PS foams
Dibromoethyldibromocyclohexane	75	75	50%-292°C	A. PS, PUR
Ethylene bis(dibromonorbornanedicarboximide)	48	300	50%-365°C	A. nylons and polydefins
Dibromoneopentyl glycol (DBNPG)	61	95	90%-240°C	R. UPE, PUR
Tribromoneopentyl alcohol (TBNPA)	72	62	50%-240°C	R. PUR
Vinyl bromide (VBr)	75	liquid	NA	R. modacrylic fibers
Ammonium bromide	82	NA	NA	A. textiles
2,4,6-Tribromophenol (TBP)	73	95	95%-330°C	R. phenolics, epoxy
Bis(tribromophenoxy)ethane (HBPE)	70	225	90%-450°C	A. ABS, PC, thermosets
Tribromophenyl allyl ether (TBP-AE)	65	75	50%-245°C	R. PS foams
Poly(dibromophenylene oxide) (PDBPO)	62	230	50%-550°C	A. similar DeBDPO
Pentabromoethylbenzene (5BEB)	82	280	NA	A. UPE, SBR, textile
Tetradecabromodiphenoxybenzene (TDBDPB)	82	370	90%-485°C	A. similar DeBDPO
Poly(pentabromobenzyl acrylate) (PBB-PA)	70	200	NA	A. polymeric, PBT
Polymer of dibromostyrene (PDBS)	59	NA	5%-355	A. PA, PBT, styrenics
Brominated polystyrene (BrPS)	60	550	50%-420°C	A. polymeric, PBT, PS

Table 1.4 Examples of Brominated Flame Retardant Loading in Polymers (V-0 Classified)

Base polymer	**Brominated flame retardant**	**BFR**	**Sb_2O_3**
		Loading %	
Polypropylene	Decabromodiphenyl oxide	23	8
"	Ethylene bis(tetrabromophtalimide)	27	8
Polystyrene	Decabromodiphenyl oxide	12	4
"	Tetrabromobisphenol A	15	4
ABS	Octobromodiphenyl oxide	20	6
"	Tetrabromobisphenol A	20	4
Polyterephthalate	Decabromodiphenyl oxide	12	4
"	Pentabromobenzyl acrylate	17	4
"	TBBPA carbonate oligomer	18	4

(R. Borms, February 1993) **Sb_2O_3 = antimony trioxide**

A number of other factors are important in the application of brominated flame retardants, such as the form in which they are commercially available and their melting range. Colourless compounds are preferred, and the possession of a well defined colour is usually a disadvantage. Compounds that are liquid at normal temperatures have certain advantages, but free-flowing, fine powders are acceptable for most purposes.

A high bromine content and high density are other obvious desirable qualities. In the case of additive flame retardants, low volatility is an important requirement, so that there is no significant loss from the polymer either under conditions of normal use or, more particularly, during the different stages of polymer processing. Other specific properties required by brominated flame retardants are dependent on the polymeric material into which they are to be incorporated.

The polymerisation procedures and processing temperatures involved, and the uses to which the flame retarded polymer is to be put, are also important factors. In this connection, any brominated (or other) flame retardants should be sufficiently stable not to break down to any appreciable extent at processing temperatures, but should nevertheless have a decomposition temperature close to that of the associated polymer. The disadvantage associated with bromine compounds is that many of them decrease the stability of certain polymers to ultraviolet light, and also affect adversely some physical and mechanical polymer properties (Cullis 1987).

According to the open literature, decabromodiphenyl oxide is incorporated in the flame retardant compounds for nearly all polymers. For an overview of the use of brominated flame retardants in polymers, see **Table 1.5**.

Table 1.5 Brominated Flame Retardants Used in Polymers

	ABS	Epoxy	EX. PS	EVA	HDPE	HIPS	LDPE	PA	PBT	PC	PET	PF	PP	PUR	PVC	UPE	Elastomer	Textile	Coating
TBBPA		X								X		X				X			
TBBPA Carbon	X								X	X	X	X							
TBBPA Epoxy	X					X			X	X		X							
TBBPA DP.E.					X		X						X						
TBBPA A.E.			X																
TBBPA H.E.									X	X									X
DeBDPO	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
OBDPO	X									X		X				X			X
PeBDPO														X				X	
DeBB	X			X		X		X	X	X	X	X	X		X	X	X		X
TBPA		X														X			X
TBPA diol														X			X		
EBTBPA	X			X	X	X	X	X	X	X			X				X		
EBTBPA imide	X							X	X	X	X								
EBTBPA Na																		X	X
HBCD	X		X		X	X	X											X	
DBEDBC			X			X								X					
DBNPG														X		X	X		
TBNPA														X					
V Br																		X	
NH_4Br																		X	
TBP		X										X							
HBPE	X	X						X	X	X	X					X		X	
TBP-AE			X																
PDBPO	X			X	X	X	X	X	X	X	X	X	X		X				
5 BDB																X		X	
TDBDPB	X			X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
PBB-PA						X		X	X	X			X						
PDBS	X					X		X									X		
BrPS	X			X	X	X	X	X	X	X			X				X		

The selection guide of brominated chemical producers suggests that ethylene bistetrabromophthalimide (EBTBP), tetradecabromodiphenoxy benzene (TDBDPB) and polydibromophenylene oxide (PDBPO) can also be incorporated as additives to a very large range of flame retardant polymers.

Inherent flame retardancy is a characteristic of the halogen or sulphur based polymers, such as polyvinyl chloride (rigid PVC), fluoropolymers, polyphenylene sulphide (PPS), etc. This is also the case for other polymers with high thermally stable chemical structures, such as polyphenylene oxide (PPO), polyamide-imides (PAI), polyphenylene, isophthalimides ("Nomex"), etc.

1.3.4 Processing of compounds into final products

The flame retardant compounds are generally transformed by injection, extrusion or cutting techniques into semi-finished parts or products (e.g. films, boxes, sheets, pipes, profiles). These parts/products are then used in the assembly of final products such as television sets, computers, telephones, building elements, etc.

1.4 World markets and demand

Worldwide, there are over 100 flame retardant chemicals on the market today with total demand equal to 600,000 tonnes per year. Brominated flame retardants represent 25 per cent of this total. Approximately 30 bromine based chemicals are in major commercial use see Section 1.3.2).

When considering the market demand for brominated flame retardants, it is necessary to consider the different polymeric applications (see, for example, **Appendix 2**, "Brominated Flame Retardants: Formulation, Application and Market Demand").

Appendix 3 contains a listing of the physical-chemical properties of the main brominated chemicals.

The worldwide demand for brominated flame retardant chemicals is estimated at 150,000 tonnes per year, valued at over US$ 500 million. OECD countries are the largest consumers.

The current demand for brominated flame retardant chemicals for use in polymer compounding is expected to change in the near future, with the anticipated entry of new products into the market. Dibromostyrene and its derivatives, brominated polystyrenes, tetrabromophthalic derivatives and decabromodiphenyl ethane are currently in commercial development and/or application development phases.

International prices for brominated flame retardant chemicals vary from US$ 3500 to over US$ 6000 per metric tonne. Of all these chemicals, decabromodiphenyl oxide is the most economical in relation to bromine content, effectiveness, and lack of adverse effects on the physical properties of the matrix.

Patterns of brominated flame retardant consumption vary among countries. Estimated consumption of brominated flame retardants in Japan (37,000 tonnes in 1992) is shown in **Table 1.6** by polymer (Sugie 1993).

The great variation in demand that exists today from country to country can partly be explained by characteristics of their national industries. For instance, while numerous polymer producers may exist in one country, polymer compounding may take place in another country.

National flame retardant regulations can also have an impact on the quantity and type of demand. Brominated diphenyl oxide use in textiles usually accounts for only 10 per cent of total national consumption of this type of flame retardant.

It is important to examine the demand for and consumption of flame retardants as pure chemicals, as part of polymer compounds, within plastics and textiles, and finally as end product components. This analysis has been made in Sweden (S. Svensson) and is reflected in **Table 1.7**. BFRs are not produced domestically in Sweden.

In the UK, over 50 per cent of the national diphenyl oxide consumption goes to textile applications. The Furniture and Furnishings Fire Safety Regulations (1988) appear to be responsible for this consumption pattern (UK Department of the Environment 1992).

Table 1.6 Estimated Consumption of Plastics and Flame Retardants in Japan

	FR Consumption in Japan	ABS	PS	PPO	EPS	PE	PP	PVC	PC	PBT	PET	PA	EPOXY	PHENOL	UPE	PU
Plastics consumption in Japan	(1000 T/Y)	50	55	20	8		10	70	20	35	10	15	30			
Bromine compounds																
Decabromodiphenyl oxide	8	x	x			x	x	x	x	x	x	x	x	x	x	x
Octabromodiphenyl oxide	1	x	x			x								x		
Tetrabromobisphenol A	15	x	x						x				x	x	x	
TBBPA PC oligomer	3	x							x	x	x			x		
TBBPA epoxy oligomer	4	x	x							x				x		
Hexabromocyclododecane	1		x		x					x	x					x
BIS (tribromophenoxy) ethane	1	x									x				x	
Ethylenebis (BR4-phthalimide)	1		x			x	x			x		x				
Brominated polystyrene	1					x	x			x		x				
Others	2	x	x			x	x			x		x	x		x	x
Examples of final products: 1: business machine housing; 2: electrical appliance housing; 3: electronics parts; 4: wire and cables; 5: circuit boards; 6: building materials; 7: cushioning materials		1, 2	1, 2	1, 2	6	4	2	4, 6	1, 2	2, 3	3	3	3, 5	5	5, 6	7

Table 1.7 Demand for BFRs in Sweden (1988) (tonnes)

Imports	BFRs
BFRs as pure chemicals	700
BFRs in plastic compounds	100
BFRs in technical laminates	50-100
BFRs in textile chemicals	50
BFRs in articles such as printed circuits, plastic covers, computers, TV sets, etc.	500-1000
Total imports	1400-2000
Exports	around 500
Apparent annual consumption	**900-1500**

CHAPTER 2

ENVIRONMENTAL FATE, TRANSPORT AND OCCURRENCE

2.1 Decabromodiphenyl oxide (DeBDPO)[1]

Photodegradation of DeBDPO occurs in organic solvents under ultraviolet radiation (UVR) or sunlight; lower brominated diphenyl oxides and brominated dibenzofurans are formed. Photodegradation also occurs, to a lesser extent, in water with sunlight; however, lower brominated diphenyl oxides and brominated di-benzofurans have not been found.

Levels of DeBDPO extracted from polymers are close to, or below, the limit of detection, depending on the polymer type and extraction solvent.

Because of its extremely low water solubility and vapour pressure, DeBDPO is likely to be transported primarily by adsorption to particulate matter. It is persistent and likely to accumulate in sediment and soil.

No data are available on its bioavailability from sediment and soil. A study on rainbow trout did not show any bioaccumulation in flesh, skin, or viscera, over 48 h. DeBDPO is unlikely to bioaccumulate because of its high relative molecular mass.

Products containing commercial DeBDPO will eventually be disposed of by landfill or incineration. DeBDPO may eventually leach from landfills. Polybrominated dibenzofurans (PBDF) and mixed halogen-dibenzofurans and -dibenzodioxins may result from landfill fires and inefficient incineration. Products containing commercial DeBDPO may contribute to these emissions.

Pyrolysis of both commercial DeBDPO itself and polymers (HIPS, PBT, industrial polypropylene) containing DeBDPO, in the presence of oxygen, produced PBDF, polybrominated dibenzodioxins (PBDD) being found to a lesser extent. The maximum formation of PBDF occurs at 400-500 °C, but it can occur at temperatures up to 800 °C, and Sb_2O_3 plays a catalytic role in the formation of PBDF and PBDD.

The formation, and amounts found, of PBDF and PBDD depend on temperature, oxygen content, and length of pyrolysis. In the absence of oxygen, mainly polybromobenzenes and polybromonaphthalenes are formed.

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[1] Text taken directly from the "Summary, Evaluation, Conclusions and Recommendations" in the International Programme on Chemical Safety (IPCS) Task Group-approved draft of Environmental Health Criteria Document No. 162 on polybrominated diphenyl ethers. EHC 162 will be published in 1994.

2.2 Octabromodiphenyl oxide (OBDPO)[1]

Components of commercial OBDPO have been found in aquatic sediment and human fat. Some lower brominated components (HxBDPO and PeBDPO) of commercial OBDPO have been found in biota. OBDPO has not been detected, but HpBDPO and NBDPO have generally not been looked for. Commercial OBDPO components are likely to be persistent but, as bromination levels rise beyond HxBDPO, they are increasingly unlikely to bioaccumulate. A bioaccumulation factor of less than 2 has been found in carp for a commercial OBDPO product.

Pyrolysis of commercial OBDPO, as such, or of polymers with OBDPO as a flame retardant (with, or without, Sb_2O_3) at 600 °C has been shown to produce PBDF and, in much lower concentrations, PBDD. Processing of ABS with OBDPO/Sb_2O_3 under different conditions, showed that under normal processing conditions, only low levels of PBDF were formed. Under abusive conditions, the concentrations were much higher. PBDD concentrations were low in both cases.

2.3 Pentabromodiphenyl oxide (PeBDPO)[1]

Components of commercial PeBDPO have been found in biota, sediment, and sewage sludge samples. Commercial PeBDPO components are likely to be persistent and bioaccumulate. A bioconcentration factor of over 10 000 has been found in carp for PeBDPO.

Pyrolysis studies with commercial PeBDPO showed that PBDF and PBDD are formed. The optimal temperature for the formation of the PBDF and PBDD was between 700-800 °C. When PeBDPO was pyrolysed in the absence of oxygen, polybromobenzenes, polybromophenols, and PBDF were formed.

2.4 Tetrabromodiphenyl oxide (TeBDPO)[1]

Components of commercial TeBDPO have been found in biota, sediment, and sewage sludge samples. Commercial TeBDPO components (containing approximately equal quantities of PeBDPO) are likely to be persistent and to bioaccumulate.

Pyrolysis studies with commercial TeBDPO showed that PBDF and PBDD are formed at 800 °C. Higher PBDF and PBDD were not found.

2.5 Polybrominated biphenyls (PBBs)[2]

Long-range transport of PBBs in the atmosphere has not been proven, but the presence of these compounds in Arctic seal samples indicates a wide geographical distribution.

The principal known routes of PBBs into the aquatic environment are from industrial waste discharge and leachate from industrial dumping sites into receiving waters and from erosion of polluted soils. PBBs are almost insoluble in water and are primarily found in sediments of polluted lakes and rivers.

Pollution of soils can originate from point sources, such as PBB plant areas and waste dumps. Once introduced into the soil, PBBs do not appear to be translocated readily. PBBs have been found to be 200 times more soluble in a landfill leachate than in distilled water; this may result in a wider distribution in the environment. The hydrophobic properties of PBBs make them easily adsorbed from aqueous solutions onto soils. Preferential adsorption of PBB congeners was noted, depending on the characteristics of the soil (e.g., organic content) and the degree and position of bromine substitution.

PBBs are stable and persistent, lipophilic, and only slightly soluble in water; some of the congeners are poorly metabolized and therefore accumulate in lipid compartments of biota. Once they have been released into the environment, they can reach the food chain, where they are concentrated.

PBBs have been detected in fish from several regions. Ingestion of fish is a source of PBB transfer to mammals and birds.

Degradation of PBBs by purely abiotic chemical reactions (excluding photochemical reactions) is considered unlikely. The persistence of PBBs under field conditions has been reported. Soil samples from a former PBB manufacturing site, analysed several years after the Michigan incident, still contained PBBs though the PBB congener composition was different, indicating a partial degradation of the PBB residues in the soil sample.

Under laboratory conditions, PBBs are easily degraded by UVR. Photodegradation of the commercial FireMaster® mixture led to diminished concentrations of the more highly substituted PBB congeners. The rates and extent of photolytic reactions of PBBs in the environment have not been determined in detail, though field observations indicate a high persistence of the original PBBs, or a partial degradation to the less brominated congeners.

In laboratory investigations, mixtures of PBBs appear to be fairly resistant to microbial degradation.

Neither uptake nor degradation of PBBs by plants has been recorded. In contrast, PBBs are easily absorbed by animals and though they have been found to be very persistent in animals, small amounts of PBB metabolites have been detected. The main metabolic

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[2] Text taken directly from the "Summary and Evaluation" in the International Programme on Chemical Safety (IPCS) Environmental Health Criteria document No. 152 on polybrominated biphenyls. EHC 152 was published in 1994.

products were hydroxy-derivatives, and, in some cases, there was evidence of partially debrominated PBBs. No investigation of sulphur-containing metabolites analogous to those of PCBs have been reported.

The bioaccumulation of PBBs in fish has been investigated. Bioaccumulation of PBBs in terrestrial animals has been investigated in avian and mammalian species. Data were obtained through field observations, evaluation of the Michigan disaster and through controlled feeding studies. Generally, the accumulation of PBBs in body fat depended on the dosage and duration of exposure.

Bioaccumulation of individual PBB congeners has been found to increase with degree of bromination up to at least tetrabromobiphenyls. Higher brominated congeners can be expected to accumulate to an even greater extent. However, no information is available for decabromobiphenyl; it is possible that it is poorly absorbed.

Brominated dibenzofurans or partially debrominated PBBs have been reported as products of the thermal decomposition of PBBs. Their formation depends on several variables (e.g., temperature, oxygen).

2.6 Tetrabromobisphenol A (TBBPA)[3]

Based on its partition coefficient and low water solubility, TBBPA in the environment is expected to sorb to a large degree onto sediment and organic matter in soil.

Accumulation studies with aquatic invertebrates and vertebrates indicate bioconcentration factors ranging from 20 up to 3200. The half-life in fish is less than 1 day, and in oysters less than 5 days. During depuration most of the accumulated TBBPA (and metabolites) will be eliminated within 3-7 days.

Biodegradability studies showed that under aerobic and anaerobic conditions in soil and in river sediment and water, TBBPA is partly degraded. Approximately 40 to up to 90% of TBBPA remained in the soils, depending on soil type, temperature, humidity and composition of the soil after 56-64 days. Under sewage treatment conditions, no biodegradation was detected as measured as BOD in 2 weeks.

Laboratory pyrolosis studies showed that polymers with TBBPA with and without the presence of Sb_2O_3, at different temperatures, presence of oxygen, etc., may form polybrominated dibenzofurans (PBDF) and, to a lesser extent, polybrominated dibenzodioxins (PBDD). The maximum temperature for the formation of PBDF and PBDD is approximately 600 °C. Mainly lower brominated PBDF and PBDD are formed. When polymers formulated with TBBPA exposed to simulating thermal processing conditions were analysed, 2,3,7,8-PBDD/PBDF were not detected. Only mono- or dibromo-substituted PBDF were detected at

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[3] Text taken directly from the "Summary and Evaluation" in the International Programme on Chemical Safety (IPCS) Task Group-approved draft of the Environmental Health Criteria document on tetrabromobisphenol A. This EHC document will be published in 1995.

up to 100 µg/kg levels in the resin. Investigation of the workplace atmosphere yielded no 2,3,7,8-substituted PBDD/PBDF (detection limit = 0.1 ng/m^3).

In recycled TBBPA-containing polymers, less than 5 µg total PBDF/PBDD/kg were detected. 2,3,7,8-substituted congeners were only found at levels of less than 0.2 µg/kg.

In a warehouse fire, in which a great quantity of polybutylene terephthalate (PBT) containing TBBPA was burnt, only low levels of 2,3,7,8-substituted tetra-, penta-, hexa-BDF/BDD (less than 5 µg/kg) were detected in burnt PBT and ash/slag samples.

CHAPTER 3

EXPOSURE

3.1 Linkages to exposure

A number of studies have explored the human and environmental exposures to brominated flame retardants. In general, these studies have focused either on direct exposure to the flame retardants themselves or to their degradation products (the most important being polybrominated dibenzofurans and dibenzodioxins), which are formed at high temperatures in the presence of oxygen or under different chemical conditions. The pathways of human exposure can be summarized as shown in **Table 3.1**.

Table 3.1 Exposure to BFRs and their Degradation Products

Worker exposure

- Production
- Compounding/transformation
- End product production

Consumer exposure

- End product use
- Fires

General population exposure

- Ambient air
- Water
- Soil
- Food intake
- Ecosystems

3.2 Environmental levels and human exposure

3.2.1 Decabromodiphenyl oxide (DeBDPO)[4]

DeBDPO has been identified in air in the vicinity of manufacturing plants at concentrations of up to 25 µg/m^3. DeBDPO was not detected in water samples collected in Japan in the period 1977-91. However, it was detected in river and estuarine sediment, collected in Japan in the same period, at concentrations of up to approximately 12 mg/kg dry weight. DeBDPO (up to 1 g/kg) was also found in the USA in river sediment close to one manufacturing plant. DeBDPO was not detected in fish samples collected in Japan, but, in one mussel sample, a level just above the level of detection was found. DeBDPO was not detected in human adipose tissue samples collected in Japan, but, in the USA, DeBDPO was found in 3 out of 5 samples of human adipose tissue.

Human exposure to DeBDPO can occur in the course of manufacture and formulation into polymers. Exposure of the general population to DeBDPO is insignificant.

Determination of occupational exposure to the breakdown products of DeBDPO during manufacture, formulation, or use, showed that air samples close to the extruder head contained high concentrations of PBDF. Lower levels were found in the air of the workroom. PBDF was also found in wipe samples. The application of good engineering techniques has been shown to reduce occupational exposure to PBDF.

Exposure of the general population to PBDF impurities in flame retarded polymers is unlikely to be of significance.

3.2.2 Octabromodiphenyl oxide (OBDPO)[4]

OBDPO and the lower brominated components of commercial OBDPO were not detected in water samples collected in Japan in 1987 and 1988. Sediment samples were also analysed and, in approximately 2-6% of the samples, OBDPO was detected in concentrations ranging from 8 to 22 µg/kg dry weight. Lower brominated components were also found in the sediment.

OBDPO was not detected in fish samples collected in Japan in 1987 and 1988.

In the USA, samples of human fat were investigated for the presence of PBDF and PBDD in 1987. The samples were derived from 865 specimens combined to form 48 composite analogues. The composite design was based on 9 census divisions and 3 age groups. In these samples, PBDPO were also identified and preliminary evidence showed the presence of OBDPO at a frequency of 60% and an estimated concentration of up to 8000 ng/kg.

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[4] Text taken directly from the "Summary and Evaluation, Conclusions and Recommendations" in the International Programme on Chemical Safety (IPCS) Task Group-approved draft Environmental Health Criteria document No. 162 on polybrominated diphenyl ethers. EHC 162 will be published in 1994.

3.2.3 Pentabromodiphenyl oxide (PeBDPO)[4]

Sediment samples taken from rivers and estuaries in Japan showed levels ranging from no PeBDPO (< 2 µg/kg) up to 28 µg/ kg dry weight. In Sweden, the concentrations in sediment samples of certain rivers were up to 1200 µg 2,2′,4,4,′5-PeBDPO/kg. Sewage sludge, analysed in Sweden also contained this PeBDPO.

In mussel and fish collected from different seashores in Japan in the period 1981-85, concentrations of 0.4 and 2.8 µg PeBDPO/kg wet weight were found in 2 out of 5 mussel samples. No PeBDPO was detected in fish (limit of determination < 0.2 µg/kg). Concentrations of 1.9-22 µg/kg, on a fresh weight basis, were reported in liver samples from cod from the North Sea. In Sweden, concentrations of between 7.2 and 64 µg 2,2′,4,4′,5-PeBDPO/kg fat were found in freshwater whitefish and herring collected at different places.

Pooled blubber of ringed seal and of grey seal collected in Sweden in 1979-85 contained average concentrations of 1.7 µg and 40 µg 2,2′,4′4′,5-PeBDPO/kg fat, respectively.

Pooled samples of muscle of rabbits, moose, and suet samples of reindeer collected in 1985-86 in Sweden contained < 0.3 µg, 0.64 µg, and 0.26 µg 2,2′,4,4′,5-PeBDPO/kg fat, respectively.

Muscle samples of osprey, collected in Sweden in 1982-86, contained an average concentration of 140 µg 2,2′,4,4′,5-PeBDPO/kg fat.

The levels of 2 PeBDPO isomers in guillemot eggs from the Baltic have increased by one order of magnitude during the last decades. The levels of these isomers in pike from a lake in Southern Sweden also showed an increase (by a factor of about 4). Baltic sediments representing different sampling years also indicate a considerable increase during the last decade.

There is minimal information on human exposure, but a rough estimate of exposure of the Swedish population through fish consumption would suggest an intake of 0.1 µg PeBDPO/person per day.

3.2.4 Tetrabromodiphenyl oxide (TeBDPO)[4]

TeBDPO was found, in Japan, in river sediment at concentrations of 12-31 µg/kg dry weight and, in Sweden, at concentrations of up to 840 µg/kg ign. loss, respectively. TeBDPO was also found in sewage sludge in Sweden, at a concentration of 15 µg/kg.

Mussels and fish, collected at different places in Japan, contained TeBDPO in concentrations ranging from < 0.1 to 14.6 µg 2,2′,4,4′-TeBDPO/kg wet weight. In Sweden, different types of fish were collected from rivers and analysed for 2,2′,4,4′-TeBDPO. The mean concentrations ranged from ND (< 0.1mg/kg) to 110 mg/kg fat. The analysis indicated that there was at least one local source of pollution in a certain river. Whitefish, arctic char, and herring, collected at different places in Sweden in 1986-87, contained concentrations of 15, 400, and 59-450 µg 2,2′,4,4′-TeBDPO/kg fat, respectively. Fish collected from rivers in Germany contained up to 1 mg TeBDPO/kg fat.

In herring and in the liver of cod, collected in the southern, central, and northern North Sea, in the period 1983-89, a decreasing trend in the concentrations of TeBDPO was found from the southern region to the northern region. In the herring, concentrations of 8.4-100 µg 2,2′,4,4′-TeBDPO/kg, on a fat basis, were found.

The muscle tissue of birds nesting and wintering in the Baltic Sea, the North Sea, and Spitzbergen, contained from 80 to 370 µg 2,2′,4,4′-TeBDPO/kg, on a fat basis. Osprey collected in Sweden in the period 1982-86, contained average concentrations of 1800 µg/kg fat.

Increasing trends in the concentrations of 2,2′,4,4′-TeBDPO have been indicated for Baltic sediments, freshwater fish, and sea bird eggs from Sweden.

The blubber of seals collected in the Baltic Sea and Spitzbergen showed concentrations of 10-730 µg 2,2′,4,4′-TeBDPO/kg, on a fat basis. The chromatographic pattern of the PBDPO was similar to that of Bromkal 70-5. Pooled samples of the blubber of ringed seals and grey seals, collected in Sweden in 1979-85 showed concentrations of 47 µg and 650 µg 2,2′,4,4′-TeBDPO/kg fat, respectively.

Pooled muscle samples of terrestrial mammals, e.g., rabbits, moose and reindeer, collected in 1985-86 in Sweden, showed average concentrations of < 2, 0.82, and 0.18 µg 2,2′,4,4′-TeBDPO/kg fat, respectively.

Levels of 2.5-4.5 µg PBDPO/kg fat, measured as Bromkal 70DE, were found in 4 samples of cow's milk in Germany. PBDPO, as Bromkal 70DE, was found in the milk of 25 women in Germany at concentrations ranging from 0.62 to 11.1 µg/kg fat.

A rough estimate of exposure via fish consumption among the Swedish population would suggest an intake of 0.3 µg TeBDPO/ person per day.

3.2.5 Polybrominated biphenyls (PBBs)[5]

Only one report is available on PBB levels in air. In this study, concentrations in the vicinity of three PBB-manufacturing or PBB-processing plants in the USA were measured.

Levels in surface waters in the same vicinity and in the Gratiot County landfill (Michigan, USA), which received over a hundred thousand kg of waste containing 60-70 per cent PBBs between 1971 and 1973, were monitored.

Groundwater monitoring data from the Gratiot County landfill have shown trace levels of PBBs even outside the landfill area, however, PBBs were not detected in drinking water wells in the area.

Data on soil pollution by PBBs are available for areas of manufacture, use, or disposal of PBBs, and for soils from fields of the PBB-contaminated Michigan farms.

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[5] Text taken directly from the "Summary and Evaluation" in the International Programme on Chemical Safety (IPCS) Environmental Health Criteria document No. 152 on polybrominated biphenyls. EHC 152 was published in 1994.

In the Michigan disaster, FireMaster® was inadvertently added to animal feed. It was almost a year later that the mixing error was discovered and the analyses indicated that PBBs were responsible. During this time (summer 1973 - May 1974), contaminated animals and their produce entered the human food supply and the environment of the state of Michigan. Hundreds of farms were affected, thousands of animals had to be slaughtered and buried, as well as thousands of tons of farm produce.

Most data available on the PBB-contamination of wildlife refer to fish and birds in the USA and Europe, primarily waterfowl, in the vicinity of industrial sites, and marine mammals.

Recent reports on the PBB-contamination of fish, terrestrial and marine mammals, and birds in the USA and Europe indicate a wide distribution of these compounds. The congener pattern found in fish samples is quite different from that found in commercial products. Many of the major peaks could well be the result of the photochemical debromination of decabromobiphenyl (BB 209), but this has not been confirmed.

Occupational exposure was found in employees in chemical plants in the USA, and in farm workers, as a result of the Michigan PBB incident. Median serum and adipose tissue PBB levels were higher among chemical workers. Information from other countries/companies on occupational exposure associated with manufacturing, formulation, and commercial uses is not available.

For most human populations, direct data on exposure to PBBs from various sources have not been documented. Widespread human exposure resulting from direct contact with contaminated feed and, primarily, from the consumption of PBBs in meat, eggs, and dairy products has been reported from Michigan, USA. At least 2000 families (primarily farmers and their neighbours) received heavy exposure. Recently, PBBs have been detected in cows' milk and human milk in Germany.

The congener patterns in these samples are different from that in fish. The relative concentration of BB 153 is higher in human milk than in fish.

The routes of exposure of the general population to PBBs are not well known. Present knowledge indicates that ambient air and water do not contain high levels. Lipid-rich food, especially from contaminated waters, is probably of great importance. There is no information on levels of exposure in indoor air and dermal exposure levels from materials containing PBB flame retardants.

The PBB congener pattern found in human milk, collected in Germany, resembled that found in cows' milk from the same region, but levels in the human samples were substantially higher.

An estimate of the daily intake of PBB via food by the general population has to be based on very few data. If it is assumed that fish contains 20 µg PBB/kg lipid and 5% lipid and that a 60-kg person eats 100 g fish/day, the intake will be 0.002 µg/kg body weight per day. A PBB concentration of 0.05 µg/kg lipid in milk (4% lipid) and a milk consumption of 500 ml/day will give the same person a PBB intake of about 0.00002 µg/kg body weight per day.

An infant of 6 kg body weight consuming 800 ml human milk (3.5% lipid) per day will have an intake of 0.01 µg PBB/kg body weight per day, if the milk contains 2 µg PBB/kg lipid.

3.2.6 Tetrabromobisphenol A (TBBPA)[6]

TBBPA was detected in some sediments in Japan and Sweden and in fish (two samples near industrialized area out of 229 samples) in µg/kg levels in Japan. In mussel and sediment the dimethoxy derivative of TBBPA could be identified. In water, TBBPA was not generally detected.

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[6] Text taken directly from the "Summary and Evaluation" in the International Programme on Chemical Safety (IPCS) Task Group-approved draft Environmental Health Criteria document on tetrabromobisphenol A. This EHC document will be published in 1995.

CHAPTER 4

INTERNATIONAL AND NATIONAL POSITIONS ON RISKS FROM BROMINATED FLAME RETARDANTS

This chapter presents evaluations, from the International Programme on Chemical Safety (IPCS), of the risks from polybrominated diphenyl oxides (PBDPOs), polybrominated biphenyls (PBBs) and tetrabromobisphenol A (TBBPA).

Also presented in this chapter are statements, provided by OECD Member countries, summarizing their perception of and concern for the risks associated with the continued production and use of certain brominated flame retardants, and the risks from exposure to the degradation products (polybrominated dioxins and furans). These statements provide the rationale for any actions the country has taken or contemplates taking to address effects associated with environmental or human exposure to brominated flame retardants.

The risk assessments and risk characterizations that have led countries to take action have a national character. Countries develop positions on the need for risk reduction activities only after they have analysed the hazard and significance of certain exposures and have factored in local social, economic and political considerations. These positions are usually arrived at after considerable debate on the numerous factors involved, and thus are not consistent across Member countries.

Some Member countries did not distinguish clearly between their *national positions on current risks* (Chapter 4) and their *mechanisms for risk reduction* (Chapter 5). A few of these national statements have therefore been included in their entirety in both chapters, for ease of reference.

4.1 International position (IPCS)

The International Programme on Chemical Safety (IPCS) is a joint venture of the United Nations Environment Programme, the International Labour Organisation, and the World Health Organization. The main objective of the IPCS is to carry out and disseminate evaluations of the effects of chemicals on human health and the quality of the environment. The Environmental Health Criteria documents prepared by IPCS contain the collective views of an international group of experts and do not necessarily represent the decisions or the stated policy of the United Nations Environment Programme, the International Labour Organisation, or the World Health Organization.

The following assessments of the risks of polybrominated diphenyl oxides (PBDPOs), polybrominated biphenyls (PBBs) and tetrabromobisphenol A (TBBPA) are taken directly from the International Programme on Chemical Safety (IPCS) Task Group-approved draft Environmental Health Criteria documents on polybrominated diphenyl ethers and tetrabromobisphenol A, and from the recently published EHC 152 on polybrominated biphenyls.[7]

Decabromodiphenyl oxide (DeBDPO)

Kinetics and metabolism in laboratory animals and humans

DeBDPO is poorly absorbed from the gastrointestinal tract and is rapidly excreted following injection.

The results of metabolic studies on the rat, using ^{14}C labelled DeBDPO, indicated a half-life for the disappearance from the body of less than 24 h and that the principal route of elimination following oral ingestion was via the faeces. No appreciable ^{14}C activity (less than 1%) was found in either urine or expired air.

Rats fed 0.1 mg/kg body weight per day, for up to two years, showed no accumulation of DeBDPO in serum, kidneys, muscle, or testes, as estimated from total bromine determination. Bromine accumulation in the liver plateaued at 30 days and was cleared within 10 days following treatment. After 180 days of treatment, the bromine level in the liver of treated rats was no greater than that in control rats. Adipose tissue accumulated low levels of total bromine, which remained after 90 days of clean diet; the nature of the retained "bromine" is not known. Since DeBDPO accounted for only 77% of the commercial mixture used, "bromine" could have been derived from NBDPO or OBDPO.

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[7] EHC 162 on polybrominated diphenyl ethers will be published in 1994. The EHC document on tetrabromobisphenol A will be published in 1995. (During technical editing of drafts, corrections may be made to the figures quoted; however, these will not affect the conclusions shown.) EHC 152 on polybrominated biphenyls was published in 1994.

Effects on laboratory mammals and in vitro test systems

The acute toxicity of DeBDPO for laboratory animals is low. The substance is not an irritant to the skin or eyes of rabbits. It is not chloracnegenic on the skin of rabbits and is not a human skin sensitizer.

The combustion products of flame retarded polystyrene containing DeBDPO and Sb_2O_3 were tested for acute toxicity and comedogenicity. The rat oral LD_{50} of the soot and char was > 2000 mg/kg body weight.

In short-term toxicity studies on rats and mice, DeBDPO (purity > 97%) at dietary levels of 100 g/kg (4 weeks) or 50 g/kg (13 weeks; equivalent to 2500 mg/kg body weight for the rat) did not induce adverse effects. A one-generation reproduction study on rats showed no adverse effects with dose levels of 100 mg/kg body weight. DeBDPO did not cause any teratogenic effects in the fetuses of rats administered a dose level of 100 mg/kg body weight. With 1000 mg/kg body weight, malformations, such as delayed ossification, were seen. DeBDPO was not shown to be mutagenic in a number of tests.

In a carcinogenicity study on rats and mice, DeBDPO (purity 94-99%) was administered at dietary levels of up to 50 g/kg. An increase in the incidence of adenomas (but not carcinomas) was found in the livers of male rats receiving 25 g/kg and female rats receiving 50 g DeBDPO/kg. In male mice, increased incidences of hepatocellular adenomas and/or carcinomas (combined) were found at 25 g/kg and an increase in thyroid follicular cell adenomas/ carcinomas (combined) at both dose levels. Female mice did not show any increase in tumour incidence. There was equivocal evidence for carcinogenicity in male and female rats and male mice only at dose levels of 25-50 g DeBDPO/kg diet. As the results of all mutagenicity tests have been negative, it can be concluded that DeBDPO is not a genotoxic carcinogen. IARC (1990) concluded that there was limited evidence for the carcinogenicity of DeBDPO in experimental animals. The very high dose levels, lack of genotoxicity, and minimal evidence for carcinogenicity indicate that DeBDPO, at the present exposure levels, does not present a carcinogenic risk for humans.

Effects on humans

No evidence for skin sensitization was found in 200 human subjects exposed to DeBDPO in a sensitization test.

A morbidity study of extruder personnel blending polybutyl-eneterephthalate containing DeBDPO, with consequently potential exposure to PBDD and PBDF for 13 years, did not reveal any deleterious effects, even though 2,3,7,8-TeBDF and -TeBDD were detected in the blood. Results of immunological studies showed that the immune system of the exposed persons was not adversely affected in 13 years.

Effects on other organisms in the laboratory and field

The EC_{50}s for the growth of 3 marine unicellular algae were greater than 1 mg DeBDPO/litre. No further information is available on the effects of DeBDPO on other organisms in the laboratory and field.

Conclusions

DeBDPO

DeBDPO is widely used incorporated in polymers as an additive flame retardant. Contact of the general population is with products made from these polymers. Exposure is very low since the DeBDPO is not readily extracted from polymers. The acute toxicity of DeBDPO is very low and there is minimal absorption from the gastrointestinal tract. Thus, risk to the general population from DeBDPO is considered to be insignificant.

Occupational exposure is to DeBDPO in particulate form. The control of dust during manufacture and use will adequately reduce the risk for workers.

DeBDPO is persistent and binds to particulate matter in the environment; it is likely to accumulate in sediment. It is unlikely to bioaccumulate. Current evidence suggests that environmental photodegradation in water does not lead to the formation of lower brominated diphenylethers or brominated dibenzofurans, but little is known about degradation in other media.

There is minimal information on the toxicity of DeBDPO for organisms in the environment.

Breakdown products

Formation of PBDF and, to some extent, PBDD may occur when DeBDPO, or products containing it, are heated to 300-800 °C. The possible hazards associated with this have to be addressed.

Properly controlled incineration does not lead to the emission of significant quantities of brominated dioxins and -furans. Any uncontrolled combustion of products containing DeBDPO can lead to an unquantified generation of PBDF/PBDD. The significance of this for both humans and the environment will be addressed in a future Environmental Health Criteria on PBDF/PBDD.

PBDF have been found in the blood of workers involved in the production of plastics containing DeBDPO. No adverse health effects have been associated with this exposure. Good engineering controls can prevent worker exposure to PBDF.

Recommendations

General

- Workers involved in the manufacture of DeBDPO and products containing the compound should be protected from exposure through the application of appropriate industrial hygiene measures, the monitoring of occupational exposure, and engineering controls.

- Environmental exposure should be minimized through the appropriate treatment of effluents and emissions in industries using the compound or products. Disposal of industrial wastes and consumer products should be controlled, to minimize environmental contamination with this persistent material and its breakdown products.

- Manufacturers should minimize levels of impurities in commercial DeBDPO products, using the best available techniques. A purity of 97% or higher is recommended.

- Incineration should only be carried out in properly constituted incinerators, running at consistently optimal conditions. Burning by any other means may lead to the production of PBDF and/or PBDD.

Further studies

- Further studies on the bioavailability and toxicity of sediment- bound DeBDPO should be performed on relevant organisms.

- Continued monitoring of environmental levels is required.

- The generation of PBDF under real fire conditions should be further investigated.

- Environmental biodegradation, and photodegradation in compartments other than water, should be further studied.

- Investigation into possible methods and consequences of re-cycling of DeBDPO-containing polymers should be made.

- Analytical methods for DeBDPO in various matrices should be validated.

Nonabromodiphenyl oxide (NBDPO)

Summary, evaluation, conclusions and recommendations

Nonabromodiphenyl oxide is not manufactured or used. No data are available on the following topics:

- Environmental transport, distribution, and transformation

- Environmental levels and human exposure

- Kinetics and metabolism in laboratory animals and humans

- Effects on laboratory mammals and *in vitro* test systems

- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

Summary and evaluation

There is no database on which to make an evaluation.

Recommendations

Levels of contamination of commercial brominated flame retardants with nonabromodiphenyl oxide should be minimized to avoid contamination of the environment and exposure of humans.

Octabromodiphenyloxide (OBDPO)

Kinetics and metabolism in laboratory animals and humans

No data are available.

Effects on laboratory mammals and in vitro test systems

The acute toxicity of commercial OBDPO for laboratory mammals is low. The substance is not irritant to the skin and gives only slight eye irritation in rabbits. In short-term toxicity studies (4-week and 13-week), rats administered dietary levels of 100 mg/kg had increased liver weights and microscopic changes characterized by enlarged centrolobular and midzonal liver parenchymal cells containing granular structures. These liver changes were more severe at higher dose levels, i.e., 1000 and 10 000 mg/kg diet. In addition, hyperplasia of the thyroid was seen. Total bromine content in the tissues increased during the study and decreased slowly during a recovery period. The liver changes were reversible. In an inhalation study with micronized dust of OBDPO (8 h/day for 14 consecutive days), no effects were observed with exposure to 1.2 mg/m^3, but a level of 12 mg/m^3 caused the liver changes described in the oral studies.

In rats, commercial OBDPO at relatively low doses increased cytochrome P450 and induced hepatic microsomal enzymes, such as UDP-glucuronyl transferase and benz[*a*]pyrene hydroxylase. Commercial OBDPO induced a porphyrinogenic effect in cultures of chick embryo liver cells.

OBDPO was tested for teratogenic potential in rats; at high dose levels (25.0 and 50.0 mg/kg body weight), resorptions, or delayed ossification of different bones and fetal malformations were observed. The malformations observed with doses of 25 mg/kg body weight and higher were most likely associated with maternal toxicity. These changes were not seen at dose levels of 15.0 mg/ kg body weight or less. In rabbits, there was no evidence for teratogenic activity, but fetotoxicity was seen at a maternally toxic dose level of 15 mg/kg body weight. Teratogenicity studies showed a no-effect level of 2.5 mg/kg body weight.

In 28-day and 90-day rat studies, 100 mg OBDPO per kg diet (equivalent to 5 mg/kg body weight) induced minimal effects in the liver. No no-effect level was established.

Results of the mutagenicity tests including an unscheduled DNA assay, *in vitro* microbial assays, and an assay for sister chromatid exchange with Chinese hamster ovary cells were all negative.

No long-term/carcinogenicity test results are available.

Effects on humans

No data are available.

Effects on other organisms in the laboratory and field

Minimal data are available.

Conclusions

OBDPO

Commercial OBDPO is a mixture of hexa-, hepta-, octa-, and nonabromodiphenyl oxide, all of which persist in the environment, largely bound to sediment.

OBDPO is widely incorporated in polymers as an additive flame retardant. Contact of the general population is with products made from these polymers. Exposure by extraction from polymers is unlikely.

The acute toxicity of OBDPO is low. There is no information on uptake and loss in mammals. OBDPO is not teratogenic or mutagenic. Long-term toxicity and carcinogenicity studies are not available.

Several components of commercial OBDPO have been identified in human adipose tissue. The acute risk for the general population is likely to be low. Risk assessment of long-term exposure is not possible, because of the lack of relevant toxicity studies.

No information is available to draw conclusions on occupational exposure to, or effects of, OBDPO.

Limited information is available on the toxicity of OBDPO for organisms in the environment. Components of the commercial OBDPO mixture with lower levels of bromination may bioaccumulate in organisms.

Breakdown products

Formation of PBDF, and to some extent PBDD, may occur when OBDPO, or products containing it, are heated to 400-800 °C. The possible hazards associated with this have to be addressed.

Exposure of the general population to PBDF impurities in flame retarded polymers is unlikely to be significant. Properly controlled incineration should not lead to the emission of significant quantities of brominated dioxins and -furans. Any uncontrolled combustion of products containing commercial OBDPO can lead to the generation of unquantified amounts of PBDF/PBDD. The significance of this for both humans and the environment will be addressed in a future EHC on PBDF/PBDD.

Recommendations

General

- Best available techniques should be used in the manufacture of commercial OBDPO, to minimize levels of hexa- and lower brominated congeners, because of their bioaccumulation potential in the environment.

- Workers involved in the manufacture of OBDPO, and products containing the compound, should be protected from exposure using appropriate industrial hygiene measures, monitoring of occupational exposure, and engineering controls.

- Environmental exposure should be minimized through the appropriate treatment of effluents and emissions in industries using the compound or products. Disposal of industrial wastes and consumer products should be controlled to minimize environmental contamination with this persistent material and its breakdown products.

- Incineration of materials, flame retarded with OBDPO, should only be in properly constituted incinerators running under consistently optimal conditions. Burning by any other means may lead to production of PBDF and/or PBDD.

Further studies

Because the present toxicological database is inadequate to evaluate the hazards of commercial OBDPO for humans and the environment, and, to support its use, the following studies should be carried out:

- Investigations on the bioavailability and ecotoxicity of sediment-bound components of commercial OBDPO using the relevant organisms

- Extended monitoring of environmental levels of components of commercial OBDPO

- Long-term toxicity and carcinogenicity studies of commercial OBDPO

- Monitoring of occupational exposure to commercial OBDPO
- Further investigations on the generation of PBDF under real fire conditions
- Further studies on environmental biodegradation and photodegradation in compartments other than water
- Investigation of possible methods and consequences of recycling of OBDPO-containing polymers
- Validation of analytical methods for OBDPO in various matrices
- Investigations on the possibility of migration from different types of polymers.

Heptabromodiphenyl oxide (HpBDPO)

Heptabromodiphenyl oxide is not manufactured or used.

There is no database on pure HpBDPO on which to make an evaluation.

No data are available on the following topics:

- Kinetics and metabolism in laboratory animals and humans
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

Because HpBDPO is the major component of commercial octabromodiphenyl oxide, the summary, evaluation, conclusions, and recommendations on commercial OBDPO, are relevant to "commercial" HpBDPO.

Hexabromodiphenyl oxide (HxBDPO)

Hexabromodiphenyl oxide is not manufactured or used, but occurs as a contaminant of commercial brominated diphenyl oxides. Such levels of hexabromodiphenyl oxide should be minimized to avoid contamination of the environment and exposure of humans.

There is no database on which to make an evaluation.

No data are available on the following topics:

- Effects on laboratory mammals and *in vitro* test systems
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

Pentabromodiphenyl oxide (PeBDPO)

Kinetics and metabolism in laboratory animals and humans

The half-life of PeBDPO has only been investigated in the perirenal fat in rats. The average half-life was between 25 and 47 days, depending on the sex of the animal and the type of isomer determined.

Effects on laboratory mammals and in vitro test systems

The acute oral toxicity of commercial PeBDPO is low in rats; the dermal toxicity in rabbits is also low. Short-term inhalation exposure in rats and the application of PeBDPO to the conjunctival sac in rabbits caused only mild, transient effects.

In short-term toxicity studies on rats (4-week and 13-week), dietary concentrations of 100 mg/kg increased liver weights and caused slight histological alterations. Changes consisted of the enlargement of hepatic parenchymal cells, which had a granular appearance and contained eosinophilic "round bodies". Dose- related increases in total bromine content in the liver occurred and levels remained elevated for as long as 24 weeks. A mild degree of thyroid hyperplasia, which was reversible, was observed.

Hepatic enzyme induction and increases in cytochrome P450 c occurred after oral administration of daily doses of PeBDPO as low as 0.78 µmol/kg body weight. The results of tests for teratogenicity and mutagenicity were negative.

No long-term/carcinogenicity studies have been reported.

Effects on humans

No data are available.

Effects on other organisms in the laboratory and field

Minimal data are available.

Conclusions

PeBDPO

Commercial PeBDPO (a mixture of 24-38% tetra-, 50-60% penta-, and 4-8% hexabromodiphenyl oxide) is persistent and accumulates in organisms in the environment.

Commercial PeBDPO is widely used, incorporated in polymers as an additive flame retardant. Contact of the general population is with products made from these polymers. Exposure by extraction from polymers is unlikely. Human exposure to PeBDPO via the food chain may occur, since the substance has been detected in organisms in the environment that are human food items, such as fish, shellfish, etc. In fish and birds from Sweden, increasing levels have been measured over the last 2 decades.

The acute toxicity of commercial PeBDPO is low. There is no information on uptake and loss in mammals. Reproduction, long-term toxicity, and carcinogenicity studies are not available.

The risk to the general population cannot be determined from the available data.

No information is available to draw conclusions on occupational exposure levels or the effects of commercial PeBDPO.

Limited information is available on the toxicity of commercial PeBDPO for organisms in the environment.

Breakdown products

PBDF and, to some extent, PBDD are formed when PeBDPO (or products containing it) are heated to 400-800 °C. The possible hazards associated with this have to be addressed.

Exposure of the general population to PBDF in polymers flame retarded with PeBDPO is unlikely to be of significance. Properly controlled incineration does not lead to the emission of significant quantities of brominated dioxins and -furans. Any uncontrolled combustion of products containing PeBDPO can lead to the generation of unquantified amounts of PBDF/PBDD. The significance of this for both humans and the environment will be addressed in a future EHC on PBDF/PBDD.

Recommendations

General

Persistence in the environment and accumulation in organisms suggest that commercial PeDBPO should not be used. However, if use continues, the following points should be taken into account:

- Workers involved in the manufacture of PeBDPO and products containing the compound should be protected from exposure using appropriate industrial hygiene measures, the monitoring of occupational exposure, and engineering controls.

- Environmental exposure should be minimized through the appropriate treatment of effluents and emissions in industries using the compound or products. Disposal of industrial wastes and consumer products should be controlled to minimize environmental contamination with this persistent and accumulating material and its breakdown products.

- Incineration of materials flame retarded with PeBDPO should only be carried out in properly constituted incinerators running consistently under optimal conditions. Burning by any other means will lead to production of toxic breakdown products.

Further studies

- Continued monitoring of environmental levels is required.

- Methods for the determination of PeBDPO in various matrices should be validated.

- Because the present toxicological database is inadequate to evaluate the hazards of commercial PeBDPO for humans and the environment, and to support its use, the following studies should be done:

    - additional toxicological, carcinogenicity, and ecotoxicological studies;
    - further investigations on the generation of PBDF under real fire conditions;
    - investigations on possible methods and consequences of recycling of PeBDPO-containing polymers;
    - studies on the possibilities of migration from flame retarded products.

Tetrabromodiphenyl oxide (TeBDPO)

Effects on laboratory mammals and in vitro test systems

There are no data on TeBDPO itself, but acute and short-term data are available for commercial PeBDPO containing 41% TeBDPO.

Kinetics and metabolism in laboratory animals and humans

Minimal data are available.

Effects on humans

No data are available.

Effects on other organisms in the laboratory and field

No data are available.

Conclusions

TeBDPO

Components of commercial TeBDPO (a mixture of 41% 2,2′,4,4′-tetra-; 45% 2,2′,4,4′,5′-penta-; 7% hexa-, and 7-8% polybrominated diphenyl oxides with an unknown structure) are persistent and accumulate in organisms in the environment.

TeBDPO as a component of pentabromodiphenyl oxide is widely incorporated in polymers as an additive flame retardant. Contact of the general population is with products made from these polymers. Exposure by extraction from polymers is unlikely. Human exposure to TeBDPO, via the food chain, may occur, because the substance has been detected in organisms in the environment that are human food items, such as fish, shellfish, etc. In fish and birds from Sweden, increasing levels have been measured over the last two decades.

There is a lack of information concerning short-, long-term toxicity/carcinogenicity, and reproduction studies. Furthermore, information on kinetics and metabolism in laboratory animals and humans is not available.

The risk for the general population cannot be determined on the basis of available data.

No information is available to draw conclusions on occupational exposure levels or the effects of TeBDPO.

No data are available on the toxicity of commercial TeBDPO for organisms in the environment.

Breakdown products

PBDF and PBDD are formed when TeBDPO are heated to 800 °C. The possible hazards associated with this have to be addressed.

Exposure of the general population to PBDF in polymers, flame retarded with TeBDPO, is unlikely to be of significance. Properly controlled incineration does not lead to the emission of significant quantities of brominated dioxins and furans. Any uncontrolled combustion of products containing TeBDPO can lead to the generation of unquantified amounts of PBDF/PBDD. The significance of this for both humans and the environment will be addressed in a future EHC on PBDF/PBDD.

Recommendations

General

Because of their persistence in the environment and accumulation in organisms, it is recommended that TeBDPO should not be used. However, should use continue, the following points must be taken into account:

- Workers involved in the manufacture of TeBDPO and products containing the compound should be protected from exposure using appropriate industrial hygiene measures, the monitoring of occupational exposure, and engineering controls.

- Environmental exposure should be minimized through the appropriate treatment of effluents and emissions in industries using the compound or products. Disposal of industrial wastes and consumer products should be controlled to minimize environmental contamination with this persistent and accumulating compound and its breakdown products.

- Incineration of materials, flame retarded with TeBDPO, should only be carried out in properly constituted incinerators running under optimal conditions. Burning by any other means will lead to the production of furan breakdown products.

Further studies

- Continued monitoring of environmental levels is required.

- Analytical methods for TeBDPO in various matrices should be validated.

- Because the present toxicological data base is inadequate to evaluate the hazards of commercial TeBDPO for humans and the environment, if use is continued, the following studies should be done:

    - additional toxicological, carcinogenicity, and eco-toxicological studies;

    - further investigations on the generation of PBDF under real fire conditions;

    - investigation into possible methods and consequences of recycling of TeBDPO-containing polymers;

    - investigations of the possibility of migration from flame retarded products.

Tribromodiphenyl oxide (TrBDPO)

Tribromodiphenyl oxide is not manufactured or used.

No data are available on the following topics:

- Environmental transport, distribution, and transformation
- Kinetics and metabolism in laboratory animals and humans
- Effects on laboratory mammals and *in vitro* test systems
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

Summary and evaluation

There is no database on which to make an evaluation.

Recommendations

Levels of contamination of commercial products with tribromodiphenyl oxide should be minimized to avoid contamination of the environment and the exposure of humans.

Use of such commercial products leading to environmental contamination should be avoided.

Dibromodiphenyl oxide (DiBDPO)

Dibromodiphenyl oxide is not manufactured or used.

No data are available on the following topics:

- Kinetics and metabolism in laboratory animals and humans
- Effects on humans
- Effects on other organisms in the laboratory and field
- Previous evaluations by international bodies.

Summary and evaluation

There is no database on which to make an evaluation.

Recommendations

Contamination of commercial products with dibromodiphenyl oxide should be minimized to avoid contamination of the environment and exposure of humans.

Use of such commercial products leading to environmental contamination should be avoided.

Polybrominated biphenyls (PBBs)

Conclusions

Most of the PBB congeners found in commercial flame retardants are lipophilic, persistent and bioaccumulating. These compounds are biomagnified in environmental food webs and pose a threat, especially to organisms in the higher levels of these webs. Furthermore, some PBB products are precursors to toxic polybrominated dibenzofurans in combustion processes.

In addition to emissions during manufacture and use, PBB will enter the environment from the widespread use of flame retardant products. A considerable part of the PBB produced will probably reach the environment because of the high stability of these compounds.

PBBs are also found in environmental and human samples from places far from known point sources. The congener pattern in the environmental samples does not match those found in the technical products, which indicates an environmental alteration, possibly a photochemical debromination.

Very little information is available at present on the extent of exposure of the general population to PBBs. However, in the few instances where measurements were made, trace amounts of PBBs were identified. At present, this exposure does not give rise to concern, but further build-up should be avoided. Human data from the Michigan episode suggests that exposures in Michigan were several orders of magnitude higher than the exposure of the general population. No definitive health effects that could be correlated with PBB exposure in the Michigan population have been identified, though the follow-up period has not been long enough for the development of cancer. Since PBB levels in adipose tissue and serum remain high in the Michigan population, their internal exposure continues. In contrast, toxicity was observed in cattle in Michigan. This discrepancy is explained by differences in the extent of the exposure of the cattle.

Occupational exposure has only been examined in two plants in the USA. It appears that chloracne-like lesions may develop in workers producing PBB, and hypothyroidism in workers exposed to DeBB. No studies have been conducted in workers incorporating the deca- or octa-/nona-bromobiphenyl into commercial products.

PBBs are extremely persistent in living organisms and have been shown to produce chronic toxicity and cancer in animals. Although the acute toxicity was low, cancer was induced at a dose of 0.5 mg/kg body weight per day and the no-observed effect level was 0.15 mg/kg body weight per day. A number of chronic toxic effects have been observed in experimental animals at doses of around 1 mg/kg body weight per day following long-term exposure.

Recommendations

General

The Task Group is of the opinion that human beings and the environment should not be exposed to PBBs in view of their high persistence and bioaccumulation and potential adverse effects at very low levels after long-term exposure. Therefore, PBBs should no longer be used commercially.

Because of the limited toxicity data on DeBB and OcBB, their extreme persistence and their potential break-down in the environment, and the more toxic persistent compounds formed through combustion, they should not be used commercially, unless their safety has been demonstrated.

It is known that observations on the Michigan cohort are still continuing. Publication of these data is required.

Future research

Future human and environmental PBB monitoring, including workplace monitoring in the manufacture and user industries, should be expanded, should be congener specific, and should include OcBB/NoBB and DeBB. These compounds should be included in monitoring programmes in progress for other halogenated compounds. The time trends and geographical distribution of PBB levels in the environment should continue to be monitored. Release of PBBs into the environment from waste disposal sites should be surveyed.

Thermolysis experiments simulating conditions of accidental fires and municipal incineration should be conducted. Additional research should be continued on the mechanisms of toxicity and carcinogenicity of PBBs and related compounds. PBBs may serve as model compounds for such mechanistic research. Purified congeners should be used in these studies.

The effects of PBBs on reproduction are not well elucidated. Therefore, well-designed, long-term, reproductive studies at low doses, using a sensitive species, should be performed.

There is also a need for more information on the bioavailability and toxicokinetics of OcBB/NoBB, DeBB, and selected congeners.

Tetrabromobisphenol A (TBBPA)

Kinetics and metabolism in laboratory animals and humans

In rats, TBBPA is poorly absorbed from gastro-intestinal tracts. Once absorbed, it and/or its metabolites appear to be distributed throughout most organs of the body. In rat, the maximum half-life in any tissue was less than 2 1/2 days.

Effects on laboratory mammals and in in vitro test systems

The acute oral toxicity is low. The oral LD_{50} for the rat is > 5g/kg body weight and the oral LD_{50} for mice is 10g/kg body weight. The dermal LD_{50} for the rabbit is > 2g/kg body weight. The inhalation LC_{50} in mice, rats and guinea-pigs is > 0.5 mg/litre. A single dermal application of TBBPA on the skin of rabbits and guinea-pigs did not induce local or systemic effects at a concentrations of up to 3.16 g/kg body weight. TBBPA was not irritating to rabbit skin or eyes. No sensitization reaction was observed in a few studies with guinea-pigs. TBBPA was also tested for chloracnegenic activity in rabbit ears. No such reaction was observed.

In a 3-week dermal toxicity study with clipped and abraded skin of rabbits exposed up to 2500 mg/kg body weight showed only slight skin erythma. No other compound-related changes were observed.

Rats were exposed to up to 18 mg/litre (18 000 $mg/m^{3)}$) micronized TBBPA for 4 h/day, 5 days/week for 2 weeks. No effects on body weight, histopathology, haematology, serum chemistry or urinalysis were observed.

Oral doses in rats up to 1000 mg TBBPA/kg diet for 28 days produced no adverse effects. Total bromine content in the liver was not different between the control and high dose (1000 mg/kg) groups.

In an oral 90-day toxicity study in rats, dose levels up to 100 mg TBBPA/kg body weight did not induce adverse effects on body weight, haematology, clinical chemistry, urinalysis, organ weights and, gross and microscopic examinations.

In an oral 90-day toxicity study in mice, a dose of 4900 mg/kg of diet (approximately 700 mg/kg body weight per day) caused no adverse effects; a dose of 15 600 mg/kg of diet (approximately 2200 mg/kg body weight per day) caused decreased body weight, increased spleen weight, and reduced concentration of red blood cells, serum proteins, and serum triglyceride.

Two teratogenicity studies were carried out with rats; one with dose levels up to 10 g/kg body weight by gavage from gestation day 6 though day 15 and a second with dose levels up to 2.5 g/kg body weight administered from day 0 to day 19 of gestation. In the first study with 10 g/kg 3/5 animals died, but with 3 g/kg no signs of toxicity were noticed. No teratogenic effects were observed. In the second study no abnormalities were found.

TBBPA was not mutagenic in various studies with *Salmonella typhimurium* strains TA 1535, TA 1537, TA 1538, TA 98 and TA 100 with metabolic activation with S9 mix of Aroclor-induced rats and Syrian hampsters. The concentrations tested were up to 10 000 μg/plate. Two tests with *Saccharomyces cerevisiae* with and without microsomal enzyme preparation from Aroclor-induced rats were also negative.

No carcinogenicity or long-term toxicity studies were reported.

Effects on humans

TBBPA produced no skin irritation or sensitization in 54 human volunteers.

No epidemiological study or other data on the effects on man are available.

Effects on other organisms in the laboratory and field

TBBPA was not very toxic to marine algae. In 28 subchronic studies the EC_{50}'s were in the range on 0.1 to 1.0 mg/litre, while fresh water algae did not show growth inhibition even with 9.6 mg/litre.

An acute 48-h LC_{50} to *Daphnia magna* was reported as 0.96 mg/litre, and at 0.32 mg/litre 5% of organisms died. In a 21-day subchronic study, EC_{50} for survival and growth of Daphnia magna was > 0.98 mg/litre. Based on TBBPA's effect on daphnid reproduction in this 28-day study, a Maximum Acceptable Toxicant Concentration (MATC) was between 0.30 and 0.98 mg/litre. Mysid shrimp (age < 1, 5 and 10 days old) showed 96-h LC_{50} values of 0.86, 1.1 and 1.2 mg/litre, respectively.

The 96-h acute EC_{50} (reduction of shell deposition) in Eastern oysters was calculated to be 0.098 mg/litre with a no-observed-effect concentration (NOEC) of 0.0062 mg/litre.

The 96-h LC_{50} of TBBPA for bluegill sunfish, rainbow trout and fathead minnow was 0.51, 0.40 and 0.54 mg/litre respectively. The no effect concentrations for these three fish species were 0.10, 0.18 and 0.26 mg/litre. Fathead minnow (embryos and larvae) were exposed for 35 days to TBBPA and showed a MATC between 0.16 and 0.31 mg/litre, based on adverse effects on embryo and larvae survival.

The 14-day no-effect levels to the sediment invertebrate midge *Chironomous tentans* was 0.039, 0.045 and 0.046 mg TBBPA/litre water in low, medium and high organic carbon sediments, respectively.

Most of the studies in aquatic systems have been performed at pHs around the pKai. The behaviour of TBBPA in acidic waters may be different.

Conclusions

General population

TBBPA is widely used and incorporated in polymers as a reactive or additive flame retardant. Contact of the general population is with products made from these polymers and would not result in significant uptake of TBBPA. Furthermore, the acute and repeated dose toxicity of TBBPA is very low. TBBPA is poorly absorbed from the gastrointestinal tract. Risk to the general population from TBBPA is, therefore, considered to be insignificant.

Occupational exposure

Occupational exposure to TBBPA is primarily as particulates during packaging or mixing operations. The control of dust through the use of local ventilation and other engineering methods will reduce the risk to workers. If dust cannot be adequately controlled, respiratory protection should be used.

The environment

Where detected in the environment, TBBPA is mainly found in soil and sediment samples. A relatively high bioconcentration factor seems to be balanced by a rapid excretion and the compound has not normally been found in environmental biological samples.

The phenolic groups of TBBPA may be methylated in the environment and the resulting Me_2-TBBPA is more lipophilic. This compound has also been found in sediment, fish and shellfish.

Breakdown products

PBDD and PBDF have been found as trace impurities in TBBPA; however, the presence of 2,3,7,8-congeners has not been demonstrated. Under laboratory pyrolysis conditions, PBDF/PBDD are formed from TBBPA.

A limited number of studies have shown that only trace quantities of PBDD/PBDF may be produced during processing and recycling of polymers containing TBBPA as an additive flame retardant. Proper ventilation and other engineering controls can prevent worker exposure.

Recommendations

General

- workers in the manufacture of TBBPA and products containing the compound should be protected from exposure with engineering controls, monitoring of occupational exposure and appropriate industrial hygiene measures.

- environmental exposure should be minimized through the appropriate treatment of effluents and emissions in industries using the compound or products. Disposal of industrial wastes and consumer products should be controlled to minimize environmental contamination with this material and its breakdown products.

- If TBBPA-treated material is incinerated, it has to be done in properly constituted incinerators running at consistently optimal conditions.

Further studies

- Monitoring of environmental samples for TBBPA, Me_2-TBBPA and PBDD/PBDF should be continued, and if these compounds are found there, human monitoring should also be done.

- monitoring should be conducted to measure occupational exposures to respirable particles of TBBPA; if indicated by workplace monitoring, a subchronic inhalation study in rats should be conducted.

- studies on PBBD/PBDF formation from TBBPA-treated material at incineration, accidental fires and under conditions simulating fire, should be conducted.

- long-term studies of the fate of polymers containing TBBPA (both added and reacted into the polymer, especially in land fills, should be conducted).

- environmental conversion of TBBPA to its dimethyl derivative, especially in sediments, should be studied.

- Studies into the recyclability of TBBPA-containing polymers should be continued, paying attention to break-down products.

- Since there are no data, an addition in vitro test with TBBPA for cytogenetic damage is required. If this test is positive, additional in vivo studies will be necessary. If the cytogenic testing in vivo shows positive results, additional subchronic or long-term testing is required.

- Since there are no data, a test for reproductive toxicity in rats is required.

4.2 National positions

Austria

Because of their high persistency and bioaccumulation, as well as their ability to form PBDD/Fs at elevated temperatures, polybrominated biphenyls (PBBs) have been banned in Austria by an ordinance (BGB1.No.210/1993) together with other halogenated biphenyls.

Since other brominated flame retardants (BFRs), especially the polybrominated diphenyl oxides (PBDPOs), also show negative effects on man and the environment, risk reduction for BFRs is a very important issue. In addition it should be stated that for a large number of applications halogen-free alternatives (aluminium, magnesium, phosphorous, nitrogen compounds etc.) exist and that the use of BFRs should be limited to those applications where they may be essential (e.g. aircraft). Nevertheless, restrictions in this field should take place on an international basis, bearing in mind that these substances are present in a large number of different products distributed by worldwide trade.

Belgium

- No specific actions have been taken to ban certain uses of selected BFRs or to implement major measures to control, limit or reduce their risks.

- No information is available on brominated flame retardant risk reduction case studies for projects initiated by government and/or industry.

- Further revision of existing and new studies on the effect of brominated flame retardants is needed before a national statement of the risk of various brominated flame retardants will be defined.

- The implementation of national actions could still be deferred at this stage of the investigations and should in no way harm the coordinated action adopted in this matter at an international level and more particularly, as regards Belgium, the legislative measures adopted by the European Commission.

- An international strategy would seem appropriate in respect of the evaluation of standardized flame retardant properties and of the conformity of the tests to the standards.

Denmark

Denmark has banned the use of polybrominated biphenyls (PBBs) in textiles by implementation of EC Directive 89/677.

The use of polybrominated diphenyl oxides (PBDPOs) in different types of plastics and textiles is proposed to be banned by an EC Directive. Seven non-commercial PBDPOs are planned to be banned immediately, and the remaining three commercially used PBDPOs are planned to be banned five years later.

Denmark supports the Directive, and is considering issuing national regulations on the PBDPOs if the above Directive isn't adopted within a reasonable time.

Additionally, Denmark is considering introducing a general ban on PBBs, because the ban on PBDPOs may increase the application of PBBs as an alternative to the flame retardants based on PBDPOs. Denmark therefore supports risk reduction activities going further than the proposed EC Directive, e.g. the German statutory order introducing limits for the formation of brominated dioxins and dibenzofurans, and the Dutch proposal for banning PBBs and the PBDPOs.

Denmark hasn't actually carried out any risk reduction case studies on the PBBs and PBDPOs. But the Danish EPA is presently planning a programme to monitor the occurrence and amounts of PBBs and PBDPOs spread in the different environmental compartments.

The Danish risk reduction activity on the brominated flame retardants is based on a concern both for man and the environment. Recently, the activity has focused attention on PBBs and PBDPOs, and Denmark is considering extending this activity to include also the other brominated flame retardants.

In general, the BFRs are persistent substances that tend to accumulate in different environmental compartments. They bioaccumulate in different organisms, and several observations of biomagnification have been reported.

Today's use of BFRs in products results in a wide spread in different compartments. The main picture is that BFR-contaminated industrial waste flows end up in surface waters and sludge. These compounds are absorbed by water organisms and may eventually reach the human food chain.

The incineration of plastic waste containing PBBs and PBDPOs may present a particular threat to man and the environment through the emission of brominated dioxins and dibenzofurans. Several studies indicate that the amounts of dioxins and dibenzofurans formed depends strongly on conditions in incineration plants. Other studies show that introduction of modern incineration plants is a means to risk reduction.

Denmark has the point of view that, in principle, risk reduction of the BFRs should primarily address the source, and not-end-of pipe technologies.

The Danish risk reduction measures on BFRs are to phase out the most harmful BFRs, here PBBs and PBDPOs, and systematically evaluate the hazards and risk of others. Possible actions are legislation and voluntary agreements, and the means in preferential order are: substitution of flame retardant; substitution of the material; and, with lowest priority, recycling and incineration.

Risk reduction for the BFRs is clearly an international issue. Trade is spreading the substances worldwide, and the substances have applications in many different products. International action is therefore necessary to eliminate the use of the most harmful BFRs.

France

France has implemented the EC Directive concerning PBBs and their use on textiles.

In connection with the draft EU Directive aimed at banning PBDPOs from the market, France and the UK will jointly undertake the risk assessment of octa- and decabrominated compounds within the context of Regulation 793/93/EEC on the evaluation and management of risks of existing substances.

As in the case of PBDPOs, the specificity of each individual member of the PBBs group should be taken into account. The preliminary results of a recent study (report available) on the phototransformation of decabromobiphenyl support this stipulation. The study showed that this compound, following adsorption on silica, was photohydrolized to polar compounds probably containing a hydroxyl function. Thus biphenyls substituted with fewer bromine atoms, which are of much greater concern, would not be formed.

Germany

Polybrominated diphenyls (and diphenyloxides) are regulated in a less direct way than under other European initiatives. In Germany, a second modification of the Chemicals Prohibition Ordinance was adopted in 1994. It imposes limits on chlorinated dioxins and furans and, for the first time, imposes limits on new *brominated* dioxins and furans. Prohibitions are placed on products and finished articles that contain greater than 100 ppb of 17 different 2,3,7,8-substituted PCDD/PCDF congeners and greater than 5 ppb of eight different PBDD/PBDF congeners. During an interim period of five years, the limit for the PBDD/PBDF will be 60 ppb.

Elsewhere in Germany, the Federal Institute for Workers’ Protection (BAU) drafted a guide value in 1989 for tolerable workplace concentrations of 2,3,7,8-TCDD equivalents (TEQ) not to exceed less than 15 pg/m^3 TEQ. The BAU has proposed that similar limits be placed on exposure to PBDD/PBDF.

The German Government believes that a rigid regulation banning PBDPOs is necessary. German industry has shown since the late 1980s that it is possible to substitute these flame retardants with other halogen-containing substances or halogen-free substances, or develop more stable polymers or copolymers.

Prior to implementation of the regulation, declaration of PBDPO-containing plastic material may be a helpful instrument to protect consumers from PBDPOs and its degradation products.

Since the recycling of PBDPO-containing products increases the rate of dioxin and furan formation, such products must be destroyed in well equipped chemical waste incinerators until the production, marketing and application of PBDPOs has been prohibited.

The German Government strongly supports the regulatory activities of the EU.

Because of their high persistency and bioaccumulation it is necessary to ban the brominated biphenyls (PBBs), too. Furthermore, this group of chemicals is a potential precursor for the producing of PBDD/F at elevated temperatures.

Italy

So far, no action has been officially taken by Italy to ban uses of brominated flame retardants (BFRs) or control their risks. At present, some risk reduction measures have been taken, on a voluntary basis, by some public organizations and industries. Examples are the following internal standards adopted by: ENEL – National Agency for Electric Energy – and FS – National Railway – (CEI 20-37 standard); Milano City Underground (standard based on Sheet G 8998); and Marina Militare (NAVI 3A075 standard). The achievement of these standards tends to exclude the use of halogenated flame retardants.

Concerning the risk of BFRs, the following observations can be made:

- The use of polybrominated biphenyls (PBBs) should be avoided because of their intrinsic toxicity and bioaccumulation;

- Polybrominated diphenyl oxides (PBDPOs) are good substitutes for PBBs because of their lower toxicity and good biodegradability. However they can produce brominated dioxins and furans at some stage of their life cycle (e.g. manufacture and combustion);

- Banning of PBDPOs does not altogether exclude the formation of halogenated dioxins in cases of fires or incineration. In such cases, in fact, several halogenated compounds can provide a source for halogenated dioxins;

- The problems deriving from PBBs and PBDPOs are presently "gone round" by using other brominated or chlorinated organics; but these problems are not solved. In fact, the reasons why halogenated FRs should be banned is the production, on heating, of corrosive and toxic halogen acids, plus high optical density smoke;

- New FRs are proposed which are promising substitutes for halogenated FRs, but they need to be tested and evaluated in detail.

In conclusion, it would seem reasonable to: ban the use of PBBs and limit the use (the concentration) of PBDPOs and other halogenated FRs; to find other solutions when high concentrations of these additives are necessary; to stimulate and support research in this area and test/evaluate new available FRs.

Finally, it would be desirable, in our opinion, to address the problem of FRs in general, not just focus on the group of BFRs.

Japan

Polybrominated biphenyls (PBBs)

Small quantities of this substance were imported from the United States and used as a flame retardant in plastics for electric appliances. It has not been used since the late 1970s in Japan, when the US industries voluntarily stopped production and use because of suspicion of its toxicity and ability to bioaccumulate. Japanese industries have also voluntarily restricted their attempt to manufacture and use these products since then.

Decabromodiphenyl oxide (DeBDPO)

This substance appeared on the market in the 1970s as a highly safe substitute for PBBs. A broad range of tests were carried out on this substance, including a two year chronic toxicity test.

In Japan, DeBDPO was registered as an "existing chemical" under the Chemical Substances Control Law in 1974. It was identified as a "low accumulative substance" in 1978, based on the accumulation test in fish conducted by the government.

Concentration of DeBDPO in the environment has been monitored in Japan by the Environment Agency in 1977, 1987 and 1988. DeBDPO’s detection in the environment is largely limited to sediment, and not in water or fish.

Octabromodiphenyl oxide (OBDPO)

In Japan, OBDPO was registered as a "new chemical" under the Chemical Substances Control Law in 1983. It was identified as a "low accumulative substance", based on tests on fish.

Hexa- and tetrabromodiphenyl oxide (HxBDPO and TeBDPO)

Though HxBDPO and TeBDPO were used for a variety of plastics until the late 1980s, Japanese industries voluntarily restricted their production and use due to the fear of high bioaccumulation and the increasing concern for dioxin formation in combustion.

The Netherlands

During 1990-1991 a risk assessment (R.A.) of the polybrominated biphenyls and the polybrominated diphenyloxides (PBBs and PBDPOs) was carried out in the Netherlands. On the basis of this R.A., the Dutch government proposed a draft resolution governing these PBBs and PBDPOs. In 1994 a re-evaluation was carried out on the most important aspects of the risks of these compounds. The results of the recent risk re-evaluation show that risks are less than formerly assumed. The conclusions are as follows:

- One can expect an increase in PBDD/F and PCDD/F formation in a Municipal Waste Incinerator (MWI) as a consequence of the input of these brominated flame retardants. However, it is not possible to draw strict conclusions from this supposition. Since the products of incineration in a MWI form a complex function of process conditions, no calculations of input/yield can be done.

- Modern plants for municipal waste incineration equipped with at least a dry absorber and a fabric filter, can meet the latest environmental standards (PCDD/F concentration in the flue gas of less than 0.1ng I-TEQ/m^3). A possible increase in formation of dioxins/furans can be compensated by an extra heavy (activated carbon + fabric filter) unit in the cleaning train.

- Because of a danger of a higher degree of contamination of ESP ash with hazardous halogenated organic compounds, the novel techniques of ash decontamination and immobilization should be more broadly implemented.

- DeBDPO, OBDPO, PeDBPO and PBBs can be classified as persistent chemicals. Photodegradation of DeBDPO and PBBs in water will probably not be an important route of degradation since most of the DeBDPO and the PBBs end up in the sediment where sunlight intensity is low. Biodegradation of the DeBDPO, aerobic as well as anaerobic, has not been studied. Both routes may be of low relevance, but it can be expected that the rates will be low. With the PBBs, aerobic biodegradation of the higher substituted congeners hardly occurs. Reduction dehalogenation of the higher PBBs occurs in anaerobic sediments. However, half-lives are expected to be in the order of decades.

- Biomagnification of commercial PeBDPO does occur in significant quantities. PeBDPO is a widespread contaminant in the Dutch environment. Based on actual levels in fish and sediment, and taking into account secondary poisoning of predators via consumption of fish, the risk was between the Maximum Permissible Concentration and the Negligible Concentration. Through lack of data, no risks could be assessed for fish-eating birds.

- Accidental fires in buildings can form a source of pollution with brominated flame retardants or the products of their thermal degradation.

Sweden

In 1991, the Parliament stated that the use of brominated flame retardants was to be restricted. Work should focus on rapid phasing out of the substances that are most harmful to man and the environment.

Sweden’s concern regarding brominated flame retardants is mainly based on the following:

There is widespread use of flame retarded products. The widespread use raises concern over diffuse exposures which are difficult to control.

PBDPOs are widespread contaminants in the Swedish environment. PBDPOs are found in biological samples representing different ecosystems and trophic levels, as well as from rural areas, industrialized areas and near possible sources. The spatial trend along the Swedish coast is similar to that of PCBs and DDTs. The concentrations of PBDPOs are increasing over time and there are indications of airborne pollution. Even in remote areas without known local sources, low concentrations of PBDPOs have been found in environmental samples. Examples are white fish in northern Sweden and ringed seal at Spitzbergen, off the north coast of Norway.

The ability of these compounds to bioaccumulate and persist raises concern over the potential effects of chronic exposure to organisms.

The potential for dioxin/furan formation when materials are heated also raises concern.

A project is in progress aiming at an evaluation of the risks associated with the use of flame retardants in Sweden. This work is not limited to brominated substances. All major chemical groups used as flame retardants are included. The goal is to propose risk reduction measures for those flame retardants posing unacceptable risks. Concerning the PBDPOs, a final judgement on the risk situation in Sweden will be made and appropriate measures will be proposed.

Switzerland

Polybrominated biphenyls (PBBs)

According to their chronic toxicity, PBBs are classified in Switzerland in toxicity class 1 (most dangerous chemicals). This classification is supported by several studies published after the accidental misuse in Michigan (cattle food) in 1973 (e.g. US EPA position paper on polybrominated biphenyls; W.A. Coniglio and B. Norkin 1977).

The best documented effect of PBBs in humans is their strong immunotoxic potential. Immunodiagnostic investigations in case of the accidentally exposed Michigan farmers revealed a significant decrease in the numbers and changes in the functional integrity of both T-and B-lymphocytes. The repeat of these immunodiagnostic tests five years after the disaster showed a virtually complete persistence of the immune dysfunction (J. Roboz et al., Environmental Health Persp., 60:107-113, 1985; J.G. Bekesi, et al., Science, 199: 1207-1209, 1978).

PBBs also appear among the most effective porphyrogenic chemicals. Heme production in bone marrow and liver produces porphyrins as by-products of this biosynthetic process. Porphyrins therefore occur in low concentrations in urine and body fluids.

Long-term exposure to PBBs in animals has also been associated with an increased risk of cancer, i.e. the induction of neoplastic nodules in the liver and in some cases hepatocellular carcinoma (E.M. Silberhorn, Crit. Rev. Toxicol., 20: 440-496, 1990).

More recently, developmental neurotoxic properties of PBBs have been documented in a study with C57B1/6 mice using FireMaster (FF-1), a commercial mixture of PBBs suspended in corn oil. In the absence of any significant effect of perinatal PBBs on weight gain of dams during gestation and postnatal body weight gain in pups, PBBs were found to significantly affect functional behaviour endpoints in offspring of both sexes, including sensory, motor and learning/memory (H.A. Tilson, Neurotoxicology and Teratology, 14:199-203, 1992). In the case of the Michigan farmers exposed to PBBs, neurotoxicity did not seem to be a problem.

These findings show that PBBs are immunotoxic in humans and porphyrogenic in animal models. PBBs were associated with an increased risk of cancer in animal experiments. Developmental neurotoxic properties were observed in animal experiments, but neurotoxicity was no problem in adult humans exposed to PBBs. Furthermore, PBBs seem to exhibit somewhat unclear effects on reproduction.

As PBBs are present in the environment and can be found in human milk and body fat samples, the toxicological and toxicokinetic pattern should be assessed and the presence of different PBB congeners should be thoroughly analysed in humans. An excellent possibility to obtain data on the PBB congener pattern in humans by non-invasive technique is the analysis of human milk (Dr Margret Schlumpf, Institute of Pharmacology, University of Zurich).

PBBs are persistent and accumulate in biota. Furthermore, they form dioxins and furans during incineration.

Polybrominated diphenyl oxides (PBDPOs)

Risk to human health: There are limited data on PBDPOs, but it seems that they do not present a major direct risk to human health. Therefore, according to Swiss toxic substances legislation, they are classified in class 4 (not very toxic). Evidence for this classification is also given by the UK risk-benefit study (John Rea, UK Department of Environment; part III – the PBDPO case study, 1993).

Risk to the environment: PBDPOs are supposed to form polyhalogenated dioxins and furans during incineration at low temperatures. Only recently the structures of some of the congeners have been identified. The toxicity of most of the possible (several thousand) congeners is unknown. Therefore, the most important congeners have to be identified before risk assessment of this group of compounds can be achieved.

United Kingdom

The Furniture and Furnishings (Fire) (Safety) Regulations 1988 require furniture and fillings and covers to meet specified performance requirements for ignition. Since their introduction, the number of deaths resulting from upholstery fires in the home has been dramatically reduced (245 in 1988, 150 in 1991). While part of this reduction may be due to other initiatives, such as the increased use of smoke alarms, the UK firmly believes that the improved flame retardancy of soft furnishings has saved many lives. The Regulations do not specify the use of any particular flame retardant system, but synthetic (non-cellulosic) textile covers currently appear to require the use of polybrominated diphenyl oxides (PBDPOs) to pass the tests.

The proposed 12th amendment to the EC Marketing and Use Directive (76/769/EEC) would ban the marketing and use of seven PBDPO congeners immediately, with the three remaining congeners following suit after five years. The proposal was considered by a UK Parliamentary Committee on 17th July 1991. The Committee endorsed the UK Government's view that PBDPO should not be banned until adequate and properly assessed alternatives with lower overall risk become available. An important consideration was the lack of evidence that the risks to humans and the environment associated with the use of PBDPO outweighed the benefits from increased flame retardancy.

The UK controls dioxin and furan emissions from municipal solid waste (MSW) incinerators by ensuring efficient operating conditions under the Environmental Protection Act (1990), using the concept of Integrated Pollution Control and BATNEEC (Best Available Techniques Not Entailing Excessive Cost).

Occupational exposures are subject to the Health and Safety at Work etc. Act (1974), and specifically the Control of Substances Hazardous to Health Regulations (1988).

The UK Department of the Environment has commissioned research aimed at developing techniques for risk-benefit analysis. PBDPO has been studied in a pilot project. Furan generation in fires and the possible bioaccumulation of PBDPO degradation products through the food chain are issues of concern that the UK believes should be investigated further.

The UK welcomes the work done by the IPCS to evaluate the available data on all brominated flame retardants. In addition, the UK and France have volunteered to act as rapporteurs for OBDPO and DeBDPO as priority substances under the EC Regulation No. 793/93 on the Evaluation and Control of the Risks of Existing Substances. This will lead to an EC risk assessment on these substances, building on the IPCS report, and includes the possibility of mandatory data generation if any further testing is considered necessary to refine these assessments.

United States

Polybrominated biphenyls (PBBs)

PBBs have been used as flame retardants in plastic for electrical equipment housing and a variety of other plastic products. The US Environmental Protection Agency (EPA) prepared a hazard assessment of the PBBs in 1979, which indicated that they are teratogenic, embryotoxic, and immunosuppressive in mice and rats, and carcinogenic in rats. In 1980, EPA published the results of a medical evaluation on 42 workers employed in a PBB production plant which showed that there was a higher prevalence of primary hypothyroidism among the PBB workers than in a control group. In addition, PBBs are persistent, accumulate in the environment and show similar toxicity to polychlorinated biphenyls. Industry found appropriate substitutes to the PBBs in the late 1970s and discontinued their production and use. To assure that industry did not resume the production and use of PBBs, EPA issued a significant new use rule (SNUR) (US *Federal Register* 52:2699) under section 5(a)(2) of the Toxic Substances Control Act (TSCA) that required anyone intending to resume the manufacture of eight specified PBBs to notify EPA 90 days prior to manufacture. This would give EPA an opportunity to review the information submitted regarding the intended production and use and take appropriate regulatory action. The PBBs subject to the SNUR and their CAS numbers are: 4-Bromo-1,1'-biphenyl (92-66-0); 4,4'-Dibromo-1,1'biphenyl (92-86-4); 2-Bromo-1,1'-biphenyl (2052-07-5); 3-Bromo-1,1'-biphenyl (2113-57-7); Decabromo-1,1'-biphenyl (13654-09-6); Nonabromobiphenyl (27753-52-5); Octabromobiphenyl (27858-07-7); and Hexabromobiphenyl (36355-01-8).

Polybrominated diphenyl oxides (PBDPOs)

Under section 4 of TSCA on June 25, 1991, EPA proposed (US *Federal Register* 56: 29140) that manufacturers of five brominated flame retardants test these substances for a variety of health effects (including cancer, chronic effects, reproductive toxicity, neurotoxicity, developmental toxicity, and mutagenicity), environmental toxicity, and chemical fate. The substances covered by this proposed rule and their CAS numbers are: decabromo diphenyl oxide (1163-19-5), hexabromocyclododecane (3194-55-6), pentabromodiphenyl oxide (32534-81-9), octabromodiphenyl oxide (32536-52-0) and 1,2-bis(2,4,6-tribromophenoxy)ethane (37853-59-1). We anticipate that this testing program will begin in 1994.

Eight brominated flame retardants are also subject to a TSCA test rule which requires that they be analyzed for the presence of brominated dioxins and furans. The rule was published June 5, 1987 (US *Federal Register* 52: 21412). The eight substances are: decabromo diphenyl oxide (1163-19-5), octabromo diphenhyl oxide (32536-52-0), pentabromo diphenyl oxide (32534-81-9), tetrabromobisphenol-A (79-94-7), tetrabromobisphenol-A-bis(ethoxylate) (4162-45-2), tetrabromobisphenol-A allyl oxide (25327-89-3), 2,4,6-tribromophenol (118-79-6), and 1,2-bis(2,4,6-tribromophenoxy) ethane (37853-59-1). The level of detection required by the rule is 0.1 ppb. for the tetrahalogenated dioxin; the range for the other contaminants ranges from 0.5 to 1000 ppb. All analyses required by the rule for the eight flame retardants should be completed by early 1994. Risk assessment activities will continue well into 1994.

Brominated flame retardant risk reduction case studies

In administering its authority to review new chemicals under the Toxic Substances Control Act (TSCA), the EPA, on a case-by-case basis, is requiring testing of new brominated flame retardants for dioxin and furans. The testing requirements may take the form of 1) analysis of the flame retardant for presence of dioxin and furan contaminants formed during its manufacture and/or 2) analysis of the combustion products of the flame retardant to determine if dioxins and furans are formed during combustion.

Statement of risk

In general, the US has not formed a national view concerning the risks of the brominated flame retardants because, as indicated above, we are in the process of developing additional information to better characterize risks posed by these substances.

CHAPTER 5

MECHANISMS FOR RISK REDUCTION

The brominated flame retardant risk management activities of 13 Member countries are described in this chapter. These descriptions, provided by each country, include information on steps taken in the past to reduce exposure to polybrominated biphenyls (PBBs), and proposed steps to reduce exposure to polybrominated diphenyl oxides (PBDPOs).

Country-specific risk management activities with regard to PBBs are summarized in **Annex A** to this chapter. (Similar tables for the other brominated flame retardants are not included, since no country has taken final action on these chemicals.) Lack of information in this document on a particular country indicates either that no risk reduction activities have taken place in that country, or that the country has not responded to requests for information.

In their responses, some Member countries did not distinguish clearly between their *national positions on current risks* (Chapter 4) and their *mechanisms for risk reduction* (Chapter 5). A few of these national statements have therefore been included in their entirety in both chapters, for ease of reference.

Austria

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- No specific actions have been taken to ban certain uses of selected BFRs or to implement major measures to control, limit or reduce their risks.

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Denmark has the point of view that, in principle, risk reduction of the BFRs should primarily address the source, and not-end-of pipe technologies.

The Danish risk reduction measures on BFRs are to phase out the most harmful BFRs, here PBBs and PBDPOs, and systematically evaluate the hazards and risk of others. Possible actions are legislation and voluntary agreements, and the means in preferential order are: substitution of flame retardant; substitution of the material; and, with lowest priority, recycling and incineration.

Risk reduction for the BFRs is clearly an international issue. Trade is spreading the substances worldwide, and the substances have applications in many different products. International action is therefore necessary to eliminate the use of the most harmful BFRs.

Finland

Polybrominated biphenyls (PBBs) may not be used in textile articles, such as garments, undergarments and linen, intended to come into contact with the skin (implementation of EC Directive 83/264).

France

France has implemented the EC Directive concerning PBBs and their use on textiles.

In connection with the draft EU Directive aimed at banning PBDPOs from the market, France and the UK will jointly undertake the risk assessment of octa- and decabrominated compounds within the context of Regulation 793/93/EEC on the evaluation and management of risks of existing substances.

As in the case of PBDPOs, the specificity of each individual member of the PBBs group should be taken into account. The preliminary results of a recent study (report available) on the phototransformation of decabromobiphenyl support this stipulation. The study showed that this compound, following adsorption on silica, was photohydrolized to polar compounds probably containing a hydroxyl function. Thus biphenyls substituted with fewer bromine atoms, which are of much greater concern, would not be formed.

Germany

Polybrominated diphenyls (and diphenyloxides) are regulated in a less direct way than under other European initiatives. In Germany, a second modification of the Chemicals Prohibition Ordinance was adopted in 1994. It imposes limits on chlorinated dioxins and furans and, for the first time, imposes limits on new *brominated* dioxins and furans. Prohibitions are placed on products and finished articles that contain greater than 100 ppb of 17 different 2,3,7,8-substituted PCDD/PCDF congeners and greater than 5 ppb of eight different PBDD/PBDF congeners. During an interim period of five years, the limit for the PBDD/PBDF will be 60 ppb."

Elsewhere in Germany, the Federal Institute for Workers' Protection (BAU) drafted a guide value in 1989 for tolerable workplace concentrations of 2,3,7,8-TCDD equivalents (TEQ) not to exceed less than 15 pg/m^3 TEQ. The BAU has proposed that similar limits be placed on exposure to PBDD/PBDF.

The German Government believes that a rigid regulation banning PBDPOs is necessary. German industry has shown since the late 1980s that it is possible to substitute these flame retardants with other halogen-containing substances or halogen-free substances, or develop more stable polymers or copolymers.

Prior to implementation of the regulation, declaration of PBDPO-containing plastic material may be a helpful instrument to protect consumers from PBDPOs and its degradation products.

Since the recycling of PBDPO-containing products increases the rate of dioxin and furan formation, such products must be destroyed in well equipped chemical waste incinerators until the production, marketing and application of PBDPOs has been prohibited.

The German Government strongly supports the regulatory activities of the EC.

Because of their high persistency and bioaccumulation it is necessary to ban the brominated biphenyls (PBBs), too. Furthermore, this group of chemicals is a potential precursor for the producing of PBDD/F at elevated temperatures.

Italy

So far, no action has been officially taken by Italy to ban uses of brominated flame retardants (BFRs) or control their risks. At present, some risk reduction measures have been taken, on a voluntary basis, by some public organizations and industries. Examples are the following internal standards adopted by: ENEL – National Agency for Electric Energy – and FS – National Railway – (CEI 20-37 standard); Milano City Underground (standard based on Sheet G 8998); and Marina Militare (NAVI 3A075 standard). The achievement of these standards tends to exclude the use of halogenated flame retardants.

Concerning the risk of BFRs, the following observations can be made:

- The use of polybrominated biphenyls (PBBs) should be avoided because of their intrinsic toxicity and bioaccumulation;

- Polybrominated diphenyl oxides (PBDPOs) are good substitutes for PBBs because of their lower toxicity and good biodegradability. However they can produce brominated dioxins and furans at some stage of their life cycle (e.g. manufacture and combustion);

- Banning of PBDPOs does not altogether exclude the formation of halogenated dioxins in cases of fires or incineration. In such cases, in fact, several halogenated compounds can provide a source for halogenated dioxins;

- The problems deriving from PBBs and PBDPOs are presently "gone round" by using other brominated or chlorinated organics; but these problems are not solved. In fact, the reasons why halogenated FRs should be banned is the production, on heating, of corrosive and toxic halogen acids, plus high optical density smoke;

- New FRs are proposed which are promising substitutes for halogenated FRs, but they need to be tested and evaluated in detail.

In conclusion, it would seem reasonable to: ban the use of PBBs and limit the use (the concentration) of PBDPOs and other halogenated FRs; to find other solutions when high concentrations of these additives are necessary; to stimulate and support research in this area and test/evaluate new available FRs.

Finally, it would be desirable, in our opinion, to address the problem of FRs in general, not just focus on the group of BFRs.

Japan

Risk reduction of chemical substances produced and used in Japan is principally controlled under the Chemical Substance Control Law based on their biodegradability, ability to bioaccumulate, and toxicities. Other controls include the Industrial Safety and Health Law, Poisonous and Deleterious Substance Control Law, etc.

Polybrominated biphenyls (PBBs)

Japanese industries continue to voluntarily restrict the production and use of these products.

Decabromodiphenyl oxide (DeBDPO)

In Japan, DeBDPO is currently produced and used with less than 3% of nonabromodiphenyl oxide as impurity.

DeBDPO is considered as a highly safe chemical based on the data of low toxicities and very low bioaccumulation ability.

Environmental monitoring results conducted by the Environmental Agency in Japan indicate that DeBDPO's accumulation in the environment is not at a significant level to threaten environment.

It is not necessary to take any actions to restrict the manufacture and use of DeBDPO in Japan.

Octabromodiphenyl oxide (OBDPO)

Since OBDPO is used as a mixture from hexa- to nonabromodiphenyl oxide, it has the possibility of containing the low brominated DPO as an ingredient of high bioaccumulation.

Further detailed studies will be necessary to evaluate the risk assessment of OBDPO.

Hexa and tetrabromodiphenyl oxide (HxBDPO and TeBDPO)

Japanese industries continue to voluntarily restrict the production and use of these products.

The Netherlands

The Netherlands bans the use of polybrominated biphenyls (PBBs) in textiles by implementation of the EC Directive 76/769/EEC.

Actions are taken by the industry to decrease the use of these brominated flame retardants in end products. Their use in the Netherlands has significantly decreased in the last years.

Licensing authorities are taking actions to control discharges from point sources.

A draft regulation concerning electrical devices is under way governing importers and producers' responsibility at the waste stage (including PBBs/PBDPOs).

Dioxin and furan emissions from municipal waste incinerators are controlled under "the decree on waste incineration 1993".

In the Netherlands a regulation governing these substances is under discussion. A decision on whether to promulgate this regulation is still on hold. The Dutch Ministry of Environment is in favour of promulgation, the Dutch Ministry of Economic Affairs esteems that it is highly important that these measures are taken on an international level.

In general, the Netherlands is in favour of measures governing these substances being dealt with internationally.

The Dutch government deliberately deals with the matter.

Sweden

The Swedish Government stated in a Government Bill, adopted by the Parliament in 1991, that the use of brominated flame retardants is to be restricted.

Sweden has banned the use of polybrominated biphenyls in textiles intended to come into contact with the skin, by implementation of the EC Directive 76/769.

Licensing authorities are taking actions to control discharges from point sources. Demands of substitution may be included.

Possible demands for recycling and producer responsibility concerning electrical devices are under investigation by the Swedish authorities.

Actions are taken by Swedish industry to substitute the brominated flame retardants. There are examples of substitution from, among others, the textile and the telecommunication industries.

As an example from the textile industry, a producer of fabrics for domestic and industrial uses reports that it has been possible to replace the brominated flame retardants by a new non-hygroscopic organic phosphorous/nitrogen compound in all products with one single exception. The original consumption of brominated flame retardants has been reduced by 80 per cent.

A producer of telecommunication equipment reports that, for both technical and environmental reasons, PBDPO flame retarded polybutylene terephthalate is substituted with Liquid Crystalline Polymer (LCP) in the production of male and female connectors. These connectors must achieve V-0 rating on the UL 94 Standard. LCP is halogen-free and fulfils the requirements without addition of flame retardants. The consumption of bromine will be reduced by approximately 10 per cent when the substitution is completed. The remaining part of the bromine is mainly used in printed circuit boards.

Switzerland

Summary of actions taken in Switzerland

By the Ordinance on Substances the manufacture, supply, import and use of *polybrominated biphenyls (PBBs) and terphenyls (PBTs)* and products containing these substances have been prohibited. By the same ordinance, the supply and import of capacitors and transformers containing *halogenated aromatic substances* such as polychlorinated and polybrominated biphenyls, halogenated diarylakanes or halogenated benzenes have been forbidden.

Information on brominated flame retardants risk reduction case studies

Within the scope of a quality label for non-flammable curtains developed by Swiss fire and accident prevention organisations, the Federal Office of Environment, Forests and Landscape has issued recommendations on flame retardants to be used. In accordance with these recommendations brominated aromatic flame retardants, among others, should not be used in this area.

Swiss statement on the rationale for taking actions

Polybrominated biphenyls have been generally prohibited together with all halogenated biphenyls and terphenyls. The reasons have mainly been the following:

- generally high persistency;

- accumulation in biota (e.g. adipic tissues) or other environmental compartments (e.g. sediments);

- possibility of the formation of hazardous transformation products (dioxins and furans);

- high human toxicity and high toxicity to environmental biota of some of its congeners and/or transformation products.

The prohibition of all halogenated aromatic substances in condensers and transformers is mainly based on the possible formation of hazardous transformation products at high temperatures.

Swiss legislation does not ask the environmental administration to assess all dangerous substances and applications of these substances and to propose, if necessary, regulation. But the legislation requires the manufacturer or importer of a substance, and a product/article containing such a substance, to carry out a so-called self-supervision. On that behalf he has to assess the environmental impact of what he puts on the market in order to make sure that his products/articles in their normal use do not present a hazard to the environment. This obligation also applies to the handling of any generated waste. To help the concerned people and organisations fulfil this task, the Swiss authorities have published a guide to self-supervision. As a consequence, manufacturers and importers of articles should not wait on a possible governmental action, but refrain on their own initiative from the use of critical chemicals. In assessing the environmental impact, the reasoning mentioned above on the prohibition of PBBs generally, and of halogenated aromatics in capacitors and transformers should be taken into account.

In consideration of the various problems during the manufacture, use and discarding of polybrominated diphenyl oxides (PBDPOs) and similar compounds and articles containing such chemicals, industry is urged to phase out their use as quickly as possible. One main argument is the lack – and also the factual impossibility – of an adequate waste management in practice. A 100 per cent return of used articles from the end user to a specialized collection point is not realistic; thus a high percentage of flame retarded articles ends up in municipal waste, i.e. in an incineration plant or in a landfill, both not adapted to special waste treatment.

United Kingdom

The main risk reduction mechanism affecting the use of polybrominated diphenyl oxides (PBDPO) in the UK is the Furniture and Furnishing (Fire)(Safety) Regulations 1988, which require furniture fillings and covers to meet specified performance requirements for ignition. This has led to an increase in the use of these substances to help prevent deaths in domestic fires.

The 1st and 4th amendments to the EC Marketing and Use Directive (76/769/EEC) control the use of tris (2,3-dibromopropyl) phosphate and polybrominated biphenyls (PBB) in textiles. These have been implemented in the UK.

The UK controls dioxin and furan emissions from municipal solid waste (MSW) incinerators by ensuring efficient operating conditions under the Environmental Protection Act (1990), using the concepts of Integrated Pollution Control and BATNEEC (Best Available Techniques Not Entailing Excessive Cost).

Occupational exposures are subject to the Health and Safety at Work etc. Act (1974), and specifically the Control of Substances Hazardous to Health Regulations (1988).

The UK and France have been jointly assigned DeBDPO and OBDPO as priority substances for risk assessment under the EC Regulation No. 793/93 on the Evaluation and Control of the Risks of Existing Substances. Assessments are now in hand. These may also address risks from PeBDPO. The Regulation provides for mandatory data generation if any further information, including testing, is considered necessary. This will lead to an EC-agreed risk assessment on these substances, building on the IPCS report. The Regulation requires the rapporteurs to recommend any risk reduction measures which may be needed.

United States

As discussed in the US Position on Risk [Chapter 4], the bulk of US activities concern the testing of the chemicals per se and testing to determine contaminant levels of brominated dioxins and furans. Consequently, a national view on risk reduction activities has not been defined due to the need to evaluate completed, ongoing, and planned testing. However, risk reduction activities need not wait until all testing is completed. This is because testing is occurring on these levels.

One level is testing of a number of existing flame retardants for brominated dioxin/furan contamination. This testing should be completed in 1994 and risk assessment may lead to risk management recommendations for one or more substances.

The second level is testing of certain flame retardants to determine their direct hazard potential. Final decisions on the testing required will be made in early 1994. Completion of the testing will take a number of years. Thus risk assessment/management actions are not imminent.

The third level is testing on a case-by-case basis of new brominated flame retardants for dioxin/furan contamination from manufacture and/or resulting from combustion. This testing could lead to risk management decisions on a chemical-by-chemical basis.

ANNEX A (TO CHAPTER 5)

Country-specific Actions Taken or Proposed on PBBs

Country	Actions
Australia	
Austria	Prohibits the manufacture, placing on the market, import and use of PBBs and products containing these substances.
Belgium	
Canada	Prohibits the manufacture, use, processing, offer for sale, selling or importation of PBBs for commercial, manufacturing or processing purposes.
Denmark	Implements EC Directive 89/677 banning the use of PBBs in textiles.
Finland	May not be used in textile articles intended to come into contact with the skin (in accordance with EC Directive 83/264).
France	Implements EC Directives concerning PBBs and their use on textiles.
Germany	
Greece	
Iceland	
Ireland	
Italy	
Japan	
Luxembourg	
Mexico	
Netherlands	Proposed resolution would prohibit the storage of PBBs or products or preparations containing these substances or making them available to third parties. (Exports are excluded from resolution.)
New Zealand	
Norway	
Portugal	
Spain	
Sweden	Ban on PBBs in textiles intended to come into contact with skin by implementation of EC Directive 76/769.
Switzerland	Prohibits manufacture, supply, import and use of PBBs and products containing these substances. Supply and import of capacitors and transformers containing PBBs is forbidden.
Turkey	
United Kingdom	
United States	No current production or use. Companies intending to resume manufacture must notify EPA 90 days in advance for approval.

APPENDIX 1

OVERVIEW OF FLAME RETARDANT CHEMICALS AND COMPOUNDS

This Appendix presents an overview of the flame retardant industry, in order to put the use of brominated flame retardants into perspective. Particular attention is paid to non-brominated flame retardants currently on the market.

A major source for the following data and discussions was industry literature. This Appendix does not contain a thorough analysis of environmental impacts, application status, and technical and cost comparisons. The OECD has not evaluated the substances described in this Appendix, and does not recommend them as replacements for brominated flame retardant chemicals or polymers or final products that contain brominated flame retardants.

Criteria for Selecting a Flame Retardant

Flame retardant applications cover several industrial stages, from base chemicals to materials or parts used in semi-finished or end products. Bromine based chemicals are one of the ways to achieve flame retardancy.

The choice between flame retardant chemicals is governed by several criteria:

- **Base chemical content** is related to the possible reduction of the flame retardant chemical concentration in the compound, cost reduction, and minimizing the effect on mechanical properties of the end product, such as tensility, flexibility and elongation.

- **Product price** is primarily considered as part of the total formulation costs (flame retardant chemicals + polymer + other additives + compounding) and is secondarily related to the product amount required or premium price ascribed to the end product.

- **Thermal stability** of the product during its mixing (compounding) and transformation process (moulding, extrusion, calendering, coating, etc.) is reflected by its thermogravimetric analysis (TGA factor) and is preferably similar to that of the polymer concerned.

- **Compatibility** of FR additives with the polymer or textile treated avoids their migration to the surface, which reduces the permanency of the flame retardancy treatment and results in surface disruption in the end product (blooming effect).

- **Blendability** or melting related to the impact strengths (izod) and product purity, especially with reference to electrical and electronic end uses.

- **Exposure potential** at each life cycle stage of the FR chemical:

  - production and transport of raw materials;
  - manufacturing and supply of FR chemicals;
  - compounding, formulation or FR treatment;
  - transformation or processing;
  - assembling of semi-finished products;
  - use of end products and service life; and
  - waste disposal, recycling or incineration.

Demand for Flame Retardants

The worldwide demand for flame retardant chemicals in 1992 is estimated at over 600,000 tonnes. This includes over a hundred products and can be classified according to base chemical content:

Base chemicals	Volume of FR chemicals (tonnes)
bromine	150,000
chlorine	60,000
phosphorous	100,000
antimony	50,000
nitrogen	30,000
aluminium	170,000
other	50,000

Overall, the annual growth rate in the demand for FR chemicals is expected to be far greater than that for polymers and textiles, the major substrates for FR chemicals (see below).

This is based on forecasts of greater national requests for flame retarded end products and more harmonization of FR test procedures (particularly in the EU). In addition, the current geographical distribution of worldwide production is likely to undergo major changes as companies move the production of semi-finished or finished products to countries that are only limited consumers of such products.

Application of Flame Retardants

To put the use of flame retardants into perspective, one needs to examine the demand for plastics and textiles. When broken down by geographic regions, OECD countries continue to lead in total demand; however, their rate of growth is slower than in the rest of the world.

World Main Plastics and Synthetic Fibers Demand

Polymers (million tonnes)	**1991**	**1996**	**2005**
LDPE	13.8	14.9	16.4
LLDPE	5.1	8.5	15.7
HDPE	12.1	15.5	22.3
PP	13.9	19.1	30.4
PVC	17.7	21.2	27.8
PS	9.0	11.1	14.9
ABS/SAN	2.7	3.6	5.1
Total	**74.3**	**93.9**	**132.5**
of which:			
Western Europe	21.1	24.1	30.7
US and Canada	19.0	23.7	30.6
Japan	8.3	9.4	12.0
Fibres (million tonnes)			
Polyester	9.1	11.3	15.0
Polymide	3.7	4.1	4.7
Acrylic	2.4	2.6	2.8
Polypropylene	2.6	3.2	3.9
Others	0.3	0.5	0.8
Total	**18.1**	**21.7**	**27.2**

(C. Fryer, February 1993)

Flame Retardant Chemicals (Other than Bromine Based)

Chlorinated flame retardants

Over 80 per cent of the estimated volume use of chlorine based flame retardant chemicals is for the chlorinated paraffins (CP), the most popular and comparatively inexpensive of the halogenated FR chemicals. Their aliphatic chlorine content varies, according to grade, from 40 to 70 per cent and ranges from liquid to powder form as the chlorine content increases. CP are more frequently used in powder form (70 per cent chlorine content) to limit their negative plasticizing effect.

The present demand volume of 50,000 tonnes/year seems realistic if their application as FR chemical additive for thermoplastics, thermosettings, paints, textile fabrics, rubbers, adhesives and sealants (by order of importance) alone is considered.

Other chlorinated FR chemicals include, notably, hexachloroendomethylenetetrahydrophthalic – HET – acid or anhydride, Diels-Alder derivatives of hexachlorocyclopentadiene (C-5.6) containing 55 per cent chlorine, and tetrachlorophthalic anhydride – TCPA – containing 60 per cent chlorine.

These chemicals are used as FR reactive intermediates for the esterification polymer processes, notably in unsaturated polyester (UPE) and alkyd resins.

Dodecachloropentacyclooctadecadiene, another C-5.6 adduct of cyclooctadiene, containing 65 per cent chlorine, is used as an FR additive for polyolefins and nylon compounds.

Formulations and Performance of Chlorinated Flame Retardant Polymers

Formulation based on (%):	**High Impact Polystyrene (HIPS)**	**Acrylonitrile Butadiene Styrene (ABS)**	**Nylon 66 (PA 66)**
Polymer	77	62.8	70
C-FR / C-FRH	18	16.0	20
Sb_2O_3	4	5.5	10
Other additives	1	15.7	-
Performance:			
UL-94 3.2 mm	V-0	V-0	V-0
Afterglow (sec)	0	-	-
1.6 mm	V-0	V-0	V-0
Afterglow (sec)	85	-	-
Notched izod (j/m)	100	230	-

C-FR/C-FRH = Dodecachloropentacyclooctadecadiene

(R. Markezich, January 1992)

Phosphorous-containing flame retardant chemicals

The present annual demand for phosphorus-containing FR chemicals is about 100,000 tonnes. Thirty per cent of the FR phosphorus chemicals contain halogens.

Some products of this group, generally the phosphates, are used in combination with halogenated FR chemicals to increase FR performances (synergistic effect), instead of antimony.

This use is motivated by the requirements for translucency of the end FR product. A typical example of this application is the FR formulations for translucent panels used in building roofings.

The FR chemicals included in this group are classified as follows:

FR phosphorus chemicals	**Major FR applications**
Phosphoric acid esters	Vinylic compounds
Red phosphorus	Polyamide resins
Polyphosphates	Cellulosic materials
Phosphonium salts	Textile fabrics
Phosphate polyols	Polyurethane foams
Phosphonate polyols	Polyurethane foams
Chlorinated phosphates	Polyester compounds
Phosphonium chlorides	Cellulosic materials
Chlorinated phosphonates	Polyurethane foams
Mixtures bromo-phosphates	Engineering plastics

Red phosphorus has been suggested as a flame retardant additive for a wide variety of plastics. However, it is most efficient in oxygen-containing polymers such as polycarbonate resin and polyethylene terephthalate.

Red Phosphorus Concentration Required for UL-94 VO Rating

Resin	**Concentration (%)**
Polyamide	7
Polycarbonate	1.2
Polyethylene	10
Polyethylene terephthalate	3
Polystyrene	15
Filled phenolic resin	3

(Albright and Wilson, Data Sheet)

Red phosphorus is used commercially in flame retarding nylon. High levels of colour pigments will overcome the red colour. There are risk factors working with red phosphorus including flammability and auto-ignition. Disproportionation will give toxic phosphine. Suitable stabilization and encapsulation have led to commercial concentrates with 50 per cent red phosphorus, the remainder being polymer in which the phosphorus is embedded.

Phosphates/phosphonates	**In commercial application**
Tris(chloropropyl) phosphate	Polyurethanes, resins, coatings
Triethyl phosphate	Polyurethanes, resins
Reactive amino alkyl phosphonate	Polyurethanes, resins
Tricresyl phosphate	PVC, rubber, phenolic, PUR, paints, coatings
Trioctyl phosphate	PVC, rubber, PUR, pigment pastes
Triphenyl phosphate	Phenolic, cellulose acetate, paints, coatings
Diphenylcresyl phosphate	Phenolic, polysulphide, PVC, rubber, coatings
	In developmental stage
Reactive di-functional phosphonate	Thermoplastics, polymers
Diethylethane phosphonate	Polyurethanes, resins
Non-volatile aromatic phosphate	Thermoplastics, polymers
Dimethylpropane phosphonate	Polyurethanes, resins
Non-reactive, oligomeric phosphonate	Polyurethanes, resins
Aromatic phosphinate	Polyurethanes, resins

(H.P. Laubenheimer, March 1993)

Trialkyl phosphates, phosphonates and triethyl phosphates are used in unsaturated polyester resins to reduce the viscosity of highly filled products (ATH and calcium carbonate). They also serve as a synergist in halogenated polyesters. Less volatile trialkyl phosphates are commercially available, specifically tributyl-, trioctyl- and tris-butoxyethyl phosphate.

Several high phosphorus products are available commercially. Dimethyl methylphosphonate, $CH_3P(O)(OCH_3)_2$ (25 per cent P), can also be used in highly filled unsaturated polyesters to lower viscosity and improve flame retardancy. Antiblaze 19 (mixtures $n = 1$ and 2) and 1045 ($n = 2$) are high phosphorus-containing products (21 per cent P) with lower volatility. Suggested applications for these products include urethane foam, polyester fabric and nylon.

(J. Green, December 1992)

Aryl phosphates' major commercial uses include polyvinyl chloride (PVC), cellulose acetate and modified PPO resin (Noryl). Triaryl phosphates include triphenyl (mp 49-50°C), isopropyl- and *t*-butyl-substituted triaryl, and resyl phosphates. Two alkyl diaryl phosphates are also commercially available. A diphosphate of reduced volatility is made with resorcinol as the linking group. The flame retardants used commercially are the alkylated triaryl phosphates. A UL-94 V-0 product at 1/16" is obtained with about one per cent phosphorus. Non-halogen, flame retarded polycarbonate/ABS resins use triphenyl phosphate as the flame retardant. A UL-94 V-0 product at 1/16" contains about 1.2 per cent phosphorus or about 13 per cent triphenyl phosphate.

Reactive phosphorus compounds. Phosphorus polyols have been used as reactives for rigid polyurethanes. A phosphine oxide diol and triol have also been reported and recommended as reactive for polyurethane, PET, and epoxy resin. Reactive phosphorus compounds have been used to prepare flame retardant polyester (PET) fibre.

Chloroalkyl phosphates and phosphonates. A number of chlorophosphates and diphosphates are available commercially. A major application is for flexible polyurethane foam. A bromochlorophosphate has also been suggested for flexible polyurethane application. These products are not stable to the exotherm which takes place during the foam curing, and discolouration takes place.

Brominated phosphates are recommended for use in polypropylene fibre with excellent colour, no bloom and good UV stability. No antimony oxide is required for the fibre application. Brominated phosphates contain 3-4 per cent phosphorus and 60-70 per cent bromine. Moulding resins contain 5 per cent of brominated phosphates and 2.5 per cent antimony oxide for a V-2 rating.

Applications are also suggested as flame retardants for ABS, polycarbonates, PBT, PET, and blends of PC/PBT, PC/PET or PC/ABS. Brominated phosphates melt at 110°C, are melt blendable, and function as a processing aid allowing for the mouldings with thin walls required for current day miniaturization.

Ammonium polyphosphates consist of an ammonium polyphosphate based, non-halogenated system that contains no chlorine, bromine or antimony trioxide. The absence of these chemicals significantly reduces the generation of smoke and corrosive gases typical of conventional flame retardants, which can harm electronic equipment.

These products are thermally stable at processing temperatures as high as 240 degrees C and are designed to achieve a UL-94 VO rating in thermoplastics such as polyethylene (PE), polypropylene (PP), thermoplastic polyester elastomers (TPEs), and ethylene-vinyl acetate (EVA).

(D. Scharf, October 1992)

Nitrogen based flame retardants

Nitrogen based compounds can be designed to work as flame retardant systems or to form part of flame retardant formulations in many applications. They have always attracted the attention of scientists, as one can see by the filing date of many patents. N-containing compounds are a relatively small group of flame retardants.

A logical application is nitrogen-containing polymers such as polyurethanes and polyamides, in which the flame retardant does not add any other elements to the system than are already present in the polymer. From an environmental point of view, this is significant.

Nevertheless, nitrogen-containing flame retardants are not limited to these polymers. Applications in polyolefins, polyvinylchloride, and intumescent paint systems are known. Development work for applications in polystyrene is well under way. Nitrogen-containing flame retardant systems are a commercially available alternative to halogenated flame retardants.

(Grabner, February 1993)

Melamine derivatives	**In commercial application**
Melamine cyanurate	nylons (PA); terephthalates (PET/PBT)
Melamine	polypropylene (PP); polyethylene (PE)
Melamine phosphate	terephthalates (PET/PBT)
	In developmental stage:
Melamine cyanurate	epoxy resins; polyurethanes (PUR)
Melamine phosphate	epoxy resins; polyurethanes (PUR)
Melamine salts	thermosets
Melamine formaldehyde	unsaturated polyesters (UPE)

(C. Boelens, March 1993)

Aluminium trihydroxide (ATH)

ATH is sometimes called alumina trihydrate, but more correctly aluminium trihydroxide, $Al(OH)_3$. ATH is used as a flame retardant/smoke suppressant in a wide variety of applications. It is produced industrially from bauxite. The term bauxite refers to an ore, or mixture of minerals, formed by the weathering of aluminium-bearing rocks. The parent rocks, which may be igneous or sedimentary, are often nepheline ($3Na_2O.K_2O.4Al_2O_3.9SiO_2$), serpentine, granite, diorite, basalt, dolerite, crystalline schists and limestone-containing clay minerals. Significant bauxite deposits are found in a variety of locations including Australia, Jamaica, Ghana, Brazil, India and Surinam.

ATH is manufactured from bauxite by the Bayer process, the essential features of which remain as they were when the process was invented by Karl Josef Bayer in Austria and patented by him in 1888. The bauxite is digested with caustic soda under pressure to form sodium aluminate solution. This leaves behind most of the impurities, predominantly iron oxide, titania and silica, as an insoluble residue. The clear, filtered sodium aluminate solution is diluted and cooled, and a seed of ATH is added. The sodium aluminate solution hydrolyses on the surface of the seed to form crystalline ATH. Finally, the ATH is filtered off and dried.

ATH was known as a flame retardant during the 19th century. However, despite interest during the 1920s and 1950s it was not until the mid 1960s that a sustained growth in this use began. Initial applications in unsaturated polyester carpet backings were very much as simple partial replacements for the chalk fillers that had traditionally been used.

Through the 1970s and 1980s the particular benefits of ATH, including good purity, cost effectiveness, non-corrosivity and combined flame retardancy/smoke suppression, resulted in a much wider range of applications.

(N.G. Mead and S.C. Brown, January 1993)

Magnesium hydroxide

Magnesium hydroxide offers a variety of advantageous properties such as no emission of acidic gases (only water is generated during decomposition), high thermal stability (up to 340°C) and very efficient smoke reduction. Its main disadvantage is the high loading level of more than 60 per cent to pass UL-94 V-0.

While the use of high loading levels of inorganic flame retardant fillers in the wire and cable industry have been well known for more than 15 years (with loadings up to 70 per cent), compounders in the area of thermoplastic injection moulded parts are usually not familiar with high filler amounts. Therefore the main objective is to combine the experience of the compounder, polymer producer and supplier of flame retardants, in order to adjust polymer, additives, formulation and compounding technology to meet requirements.

The flame retardant properties of magnesium hydroxide-filled ethylene vinyl acetate (EVA) demonstrate that 65 per cent loading by weight is required to yield UL-94/V-0 at 1/8". For jacketing applications, this flammability performance is usually acceptable. A slight increase in magnesium hydroxide filling rate upgrades the rating to UL-94/V-0 classification at 1/6". Magnesium hydroxide in PA 6 can achieve UL-94/V-0 performance up to 1/32", even with glass fibre reinforcement.

Additional work will be done to improve compound properties such as impact strength, elongation and heat stability (HDT). Polyamide 66 (PA 66) formulations flame retarded with magnesium hydroxide have also been developed. Commercial polyamide compounds based on the flame retardancy of special magnesium hydroxides were introduced into the market two years ago. Today various halogen-free PA compounds are available for injection moulding, allowing a UL 94 (1/32") V-0 rating.

(Kirschbaum, February 1993)

Zinc borates [$(ZnO)_x(B_2O_3)_y(H_2O)_z$], molybdenum oxide ($MoO_3$) and tin compounds ($SnO_2$)

These FR chemicals are industrially considered as complementary products or FR fillers in the compounding of plastics. The FR regulation requirements on reduction of opacity or volume of combustion gases has led to the development of the application of these FR metallic additives in plastic compounding.

The effect of zinc borates in the smoke reduction of halogen based FR plastic is well recognized, with magnesium and molybdenum derivatives also providing this function.

More recently tin compounds, SnO_2, $SnO_2.xH_2O$, $ZnSnO_3$, and $ZnSn(OH)_6$ have been introduced as smoke and carbon monoxide suppressants.

Halogen-free intumescent technology

This technology is based on various proprietary chemical products and formulations and can be a halogen-free technology for polyolefins, urethanes, polyamides and other polymers which require flame retardant applications. Base chemicals concerned are, notably, poly-triazinylpiperazine and polyimidazoidinone.

Intumescent technology has well recognized advantages in terms of flame retardant effectiveness, smoke release, corrosivity of the combustion gases, and physical properties of the polymer treated. Intumescent systems are produced in Italy, Germany, the US and Israel.

The intumescent polymer systems are suitable to produce mainly injection moulded and extruded parts, which are required to possess high flame retardant performances (V-0 or more stringent standards) as well as reduced hazard due to fire smoke and corrosive gases.

(O. Cicchetti, February 1993)

Commercial and Developmental Applications of Intumescent Flame Retardants

Commercial applications

Polypropylene:

Containers for electronic equipment
Electric trunkings and conduits
Big battery housing for industrial use
Appliance boxes and internal parts
Electric derivation boxes in buildings

Polyurethane:

Packing systems
Acoustic insulation

Developmental applications

Polypropylene:

Deflection units
Television backs
Appliance housings

Polyethylene:

Electric trunkings
Waste water pipes
Mining ducts
Pallets

Polyamides:

Multiconnectors

(O. Cicchetti, February 1993)

Flame Retardant Polymers

The German Electrotechnical and Electronic Association (ZVEI) has summarized alternatives to PBDPOs that can be used as flame retardants in several polymer based systems.

Flame Retardant Alternatives

Flame retardants:	**Brominated diphenyl oxide alternatives**	
Polymer base	**Halogenated**	**Halogen-free**
Polyethylene **(PE)**	Chloroparaffins Hexabromocyclododecane Ethylene bis(tetrabromophthalimide) Brominated polystyrene TBBPA derivative	Aluminium trihydrate Red phosphorus
Polypropylene **(PP)**	Ethylene bis(tetrabromophthalimide) TBBPA-dibromopropylether TBBPA-dibromoglycidylether	Magnesium hydroxide Red phosphorus Intumescent systems
Polystyrene **(PS)**	Chloroparaffins Hexabromocyclododecane TBBPA-dibromoglycidyelther Poly(dibromophenylenoxide) Poly(pentabromobenzylacrylate)	PS-PPO blends with phosphate esters
Acrylonitrile-Butadiene-Styrene **(ABS)**	TBBPA Hexabromocyclododecane TBBPA carbonate oligomer	ABS-PC blends with phosphate esters
Polyamides **(PA)**	Brominated polystyrene Ethylene bis(tetrabromophthalimide) Poly(dibromophenylenoxide) Poly(pentabromobenzylacrylate) "Dechlorane"[1]	Melamine-cyanurate Red phosphorus Magnesium hydroxide
Polybutylene terephthalate **(PBT)**	Ethylene bis(tetrabromophthalimide) TBBPA carbonate oligomers Poly(pentabromobenzylacrylate) Poly(dibromophenylenoxide)	
Polycarbonate **(PC)**	TBBPA carbonate oligomers TBBPA Poly(pentabromobenzylacrylate)	Phosphate esters with PTFE

(ZVEI, December 1992)

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[1] "Dechlorane" is a trade name. The chemical name is dodecachloropentacyclooctadecadiene.

Ethylene and Propylene Polymers

Polyethylenes (LDPE, HDPE), polypropylene (PP), ethylene vinyl acetate (EVA), ethylene propylene rubber (EPDM), etc. are several commercially available polymers that can use additives to achieve flame retardancy. For halogen additives, the following can be used: TBBPA derivatives, brominated imides, chloroparaffins and dodecachloropentacyclooctadiene. Halogen-free polyolefins can be made from phosphorus and/or nitrogen based chemicals or by the use of metallic hydroxides.

Low halogen content for polypropylene and its blends based on particular nitrogen/bromine-containing chemical structures does not produce corrosive acid components or free bromine during pyrolysis. In fact, due to the specific thermo-degradation mechanism, all the bromine content is evolved as ammonium bromide, which is not corrosive.

Due to the low halogen content and action mechanism, low obscurant smoke is emitted during the burning of polymer compounds with these systems. The results are similar, for V2 grades, to those for neat polymers.

(O. Cicchetti, February 1993)

Polystyrene

Brominated FR alternatives for HIPS based on DeBDPO are the compounds based on hexabromocyclododecane (HBCD), brominated polystyrene (BrPS), tetrabromobisphenol A (TBBPA) and its derivatives, and polymers of dibromostyrene. More recently, the use of decabromodiphenyl ethane and/or ethylene-bis-tetrabromophthalimide (EBTBP) is also suggested. The FR industry has also considered a non-brominated adduct of C-56 (dodecachloropentacyclooctadeca-diene) in a mixture with ammonium polyphosphate (afterglow agent) as a DeBDPO replacement alternative, as well as chlorinated paraffins.

The choice of other polymer based FR compounds can be considered as alternatives to HIPS based DeBDPO for several end uses. The main options appear to be mixtures of polyphenylene oxide (PPO) and polystyrene (PS) containing non-halogenated FR additives (phosphorus based), the FR polycarbonate (PC) based on TBBPA derivatives or phosphorus, the ABS/PVC blends, and halogen-free flame retardant polypropylene (PP). Of these compounds, halogen-free seems to be the option of choice.

These substitutions will inevitably include the cost of changing the moulds used for FR HIPS end products like back panels. Given the frequency of changes of style in the television production industry, this is economically acceptable in the adaptation of television industrial design.

An HIPS resin with approximately 5 per cent rubber content was used in the following table. It was prepared on the Haake at 220-240°C and injection moulded on the Battenfeld at 205-210°C. The formulation consisted of 12 per cent flame retardant, 4 per cent antimony oxide, and the balance resin.

Physical Properties of High Impact Polystyrene (HIPS) FR

Based on:	**DEBDPO**	**EBTBP**	**TDBDPB**
UL-94 1/8"	V-0	V-0	V-0
HDT, °C 264 psi	87	88	89
Izod, 1/8"	1.7	0.7	1.0
Moulding colour	white	yellow	white
HPUV (3-year) ΔE2	35.55	5.36	17.01

(C. Abbott and B. Sutker, Ethyl Corp.)

Acrylonitrile Butadiene Styrene

Listed below are non-diphenyl oxide brominated chemicals that can be used in the formulation of flame retardant ABS compounds:

- bis(tribromophenoxy)ethane (HBPE)
- tetrabromobisphenol A (TBBPA) and derivatives
- brominated polystyrene (BrPS)
- tetrabromophthalic (TBPA) derivatives
- polymer of dibromostyrene (PDBS)

Some of these are already in commercial use, such as the TBBPA carbonate and epoxy oligomers. Flame retardant ABS-polycarbonate (PC), modified polyphenylene oxide (PPO) and polycarbonate halogen free compounds can be considered as alternatives to brominated ABS.

(Pendleton, February 1993)

Physical Properties of Acrylonitrile Butadiene Styrene (ABS) FR

Based on:	**DeBDPO**	**OBDPO**	**TDBDPB**	**TBBPA**	**HBPE**
Oxygen index	27.1	28.3	31.2	33.7	25.8
UL-94, 1/8"	V-0	V-0	V-0	V-0	V-0
1/16"	V-0	burn	V-0	V-0	burn
Tensile, psi	5850	6350	5600	4850	5760
Flex.mod.psix10^5	2.5	2.9	3.3	3.9	2.9
Vicat, 1/8" (°C)	102	97	102	85	96
Izod, 1/8"	0.7	1.4	0.6	0.5	1.3
HPUV (3 year ΔE)	18.8	19.1	7.3	4.8	9.1
D_m	420	411	426	480	462
T_{16}, min.	2.8	3.3	3.0	2.8	3.3

D_m is the maximum smoke evolved in the ASTM E662 smoke density test when run in the radiant mode. (Low numbers signify less smoke.) T_{16} is the time it takes to obscure vision of an article 16 feet away from the smoke source. (High numbers signify more time.)

A commercial unmodified ABS resin was used. It was prepared on a Farrel Banbury type 00 mixer at 150-175°C and injection moulded on a Battenfield BSKM 100/40HK at 205°C. All flame retardants were used at a rate to provide 14 per cent aromatic bromine. Antimony oxide was used at 4 per cent, and the balance was resin.

A modification in formulation, i.e. more rubber, could permit the compounds to achieve acceptable Vicat and Izod yet retain the other benefits of TDBDPB.

(C.J. Abbott and B.J. Sutker, November 1985)

Other Flame Retardants in ABS RESIN

	PDBS-10	**DE-79**	**FF-680**	**DeBDPO**	**BA-59P**
Loading, wt. %					
Flame retardant	21.0	16.0	18.5	14.0	18.3
Sb_20_3	4.0	4.0	4.0	4.0	4.0
CPE-4213	5.0	5.0	5.0	5.0	5.0
UL-94, 1/16"	V-0	V-0	V-0	V-0	V-0
Izod impact, ft-lb/in (1/8")	1.5	3.6	4.0	1.5	1.0
HDT, F, 264 psi (1/8")	181	164	154	168	148
Melt flow, g/10 min	1.6	2.1	2.9	1.5	3.4
Tensile yield, psi	6400	6700	5200	5300	6200
Elongation, %	10	17	11	13	5
Flexural yield, psi	9500	11100	8400	9300	10500
Flexural modulus, psixE5	3.25	3.30	3.20	3.24	3.60
Hardness, R-scale	94	97	93	98	92

PDBS = poly(bromostyrene)
DE79 = OBDPO
FF-680 = bis(tribromophenoxy)ethane
BA-59P = TBBPA

(Product Information, Great Lakes, September 1992)

Thermoplastic Polyesters

Flame retardant polyethylene terephthalate (PET) can be produced without diphenyl oxide by the use of:

- ethylene-bis-tetrabromophthalimide
- tetrabromobisphenol A (TBBPA) oligomers
- brominated polystyrene (BrPS)
- poly-pentabromobenzyl acrylate
- poly-dibromophenylene oxide
- brominated epoxy oligomer

Halogen-free thermoplastic polyester flame retardant compounds are not presently on the market. Consequently, only alternatives based on other flame retardant polymers need to be considered at the end-users level, e.g. polyphenylene sulphide (PPS), polyphthalimides (PPA), halogen-free polyamides (PA) or thermosetting moulding compounds.

Physical Properties of Polybutylene Terephthalate (PBT) Flame Retardant

Based on:	**DeBDPO**	**EBTBP**	**TDBDPB**
Oxygen Index	36.1	33.7	36.4
UL-94 1/8"	V-0	V-0	V-0
UL-94 1/16"	V-2	V-2	V-2
Tensile, psi	$1.3x10^4$	1.2×10^4	1.2×10^4
Flex. mod., psi	9.6×10^5	9.5×10^5	9.0×10^5
HDT, °C 264 psi	205	210	208
Izod, 1/8"	1.02	1.00	1.19
Moulding colour	off-white	lt. yellow	off-white
Bloom, 1 week at 140°C	light	none	very light

Polyamides

Flame retardant nylons include the use of polyamides (PA) 6, 6-6, 11, 12 and several copolymers with or without glass fibre reinforcements. The most used PA 6 and PA 6-6 flame retardant grades are formulated with several flame retardant additive options based on:

- brominated (non-diphenyl oxides):
    - polydibromostyrene (PBDS)
    - poly-dibromophenylenoxide
    - tetradecabromodiphenoxybenzene
- chlorinated:
    - dodecachloropentacyclooctadecadiene
- halogen-free:
    - red phosphorus
    - melamine
    - melamine-cyanurate
    - magnesium hydroxide

Physical Properties of Polyamide (Nylon 66) FR Compounds

	DeBDPO	**TDBDPB**
FR addition level, %	10	10
UL-94, 1/16"	V-0	V-0
Tensile, psi	$1x10^4$	$1x10^4$
Elongation %	16	14
Izod, 1/8"	0.67	0.80

The resin used was a type 66 Nylon containing no filler. It was prepared on the Haake at 250°C and on the Battenfeld at 270°C. All the formulas contained 5 per cent antimony oxide, with the balance being flame retardant and resin.

Unsaturated Polyester (UPE)

Six thousand tonnes of the European flame retardant UPE market is covered by resins based on chlorinated chemicals (hexachloroendomethylene tetrahydrophthalic acid, chlorostyrene, etc.) or brominated reactive flame retardants (dibromoneopentyl glycol, tetrabromophthalic anhydride, etc.).

The replacement of unsaturated polyester by phenolic resins with inherent flame retardancy and reduced smoke generation are considered as alternatives for several end uses.

(P. Canard, February 1993)

Flame Retardant Semi-finished Products

A large number of industrial sectors that are subject to flame retardant regulations produce finished products that contain flame retardant base polymer materials. In the list that follows there are several examples, compiled by Troitzsch (CEM 1989), of flame retarded polymers in different finished products in Germany.

Flame Retarded Polymers by Application (Germany)

Construction materials	***Made of (base polymer)***
Roofing	
Roof sheeting (as roof seal vapour and wind barrier)	PE, PVC sheets
Coated fabric for inflated structures	PVC on polyester fabric
Insulating boards and sheeting (flat roof, steep roof)	PS, PUR foams
Facing	
Outer wall insulating boards (also heat retention system)	PS, PUR, PF foams
Outer wall coverings, facing elements	PVC, PC
Wind and facing elements protection boards	PC
Balcony coverings, parapets	HIPS
Interior	
Ceiling, facing and heat insulating boards	PS, PF, PUR foams
Structural sound insulating boards	PS foams
Pipes, sleeves (domestic drain pipes)	PP
Insulating tubing (pipe insulation)	PE foam, PVC elastomer
Insulating shells (pipe insulation)	PS, PE, PUR foams
Wiring conduits, ventilation ducts	PP
Curtains, decorative materials	Polyester fabric
Vertical louvres	PVC
Partition curtains	PVC
Wall coverings	PVC foam, PP
Floor coverings	PVC, PA, polyester, cotton

Transportation	***Made of (base polymer)***
Interior roof	PVC, PUR foams
Sliding roof	PMMA, PC
Interior lining	PUR foam, PVC, ABS/PVC, polyamide fabric
Head rests, seats	PUR foam, PVC, polyamide fabric
Dashboard	PUR foam, PVC
Brackets, shelves	PP, PA, PVC, PUR, ABS, PC/ABS
Instrument panel	PUR, PVC, PA, PP, PPO mod., PC/ABS
Steering wheel	ABS, PVC, PUR, PP
Heating, ventilation	PP, PA, PVC, PPO mod., ABS

(continued next page)

Electrical and electronics	***Made of (base polymer)***
Switches, plugs	PC, PBT
Sockets	PA
Switch casing	PC, PA, PET
Transformer casing	PC
Relay parts	PC, PBT
Plug-in connections, multi-point connectors	PC, PBT
Insulators	PC
Switch boxes	PC
Terminal strips, securing elements	PA
Automatic cut-outs	PA
Coil formers	PC, PA, PBT
Meter casings, electrical switch boxes	HIPS, PP
Printed circuit boards, laminates	PF, epoxy
Adhesives	epoxy
Lighting	
Lamp parts	PC
Lamp casings	PA
Light parts	PC
Light covers	PC, PMMA
Light rails	PC, PA
Cable insulations and sheaths, insulated lines	PVC, LDPE, EPDM, Elastom
Electric wiring conduits	PA, PC, pp
Office machines	
Telex machine casings	PC
Telex machine parts	PC, PBT
Parts of office machines	PC, ABS
Copying machine casings	ABS
Computer casings	PC, ABS
Computer cassettes	PC
Electrical equipment	
Measuring equipment	PC
Charging equipment	PC
Parts of electric motors and meters	PC, PA
Casings for electric tools	PA
Kitchen machine parts	PC
Heating oven parts	PC
Hair dryer parts and nozzles	PC, PBT
Radios, television sets and record players	
Radio parts	PC, ABS, HIPS
Record players	PC, ABS
TV control parts	PC
TV chassis	PC
Line output transformers	PC

Business Equipment

One manufacturer in Europe has stated that those of its products delivered to the low-end segment of the business market in Europe will be brominated diphenyl oxide-free after the first of January 1994. The so-called high-end segment is already PBDPO-free, due to the use of more expensive polymers.

(S. Looijs, February 1993)

Basic polymer options in the computer manufacturing industry are illustrated by a US computer company. Cases or housing for computers can be made from high-impact polystyrene (HIPS), ABS-polycarbonate blends, or ABS base flame retardant compounds. The main base polymer options in this industry for production of the internal components are polyphenylene sulphide (PPS), terephthalates (PBT, PET), liquid crystal polymers (LCP) and nylons.

(Cartwright, February 1993)

Consumer Products

Since the early 1980s, there has been a tremendous change in the design of consumer electronic equipment. Some companies decided that equipment should be designed that did not require the use of flame retardants. The inherent safety of the components used, the introduction of safety distances, and the demand for good solder joints are the results of this new emphasis (Looijs, February 1993).

Television sets are generally made from high-impact polystyrene. In the US, this application requires VO flame retardant, UL classification; however, in Europe only the back covers are required to meet this flame retardancy level.

General Survey of Possible Materials in the TV Sector

Basic materials	Flame retardant	TCE orientation	Why (for TCE)?
PS	no	no	
	polybromodiphenylether	suppressed	
	polybromodiphenyl		forbidden in the US
	hexabromocyclododecane	no	mechanical properties
	ethylenebistetrabromophtalimide	no	price
	bistribromophenoxyethane	in progress	
	bromoethylene	in progress	
	chlorinated paraffin	no	mechanical properties
	dechlorane	in progress	
	mineral load	no	mechanical properties
	melamines	no	mechanical properties
	PPO	in progress	
polybromostyrene	bromine per definition	in progress	
polypropylene	mineral load	no	mechanical properties
ABS	brominated	no	price
PVC	chlorine per definition	no	mechanical properties

(A. Mary, February 1993)

Printed Wiring Laminates

Tetrabromobisphenol A is the most widely used flame retardant chemical for printed wiring laminates. FR 4 type laminates based on glass fibres impregnated by epoxy resins achieve V0 (UL flame retardant classification), with 8 per cent TBBPA. Halogen-free based FR 4 materials are in the development stage. FR 3 laminates, based on paper impregnated by epoxy resins, contain TBBPA and Sb_2O_3 flame retardant systems. No information exists on FR 3 material that does not contain bromine.

The phenolic paper FR 2 laminate can also contain TBBPA and Sb_2O_3 flame retardant chemicals. The only identified alternative in commercial use is cold punchable material, currently available in single- and double-sided versions.

One manufacturer has been unable to find effective substitutes for TBBPA in such laminates despite intensive efforts.

Aircraft

In recent years, major improvements have been made in reducing the possibility of aircraft fires. Some essential rules have been issued (e.g. fire containment, seat cushion, fire blocker, NBS chamber, heat release, OSU) aimed at increasing the level of security, delaying the appearance of fire, and increasing the time required for passengers to escape.

Halogen based systems (chlorinated or brominated such as TBBPA) combined with other additives (Sb_2O_3) are among the most widely used fire retardants for structural composite organic matrices such as epoxides. For furnishings and interiors, both thermoplastic and thermoset polymers (phenolics) are used, but no attempt has been made until now to correlate the level of fire resistance to the chemical formulations of these materials. As a consequence, any strengthening of the fire prevention rules will induce a change in the formulation of the materials, which in turn will require requalification/certification of these materials at great cost.

Therefore, a complete investigation has to be made of alternative solutions before any change is made, to verify the performances and the environmental properties of the possible substitutes. Studies have been conducted on this topic within the framework of a Brite-Euram project (Brite Euram n° 4412 – CT0466) and on national levels. They have focused on the development of new halogen-free fire retarded formulations for structural or interior applications. Results of the studies indicate that it is currently difficult to substitute those materials.

An important phase of research to develop and optimize some possible brominated-free fire retardant substitutes still has to be performed before these substances can be used in new formulations. Should suppression of brominated substances occur, the resulting necessity to change the formulations would apply only to new formulations. Derogations or delay in the use of current fire retarded systems should also be considered, taking into account the cost of qualification, the relevant essential applications, and the high degree of security required in the aerospace industry.

(Costes, February 1993).

Textiles

To achieve fire retardancy in a textile, there are a number of options.

Simple phosphate salts are used in some contract areas, but are not durable and are easily removed by, for example, liquid spillages.

Reactive phosphates are durable for both washing and dry cleaning, but are fibre-specific; they will only bond onto cellulosic yarns like cotton, viscose, etc. and, if improperly applied, they can cause problems with formaldehyde.

Fire retardant yarns are available, but generally they are costly and suffer in many cases from poor wear, dyeing, weaving, etc. The combustion products of many yarns – wool, nylon, acrylic and modcrylic – can produce hydrogen chloride, cyanide, and (as with all organics) carbon monoxide.

Backcoating: The incorporation of brominated diphenyl oxides and synergist, antimony trioxide, into the aqueous backcoating composition has enabled formulators to tackle almost all fibre types and fabric constructions, and to achieve the correct level of fire retardancy.

Other systems using phosphate, halogen only, ATH, other oxides and combinations are used for specific reasons. Substitution of existing FR or alternative systems may be difficult for protective clothing. DeBDPO is the only flame retardant that allows the material to meet FR requirements.

A similar situation exists for carpets, particularly in Belgium. The majority of textiles in the UK are treated with brominated diphenyl oxide. The cost of substituting other FR is estimated to be around £150 million. For all-round FR efficiency and cost effectiveness, the antimony/halogen route is still the best and most universal finish.

(T. Matthews-Mydrin, February 1993)

APPENDIX 2

BROMINATED FLAME RETARDANTS: FORMULATION, APPLICATION AND MARKET DEMAND

Tetrabromobisphenol A (TBBPA) and derivatives

This is the most important group of brominated flame retardants in terms of actual production and/or demand, which is over 60,000 tonnes per annum. This group includes tetrabromobisphenol A as well as their dimethylether, dibromopropylether, bis(allylether), bis(2-hydroxyethyl oxide), carbonates and epoxy oligomers. The production of these brominated chemicals is concentrated in the United States, Japan and Israel.

Tetrabromobisphenol A (TBBPA) is produced by bromination of bisphenol A. TBBPA is a traditional flame retardant in the production of epoxy resins, replacing bisphenol A, partially or totally, in the reaction with epichlorhydrin. It can reach up to 48 per cent of bromine content in the polymer structure.

Commercial epoxy FR resins containing 20 per cent bromine (48 per cent if bisphenol A is totally replaced by TBBPA) are widely used in the manufacturing of rigid epoxy laminated printed circuits. A typical example is the NEMA FR-4 type printed circuit made by a combination of eight epoxy prepegs with one or two copper foils (single or double faced).

Other epoxy based TBBPA end uses are glass reinforced (GR) panels for construction, motor housings and terminal boards.

TBBPA is also a FR reactive intermediate in the production of unsaturated polyester (UPE) and polycarbonate (PC) resins, for which it is considered as a replacement for bisphenol A. This application is still less important in demand-volume than epoxy, but has increased considerably over the last decade with the development of a series of TBBPA oligomers for use as FR additives in acrylonitrile-butadiene-styrene (ABS) and engineering thermoplastic polymers.

Pure TBBPA based polycarbonates (TBBPA + phosgene) achieve V-O (the highest fire retardancy classification) in their application as an additive (7 per cent bromine in the compound) for polycarbonate resins.

Phenoxy terminated TBBPA carbonate oligomers, produced in the US, contain 51-59 per cent bromine and are also FR additives for polybutylene terephthalate (PBT) and thermoplastic elastomers.

TBBPA can also be a chemical intermediate in the production of other brominated flame retardant oxides of dibromopropyl, allyl, hydroxyethyl, etc., and carbonates or epoxy oligomers.

Japanese chemical producers introduced PBT flame retardants based on the 2,2-bis(4-(2-hydroxyethoxy)-2,6-dibromophenyl) propane or TBBPA bis(hydroxyethyl oxide) made from TBBPA, ethylene oxide and toluene (US patent 4085086).

Brominated epoxy oligomer flame retardants **(BEPO-FRs)** were first introduced in the Japanese market in 1987. Demand requirements still show rapid growth in Japan as well as in the US. BEPO-FRs are composed of tetrabromobisphenol-A (TBBPA) epoxy and tribromophenol (TBP) in certain grades.

There are two chemically different types of brominated epoxy oligomers. One has two epoxy groups at the end of the molecule, which is quite similar to epoxy resins used for printed circuit boards. The other TBBPA epoxy end-capped with tribromophenol has no reaction groups. Molecular weights vary from 700 to 50,000 and differ depending on the application and kind of plastic.

Brominated epoxy oligomers have been applied to housings for business machinery and electrical/electronics parts by injection moulding from flame retardant compounds based upon HIPS, ABS, ABS/PC or PBT alloys and PBT. A new application is use in large size TV sets moulded from HIPS.

TBBPA epoxy oligomers have seen a rapid growth demand in Japan and the US. In Japan the local demand for these oligomers is 4000 tonnes per annum (Sugie 1993).

The TBBPA epoxy oligomers are especially characterized by higher melt flow rate without blooming and better light stability than existing flame retardants such as polybrominated diphenyl oxides or others (Sugie 1993).

A type of polyester fibre is made with bis(hydroxyethyl) TBBPA ethylene glycol in reaction with terephthalic acid (TPA).

FR-polyester-cotton blends containing 30 per cent bromine, 45 per cent polyester fibres and 25 per cent cotton can be made from TBBPA, reacting with diacid chloride (terephthaloyl chloride) in methylene chloride.

Other TBBPA derivatives included in this group are TBBPA bis(2-hydroxyethyloxide), TBBPA bis(2,3-dibromopropyl) oxide and TBBPA bis(allyloxide), used for polyolefins, in particular polypropylene (PP) extrusion grade, surface coatings and polystyrene (PS) foams, respectively.

Polybrominated Diphenyl Oxides (PBDPOs)

The worldwide production of/demand for the polybrominated diphenyl oxides is the second largest in terms of FR group consumption of the brominated FR chemicals. At present, this total is estimated at over 40,000 tpa. The US, Japan and Israel are the major producer countries, but France, the UK, the Netherlands and Crimea (ex-USSR) also have manufacturing facilities.

This group of brominated flame retardants covers a chemical family in which hydrogens are replaced by bromine in the diphenyl oxide structure (from mono- to decabromination). Commercial products are not pure substances and contain different levels of brominated diphenyl oxides. Currently, the only three products on the market are deca (DeBDPO), octa (OBDPO) and pentabromodiphenyl oxides (PeBDPO).

The applications of brominated diphenyl oxides cover a large range of polymeric material. It is generally recognized that these brominated chemicals can achieve flame retardant formulations in attractive, technical, and economical ways.

Decabromodiphenyloxide (DeBDPO) is the product in the group with the largest demand (30,000 tpa). It was introduced commercially in the United States in the early 1970s when the first fire safety standards and regulations were put into force in that country, for the FR high impact polystyrene (HIPS) compounds used in the fabrication of television panels and cabinets.

Today's commercial DeBDPO is typically composed of 97-98 per cent decabromodiphenyl oxide with 0.3-3.0 per cent other brominated diphenyl oxides (BFRIP, 1992). Nonabromodiphenyloxide isomers are the major impurities. The commercial product typically contains a minimum of 81-83 per cent bromine (IARC 1990).

DeBDPO is produced by bromination of diphenyl oxide in the presence of a Friedel-Crafts catalyst (Larsen 1980). DeBDPO has been reported to be manufactured in a batch process involving closed vessels during the reaction drying cycle (US Environmental Protection Agency 1988).

Differences in manufacturing processes affect the nature and amounts of impurities in the product (Larson 1980). Today's commercial product is considerably purer than that manufactured in the past. Isomers of nonabromodiphenyloxide and octabromodiphenyl oxide have been reported as impurities in DeBDPO (Timmons and Brown 1988).

DeBDPO, produced in the early 1970s (no longer a commercial product), was composed of 77.4 per cent DeBDPO, 21.8 per cent NBDPO and 0.8 per cent OBDPO (Norris et al. 1975c). Later production of DeBDPO forms the same manufacturing range in composition, from 94-99 per cent DeBDPO with 0.3-4.5 per cent impurities (NBDPO isomers were identified as the major impurities) (US NTP 1986).

A technical product of 88.1 per cent purity containing 11 per cent NBDPO, 0.5 per cent OBDPO and 0.1 per cent hexabromobenzene has also been reported (Klusmeier et al. 1988). Other DeBDPO products have a purity of approximately 93 up to 98.5 per cent and different quantities of impurities (Davidson and Ariano 1986, de Kok et al.). Availability of a technical product of 88.1 per cent purity containing 11 per cent nona-, 0.5 per cent octabromodiphenyl oxide and 0.1 per cent hexabromobenzene has been reported (Klusmeier et al. 1988).

In Japan, DeBDPO is produced with about 3 per cent of nonabromodiphenyloxide as impurity (Watanabe and Tatsukawa 1987). EBFRIP (undated) gives 2 per cent nona- and 1 per cent octabromodiphenyloxide as impurities.

DeBDPO is stable under normal temperatures and pressures; thermal or light-catalyzed decomposition of DeBDPO may release carbon monoxide, carbonyl bromide and hydrogen bromide, lower congeners of diphenyl oxide, polybrominated dibenzodioxins and dibenzofurans. Dangerous reactions can take place with primary aliphatic amines. Exothermic reactions are difficult to control (Norris et al. 1973 1974, 1975a; Tabor and Bergman 1975; US EPA 1986, 1989; Boutonnet and Moncel 1988; Chemag Akt. Ges. 1988; Kopp 1990; IARC 1991; Great Lakes Chem. Corp. 1990b; Pijnenburg and Everts 1991; Bromine Compounds Ltd. 1992; Ethyl Corp. 1992a).

Today, DeBDPO is considered as a general purpose FR chemical. Demand for its use covers a wide range of plastics applications distributed, as a percentage of total demand, as follows:

- 30% Polystyrene (HIPS) [moulding parts, panels, sets, housing, television, appliances]
- 20% Terephthalates (PBT, PET) [moulding products, connectors, switchgears, electrical equipment]
- 15% Polyamides (PA) [injection moulding, contactors, bobbins, electrical elements]
- 10% Styrenic rubbers (SBR) [latex, carpet backing, furniture]
- 5% Polycarbonates (PC) [moulding parts, panels, housing, computers, aircraft]
- 5% Polypropylene (PP) [injection moulding, TV yocks, capacitors, TV, electronics]
- 15% Other polymer applications and end uses, notably:

  Acetate copolymer (EVA) [extrusion, coating, wire, cables, electrical distribution]

  Unsaturated polyester resins (UPE) [moulding compounds, panels, boxes, electrical equipment]

Octabromodiphenyloxide (OBDPO) is less efficient as a flame retardant than DePDPO, with a 5 per cent lower bromine content. The bulk of its applications are for compounds based on acrylonitrile butadiene styrene (ABS), where this brominated chemical offers the comparative advantage in terms of melting range and colour.

OBDPO is commercialized as a mixture of 4 per cent hexabromo-, 62 per cent hepta- and 34 per cent octabromodiphenyl oxide (de Kok et al. 1979). It is also produced as a mixture of 6.9 per cent hexabromo, 46.8 per cent heptabromo, 35.9 per cent octabromo and 10.4 per cent nonabromodiphenyl oxide.

OBDPO is synthesized by treating diphenyl oxide with eight equivalents of Br_2 in the presence of Al_2Cl_6/Al_2Br_6, first at 35°C and then at 120°C (US EPA 1986).

Pentabromodiphenyl oxide (PeBDPO) is the only commercial brominated diphenyl oxide in liquid form. Technical grade pentabromodiphenyl oxide is a mixture of tetra through hexa bromodiphenyl oxides. DE-71 is mixture of tetra-, penta- and hexabromodiphenyloxide (total > 97 per cent) and lower PBDPO <1 per cent and higher PBDPO < 2 per cent (McAllister and Ariano 1982).

Non-technical grade pentabromodiphenyl oxide is a mixture of 39 per cent tetra-, 61 per cent penta- and 9 per cent hexabromodiphenyloxide. PeBDPO can be produced as a mixture of 34.2 per cent tetra-, 59.8 per cent penta-, 5.8 per cent hexa- and 0.2 per cent heptabromodiphenyloxide, but also 41.7 per cent tetra- and 45 per cent pentabromodiphenyloxide and 7 per cent of second pentabromodiphenyloxide (Nylund et al. 1991) is reported.

A mixture with 36 per cent tetrabromo- and 74 per cent pentabromodiphenyl oxide has a bromine content of from 67-71.8 per cent (de Kok et al. 1979). It is no longer produced commercially (McAllister 1991).

Sundström and Hutzinger (1976) identified 2,4,2',4' tetra- and 2,4,5,2',4' – PeBDPO as the major components of one of the commercial PeBDPO grades. Another commercial grade is a mixture of 85 per cent PeBDPO and 15 per cent of an aromatic phosphate.

PeBDPO is synthesized by treating diphenyl oxide with five equivalents of Br_2 at 30-65 ^{o}C in the presence of Fe powder (US EPA 1986). PeBDPO is a clear, amber to pale yellow highly viscous liquid, with a typical organic smell. Under fire conditions, hydrogen bromide and/or bromine will be produced.

Rubber (conveyor belts, sheeting and flooring) and flexible polyurethane foams (in soft furnishing) account for the bulk of PeBDPO market demand. PeBDPO-containing conveyor belts are used in the UK and India; sheeting in the UK building trade; and flooring in French trains. PeBDPO- containing soft furnishings are used in many countries in Europe, Australasia and the United States. The mixture of DeBDPO – Sb_2O_3 is applied to textile materials by immersion back coating.

Generally, cellulosic/cotton based materials in the upholstery market are subject to FR regulations for furniture. One UK producer of FR formulations for textile treatment also manufactures PeBDPO.

In the UK, this industry has predicted a high growth rate; this is primarily driven by the British Furniture and Furnishing Regulations (British Standard BS 5852).

Similar predictions have been made for the European continental markets following more strict and standardized regulations particularly for end uses in public places. German consumption of FR chemicals in this sector have already experienced a high growth rate during these last two years.

In the US, the main PeBDPO application appears to be in polyurethane foams (PUR), where it is also used in mixtures with phosphate esters (40-50 per cent bromine, 6-8 per cent phosphorus).

Polybrominated biphenyls (PBBs)

The term "polybrominated biphenyls" (PBBs) or "polybrominated diphenyls" refers to a group of halogenated hydrocarbons which are formed by substituting bromine for hydrogen in biphenyl. The molecular formula is $C_{12}H_{(10-x-y)}Br_{x+y}$ (x,y = 1,5). Theoretically there can be 209 different forms (congeners) of a brominated biphenyl depending on the number and position of the bromine.

Decabromobiphenyl (DeBB) is the only brominated diphenyl that has been identified in commercial use. This chemical is produced only in France. The present demand is limited to the Benelux, France and the South European countries at a level of less than 2000 tpa.

DeBB is used (as is DeBDPO) in FR formulations for styrenic polymers and engineering plastics. It is also considered a general purpose FR additive for other polymers such as unsaturated polyester (UPE) resins, the demand for which, along with DeBDPO, amounts to 5000 tonnes per annum of this flame retardant polymer in Europe (P. Canard, February 1993).

Tetrabromophthalic anhydride (TBPA) and derivatives

This group includes the tetrabromophthalic anhydride as well as other flame retardants produced by reaction of this anhydride with alcohols, imides or sodium chemicals. The US, France, Japan and Israel are the only identified producer countries.

The market demand for tetrabromophthalic anhydride (TBPA) also includes their derivatives such as ethylene bis. imide, imide, diester-ether diols and TBPA disodium salts.

Tetrabromophthalic anhydride (TBPA), a reactive FR, can replace phthalic anhydride in the esterification polymer process, offering a high content of aromatic bromine fixed into the polymer chain. Brominated UPE and alkyds resins are typical application examples of TBPA.

The mixed ester of TBPA with diethylene glycol (DEG), and propylene glycol (PG), are liquid FR diols which react with isocyanates in the manufacturing of FR rigid polyurethane (PUR) foams. A US patented product, based on TBPA and glycerol (US patent 3989653) is part of this family.

Ethylene bis(tetrabromophthalimide) (EBTBP), produced in the US, is a well known FR additive with a similar application profile to DeBDPO.

The most significant advantage may be that EBTBP produces no detectable brominated dibenzodioxins and very low concentrations of 2,3,7,8-substituted brominated dibenzofurans under pyrolysis conditions, in contrast to DeBDPO. In addition, EBTBP has increased deflection temperature under load and better UV stability. The improved UV performance of EBTBP allows HIPS to compete in markets where it traditionally has not (F.A. Pettigrew, S.D. Landry and J.S. Reed, February 1992).

The **disodium salt of TBPA** (content 15 per cent bromine), is used in aqueous solution for the FR treatment of textile fabrics and surface coatings.

Brominated alicyclics

The most common commercially used alycyclic FR additives, discussed below, include hexabromocyclododecane, dibromoethyldibromocyclohexane or tetrabromovinylcyclohexane, and ethylene bis(dibromonorbornanedicarboximide).

Hexabromocyclododecane (HBCD), produced in the US and France, was first applied in Germany and the US (US patent 3093599) in their production of FR polystyrene (PS) foams. HBCD based FR PS foams, without Sb_2O_3, achieve the flame retardancy required for building insulations, which is a major end use of this product.

Dibromoethyldibromocyclohexane and **tetrabromovinylcyclohexane** have similar bromine contents (75 per cent) to HBCD and are in competition with HBCD in FR-PS insulation product applications. They are also used in polyurethane (PUR) foams manufacturing.

Ethylene bis(dibromonorbornanedicarboximide), produced in the US, is used in polypropylene and polyamides. These polymers can reach a V-2 flame retardancy rating with low addition (4 per cent) to the FR polymer compounds.

Pentabromochlorocyclohexane and **hexachlorocyclopentadienyl-dibromocyclooctane**, the other two brominated flame retardants included in this group, also contain chlorine in their clycloaliphatic (cyclohexane) or heterocyclic (C 5.6, cyclooctane) forms.

Brominated aliphatic and inorganic

This group includes aliphatic, alcohol terminated products used as flame retardant chemical intermediates or reactives in the production of flame retardant urethanes or esterified plastics.

Brominated ethylene, a reactive flame retardant, and ammonium bromide, an additive FR, are mainly applied in the fibre and textile industries, and are also included in this group.

Dibromoneopentyl glycol (DBNPG) was introduced as a flame retardant chemical in the production of FR unsaturated polyesters (UPE), and still provides a way of introducing stable bromine into this polymer through DBNPG reaction with phthalic (PA) and maleic (MA) anhydrides reticulated by styrene monomer. These formulations achieve M-2 (France) or class 1 (UK) flame retardancy classifications without filler with a high smoke index (FJ). (P. Canard, Neuchâtel, February 1993).

As a reactive diol, DBNPG is also applied in the FR formulation of polyurethane (PUR) rigid foams and elastomers.

DBNPG is available in pure (98.1 per cent) as well as mixture with monobromopentaerythritol and tribromoneopentyl alcohol (TBNPA). Dibromoneopentyl glycol (DBNPG) has a bromine content of 61 per cent and decomposition occurs at 235°C with the release of toxic, irritant hydrogenbromide and bromine fumes.

Tribromoneopentyl alcohol (TBNPA) with the highest bromine content is also used, alone, as polyol in the formulations of rigid PUR foams.

TBNPA is an off-white crystalline solid or free-flowing powder with 97 per cent purity. The substance decomposes at approximately 160°C. (Kopp 1990)

Vinyl bromide (VBr) aliphatic chlorides (i.e. vinychloride) are converted to their respective bromides in high yields by reaction with NaBr, $BaBr_2$, NH_4Br, etc. in a dialkyl amide solvent with the inorganic chloride being precipitated.

Vinyl bromide is prepared by treating acetylene with the hydrogenbromide in the presence of a catalyst such as halides of mercury, cesium or copper. In Japan it is prepared by the reaction of potassium hydroxide on ethylene dibromide (IARC 1979). VBr has been detected as an impurity in commercial vinyl chloride. VBr, which is commercially available in the US, has a purity of 99.5 per cent. VBr is a colourless gas at ambient temperature and pressure; it is a reactive flame retardant monomer. Through its vinyl functionality, this monomer is capable of homopolymerization or copolymerization with other reactive monomers such as in the production of flame retandant modacrylic fibres. A typical composition is based on acrylonitrile, vinylidene chloride, VBr (71 per cent), acrylamide and antimony trioxide (3 per cent).

Ammonium bromide, a white crystal containing 82 per cent bromine, is used in photography and pharmacology; however, as a flame retardant, its main application is for the treatment of textile fabrics.

Tetrabromodipentaerythritol, an off-white to beige crystalline powder with a purity of 96 per cent, is also included in this group of brominated flame retardant chemicals.

Bromophenols and derivatives

Di, tri and pentabromophenol are used as reactive flame retardants for polycondensated or esterificated polymers such as phenolic or polyester resins.

Tribromophenol (TBP) and **dibromophenol (DBP)** are reactive flame retardants with a high content of aromatic bromine (72 per cent and over 63 per cent, respectively). The most used, tribromophenol (TBP), is also an intermediate in the production of several FR additives.

Bis(tribromophenoxy)ethane (BTBPE) or **hexabromophenoxy ethane (HBPE)**, produced in the US, is commercialized for application as flame retardant additive in the acrylonitrile-butadiene-styrene (ABS) and engineering thermoplastic FR compounds.

TBTBPE/HBPE is a white to off-white crystalline powder with slightly antiseptic odour and contains 70 per cent bromine. At combustion in the presence of other fuels, it may result in release of hydrogenbromide and/or bromine.

Tribromophenyl allyl oxide (TBP-AE) is used in the manufacturing of FR expandable polystyrene (PS foams), and also in combination with hexabromocyclododecane (HBCD). TBP-AE is a white crystalline free-flowing powder.

Poly-dibromophenylene oxide (PDBPO) containing 62 per cent bromine is a general purpose type FR additive for thermoplastic compounding, with characteristics comparable to decabromodiphenyl oxide.

PDBPO is a very fine powder, light tan in colour with a slightly phenolic smell. Poly-(2,6-dibromophenylene oxide) in circumstances of combustion may release hydrogen bromide and/or bromine, in the presence of other fuels.

Brominated benzene and styrene derivatives

Amongst several other aromatic brominated flame retardants produced, the most commercially important are pentabromotoluene (5BT), pentabromoethylbenzene (5BEB) and tetradecabromodiphenoxybenzene (TDBDPB), which are produced in Israel, France and the US respectively. Poly(pentabromobenzyl acrylate) (PBB-PA) is an Israeli product, dibromostyrene (DBS) and derivatives (PDBS) were developed in the US, and the brominated polystyrenes are manufactured in the US and France.

Hexabromobenzene (HBB), a flame retardant used in mixtures for polyester fibres and thermosets, is fabricated in Crimea and Israel and also included in this group of chemicals.

Pentabromoethyl benzene (5BEB) and **pentabromotoluene (5BT)** are similar brominated chemicals used in the formulation of glass reinforced (GR) unsaturated polyester (UPE) compounds used in electrical applications as FR bulk moulding compounds (BMC).

Tetradecabromodiphenoxybenzene (TDBDPB) is a white odourless powder and contains as impurities hexabromobenzene, decabromodiphenyl oxide, pentabromophenyl tribromotolylether (in total < 1 per cent) and 73 mg ± 8.5 octabromodibenzo-p-dioxin/kg product. A second analysis by another laboratory found only 1/100 of this quantity of OBDD (Naismith and Matthews 1985). Decomposition takes place above 350°C.

TDBDPB with a similar bromine content (82 per cent) and chemical structure to DeBDPO has a comparative advantage on UV stability. Its present major application is in the formulation of engineering thermoplastics, where its premium price with respect to DeBDPO is more acceptable.

Poly(pentabromobenzyl acrylate) (PBB-PA) is produced in the form of a white free-flowing powder. PBB-PA contains a minimum of 95 per cent polypentabromo- benzylacrylate, < 1 per cent pentabromobenzylalcohol, < 1 per cent pentabromobenzylbromide and < 1 per cent pentabromobenzylacrylate (Kopp 1990).

PBB-PA was introduced in the FR compounding of glass reinforced (GR) engineering thermoplastic. GR polyamides (PA) 6 and 6/6 and GR polybutylene terephthalate (PBT) containing 17 per cent PBB-PA with 5 per cent Sb_2O_3 (equivalent at 10 per cent bromine content into the compound) can obtain a V-0 FR level. This brominated polymeric FR additive allows the high impact polystyrene (HIPS) compounds based on 12 per cent PBB-PA and 3 per cent Sb203 to be classified V-0 for FR.

Dibromostyrene (DBS), produced in the US, is a reactive styrene monomer containing 59 per cent aromatic bromine. Its reactivity profile is similar to a conventional styrene monomer, yet it is stable when inhibited with conventional stabilizers. DBS will readily homo or copolymerize in conventional processing equipment.

A polymer of dibromostyrene, **Poly-dibromostyrene- (PDBS)** flame retardant is a developmental additive for thermoplastic polyesters (PBT and PET), polyamides (Nylon 6,6 and Nylon 6) and polystyrene (HIPS) (Product Information, Great Lakes, September 1992).

Brominated polystyrene (BrPS) flame retardant additive, produced in the US and France, is a low molecular weight brominated polystyrene (BrPS) range of products. The use of these polymeric additives for FR thermoplastics. content of 66 per cent bromine, can achieve a V-0 or V-2 FR level in HIPS compounds, when BrPS are used in combination with antimony trioxide (Sb_2O_3).

BrPS can be substituted for all known Deca and Octa applications. The benefits provided by BrPS are acceptable environmental performance, improved mouldability, resistance to discolouration by actinic light and no migration, or blooming. The negative performance feature is increased cost over the more inexpensive Deca and Octa (F.J. Quinn and T. Kelley, March 1993).

Others

The production and uses of other brominated chemicals are limited to a single product, covered by patent and/or not identified as being significant as flame retardants at the present time (less than 100 tpa):

- **bis-cyclohexenyl-ethylene (BCE) hexabromide** for PP and fibres;
- **brominated hydroxymethyl phenol** in butyl-grafted polyethylene;
- **brominated ortho-cresol (BROC)** for epoxy and phenolic resins;
- **dibromobutenediol** as an intermediate producer of FR chemicals;
- **dibromopolybutadiene**, a flame retardant for electrical potting;
- **dibromopropanol**, basic intermediate in the production of T23P;
- **dibromopropyl acrylate** in the manufacturing of acrylic fibres;

- **dibromoterephthalic acid** for thermoplastic polyesters and fibres;
- **organobromosilicone fluids** for cellulosic materials;
- **pentabromomonochlorocyclohexane** in PS foams and polypropylene;
- **pentabromopentyl alcohol** for polyurethane (PUR) flexible foams;
- **tetrabromoxylene**, a flame retardant for plastics and textiles;
- **tribromophenoxy-dibromopropane** for extrusion grade of polypropylene.

In textile applications, other than penta- and decabromodiphenyl oxides, the brominated chemical producers suggest the use of hexabromocyclododecane (HBCD), bis(tribromophenxy)ethane (HBPE), tetrabromophthalate esters and salts (TBPA derivatives), ethylene bis(dibromonorbornanedicarboximide), pentabromotoluene (5BT) and ammonium bromide.

APPENDIX 3

PHYSICAL-CHEMICAL PROPERTIES OF BROMINATED FLAME RETARDANTS

Tetrabromobisphenol A

Chemical formula: $C_{15}H_{12}Br_4O_2$
Relative molecular mass: 543.92
CAS registry number: 79-94-7
Melting point: 178-180°C (180-184°C)
Boiling point: 316°C (approximately)
Specific gravity: 2.18
Flash point: 178°C
Vapour pressure: < 1 mm Hg at 20°C
Solubility: 0.72 mg/litre water at 15°C

(Kopp 1990)

TBBPA bis(2,3-dibromopropyl oxide)

Chemical formula: $C_{21}H_{20}Br_8O_2$
CAS registry number: 21850-44-2
Melting point: 90-100°C
Solubility: 1 g/litre water at 25°C

TBBPA bis (allyl oxide)

Chemical formula: $C_{21}H_{20}Br_4O_2$
CAS registry number: 25327-89-3
Melting point: 115-120°C
Specific gravity: 1.8 g/cm^3
Solubility: < 1 g/litre water at 25°C

TBBPA bis (2-hydroxyethyl oxide)

Chemical formula: $C_{19}H_{20}Br_4O_4$
CAS registry number: 4162-45-2
Melting point: approximately 112°C
Specific gravity: approximately 1.80 g/cm^3

TBBPA methyl ethyl

Chemical formula:	$C_{17}H_{16}Br_4O_2$
CAS registry number:	37853-61-5

TBBPA carbonate oligomer

	BC52	BC58
Chemical formula:	$(C_7H_5O)(C_{16}H_{10}Br_4O)x$ x = 3-5	$(C_7H_2Br_3O_3)(C_{16}H_{10}Br_4O_2)x$ x $(C_6H_2Br_2)$
CAS registry number:	94334-64-2	71342-77-3
Melting point:	210-230°C	230-260°C
Solubility:	< 0.1% in water at 25°C	negligible in water

(Kopp 1990)

TBBPA epoxy oligomer

	EP Type	EC Type
Molecular weight:	1300-40,000	1400-3000
Appearance:	Light yellow powder	Light yellow powder
Colour (Gardner):	2	2
Specific gravity:	1.8	1.9
Bromine contents:	50-52	59-55
Softening point (°C):	103->200	99-140

(Sugie, February 1993)

Decabromodiphenyl oxide (DeBDPO)

Chemical formula:	$C_{12}Br_{10}O$
Relative molecular mass:	959.22
CAS registry number:	1163-19-5 (61345-53-7) (mixture of DeBDPO and Sb_2O_3)
Melting point:	290-306°C (295-310); 300-305°C
Boiling point:	425°C (not applicable under standard conditions)
TGA (% wt. loss at °C):	1% at 319, 5% at 353, 10% at 370, 50% at 414, 90% at 436
Specific gravity:	3.04 at 20 °C (23.25)
Vapour pressure, mm Hg:	250 °C < 1, 278 °C 2.03, 306 °C 5.03
Solubility at 25 °C:	water 20-30 µg/litre

Octabromodiphenyl oxide (OBDPO)

Chemical formula:	$C_{12}H_2OBr_8$
Relative molecular mass:	801.47
Melting point:	200 (167-257) ^{o}C
Vapour pressure:	8.78-9.04 Torr at 25 ^{o}C
Solubility 25 ^{o}C in g/litre:	water < 1
Specific gravity:	2.76 (2.63)

(Great Lakes 1990a; US EPA 1986; Pijnenburg and Everts 1991; Ethyl Corp. 1992b; Norris 1974; Tabor and Bergman 1975; IARC 1990)

Pentabromodiphenyl oxide (PeBDPO)

Chemical formula:	$C_{12}H_5Br_5O$
Relative molecular mass:	564.75
CAS registry number:	32534-81-9
Melting point:	202 ^{o}C (estimated).
Boiling point:	> 300 ^{o}C (decomposition starts above 200 ^{o}C)
Specific gravity:	2.28 at 25 ^{o}C; 1.78 at 40 ^{o}C
Vapour pressure:	9.3 mm Hg at 22 ^{o}C (6.26-6.66) Torr at 25 ^{o}C)
Solubility:	Insoluble in water (9 x 10-7 mg/litre at 20 ^{o}C)
Viscosity at 50 ^{o}C.	1-6 Pa (150,000 cp at 25 ^{o}C; 1500 cp at 60 ^{o}C)

(IRPTC 1998; Great Lakes, undated; Chem. Fabr. Kalk 1982; Kopp 1990; US EPA 1989; Pijnenburg and Everts 1991)

Decabromobiphenyl (DeBB) – commercial product

Appearance:	Powder
Colour:	White to light beige
Particle size:	3 to 5 (micron)
Real density, 20 ^{o}C (estimated):	approx. 3.2 (g/cm^3)
Melting point:	360-380 ^{o}C
Colour Yi:	12 maxi (ASTM E 313-3 Std)
Colour Wi:	60 mini (Hunterlab D25/M)
Volatiles:	0.2 maxi (%)
Sieve refusal 400 mesh:	0.2 maxi (%)
Bromine content:	84 mini (%)

(From Ceca data sheet)

Tetrabromophthalic anhydride (TBPA)

Chemical formula:	$C_8Br_4O_3$
CAS registry number:	632-79-1

TBPA derivatives:

TBPA diester/ether diol (TBPA Diol)1)

Chemical formula: $C_{15}H_{16}Br_4O_7$
CAS registry number: 20566-35-2

Ethylene bis(tetrabromophthalimide) (EBTBPA)2)

Chemical formula: $C_{18}H_4Br_8N_2O_4$
CAS registry number: 32588-76-4

N,N’-bis(tetrabromophthalimide) (TBPA-Imide)3)

Chemical formula: $C_{16}Br_8N_2O_4$
CAS registry number: 26040-45-9

Disodium salt of tetrabromophthalate4)

Chemical formula: $C_8Br_4O_4Na_2$
CAS registry number: 25357-79-3

Properties of TBPA Products

	TBPA	**Diol1)**	**EBTBPA2)**	**Imide3)**	**Na Salt4)**
Form	powder	liquid	powder	powder	liquid
Specific gravity	2.87	1.8	-	-	1.33
Melting point (°C)	276-280	-	446	NA	-
Vapour pressure (Pa at 20°C)	14.67		-	10-3 mbar	-
Solubility	insoluble in water; soluble in nitrobenzene	insoluble in water	in water negligible	insoluble in water; soluble in toluene and xylene 0.2 g/l	miscible with water (pH value at 210g/l at 20°C, 6-65)

Brominated cycloaliphatics and heterocyclics:

Hexabromocyclododecane (HBCD)

Chemical formula:	$C_{12}H_{18}Br_6$
Relative molecular mass:	641.77
CAS registry number:	25637-99-4 or 3194-55-6
Melting point:	170-180°C (decomposition > 200°C)
Flash point:	162-171°C
Specific gravity:	2.24 (2.38 at 20°C)
Solubility:	insoluble in water
Vapour pressure:	< 133 Pa at 20°C

Dibromoethyldibromocyclohexane

Chemical formula:	$C_8H_{12}Br_4$
CAS registry number:	3322-93-6
Melting point:	70-75°C
Density:	2.27 at 20°C
Solubility:	0.05% in water at 20°C

Ethylene bis(dibromonorbonanedicarboximide) (EBDNDC)

Chemical formula:	$C_{20}H_{20}Br_4N_2O_4$
CAS registry number:	41291-34-3 (52907-07-0)
Melting point:	294°C
Density:	2.07 at 20°C
Solubility:	negligible in water

Pentabromochlorocyclohexane (Br/Cl cyclohexane)

Chemical formula:	$Cl_6H_6Br_5Cl_1$
CAS registry number:	87-84-3
Melting point:	202°C
Boiling point:	235°C (with decomposition
Vapour pressure:	< 0.1 mm Hg at 20°C
Solubility:	in water < 1 g/litre
Stability:	incompatible with acids, oxidizing material, and reducing metals such as aluminium

Hexachlorocyclopentadienyl dibromocyclooctane (C 56 Br. cyclooctane)

Chemical formula:	$C_{13}H_{12}Br_2Cl_6$
CAS registry number:	51936-55-1
Melting point:	200°C

Brominated aliphatic and inorganic:

Dibromoneopentyl glycol (DBNPG)

Chemical formula: $C_5H_{10}Br_2O_2$
Relative molecular mass: 261.97
CAS registry number: 3296-90-0
Melting point: 109-110°C (112°C)
Boiling point: 134°C at 1 mm Hg
Vapour pressure: 10 mm Hg at 178°C; 25 mm Hg at 200°C
Specify gravity: 2.23 (solid)
Solubility: 20 g/litre water at 25°C;

(Humiston et al. 1973; Kopp 1990)

Tribromoneopentyl alcohol (TBNPA)

Chemical formula: $C_5H_9Br_3O$
Relative molecular mass: 324.92
CAS registry number: 36483-57-5
Melting point: 62-67°C
Specific gravity: 2.28 at 20°C
Solubility: 2 g/litre water at 25°C

Tetrabromodipentaerythritol

Chemical formula: $C_{10}H_{18}Br_4O_3$
Relative molecular mass: 506
CAS registry number: 109678-33-3
Melting point: 80-82°C
Specific gravity: 2.0
Solubility: soluble in water 1 g/litre; in ethanol 400 g/litre; methanol 1000 g/litre and toluene 10 g/litre at 20°C

Vinyl bromide (VBr)

Chemical formula: C_2H_3Br
Relative molecular mass: 106.96
CAS registry number: 593-60-2
Melting point: 139.5°C
Boiling point: 15.8°C
Flash point: 13°C
Auto-ignition point: 472°C
Vapour pressure: 1.3447 at 25°C
Specific gravity (d 20/4): 1.4933
Solubility: insoluble in water
Stability: inflammable, polymerizes rapidly in light

Ammonium bromide

Chemical formula:	NH_4Br
CAS number:	12124-97-9
Appearance:	white crystals
20% solution-pH: 4.5 to 6.0:	water white
Density:	2.429 (20°C)
Boiling point:	(pressure 760 mm of Hg) sublimes without melting (452°C)
Solubility (20°C):	556 gr/cm^3 – hygroscopic material

2,4,6 – Tribromophenol

Chemical formula:	$C_6H_3Br_3O$
Relative molecular mass:	331
CAS registry number:	118-79-6
Melting point:	96°C
Boiling point:	244°C
Specific gravity:	2.55 at 20°C
Solubility:	approx. 0.07 g/l (water at 15°C)

2,4 – Dibromophenol

Chemical formula:	$C_6H_4Br_2O$
Relative molecular mass:	251.92
CAS registry number:	615-58-7
Melting point:	254°C
Boiling point:	37°C
Specific gravity:	2.042 (liquid 40°C/25°C)?
Solubility:	< 1 g/litre (water at 25°C)

Bis(tribromophenoxy)ethane (BTBPE)

Chemical formula:	$C_{14}H_8Br_6O_2$
CAS registry number:	37853-59-1
Relative molecular mass:	687.66
Melting point:	223-225°C
Specific gravity:	2.58 g/cm^3
Solubility:	insoluble in water (0.2 mg/litre at 20°C)

Tribromophenyl allyl oxide (TBP-AE)

Chemical formula:	$C_9H_7Br_3O$
CAS registry number:	NA
Relative molecular mass:	371
Melting point:	75-76.5°C
Specific gravity:	2.2

Poly(dibromophenylene oxide) (PDBPO)

Chemical formula:	$(C_6H_2Br_2O)x$
CAS registry number:	69882-11-7
Melting point:	210-240°C
Specific gravity:	2.07
Solubility:	1.6 mg/litre (water at 25°C)

Hexabromobenzene (HBB)

Chemical formula:	C_6Br_6
Relative molecular mass:	552
CAS registry number:	87-82-1
Flash point:	325-336°F

Pentabromotoluene (5BT)

Chemical formula:	$C_7H_3Br_5$
CAS registry number:	87-83-2
Melting point:	299°C
Flash point:	280-282°F
Specific gravity:	3.15 at 20°C
Solubility:	insoluble in water

Pentabromoethylbenzene (5BEB)

Chemical formula:	$C_8H_5Br_5$
CAS registry number:	85-22-3
Melting point:	136-138°C
Solubility:	insoluble in water

Poly(pentabromobenzyl acrylate) (PBB-PA)

Chemical formula:	$(C_{10}H_5Br_O2)_n$
Relative molecular mass:	34,000
Melting point:	205-215°C
Vapour pressure:	< 0.075 mm Hg at 20°C
Specific gravity:	2.05 g/cm^3 at 20°C
Solubility:	3.5-3.8 mg/litre in water

Dibromostyrene (DBS) and derivatives (PDBS)

	DBS	**PDBS-10/80**
Appearance	light yellow liquid	off-white powder
Bromine content	59%	58-60%
Boiling point	95°C	-
Melting range	-	155-160°C (10), 220-240°C (80)
Thermal stability	-	355°C

(Great Lakes, September 1991)

Brominated polystyrene (BrPS -68-60-LM)

	68PB	60PB	LM
Bromine content (%):	66	60	66
Chlorine content (%):	1	1	2
Volatiles content (%):	0.007	0.07	0.2
Tg. (°C):	195	160	135
Specific gravity:	2.1	2.0	2.1
Appearance:	powder	granules	powder

(Ferro Corp., September 1992)

APPENDIX 4

SOME ABBREVIATIONS USED IN THIS DOCUMENT

ABS	Acrylonitrile butadiene styrene
APP	Ammonium polyphosphate
ATH	Aluminium trihydroxide
BBE	Brominated biphenyl ethers
BCE	Bis-cyclohexenyl-ethylene
BCF	Bioconcentration factor
BFR	Brominated flame retardant
BrPS	Brominated polystyrene
BTBPE	Bis-tribromophenoxy-ethane
BVDU	Bromovinyldeoxyuridine
CF	Continuous filament
COSHH	Control of substances hazardous to health
DBNPG	Dibromoneopentyl glycol
DBP	Dibromophenol
DBS	Dibromostyrene
DeBB	Decabromodiphenyl
DeBDPO	Decabromodiphenyl oxide
DEG	Diethylene glycol
EBTBP	Ethylenebistetrabromophthalimide
EDB	Ethylene dibromide
EG	Ethylene glycol
EHC	Environmental Health Criteria
EPDM	Ethylene propylene rubber
EPS	Expanded polystyrene
EVA	Ethylene vinyl acetate
FR	Flame retardant
HBB	Hexabromobenzene
HBr	Hydrogen bromide
HBCD	Hexabromocyclododecane
HBDPE	Hexabromodiphenoxy ethane
HBPE	Bis-tribromophenoxy-ethane
HpBDPO	Heptabromodiphenyl oxide
HxBDPO	Hexabromodiphenyl oxide
HCl	Hydrogen chloride
HCN	Hydrogen cyanide
HDPE	High density polyethylene
HIPS	High impact polystyrene
IEC	International Electrotechnical Commission
LCP	Liquid crystalline polymers
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MA	Maleic anhydride
MPPO	Modified polyphenylene oxide

NBDPO	Nonabromodiphenyl oxide
OBDPO	Octabromodiphenyl oxide
OI	Oxygen index
PA	Polyamide
PAI	Polyamide-imide
PBB	Polybrominated biphenyl
PBB-PA	Poly-pentabromobenzyl acrylate
PBDD	Polybrominated dibenzo dioxin
PBDF	Polybrominated dibenzo furan
PBDPO	Polybrominated diphenyl oxide
PBT	Polybutylene terephthalate
PC	Polycarbonate
PCDD	Polychlorinated dibenzo dioxin
PCDF	Polychlorinated dibenzo furan
PDBPO	Poly-dibromophenylene-oxide
PDBS	Polydibromostyrene
PeBDPO	Pentabromodiphenyl oxide
PES	Polyester fibres
PET	Polyethylene terephthalate
PF	Phenol-formaldehyde resins
PG	Propylene glycol
PMMA	Polymethylmethacrylate
PP	Polypropylene
PPO	Polyphenylene oxide
PPS	Polyphenylene sulphide
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PUR	Polyurethane
PVC	Polyvinyl chloride
SAN	Styrene acrylonitrile
Sb_2O_3	Antimony trioxide
SBR	Styrene butadiene rubber
TBPA	Tetrabromophthalic anhydride
TBBPA	Tetrabromobisphenol A
TBNPA	Tribromoneopentyl alcohol
TBP	Tribromophenol
TBP-AE	Tribromophenyl allyl ether
TBS	Tribromosalicylanilide
TCDD	Tetrachlorodibenzodioxin
TDBDPB	Tetradecabromodiphenoxybenzene
TeBDPO	Tetrabromodiphenyl oxide
TEQ	Toxic Equivalent
TGA	Thermal gravimetric analyses (TGA factor)
TPA	Terephthalic acid
VBr	Vinyl bromide
VCI	German Chemical Association
V-O	Highest fire retardancy classification
UPE	Unsaturated polyesters

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AND
APPENDIX 1, 2 AND 3

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