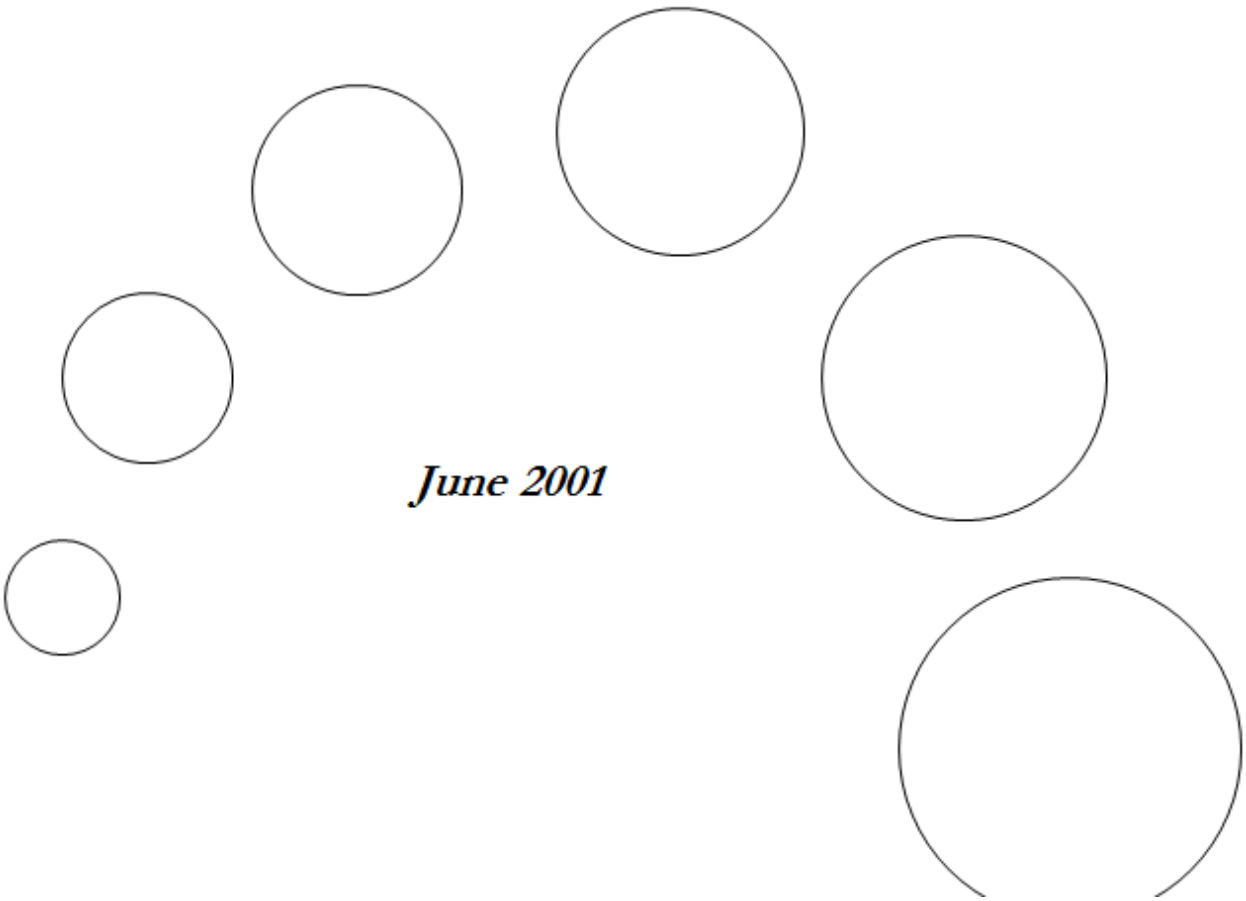
National Industrial Chemicals Notification and Assessment Scheme

Polybrominated Flame Retardants (PBFRs)

Priority Existing Chemical Assessment Report No. 20



June 2001

ISBN 0 642 70987 4

Preface

This assessment was carried out under the National Industrial Chemicals Notification and Assessment Scheme (NICNAS). This Scheme was established by the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), which came into operation on 17 July 1990.

The principal aim of NICNAS is to aid in the protection of people at work, the public and the environment from the harmful effects of industrial chemicals.

NICNAS assessments are carried out in conjunction with Environment Australia and the Therapeutic Goods Administration, which carry out the environmental and public health assessments, respectively.

NICNAS has two major programs: the assessment of the health and environmental effects of new industrial chemicals prior to importation or manufacture; and the other focussing on the assessment of chemicals already in use in Australia in response to specific concerns about their health/or environmental effects.

There is an established mechanism within NICNAS for prioritising and assessing the many thousands of existing chemicals in use in Australia. Chemicals selected for assessment are referred to as Priority Existing Chemicals.

This Priority Existing Chemical report has been prepared by the Director (Chemicals Notification and Assessment) in accordance with the Act. Under the Act manufacturers and importers of Priority Existing Chemicals are required to apply for assessment. Applicants for assessment are given a draft copy of the report and 28 days to advise the Director of any errors. Following the correction of any errors, the Director provides applicants and other interested parties with a copy of the draft assessment report for consideration. This is a period of public comment lasting for 28 days during which requests for variation of the report may be made. Where variations are requested the Director's decision concerning each request is made available to each respondent and to other interested parties (for a further period of 28 days). Notices in relation to public comment and decisions made appear in the *Commonwealth Chemical Gazette*.

In accordance with the Act, publication of this report revokes the declaration of this chemical as a Priority Existing Chemical; therefore manufacturers and importers wishing to introduce this chemical in the future need not apply for assessment. However, manufacturers and importers need to be aware of their duty to provide any new information to NICNAS, as required under section 64 of the Act.

For the purposes of Section 78(1) of the Act, copies of Assessment Reports for New and Existing Chemical assessments may be inspected by the public at the library of the National Occupational Health and Safety Commission (NOHSC). Summary Reports are published in the *Commonwealth Chemical Gazette*, which are also available to the public at the NOHSC library.

Copies of this and other Priority Existing Chemical reports are available on the NICNAS website. Hardcopies are available from NICNAS either by using the prescribed application form at the back of this report, or directly from the following address:

GPO Box 58

Sydney

NSW 2001

AUSTRALIA

Tel: +61 (02) 9577 9437

Fax: +61 (02) 9577 9465 or +61 (02) 9577 9465 9244

Other information about NICNAS (also available on request) includes:

- NICNAS Service Charter;
- information sheets on NICNAS Company Registration;
- information sheets on PEC and New Chemical assessment programs;
- safety information sheets on chemicals that have been assessed as PECs;
- subscription details for the NICNAS Handbook for Notifiers; and
- subscription details for the Commonwealth Chemical Gazette.

More information on NICNAS can be found at the NICNAS Web site:

http://www.nicnas.gov.au

Other information on the management of workplace chemicals can be found at the website of the National Occupational Health and Safety Commission:

http://www.nohsc.gov.au

Overview

The polybrominated flame retardants (PBFRs) including polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDPEs) were declared Priority Existing Chemicals for preliminary assessment as a group on 7 March 2000, primarily due to concerns over the bioaccumulative and persistent nature of some PBFRs and therefore potential to impact adversely on the environment and human health. The focus of this report is on use patterns and potential exposure to members of this class of chemicals in Australia.

The PBFRs are not manufactured in Australia, but are imported as pure chemicals or mixtures, or in polymer resins or extruded polystyrene foam boards. The PBFRs may be introduced into Australia in other finished products or articles, however, no reliable estimates of the quantity are available. These chemicals are used exclusively as flame retardants, typically in concentrations ranging from 3 to 12% depending on the product, although concentrations above and below this range are also used.

For this assessment, the physico-chemical, toxicological and environmental properties of PBFRs were summarised from peer reviewed hazard assessments by international organisations, such as the International Agency for Research on Cancer (IARC), the International Programme on Chemical Safety and the Organisation for Economic Cooperation and Development (OECD). Primary sources of toxicological data were also used for some of the chemicals.

The primary health concerns revolve around the potential of some PBFRs to act as carcinogens, endocrine disruptors and neurodevelopmental toxicants and the lack of adequate toxicological data for others to fully assess their hazards. In addition, their structural similarities to the polychlorinated diphenyl ethers (PCDEs), nitrofen and polychlorinated biphenyls lends further support to concerns for health effects exerted by these chemicals. Of the commercially and commonly used PBFRs, penta- and tetra-bromodiphenyl ethers which are components of the commercial product known as "pentabromodiphenyl ether" appear to be of greatest significance where health effects are concerned. Evidence indicates that from the available data, the liver, and possibly the thyroid, are the most sensitive organs to the brominated diphenyl ethers assessed in this report. The two other chemicals with significant adverse health effects are tris-(2,3-dibromopropyl phosphate) (TDBPP) and the PBBs. Although both have relatively low acute toxicity in experimental animals, supportive evidence for carcinogenicity, endocrine disruption and reproductive effects exists. Overseas commercial manufacture of both TDBPP and the PBBs has been discontinued, although articles containing these chemicals may still be in use. IARC has classified TDBBP as Group 2A carcinogen and the PBBs as Group 2B carcinogens.

Few PBFRs are classified for health effects, however a number are undergoing further testing and review internationally, which will enable classification to occur for those chemicals. The National Occupational Health and Safety Commission and industry will need to ensure classifications reflect the latest data.

It is expected that a large number of workers may be employed nationwide in the flame retarding industry, mostly in the production of flame retarded articles and less so in the formulation of flame retardant polymers and resins. Potential for exposure during transport is expected to be minimal and restricted to accidents.

There is a potential for exposure of workers involved in the formulation of flame retarded resins and polymers, particularly where weighing and mixing are carried out in manual and open systems, and where minimal personal protective equipment is used.

Downstream fabricators of articles are also at risk of exposure to PBFRs in resin and polymer formulations, though to a lesser degree than formulators. PBFRs may diffuse from treated articles, a process generally referred to as "blooming" which is dependent on a number of factors, including molecular weight and structure, the chemical nature of the compound (reactive or additive) and the structure of the polymer matrix of the article. Such articles are likely to be used to a great extent in private and/or commercial premises, with potential for long term occupational exposure. A number of recent overseas reports describe exposure to PBFRs in different occupations, although potential health risks have not been assessed. Despite the lack of exposure data, some assessments indicate negligible risks for some PBFRs/use scenarios (National Academy Press 2000; IPCS 1994b).

Little information is available on emission and release of PBFRs into the Australian environment. PBBs and PBDEs, may be persistent in the environment. The introduction of PBDPEs into widespread products may provide a long-term and diffuse source of emissions and release into the environment. Tetra- and pentabromodiphenyl ethers bioaccumulate in fish eating birds. Although biomagnification may occur in fish eating birds the evidence for this is equivocal. Some volatilisation and long range transport may also occur. Evidence in support of this is available for tetra- and pentabromodiphenyl ether.

Based on limited data, some PBDPEs may be considered highly acutely toxic to some aquatic organisms, though chronic toxicity seems limited. Under the EU's Existing Chemical Regulation (reflected in OECD's Screening Information Data Set (SIDS) assessment program), work is underway with testing on soil, sediments, waste water treatment plants and biodegradation for a number of these compounds. Additional data on the brominated flame retardants will be required for a comprehensive assessment of their possible adverse impact on the Australian environment.

At present, knowledge of long-term effects resulting from public exposure to PBFRs and their breakdown products is limited. Given the widespread public contact with products containing PBFRs in Australia, and the lack of information about exposure levels for the general public, it is currently not possible to determine whether their use poses an unacceptable risk.

In conclusion, due to the identified health and environmental effects of concern with some PBFRs, the lack of adequate data on others and their wide use it is recommended that a full (risk) assessment be considered when hazard data is available from international assessments. On the basis of the known hazards for specific PBFRs, it is recommended that labels, material safety data sheets and other hazard communication materials be revised to reflect the information on hazards already available for these chemicals from international assessments and summarised in this report.

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Acronyms and Abbreviations

ABS	acrylonitrile-butadiene-stryrene
ADG CODE	Australian Dangerous Goods Code
AICS	Australian Inventory of Chemical Substances (NICNAS)
BDBPP	bis (2,3-dibromopropyl) phosphate
bw	body weight
CAS	Chemical Abstracts Service
CHO	Chinese hamster ovary
DBDPE	decabromodiphenyl ether
DMF	dimethylformamide
DMSO	dimethyl sulphoxide
EC	European Commission
EC_{50}	median effective concentration
EU	European Union
ECL	Korean Existing Chemicals List
EINECS	European Inventory of Existing Commercial Chemical Substances
ENCS	Japanese Existing and New Chemical Substances
FM	Flame retardant
g	grams
h	hour
HBCD	hexabromocyclododecane
HBDPE	hexabromodiphenyl ether
HpBDPE	heptabromodiphenyl ether
hPa	hectopascal
IARC	International Agency for Research on Cancer
IPCS	International Programme on Chemical Safety
kg	kilogram
K_{ow}	octanol/water partition coefficient
L	litre
LC_{50}	median lethal concentration

LD_{50}	median lethal dose
LOAEL	lowest-observed-adverse-effect level
LOEL	lowest-observed-effect level
mg	milligram
mg/cm^3	milligrams per cubic centimetre
mg/kg bw	milligrams per kilogram body weight
mg/kg bw/d	mg/kg body weight/day
mL	millilitre
µg	microgram
MATC	Maximum acceptable toxicant concentration
MSDS	Material Safety Data Sheet
MTL	Master Testing List
NBDPE	nonabromodiphenyl ether
ng	nanogram
NOAEL	no-observed-adverse-effect level
NOEC	no-observed-effect concentration
NOEL	no-observed-effect level
NOHSC	National Occupational Health and Safety Commission
NTP	National Toxicology Program (USA)
OBDPE	octabromodiphenyl ether
OECD	Organisation for Economic Cooperation and Development
OPPT	Office of Pollution Prevention and Toxics
Pa	pascals
PBFRs	polybrominated flame-retardants
PBB	polybrominated biphenyls
PBDE	polybrominated diphenyl ethers
PBDPE	polybrominated diphenyl ethers
PDBD	p-dibenzodioxins
PDBF	p-dibenzofurans
PeBDPE	pentabromodiphenyl ether
PEC	Priority Existing Chemical
PEC	predicted environmental concentration

pg	picogram
PIC	Prior Informed Consent
ppb	parts per billion
ppm	parts per million
PPO	polyphenylene oxide
PS	polystyrene
QSAR	quantitative structure-activity relationship
SCE	sister chromatid exchange
SIAR	SIDS Initial Assessment Report
SIAM	SIDS Initial Assessment Meeting
SIDS	Screening Information Data Set
SUSDP	Standard for the Uniform Scheduling of Drugs and Poisons
TBBPA	tetrabromobisphenol A
TBDPE	tetrabromodiphenyl ether
TDBPP	tris (2,3-dibromopropyl) phosphate
TrBDPE	tribromodiphenyl ether
TSCA	Toxic Substances Control Act (US EPA)
TTBP	tris (tribromoneopentyl) phosphate
TWA	time-weighted average (NOHSC)
UDS	unscheduled DNA synthesis
US EPA	Environmental Protection Agency of the USA
VIC	Voluntary Industry Committment
WHO	World Health Organization

1. Introduction

1.1 Declaration

The polybrominated flame retardants (PBFRs) encompassing polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDPE) and a range of other chemicals were declared Priority Existing Chemicals (PEC) for preliminary assessment under the *Industrial Chemicals (Notification and Assessment) Act 1989* by notice in the Chemical Gazette of 7 March 2000. The declaration applied to the flame retardant uses of the chemicals.

The reason for declaration was concern over "the widespread use of polybrominated flame retardants in numerous household and industrial items such as printed circuit boards, polystyrene and other plastics. This large number of dispersive uses provides many ways for these to enter the environment. Some polybrominated flame retardants can be expected to be persistent, lipophilic and bioaccumulative and therefore potentially have adverse impacts on the environment and human health. Certain countries have banned or severely restricted use of specific polybrominated flame retardants. OECD countries are coordinating hazard testing of a number of these substances. Australian use information is needed to put the hazard data on PBFRs into perspective with respect to potential risk."

1.2 Scope of the assessment

The assessment is a preliminary one, focussing on manufacture/import volumes, identifying downstream users and use patterns and the potential for occupational, public health and environmental exposure to the chemicals in Australia. All sectors manufacturing, importing, using or potentially using PBFRs are investigated as potential sources of human and environmental exposure. These chemicals are assessed as a class. Summary information on health and environmental effects is included. The Act prescribes that risk assessment and risk management (see below) are not covered in preliminary assessments. However, as an outcome of a preliminary assessment, the Act requires NICNAS to determine the significance of the assessment findings for risk. If the findings indicate that there may be a significant risk of adverse health, safety or environmental effects, then a full (risk) assessment may be recommended.

This assessment, although focusing on PBFRs as a single class of chemicals, acknowledges that the chemicals comprising this class are a structurally diverse group of chemicals. In addition, it is recognised that some PBFRs are either mixtures of different congeners (e.g. PBDPEs) or polymers of variable composition. As such, PBFRs do *not* necessarily have similar chemical, physical, toxicological or environmental properties. Every attempt has been made to clarify this issue, where relevant, in the body of the report. However, where data are either lacking or were not available for assessment, the default, by necessity, was to adopt a more generic approach.

The aim of a 'preliminary' PEC assessment is not to undertake a comprehensive evaluation of all available data (i.e. as required in a full risk assessment) or to recommend risk reduction measures beyond those that are currently adopted under relevant Australian regulations (e.g. NOHSC hazard classification) or have been initiated by international treaties or promulgated by expert international organisations (e.g. EU, OECD).

1.3 Objectives

The objectives of the assessment are to:

- identify the manufacture/import volumes and the likely or potential uses of polybrominated flame retardants;
- review the properties of PBFRs;
- review and summarise any adverse health or environmental effects of PBFRs; and
- determine the potential for public and occupational exposure and exposure to the environment resulting from use; and
- determine the need for a full risk assessment in light of the conclusions on the risk of adverse health or environmental effects.

1.4 Sources of information

Information for the assessment was obtained from a number of sources.

Industry

Manufacturers and importers of PBFRs and mixtures containing PBFRs were requested to apply for assessment and supply data. Industry supplied information on:

- volumes being, or proposed to be, imported, manufactured and/or formulated into products;
- mixtures already, or proposed to be, imported and/or formulated which contain PBFRs;
- known uses and potential uses;
- methods used or proposed to be used in handling, storage, manufacture and disposal;
- information on human and environmental exposure to PBFRs; and
- a list of end users.

Importers of PBFRs and PBFR products on-sell them and were unable to provide data on potential exposure and disposal during use of the chemicals. An external consultant, Professor Ian Rae, was therefore appointed to facilitate data collection and to investigate use patterns and potential occupational, public and environmental exposure during use of PBFRs in Australia.

Literature review

The major sources of information on the toxicology of PBFRs were the World Health Organisation (WHO) Environmental Health Criteria (EHC) monographs published under the International Programme on Chemical Safety (IPCS). Other sources of toxicological data were draft risk assessments on pentabromodiphenyl ether (PeBDPE), octabromodiphenyl ether (OBDPE), decabromodiphenyl ether (DBDPE) and hexabromocyclododecane (HBCD) carried out by the UK, France/UK and Sweden, respectively, and prepared for the OECD Existing Chemicals Screening Information Data Set (SIDS) program, a report by the National Research Council commissioned by the USA National Academy of Sciences, a report by the Swedish National Chemicals Inspectorate and a report under the Voluntary Industry Commitment by the US and European Producers of Selected Brominated Flame Retardants under the OECD's Risk Reduction Programme.

Other relevant data for the assessment were obtained from literature searches of publicly available databases, and other bibliographic sources.

Due to the availability of a number of overseas reports and the preliminary nature of this assessment, not all primary sources of data were evaluated.

No published reports were available for brominated polystyrene; 1,2-bis (tribromophenoxy) ethane; ethylene bis-(tetrabromophthalimide); 2-propenoic acid (pentabromophenyl) methyl ester; disodium tetrabromophthalate; phosphoric acid, mixed 3-bromo-2,2-dimethylpropyl and 2-bromoethyl and 2-chloroethyl esters. However, primary study reports were identified and obtained for these chemicals.

No sources of information were publicly available for:

Tetradecabromo (p-diphenoxy benzene);

Bis-(2,4,6-tribromophenyl) carbonate;

3,4,5,6-Tetrabromophthalic anhydride, ethylene glycol, propylene oxide reaction products; and

TBBPA, 2,2-bis [4- (2,3-epoxypropyloxy) dibromophenyl] propane polymer.

An assessment report (NA/672) published by the New Chemicals Assessment Program, the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) was used as the main source of information for tris (tribromoneopentyl) phosphate (TTBP).

Literature searches were conducted utilising Medline, PubMed, Toxline, Scifinder and Tomes CPS. The last literature search for this assessment was conducted on 27 November 2000.

1.5 Peer review

The report has been subjected to internal peer review by NICNAS, Environment Australia (EA) and Therapeutic Good Administration (TGA) during all stages of preparation. External peer review was not undertaken because the primary sources

of the hazard information has already been subject to significant international peer review.

2. Background

Polybrominated flame retardants comprise about 25% of the volume of flame retardants used on a global scale. As a class, they are structurally diverse and include aromatic diphenyl oxides (a.k.a. ethers), cyclic aliphatics, phenolic derivatives, aliphatics, phthalic anhydride derivatives and others. The PBFRs share one common characteristic – they all contain bromine. The bromine portion of the compound is responsible for the molecule's flame retardant activity and is unique in its ability to provide flame retardancy in the gas phase. Most brominated flame retardants have fairly specific applications; few are broad spectrum across-the-board flame retardants. Their specific applications are determined by many factors including the type of resin requiring flame retardancy, the level of flame retardancy required, the properties of the resin and its additives, and the items' use. For example, DBDPE is used primarily in electronics and electronic equipment housings, OBDPE in one resin (ABS) in electronic equipment housings, PeBDPE to flame retard flexible polyurethane foam used as cushioning in upholstery, and HBCD in upholstery textiles and rigid plastic foam.

Brominated flame retardants are used in applications requiring high FR performance or in resins needing a FR active in the gas phase of a fire. Examples of applications requiring high FR performance (e.g. the ability to meet V0 or FR4 requirements) are electronic equipment and printed circuit boards. Resins requiring gas phase flame retardancy are those which melt, drip, and de-polymerize to form volatile monomers, dimers and trimers when exposed to heat (e.g. styrenic polymers). Styrenic polymers include polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), polyphenylene oxide/polystyrene blends (modified PPO) and polycarbonate/ABS blends. Flame retardants that act in the gas phase are limited to those containing halogens, and in practice this means bromine or chlorine-containing flame retardants.

Two PBFRs account for approximately 50% all PBFR usage globally. These two PBFRs are Tetrabromobisphenol A (TBBPA) (#1 in volume globally) and DBDPE (#2 in volume globally). The remaining 50% of the global volume of PBFRs is composed of a number of different PBFR structural types and includes the two other commercial PBDPE flame retardants: OBDPE and PeBDPE. The OBDPE and PeBDPE commercial products are produced and used in substantially smaller quantities than DBDPE. Not all PBDPEs are used as flame retardants, nor are all PBDPEs components of these three commercial PBDPE products.

The brominated flame retardants have a high bromine content of 50 to 85% and a relative molecular mass ranging from 200 to that of larger polymers. They represent over 90% of the broad category of halogenated flame retardants.

Bromines are incorporated into organic molecules in three ways - addition to carbon-carbon double bonds, substitution in aliphatic hydrocarbons, or substitution in aromatic compounds in which the aromatic is usually activated towards such substitution by existing oxygen (phenol or ether) substituents.

The third class, namely substitution in aromatic compounds, may be subdivided into additive and reactive flame retardants:

- the additive substances include polybromodiphenyl ethers (PBDPEs) including the mono- to decabromodiphenyl ethers and polybromobiphenyls (PBBs), which are discrete molecules with molar masses in the range of approximately 240 to 1000 Dalton. Also in this group are esters of pentabromobenzoic acid and tetrabromophthalic acid and derivatives of tetrabromophthalimide.
- the reactive flame retardants include bromo-derivatives of bisphenol A which, because of the presence of free hydroxy groups in the molecule, may be incorporated into polyesters and epoxy resins in the same way as the regular monomer, bisphenol A, thus imparting flame retardancy to the polycarbonate product. Esters of propenoic (acrylic) acid or 2-methylpropenoic (methacrylic) acid having bromine in the ester moiety, for example derived from a pentabromobenzene moiety, can give rise to ethylenic polymers which are flame retardant. A third type is exemplified by tetrabromophthalic anhydride, which may take the place of a proportion of the phthalic anhydride component of an alkyd resin. Finally, the brominated polystyrenes are another member of this class, although the brominated units are created by bromination of a polymer rather than preformation and incorporation through the polymerisation process.

Two aromatic brominated retardants represent the highest volumes in use today in Australia, namely DBDPE followed by PeBDPE. HBCD, a cycloaliphatic chemical, is another commonly used brominated flame retardant in Australia.

2.1 International perspective

Worldwide, PBFRs are used in numerous products including electrical and electronic equipment, coatings, in automotive parts, upholstery textiles, furniture, building materials and thermal insulation used in buildings.

Over 55% of the world bromine is produced by the OECD countries, with much of the remainder produced by Israel and the ex-USSR. Approximately 20% of world bromine is used in the manufacture of flame retardants. PBFRs make up approximately 25% of all flame retardants sold globally.

The wide scattered use of PBFRs together with concern over their impact on the environment and human health have attracted international attention to assess the risks associated with their use. The PBBs, PBDPEs and tetrabromobisphenol A (TBBPA) have been the most widely studied brominated flame retardants. For PBBs, industry advise that since the 1970's, only decaBB has been manufactured commercially, which ceased in 2000 and accounted for around 1% of all PBFR use. Currently, TBBPA and DBDPE are the most widely used PBFRs. According to the EU, the TBDPE congener makes up approximately 70% of PBFRs detected in environmental samples.

Concerted efforts by international organisations to implement risk reduction measures have been initiated. For example, the manufacture and use of some brominated flame retardants have been restricted or prohibited, through government legislation or voluntary action by industry.

Europe

The Swedish government has proposed a phase out of PBDPEs and PBBs. The National Chemicals Inspectorate (Kemi, 1995, 1999) was commissioned by the Swedish government to prepare and submit proposals for the phasing out of PBDPEs and PBBs; reporting was prepared within the framework of a risk reduction plan process. In Germany, these chemicals are restricted through the Dioxin Ordinance and by voluntary agreements with industry. Dioxins may be formed during the production and/or incineration of flame-retarded plastics, and thus the requirements for the Ordinance restrict indirectly the use of PBDPEs and PBBs (Kemi, 1999). The production of PBDPEs has ceased in Germany, but their use as chemical products and in imported products continues. In Germany and Denmark, projects are in progress to investigate the use and fate of brominated flame retardants and substitution possibilities. In the Netherlands, industry has given a voluntary undertaking to phase out PBDPEs and PBBs (Kemi, 1999).

Brominated flame retardants are proposed for consideration under the Oslo and Paris Convention for the Prevention of Marine Pollution (OSPAR). Under the Esbjerg Declaration, Environment Ministers agreed at the Fourth North Sea Conference (1995) on common action to be taken within the international organisations to replace brominated flame retardants with less hazardous substances where alternatives were available.

In the European Commission, work is in progress on drafting a Directive concerning waste from electronics and electrical products.

PBBs and tris-(2,3-dibromopropyl phosphate) (TDBPP) are subject to the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade. This procedure aims to facilitate informed decision making on the export and import of potentially hazardous chemicals and to promote the protection of human health and the environment from the harmful effects of such chemicals. This is achieved via the provision of a list of chemicals of particular concern summarising relevant information on each chemical. Many overseas countries have not consented to the importation of these chemicals.

The PBBs have been added to the chemicals banned or severely restricted to certain uses by the European Community due to their effects on human health and the environment (CEC, 1988 cited in IPCS 152, 1994). Similarly, many European member countries have implemented EC Directives restricting or banning the use of TDBPP and bis (2,3-dibromopropyl) phosphate (BDBPP) in children's clothing.

Other measures and activities of risk management in various countries include identifying alternatives and substitutes, discussions to restrict the use of brominated flame retardants and eco-labelling of equipment containing flame retardants (Kemi, 1999).

USA

In the USA, the production and use of PBBs was discontinued voluntarily by industry in the late 1970s. Also, a Significant New Use Rule was introduced by the Environment Protection Agency (US EPA) to govern intended resumption of the manufacture of specified PBBs. In 1977, the use of TDBPP in children's clothing was banned by the US Consumer Product Safety Commission. Since then, its use

as a flame retardant has been severely restricted in consumer products and prohibited in textiles.

A number of PBFRs are listed on the US EPA Office of Pollution Prevention and Toxics (OPPT) Master Testing List (MTL), which is a consolidated listing of the existing chemical testing priorities of the OPPT (US EPA, 2000). The PBFRs currently listed include:

- 2,4,6-tribromophenol, TSCA Section 4 Final Rule-Making testing program completed, but the chemical remains on MTL because of additional testing actions;
- pentabromophenol, currently under TSCA section 4 Final Rule Making, product analysis underway;
- 2,4-dibromophenol, currently under TSCA section 4 Final Rule Making;
- decabromodiphenyl ether, TSCA Section 4 Final Rule-Making testing program completed, but the chemical remains on MTL because of additional testing actions for OECD/SIDS;
- 4-bromo-2,5-dichlorophenol, currently under TSCA section 4 Final Rule Making, product analysis underway;
- tetrabromobisphenol A diglycidyl ether,2,2',6,6'-, Testing Action Development Underway;
- cyclododecane,1,2,5,6,9,10-hexabromo-, Testing Action Development Underway;
- tetrabromobisphenol A bis(ethoxylate), TSCA Section 4 Final Rule-Making testing program completed, but the chemical remains on MTL because of additional testing actions;
- dibromophenyl glycidyl ether, 2,4-, Testing Action Development Underway;
- tetrabromobisphenol A bis(2,3-dibomopropyl ether), currently under TSCA section 4 Final Rule Making, product analysis underway;
- dibromo-4-methylphenyl glycidyl ether,2,6-, Testing Action Development Underway;
- tetrabromobisphenol A, ally ether, TSCA Section 4 Final Rule-Making testing program completed, but the chemical remains on MTL because of additional testing actions;
- pentabromodiphenyl ether, TSCA Section 4 Final Rule-Making testing program completed, but the chemical remains on MTL because of additional testing actions for OECD/SIDS;
- octabromodiphenyl ether, TSCA Section 4 Final Rule-Making testing program completed, but the chemical remains on MTL because of additional testing actions for OECD/SIDS;
- tetrabromobisphenol A diacrylate, currently under TSCA section 4 Final Rule Making, product analysis underway;

- tetrabromobisphenol B, currently under TSCA section 4 Final Rule Making, product analysis underway;
- 2,4-dibromo-6-methyl-phenyl glycidyl ether, Testing Action Development Underway.

In addition, under the auspices of the Toxic Substances Control Act (TSCA), the Interagency Testing Committee (ITC) has made testing decisions for 129 chemicals since 1978 (Walker, 1994). A number of criteria, such as the needs of the US government organisations represented on the ITC and the section 4(e) criteria of TSCA (e.g quantities of chemical manufactured, released into the environment, workers exposure and potential to cause adverse health effects) are usually considered prior to decisions on designations/recommendations, deferrals and/or removals of chemicals from the Priority Testing List (PTL).

OECD-Industry program

In 1990, the OECD established a pilot program aimed at reducing the risks from chemicals. Of five chemicals nominated for study the PBBs, PBDPE and TBBPA were selected as a group. The Brominated Flame Retardant Industry Panel (BFRIP), a US Chemical Manufacturers Association (CMA) panel and the European Brominated Flame Retardant Industry Panel (EBFRIP) participated in the pilot risk reduction programme on the selected brominated flame retardants providing comments on OECD draft reports and participating in workshops.

In response to concerns expressed by OECD member states, a Voluntary Industry Commitment (VIC) by the major brominated flame retardant producers of the USA, Europe and Japan was proposed, accepted by the OECD and officially initiated in 1996. The member companies participating in the VIC are Albermarle Corporation, Ameribrome Inc. and Great Lakes Chemical Corporation all of which are members of the CMA BFRIP. Akzo Nobel Chemicals Inc is an associate member. European EBFRIP members of the VIC include Albermarle S.A., Elf Atochem, Eurobrom B.V. and Great Lakes Chemical (Europe) Ltd. Japan's member companies include Asahi Glass Co., Albermarle Asano Corporation, Teijin Chemicals Ltd., Tosoh Corporation, Nippoh Chemicals Co. Ltd., Bromoken (Far East) Ltd, Manac Incorporated, Miki & Co. Ltd. and Mitsui Toatsu Fine Chemicals Inc.

The brominated flame retardants covered by the OECD's Risk Reduction Program and the VIC are decabromodiphenyl ether (DBDPE), octabromodiphenyl ether (OBDPE), pentabromodiphenyl ether (PeBDPE), TBBPA and the PBBs.

Through the VIC, industry committed to:

- not manufacture as individual flame retardants lower brominated diphenyl ethers (except as components of the three commercial PBDE products) and not initiate the manufacture of any PBB (the exception was the continued production of DecaBB by one manufacturer who would re-evaluate the need for the product in the year 2000), and agreed not to import and/or export these compounds;
- minimise contamination of PBDPEs with lower brominated diphenyl ethers, pollution prevention and controlled release of the PBFRs in the VIC; and

- conduct regular toxicology and environmental assessment and reporting on the specified brominated compounds.

Although members of the VIC did not commit to undertake particular tests, they agreed to continue with on-going tests and initiate new tests as suggested by the IPCS or required by the US EPA or the EU.

At the 30th OECD Joint Meeting (February 2000), a summary of the developments on the VIC together with update reports from manufacturers of PBFRs were provided. It was also noted that reductions in emissions had been achieved as a result of cessation of production of PBBs, rationalisation of manufacturing sites together with other control measures. It was noted at the 31st OECD Joint Meeting (October 2000) that when the current EU reviews on a number of PBFRs have been completed (see section 2.3), the Joint Meeting will consider whether any further OECD action is required.

2.2 Australian perspective

There are no restrictions on the manufacture, import and use of these chemicals in Australia.

Prior to this assessment, little was known about the extent of exposure of the Australian environment to these chemicals. Given their incorporation into a variety of end use articles, they are expected to be broadly distributed across Australia. They are likely to be imported as raw materials in the form of pure chemicals or in chemical resin mixtures, or in market-ready consumer products. In addition, little was known about the extent of human exposure, either directly through working with these substances, or arising from environmental exposure.

None of the chemicals in this class are currently listed on the NOHSC *List of Designated Hazardous Substances* (National Occupational Health and Safety Commission, 1999a) or the *Standard for Uniform Scheduling of Drugs and Poisons* (Australian Health Ministers Advisory Council, 2000). PBFRs are not listed in the Australian Dangerous Goods Code (FORS, 1998).

One of the PBFRs has been assessed by the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) under the New Chemicals Assessment Program.

2.3 Assessment by overseas national or international bodies

The International Programme on Chemical Safety (IPCS) has prepared several Environmental Health Criteria (EHC) monographs on several flame retardants including the brominated groups. The PBFRs reviewed by EHC are the PBDPEs (IPCS 162), TBBPA and its derivatives (IPCS 172) and the PBBs (IPCS 152).

The EU is currently conducting risk assessments on specific PBFRs under their Existing Chemicals Regulation Program. The chemicals under assessment are: TBBPA and PeBDPE (UK); DBDPE and OBDPE (UK/France) and HBCD (Sweden). In all cases the commercial products are being assessed.

The EU risk assessment on PeBDPE was finalised in August 2000. The classification for human health is Xn: Harmful with the risk phrase R 48/21/22 - danger of serious damage to health by prolonged exposure in contact with skin or if swallowed and R64 - may cause harm to breast fed babies. The classification for the environment is R50/53 - very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. These classifications have now been adopted by EU member states. The report concluded that there is a need for further testing and risk reduction measures. The additional testing required includes toxicity to sewage micro-organisms, toxicokinetic data on dermal absorption and uptake/excretion in breast milk and a multi-generation reproduction study. A draft risk reduction strategy has been developed which proposes a restriction on marketing and use of PeBDPE under EU Directive 76/769/EEC.

These four chemicals are also being assessed under the OECD Screening Information Data Set (SIDS) Programme, whereby UK, France and Sweden are conducting the evaluations. Australia is involved in this program and will be considering these assessments. Draft SIDS reports have been prepared for DBDPE and OBDPE in which existing toxicity data have been assessed and the OECD agreed on testing to fill remaining SIDS data gaps. A proposal to classify OBDPE as a hazardous substance is to be considered pending the outcome of further toxicity studies (undergoing). Additional testing required includes sediment and soil toxicity, anaerobic degradation/debromination, chronic inhalation toxicity with appropriate examination of reproductive endpoints and genotoxicity.

The final SIDS report for PeBDPE was discussed at the eleventh SIDS Initial Assessment Meeting (SIAM 11) in January 2001. The EU risk reduction proposals were noted (see above) and it was recommended that OECD member states review the exposure situation in their respective countries to determine the need for similar measures. A SIDS Initial Assessment Report (SIAR) has been prepared for HBCD which has been discussed and will be finalised following completion of additional testing for a range of end points.

Other reviews (contracted studies) of certain flame retardants have been carried out for the European Commission. For example, the Binetti Report (1992), which evaluated the toxicology of flame retardants used in upholstery in Europe, concluded that their use was compatible with protection of health and the environment. A risk benefit analysis for PBDPEs, conducted for the UK Department of Environment in 1992, found that risks to the environment or humans were uncertain, no chronic effects were observed in the environment and no significant human health effects were identified. Another study, the 1993 Techno-economic study on brominated flame retardant emissions in the EU, concluded that releases of PBBs, PBDPEs and TBBPA from production processes are minimal and that those from the plastics industry can be adequately controlled. It also concluded that greater potential for release was associated with transportation and storage due to accidents.

3. Applicants

Following the declaration of polybrominated flame retardants as a PEC, eight companies importing or using chemicals within this class into Australia for use as flame retardants applied for assessment of these chemicals. In addition, an application was also received from an interested party. Companies supplied information on import volumes as pure chemicals or in mixtures; information on volumes used in formulation were also supplied where relevant. Details of customers and uses of the chemicals were also provided. Data for assessment were also provided by companies that purchase the chemicals in Australia for formulation into a variety of products. In accordance with the *Industrial Chemicals (Notification and Assessment) Act 1989*, NICNAS provided the applicants with a draft copy of the report for comments during the statutory consultation phases of the assessment.

The applicants were as follows:

Australian Council of Trade Unions
393 Swanston Street
Melbourne
VIV 3000

Dow Chemical (Australia) Ltd
Private Bag No 1
Altona
VIC 3018

Dupont (Australia) Ltd
49-59 Newton Road
Wetherill Park
NSW 2164

Huntsman Chemical Company Australia Pty Ltd
PO Box 62, West Footscray
VIC 3012

International Sales and Marketing Pty Ltd
PO Box 544
South Hurstville
NSW 2221

Marchem Australasia Pty Ltd
PO Box 242, North Braybrook
VIC 3019

Plastral Fidene
PO Box 1095
Waterloo DC
NSW 2017

Swift & Co
PO Box 600
Abbotsford
VIC 3067

T.R. Chemicals (Australia) Pty Ltd
PO Box 453
Wentworthville
NSW 2145

4. Chemical Identity, Composition and Physical and Chemical Properties

4.1 Chemical identities and physicochemical properties

Details of chemical names, registry numbers including chemical abstract service (CAS) number, EINECS number, ENCS number and ECL number, other names and trade names, molecular and structural formulae and molecular weight for each of the PBFR chemicals assessed are described in Appendix A.

The physical and chemical properties for the chemicals are also detailed in Appendix A. Unless otherwise specified, these properties are provided for the pure chemicals. As indicated earlier (Section 1.2), the PBFRs are a diverse class of chemicals that differ in their physicochemical characteristics, details of which are provided in Appendix A. However, a brief summary is presented in this section with ranges described, where available, for the different properties (see also Table 2).

The PBDPE are stable compounds with high boiling points ranging between 310^{o} and 425^{o} C and low vapour pressures in the range 6.5 x 10^{-6} to 4.5 x 10^{-5} Pa at 20 to 25^{o} C. They exhibit poor solubility in water (0.0001 to 0.01 mg/L) and in most organic solvents, with *n*-octanol/water partition coefficients (log P_{ow}) between 4 and 10. No formal fat solubility studies were available for assessment, but pharmacokinetic studies indicate significant differences between congeners e.g., <1% DBDPE was identified in fatty tissue, whereas the majority of TBDPE was retained in adipose tissue.

The chemical stability of the PBBs is dependent, in part, on the degree of bromination and the specific substitution patterns. In general, the highly brominated PBBs are more rapidly degraded by UV radiation. Their solubility in water is low and decreases with increasing bromination. Melting points, where determined, range from a low of 72^{o} C to a high of 380^{o} C. Like the PBDPEs, the PBBs have low vapour pressures.

Little information is available for the other brominated flame retardants covered in this review. The available data indicate that low vapour pressures are also characteristic of other PBFRs.

4.2 Thermal degradation

Considerable laboratory experimentation has gone into the investigation of the thermal degradation, pyrolysis and combustion products of PBFRs, mainly because of concern that polybromodibenzo-dioxins (PBDD) and -furans (PBDF) might be formed. Close analogies have been drawn with the formation under similar conditions of polychlorodibenzo- dioxins and -furans from organochlorine substances and with the toxicity of these derived ‘dioxins’.

Neither the commercial flame retardant DBDPE, nor plastic materials incorporating it, contain measurable amounts of the highly toxic polybromodibenzo-dioxin and -furan contaminants. Partial combustion of the material containing the flame retardant (and usually also antimony trioxide) produced polybromodibenzo-dioxins and -furans, but these were mainly heavily brominated and congeners with the substitution pattern of most concern - 2,3,7,8 - were minor components of the congener mixture (Thoma et al, 1987).

Analysis of 2-propenoic acid (pentabromophenyl) methyl ester; tris (tribromoneopentyl) phosphate and TBBPA bis (2,3-dibromopropyl) ether for contamination of polybrominated p-dibenzodioxins and dibenzofurans indicated that the PBDD/PBDF levels were below the level of quantification specified by US EPA Toxic Substances Control Act (TSCA) 40 CFR 766.27. The levels of PDBD/PDBF in incineration gas were also below the US EPA level (DSBG, 2001). No details were provided on the combustion products of tris (tribromoneopentyl) phosphate and TBBPA bis (2,3-dibromopropyl) ether.

In an early study, brominated flame retardants were heated in open quartz tubes and the pyrolysis residues were analysed by gas-liquid chromatography (Thoma et al., 1986). Maximum yields of dibenzodioxins and furans were observed for reactions conducted at 800^{o}C, but none could be isolated from the residues of tetrabromo phthalic anhydride.

Table 1 shows measured releases of dibenzo-dioxins and -furans from some brominated flame retardants (adapted from Thoma et al., 1986).

Table 1 -Dibenzodioxins and dibenzofurans (ppm) from flame retardants

	2,4,6-tribromophenol	**pentabromophenol**	**TBBPA**
Dibenzodioxin			
dibromo	n.d.	n.d.	233
tribromo	40898	n.d.	109
tetrabromo	896000	n.d.	27
pentabromo	3053	375	n.d.
hexabromo	n.d.	1840	n.d.
heptabromo	n.d.	3621	n.d.
octabromo	n.d.	1672	n.d.
Dibenzofuran			
monobromo	n.d.	n.d.	270
dibromo	n.d.	n.d.	623
tribromo	n.d.	n.d.	236
tetrabromo	8950	n.d.	21
pentabromo	n.d.	n.d.	n.d.
hexabromo	n.d.	n.d.	n.d.
heptabromo	n.d.	7042	n.d.

Subsequent work by Thoma and coworkers (Thoma et al., 1987) showed that yields of mixed polybromodibenzofuran congeners as high as 90% could be realised by the pyrolysis of neat bromodiphenyl ethers, and lesser yields when the flame retardants were incorporated into polystyrene or polyethylene. Gas-phase pyrolysis of a number of PBFRs, including polybrominated diphenyl ethers, has demonstrated the formation of bromobenzenes, bromophenols and dioxins and furans at intermediate temperatures. However, these were destroyed when the thermal degradation reactions were carried out at 800°C (Striebich et al., 1991). Similar experiments with decabromodiphenyl and tetrabromobisphenol A showed the presence in the pyrolysates of polybrominated dibenzo-dioxins and –furans, the latter in greater amounts. Only small proportions of these products had the 2,3,7,8-tetrasubstitution pattern, which is associated with the greatest toxicity. Formation of the dioxins and furans was greatest at 600°C (Luijk & Govers, 1992). Similar results were reported for thermal degradations conducted in a device, which simulated the operation of a municipal waste incinerator (Riggs et al., 1992).

In other thermal degradation experiments it has been observed that bromine from the PBFRs may be transferred to fragments derived from other components of commercial mixtures. For example, bromoethane formed in this way has been reported (Dave & Israel, 1989, 1990) the two-carbon moiety sourced to the nylon into which the flame retardant had been incorporated. In general polymeric materials containing bromine, such as poly(pentabromobenzyl acrylate), decompose above 300°C with release of hydrogen bromide and other toxic substances.

Similar studies continue to be reported and it is clear that combustion of material containing PBFRs, except in high temperature incinerators operated specifically so as to minimise dioxin emissions, will result in dispersal of polybromodibenzodioxins and furans into the environment.

4.3 Blooming potential

Blooming is defined as the migration (or more appropriately, diffusion) of an ingredient (e.g., plasticiser or flame retardant) in rubber or plastic material to the outer surface after curing. It is sometimes incorrectly referred to as ‘leaching’ or ‘degassing’. Diffusion is generally considered to be a slow process.

Blooming has been identified as a source of potential exposure (human and environmental) to PBFRs, particularly for low molecular weight additive PBFRs, although there appears to be a lack of data on the propensity for blooming for the chemicals reviewed in this report.

It is generally accepted that ‘reactive’ PBFRs such as TBBPA (and derivatives) and esters of acrylic (propenoic) acid, which are directly incorporated into polymers (e.g., polyester or epoxy resins) via chemical reaction (i.e., covalent binding) have a low or negligible blooming potential, although such chemicals can also be used as non-reactive (i.e., additive) ingredients.

So-called ‘additive’ PBFRs (e.g., PBDPEs, PBBs, HBCD) are more likely to be subject to blooming, as these compounds are not chemically bound to the polymer backbone. Additive PBFRs reside within the polymer matrix as discrete molecules, but may be subject to weak Van der Waals and electrostatic interaction

both between PBFR molecules and with the polymer backbone. High molecular weight polymeric additive flame retardants such as brominated polystyrene are more likely to remain within the matrix due to the slow rate of diffusion.

Other PBFRs may undergo both reactive and/or additive reactions with polymer matrices e.g., tetrabromophthalic anhydride and brominated polystyrenes.

The degree (i.e., rate) to which blooming may occur (for additive PBFRs) is dependent on a number of factors, which include:

- size and shape of the PBFR molecule/polymer;
- geometric structure of the plastic matrix;
- stability of PBFR in the 'melt' i.e., compatibility of PBFR with plastic polymer;
- solubility (octanol/water partition coefficients) of the PBFR molecule/polymer;
- volatility (vapour pressure) of the PBFR molecule/polymer; and
- temperature (generally increased temperature will increase blooming potential).
- stability of polymer matrix in contact with solvents e.g., swelling

The specific combination of these properties for a particular PBFR and polymer matrix will determine whether, or to what extent, blooming is likely to occur.

It is beyond the scope of this report to provide an in depth evaluation of these properties as they relate to blooming potential for each chemical in this report. In addition, lack of experimental data precludes firm conclusions. It was however considered appropriate to discuss some of these properties and their likely impact on blooming potential of some 'additive' PBFRs assessed in this report.

It is generally considered that high molecular weight compounds e.g., brominated polystyrenes and other brominated polymers will have a significantly lower potential for blooming than low molecular weight compounds e.g., brominated trisphosphates, PBBs and PBDPEs, due to the fact that the larger (long chain) structures will become more 'entangled' (fixed) in the compounded plastic/resin matrix. However, other considerations, in particular, the oligomeric composition of PBFR polymers are important in the overall evaluation, as these low molecular weight (LMW) species are likely to be more mobile than the parent PBFR polymer in the plastic/resin matrix. The distribution of these LMW species may also vary for the same polymer, depending upon the intended use. This is also an important issue in the evaluation of the toxicity profiles of polymeric compounds.

The geometry of the polymer matrix is also an important determinant in blooming potential. For example, flexible polyurethane foams consist of multiple small 'open cells', affording the polymer a larger surface area than, for example, rigid foams. Larger surface area is associated with increased contact between ingredients of the foam and the environment/atmosphere, and may facilitate movement of component PBFRs out of the foam.

A more contentious issue is the relationship of PBFR solubility and volatility to blooming potential. It appears that some confusion exists in relation to these properties, i.e., over the issues of potential for blooming and potential for movement/partitioning in environmental media. Although it is likely that PBFRs that exhibit low solubilities in water and organic compounds and low vapour pressures will have a low propensity to be removed from the surface of the polymer, abrasion/movement during use/cleaning of the plastic may result in depletion of some PBFR (if present) at the material surface, thereby maintaining a concentration gradient, the net effect of which would be to propagate any blooming potential. Some applications requiring flame retardants are not subject to cleaning or abrasion during their entire useable life. Similarly, although leaching of PBFRs exhibiting low water solubility might be expected to be minimal from landfilled polymer materials, this would be dependent on the rate of 'flow' (i.e., quantity) of water across the polymer surface, which would provide a 'driving force' for migration of the PBFR. In addition, some solvents may affect the stability of certain polymer matrices causing, for example swelling, which may also facilitate PBFR migration. This may also apply in certain cleaning operations.

Increased temperature is also associated with an increase in the rate of PBFR migration. Release of PBFRs or degradation products may occur at high temperatures during thermal processing or recycling e.g. PBDPEs emissions have been reported during thermal recycling activities (Sjodin et al 1999).

In summary, the potential for blooming of PBFRs is highly variable and related to a combination of physicochemical and structural parameters. Table 2 provides pertinent physicochemical data upon which tentative judgments can be made for those PBFRs used in Australia. However, no studies citing the degree of migration for PBFRs were provided for assessment, and as such, definitive conclusions on blooming potential are not possible for the majority of the chemicals reviewed in this report.

Table 2 - Physicochemical parameters of the main PBFRs used in Australia.

PBFR	Molecular weight (daltons)	Vapour Pressure (Pa)	Log K_{ow}	Water solubility (mg/L)	Reaction type*
Tetradecabromo (p-diphenoxybenzene)	1368	NA	NA	NA	A
2-Propenoic acid (pentabromophenyl) methyl acrylate, polymer	10,000 – 80,000	< 0.075 mm Hg	NA	3.5 – 3.8	R
2-Propenoic acid (pentabromophenyl) methyl ester, oligomer[1]	~ 3000	NA	NA	NA	LMW
TeBDPE	486	2.42×10^{-7} mm Hg	6.77	<0.011	A
PeBDPE	565	4.69×10^{-5}	6.58	<0.013	A
HBDPE	644	NA	6.86-7.92**	NA	A
OBDPE	802	6.59×10^{-6}	6.29	<0.001	A
DBDPE	960	4.63×10^{-6}	6.26	<0.0001	A
Brominated polystyrene	80,000 – 800,000	NA	NA	NA	A/R
Monobromo styrene[2]	360	30	3.78	NA	LMW
Dibromo styrene[2]	520	2	4.68	NA	LMW
Tribromo styrene[2]	800	0.1	5.57	NA	LMW
TBBPA	544	$< 1.3 \times 10^{-6}$	4.54	<0.08	R
TBBPA bis(2,3-dibromopropyl) ether	948	NA	NA	1000	R/A
1,2-Bis (2,4,6-tribromophenoxy) ethane	688	NA	NA	1000	A
HBCD	642	6.3×10^{-5}	5.62	0.0034	A
Tris (3-bromo-2,2 -bis(bromomethyl) propyl) phosphate	1019	2.75×10^{-5}	3.7	0.9	A

* Type of incorporation into plastic/resin polymer matrix [A = additive, R = Reactive] ** Log Pow

LMW = Low molecular weight component of parent polmer

[1] LMW component of 2-propenoic acid (pentabromophenyl) methyl acrylate, polymer.

[2] LMW component of brominated polystyrene.

NA = not available

5. Manufacture, Importation and Use

5.1 Manufacture and importation

PBFRs chemicals are not manufactured in Australia, but are imported mainly from the USA, Japan, Singapore, Israel, Netherlands, Germany and other European countries. They are imported as pure chemicals or as mixtures with additives such as antimony trioxide, non-halogenated triaryl phosphate or other flame retardants and water. Polystyrene, epoxy polymer resins or extruded polystyrene foam boards containing brominated flame retardants are also imported. In addition, the flame retardant is incorporated along with other additives such as pigments into resins of various kinds.

Besides pure brominated chemicals, powdered mixtures containing between 45 and 60% of PBFRs are also imported, with additives like other flame retardants or water composing the rest of the mixture. Imported brominated polymer resins may contain 1 to 30% of brominated flame retardants, eg. some members of the Crastin® range, Hytrel® polyester elastomer, Rynite® polyester resins and Zytel® resins may have PBFRs content of 10 to 30%. Flame retardant modified grades of Austrex® polystyrene resins may contain 5 to 20% of PBFRs. Styrofoam® extruded insulation boards have PBFR concentrations varying from 1 to 4% depending on the specific grade and some Derakane® resins contain up to 20% of BFR in the form of a brominated polymer. Spacel® fire retardant modified expandable polystyrene (EPS) contains less than 1% PBFR.

It is also possible that a variety of market-ready products containing brominated flame retardants such as computer casings are imported, however, no reliable estimates are available of the quantities of flame retardants imported in this manner. The content of PBFRs in articles imported into Australia may vary widely, but may nonetheless present a large source of introduced flame retardants.

The PBFRs distribution chain is depicted in Figure 1.

Table 3 provides details of PBFR chemicals that are imported into Australia. Import volumes were calculated from volume estimates supplied for the commercial mixtures using the percent content of PBFRs identified in each commercial product.

The moulding industry is declining in Australia, as manufacturing moves off-shore, and so sales volumes of PBFR chemicals and mixtures containing them are decreasing and expected to continue to decrease at approximately 5% a year.

Two changes in imports merit further comment. In the case of CAS No. 125997-20-8, the mixed halogenated phosphate esters, production has ceased and there will be no further importation or use. Brominated polystyrene (CAS No. 88497-56-7) was used in the production of stadium seating at the Sydney 2000 Olympics, so imports during the period of construction greatly exceeded those expected to characterise normal levels of business.

Figure 1 - Distribution chain of brominated flame retardants and products.

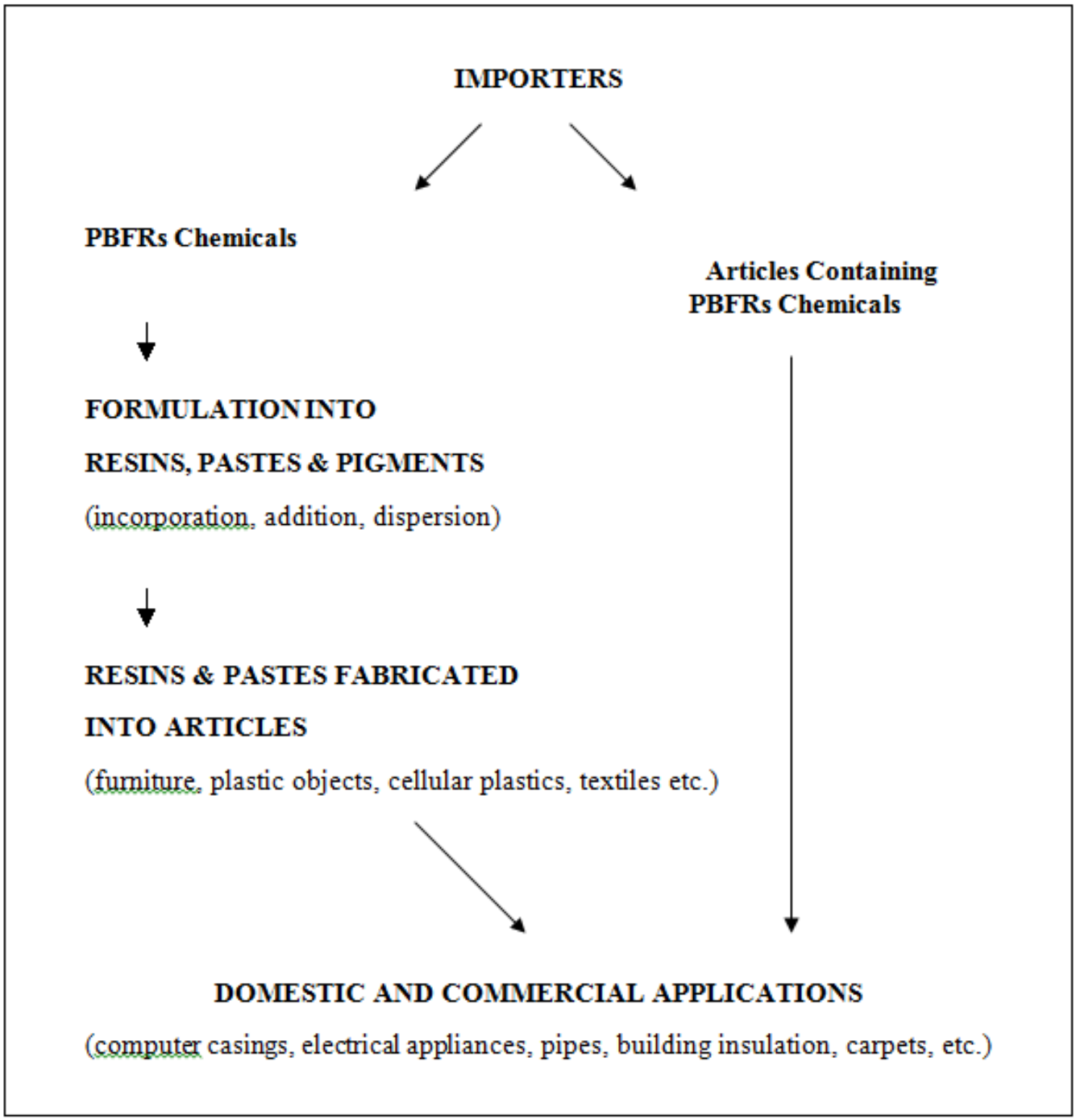

Table 3 - Identified PBFRs, current and estimated future import volumes.

Substance	CAS Number	1998/1999 (tonne/year)	^Future Estimates (tonne/year)
Decabromodiphenyl ether	1163-19-5**	177	165
Pentabromodiphenyl ether	32534-81-9**	72	119
Phosphoric acid, mixed 3-bromo-2,2-dimethyl propyl and 2-chloroethyl esters	125997-20-8	60	nil
Octabromodiphenyl ether	32536-52-0**	47	57
Hexabromocyclododecane	25637-99-4	36	59
Tetrabromobisphenol A	79-94-7	32[#]	15
TBBPA bis-(2,3-dibromopropyl) ether	21850-44-2	29	8
Polystyrene, brominated	88497-56-7/ 148993-99-1[$]	26	10
Tetrabromodiphenyl ether	40088-47-9*	22	36
2-propenoic acid (pentabromophenylmethyl) ester, homopolymer	59447-57-3	22	20
1,2-bis(2,4,6-tribromophenoxy)ethane	37853-59-1	17	12
Hexabromodiphenyl ether	36483-60-0*	10	15
Nonabromodiphenyl ether	63936-56-1*	>5	>5
TBBPA,2,2-bis[4-(2,3-epoxypropyloxy) dibromophenyl] propane polymer	68928-70-1	5	7
Tris (tribromoneopentyl) phosphate)	19186-97-1	4	12
Tribromodiphenyl ether	49690-94-0*	4	6
Disodium tetrabromophthalate	25357-79-3	4	5
Polymer of TBBPA, phosgene, and phenol	94334-64-2	2	2
2,4,6-Tribromophenyl terminated TBBPA carbonate oligomer	71342-77-3	1	1
3,4,5,6-Tetrabromophthalic anhdride, ethylene glycol, propylene oxide reaction products	20566-35-2/ 77098-07-8[$]	1	1
Tris (2,3-dibromopropyl) phosphate	126-72-7	nil	nil
Bis-(2,3-dibromopropyl) phosphate	5412-25-9	nil	nil
Tetradecabromo (p-diphenoxy benzene)	58965-66-5	nil	nil

*None of these compounds are imported individually or used/sold individually as flame retardants.
**Manufacturer's advice indicates that typical compositions for these 'commercial' products may be:
DBDPE: DBDPE (~97%), NBDPE (~3%), OBDPE (<1%)
PeBDPE: PeBDPE (~55%); TBDPE (~30%); HBDPE (~10%); TrBDPE (<5%)
OBDPE: OBDPE (no data), NBDPE (no data), HBDPE (~6%); DBDPE (<0.1%)
These compositions were used to estimate the quantities of HBDPE; TBDPE and TrBDPE and NBDPE introduced into Australia in Table 3.

[$] The two CAS numbers refer to the same chemical, but one is a generic reference whereas the other is specific.

^ Data estimates were obtained from Industry

[#]Estimates of imported quantities of TBBPA include polymer resins

5.2 Uses and exports

Most brominated flame retardants have fairly specific applications; only a few are broad spectrum across-the-board flame retardants. Their specific applications are determined by many factors including the type of resin requiring flame retardancy, the level of flame retardancy required, the properties of the resin and its additives, and the items' use.

PBFRs are generally used in the fabrication of products ranging from textiles/fabrics for automotive seating, curtains, awnings and floor coverings, in furniture such as seating and cushioning and in electronic/electrical applications, e.g., plastic casings for power tools, business equipment and thermal insulation boards.

In Australia, the imported pure- and mixture- based PBFR chemicals are incorporated together with other polymers to formulate flame-retarded resins for use in the production of articles such as furniture, moulded hard/dense plastics like plastic sheeting and rigid cellular plastic blocks and sheeting which have applications in the building and construction industry such as thermal insulation, concrete void formers, soil stabilisers in road construction and to laminate metal sheetings. Flame retarded resins are also used in electronic housings and circuit boards, containers and cellular polystyrene products. PBFRs may be blended with polypropylene and extruded into fibres for production of carpets and other flexible furnishings. Some are used in the production of chemical-resistant fiberglass items such as pipes and automotive components. Consumer products have lifetimes in the range of 10 to 20 years.

Imported brominated resins have similar applications in the production of flame-resistant plastics and other items.

The only instances of export reported were a one-off shipment of 18 tonnes of TBBPA, and continuing export to New Zealand of products containing DBDPE.

6. Potential for Exposure

6.1 Environmental exposure

Landfill will be the predominant means by which the environment is exposed to PBFRs, as incineration is seldom practised in Australia. As products containing these chemicals reach the end of their useful lives, due to the lack of incineration in Australia, and the apparent lack of recycling of these materials at this stage, landfill presents the only real option for disposal.

Once in landfill, the potential exists for PBFRs, particularly additive compounds such as the PBDPEs, to leach out of the articles in a process known as blooming (see Section 4.3). Where this occurs, in a landfill situation, the PBFRs would not be expected to migrate far due to their low solubility and high affinity for adsorbing to organic carbon.

However, during use of products, there is the potential for exposure to aquatic systems through blooming. Blooming may occur for some flame retardants during the life of a product. For such chemicals, removal of surface PBFRs from plastic/resin materials during cleaning operations is possible, although their low water solubilities would limit their dissolution. Any PBFRs in wash water would enter the sewer system, where mostly, they would be expected to be removed through binding to the sludge component.

PBFRs (e.g. DBDPE and HBCD) are used to flame retard textiles. The process of applying the polymer backcoat to the upholstery textile utilises water and is a potential source of environmental release. Further potential for environmental exposure is when these textiles are washed, although this would be limited by the infrequency of cleaning such products; the low concentration of BFR used in textiles and their extremely low water solubilities. It is also generally understood that for a flame retardant to be used in any kind of textile, it must be demonstrated to withstand washing (if appropriate for the particular textile). Again, release is likely to go to sewer.

The following discussion on environmental fate largely centres around PBDPEs, namely the commercial PeBDPE, OBDPE and DBDPE products which represent almost three quarters of PBFRs expected to be imported into Australia.

One chemical, HBCD, has been identified as being increasingly used in significant quantities. The OECD/SIDS draft report was used to summarise environmental data on this chemical.

Information has primarily been extracted from IPCS EHC monograph 162 (1994) and the draft OECD SIDS report for PeBDPE (OECD, 2000). It should be noted that, for the purpose of this preliminary assessment, the data has been summarised and is discussed for this class of chemicals generally (See Section 1.2 for further details). In some cases, for example, where relevant additional reference material or study summaries have been provided by applicants during the public comment stage, these have been included and cited appropriately.

No studies appear to be available on the fate of PBDPE-containing products in landfills, although there is concern that PBDPEs may eventually leach out. PBDPEs, particularly as levels of bromination increases, are persistent in the environment and the introduction of these compounds into widespread products will provide a long-term and diffuse source of emissions to the environment.

Three commercial PBDPE products exist: DBDPE, OBDPE, and PeBDPE. The DBDPE product is >97% DBDPE (the remainder is nona-BDPE with trace amounts of octa-BDPE). The OBDPE product is a mixture of congeners ranging from penta- to nona-BDPE. The PeBDPE product is a mixture consisting primarily of 2,2,4,4,5-PeBDPE and 2,2,4,4-TBDPE with congeners ranging from tetra- to hexa-BDPE. The environmental distribution of each PBDPE commercial product will be dependent on the physicochemical properties of the individual components and its uses. Therefore, with respect to diphenyl ethers, data for all levels of bromination should be considered. Similar considerations should also be given to other types of brominated flame retardants where isomers/congeners are present and/or where used as mixtures.

Overall, it has been determined that varying the physico-chemical properties of $LogP_{ow}$, water solubility and vapour pressure over a wide range had little effect on distribution to the aquatic and terrestrial compartments. However, a much larger effect was noticed in the atmospheric compartment (OECD, 2000). More specific discussion on distribution in the environment is presented in the following sub-sections.

6.1.1 Atmospheric fate

The PBDPE commercial products have low vapour pressures (see Appendix A), that decrease with increasing bromination. Based on the scale of Mensink (Mensink et al., 1995), they may be considered slightly to very slightly volatile. Accordingly, PBDPE compounds with a higher level of bromination, when released to land, are more likely to bind to soils than volatilise. Whether other highly brominated flame retardants of low vapour pressure have the same fate, cannot be determined due to the lack of sufficient data. However, this may not be the case where release is to water as the substances have very low water solubilities. Detailed assessment of the potential for volatilisation, adsorption to particles, and transport in the environment is not within the scope of this assessment.

PeBDPE has a rate constant of 1.27×10^{-12} cm^3/molecule.sec for reaction with atmospheric hydroxyl radicals (OECD, 2000). Using the accepted global average atmospheric concentration of hydroxyl radicals as 5×10^5 molecules/cm^3, an atmospheric half-life of around 12.6 days can be estimated. This is of sufficient time for long-range atmospheric transport to occur. PeBDPE has been identified in air samples from Swedish background sites on the island of Gotland and in the Scandinavian mountain range (Kemi, 1999). Similarly, HBCD levels up to 5.7 pg/m^3 were measured in Sweden during 1990 and 1991 at locations far from known point sources (OECD, 1999).

Air concentrations of tri- and hexa-BDPE in the range of 7.1 to 53 pg/m^3 near metal recycling plants in Taiwan and Japan, and of tetra- and penta-BDPE (combined) in the range 1 to 8 pg/m^3 and HBCD of 5.3 to 6.1 pg/m^3 in Swedish air samples have been reported (cited in de Wit, 1999).

6.1.2 Aquatic fate

There appears to be limited scope for release to aquatic systems within Australia. However, increasing reports of PBDPEs detected in fish in the northern hemisphere (there are no data for Australia) show that aquatic exposure does occur, which may be attributed to local industries. For example, in Virginia, USA, muscle tissue of several fish species contained PBDPEs. While the sample area was not heavily industrialised, it is home to considerable furniture manufacturing activities. In Sweden, fish with detectable PBDPEs and HBCD concentrations were caught downstream of textile industries and sewage treatment plants (OECD, 1999; Renner, 2000b). This may be possible in Australia.

There is little information available on the abiotic degradation of PBDPEs in aqueous solutions. Ethers are not likely to hydrolyse readily in the normal environmental pH range. PeBDPE is reported to be hydrolytically stable under conditions found in the environment (OECD, 2000).

Volatilisation from water may be predicted by considering the Henry's Law Constant for these compounds. Table 4 provides estimates of Henry's Law Constants for 10 representative PBDPEs (OECD, 2000).

Table 4 - Estimated Henry's Law Constants for representative PBFRs*

Chemical Substance	Henry's Law Constant ($atm.m^3/mole$)
4-bromodiphenyl ether	$1.17 \times 10^{-4} – 4.69 \times 10^{-5}$
4,4'-dibromodiphenyl ether	$1.87 \times 10^{-5} – 4.88 \times 10^{-5}$
2,4,4'-tribromodiphenyl ether	$2.03 \times 10^{-5} – 7.45 \times 10^{-6}$
2,2',4,4'-tetrabromodiphenyl ether	$2.97 \times 10^{-6} – 8.48 \times 10^{-6}$
2,2',4,4',5-pentabromodiphenyl ether	$1.18 \times 10^{-6} – 3.54 \times 10^{-6}$
2,2',4,4',5,5'-hexabromodiphenyl ether	$1.47 \times 10^{-6} – 4.71 \times 10^{-6}$
2,2',4,4',5,5',6-heptabromodiphenyl ether	$1.88 \times 10^{-7} – 6.14 \times 10^{-7}$
2,2',4,4',5,5',6,6'-octabromodiphenyl ether	$2.56 \times 10^{-7} – 7.48 \times 10^{-8}$
2,2',3,4,4',5,5',6,6'-nonabromodiphenyl ether	$1.07 \times 10^{-7} – 2.98 \times 10^{-8}$
decabromodiphenyl ether	$1.19 \times 10^{-8} – 4.45 \times 10^{-8}$
hexabromocyclododecane	2.96×10^{-5}

* Reproduced from the OECD/SIDS Draft report on PeBDPE and HBCD.

Chemicals with a Henry's Law Constant in the range 2.45×10^{-7} to 7.34×10^{-4} $atm.m^3/mole$ are considered moderately volatile from water (Mensink et al., 1995). It is apparent from the values presented above that most of the PBDPEs and HBCD can be considered moderately volatile. The highly brominated compounds may be expected to be less volatile, with the three most highly brominated substances being considered only very slightly volatile from water. This is supported by the long half-lives of volatilisation (from rivers and lakes) for DBDPE, HBCD and TBBPA (Syracuse Research Corporation EPIWIN modelling).

This suggests that where release occurs to water and the compounds do not fully partition to sediments or biota, the PBFRs, particularly those with relatively low low levels of bromination, may volatilise to the atmosphere and thereby be available for atmospheric transport.

6.1.3 Terrestrial fate

Most PBFRs have specific applications which are determined by a number of factors (see Section 2). Nonetheless, information provided by industry for this assessment suggests that these chemicals and others are used more broadly.

In Australia, the vast majority of end-products containing PBFRs will be disposed of to landfill over the lifetime of products containing these compounds. PBDPEs are currently used in plastic components of a diverse range of products. The difference between additive and reactive uses is important. Reactive fire retardants like TBBPA are covalently bonded to the plastic itself. However, additives such as PBDPEs are only dissolved in the material, and are not covalently bound. Thus, the potential for migration from end-use plastics is greater for the additive flame retardants than for the reactive flame retardants. The potential for leaching or volatilising of additive PBFRs from end-use products is dependent on a number of physicochemical factors (see Section 4.3 for further discussion).

High octanol-water partition coefficients have been determined for various PBDPEs (see Appendix A). Chemicals with $LogK_{oc}$ values greater than 3.6 are considered to be immobile (McCall et al., 1980). Therefore, where released to soils, PBFRs may generally be considered to bind strongly and be immobile. Leaching from soil is unlikely to occur. The results show that sorption tendencies increase as the level of bromination increases. This indicates that mobility, albeit very limited, is likely to be greater with the lower brominated compounds.

HBCD is expected to adsorb to soils and sediments as indicated by its low water solubility, log K_{ow} (5.625) and its low vapour pressure ($6.3X10^{-5}$ Pa at $20^{o}C$). Its log K_{oc} has been calculated to be 4.66 (OECD, 1999).

6.1.4 Degradation

The three commercial PBDPE products have each been tested for "ready biodegradability", e.g. for degradation by sewage sludge within a 28 day timeframe. Neither the DBDPE, OBDPE nor PeBDPE commercial products were readily biodegradable.

Although little information on biological degradation for PBDPEs is available, it is suggested that reductive dehalogenation occurs under some conditions (OECD, 2000). Testing on soil, sediment and waste water treatment plant and degradation is currently underway for OBDPE and DBDPE (UK).

Although DBDPE accounts for the bulk of PBFR consumption, it is the lower congeners, particularly tetra- and penta-BDPE, which are most commonly found in the environment. Historic emissions may account for these findings, e.g. PeBDPE was used for off-shore oil drilling in the early 1990s and in hydraulic fluids in the coal industry until the late 1980s (Renner 2000a). Although environmental breakdown to lower congeners is also a possibility, no anaerobic biodegradation of DBDPE was seen in sediment for up to 2 years (de Wit 2000). The brominated flame retardant industry is currently conducting a 32-week anaerobic sediment

degradation and solid-surface photolysis studies on DBPDE as a part of the EU risk assessment.

Heating/pyrolysis of PBDPEs may lead to the release of brominated dibenzofurans and brominated dibenzodioxins.

TBBPA has been shown to partly degrade under both aerobic and anaerobic conditions in a range of soil types and in sediment water. After 64 days approximately 35 to 80% of TBBPA remained in soil under aerobic conditions, with 40 to 90% remaining under anaerobic conditions, with the highest levels measured in sandy loam and lowest in silty loam. A recent sequential anaerobic/aerobic soil study demonstrated complete degradation of TBBPA after 45 days to the non-brominated bisphenol A, which was resistant to further degradation (Ronen and Abeliovich, 2000). Under aerobic conditions, TBBPA degraded in river sediment/water with between 45% and 60% remaining in sediment at test concentrations between 0.01 mg/L and 1 mg/L. No biodegradation of TBBPA (test concentration 100 mg/L) was detected after 2 weeks under sewage treatment conditions (IPCS, 1995a). In has been estimated that in a wastewater treatment plant, TBBPA would be removed mainly by sludge adsorption with < 1% biodegradation (Syracuse Research Corporation EPIWIN modelling).

The phenolic groups of TBBPA may be methylated in the environment and the resulting metabolite is potentially more lipophilic. This compound has been found in sediment, fish and shellfish (IPCS, 1995a). Two out of 19 samples of fish and shellfish collected in Osaka bay contained 0.8 and 4.6 ug/kg wet weight. The methylated derivative was reported in sediment collected in Sweden.

HBCD has been tested and found not ready biodegradable. The biodegradation of HBCD was examined after exposure of samples to bacterial medium for 5, 7 and 15 days. Some biodegradation was indicated (Kemi, 1995). Further studies analysed in the OECD SIDS draft assessment report indicated that HBCD may be considered not readily biodegradable (OECD, 1999).

6.1.5 Bioaccumulation

The bioaccumulation of a commercial PeBDPE product containing TBDPE, PeBDPE (2 isomers) and HBDPE (2 isomers) was studied in Carp (OECD, 2000). An overall LogBCF of 4.16 was estimated. The BCF for 2-propenoic acid (pentabromophenyl) methyl ester in carp was measured to be a maximum of 12 at any level (0.2 ppm, 2 ppm) over an 8-week period (Chemicals Inspection and Testing Institute, 1983).

Studies indicate that as bromination levels increase beyond HBDPE, PBDPEs show a decreasing tendency for bioaccumulation (IPCS, 1994b). Tetra- and penta-BDPEs, in particular, have a high potential for bioaccumulation. Monitoring data from the Baltic and elsewhere suggest the presence of high concentrations of these compounds higher up in the food chain (Kemi, 1999).

Where OBDPE and DBDPE are concerned, no significant bioaccumulation has been demonstrated in fish and BCF varied between about 5 and less than 50. This is due to low uptake. OBDPE and DBDPE are larger molecules and, consequently, are less readily absorbed than PeBDPE. A recent Swedish study showed that DBDPE is minimally absorbed from food by fish and reported that DBDPE was possibly metabolised to lower-brominated diphenyl ethers. However, the uptake was low with only about 0.02 to 0.13% of the dose found in muscle tissue. Low absorption of DBDPE from diet administered to rats was also indicated (see Section 7.1.1).

Studies with aquatic invertebrates and vertebrates with TBBPA indicate bioconcentration factors (BCF) ranging from 20 up to 3200 depending on the test conditions and organisms. Although the BCFs are high, studies indicate that in some species TBBPA is rapidly excreted. Methylated TBBPA have been detected in 2/19 samples of fish and shellfish in Japan (IPCS, 1995a).

In a Swedish study, relatively high concentrations of HBCD were detected in sediment and fish samples analysed from a number of locations, suggesting potential for bioaccumulation (OECD, 1999).

Besides concentrating ability, bioaccumulation is also dependent on the depuration rate. Depuration half lives for the hexa-, penta-, and tetra- components of commercial PeBDPE examined in the blue mussel *Mytilus edulis* were determined to be similar at 5.6 to 8.1 days (OECD, 2000).

6.1.6 Summary of environmental fate

Release to the environment will be slow and diffuse over the life of products containing PBFRs. However, use is widespread and varied and significant quantities of PBFRs, particularly PBDPEs, are used in Australia giving potential exposure to the wider environment. The most significant environmental source for Australia is in the processing of the flame retardant into the resin. The particular application with the highest anticipated release is the textile backcoating process due to the use of water during processing.

Where released to the environment, some PBFRs are expected to be stable, both microbially and abiotically. When released to land, they should bind strongly to the organic component of soils and be immobile. In the event of release to water, movement from the water column is likely to be rapid with the compounds partitioning to sediments and biota, where bioaccumulation is expected from the commercial pentabromo diphenyl ether compounds (tetra- to hexa-) (OECD, 2000). Bioaccumulation is not anticipated with OBDPE and DBDPE while HBCD has the potential to bioaccumulate. A relatively high bioconcentration factor for TBBPA is balanced by rapid excretion and the compound has not been found in environmental biological samples.

Components of commercial PeBDPE may volatilise to the atmosphere from water. It is speculated that they may bind to atmospheric particles with the potential to undergo long-range atmospheric transport.

However, no data were available on levels of PBFRs in the Australian environment including in biota.

6.2 Occupational exposure

6.2.1 Routes of exposure

Occupational exposure to PBFRs in Australia may result from direct use of these chemicals or mixtures containing them, or indirectly during the formulation of PBFR treated products, or from end-use of such products. Other potential sources of exposure are during transport and storage and during disposal of the contaminated containers. Occupational exposure to PBFRs is discussed for importation, formulation and end-use of flame retarded products in the following sections.

6.2.2 Importation

The PBFRs, mostly in solid powder form, are imported in 25 kg to 1 tonne capacity polyethylene lined paper bags or polypropylene bags, or in 200 L steel drums. They are either stored by importers at their sites in warehouses alongside other additives such as pigments and fillers or warehouse facilities of contractors who arrange for transport to designated facilities. Some PBFRs may be stored in special areas designated for specific requirements, such as flammable goods. The imported flame-retardant chemicals are distributed to formulators of products by licensed carriers who deliver the materials by road transport.

A diverse range of flame retardant treated articles are also imported into Australia, which are distributed by road and/or rail nationwide.

Exposure during transport and storage of packaged chemicals is unlikely to occur, except in cases where packaging is breached.

6.2.3 Formulation of brominated flame retarded polymers

A wide range of PBFR chemicals are formulated into a myriad of polymeric resins such as polycarbonate, epoxy resins, polypropylene, vinyl ester polymers, polyester reinforced with glass fibre and polystyrene.

Formulation processes are generally similar across industry and are conducted mostly on a batch basis in enclosed and largely automated systems. Formulation of resins containing the flame-retardant chemicals consists of weighing or pumping, mixing and blending, processing/extrusion and cutting and packaging of the granular pellets or liquid resins. Pellets and resins are formulated according to customer specifications, and are further used in the fabrication of plasticised articles or in the textile industry. The primary and secondary formulation processes are briefly described below.

The PBFRs are compounded with the appropriate polymer (polypropylene or polystyrene) to produce a masterbatch containing up to 30% of the flame-retardant. It is possible that more than one flame-retardant chemical may be used in the formulation process. For example, antimony oxide is often used in conjunction with the PBFRs as it is thought to have a synergistic effect.

In the blending plant, weighed amounts of the powdered or granulated polymeric material are transferred to rotary mixers/blenders. Weighing is a manual process, whereby workers transfer the flame retardant by tipping the drums or bags in specially designed dispensary. Weighed quantities of flame retardant, pigment and

other additives are added either via a closed transfer system or through a chute with a vacuum collar or under local exhaust ventilation to remove dust. During weighing and handling of the powdered chemical, dust is generated. Data supplied for this assessment indicated that significant dust levels, exceeding the 12 h occupational exposure standard for dusts of 5 mg/m^3 (4.85 to 7.81 mg/m^3 personal results; 5.9 mg/m^3 static results), have been measured in an occupational setting around blending areas. Although the report indicated that this may be related to faulty dust extraction system on the charge floor, the findings indicate that potential for dust generation, and exposure, during such incidents is of concern.

The most likely routes of exposure are inhalation and ocular exposure to the dust and dermal exposure to the powdered solid or dust, during weighing, transfer (if not enclosed) and equipment cleaning and maintenance.

In cases where the brominated chemical is a liquid, a dip-tube is inserted into the container and the chemical is automatically pumped into the mixing vessel. Dermal exposure to the chemicals from drips and spills is the main route, though indirect ocular exposure may also occur.

Exposure by inhalation of dust and dermal contact is also possible, when empty containers and bags are compacted for transfer to landfill. Dust arising from the compaction operation goes to the dust collection system, which is emptied regularly by specialist contractors. This presents another potential source for exposure. Exposure to dusts is controlled through the use of engineering controls designed to standards suitable for hazardous chemicals like antimony trioxide, which is a common additive to the PBFRs preparation.

Similarly, dermal exposure to PBFRs in solution is possible when handling empty containers with residual resin.

The blended material is discharged to a collection bin, usually either in an enclosed system or under local exhaust ventilation and transferred to an extruder, whereby the mixture is extruded under high temperatures to form strips, which are cooled then cut into small pellets or granules with the desired concentration of flame retardant. These are bagged and dispatched to customers. Low levels of PBFR (less than 1%) may also be incorporated into polystyrene during the manufacture of fire retardant modified expandable polystyrene (EPS) beads.

The extrusion reaction (or polymerisation) is also used to produce a resin solution containing the brominated retardant, which can then be further polymerised with other monomers through the addition of suitable initiators. Release of fumes during extrusion is possible, but the low vapour pressure of the PBFRs and extraction ventilation would minimise emissions. During extrusion, the brominated chemicals become immobilised by encapsulation within the polymer matrix. Given the enclosed and automated nature of the extruder, exposure to the chemicals is unlikely to occur. Alternatively, the PBFRs are formulated into pastes by dispersion with other additives. The likelihood for exposure during the latter process is minimal.

The brominated resin or pellet material is produced according to customer specification, with the early portion of each extrusion checked for specification and recycled, if necessary.

6.2.4 Production of articles

At the product manufacturing factory, masterbatch granules containing the flame retardant are fed into the hopper of a blender. These are then mixed with polymer resins and other additives, extruded, moulded or spun to produce the finished product, containing between 3 and 30% of the brominated flame retardant chemical according to end-use specifications. Transfer of the masterbatch granules into the mixer occurs under local exhaust ventilation. Given that handling of these is intermittent and as the brominated chemicals are present in encapsulated form, exposure would be significantly less than would otherwise occur.

Fire retardant modified expandable (cellular) polystyrene mouldings are made by heating expandable polystyrene beads in a mould with steam until the polymer softens and the pentane blowing agent in the beads is released. As the low level of PBFR is bound within the cellular polymer matrix, exposure to the PBFR when handling the mouldings during production and in use is expected to be very low. Also, low level exposure to thermal decomposition products of non-diphenyl ether PBFR is possible during hot wire cutting of moulded cellular polystyrene block and sheeting product. The hot wire cutting operation is normally conducted in well ventilated areas during manufacture and in open areas when used as insulation, void formers and soil stabilisers in the building and construction industry.

Injection moulders apply high temperatures, similar to those used in extrusion, and thus fumes may be generated. However, the low vapour pressure of the PBFRs and the use of appropriate ventilation and engineering controls in the workplace should minimise worker exposure to vapours. In one facility, where moulding of polyamide containing brominated polystyrene flame retardant was carried-out, mixed (mono-, di- and tri-) brominated styrenes were detected (below 300 ppb) in air samples from around moulding machines (Dupont 2001).

In the textile industry, the emulsion of PBFRs is applied to heavy fabrics, eg. cotton, of the kind used in tarpaulins or screens such as those used in welding booths. It is only applied when the use of the fabric requires flame retardancy. Two application methods are used. The flame retardant emulsion is diluted with water and sprayed onto the fabric, with the excess squeezed off by passage through rollers. This also tends to squeeze the emulsion into the fabric. Inhalation exposure from aerosols is expected, particularly if spraying is undertaken in open or not fully enclosed systems. Dermal contact is also possible during dilution of the emulsion and from aerosols.

Alternatively, the emulsion flows onto the fabric as it passes under a doctor blade/knife. This presses the emulsion into the fabric in much the same way as the rollers used in combination with spraying. No inhalation exposure is expected from this process, but dermal contact with the emulsion is possible. These systems are expected to be automated and enclosed, thus reducing the need for manual operations and hence exposure.

The flame retardant is bound to the fabric, which retain their flame retardancy over their lifetime (usually some years). Resins containing flame retardants can be also applied using the doctor blade process. There are no measurements on the fixation rate or for the availability and/or release of these chemicals from treated textiles. Exposure, mostly by dermal contact, from handling treated fabric or during rinsing and cleaning operations may occur from excess unbound chemicals. Although the

lack of such data does not permit an accurate estimate of the level of exposure, it is possible that low level exposure will occur.

Cleaners and maintenance workers may be involved in all of the above formulation industries. The potential for exposure to resin residues, spillage and/or dust accumulating on equipment and other surfaces exists for these workers. However, the use of appropriate engineering controls, such as ventilation, bunding and closed operating systems, reduces the level of waste. Thus, exposure during these operations is expected to be low.

Ready to use flame-retarded materials such as foam boards containing up to 4% PBFR are used for thermal insulation in buildings or laminated to sheet metal facings. Exposure from handling such materials would be dependent on the PBFR used i.e. its degree of binding within the polymer matrix (see Section 4.3).

Brominated flame retardant compounds are mostly used as additives, in which they physically, rather than chemically, combine with the treated materials. Accordingly, they are subject to "blooming", which is a slow release process of the brominated chemical to the surface of the article. The articles containing the brominated chemicals are likely to be used to a great extent in private and/or commercial premises, and there is likely to be occupational exposure of workers, eg. office clerks, factory labourers, builders, cleaners etc., to low levels of flame retardants over extended time periods.

Recycling of finished articles containing the flame retardants is likely. Little recycling activities exist in Australia and thus, it is not possible to evaluate exposure from the recycling industry. However, significant exposure by inhalation of dusts and dermal contact with articles containing these chemicals has been shown to occur elsewhere.

Two recent Swedish reports described the detection of DBPDE and other polybrominated diphenyl oxide isomers in workers dismantling electronic equipment (Sjodin et al, 1999) and in computer technicians (Hagmar et al, 2000). Sjodin et al. (1999) investigated the concentration of PBDPEs in the serum of Swedish subjects from three occupational backgrounds including electronics-dismantling workers, office staff with full-time use of computers and hospital cleaners. The median and range serum concentrations of tetra-, two hexa-, hepta, and decabromodiphenyl ethers for the three groups of workers are summarised in Table 5 (Reproduced from Sjodin et al., 1999).

Quantitative measurements of PBDPEs in ambient air at the electronics-dismantling plant, see above, showed hepta- and decabromodiphenyl ether concentrations in the range 6.3 to 87 and 12 to 200 ng/m^3, respectively. Tetrabromodiphenyl ether concentrations were reported to be much lower at 1.2 to 2.1 ng/m^3 (Sjodin et al., 1999).

Table 5 - Median and range serum concentrations (pmol/g lipid weight with ng/g lipid weight in parenthesis) of five PBDPE congeners measured for subjects from three occupational settings.

	Hospital Cleaners (n=20)		Office Staff (n=20)			Electronics Dismantlers (n=19)		
Compound	Median	Range	Median	Range	*p*	Median	Range	*p*
TBDPE	3.2 (1.6)	< 1-34	3 (1.5)	< 1-10	> 0.5	5.9 (2.9)	< 1-47	0.02
HBDPE-1	0.89 (0.57)	0.64-7.6	1.3 (0.85)	0.8-5.1	0.02	7 (4.5)	3.2-19	< 0.001
HBDPE-2	0.59 (0.38)	0.25-1.4	0.79 (0.51)	0.43-1.5	0.04	1.9 (1.2)	0.74-7.4	< 0.001
HpBDPE	0.16 (0.12)	0.025-0.39	0.24 (0.18)	< 0.02-1.4	0.02	11 (7.8)	3.1-26	< 0.001
DBDPE	< 0.7 (< 0.7)	< 0.3-3.9	< 0.7 (< 0.7)	< 0.3-8	> 0.5	5 (4.8)	< 0.3-9.9	< 0.001
SPBDPE	5.4 (3.3)	3.1-39	7.1 (4.1)	3.9-17	0.1	37 (26)	15-75	< 0.001

Abbreviations: TBDPE- 2,2',4,4'-tetrabromodiphenyl ether;
HBDPE1- 2,2',4,4',5,5'-hexabromodiphenyl ether;
HBDPE2- 2,2',4,4',5,6'-hexabromodiphenyl ether;
HpBDPE- 2,2',3,4,4',5',6-heptabromodiphenyl ether;
DBDPE- 2,2',3,3'4,4',5,5',6,6'-decabromodiphenyl ether;
sPBDPE- polybromodiphenyl ether (sum).

p: Level of significance derived from Mann-Whitney *U*-test (for details, see Sjodin et al., 1999).

6.3 Public exposure

Due to the ubiquitous nature of the plastic/textile products containing PBFRs, there is potential for widespread and prolonged public exposure. Most PBFRs from extrusions or mouldings will be encapsulated within an inert, very high molecular weight plastic matrix. However, there may still be inhalation and dermal exposure to some types of PBFRs in these products via "blooming" and emissions, although there is little data to show the magnitude of these processes (see Section 4.3). There is the potential for oral exposure via ingestion of some PBFRs in the food chain.

Dermal exposure may occur on surface contact and dispersion into the atmosphere may lead to inhalation exposure. These exposures will be mitigated by such factors as PBFR concentrations, ambient temperatures, the operating temperature of PBFR-containing appliances, the extent of ventilation and the potential (e.g. molecular weights/size and solubility) for the individual PBFR to be absorbed through the skin.

Around 2% of PBFRs and resins containing PBFRs are disposed of to land-fill, and most plastic/textile products containing PBFRs are likely to be disposed of to land-fills. Although vapour pressures are low, there is the potential for PBFRs to evaporate into the atmosphere and to photodegrade over time. However, their potential for photodegradation has not been evaluated.

Some PBDPEs are environmental contaminants. TBDPE and PeBDPE appear to be the most commonly reported PBFRs occurring in animal and human tissues (Kemi, 1999). PBDPE residues, predominantly tetra- to hexa-BDPE, have been detected in fish and animal tissue (Hooper & McDonald, 2000; IPCS, 1994b).

Information on public exposure to PBFRs is limited. Values of 25, 4, and 1 pg/m^3 were recorded for television set emissions of tri-, tetra-, and penta-BDPE, respectively (IPCS, 1994a, 1994b). Emissions measured in computer halls were 90, 30, and 30 pg/m 3 for tetra-, penta-, and hexa-BDPE, respectively (Lindstrom, personal communication).

The highest atmospheric and surface concentrations of PBFRs in automotive interiors from plastics/fabrics are likely to correlate with high interior temperatures (of up to 80°C in Australian conditions). There may be an increased risk of inhalation or dermal exposure under such circumstances. There is no information regarding the automotive interior concentrations of PBFRs under Australian, or other, conditions.

7. Health Effects and Hazard Classification

The following health effects summaries for the brominated diphenyl ethers have been extracted mainly from IPCS EHC monograph 162 (IPCS, 1994b). Additional information for penta-, octa- and deca-BDPE was also obtained from the OECD draft SIDS reports (OECD, 1997a, OECD, 2000 and OECD, 1997b and OECD, 1997c). For HBCD, an OECD draft SIDS report (OECD, 1999) and a study report conducted by the US National Research Council of the National Academy of Sciences and National Academy of Engineering were utilised as the main source of information (National Academy Press, 2000). IPCS EHC monographs 152 (IPCS, 1994a), 172 (IPCS, 1995a), 173 (IPCS, 1995b) were used for the PBBs, TBBPA and derivatives and tris and bis-DBPP, respectively. Tris (tribromoneopentyl) phosphate (TTBP) health effects were summarised from a NICNAS new chemical assessment (NA/672, NICNAS, 1999).

Other literature sources were also used in the preparation of the health effects summary, details of which are cited where relevant. Only a summary of health effects is presented in this assessment, for which primary data sources were not consulted unless otherwise mentioned.

The classification of chemicals by national and international regulatory authorities, where available, is described in the relevant sections of this summary.

No toxicology data or other information were available in the published literature for the following chemicals:

Tetradecabromo (p-diphenoxy benzene)[1];

Bis-(2,4,6-tribromophenyl) carbonate;

3,4,5,6-tetrabromophthalic anhydride, ethylene glycol, propylene oxide reaction products; and

TBBPA, 2,2-bis[4-(2,3,epoxypropyloxy)dibromophenyl] propane polymer.

7.1 Polybrominated diphenyl ethers

7.1.1 Decabromodiphenyl ether commercial product

Industry advised that nonabromodiphenyl ether (NBDPE) congeners are present in the DBDPE and OBDPE commercial products.

Studies in rats indicated that DBDPE was minimally absorbed (< 2%) in the gastro-intestinal tract, with the majority being excreted via faeces. Neither absorption nor elimination were affected by the dose administered. DBDPE deposits in the liver

1Chemical not notified as being imported into Australia.

were identified to be less than 1% of the administered dose and only trace amounts were identified in kidneys, spleen, lung, brain, fat and skin.

Dietary long-term exposure in rats revealed significant increase in total bromine content of adipose tissue in response to increased dose and time of exposure. However, conclusions regarding the source of the increased bromine levels were confounded by the purity of the test substance, which also contained around 20% NBDPE and OBDPE congeners.

No information was available on metabolites in animals fed DBDPE. Radiolabelled ^{14}C-DBDPE studies in rats indicated that the elimination of DBDPE is a rapid process with a half-life of less than 24 h.

DBDPE is of low acute oral toxicity with LD_{50} in rats > 5 g/kg, with no indication of toxicity, gross pathological changes or mortality over a 14-day observation period following single dose.

The acute dermal LD_{50} in rabbits is > 2 g/kg with no associated mortalities. No information on skin irritation was reported. The acute inhalation LC_{50} in rats is > 48.2 mg/L; although no mortalities were reported, respiratory difficulties, eye squint and ocular discharge and increased motor activity, were observed in a 14-day inhalation study.

Application of DBDPE to the shaved skin of rabbits resulted in no irritation to intact skin and no, or only slight, irritation to abraded skin. Similarly, only transient redness and chemosis of the conjunctival membrane of rabbit eyes resulted from application of DBDPE, which resolved after 24 h.

A variety of samples of DBDPE were evaluated for chloracnegenic activity on the rabbit ear and found to be negative. DBPDE did not induce skin sensitisation in a human patch test (Norris et al, 1975)

In general, short- and long-term studies in mice and rats provided no evidence of compound-related effects on clinical, physiological or pathological parameters, with a few exceptions. Increased liver weights and pathological changes in kidneys and lungs following inhalation exposure were reported. In mice and rats, the LOAELs for orally administered DBDPE were determined to be 9 000 mg/kg bw/day and 3 350 mg/kg bw/day, respectively, obtained in 90 days studies. The NOAELs (oral) were determined to be 3 500 mg/kg bw/day and 1 100 mg/kg bw/day in mice and rats, respectively. Effects reported in 2 year oral studies included liver degeneration and fibrosis of spleen in rats and liver hypertrophy and follicular cell hyperplasia in mice. Neoplastic effects are discussed below.

DBDPE was not mutagenic in *Salmonella typhimurium* or *Saccharomyces cerevisiae* assays in the presence or absence of exogenous metabolic activation. Similarly, it was neither mutagenic in mouse lymphoma cells nor caused chromosomal aberration or sister chromatid exchanges (SCE) in Chinese hamster ovary cells. The absence of cytogenetic effects by DBDPE was also reported in bone marrow cells recovered from a reproduction study.

Carcinogenicity bioassays (2 year) have been conducted on DBDPE in mice and rats. A significant increase in the combined incidence of hepatocellular adenomas and carcinomas was reported in mice (males) when compared to control animals, but not when compared to historical control groups. The combined incidence of thyroid gland follicular-cell adenomas and carcinomas was also increased at low

and high doses, though not significantly. No significant differences in the number of rats developing tumours, the total number of tumours or specific type of tumours were observed between treated and control animals fed up to 1 mg/kg DBDPE over 2 years. In another report, rats fed doses up to 50 g/kg of DBDPE over two years showed significant increases in the incidence of liver adenomas. However, no significant differences were identified among the groups in the incidence of hepatocellular carcinomas or acinar-cell adenomas of the pancreas.

The International Agency for Research on Cancer (IARC) has classified DBDPE as a Group 3 carcinogen: Unclassifiable as to carcinogenicity to humans. No epidemiological data relevant to the carcinogenicity of DBDPE were available. There is limited evidence in experimental animals for the carcinogenicity of DBDPE (IARC, 1999). IARC classifications are not made for regulatory purposes.

No reproductive or other toxicological effects were observed in adults or neonates treated with DBDPE in a one generation study. The reproductive NOAEL was determined to be 100 mg/kg bw/day for parents and conceptus. However, the authors questioned the study and indicated that higher doses should have been tested (OECD, 1997b). In a developmental study, significant increase in resorption at 3 and 30 mg/kg, but not at 100 mg/kg, was reported. Also, subcutaneous oedema and delayed ossification of bones and skull were reported at the high dose. The NOAEL for developmental effects was 1,000 mg/kg bw/day for the dams and 100 mg/kg bw/day for the conceptus. These estimates are questionable as only a summary of the study was available and the test substance was of low purity (OECD, 1997b). A more recent study[2] on a current commercial DBDPE product (97.34% DBDPO, 2.66% nona- and octabromodiphenyl oxide) found no evidence of material toxicity or foetal effects at 1,000 mg/kg (Schroeder, 2000).

DBDPE was detected in the serum of workers in the recycling industry dismantling electronic waste (Sjodin et al., 1999).

Human studies indicated that DBDPE is not a skin sensitiser when applied repeatedly to the skin of human volunteers, though signs of skin irritation were reported in a small group of volunteers (9 out of 50 individuals).

The available epidemiological reports indicate that no adverse health effects were observed from occupational exposure to DBDPE. However, a health assessment of workers exposed to PBB and PBDPEs revealed the prevalence of primary hypothyroidism and significant reduction in sensory and fibula motor velocities. Thyroid nodules were also observed in 16% of workers exposed to PBB and DBDPE, with the effects reportedly dependent on the content of the mixes. No direct correlation between the effects and chemicals could be established, given that exposure to both may have occurred at the same plant.

Hazard classification:

In Australia and the European Union DBDPE has not been classified. Current testing may lead to consideration for classification.

2 Only the study summary was provided to NICNAS for assessment.

7.1.2 Octabromodiphenyl ether commercial product

Industry advised that nonabromodiphenyl ether (NBDPE) congeners are present in the DBDPE and OBDPE commercial products.

No data were available on kinetics and metabolism of OBDPE. Following oral treatment, total bromine increased in the liver during the study period, but decreased slowly following suspension of treatment, but remained higher than the controls after one year of withdrawal (OECD, 1997c). Similarly, total bromine concentrations in the lung, liver and fat were higher in treated animals than in controls following 14 day inhalation exposure (OECD, 1997c).

OBDPE is of low acute oral and dermal toxicity with LD_{50} > 28 g/kg in rats and > 2 g/kg in rabbits, respectively. Inhalation exposure caused similar effects to those observed with DBDPE. The LC_{50} in rats is > 50 mg/L. Tachypnea was also noted in animals exposed to 60 mg/L of OBDPE.

OBDPE was not a skin irritant and only transient eye irritation was observed in rabbits.

Inhalation of up to 1200 mg/m^3 of OBDPE over 14 days caused a non-persistent increase in breathing pattern. Significant dose-related increases in relative liver weights accompanied with histopathological lesions were also observed.

Short-term feeding studies over 4 and 13 weeks showed more pronounced effects on animals treated with OBDPE than was observed with DBDPE. Increased liver weights and microscopic changes in liver tissue were identified and found to be dose-related and reversible. Hyperplasia of the thyroid was also observed in the treated animals.

Changes in absolute and relative liver and thyroid weights were also reported in rats administered commercial preparations of OBDPE over 90 days. The NOAELs for orally administered OBDPE were not determined from the available studies, however, the LOAEL in rats was determined to be 100 ppm (28 and 90 day studies).

OBDPE was reported to be non-mutagenic in the microbial and eukaryotic cell systems tested.

No study reports investigating the potential for carcinogenicity of OBDPE are available.

Three developmental toxicity studies have been performed using commercial OBDPE. In one rat study, malformations and foetal variations were observed at 50 mg/kg, which were considered secondary to maternal toxicity. No compound-related effects were observed in the 15 mg/kg or lower dose groups (IPCS 1994b). In a second rat study, the test substance was found to be more toxic to the conceptus than the dam, with malformations and/or foetal variations seen at and above 10 mg/kg. The NOEL for developmental effects was determined to be 2.5 mg/kg. In a study in rabbits, no evidence of teratogenic activity was reported but slight foetotoxicity was observed at a maternally toxic dose of 15 mg/kg (IPCS 1994a; OECD, 1997c).

Hazard classification:

OBDPE is not currently classified in the EU or Australia. However, it is noted the OECD/SIDS draft risk assessment report (OECD, 1997c) includes an EU proposal to classify the chemical as Toxic for Reproduction Cat. 3 and labelled as Xn, R63 (Possible risk of harm to the unborn child).

7.1.3 Hexabromodiphenyl ether

Industry has advised that hexabromodiphenyl ether (HBDPE) is not produced commercially for use as a flame retardant. HBDPE congeners may be present in the commercial OBDPE (~6%) and PeBDPE (~4-8%) products.

Limited kinetic details are available for HBDPE. The half-life for two HBDPE congeners in rats was reported to range between 45 to 55 and 90 to 119 days depending on the sex of the animal and the chemical isomer tested.

No toxicity data are available for HBDPE.

Hazard classification:

Has not been considered.

7.1.4 Pentabromodiphenyl ether commercial product

Industry has advised that the 2,2',4,4'-TBDPE isomer is a major component of the PeBDPE commercial product (see Section 7.1.5 below). Also, tribromodiphenyl ether (TrBDPE) may be present in very limited amounts in the commercial PeBDPE product.

Limited kinetics data were available for PeBDPE. The half-lives for 2 isomers of commercial PeBDPE in rats perirenal fat were around 25 days and 42 days. Half-lives for the other components of the commercial product were not reported.

PeBDPE was reported to be of low acute oral and dermal toxicity in rats, although clinical and hepatic histopathological effects were observed with oral administration. Mild and transient effects, including affected motor activity and clinical signs were observed in rats in an inhalation study. The severity of the reported signs appeared to be concentration related.

PeBDPE caused no or only very slight erythema to the skin of rabbits, but was slightly irritating to the eyes causing redness, chemosis and discharge.

Short-term, 4- and 13-weeks, dietary intake of PeBDPE in rats resulted in increased liver weights and histopathological alterations. Reversible thyroid hyperplasia was also observed. Dose-related increase in tissue total bromine persisted beyond treatment-free period. The NOAEL for orally administered PeBDPE (30 days) in rats was determined to be 1 mg/kg bw/day (OECD, 1997a, 2000).

PeBDPE was reported to be non-mutagenic in the microbial and eukaryotic cell systems tested.

No study reports investigating the potential for carcinogenicity of PeBDPE are available.

PeBDPE effects on thyroid hormone levels have been reported in three studies, which were recently reveiwed by Hooper & McDonald (2000). In mice, thyroid hormone (T_4) levels were significantly reduced following a single exposure to 0.8 mg/kg of PeBDPE (Fowles et al., 1994). A commercial-grade of PeBDPE was reported to cause a reduction in thyroid hormone levels and increased incidences of thyroid hyperplasia in rats at all dose levels (TRIAGE Chemical Studies Database, cited in Hooper & McDonald, 2000; references therein). Reduced thyroid hormone levels were also observed in female rats administered PeBDPE (Hallgren & Darnerud, 1998). The draft OECD assessment of PeBDPE considered the effects on thyroid hormone levels to be indirect consequences of the induction of liver enzymes. Developmental effects were observed at high doses in rats, which were accompanied by severe maternal toxicity.

Neonatal exposure to a PeBDPE congener resulted in permanent behavioural changes affecting motor activity and reduced learning and memory abilities in adult mice (Eriksson et al., 1998).

No teratogenic effects were reported when PeBDPE was administered to pregnant female rats.

Hazard classification:

In Australia PeBDPE has not been considered for classification.

PeBDPE is classified in Annex I to EU Directive 67/548/EEC as follows:

R 48/21/22 Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed.

R64 Harmful: May cause harm to breastfed babies.

The EU classification should be adopted by Australia in accordance with the NOHSC procedure, when the *NOHSC List of Designated Substances* (National Occupational Health and Safety Commission, 1999a) as soon as possible.

7.1.5 Tetrabromodiphenyl ether

Tetrabromodiphenyl ether (TBDPE) is not produced as an individual product. The 2,2',4,4'-TBDPE isomer is a major component of the PeBDPE commercial product.

Significant absorption of TBDPE in the gastro-intestinal tract of rats and mice occurs after oral administration (Orn & Klasson-Wehler, 1998). The main excretory pathway for rats is via faeces, whereas excretion in the mouse is equally distributed in faeces and urine. Although a number of TBDPE metabolites were detected in different tissues, the majority of the administered dose was retained in adipose tissue, mainly as the parent compound, for five days following administration. In the rat, the lung had the second highest concentration of TBDPE and its metabolites.

The authors postulated that similarities between these metabolites and thyroxine may be biologically and toxicologically relevant, whereby structural similarities may enable them to compete for binding sites on transport proteins. TBDPE and commercial mixtures containing it have been shown to lower serum and total T_4 (Orn & Klasson-Wehler, 1998).

TBDPE was shown to induce statistically significant increases in the recombination frequency in the SPD8 duplication cell line (Helleday et al., 1999).

Exposure to TBDPE during active brain growth, ie. on day 10 postnatally, in mice led to permanent behavioural changes involving motor activity in adult animals (Eriksson et al., 1998).

A recent study showed a correlation between the risk for non-Hodgkin's lymphoma among Swedish hospital patients and the levels of a TBDPE congener in adipose tissue (Hardell et al., 1998).

No other data are available on TBDPE, and accordingly no additional conclusions as to its toxicity profile may be formulated.

Hazard classification:

Has not been considered.

7.1.6 Nona- and tri-bromodiphenyl ether

Industry has advised that nona- and tri-BDPE are not produced commercially as individual commercial products. Nonabromodiphenyl ether (NBDPE) congeners are present in the DBDPE and OBDPE commercial products. Tribromodiphenyl ether (TrBDPE) may be present in very limited amounts in the commercial PeBDPE product.

No data are available on the kinetics and metabolism in laboratory animals or humans or the effects of NBDPE or TrBDPE in laboratory mammals and *in vitro* test systems.

Hazard classification:

Has not been considered.

7.2 Tetrabromobisphenol A and derivatives

Like most of the diphenyl ethers, TBBPA is poorly absorbed from the gastro-intestinal tract and is mainly (~95%) eliminated via faeces. Blood and tissue levels were low at all time points measured, with liver and gonads being the main tissues for TBBPA deposition. Tissue half-lives varied from 20 hours to 3 days. Rapid elimination was seen in rats, with >95% of dose excreted within 72 h.

TBBPA is of low acute oral and dermal toxicity with LD_{50} in the range > 2 g to > 5 g/kg and > 1 g to > 2 g/kg, respectively depending on the animal species tested. TBBPA is not acutely toxic via inhalation with a 2 h LC_{50} in rats of 2.5 mg/L. Single inhalation exposure to 0.5 mg aerosol/L of air revealed no symptoms of local or systemic toxicity in guinea pigs.

It was neither irritating to the abraded or intact skin of rabbits and rats, nor to the eyes of rabbits. Similarly, TBBPA was not sensitising in guinea pigs and noncomedogenic in rabbit ear test. Testing in human volunteers showed no evidence of irritation or induction of skin sensitisation.

Inhalation exposure to TBBPA over two weeks to rats, resulted in salivation, nasal discharge and lacrimation at the highest doses as well as suspected compound-

related decrease in relative liver weights. In a three week dermal exposure study, only very slight erythema was reported when TBBPA was applied to rabbit skin.

Repeated oral dose studies on TBBPA in rats including 14-day inhalation and 28 and 90-day oral studies and a 21-day dermal study in rabbits, resulted in no gross or microscopic lesions or symptoms of systemic toxicity. Similar findings were reported for mice, however, concentrations of approximately 70 times those administered to rats lead to death and other toxic effects. The NOAEL reported for this latter study was 700 mg/kg/day.

TBBPA was neither teratogenic in rats, nor mutagenic when tested in microbial and eukaryotic systems. No study reports investigating the long-term effect or potential for carcinogenicity of TBBPA are available.

TBBPA carbonate oligomers, eg. polymer of TBBPA, phosgene, phenol and 2,4,6-tribromophenyl terminated TBBPA, are also used as flame retardants, but very little data is available to enable an appropriate evaluation of health effects associated with their use. The oral LD_{50} in rats was > 5 g/kg and the dermal > 2 g/kg in rabbits. Both carbonate oligomers were not primary skin or eye irritants and were determined not to be mutagenic in the *Salmonella typhimurium in vitro* assay. No other data for short- or long-term exposures and possible toxicological effects are available.

TBBPA carbonate oligomer tested negative in the salmonella *in vitro* test system. No other data on its effects on laboratory animals, *in vitro* test systems, or kinetics and metabolism in animals or humans are available.

TBBPA-bis 2,3-dibromopropyl ether is another derivative with low acute oral and dermal toxicity in mice with LD_{50} > 20 g/kg. It is not irritant to skin, but was a slight eye irritant in rabbits. It did not induce dermal sensitisation in guinea pigs (Safepharm Laboratories Ltd, 1997a). Administration of 200 or 2000 mg/kg bw of the compound to mice in the diet over a 90-day period had no abnormal effects on gross pathological examination and no deaths were reported. TBBPA-bis 2,3-dibromopropyl ether was mutagenic in salmonella *in vitro* tests both with and without metabolic activation (S9 mix) (Safepharm Laboratories Ltd, 1997b). It did not induce unscheduled DNA synthesis (UDS) or sister chromatid exchange (SCE) in *in vitro* test systems.

Hazard classification:

Has not been considered.

7.3 Hexabromocyclododecane

Although significant dermal absorption of HBCD is not expected from its physicochemical profile, evidence indicates that rapid absorption occurs from gastro-intestinal tract. HBCD undergoes metabolism and elimination, mainly in faeces within 72 h. HBCD is distributed primarily to fatty tissues.

No reports on its potential as a dermal or ocular irritant in animals were available. Its potential for sensitisation in guinea pigs remains to be clarified as conflicting findings have been reported.

Dietary intake of HBCD over 28- and 90-days resulted in dose-related increase in absolute and relative liver weights and increased incidence and severity of fatty accumulation in the livers of rats. Thyroid related hyperplasia was also reported. The LOAELs from these studies were 900 mg/kg/day and 925 mg/kg/day, respectively. A NOAEL of 450 mg/kg/day was determined from the 90-day repeated dose study. Although other studies did not establish a NOAEL following oral administration of HBCD, a LOAEL of 80 mg/kg bw/day in rats was determined from a 90-day study (OECD, 1999). These studies have recently been reviewed by EU (report at draft stage). The US Albemarle Corporation has provided EU with comments criticising the validity of the dose estimates and LOAELs reported for these studies. A recent 28-day gavage study[3] for HBCD in CD BR rats found no microscopic or gross lesions (including thyroid), except a 'reversible' increase in relative and absolute liver weights in mid and high dose groups. A NOAEL of 1000 mg/kg bw/day was determined in this study (WIL Research Laboratories, 1997).

It was not genotoxic as revealed from eukaryotic and prokaryotic *in vitro* systems, although it caused a significant increase in recombination frequency in Sp5 and SPD8 duplication cell lines (Helleday et al., 1999).

An 18 month study in mice fed HBCD in diet provided no evidence of carcinogenicity.

HBCD had no effects on reproduction or foetal development in rats with a developmental maternal NOAEL of 50 mg/kg bw/day. However this study was considered to be inadequate as it was not conducted according to good laboratory practice.

Carcinogenicity and reproduction studies have been questioned by the OECD/SIDS risk assessment, and further testing is currently in progress to answer ambiguous findings (OECD, 1999).

HBCD is non-irritant to human skin.

Hazard classification:

Has not been considered.

7.4 Tris (2,3-dibromopropyl) phosphate and metabolites

TDBPP is readily absorbed from the gastro-intestinal tract and to a lesser extent from the skin. Once absorbed, it is usually distributed throughout the blood, liver, kidneys, muscles, fat and skin. It is readily metabolised and eliminated mainly in urine with smaller amounts excreted in faeces and exhaled carbon dioxide. Up to six metabolites, known to be genotoxic intermediates, have been identified in urine, with very little of the parent compound present.

TDBPP is of low acute oral and dermal toxicity with LD_{50} for rats > 2 g/kg and LD_{50} for rabbits > 8 g/kg, respectively.

It is neither a skin or eye irritant in rabbits, nor a skin sensitiser in guinea pigs.

3 Only the study summary was provided to NICNAS for assessment.

Twenty eight- and 90-day oral studies showed dose-related increase in the incidence and severity of chronic nephritis in rats. Dermal application caused degenerative changes in the liver and kidneys and led to death within 28 days. Kidney changes, testicular atrophy and aspermatogenesis, but not death, were reported in rabbits treated dermally with TDBPP for 90 days. No NOAELs were established from the available studies.

TDBPP and its metabolites are reactive molecules that bind to protein and DNA and are genotoxic and mutagenic in a variety of in vitro/in vivo test systems. Animals administered TDBPP experienced extensive DNA damage in a variety of organs and tissues.

Two-year carcinogenicity studies have been reported in mice and rats treated orally or dermally with TDBPP. Dietary intake of TDBPP caused an increase in the incidence of squamous-cell carcinomas and papillomas of the fore-stomach and adenomas and carcinomas of the lungs in mice. The incidence of renal tubular cell adenomas and adenocarcinomas and liver cell adenomas and carcinomas also increased in male and female mice, respectively. Similarly, TDBPP resulted in an increase in renal tubular cell adenomas in rats of both sexes, but tubular cell adenocarcinomas increased only in male rats. Dermal application of TDBPP resulted in significant increase in skin papillomas and/or carcinomas in mice and squamous cell carcinomas, papillomas and carcinomas at other sites. The latter included mainly tongue, gingival area and fore-stomach.

Administration of TDBPP to male rats caused significant does-related effects on the reproductive system, but no NOAEL were determined. Although TDBPP administered to pregnant rats led to significant increase in skeletal variations in foetuses at high doses and to lower viability index at low doses, it was not considered to be teratogenic. Maternal toxicity was also reported at the highest dose. No NOAELs were determined.

Tests on human volunteers revealed that TDBPP has a low sensitisation potential in humans, with the degree of sensitisation dependent upon the availability of the chemical at the surface of the fibre.

Bis (2,3-dibromopropyl) phosphate (BDBPP) is a metabolite of TDBPP and shares similarities in its tissue distribution and elimination. Single exposure to BDBPP or its magnesium salt affected kidneys, both macroscopically and microscopically, and exerted effects on some blood/plasma parameters. Investigations into the toxic effects of short-term exposure of 45 days to BDBPP revealed that the chemical is a renal toxicant. No NOAEL was determined.

No data are available on its potential as an irritant to skin and eyes or as a sensitiser. The free acid of BDBPP is mutagenic in some salmonella strains as are the magnesium and ammonium salts, which exert a greater mutagenic potential than the free acid. The ammonium salt possesses the greatest mutagenic potential. Two-year studies suggest that the magnesium salt of BDBPP is a potential carcinogen when administered in diet to rats. A high incidence of tumours, papillomas and adenocarcinomas in the digestive system as well as hepatocellular adenomas and carcinomas in the liver were reported.

The International Agency for Research on Cancer (IARC) has classified TDBBP as Group 2A: Probably carcinogenic to humans (IARC, 1999) on the basis that there is inadequate evidence in humans for the carcinogenicity of TDBBP and that TDBBP is consistently active in a wide range of mammalian *in vivo* and *in vitro* test systems.

It is also listed in the National Toxicology Program (NTP) Ninth Report on Carcinogens as Reasonably Anticipated to be Human Carcinogen (National Toxicology Program, 2000).

Reproductive toxicity, embryotoxicity and teratogenicity have not been investigated.

Hazard classification:

TDBBP has not been classified in Australia and the European Union.

7.5 Tris (tribromoneopentyl) phosphate (TTBP)

The acute oral and dermal toxicity in rats is low with LD_{50} > 5 g/kg and LD_{50} > 2 g/kg, respectively. The limit test for the acute inhalation toxicity used a maximum achievable concentration of the chemical (1.81 ± 0.50 mg/L) indicating that the inhalation toxicity would be at most moderate. However, the lack of clinical signs suggests that the true LC_{50} is likely to be higher.

TTBP is not irritating to rabbit skin, but is a slight irritant to rabbit eyes. It is not a skin sensitiser in guinea pigs according to the Buehler test.

TTBP is a phosphate ester and is similar to a number of chemicals that have been shown to produce polyneuropathy. However, it tested negative in an acute delayed neurotoxicity study in hens administered a single dose of 2 g/kg.

No significant treatment-related findings were reported in a 28 day feeding study in rats. The NOEL was 20 000 ppm, which is equivalent to 1 635 mg/kg/day for males and 1 858 mg/kg/day for females.

Increased food consumption accompanied by increase in body weight of male rats were the only effects observed in a 90-day feeding study. A NOAEL of 20 000 ppm, or 1 358 mg/kg/day for males and 1 685 mg/kg/day for females, was established.

It was not mutagenic as indicated by the findings from *in vitro* genotoxicity tests in *Salmonella typhimurium* reverse mutation assay, chromosomal aberrations in CHO cells and mouse lymphoma forward mutation assay.

Hazard classification:

Not hazardous according to NICNAS (NA/672) with reference to the *National Occupational Health and Safety Commission Approved Criteria for Classifying Hazardous Substances* (National Occupational Health and Safety Commission, 1999b), for the end points for which data were available. No data on chronic toxicity, carcinogenicity or reproductive end-points were available.

7.6 Brominated polystyrene

No data were available on the pharmacokinetics of brominated polystyrene. However, a study by Monte (1983) on radiolabelled polystyrene (average MW of 100,000) administered orally (dissolved in lemon oil) to rats, indicated that 99% of radioactivity was recovered in rat faeces (without GI absorption) in 48 h. Although skin permeation data was unavailable for brominated polystyrene, physicochemical properties (e.g. molecular weight, water solubility and o/w partition coefficient) of the commercial fire-retardant polymers notified for this assessment, indicate a low potential for skin absorption.

Molecular weight (MW) distribution data for a dibromostyrene polymer (PDBS 80) flame retardant was provided by one supplier. The data indicated that this polymer (MW = 80,000) met NICNAS criteria for a polymer of low concern (PLC) with regard to potential health hazards. It was however noted by the supplier that the degree of polymerisation and hence the MW distribution of component oligomers can vary. In addition, brominated polystyrene may be thermally degraded at processing temperatures (>300 deg C) forming an aerosol of mixed brominated mono- di- and tri- brominated styrenes. In this regard, US Dupont Haskell Laboratory provided a number of study summaries for a brominated styrene mixture (containing ~85% dibromostyrene, ~15% monobromostyrene and ~5% tribromostyrene) and for dibromostyrene (Dupont 2001). Although the quality of these studies could not be determined, they have been included in this section for completeness.

Different commercial preparations containing brominated polystyrene have been tested for toxicity in animals. Only one study disclosed the composition of the examined product, which was reported to contain 16% of brominated polystyrene fire retardant (Larson, 1987a).

Brominated polystyrene was of low acute oral and dermal toxicity with LD_{50} for rats of > 5 and > 15 g/kg respectively (Scibor, 1977; Rush, 1990b) and LD_{50} for rabbits of > 2 g/kg and > 3 g/kg (Larson, 1987a), respectively. The acute inhalation LC_{50} in rats was > 1.9 to > 5.2 mg/L based on two different commercial products (Dreier, 1977; Rush, 1990c). The acute LC_{50} of a brominated styrene mixture was > 3.1 mg/L air (Dupont 2001). No mortality, significant clinical signs, or histopathological changes were observed in the test animals following exposure. Body weight loss was noted in a few animals (Rush, 1990c) and red nasal discharge, which persisted for one day (Dreier, 1977).

Brominated polystyrene is a slight to moderate eye irritant in rabbits (Scibor, 1977; Larson, 1987e; Rush, 1989) and a slight skin-irritant in rabbits (Rush, 1990a). Dibromostyrene was reported as a moderate to severe skin irritant in rabbits (Dupont 2001). Its potential for dermal sensitisation in guinea pigs is inconclusive as conflicting findings have been reported (Larson, 1987c; Rush, 1990d; Dupont 2001).

In a 28-day gavage study in rats systemic toxicity was seen with dibromostyrene at 1600 mg/kg with clinical signs and changes in body and absolute and relative liver weights. Clinical signs such as salivation and staining around the mouth and ventral body surface were reported at 400 and 800 mg/kg. A NOAEL of 200 mg/kg was identified for this study (Dupont 2001).

Administration of dibromosytrene by gavage to rats over 90 days at 130 to 1600 mg/kg resulted in an increase in absolute and relative liver weights. Microscopic changes in the liver such as minimal hypertrophy of the centrilobular parenchymal cells (700 and 1600 mg/kg), areas of nephrosis in the kidneys and an increased incidence of minimal hyperplasia of the urinary bladder epithelium were reported at 1600 mg/kg. Clinical signs were reported at all doses. A NOAEL could not be identified for this study (Dupont 2001).

Dibromostyrene had no effects on reproduction and foetal development in rats in one study with a NOAEL for maternal toxicity of 150 mg/kg bw/day. In another developmental study maternal toxicity was seen at all doses ranging from 100 to 1600 mg/kg/day. The NOAEL for foetal developmental toxicity was identified as 100 mg/kg/day. In a two-generation reproductive study in rats, dibromostyrene by gavage, produced decreased male fertility in the F1 generation at the highest dose of 1600 mg/kg. Increased liver and renal weights at 400 and 1600 mg/kg and microscopic changes in the kidneys at 1600 mg/kg were reported in the F0 and F1 animals. Renal changes included tubular dilatation, nephrosis and/or papillary necrosis. The NOAEL for F0 and F1 animals, based on increased liver and renal weights, was 200 mg/kg/day (Dupont 2001).

Different commercial preparations of brominated polystyrene were shown to be mutagenic to certain strains of salmonella only in the absence of metabolic activation (Microbiological Associates, 1979a; Microbiological Associates, 1979b; Lawler & Valentine, 1989a; Lawler & Valentine, 1989b). These findings were subsequently shown to result from the presence of contaminants in the examined preparations, which induced point mutations in the test strains (Gill & Leber, 1990). Accordingly, brominated polystyrene is considered non-mutagenic to salmonella. Dibromostyrene was not mutagenic in the *in vitro* salmonella assay and tested negative for Unscheduled DNA Synthesis in rat hepatocytes. Results on clastogenicity in Chinese Hamster Ovary (CHO) cells were equivocal (Dupont 2001).

No data for long-term exposures in animals or humans were available.

Hazard classification:

Has not been considered.

7.7 1,2-Bis (tribromophenoxy) ethane

A twenty eight-day dietary intake study revealed accumulation of the substance in fat, liver and muscle of rats, which disappeared following cessation of dosing (National Toxicology Program, 1987). Another study indicated poor absorption in the gastro-intestinal tract with up to 80% of a single orally administered dose excreted in faeces and 5% in urine within 96 h following dosing (Diaz & Atallah, 1978).

The compound does not bioaccumulate in fat, with a short half-life in different tissues averaging 4 days and that in blood being 36 h (Diaz & Atallah, 1978). Excretion in faeces and poor absorption from the gastro-intestinal tract was confirmed in a separate 1 and 10-day feeding study in rats (Nomeir et al., 1993).

1,2-bis (tribromophenoxy) ethane is structurally similar to 2,4,5,2',4',5'-hexabromobiphenyl, which was shown to be readily absorbed from the gastro-intestinal tract of rats following oral administration. The discrepancy in the rate of absorption between two structurally similar compounds may be explained by differences in dose formulations and delivery vehicle used in the different studies.

1,2-bis (tribromophenoxy) ethane is of low acute oral toxicity in rats and dogs with LD_{50} > 10 g/kg and low acute dermal toxicity with LD_{50} > 2 g/kg and > 10 g/kg for rats and rabbits, respectively (Nomeir et al., 1993).

The acute inhalation LC_{50} in rats was > 13.08 mg/L air; no mortality, clinical, or pathological treatment-related changes were detected in the test animals (Horath, 1976).

No toxic effects were observed in rats fed a 10% preparation of the chemical for 14 days (Nomeir et al., 1993). Rabbits treated dermally with 5 g/kg of the chemical for 28 days showed no signs of dermal toxicity (Nomeir et al., 1993). No gross pathological observations were reported in rats exposed to 5 or 20 mg/L in the atmosphere for 21 days, but unspecified histopathology lesions were identified in the lungs of rats (Nomeir et al., 1993). No NOAELs were determined.

It is not mutagenic to salmonella or saccharomyces strains (Brusick, 1990).

Neither appearance, nor behavioural treatment-related changes were observed in pregnant female rats treated with 1,2-bis (tribromophenoxy) ethane (Goldenthal, 1979). Slight reduction in mean maternal body weight and red vaginal discharge were the only changes observed at the highest dose administered. No treatment-related effects on the number of foetuses with anomalies were observed (Goldenthal, 1979). No NOAELs were determined.

Hazard classification:

Has not been considered.

7.8 Ethylene, bis-(tetrabromophthalimide)

Following oral administration, it was mainly excreted in rat faeces with approximately 15% of the radioactivity detected in urine (Cannon Laboratories Inc, 1978a). Residues of the radioactively labelled compound were detected in all tissues, with the highest concentrations found in kidneys and liver. Only one animal in the study was determined moribund and was euthanased prior to the termination of the study. Pathological examination of tissues from the latter revealed inflamed intestines.

Ethylene, bis-(tetrabromophthalimide), also known as 1H-isoindole-1,3(2H)-dione,2,2'-(1,2-ethaediyl)bis[4,5,6,7-tetrabromo-], is of low acute oral toxicity in rats with LD_{50} > 7.5 g/kg (Gabriel, 1976a) and low acute dermal toxicity with LD_{50} > 2 g/kg in rabbits (Biosearch Inc, 1976). It is an irritant to rabbit eyes (Mallory, 1983), but not irritating to rabbit skin (Gabriel, 1976b). Acute inhalation study in rats conducted at a concentration of 203 mg/L resulted in dyspnea and nasal discharge, the former lasting five days post (International Research & Development Corporation, 1981). Necropsied animals revealed red foci in the lungs.

A 28-day repeated dose toxicity study in rats revealed no clinical, physiological or pathological effects on treated animals (Warf Institute, 1976). The incidence and severity of tissue alterations were reported to be minimal and not treatment-related. Reported effects in a 90-day feeding study were swelling of jaws and body weight differences observed in some treatment groups (Cannon Laboratories Inc, 1978b). No other effects were reported. No NOAELs were established.

Ethylene, bis-(tetrabromophthalimide) is not mutagenic to salmonella, *E. coli* or saccharomyces strains (Cannon Laboratories Inc, 1978c).

When administered orally during the period of organogenesis, it was neither maternally or embryo/foeto-toxic nor teratogenic in pregnant rats and rabbits at doses as high as 1 g/kg/day (Rodwell, 1988a/b). Although some malformations were identified in rabbit foetuses, their type was known to occur spontaneously in this species and the increased incidence was not statistically significant.

Hazard classification:

Has not been considered.

7.9 Disodium tetrabromophthalate

Disodium tetrabromophthalate is of low acute oral toxicity in rats with an LD_{50} of 2.7 g/kg in females and 3 g/kg in males (Naas, 1987). Besides mortality, which occurred on the first day after dosing, treatment-related clinical observations included salivation, urogenital staining, lethargy and ataxia. In addition, brain haemorrhage, reddened intestines and adrenal glands and darkened kidneys were reported in the animals. Although thymic changes, dark purple spleens and reddened gastric mucosa were observed in some animals, the former were considered not treatment related whereas the latter findings were equivocal.

Hazard classification:

Has not been considered.

7.10 Phosphoric acid, mixed 3-bromo-2,2-dimethylpropyl and 2-bromoethyl and 2-chloroethyl esters

A dietary one-generation reproductive toxicity study was conducted with the compound to determine its potential effects on fertility and reproduction (Nemec, 1991). With the exception of 7 female deaths occurring between lactation days 12 and 19 in the 400 mg/kg/day group, all F0 animals survived treatment at all doses till scheduled necropsy. Although no clear biological significance was identified for the mortalities, the lack of deaths at other doses and the absence of microscopic correlates suggests no association with the dietary administration of the compounds.

Dietary consumption of 64 mg/kg/day of the compound had no adverse effects on F0 males and females. Tan staining was observed in males treated with 1000 mg/kg/day and tan-coloured faeces were observed in females administered 400 and 1000 mg/kg/day. At the high dose, male fertility indices were adversely affected, whereas that for females was not affected by treatment at any doses.

Adverse effects on body weight, food consumption and thyroid hormone assays in the F0 groups were found to be dose-responsive. Reduced organ weights were also identified, which appeared to correlate with the decline in body mass. Small seminal vesicles were identified in some males at the medium and high dose levels, but no microscopic cellular alterations were recognised. In the high dose groups, treatment-related lesions in the kidneys, characterised by nuclear atypia in the tubules of the outer portion of the medulla and/or nephrosis of the proximal and distal tubules, were noted.

No treatment-related adverse effects were observed in the F1 generation descendants of F0 treated males. However, treatment-related adverse effects including pup survival and general physical conditions, were apparent in the high dose group of descendants of F0 treated females. Also noted was a dose-related reduction in mean body weights of pups beginning from lactation day 1.

A dose related increase in bromide was detected in serum of both sexes in F0 adults, but no signs of toxicity were identified in the low dose groups; ie. 64 mg/kg/day. This was determined to be the NOAEL for parental toxicity (for treated males and females). The NOAEL for reproductive toxicity was determined to be 400 mg/kg bw/day for treated males and 1000 mg/kg bw/day for treated females. The NOAEL for neonatal toxicity was considered to be 1000 mg/kg bw/day (treated males) and 64 mg/kg bw/day (treated females).

Hazard classification:

In Australia and the European Communities (EU) phosphoric acid, mixed 3-bromo-2,2, dimethylpropyl and 2-bromoethyl and 2-chloroethyl esters has not been considered for classification.

International Sales & Marketing[4] Pty Ltd has classified the substance as:

R 22 Harmful if swallowed

R40 Possible risks of irreversible effects

(Source: Material Safety Data Sheet)

7.11 2-Propenoic acid (pentabromophenyl) methyl ester

2-Propenoic acid (pentabromophenyl) methyl ester, homopolymer is of low acute toxicity with oral LD_{50} for rats >5000 mg/kg (Safepharm Laboratories Ltd, 1994a). No signs of systemic toxicity were noted.

It is not a skin irritant and is a slight eye irritant in rabbits. It did not produce dermal sensitisation in guinea pigs (Safepharm Laboratories Ltd, 1994b-d). 2-Propenoic acid (pentabromophenyl) methyl ester tested negative in the salmonella *in vitro* test both with and without S9 mix (Huntingdon Research Centre, 1983).

Molecular weight (MW) distribution data for pentabromobenzyl polyacrylate (PBBPA) was confidentially provided by one supplier. The data provided, indicated that this polymer (MW = ~80,000) met NICNAS criteria for a polymer of low concern (PLC) with regard to potential health hazards.

[4] No evidence or explanatory data were supplied in support of this classification.

Hazard classification:

Has not been considered.

7.12 Polybrominated biphenyls (PBBs)

Most of the studies available for PBBs have been conducted on commercial mixtures, namely FireMaster BP-6 and FF-1 containing hexa- and hepta-bromobiphenyl as their main constituents together with minor ingredients of lower brominates.

Like the brominated diphenyl ethers, absorption of PBBs from the gastro-intestinal tract increases as the level of bromination decreases. PBBs are poorly metabolised, persistent in biological systems and generally bioaccumulate in adipose tissues as well as in liver. Relatively high levels of the more toxic congeners have been found in the liver. *In vitro* studies indicate that the rates of metabolism of PBB congeners depend on the position of bromine and the type of cytochrome induced. Elimination of PBBs is a slow process and occurs primarily via the bile and the intestine into the faeces.

Partitioning ratios of various PBB congeners differ between tissues. PBBs have been shown to pass readily through the placental barrier into the developing foetuses in animals. It is also transferred to offspring through milk. These modes of transfer also occur in humans. There are no quantitative data on PBB absorption in humans.

The half-life for some PBBs has been estimated to range from approximately 1 to > 4 years in rats and rhesus monkeys, respectively, and between 8-12 years in humans.

Commercial mixtures of PBBs are of relatively low acute toxicity with an LD_{50} of > 1 g/kg in rats, rabbits and quails following oral or dermal administration. The extent of toxicity correlates with the total dose administered, irrespective of exposure patterns. The acute health effects and death were usually delayed. Death, following acute or short-term studies, was ascribed to a wasting syndrome associated with reduced intake of feed rather than to specific organ pathologies.

Although a number of studies indicated that PBB mixtures were not, or only mildly, skin or eye irritants, hyperkeratosis and hair loss and lesions similar to chloracne were reported in cattle and rhesus monkeys, respectively. Hyperkeratosis of the inner ear was also observed in rabbits following treatment with a commercial PBB mixture. PBBs are not skin or respiratory sensitisers.

The liver is the target organ, with significant morphological and histopathological changes. The changes include extensive swelling and vacuolation of hepatocytes, proliferation of smooth endoplasmic reticulum and single cell necrosis. The weights of some organs increased following consumption of some congeners.

Oral administration of PBBs at doses as low as 0.3 mg/kg bw per day lead to porphyria in rats and male mice, with a NOEL of 0.1 mg/kg/day.

In vitro and *in vivo* tests in a variety of microbial and mammalian systems revealed that it is neither mutagenic nor genotoxic.

The liver appears to be the principal site of carcinogenic effects of PBBs in long-term toxicity studies. Hepatocellular carcinomas were significantly increased in male and female mice and rats treated orally with a PBB mixture. For example, FireMaster FF-1 induced hepatocellular carcinomas in mice and rats and cholangiocarcinomas and neoplastic nodules of the liver in rats. Administration via gastric intubation induced trabecular hepatocellular carcinomas and neoplastic nodules of the liver in female rats. Trabecular hepatocellular carcinomas were also detected in male and female offspring of female rats exposed orally to FF-1. The ability to promote tumour formation differs for different congeners.

Foetal mortality and reduced offspring survivability were the main adverse effects on reproduction associated with consumption of PBB mixtures. Most of the available data are for FireMaster mixture, with some studies examining the effects of only single doses. No NOAELs were established. Low brominated biphenyls, namely tetra- to heptaBB, exhibit high toxicities similar to those exerted by the chlorinated dioxins and coplanar polychlorinated biphenyls. These include malformations, liver injuries, immune suppression, reproductive disturbances, thyroid dysfunction, skin injuries and severe weight loss at acutely toxic doses.

PBBs are known to interact with the endocrine system and to affect the levels of steroid hormones. Oral administration of FireMaster FF-1 to rats showed a dose-related hypothyroidism measured by decreased serum thyroxine (T_4) and triiodothyronine (T_3) levels. In addition, PBBs have been shown to inhibit intercellular communication *in vitro* at non-cytotoxic concentrations.

Reports of PBB effects on humans exist mainly from the poisoning incident in Michigan, USA, 1973. Two major epidemiological studies were conducted following this incident, which were used to evaluate the relationship between exposure to PBB and a diverse range of adverse effects reported in the exposed populations.

In studies conducted by the Michigan Department of Public Health (1974 and 1978), no correlation between the reported symptoms and PBB body-burden was identified. The study reported an absence of a positive association between serum concentrations of PBB and symptom or disease frequencies. No abnormalities in major organ functions or other medical conditions were found. Other studies conducted by the Environmental Science Laboratory, Mount Sinai School of Medicine (NY) indicated that Michigan farmers accidentally exposed to PBB had a higher prevalence of skin, neurological and musculoskeletal symptoms when compared with unexposed subpopulations from another locality (1976 and 1977). Despite the reported discrepancies, both studies demonstrated the absence of a dose-response correlation between PBB levels in serum and/or adipose tissue and the prevalence of clinical symptoms and measurements.

These findings should be considered with caution as the studies suffered design problems that introduced a number of confounding factors. Besides follow up studies to assess cancer risk (see below), no long-term follow up studies are available to assess other adverse health effects following exposure to PBB in humans.

A recent study revealed that perinatal exposure to PBBs may alter pubertal development in female offspring of women exposed to PBBs during the Michigan accident (Blanck et al., 2000). The onset of menses and pubic hair development appeared to be affected. However, little association between exposure to PBBs and

breast development was identified. Exposure to PBBs may interfere with the endocrine feedback loop and influence circulating hormone levels and thus affect pubertal developments. Despite acknowledged limitations, the study nonetheless shows an association between pubertal events and pre- and postnatal exposure to organohalogens (Blanck et al., 2000).

Occupational exposure to PBB mixtures resulted in chloracne and hypothyroidism, with 13% and 11.4% of cases identified in independent studies, respectively. Thyroid nodules were also observed in 16% of workers exposed to PBB and DBDPE. These effects were reported to be dependent on the congeners present in the mixes.

Michigan farmers exposed to PBBs were examined for the prevalence of carcinogenic embryonic antigen (CEA) titres in serum, which were found to be elevated and higher than the matched controlled group of unexposed population. However, the difference was not statistically significant. Nonetheless, a positive correlation was identified between serum PBB concentrations and CEA titres. Workers exposed to PBB for more than five years had a higher prevalence of elevated CEA titres than farmers exposed as a result of the Michigan incident.

A follow up nested case-control evaluation of the association between site-specific cancer risk and serum PBB levels was undertaken among the accidentally exposed Michigan population. This study revealed an increasing dose-response relationship between the risk of two cancer sites, namely digestive system and lymphoma, and serum PBB levels (Hoque et al., 1998). Similar association was also reported for breast cancer (Henderson et al., 1995). The International Agency for Research on Cancer (IARC) has classified PBB as Group 2B: Possibly carcinogenic to humans (IARC, 1986; IARC, 1987). The basis for the classification is that no data were available on the genetic and related effects of polybrominated biphenyls in humans, inadequate evidence for the carcinogenicity of polybrominated biphenyls to humans and sufficient evidence for the carcinogenicity of commercial mixtures of polybrominated biphenyls to experimental animals.

Hazard classification:

PBB has not been classified in Australia and the EU.

8. Effects on Organisms in the Environment

Until recently, the ecotoxicity of the PBDPEs has mainly been studied for PeBDPE with limited data available for OBDPE and DBDPE. In general, toxicity in short-term tests appears to be higher at lower levels of bromination (Kemi, 1999).

8.1 Avian toxicity

PBFRs (PeBDPE, TBDPE, dibromodiphenyl ether) have been detected in birds. No toxicity data have been found. Although there is no evidence, the possibility exists for biomagnification, which may be an issue for fish eating birds. According to preliminary assessments under the EU's existing substances programme, PeBDPE may pose a risk to aquatic and terestrial organisms and lead to secondary poisoning, e.g. of fish-eating birds or mammals (Kemi, 1999).

8.2 Aquatic toxicity

Unless otherwise stated, the ecotoxicity described in this section has been summarised from the OECD/SIDS draft reports.

8.2.1 Toxicity to fish

Acute ecotoxicity findings for a number of PBFRs are summarised in Table 6.

Table 6 - Acute aquatic toxicity of some PBFRs

Test	Substance	Species	Result	Reference
1	Pentabromodiphenyl ether[1]	Orange-red killifish	48 h LC50>500 mg/L	OECD, 2000
2	Pentabromodiphenyl ether[1]	Rainbow trout	96 h LC50>21 μg/L	OECD, 2000
3	Tetrabromobisphenol A	Bluegill sunfish	96 h LC50=0.51 mg/L	IPCS, 1995
4	Tetrabromobisphenol A	Rainbow trout	96 h LC50=0.4 mg/L	IPCS, 1995
5	Tetrabromobisphenol A	Fathead minnow	144 h LC50=0.54 mg/L	IPCS, 1995
6	Hexabromocyclododecane	Bluegill sunfish	96 h LC50 >100 mg/L	Kemi, 1995
7	Poly (pentabromo benzyl) acrylate[2]	Orange-red killfish	48 h LC50>250 mg/L	Bromine Compounds Ltd, 2000
8	Tris (tribromoneopentyl) phosphate	Rainbow trout	96 h LC50>100 mg/L	Bromine Compounds Ltd, 1998

[1] Commercial substance containing 33.7% tetrabromodiphenyl ether, 54.6% pentabromodiphenyl ether and 11.7% hexabromodiphenyl ether.

[2] Full study not provided only results were supplied.

Test 1. This test was carried out as part of a bioaccumulation study on adult orange-red killifish (*Oryzias latipes*). The reported 48 h LC_{50} >500 mg/L is much higher than the water solubility of the substance. PeBDPE was dispersed in water with dimethyl sulphoxide (DMSO) and a dispersing agent at levels well above those recommended for solubilising agents, given in the EU test methods.

Test 2. Rainbow trout (*Oncorhynchus mykiss*) was exposed over 96 h using a flow-through test system. Dimethylformamide at a concentration of 0.1 ml/L was used as a cosolvent. The mean test concentrations measured were 1.1, 2.3, 3.9, 7.8 and 21 µg/L. No mortalities or overt signs of toxicity were seen at any exposure concentration and the 96 h LC_{50} and NOEC were greater than the water solubility of the substance.

A fish early life stage chronic toxicity study was carried out with rainbow trout (*Oncorhynchus mykiss*) using a substance with the following composition: 0.23% TrBDPE, 36.02% TBDPE, 55.10% PeBDPE and 8.58% HBDPE. Mean measured concentrations determined over the test period for the 5 treatments respectively were 1.2, 2.5, 4.0, 8.9 and 16 µg/L and the test was performed under flow-through conditions. Dimethylformamide (DMF), at a concentration of 0.10 ml/L, was used as a cosolvent. Controls (no test substance or DMF) and solvent controls (DMF at 0.1 ml/L) were also run (OECD, 2000).

The following endpoints were determined in the test: embryo survival (hatching success); time to hatch; time to swim-up of larvae; post-hatch growth (weight and length); and post hatch survival. For all endpoints except post hatch growth, there were no statistically significant differences ($p>0.05$) between the control groups and any treatment. For post hatch growth, the mean length, wet weight and dry weight of fish exposed to 16 µg/L was statistically significantly reduced ($p<0.05$) compared to controls. The overall NOEC from the study was determined to be 8.9 µg/L, with statistically significant effects being seen on juvenile fish length and weight by day 60 post-hatch at a concentration of 16 µg/L.

A study to examine the effects of PeBDPE on the liver morphology and cytochrome P450 activity in fry of rainbow trout used commercial PeBDPE Bromkal 70. One week prior to hatching, trout embryos in each exposure group (0.08, 0.8 and 4 µg/egg – equivalent to 1, 10 and 50 µg/g fresh weight at the start of the experiment) were injected with a solution of the test substance in DMSO. Two control groups were used, one receiving no treatment and one being injected with DMSO alone. Six weeks after the embryos were exposed the morphology and the EROD activity of the liver of the fry was examined. Cumulative mortality in the 4 µg/egg group (54% mortality) was slightly higher than that seen in the DMSO control group (33% mortality) but both were significantly higher than the untreated control group (<5% mortality), indicating that at least some of the mortality seen in the treated groups could be due to the method of administration. Some changes in liver morphology were noted at 4 µg/egg and a slight increase (2-3 times) in EROD activity was found at 0.8 µg/egg, but not at 0.08 or 4 µg/egg (OECD, 2000). These effects were much less than those produced by known P450 inducers using the same test system (e.g. a dose related increase of up to 35 times the control hepatic EROD activity was seen for polychlorinated diphenyl).

A rainbow trout early lifestage mortality bioassay was undertaken to compare the potency of individual polybrominated diphenyl ether isomers with that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The compounds studied in the test were

2,2'4,4'-tetrabromodiphenyl ether, 2,2',3,4,4'-pentabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether. All isomers were >98% purity. The test substances were dissolved in chloroform and then incorporated into phosphatidylcholine liposomes using a thin-film hydration method. Test substances were then injected into eggs 24 to 50 h after fertilisation, and the eggs were placed in flowing water at 11°C. The eggs and fry were observed 3 times/week and mortality was scored as either positive or negative for signs of TCDD-like toxicity. The polybrominated diphenyl ethers tested did not cause sac-fry mortality or signs of TCDD-like toxicity at concentrations up to 12 µg/g egg (OECD, 2000).

The effect of food contaminated with PeBDPE (Bromkal 70-5DE) on reproduction was studied using the three-spined stickleback (*Gasterosteus aculeatus*). Female fish were fed freeze-dried chironomids at approximately 2% of body weight/day contaminated with PeBDPE for three months. Two exposure concentrations were used, 6.29 and 10.39 mg of PeBDPE. These concentrations are equivalent to initial exposure concentrations (doses) in food of 3.5 mg/kg food/day and 5.8 mg/kg food/day. Following exposure, around half the females from each group were transferred to spawning aquaria containing unexposed males. Spawning was considered to be successful if it occurred within 24 h. After spawning, the eggs were collected. One week after hatching the number of fry and non-hatched eggs were counted. No changes in feeding patterns or behaviour were noted during the exposure period and no dose related mortality was seen from the start of exposure until spawning. On examination of the livers, exposed fish showed intracellular lipid accumulation. No significant difference between exposed fish and controls was seen in spawning success (OECD, 2000).

The effects of TBBPA on fathead minnow (*Pimephales promelas*) were evaluated following exposure to concentrations ranging from 0.024 to 0.31 mg/L over 35 days. Parameters measured included the survival of organisms at hatch and survival and growth of larvae after 30 days post hatch. Survival at the end of the hatching period (day) at the highest concentration was 28% compared to 84% in the controls. Survival in all other concentrations was unaffected compared to controls. All larvae in the highest concentration died within the initial week of the post hatch exposure period. Again, other exposure groups were unaffected compared to controls. At test termination, surviving fish in all treatments grew at rates comparable to those in the control groups. The NOEC for this experiment was 0.16 mg/L, and the MATC determined to be between 0.16 and 0.31 mg/L (geometric mean 0.22 mg/L) (IPCS, 1995a).

Three studies were evaluated in the SIDS draft report for HBCD. Two studies reported EC_{50} (96 h) of > 100 mg/L and 10,000 mg/L in bluegill fish and golden orfe, respectively (OECD, 1999). No abnormal behaviour were reported for either test study. In the same SIDS draft assessment report, a third reported study, which used a composite sample of HBCD, indicated that HBCD is not acutely toxic to rainbow trout at a concentration of approximately 2.5 µg/L which is closer to its water solubility limit.

8.2.2 Toxicity to aquatic invertebrates

A composite sample containing of 33.7% TBDPE, 54.6% PeBDPE and 11.7% HBDPE was tested on *Daphnia magna* over 48 h using a flow-through system. DMF at a concentration of 0.1 ml/L was used as a cosolvent. Exposure levels

consisted of mean measured concentrations of 1.2, 2.4, 4.9, 9.1 and 20 µg/L. The 48 h EC_{50} was determined to be 14 µg/L and the NOEC was 4.9 µg/L, based on the mean measured concentrations. It was stated in the test report that the effects seen could have been due to physical impairment (undissolved test substance adsorbing onto the daphnids and adversely affecting respiration, swimming etc.) rather than a direct toxic effect (OECD, 2000).

The effects of PeBDPE were also studied in a 21-day life-cycle study under flow-through conditions using the same composite test substance described above. The concentration of DMF in the test chambers was 0.08 ml/L, and a solvent control using the same concentration, as well as a control without solvent, was also run. Five test concentrations were used: 1.4, 2.6, 5.3, 9.8 and 20.0 µg/L, based on the mean measured concentration during the test. No significant ($p>0.05$) differences between the control and solvent control daphnids were seen for any endpoint studied and so effects in the exposed daphnids were compared against the pooled effects seen in the controls and solvent controls. No significant ($p>0.05$) mortality was seen in the 1.4, 2.6, 5.3 and 9.8 µg/L treatments when compared to controls. However, by day 7 of the test, 100% mortality of the daphnids in the 20 µg/L treatment was seen. The EC_{50} for mortality/immobilisation was found to be 17 µg/L after 96 h and 14 µg/L between days 7 and 21. No significant effects ($p>0.05$) on reproduction were seen in the 1.4, 2.6, 5.3 and 9.8 µg/L treatments compared to controls. No young were produced in the 20 µg/L treatment as all test organisms died before the first brood was produced (day 8). The EC_{50} for this endpoint was estimated at 14 µg/L at days 14 and 21. The final endpoint considered in the study was growth of the first generation organisms. Here, a small but significant ($p<0.050$) reduction in mean length of the organisms was found in the 9.8 µg/L treatment group. A slight reduction in mean dry body weight was also found but this was not statistically significant ($p>0.05$) when compared to controls. Overall, the NOEC from the study was found to be 5.3 µg/L and the LOEC was found to be 9.8 µg/L (OECD, 2000).

The 48 h LC_{50} for *Daphnia magna* exposed to TBBPA is 0.96 mg/L. *Daphnia magna* were exposed under flow through conditions for 21 days to 0.056-0.98 mg/L of TBBPA. At termination of the study, daphnid survival at all concentrations was 95-100% compared with 98% in the control. Daphnid growth also appeared unaffected at any dose level. However, there was an adverse impact on reproduction with 21 offspring per female at the highest level tested compared to 60 offspring per female in the control. Other dose levels did not appear affected. The MATC was therefore determined to be between 0.3 and 0.98 mg/L (geometric mean 0.54 mg/L) (IPCS, 1995a). Dissolved humic material has been shown to have no effect on the toxicity of TBBPA for *Daphnia magna* in a 48 h exposure test.

Mysid shrimp, *Mysidopsis bahia*, were exposed to TBBPA in a flow-through system for 96 h. Three live stages were tested, <1, 5 and 10 days old. Test concentrations do not appear to be specifically stated, but the 96 h LC_{50} values for the three stages were 860, 1100 and 1200 µg/L respectively indicating moderate to high toxicity (IPCS, 1995a).

Using reduction of shell deposition as the endpoint, eastern oysters, *Crassotera virginica*, were exposed under flow through conditions to 0.018-0.15 mg/L TBBPA. The EC_{50} was calculated to be 0.098 mg/L indicative of high toxicity. No effects were observed at the lowest concentration (IPCS, 1995a).

The 48 h EC_{50} of HBCD to *Daphnia magna* was determined to be 146.34 mg/L. The NOEC was 1 mg/L, and the lowest tested concentration with 100% effect was more than 1000 mg/L. The reliability of this test is uncertain. The results are several orders of magnitude greater than the water solubility of this substance (3.4 ppb), and not much would be expected to dissolve (Kemi, 1995; OECD, 1999). A chronic toxicity study report indicated that a composite sample of HBCD had no statistically significant effects on survival, reproduction or growth of *Daphnia magna* exposed to µg/L over 21 days. The NOEC was determined to be 3.1 µg/L. However, daphnids exposed to 11 µg/L had statistically significant reduced lengths, dry weight and fewer young. At 5.6 µg/L for 21 days, daphnids had statistically significant reduced mean lengths and thus the LOEC was determined to be 5.6 µg/L (OECD, 1999).

8.2.3 Toxicity to algae

The toxicity of a commercial mixture of PeBDPE comprised of 33.7% TBDPE, 54.6% PeBDPE and 11.7% HBDPE was determined over 96 h using the freshwater algae, *Selenastrum capricornutum*. A static test system was used and DMF at a concentration of 0.1 ml/L was used as cosolvent. Mean measured concentrations at the start of the test were 1.7, 3.1, 5.9, 12 and 26 µg/L, but by the end of the test the concentration of the test substance was below the detection limit (<0.8 µg/L) in all exposures (presumably the substance had adsorbed onto or was taken up by the biomass). Over the 96 h exposure period, no statistically significant ($p<0.05$) differences between treatment and control groups were seen in either cell densities or areas under growth curves. However, at 24 h a slight, but statistically significant, inhibition of growth was seen in the higher exposure groups and a 24 h EC_{10} of 3.1 µg/L based on cell density and 2.7 µg/L based on area under the growth curve was calculated. By 48 h and longer, no significant difference was seen between controls and any exposure group (OECD, 2000).

The results of the algal toxicity test are difficult to interpret since the test concentration declined during the test, presumably by adsorption onto the algae. Although this itself does not invalidate the test, it does make it difficult to determine at what concentrations effects may occur through continuous exposure over longer periods.

Marine unicellular algae, *Skeletonema costatum, Thalassiosira pseudonana* and *Chlorella* sp., were exposed to TBBPA in 6 algal growth media for periods of 72 h, 72 h and 96 h, respectively. Growth of *Chlorella* sp. was not inhibited by as much as 50% at 1500 µg/L. However, TBBPA was toxic to *S. costatum* and *T. pseudonana* with EC_{50} values between 90-890 µg/L and 130-1000 µg/L, respectively. TBBPA may be classified as very highly toxic to marine algae based on these results (IPCS, 1995a).

The freshwater green algae, *Selenastrum capricornutum* was exposed to TBBPA at measured concentrations of 0.34-5.6 mg/L for 96 h. Growth was not reduced at any dose level suggesting at worst, TBBPA is moderately toxic to this species (IPCS, 1995a).

Marine unicellular algae, *Skeletonema costatum* and *Thalassiosira pseudonana* were exposed to HBCD in 6 growth media. The EC_{50} for *S. costatum* ranged from 9.3-12 µg/L indicating very high toxicity. The EC_{50} (96 h) measured for another algae, *Chlorella* sp., was > 1500 µg/L (OECD, 1999). *T. pseudonana* was less

sensitive with the EC_{50} ranging from 0.05-0.37 mg/L. Nonetheless, this is still indicative of very high toxicity. These results are higher than the water solubility of this compound (Kemi, 1995).

8.2.4 Micro-organisms

No data have been found on the toxicity of PBFRs to micro-organisms.

Although HBCD was reported to have low toxicity to micro-organisms, the nominal test concentrations used were above the water solubility of HBCD (OECD, 1999).

8.2.5 QSAR data

The high octanol-water partition coefficient of PeBDPE (log K_{ow} = 6.46-6.97) means that it is not ideally suited for QSAR predictions (generally only valid for substances with log K_{ow} between 1 and 6). Because of this and due to tested results being available, QSAR values determined in the SIDS report have not been reported here.

8.2.6 Sediment organisms

The following sediment toxicity studies were carried out for PeBDPE and/or TBBPA. The PeBDPE test substance was composed of 0.23% TrBDPE, 36.02% TBDPE, 55.10% PeBDPE and 8.58% HBDPE. Tests for PeBDPE were carried out as a result of the initial risk assessment for PeBCPE by the EU (OECD, 2000).

Hyalella azteca

A prolonged sediment toxicity test using spiked sediment has been carried out with the amphipod *Hyalella azteca* using a flow-through system. The sediment used in the test was an artificial sediment consisting of 1% humic acid and dolomite, 5% alpha cellulose, 14% silt and kaolin and 80% industrial quartz sand. The sediment had a mean organic matter content of <2%, a water holding capacity of 11%, a pH of 6.6 and a particle distribution of 83% sand, 6% silt and 11% clay. PeBDPE test substance was added to the sediment as a solution in DMF (final concentration of DMF was 0.1 ml/kg dry sediment). Groups of 12-day old amphipods were exposed to a series of 5 test concentrations (3.1, 6.3, 13, 25 and 50 mg/kg dry weight nominal), a solvent control and control sediment for 28 days at 23°C. The concentrations were well maintained throughout the test.

The endpoints determined in the study were: percent mortality and growth (dry body weight). Mortalities at 28 days were 30% in the controls, 34% in the solvent controls, and 37%, 30%, 56%, 41% and 44% in the 3.1, 6.3, 13, 25 and 50 mg/kg dry weight treatment groups respectively. Mortalities were reported to be variable within and between treatment groups and in the controls. From these results it was determined that a slight increase in mortality relative to controls was seen at the three highest concentrations tested, but that this increase was only statistically significant ($p<0.05$) compared to the pooled controls in the 13 mg/kg dry weight treatment group.

The weights of individuals within and between treatment groups, including the controls, were highly variable, but any reduction in weight in comparison with the pooled controls was not concentration-dependent or statistically significant ($p>0.05$). Due to the variability of responses seen in this study it is not possible to derive exact values for the NOEC and LOEC. The report indicates that the 28-day EC_{50} is >50 mg/kg dry weight and that the LOEC is ≥13 mg/kg dry weight, based on the general increase in mortality seen at and above this concentration. The NOEC is therefore around 6.3 mg/kg dry weight.

Chironomus riparius

A prolonged sediment toxicity test using spiked sediment has been carried out with the midge *Chironomus riparius*. The sediment used was as described above but the test was undertaken under static conditions.

Groups of midge larvae were exposed to a series of 5 test concentrations (3.1, 6.3, 13, 25 and 50 mg PeBDPE test substance per kg dry weight nominal), a solvent control and control sediment for 28 days at 20°C. The larvae used in the test were first-instar larvae, approximately 3 days old. The concentrations were reasonably well maintained throughout the test.

Data obtained in this test allowed a sediment-water partition coefficient to be estimated for PeBDPE for the sediment used in this study. Kp_{sed} ranged from around 490 L/kg for the low exposure concentration and approximately 4,516 L/kg for the high exposure concentration.

The endpoints determined in the study were: percent mortality, mean development time, emergence rate and development rate. The overall NOEC from this study is 25 mg/kg dry weight (nominal) based on a statistically significant ($p<0.05$) decrease in the mean development rate of the 50 mg/kg dry weight treatment groups. The LOEC is 50 mg/kg dry weight (nominal). The actual measured concentrations appear to be slightly lower than the nominal concentrations in this study, and the same results based on the mean measured concentration would give the LOEC to be around 28 mg/kg dry weight and the NOEC to be around 16 mg/kg dry weight (assuming that the actual concentration in the 25 mg/kg treatment is 65% of the nominal value).

Lumbriculus variegatus

A prolonged sediment toxicity test using spiked sediment has been carried out with the oligochaete Lumbriculus variegatus using a flow-through test system. The sediment and test system used was the same as in the *Hyalella azteca* test above.

Groups of adult oligochaetes were exposed to a series of 5 test concentrations (3.1, 6.3, 13, 25 and 50 mg PeBDPE test substance per kg dry weight nominal), a solvent control and control sediment for 28 days at 23°C. The concentrations were well maintained throughout the test.

The endpoints determined in the study were: survival/reproduction (total number of organisms present at end of study; as it is not possible to distinguish between adults and young this is a combination of parent survival and number of young produced); and growth (dry body weight).

Statistically significant differences ($p<0.05$) in the mean dry weight data of individuals were observed between the control and solvent control groups and so the two groups were not pooled. The solvent control group was used for comparison with the responses seen in the treatment groups.

During the test, no observations of mortality or abnormal behaviour of oligochaetes were seen in any of the replicates or control groups. At the end of the test, an increase in the numbers of oligochaetes was found in each replicate (experiment started with 10/replicate) indicating that reproduction had occurred. The reduction in the number of worms/replicate in the three highest treatments were statistically significantly different ($p<0.05$) from the solvent controls. There was no concentration-dependent or statistically significant difference in dry weights determined. The report indicates that the 28-day EC_{50} is >50 mg/kg dry weight and that the LOEC is 6.3 mg/kg dry weight, based on the survival/reproduction. The NOEC is therefore 3.1 mg/kg dry weight.

Chirononous tenans

The following study on the sub-chronic effects of TBBPA on the benthic invertebrate midge *Chirononous tenans* was reported in IPCS 1995a. The study consisted of a series of three 14-day (partial life cycle tests) under flow through conditions. Each test was conducted with sediment containing different organic carbon levels. The three sediments were of high (6.8% organic carbon), mid (2.7%) or low (0.25%) organic carbon content. The mean, measured concentrations of TBBPA in high organic carbon (HOC), medium organic carbon (MOC), and low organic carbon (LOC) sediments were 0.0044-0.046, 0.0075-0.045, and 0.0078-0.046 mg/L, respectively.

The highest NOEL was established at an interstitial water concentration of 0.046 mg TBBPA/L, which was the highest concentration attained in the HOC treatment. The TBBPA concentration in the HOC sediment was 340 mg/Kg. The NOELs in the interstitial waters of MOC and LOC treatments were 0.045 and 0.046 mg TBBPA/L. The TBBPA concentrations of the sediments in MOC and LOC treatments were 240 and 230 mg/kg. Bioconcentration factors in the midge ranged from 240 to 510 in the HOC sediments, 490 to 1100 in the MOC sediments, and 650 to 3200 in the LOC sediments. A high organic content in the sediment reduced accumulation. No adverse biological effects resulted from the increased TBBPA body burden. No relationship was observed between the sediment concentration of TBBPA and midge body burden. (IPCS, 1995a).

8.3 Terrestrial toxicity

In the following following tests, the PeBDPE test substance was composed of 0.23% TrBDPE, 36.02% TBDPE, 55.10% PeBDPE and 8.58% HBDPE (OECD, 2000). These tests were all carried out as a result of the initial EU risk assessment.

8.3.1 Micro-organisms

The toxicity of commercial PeBDPE to soil micro-organisms was studied using Nitrogen Transformation Test (OECD, 2000). The soil used was a sandy loam of pH 6.8 and 1.0% organic carbon content. The moisture content of the soil was 11.4% as supplied, and the maximum water holding capacity (MWHC) was 41.9%. Before use in the test, the soil moisture content was adjusted to approximately 40%

of the MWHC (i.e. the soil water content was around 17%), and this level was maintained throughout the test. The soil samples were treated with the test material using quartz sand as carrier. The test substance was added to sand as an acetone solution, and once the acetone had evaporated, the sand was thoroughly mixed into the soil samples. The concentrations tested were 0.01, 0.03, 0.10, 0.33 and 1.00 mg/kg dry soil weight. Lucerne meal (0.5% w/w) was then added to the soil and the samples were incubated at 20±2°C for 28 days under aerobic conditions. Nitrate production was determined after 0 to 3 h and 28 days incubation. Increasing concentrations of test material were found to have no effect on the levels of nitrate produced. The variation in nitrate concentration between replicate control samples was <15% at 0-3 hours and 28 days (actual variation was 1.7% and 0.4% respectively), indicating a valid test. The NOEC from this test is therefore >1 mg/kg dry weight (OECD, 2000).

8.3.2 Plants

Artificial sandy soil produced by mixing kaolinite clay, industrial quartz sand and peat in the weight ratio 4:50:5, respectively, was used in testing the toxicity of PeBDPE. Crushed limestone and a slow-release fertiliser were also added. The particle size distribution of the soil was 92% sand, 0% silt and 8% clay, and the soil had a pH of 7.5 and an organic matter content of 2.9% (OECD, 2000).

Six plant species were tested: monocots; corn (*Zea mays*), onion (*Allium cepa*), rye grass (*Lolium perenne*): dicots; cucumber (*Cucumis sativa*), soybean (*Glycine max*), tomato (*Lycopersicon esculentum*). The nominal concentrations tested were 62.5, 125, 250, 500 and 1000 mg/kg dry soil.

During the 21-day test, weekly observations of emergence were made (number of emerged seedlings per pot). In addition, a qualitative assessment of the condition of each seedling was made (i.e. presence or absence of signs of phytoxicity such as colour changes, necrosis, leaf curling, plant lodging or plant stunting). At the termination of the test, the growth of the emerged seedlings was evaluated in terms of the mean shoot height and mean shoot fresh weight. Only corn and tomatoes showed effects and these are described below.

Corn: No statistically significant effects ($p>0.05$) on the emergence of seedlings were noted in any treatment group compared with the control group. The emerged seedlings generally appeared normal throughout the test, although there were isolated individuals which displayed signs of phytotoxicity. Effects were seen on the mean shoot height and mean shoot weight after 21-days compared with the control group. The mean shoot height was statistically significantly reduced ($p<0.05$) in the 250, 500 and 1,000 mg/kg dry weight groups over the controls, although the EC_{25} for this endpoint was estimated to be >1,000 mg/kg dry weight. The mean shoot fresh weights were found to be statistically significantly reduced ($p<0.05$) in all treatment groups compared with the controls. Based on the dose-response seen an EC_{25} of 154 mg/kg dry weight was calculated. Since significant effects were seen at the lowest concentration tested, it is not possible to obtain a NOEC directly from the results. However, an EC_5 of 16 mg/kg dry weight was calculated in the test report and this approximates the NOEC.

Tomato: No statistically significant differences ($p>0.05$) were seen in emergence in the treatment groups compared with the control groups. The emerged seedlings generally appeared normal throughout the test. Effects were seen on the mean seedling height and mean seedling fresh weight. A dose-responsive decrease in the mean seedling height was observed, but this was only statistically significantly different ($p<0.05$) from the control group in the 500 mg/kg dry weight treatment group. The EC_{25} for this endpoint was calculated as 369 mg/kg dry weight. The mean shoot fresh weights were found to be statistically significantly ($p<0.05$) reduced in the 250, 500 and 1,000 mg/kg treatment groups when compared to controls. The EC_{25} was calculated to be 136 mg/kg dry weight and the EC_{50} was calculated to be 217 mg/kg dry weight for this endpoint. Overall, the NOEC for this species was 125 mg/kg dry weight.

8.3.3 Earthworms

The earthworm, *Eisenia fetida*, was used in the following studies. The soil used in the test was an artificial soil prepared by mixing sand (70%), kaolin (20%) and sphagnum peat (10%). The pH of the soil was adjusted to 6. The test substance was dissolved in DMF. The water content of the soil was adjusted to 33% by weight and then mixed for 20 minutes to allow the solvent to evaporate. A solvent control soil was also prepared in the same way by adding DMF alone to the soil. On day 7 of the test (total duration of test was 14 days), the content of each test chamber was removed to determine the number of surviving worms and to observe any behavioural or pathological abnormalities. Following these observations, the test soil was returned to the chambers and worms replaced on the soil surface in order to observe burrowing behaviour. At the end of the test, the number of surviving worms, and also the average body weight of the worms was determined (OECD, 2000).

The test was carried out over two phases. In the first phase, earthworms were exposed to concentrations of 3.1, 6.3, 13, 25 and 50 mg/kg dry weight over 14 days. In the second phase, higher concentrations of 100, 300 and 500 mg/kg dry weight were tested. Test concentrations were maintained during the study.

The earthworms were monitored for signs of mortality and toxicity after 7 and 14 days exposure. In the first phase of the test, the mortality seen in the control and solvent control was 5% and 10% respectively after 14 days. In the second phase, the mortality seen in the control and solvent control was 10% and 12.5% (the test guideline indicates that mortality in controls should not exceed 10%). Mortalities in the treatment groups were comparable to those observed in the control groups and were not considered treatment related.

No significant treatment-related effects were observed in this study and the NOEC is determined to be >500 mg/kg dry weight.

8.4 Summary of environmental effects

While there is a distinct lack of data for avian toxicity, biomagnification in fish eating birds may occur particularly for the tetra- and penta-BDPE, which have been detected in fish as well as in fish eating birds.

Due to the very low solubility of the highly used PBDPEs, namely penta-and deca-BDPE, toxicity to aquatic organisms is difficult to determine. Acute toxicity in fish up to the limit of solubility has not been observed. Some chronic effects may occur, but these appear to be limited.

Aquatic invertebrates and algae appear susceptible to PBDPEs based on the limited data available, and PBDPEs may be considered highly toxic to these organisms. There is only one acute effect available for daphnia following exposure to commercial PeBDPE and evidence suggests the effect may have been physical rather than toxic, so conclusions are uncertain. Based on two test results, TBBPA can be described as moderately to highly toxic to aquatic invertebrates.

Sediment testing conducted as a result of the initial risk assessment conducted on PeBDPE in the EU demonstrated a lack of toxicity to three sediment dwelling organisms. Further sediment testing is currently underway in the EU on two other PBDPEs (octa- and deca-). No adverse biological effects resulted from the increased TBBPA body burden in a single sediment organism study.

Based on the commercial PeBDPE, PBDPEs are not toxic to soil micro-organisms, earthworms or plants.

Little data are available for HBCD. Based on limited results, it does not seem to be acutely toxic to fish and aquatic invertebrates and algae. However, the data are possibly unreliable with effects being observed at concentrations greatly exceeding the water solubility of this compound.

9. Discussion and Conclusions

9.1 Importation and uses

PBFRs are not manufactured in Australia, but a variety of flame retardant chemicals are imported either in pure solid form or as solid and/or liquid resin mixtures. Approximately 500 tonnes per annum PBFRs are imported into Australia. Data indicate that DBDPE and PeBDPE represent the majority of the imported flame retardants followed by HBCD and OBDPE. Approximately 57, 165 and around 120 tonnes per annum of OBDPE, DBDPE and PeBDPE, respectively, are imported. In addition, import volumes of approximately 60 tonnes per annum of HBCD are estimated, with a trend towards increasing use. In the future, these may be expected to comprise almost three quarters of PBFRs used. The rest of the notified PBFRs are imported in small volumes representing a minor proportion of all imports.

The overall quantities of PBFRs used are predicted to decrease in the future, however, information provided on future imports indicate increases in the volumes of OBDPE and PeBDPE. DBDPE will still be the highest imported chemical for use as a flame retardant.

Information on imported articles containing PBFRs is not available, but may be occurring. However, the absence of reliable data does not permit quantitative estimates.

PBFRs and resin mixtures containing these chemicals are used in the production of flame resistant articles and textiles for commercial and consumer market applications.

There are eight importers of these chemicals, some of whom supply a large number of customers with either the pure form or resin mixtures for down stream formulations and applications.

Regulations require flame retardancy for certain articles as an essential safety feature to protect human health and property.

9.2 Environment

PBDPEs, may be persistent in the environment and the introduction of these compounds into widespread products may provide a long-term and diffuse source of emissions and release into the environment. TBBPA's main use in epoxy resin circuit boards, where it is covalently reacted into the polymer backbone, will not serve as an environmental source of TBBPA.

As products containing PBFRs reach the end of their useful lives, landfill presents the only option for disposal, as incineration and recycling are not practised in Australia. Accordingly, landfill is the predominant means by which the environment is exposed to PBFRs. Potential for environmental exposure also exists as the chemicals leach out from the soil compartment, from maintenance and cleaning of end use flame-proofed products and from textiles as the chemical migrates to the surface (blooming effect) into aquatic systems.

Although PBFR release to the environment is expected to be slow and diffuse, the widespread, varied and significant quantities of PBFRs, particularly PBDPEs, used in Australia indicate that exposure to the wider environment may occur.

Generally, where released to the environment, PBFRs are expected to be stable, both microbially and abiotically. Others, such as TBBPA, have been found to partly or completely degrade (Ronen and Abeliovich, 2000), whereas limited potential for degradation has been indicated for HBCD. In land, they are expected to bind strongly to organic component of soils and be immobile. In water, the compounds are expected to partition to sediments and/or biota. Commercial PeBDPE is expected to bioaccumulate. Components of the PeBDPE commercial product may also have a tendency to volatilise to the atmosphere and may undergo long-range transport.

Highly brominated diphenyl ethers have low water solubilities and thus toxicity to aquatic organisms is difficult to assess. Based on limited ecotoxicity data, the PBDPEs appear to be highly toxic to some aquatic organisms. TBBPA has been reported to be moderately to highly toxic to aquatic invertebrates, but non-toxic to a single sediment dwelling organism. PeBDPE was non-toxic to three sediment dwelling organisms. Similarly, PBDPEs were shown to be non-toxic to soil micro-organisms, earthworms and plants. However, biomagnification in fish eating birds may occur, particularly for the medium brominated diphenyl ethers.

Further assessment of the PBDPEs in particular, with respect to their exposure in Australia is warranted, but should await the outcome of overseas testing efforts (see Section 9.6 below).

No further work is recommended on TBBPA for the environment. The use of this compound appears to be declining. Further, it is a reactive flame retardant and thus is chemically bound to the polymers into which it is incorporated. Accordingly, its potential for release into the wider environment is reduced.

9.3 Health hazards

Toxicity data available for the PBFRs assessed in this study are summarised at Table 7. It is apparent that for some PBFRs comprehensive data on toxicology is lacking. This hinders an in depth evaluation of their potential to affect the health of animals and humans adversely either directly or indirectly. Although the PBFRs share the same end use to confer resistance to flame on materials and share some health effects, significant differences exist in the overall toxicity of this group of chemicals.

The primary health concerns revolve around the potential of PBFRs to act as carcinogens, endocrine disruptors and neurodevelopmental toxicants based on data for some members of this class of chemicals. In addition, their structural similarities to the polychlorinated diphenyl ethers (PCDEs), nitrofen and polychlorinated biphenyls lends further support to concerns for health effects exerted by these chemicals.

Three PBFRs, the penta-, octa- and decaBDPEs, have been and remain of significant commercial interest. Nonetheless, the field of PBFRs is expanding and a diverse range of these chemicals are now available. Due to the diverse and complex nature of the PBFRs as a class, the most significant health effects shared by these chemicals are described here. Emphasis in this assessment is directed to

certain chemical compounds within this class, namely DBDPE, PeBDPE, OBDPE and HBCD, because they represent the bulk of PBFRs imported into Australia and because of the significance of some of the identified health effects associated with exposure to them. Also discussed are the PBBs and TDBPP, though no longer used, due to their significant adverse health effects.

The PBFRs are a structurally diverse group of chemical compounds, some of which share similarities in chemical structure while others vary significantly. Pharmacokinetic studies are limited for most of the chemicals reviewed in this report. However, the available information indicates that some brominated flame retardants such as TBDPE, HBCD, TDBPP and PBBs are readily absorbed via the gastrointestinal tract. Data available for the PBDPEs and PBBs indicate that the degree of gastrointestinal absorption is inversely proportional to the level of bromination. Dermal absorption has also been reported for TDBPP.

They are generally of low acute toxicity with no or slight and transient irritation to the skin and eyes of experimental animals. Inhalation studies in animals revealed that exposure to PBDPEs caused transient respiratory difficulties.

Like the PBDPEs, TBBPA and its derivatives have low acute and repeated dose toxicity. They are neither skin or eye irritants nor skin sensitisers in experimental animals. Reversible respiratory effects were reported following inhalation exposure.

With a few exceptions, mutagenicity studies indicate that the majority of the chemicals evaluated in this assessment are neither mutagenic to microbial or eukaryotic organisms nor genotoxic in experimental *in vivo* and *in vitro* systems. TBDPE and HBCD caused an increase in the recombination frequency in some cell lines.

Of the commercially and commonly used PBFRs, penta- and tetra-bromodiphenyl ethers appear to be of greatest significance where health effects are concerned. Evidence indicates that the liver, and possibly the thyroid, are the organs most sensitive to these chemicals. According to available data, they are endocrine disruptors and neurodevelopmental toxicants in experimental animals. Whether neurodevelopmental effects are a consequence of changes in thyroid hormone levels or are caused by direct neurotoxicity remain to be elucidated. The absence of clinical, physiological and biochemical correlates precludes any conclusions as to the nature of the mechanisms involved. PeBDPE has been classified as a hazardous chemical, Harmful- Danger of Serious Damage to Health by Prolonged Exposure in Contact with Skin and if Swallowed. A similar toxicity profile is apparent for TBDPE. OBDPE is another chemical of concern due to its adverse effects on reproduction in experimental animals.

The two other groups with significant adverse health effects are TDBPP and PBBs. Although both have relatively low acute toxicity in experimental animals, evidence for carcinogenicity, endocrine disruption and reproductive effects exists.

Little human data is available, however, epidemiological reports and follow up studies indicate that PBDPE, TDBPP and PBBs are absorbed and can be detected in the serum, adipose tissue and breast milk of directly and/or indirectly exposed individuals. The available evidence indicates that, in some countries, levels of these chemicals are increasing in animal and human tissues (including breast milk), which suggests they are bioaccumulative and persistent. Thyroid effects appear to

be the major adverse health effect, with hypothyroidism seen in animals (e.g. OBDPE and PeBDPE, HBCD and PBB) and humans (e.g. DBDPE and deca-BB), although some PBFRs (e.g. DBDPE, TDBPP, HBCD and PBB) elicit carcinogenic effects in animal studies.

9.4 Occupational health and safety

Although detailed information on the number of workers and duration of exposure were not collected for this preliminary assessment, analysis of information allows for some conclusions about worker exposure to be drawn.

The main routes of exposure to these chemicals are dermal and inhalation, the latter is of concern with the powder forms. Some ocular exposure is also expected, resulting from indirect contact with the solid powder or from dusts generated during handling of the solid. Dermal contact is the main route of exposure with the resin or emulsion solutions.

The risk of exposure of transport and storage workers is minimal and restricted to accidents. Workers in the formulation industry, that is those involved in the formulation of flame retarded resins, have the greatest risk of exposure since they weigh, transfer and mix the solid powder or liquid resins containing pure/concentrated PBFRs. Downstream fabricators who handle the formulated resins, emulsions and/or polymers are also expected to be exposed to the PBFRs. Dermal contact is the main route of exposure resulting from contact with these solutions. Given that the PBFRs are non-volatile, exposure by inhalation is expected to be minimal when handling liquid resins. However, potential for exposure by inhalation of dust generated while handling powder compounds is high. Some release of volatile, thermal degradation products of some PBFRs may occur during moulding of polymer at processing temperatures. The control of dust and potential aerosols through the use of local and exhaust ventilation and other engineering methods will reduce the risk of exposure and thus potential adverse health effects to workers. However, given the potentially hazardous nature of the commonly used PBFRs, namely DBDPE, OBDPE, PeBDPE and HBCD, the risk of adverse health effects to workers cannot be excluded.

PBFRs may diffuse from treated articles, a process generally referred to as blooming. The slow release of PBFRs from such materials is influenced by a number of factors (see Section 4.3). Flame retarded materials are likely to have significant use in private and/or commercial premises, and hence the possibility exists for exposure to workers in occupancy over extended time periods.

For example, occupational exposure to PBFRs from recycling activities was recently described in a number of studies. High levels of PBDPE have been detected in serum of workers at industrial plants for dismantling electronics (Sjodin et al., 1999). In the same study, office staff working full-time at computer screens had relatively high levels of some PBFRs in their blood serum, though they were significantly lower than the former group (Sjodin et al., 1999). Although the study indicates that computer work may be a potential source of exposure, further work is needed to confirm these findings. Monitoring studies on PBDPE concentrations in indoor and outdoor air have been carried out for a number of environments, which revealed significant levels in some settings (de Wit, 1999; Lindstrom, 1999). However, no Australian monitoring data are available. Accordingly, it is not possible to assess the potential for exposure and possible risks to workers.

One of the main concerns with PBFR treated materials is the emission of dioxins and furans, when such items are incinerated. Emission control technology is available for incinerators that can be used to reduce the amounts of these substances formed in the process to acceptable levels (OECD, 2000). Information collected for this assessment indicates that high temperature incineration is not practised in Australia and flame retarded articles are mostly disposed of to landfill. Exposure to thermal degradation products may occur from fires. As landfill fires and other fires are considered to be accidental, no such emission control technology exists for these (OECD, 2000). However, the risk of exposure to thermal degradation products is considered to be low.

The human health risk assessment conducted under the EU Risk Assessment process and the OECD/SIDS program for PeBDPE indicated the need for additional information. The author (UK) for PeBDPE, a final draft report which will be discussed in January 2001 by the OECD, proposes that information is needed on the extent of dermal exposure in workers together with quantitative data for dermal absorption. Also required are health surveillance data to investigate signs of chloracne in workers and information on the effects of prolonged (e.g. lifetime) exposure since this compound has the potential to accumulate in the body.

The draft EU Risk Assessment (yet to be discussed at the OECD) of DBDPE and OBDPE indicated a need for additional testing. For DBDPE, a teratology study was required and for OBDPE, a 90-day inhalation study was required. For HBCD, a 90-day oral study and an *in vivo* bone marrow micronucleus test were required. Industry has advised that these studies have now been completed and final reports are due later this year. Additional data on carcinogenic mechanisms and inhalation exposure in occupational settings were also requested.

9.5 Public health

There is no direct public use of PBFRs. Of the PBFRs, those with greatest toxic concerns are PBBs and TDBPP. However, PBBs and TDBPP (and their flame retardant resins) are not imported into Australia. Consequently, public exposure will only arise from imported plastics containing PBBs or TDBPP as flame retardants.

TBBPA is of low toxicity generally, although there are data gaps for chronic toxicity and carcinogenicity, therefore the toxic hazard to the public from TBBPA exposure is considered to be minimal. HBCD is of low acute toxicity, with no data on chronic toxicity. PBDPEs are of low acute toxicity, and are generally not genotoxic. There was equivocal evidence of carcinogenicity for DBDPE in chronic studies in rats and mice at 25-50 g/kg in the diet, and it is non-genotoxic. There is little chronic/carcinogenicity data for other PBDPEs. There is one report of association between 2,2',4,4'-TBDPE adipose levels and non-Hodgkin's lymphoma (Hardell et al., 1998). As there is little or no exposure data (none under Australian conditions), the risks associated with PBDPE products and HBCD exposure are difficult to estimate.

The OECD/SIDS draft report (OECD, 1999) indicated that to conduct an in depth health risk assessment for consumer exposure to HBCD, additional information and testing on reproductive toxicity, mutagenicity and carcinogenicity of HBCD is needed.

A recent study assessing the health risks from the use of flame retardants used in upholstery textiles (National Academy Press, 2000) concluded that DBDPE and HBCD, despite the lack of complete toxicological information, can be used on residential furniture with minimal risk to health. This decision was arrived at following in-depth analysis and taking into consideration worst-case exposure scenarios. However, a range of PBFRs may be present in consumer articles, and overall, further work in this area is indicated.

9.6 Further assessment

As a member country, Australia is involved in the OECD/SIDS discussion forums and contributes to the assessment process. Information collected on these chemicals, their toxicity profiles and the outcomes of the human health hazard assessment are of importance to the assessment of PBDPEs in the Australian context. In considering whether and when a full (risk) assessment should be conducted in Australia, it is relevant to consider which chemicals are in actual use, which are undergoing further testing or require further data and whether concerns are such that the chemicals are restricted elsewhere. Table 8 provides a summary of this information for the PBFRs in use in Australia. Consequently, conclusions on the need for full (risk) assessment for environmental, occupational health and safety and public health are as follows:

- There has been sufficient information on TDBPP and PBBs for a number of countries to ban these substances and for their inclusion under the PIC Procedure. The PIC process is an international treaty known as the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (see Section 2.1 International perspective). Although a signatory to the Rotterdam convention, Australia is yet to make a decision on ratification. If the Australian government were to ratify the Convention, national legislation may be formalised not to import these chemicals. These chemicals are not currently imported or manufactured in Australia. Should Australia ratify the PIC Treaty, there is considered to be sufficient information for Australia to consider prohibitions of these substances to ensure import/manufacture do not resume in future.
- DBDPE, OBDPE, PeBDPE and HBCD are undergoing testing and assessment within the EU under the Existing Chemicals Regulation and within the OECD SIDS Program, in which Australia participates. These flame retardants currently make up the bulk of PBFRs imported into Australia. This PEC exposure assessment will enable consideration of the OECD agreed hazard assessments in the Australian context, as soon as they are available. Where there are concerns, further work to enable any necessary risk management recommendations can then occur. In addition, a similar assessment of TBBPA within the EU Risk Assessment program will be initiated in 2001. The UK is the lead country performing the assessment.

- Additional hazard (health and environment) and exposure (monitoring) data are required to enable further assessment of the remaining PBFRs used in Australia. International efforts in facilitating industry generation of these data will be key to these data becoming available. It is essential to ensure that any prohibitions/restrictions arising from testing on widely used PBFRs do not lead to replacement with PBFRs of unknown toxicity. NICNAS will continue to monitor the import and use of these substances, with a view to recommending further work where indicated.

9.7 Data gaps

Given the concerns regarding toxicity of some PBFRs and the lack of data on most PBFRs, industry must continue its efforts in testing these substances. Sufficient hazard data have been available on TDBPP and PBBs for regulatory decision-making. DBDPE, OBDPE, PeBDPE and HBCD have agreed test plans for further testing under the OECD SIDS program. A similar plan will be developed soon for TBBPA under the EU Risk Assessment program. Given concerns for repeat dose toxicity, there is insufficient information for assessment, and no known plans to generate such information, for the other PBFRs. However, as data become available it may be possible to exclude some chemicals from test plans on the basis of available information on closely related chemicals.

It is not known whether there are any common mechanisms of toxicity for chemicals within the PBFRs group, therefore any effects may be additive.

Additional subchronic and long term studies examining end points involving pharmacokinetic, carcinogenicity, thyroid function, neurodevelopmental, and reproductive effects are needed. More importantly, biological assays and epidemiological follow up studies that monitor the levels of PBFRs in animal and human tissues and identify toxicological correlates are essential. The available evidence reveals increasing levels of some PBFRs in human and animal tissue, which suggests they may be bioaccumulative and persistent.

Of equal importance, is information on emissions and releases of PBFRs from articles under variable conditions and environments. Such details are essential and will be required to conduct a full (risk) assessment.

Also needed for a full (risk) assessment is a complete list of articles/products containing PBFRs, their PBFR content, details of the method of PBFR incorporation into articles, the use of the articles/products and their availability in the public domain.

Table 7 - Summary of toxicity data for PBFRs.

PBFRs	Acute	Irritation	Sensitisation	Repeated exposure	Reproduction	Genotoxicity	Carcinogenicity
DBDPE	Low- oral, dermal animals	No/slight- skin, eye animals	No- skin human	28-days 90-days 2-years	No effects on reproduction Not teratogenic	Negative	Animals: Equivocal evidence (IARC- 3)
OBDPE	Low- oral, dermal animals	No- skin, eye animals	No- skin human	28-days 90-days	Toxic (SIDS-repeat inhalation needed) Not teratogenic	Negative	No data
HBDPE	No data	No data	No data	No data	No data	No data	No data
PeBDPE	Low- oral, dermal animals	No/slight- skin Slight- eye animals	No- skin animals	28-days 30-days 90-days	Not Toxic	Negative	No data
TBDPE	No data	No data	No data	No data	No data	Induces recombination in SPD8 cell line	No data; Correlation with Non-Hodgkin's Lymphoma (human, epidemiology)
NBDPE	No data	No data	No data	No data	No data	No data	No data
TrBDPE	No data	No data	No data	No data	No data	No data	No data
TBBPA	Low- oral, dermal animals	No- skin, eye animals	No human, animals	28-days 90-days	Not teratogenic Animals	No data	No data

Table 7 - Summary of toxicity data for PBFRs (contd).

PBFRs	Acute	Irritation	Sensitisation	Repeated exposure	Reproduction	Genotoxicity	Carcinogenicity
TBBPA-bis2,3-dibromopropyl ether	Low (oral, dermal)	No data	No data	90-days	No data	Negative	No data
Polymer of TBBPA, phosgene, phenol	Low- oral, dermal Animals	No- skin, eye animals	No data	No data	No data	Negative	No data
2,4,6-Tribromophenyl terminated TBBPA carbonate oligomer	Low- oral, dermal animals	No- skin, eye animals	No data	No data	No data	Negative	No data
HBCD	Low- oral, dermal animals	No- skin No/slight- eye animals	Equivocal animals	28-days 90-days 18-months	Insufficient data; SIDS testing underway	Induces recombination in Sp5 and SPD8 cell lines	No Insufficient evidence
TDBPP	Low- oral, dermal animals	No- skin, eye animals	No- skin animals Yes- skin human	28-days 90-days 2-years	Affects reproductive system; Not teratogenic Animals	Positive	Yes (IARC- 2A) (NTP- R)*
BDBPP	No data	No data	No data	45-days	No data	Positive	Yes. Insufficient evidence in animals

* Reasonably Anticipated to be a Human Carcinogen

Table 7 - Summary of toxicity data for PBFRs (contd).

PBFRs	Acute	Irritation	Sensitisation	Repeated exposure	Reproduction	Genotoxicity	Carcinogenicity
Tris (Tribromoneopentyl) phosphate	Low- oral, dermal Animals	No– skin Slight- eye animals	No animals	28-days 90-days	No data	Negative	No data
Brominated polystyrene	Low- oral, dermal animals	No/slight- skin Slight/moderate- eye animals	Equivocal animals	14-days 21-days 28-days	No data	Negative	No data
1,2-Bis(2,4,6-tribromophenoxy)ethane	Low- oral, dermal animals	No data	No data	14-days	No effects (Insufficient, 1 study)	Negative	No data
Hytrel polyester Elastomer; 1H-Isoindole-1,3(2H)-dione, 2,2'-(1,2-ethanediyl)bis[4,5,6,7-tetrabromo-	Low- oral, dermal animals	Yes- skin No- eye animals	No data	28-days 90-days	Not foetotoxic Not teratogenic	Negative	No data
Disodium tetrabromophthalate	Low-oral Animals	No data	No data	No data	No data	No data	No data
Phosphoric acid, mixed 3-bromo-2,2, dimethylpropyl and 2-bromoethyl and 2-chloroethyl esters	No data	No data	No data	No data	Toxic (1 study)	No data	No data

Table 7 - Summary of toxicity data for PBFRs (contd).

PBFRs	Acute	Irritation	Sensitisation	Repeated exposure	Reproduction	Genotoxicity	Carcinogenicity
PBBs	Relatively low-oral, dermal	Slight- skin, eye Hyperkeratosis etc. animals; human	No- skin, respiratory animals	Variable 14-days 28-days 90-days 2-years	Yes animal studies	Negative	Yes; Sufficient animal data IARC (2B)
Tetradecabromo (p-diphenoxybenzene)	No data	No data	No data	No data	No data	No data	No data
2-propenoic acid (pentabromophenyl) methyl ester, homopolymer	Low (Oral)	No-skin Slight-eye animals	No-skin animals	No data	No data	Negative-Ames, E. Coli	No data
Bis(2,4,6-tribromophenyl) carbonate	No data	No data	No data	No data	No data	No data	No data
3,4,5,6-Tetrabromophthalic anhydride, ethylene glycol, propylene oxide reaction products	No data	No data	No data	No data	No data	No data	No data
TBBPA-bis 2,3-dibromopropyl ether	Low (oral, dermal)	No-skin; Slight-eye animals	No-skin animals	90-days	No data	Positive-Ames test*	No data
TBBPA-2,2-bis[4-(2,3-epoxypropyloxy)dibromophenyl] propane polymer	No data	No data	No data	No data	No data	No data	No data

* may be due to impurities – Ames test to be repeated (DSBG 2001).

Table 8 - PBFRs used in Australia and regulatory information (contd).

PBFRs*	CAS No	AICS	Import-$ Pure	Import-$ formulation	Undergoing further testing#	Restrictions¥
2,4,6-Tribromophenyl terminated TBBPA carbonate oligomer	71342-77-3	√	-	√	No information	No known restrictions
HBCD	25637-99-4	√	√	√	OECD-SIAR Preliminary discussion; US EPA/OPPT MTL	No known restrictions
TDBPP	126-72-7	√	-	-	No information	Banned in USA; Banned in EU; PIC-listed chemical No restrictions in Australia
BDBPP	5412-25-9	√	-	-	No information	No known restrictions
Tris (Tribromoneopentyl) phosphate	19186-97-1	NC	√	-	No information	No known restrictions
Polystyrene, brominated	88497-56-7	√	√	√	No information	No known restrictions
1,2-Bis(2,4,6-tribromophenoxy)ethane	37853-59-1	√	√	-	US EPA/OPPT MTL	No known restrictions
Hytrel polyester Elastomer; 1H-Isoindole-1,3(2H)-dione, 2,2'-(1,2-ethanediyl)bis[4,5,6,7-tetrabromo-	32588-76-4	√	-	√	No information	No known restrictions
Disodium tetrabromophthalate	25357-79-3	√	√	-	No information	No known restrictions
Phosphoric acid, mixed 3-bromo-2,2, dimethylpropyl and 2-bromoethyl and 2-chloroethyl esters	125997-20-8	√	-	√	No information	No known restrictions

10. Recommendations

Recommendation 1: Further assessment

A full (risk) assessment to assess occupational, public and environmental exposure and consequently risks to human health and environment will be considered when testing of PBFRs is completed under the OECD Program. Selection of PBFRs for a full assessment will depend on the outcomes of the testing and the chemicals in use in Australia.

A full risk assessment would also need to balance consideration of any adverse effects of these chemicals against the need for fire retardancy for certain articles and use situations to protect human heath and property.

Recommendation 2: Hazard classification

PeBDPE has been determined to be hazardous and is classified in the EU as R 48/21/22 - Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed; R64 - may cause harm to breast fed babies; R50/53 - very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. It is recommended that this classification be included in the *NOHSC List of Designated Hazardous Substances* as soon as possible.

It is recommended that NOHSC adopt classifications for the other PBFRs currently undergoing testing, as soon as the EU classifications are available.

TDBPP and PBBs do not require classification while they are not imported or manufactured in Australia.

Recommendation 3: Selection of PBFRs by industry

It is recommended that industry carefully consider the selection of PBFR compounds for use, to ensure that those known to be hazardous are avoided, and that PBFRs of unknown hazard are not introduced. TBBPA is generally of low toxicity, however lacks data on chronic effects and carcinogenicity. Although no PBFR has a complete data set, chemicals where adverse effects have been reported are less preferred than where testing has occurred and effects are not observed. Table 7 summarises the available toxicology data. In considering reported effects, no PBFR has acute toxicity that would warrant discrimination. In addition, irritant and sensitising effects reported for some are of lesser importance than any chronic, reproductive or carcinogenic effects. Chronic, reproductive and carcinogenic effects should be given most weight. TDBPP and the PBBs are not currently used in Australia and the adverse health effects data available do not support their re-introduction. It is recommended that relevant companies ensure they are aware of current findings arising from the work of the industry OECD Voluntary Industry Commitment.

Recommendation 4: Hazard communication and Workplace Controls

It is recommended that manufacturers and suppliers update their MSDS, labels and training materials to reflect the information in this report, paying particular attention to the health effects information for specific PBFRs and the recently adopted EU classification for PeDBPE. It is recommended that this be followed up by OHS jurisdictions. Industry needs to comply with the requirements of the Workplace Hazardous Substances Regulations, including implementing control measures, based on the NOHSC hierarchy of controls, to minimise exposure during use of PBFRs.

11. Secondary Notification

Under Section 65 of the *Industrial Chemicals (Notification and Assessment) Act 1989*, secondary notification of the PBFRs is required where a person becomes aware of any circumstances that may warrant a reassessment of its hazards and risks. Specific circumstances include:

- manufacture of PBFRs has begun in Australia;
- significant new information about the adverse health or environmental effects become available;
- the use of PBFRs has increased, or is likely to increase significantly.
- PBB and TDBPP are imported or manufactured in Australia.

The Director must be notified within 28 days of the introducer becoming aware of any of the above or other circumstances prescribed under Section 65 of the Act.

Appendix A: Chemical Identity, Composition and Physical and Chemical Properties

A.1 Tetrabromobisphenol A

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-].

Registry numbers

CAS number	79-94-7
EINECS number	201-236-9
ENCS number	4-205
ECL Serial number	KE-23971

Other names

2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol

2,2-Bis(4'-hydroxy-3',5'-dibromophenyl) propane

4,4'-(1-Methylethylidene)bis[2,6-dibromophenol]

2,2',6,6'-Tetrabromobisphenol A

2,2-Bis(3,5-dibromo-4-hydroxyphenyl) propane

2,2-Bis(4-hydroxy-3,5-dibromophenyl) propane

3,3',5'5'-Tetrabromobisphenol A

3,5,3',5'-Tetrabromobisphenol A

4,4'-(1-Methylethylidene)bis[2,6-dibromophenol]

4,4'-Isopropylidenebis(2,6-dibromophenol)

Phenol, 4,4'-isopropylidenebis(2,6-dibromo-)

Tetrabromodian

TBBPA

Tetrabromodiphenylolpropane

Trade names

Derakane

Molecular formula

$C_{15}H_{12}Br_4O_2$

Structural formula

$C_{15}H_{12}Br_4O_2$

Molecular Weight

544

Physical properties

Appearance:	White crystalline powder with slight odour
Melting point:	181-182°C
Boiling point:	316°C (decomposes)
Vapour pressure:	<1.3 hPa at 20°C
Relative density:	2.17
Solubility in water:	<0.08 mg/L (BSEF, 2000)
Soluble in:	acetone 240 g/100g at 25°C, methanol 92g/100g at 25°C
log K_{ow}:	4.54

A.2 Tris (2,3-dibromopropyl) phosphate

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as 1-propanol, 2,3-dibromo-phosphate (3:1).

Registry numbers

CAS number	126-72-7
EINECS number	204-799-9
ENCS number	2-1955/2-2188
ECL Serial number	KE-34800

Other names

Tris(2,3-dibromopropyl) phosphate

Trade names

Numerous

Molecular formula

$C_9H_{15}Br_6O_4P$

Structural formula

$(BrCH_2CHBrCH_2O)_3P=O$

Molecular weight

694

Physical properties

This substance is not described in the research literature and since it has long been withdrawn from sale the physical and chemical data relating to it are unavailable from industrial databases.

Melting point:	The viscous liquid is reported to crystallise at low temperatures
Boiling point:	Decomposes above 200°C
Flash point:	>112°C
Relative density:	2.24
Viscosity:	9,500 centipoise at 27°C

A.3 Bis (2,3-dibromopropyl) phosphate

Chemical name

This substance is a new chemical that was recently notified to NICNAS. It is not yet listed on the Australian Inventory of Chemical Substances.

Registry numbers

CAS number	5412-25-9
EINECS number	226-493-4
ENCS number	2-1987X (class/category 2-1987)

Other names

1-Propanol, 2,3-dibromo-, hydrogen phosphate

Bis(2,3-dibromopropyl) hydrogen phosphate

Trade names

No trade names are listed for this substance.

Molecular formula

$C_6H_{11}Br_4O_4P$

Structural formula

$(BrCH_2CHBrCH_2O)_2P(=O)OH$

Molecular weight

498

Physical properties

No data available for this substance.

A.4 Tetradecabromo (p-diphenoxybenzene)

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as benzene, 1,2,4,5-tetrabromo-3,3-bis(pentabromophenoxy)-.

Registry numbers

CAS number	58965-66-5
EINECS number	261-526-6
ENCS number	3-4206

Other names

1,2,4,5,-Tetrabromo-3,6-bis(pentabromophenoxy) benzene

Perbromo(1,4-diphenoxybenzene)

1,4-Bis(pentabromophenoxy) tetrabromobenzene

Perbromo-1,4-diphenoxybenzene

Trade names

BT 120

BT 120 (fireproofing agent)

Saytex 120

Molecular formula

$C_{18}Br_{14}O_2$

Structural formula

C_6Br_5-O-C-C_6Br_4-O-C_6Br_5

Molecular weight

1368

Physical properties

No source of chemical or physical data for this substance could be located.

A.5 Decabromodiphenyl ether

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as benzene, 1,1'-oxybis(2,3,4,5,6-pentabromo)-.

Registry numbers

CAS number	1163-19-5
EINECS number	214-604-9
ENCS number	3-2846
ECL Serial number	KE-27715

Other names

Bis(pentabromophenyl) ether

Decabromodiphenyl ether

1,1'-Oxybis(2,3,4,5,6-pentabromobenzene)

2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether

Decabromobiphenyl ether

Decabromobiphenyl oxide

Decabromodiphenyl ether

Decabromodiphenyl oxide

Decabromophenyl ether

Ether, bis(pentabromophenyl)

Pentabromophenyl ether

Trade names

Numerous

Molecular formula

$C_{12}Br_{10}O$

Structural formula

C_6Br_5-O-C_6Br_5

Molecular weight

960

Technical mixtures

Commercial DBDPE product is reported to comprise : ≥97% DBDPE, ~3% NBDPE and < 1% OBDPE.

Physical properties

Appearance:	White odourless powder,
Melting/softening:	300^{o}C approx.
Vapour pressure:	4.63x10^{-6} Pa at 20^{o}C
Specific gravity:	3.3
Solubility in water:	<0.1 ug/L
log K_{ow}:	6.265

A.6 Nonabromodiphenyl ether

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as benzene, pentabromo(tetrabromophenoxy)-.

Registry numbers

CAS number	63936-56-1
EINECS number	264-565-7
ENCS number	3-3716X (class/category 3-3716)

Other names

Pentabromo(tetrabromophenoxy) benzene

Nonabromodiphenyl oxide

Nonabromobiphenyl oxide

Nonabromodiphenyl ether

Nonabromophenoxybenzene

Trade names

No trade names are listed for this substance, which is not itself a commercial product but is a component of mixtures with other bromodiphenyl oxide designations.

Molecular formula

$C_{12}HBr_9O$

Structural formula

C_6Br_5-O-C_6HBr_4. Three structural isomers are possible, with the lone hydrogen in position 2,3 or 4 of the less-substituted benzene ring. These isomers are not differentiated in the specifications of this substance.

Molecular weight

881

Physical properties

This substance has not been separately characterised.

A.7 Octabromodiphenyl ether

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as benzene, 1,1'-oxybis-, octabromo derivate.

Registry numbers

CAS number	32536-52-0
EINECS number	251-087-9
ENCS number	3-3716X (class/category 3-3716)
ECL Serial number	KE-26268

Other names

Diphenyl ether, octabromo derivative

Octabromodiphenyl oxide

Octabromobiphenyl oxide

Octabromodiphenyl ether

Phenyl ether, octabromo derivative

Trade names

Bromkal 79-8DE

CD 79

DE 79

EB 8

FR 1208

FR 143

Tardex 80

Molecular formula

$C_{12}H_2Br_8O$

Structural formula

$C_6H_nBr_{5-n}$-O-$C_6H_{2-n}Br_{3+n}$

Molecular weight

802

Technical mixtures

The OBDPE commercial product is composed of brominated diphenyl ether congeners ranging from hexa- to nona- with minor amounts (<0.1%) of deca- BDPE.

Physical properties

Appearance:	white to light yellow, odourless powder
Melting point:	85-89^{o}C
Vapour pressure:	$6.59x10^{-6}$ Pa
Relative density:	2.8
Water solubility:	<1 µg/L at 25^{o}C
Soluble in:	benzene, 20g/100g at 25^{o}C
log K_{ow}:	6.29

A.8 Hexabromodiphenyl ether

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as benzene, 1,1'-oxybis-, hexabromo derivative.

Registry numbers

CAS number	36483-60-0
EINECS number	253-058-6
ENCS number	3-2845
ECL Serial number	KE-27677

Other names

Diphenyl ether, hexabromo derivative

Hexabromodiphenyl ether

1,1'-Oxybisbenzene hexabromo derivative

Hexabromodiphenyl ether

Hexabromodiphenyl oxide

Hexabromophenoxybenzene

Trade names

BR 33N

HR 60P

Molecular formula

$C_{12}H_4Br_6O$

Structural formula

$C_6H_nBr_{5-n}$-O-$C_6H_{4-n}Br_{1+n}$

Molecular weight

644

Technical mixtures

HBDPE is not produced as an individual flame retardant. HBDPE congeners are reported components of the commercial OBDPE and PeBDPE products.

Physical properties

No data available.

A.9 Pentabromodiphenyl ether

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as benzene, 1,1'-oxybis-, pentabromo derivative.

Registry numbers

CAS number	32534-81-9
EINECS number	251-084-2
ECL Serial number	KE-27858

Other names

Diphenyl ether, pentabromo derivative

Pentabromodiphenyl oxide

Pentabromodiphenyl ether

Pentabromophenoxybenzene

Trade names

Bromkal G 1

DE 60FTM

Planelon PB 501

Saytex 125

Molecular formula

$C_{12}H_5Br_5O$

Structural formula

$C_6H_nBr_{5-n}$-O-$C_6H_{5-n}Br_n$

Molecular weight

565

Technical mixtures

A great many isomers of 'pentabromodiphenyl ether' are theoretically possible and these have not been characterised individually. The composition of commercial PeBDPE has been reported as a mixture of penta- (~55%), tetra- (~30%), hexa- (~10%) and tri (<5%) BDPE congeners. 2,2',4,4',5-PeBDPE and 2,2',4,4'-TBDPE are the predominant isomers in the commercial PeBDPE product.

Physical properties

Relative density:	2.3 at 25^{o}C
Vapour pressure:	4.69x10^{-5} Pa
Water solubility:	13.3 μg/L at 25^{o}C
Soluble in:	toluene, dichloromethane, methyl ethyl ketone
log K_{ow}:	6.58

A.10 Tetrabromodiphenyl ether

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as benzene, 1,1'-oxybis-, tetrabromo derivative.

Registry numbers

CAS number	40088-47-9
EINECS number	254-787-2
ENCS number	3-61X (class/category 3-61)
ECL Serial number	KE-27680

Other names

Diphenyl ether, tetrabromo derivative

1,1'-Oxybisbenzene tetrabromo derivative

Tetrabromobiphenyl ether

Tetrabromodiphenyl ether

Tetrabromodiphenyl oxide

Trade names

Pyrogard SR 900

SR 900

Molecular formula

$C_{12}H_6Br_4O$

Structural formula

$C_6H_nBr_{4-n}$-O-$C_6H_{6-n}Br_n$

Molecular weight

486

Technical mixtures

A great many isomers of 'tetrabromodiphenyl ether' are theoretically possible and these have not been characterised individually. TBDPE is not produced as an individual flame retardant. TBDPE congeners are components of the commercial PeBDPE product. The 2,2',4,4'-TBDPE isomer is the predominant TBDPE isomer in the commercial PeBDPE product.

Physical properties

Water solubility: <0.011 mg/L at 25^{o}C

No other physical or chemical data were available for this substance, which is present as a component of commercial mixtures.

A.11 Tribromodiphenyl ether

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as benzene, 1,1'-oxybis-, tribromo derivative.

Registry numbers

CAS number 49690-94-0

EINECS number	256-431-1
ENCS number	3-61X (class/category 3-61)
ECL Serial number	KE-27682

Other names

Diphenyl ether, tribromo derivative

1,1-Oxybisbenzene tribromo derivative

Tribromodiphenyl ether

Trade names

No trade names are known for this substance, which is normally only found as a component of mixtures prepared by varying degrees of bromination of diphenyl ether.

Molecular formula

$C_{12}H_7Br_3O$

Structural formula

$C_6H_nBr_{3-n}$-O-$C_6H_{7-n}Br_n$

Molecular weight

407

Technical mixtures

A number of 'tribromodiphenyl ether' isomers are theoretically possible and these have not been characterised individually. TrBDPE is not produced as an individual flame retardant, but is reported to be present at < 5% in the commercial PeBDPE product.

Physical properties

No physical or chemical data are available for this substance, which is present as a component of commercial mixtures.

A.12 2-Propenoic acid (pentabromophenylmethyl) ester, homopolymer

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as 2-propenoic acid, (pentabromophenyl)methyl ester, homopolymer.

Registry numbers

CAS number	59447-57-3

ENCS number 6-1671

ECL Serial number KE-28933

Other names

Poly(2,3,4,5,6-pentabromobenzyl acrylate)

Polymer of 2,3,4,5,6-pentabromobenzyl acrylate

Pentabromobenzyl acrylate homopolymer

Poly(pentabromobenzyl acrylate)

Trade names

Ameribrom FR 1025

FR 1025

FR 1025P

PBB-PA

Molecular formula

$(C_{10}H_5Br_5O_2)_x$

Structural formula

The single component of this polymer is the monomeric ester, $C_{10}H_5Br_5O_2$, ($C_6Br_5CH_2O$-CO-CH=CH_2),CAS number 59447-55-1

Molecular weight

~ 80,000 daltons

Physical properties

Appearance:	White odourless powder
Melting point:	190-220^{o}C
Vapour pressure:	<10 Pa at 20^{o}C
Relative density:	2.05
Solubility in water:	3.5-3.8 mg/L at 20^{o}C

A.13 Polystyrene, brominated

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as benzene, ethenyl-, homopolymer, brominated.

Registry numbers

CAS number	88497-56-7
EINEC number	P 79-11
ENCS number	6-1579
ECL Serial number	KE-03604

Other names

Polystyrene, brominated

Brominated ethenylbenzene homopolymer

Trade names

PDBS 80

Molecular formula

$(C_8H_{8-n}Br_n)_x$

Structural formula

Unspecified.

Molecular weight

80,000 – 800,000 daltons.

Related substances

The substance with CAS No. 88497-57-3 is a generic 'brominated polystyrene' category, which may include the products of bromination of pre-formed polystyrene as well as a range of polymers produced from brominated styrene monomers. There are also specific CAS numbers for several such polymers, for example that from dibromostyrene has CAS No. 148993-99-1, and that from a related tribromostyrene has CAS No. 57137-10-7 (marketed as Pyrocheck 68).

Physical properties

No physical or chemical data available. The substance is imported only as a component of resins.

A.14 TBBPA bis (2,3-dibromopropyl) ether

Chemical name

Benzene, 1,1'-(1-methylethylidene)bis[3,5-dibromo-4-(2,3-dibromopropoxy)-.

Registry numbers

CAS number	21850-44-2

EINECS number	244-617-5
ENCS number	4-212
ECL Serial number	KE-23970

Other names

1,1'-(Isopropylidene)bis[3,5-dibromo-4-(2,3-dibromopropoxy)benzene

2,2-Bis[4-(2,3-dibromopropoxy)-3,5-dibromophenyl]propane

1,1'-(1-Methylethylidene)bis[3,5-dibromo-4-(2,3-dibromopropoxy)-benzene]

2,2-Bis[3,5-dibromo-4(2,3-dibromopropoxy)phenyl]propane

2,2-Bis[3,5-dibromo-4-(2,3-dibromopropyloxy)phenyl]propane

3,3',5,5'-TetrabromobisphenolA bis92,3-dibromopropyl) ether

4,4'-Isopropylidenebis[2,6-dibromo-1-(2,3-dibromopropoxy)benzene]

Bis(2,3-dibromopropoxy)tetrabromobisphenol A

Propane, 2,2-bis[3,5-dibromo-4-(2,3-dibromopropoxy)phenyl]-

Tetrabromobisphenol A 2,3-dibromopropyl ether

Tetrabromobisphenol A bis(2,3-dibromopropyl ether)

Tetrabromobisphenol A bis(2,3-dibromopropyl) ether

Trade names

FR 720

Molecular formula

$C_{21}H_{20}Br_8O_2$

Structural formula

$BrCH_2CHBrCH_2O\text{-}C_6H_2Br_2\text{-}C(CH_3)_2\text{-}C_6H_2Br_2\text{-}OCH_2CHBrCH_2Br$

Molecular weight

944

Physical properties

Appearance:	white crystalline powder with characteristic odour
Melting point:	114^oC
Vapour pressure:	Not available
Relative density:	2.3
Water solubility:	<0.1 g/100 mL at 25^oC

Soluble in:	toluene, dichloromethane
log K_{ow}:	not provided

A.15 Bis(2,4,6-tribromophenyl) carbonate

Chemical name

This substance is listed in the Australian Inventory of Chemical Substances as phenol, 2,4,6-tribromo-, carbonate (2:1).

Registry numbers

CAS number	67990-32-3
EINECS number	268-053-4

Other names

Bis(2,4,6-tribromophenyl) carbonate

Trade names

No trade names are recorded for his substance. It occurs as an impurity in a tribromophenol-terminated oligomer (see Section 4.2.12) below.

Molecular formula

$C_{13}H_4Br_6O_3$

Structural formula

$(C_6H_2Br_3O)_2C=O$

Molecular weight

688

Physical properties

No separate physical or chemical data are available for this substance, which is present as an impurity in other products such as the tribromophenyl terminated oligomer (CAS No. 71342-77-3) described below in Section 5.2.12.

A.16 1,2-Bis(2,4,6-tribromophenoxy) ethane

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as benzene, 1,1'-[1,2-ethanediylbis(oxy)]bis[2,4,6-tribromo]-.

Registry numbers

CAS number	37853-59-1
EINECS number	253-692-3
ENCS number	3-3461
ECL Serial number	KE-13205

Other names

1,1'-(Ethane-1,2-diylbisoxy)bis(2,4,6-tribromobenzene)

1,2-Bis(2,4,6-tribromophenoxy)ethane

1,1'-[1,2-Ethanediylbis(oxy)]bis[2,4,6-tribromobenzene]

Bis(2,4,6-tribromophenoxy)ethane

Bis-1,2-(2,4,6-tribromophenoxy)ethane

Trade names

FF680

FireMaster 680

FireMaster FF 680

Molecular formula

$C_{14}H_8Br_6O_2$

Structural formula

$C_6H_2Br_3O\text{-}CH_2CH_2\text{-}OC_6H_2Br_3$

Molecular weight

688

Physical properties

Appearance:	White crystalline powder with slight characteristic odour
Melting point:	224^oC
Vapour pressure:	Not available
Relative density:	2.6
Water solubility:	<0.1 g/100 mL

A.17 Disodium tetrabromophthalate

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as disodium tetrabromophthalate.

Registry numbers

CAS number	25357-79-3
EINECS number	246-890-6
ENCS number	3-3840

Other names

1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, disodium salt

Phthalic acid, tetrabromo-, sodium salt

Tetrabromophthalic acid, sodium salt

Trade names

FR 756

Molecular formula

$C_8Br_4O_4Na_2$

Structural formula

$C_8H_2Br_4O_4.2Na$

Molecular weight

526

Physical properties

Solution pH value:	6-6.5
Melting point:	>500^{o}C
Vapour pressure:	N.A.
Relative density:	2.8
Water solubility:	21 g/100 mL at 25^{o}C

A.18 1H-Isoindole-1,3(2H)-dione, 2,2'-(1,2-ethanediyl)bis[4,5,6,7-tetrabromo]

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as 1H-isoindole-1,3-(2H)-dione, 2,2'-(1,2-ethanediyl)bis [4,5,6,7-tetrabromo]-.

Registry numbers

CAS number	32588-76-4
EINECS number	251-118-6

ENCS number 5-5550

ECL Serial number KE-13207

Other names

1*H*-Isoindole-1,3(2*H*)-dione,2,2'-(1,2-ethanediyl)bis[4,5,6,7-tetrabromo]-

N,N'-Ethylenebis(3,4,5,6-tetrabromophthalimide)

N,N'-Ethylenebis[3,4,5,6-tetrabromophthalimide]

2,2'-(1,2-Ethanediyl)bis[4,5,6,7-tetrabromo-1H-isoindole-1,3(2H) dione

1,2-Bis(tetrabromophthalimido)ethane

3,3',4,4',5,5',6,6'-Octabromo-*N,N'*-ethylenediphthalimide

Ethylene bis(tetrabromophthalimide)

Phthalimide, *N,N'*-ethylenebis[tetrabromo]-

Trade names

BT 93

BT 93W

Citex BT 93

Saytex BT 93

Saytex BT 93W

Molecular formula

$C_{18}H_4Br_8N_2O_4$

Structural formula

$C_{18}H_4Br_8N_2O_4$

Molecular weight

952

Physical properties

No physical or chemical data available. The substance is imported only as a component of resins.

A.19 Hexabromocyclododecane

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as cyclododecane, hexabromo.

Registry numbers

CAS number	25637-99-4
EINECS number	247-148-4
ENCS number	3-2254X (class/category 3-2254)
ECL Serial number	KE-18397

Other names

Hexabromocyclododecane

Trade names

Numerous

Molecular formula

$C_{12}H_{18}Br_6$

Structural formula

$C_{12}H_{18}Br_6$

Molecular weight

642

Related substances

The CAS No. 3194-55-6 refers to a specific isomer, 1,2,5,6,9,10-hexabromocyclododecane, whereas CAS No. 25637-99-4 represents the generic class of hexabromocyclododecanes. Manufacturers are changing their information sheets to reflect a change from the generic to the specific product.

Physical properties

Appearance:	off-white powder with slight characteristic odour	
Melting point:	190°C	
Vapour pressure:	6.27×10^{-5} Pa at 20°C	
Relative density:	2.2	
Water solubility:	3.4 µg/L	at 25°C
log K_{ow}:	5.625	

A.20 3,4,5,6-Tetrabromophthalic anhydride, diethylene glycol, propylene oxide reaction products

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as 1,2-benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, mixed esters with diethylene glycol and propylene glycol.

Registry numbers

CAS number 77098-07-8

Other names

3,4,5,6-Tetrabromo-1,2-benzenedicarboxylic acid, mixed esters with diethylene glycol and propylene glycol

Trade names

No trade names are listed for this substance.

Molecular formula

The three components are $C_8H_2Br_4O_4$, $C_4H_{10}O_{3,}$ and $C_3H_8O_2$.

Structural formula

Undefined**.**

Molecular weight

Undefined.

Related entry

While the above details apparently relate to an alkyd-type polymer formed from the three components listed, the discrete mixed ester derived from the same three components is listed under CAS Number 20566-35-2, with Trade Names Saytex RB 79 and PHT 4-DIOL.

Physical properties

Related to 3,4,5,6-Tetrabromophthalic anhydride, diethylene glycol, propylene oxide reaction products. It is a viscous liquid has no definite melting point or boiling point.

Relative density: 1.8

Solubility in water: negligible

Viscosity: 100 Pa at 25^{o}C

A.21 Tris(tribromoneopentyl) phosphate

Chemical name

This substance is not listed on the Australian Inventory of Chemical Substances.

Registry numbers

CAS number	19186-97-1
ENCS number	2-1941X (class/category 2-1941)
ECL Serial number	97-3-169

Other names

1-Propanol, 3-bromo-2,2-bis(bromomethyl)-, phosphate (3:1)

3-Bromo-2,2-bis(bromomethyl)propan-1-ol, phosphate (3:1)

Tris[3-bromo-2,2-bis(bromomethyl)propyl]phosphate

Tris(tribromoneopentyl) phosphate

Tris[2,2-bis(bromomethyl)-3-bromopropyl] phosphate

Tris[3-bromo-2,2-bis(bromomethyl)propyl] phosphate

Trade names

CR-900

Flame Cut 175R

TPB 3070

FR 370

FR 372

Molecular formula

$C_{15}H_{24}Br_9O_4P$

Structural formula

$[(BrCH_2)_3CH_2O]_3P=O$

Molecular weight

1019

Physical properties

Appearance:	white powder with slight odour
Melting point:	182-184^{o}C
Solubility in water:	0.09 mg/100 mL
Specific gravity:	2.28
log K_{ow}:	3.7

A.22 Phosphoric acid, mixed 3-bromo-2,2-dimethylpropyl and 2-bromoethyl and 2-chloroethyl esters

Chemical name

This substance is listed on the Australia Inventory of Chemical Substances as phosphoric acid, mixed 3-bromo-2,2-dimethylpropyl and 2-bromoethyl and 2-chloroethyl esters.

Registry numbers

CAS number	125997-20-8
ECL Serial number	KE-28600

Other names

No other names are listed for this substance.

Trade names

FM-836

FM-86

Molecular formula

Three components: $C_{15}H_{30}Br_3O_4P$, $C_6H_{12}Br_3O_4P$, $C_6H_{12}Cl_3O_4P$.

Structural formula

$[BrCH_2C(CH_3)_2CH_2O]_3P=O$, $(BrCH_2CH_2O)_3P=O$, $(ClCH_2CH_2O)_3P=O$

Molecular weight

Approximately 550

Physical properties

Appearance:	colourless to light yellow liquid with characteristic odour
Melting point:	$<-100^oC$ (HP-36)
Boiling point:	203^oC (HP-36)
Vapour pressure:	2.75×10^{-6} hPa at 20^oC (HP-36)
Relative density:	1.60 at 20^oC
log K_{ow}:	3.05

A.23 TBBPA, 2,2-bis[4-(2,3-epoxypropyloxy)dibromophenyl] propane polymer

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as 2,2'-[(1-methylethylidene)bis[(2,6-dibromo-4,1-phenylene) oxymethylene]]bis[oxirane].

Registry numbers

CAS number	68928-70-1
ENCS number	7-1267X (class/category 7-1267)
ECL Serial number	KE-23977

Other names

Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo]-, polymer with 2,2'-[(1-methylethylidene)bis[(2,6-dibromo4,1-phenylene)oxymethylene] bis(oxirane)

4,4'-[(1-Methylethylidene)bis[2,6-dibromophenol] polymer with 2,2'-[(1-methylethylidene)bis[(2,6-dibromo-4,1-phenylene) oxymethylene]]bis[oxirane]

Tetrabromobisphenol A -tetrabromobisphenolA diglycidyl ether copolymer

Tetrabromobisphenol A diglycidyl ether - tetrabromobisphenol A

copolymer

Trade names

FR 2400E

FR 2016

Molecular formula

$(C_{21}H_{20}Br_4O_4.C_{15}H_{12}Br_4O_2)_x$

Structural formula

Undefined.

Molecular weight

Undefined

Physical properties

Two commercial products described by this CAS Number are polymers of different molecular sizes (approximately 1600 and 28,000-35,000) with little differences in properties.

Appearance:	white powder to light yellowish irregular particles (higher weight)
Melting point/range:	105-115oC and 150±5oC (higher weight)
Solubility in water:	insoluble

Specific gravity:	ca. 1.8
log K_{ow}:	not provided

A.24 Polymer of TBBPA, phosgene, and phenol

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as carbonic dichloride, polymer with 4,4'-(1-methylethylidene)bis[2,6-dibromophenol] and phenol.

Registry numbers

CAS number	94334-64-2
ECL Serial number	KE-04737

Other names

Polymer of tetrabromobisphenol A, phosgene and phenol.

Trade names

BC-52

Molecular formula

$(C_{15}H_{12}Br_4O_2.C_6H_6O.CCl_2O)_x$

Structural formula

Undefined

Molecular weight

Undefined

Physical properties

The commercial product is the only one for which chemical and physical data are available. It is described as a polycarbonate oligomer with 3-5 TBBPA units and end groups derived from phenol. The molecular weight would thus be in the range 1900-3100.

Appearance:	white, odourless powder
Melting range:	210-230 ^{o}C
Relative density:	2.2
Water solubility:	negligible
Soluble in:	dichloromethane, toluene, methyl ethyl ketone.

A.25 2,4,6-Tribromophenyl terminated carbonate oligomer

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as carbonic dichloride, polymer with 4,4'-(1-methylethylidene) bis[2,6-dibromophenol], 2,4,6-tribromophenyl ester.

Registry numbers

CAS number	71342-77-3
ECL Serial number	KE-04738

Other names

Phosgene-tetrabromobisphenol A polymer 2,4,6-tribromophenyl ester

Phosgene-tetrabromobisphenolA-tribromophenol copolymer

Trade names

BC-58

Molecular formula

$(C_{15}H_{12}Br_4O_2.CCl_2O)_x.2C_6H_3Br_3O$

Structural formula

Undefined.

Molecular weight

Undefined. Commercial product BC-58 specifies five TBBPA units in the oligomer which would thus have molecular weight approximately 3200.

Physical properties

The commercial product is the only one for which chemical and physical data are available. It is an oligomer containing five TBBPA units in each molecule, with tribromophenyl ester end groups, giving it a molecular weight of 3854.

Appearance:	odourless white powder
Melting point/range:	230-260 ^{o}C
Vapour pressure:	very low
Relative density:	2.2
Water solubility:	negligible
Soluble in:	dichloromethane, toluene, methyl ethyl ketone

A.26 Polybromobiphenyls

The only registry listing of this general class of substances is ENCS 4-18. However, a number of individual congeners have been listed, and are described in this section.

A.26.1 Decabromobiphenyl

Chemical name

This substance is listed on the Australian Inventory of Chemical Substances as 1,1'-biphenyl, 2,2',3,3',4,4',5,5',6,6'-decabromo.

Registry numbers

CAS number	13654-09-6
EINECS number	237-137-2
ENCS number	4-799
ECL Serial number	KE-09378
Swiss number	G-6910

Other names

Decabromo-1,1'-biphenyl

Decabromobiphenyl

2,2',3,3',4,4',5,5',6,6'-Decabromobiphenyl

Perbromobiphenyl

Biphenyl, decabromo-

PBB 209

Trade names

Adine 0102

Berkflam B 10

Flammex B 10

Molecular formula

$C_{12}Br_{10}$

Structural formula

C_6Br_5-C_6Br_5

Molecular weight

944

A.26.2 Pentabromobiphenyl

Chemical name

This substance is not listed on the Australian Inventory of Chemical Substances.

Registry numbers

CAS number 67888-96-18X

ENCS number 4-18X (class/category 4-18)

Other names

2,2',4,5,5'-Pentabromobiphenyl

2,2',4,5,5'-Pentabromo-1,1'-biphenyl

2,4,5,2',5'-Pentabromo-1,1'-biphenyl

2,4,5,2',5'-Pentabromobiphenyl

Trade names

No trade names are listed for this substance.

Molecular formula

$C_{12}H_5Br_5$

Structural formula

$C_{12}H_5Br_5$

Molecular weight

549

A.26.3 Tetrabromobiphenyl

Chemical name

This substance is not listed on the Australian Inventory of Chemical Substances.

Registry numbers

CAS number 60044-24-8

ENCS number 4-18X (clas/category 4-18)

Other names

1,1'-Biphenyl, 2,2'4,5'-tetrabromo

2,2',4'5-Tetrabromobiphenyl

2,2',4,5'-Tetrabromobiphenyl

2,4,2',5'-Tetrabromobiphenyl

Trade names

No trade names are listed for this substance.

Molecular formula

$C_{12}H_6Br_4$

Structural formula

$C_{12}H_6Br_4$

Molecular weight

470

A.26.4 Dibromobiphenyl

Chemical name

This substance is not listed on the Australian Inventory of Chemical Substances.

Registry numbers

CAS number	92-86-4
EINECS number	202-198-6
ENCS number	4-18X (class/category 4-18)

Other names

1,1'-Biphenyl, 4,4'-dibromo

4,4'-Dibromobiphenyl

4,4'-Dibromo-1,1'-biphenyl

Biphenyl, 4,4'-dibromo

p,p'-Dibromobiphenyl

Trade names

No trade names are listed for this substance.

Molecular formula

$C_{12}H_8Br_2$

Structural formula

$C_{12}H_8Br_2$

Molecular weight

312

A.26.5 Bromobiphenyl

Chemical name

This substance is not listed on the Australian Inventory of Chemical Substances.

Registry numbers

CAS number	2052-07-5
EINECS number	218-141-3
ENCS number	4-18X (class/category 4-18)

Other names

1,1'-Biphenyl, 2-bromo

2-Bromobiphenyl

1-Bromo-2-phenylbenzene

2-Biphenylyl bromide

2-Bromo-1,1'-biphenyl

Phenylbromobenzene

o-Bromobiphenyl

Trade names

No trade names are listed for this substance.

Molecular formula

$C_{12}H_9Br$

Structural formula

$C_{12}H_9Br$

Molecular weight

233

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