NICNAS

POLYCHLORINATED STYRENES

July 2002

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME
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1. INTRODUCTION

1.1 Nomination reason

The chemical group chlorinated styrenes (or polychlorinated styrenes, PCSs) including octachlorostyrene (CAS 29082-74-4), was nominated during the National Industrial Chemicals Notification and Assessment Scheme's (NICNAS) public call for nomination of chemicals of concern in February 1999. During screening of the nominated chemicals other PCSs belonging to this group were identified. Three other chemicals were identified and these are *m*-chlorostyrene (CAS 2039-85-2), *o*-chlorostyrene (CAS 2039-87-4) and *p*-chlorostyrene (CAS 1073-67-2).

The reason for nomination and selection of these chemicals for further work included concerns surrounding their potential to persist and bioaccumulate in the environment.

An initial call for information under section 48 of the *Industrial Chemicals (Notification and Assessment) Act 1989* (Cwlth) (the Act) was carried out for PCSs in August 1999. No information was received by NICNAS as a result of this call for information. Subsequently a second call for information was published in the *Commonwealth Chemical Gazette* of January 2002.

1.2 Objectives of report

The objectives of the report are to identify the quantities of PCS or PCS products imported into Australia, quantities of PCS manufactured here and uses of PCSs and PCS products. Amounts of PCSs produced and/or released as by-products of processing and/or manufacture and use were also investigated.

In addition to the uses and amounts, the report includes information on the physico-chemical characteristics of these chemicals and overseas regulatory initiatives pertaining to these chemicals.

2. SEARCH STRATEGY

2.1 Industry

In accordance with section 48 of the Act, a notice was published in the *Commonweatlh Chemical Gazette* of January 2002. The notice was directed at all persons who have manufactured or imported one or more of the chemicals or products containing the listed chemicals since August 1999. The information required in the section 48 notice was:

- quantities imported and/or manufactured;
- amounts produced and/or released as by-products of processing and/or manufacture;
- products imported containing the chemicals and quantities of the chemicals in the products; and
- uses of the chemicals or the products containing the chemicals.

It also encouraged any other persons with information on these chemicals including users, past importers or manufacturers to provide this information.

A total of 31 companies identified as being potentially involved with this group of chemicals were contacted. The companies are listed in Appendix 1.

Potential manufacturers and importers of these chemicals were identified from a search of:

- overseas use information;
- published literature (eg books, manuals and encyclopaedias);
- NICNAS Company Registration Database (NICNAS, 2002); and
- web site sources such as MSDSOnline (MSDSOnline, 2002), SciFinder (SciFinder, 2000) and TOMES Plus (TOMES Plus 2002).

Throughout this process if information became available on a particular use, or industry that may use, or be associated with the chemical, then further focused searching was conducted in that specific area.

2.2 Organisations

Organisations contacted included non-government organisations (NGO) including industry associations, and unions (Appendix 2) as well as government agencies at the Federal, State and Territorial levels.

NGOs were identified from the Directory of Australian Associations March 2002-July 2002 (Current Contents, 2002).

In addition, the Organisation for Economic Cooperation and Development (OECD), United States Environmental Protection Agency (US EPA) and the European Chemicals Bureau (ECB) were contacted for international use information.

2.3 Literature sources

Chemical identity search was conducted using a variety of databases to identify other chemicals within this group. SciFinder (2000) was used to identify chemicals with the same molecular structure, and chemical dictionaries and encyclopaedias were used to further identify the specific chemicals constituents within the group of PCSs.

3. CHEMICAL IDENTITY

PCSs are a class of compounds in which chlorine atoms displace hydrogen atoms in the styrene (vinyl benzene) structure (US EPA, 2000). The group contains 159 theoretically possible isomeric PCSs containing one to eight chlorine atoms (Steinwandter and Zimmer, 1983). Very little data is available on the isomers.

The identities of the four PCSs are presented in Table 1.

4. PHYSICAL AND CHEMICAL PROPERTIES

PCSs are colourless liquids at room temperature and have a high thermal conductivity (HSDB, 2000).

The physical-chemical properties of the four PCSs are presented in Table 2.

Table 1 - Chemical identity

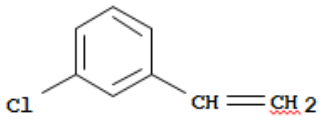
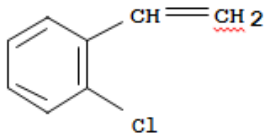
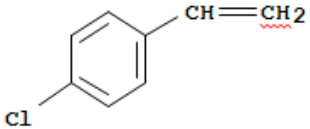
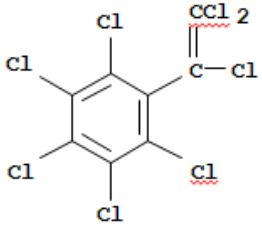
Chemical Name	*m*-Chlorostyrene	*o*-Chlorostyrene	*p*- Chlorostyrene	Octachlorostyrene	References
CAS number:	2039-85-2	2039-87-4	1073-67-2	29082-74-4	(HSDB, 2000)
EINECS Number	218-024-7	218-026-8	214-028-8	Not available	(HSDB, 2000)
AICS	No	No	Yes	Yes	(AICS, 1999)
Synonyms	Benzene, 1-chloro-3-ethenyl- (9CI) Styrene, M-chloro- (8CI) Styrene, 3-chloro- 3-Chlorostyrene	Benzene, 1-chloro-2-ethenyl- (9CI) 2-chlorostyrene Styrene, o-chloro Styrene, 2-chloro Ortho-chlorostyrene	Styrene, P-chloro- (8CI) Benzene, 1-chloro-4-ethenyl- 4-Chlorostyrene Parachlorostyrene Styrene, 4-chloro-	Benzene, pentachloro(trichloro ethenyl)- Styrene, octachloro- Trichlorovinalpenta chlorobenzene	(HSDB, 2000)
Molecular weight	138.60	138.60	138.60	379.68	(HSDB, 2000)
Molecular formula	C_8H_7Cl	C_8H_7Cl	C_8H_7Cl	C_8Cl_8	(HSDB, 2000)
Structural formula CI=CAS Index					(SciFinder 2000)

Table 2 - Physical-chemical properties

Chemical Name	*m*-Chlorostyrene	*o*-Chlorostyrene	*p*- Chlorostyrene	Octachlorostyrene	References
CAS number	2039-85-2	2039-87-4	1073-67-2	29082-74-4	(HSDB, 2000)
Melting point (^{o}C)	Not available	-63.1	-15.9	Not available	(HSDB, 2000)
Boiling point (^{o}C)	62 to 63	188.7	192.0	Not available	(HSDB, 2000)
Density (at 20 ^{o}C)	1.1168	1.1000	1.0868	Not available	(HSDB, 2000)
Vapour pressure (at 25 ^{o}C)	Not available	9.6 x 10^{-1} mm Hg	1.5 mm Hg	Not available	(HSDB, 2000)
Water solubility	Insoluble in water	Not available	Insoluble in water.	Insoluble in water *	(HSDB, 2000) * (US Dept. of Health and Human Services, 1995)
Henry's Law constant (@25^{o}C)	2.39 X 10^{-3} atm m^3/mole (estimated)	2.39 X 10^{-3} atm m^3/mole (estimated)	2.39 X 10^{-3} atm m^3/mole (estimated)	1.3 X 10^{-4} atm m^3/mole	(HSDB, 2000)
Log (BCF) (Bioconcentration factor)	2.49 (estimated)	2.49 (estimated)	2.49 (estimated)	6.15 (trout measured) 3.91 (trout estimated) 4.52 (minnow estimated)	(HSDB, 2000)
Log Kow (Octanol/Water partition coefficient)	3.58 (estimated)	3.58 (estimated)	3.58 (estimated)	6.29 (estimated)	(HSDB, 2000)
Volatilisation t ½ (river)	4 hour (estimated)	4 hour (estimated)	4 hour (estimated)	18 hour (estimated)	(HSDB, 2000)
Volatilisation t ½ (pond)	15 days (estimated)	15 days (estimated)	15 days (estimated)	5 years (estimated)	(HSDB, 2000)
Photolysis half life	14 hour (estimated)	14 hour (estimated)	14 hour (estimated)	17 days (estimated)	(HSDB, 2000)
Ozone half life	13 hour (estimated)	13 hour (estimated)	13 hour (estimated)	Not available	(HSDB, 2000)
Log Koc (Octanol/Carbon coefficient)	2100 (estimated)	2100 (estimated)	2100 (estimated)	62900 (estimated)	(HSDB, 2000)

5. INTERNATIONAL PERSPECTIVES

5.1 Uses and emissions

o-Chlorostyrene

o-Chlorostyrene is produced commercially as a monomer from *o*-chloroethylbenzene and is also produced as a mixture with *p*-chlorostyrene (HSDB, 2000).

International uses of *o*-chlorostyrene include:

- the manufacture of polychlorostyrene which is a clear, colourless plastic with good foaming, heat distortion and flame-retardant properties (HSDB, 2000);
- the incorporation into polyesters providing reduced flammability and heat resistant qualities to the formulations (HSDB, 2000); and
- the formulation of plastics, rubber and resin (NTP, 2001).

o-Chlorostyrene is likely to be released to the environment via effluents at the site where it is produced or used (HSDB, 2000).

m-Chlorostyrene

No information on manufacture or use of *m*-chlorostyrene internationally was found.

p-Chlorostyrene

p-Chlorostyrene is produced commercially as a monomer from *p*-chloroethylbenzene by an oxidation technique and as a mixture with *o*-chlorostyrene (HSDB, 2000).

The uses of *p*-chlorostyrene are similar to *o*-chlorostyrene and include:

- manufacture of polychlorostyrene;
- incorporation into polyesters; and
- formulation of chlorostyrene polymers.

Octachlorostyrene

Octachlorostyrene is not produced commercially for any application. In addition to the lower PCSs, octachlorostyrene is mainly formed as an accidental by-product of high temperature industrial processes involving chlorine. US EPA (2000) indicated that the processes that combine chlorine, carbon and high temperatures are the main source of its unintentional production.

Fly ash containing octachlorostyrene can be released to the atmosphere via waste incineration (Kaminsky & Hites, 1984; King & Sherbin, 1986; Junk & Ford, 1980; HSDB, 2000).

Octachlorostyrene has structural similarities to hexachlorobenzene (CAS 118-74-1) and dioxins/furans and is produced in the same processing circumstances that emit these substances. It has been suggested that the measured emissions of these structurally similar chemicals can be related to octachlorostyrene via ratios and therefore, estimates of octachlorostyrene production can be calculated (USEPA, 2000).

Electrolytic production of chlorine gas or magnesium, and the chlorination and distillation processes of niobium and tantalum production have all been identified as potential sources for octachlorostyrene release (HSDB, 2000). Niobium and tantalum are used as alloys in steel making. Octachlorostyrene has also been measured as part of the chlorine fluxing of aluminium to remove hydrogen and undesirable metallic impurities in aluminium foundries. This technique has largely been replaced by fumeless fluxing procedures (Howe-Grant, 1991).

Octachlorostyrene emissions into the environment have been shown to occur largely through the wastewater effluents of these operations. Octachlorostyrene has also been released to ground water via leachate from a landfill where chlorinated tars were deposited and via the sedimentation basin of aluminium smelters treated with hexachloroethane and chlorine gas (HSDB, 2000).

5.2 International initiatives

PCSs have gained international attention because of their potential to persist and bioaccumulate in the environment. However, little work has been done in qualifying and quantifying this, possibly due to the scarcity of data concerning the toxic effects of this group of chemicals in humans and the adverse effects on wildlife.

United States

The U.S. Environmental Protection Agency's (EPA) Persistent, Bioaccumulative, and Toxic (PBT) program was initiated in November 1998. The PBT Program is an integrated approach addressing widespread problems associated with toxic pollutants that persist and bioaccumulate in the environment.

The US EPA outlined a plan of action for chemicals on the PBT list to reduce risks to human health and the environment. These priority actions and supporting assessments are embodied in reports called national action plans. These plans are being developed and reviewed through an Agency-wide process and are consistent with international efforts involving Canada, Mexico and the United States.

Octachlorostyrene is listed in the priority 1 series of chemicals considered under the PBT program. The US EPA's Action Plan on octachlorostyrene acknowledges levels of octachlorostyrene in the environment are decreasing. Therefore the action plan mainly focuses on identifying sources, releases and potential for exposure from this chemical and also on the promotion of voluntary pollution prevention efforts where appropriate. Information is available from the US EPA's website at http://www.epa.gov/pbt/octa.htm.

Octachlorostyrene is not specifically listed as a hazardous waste in the US under the Resource Conservation and Recovery Act (RCRA) (US Dept of Health and Human Service, 1995).

The American Conference of Governmental Industrial Hygienists (ACGIH) has set exposure standards for *o*-chlorostyrene. These are a short term exposure limit (STEL) of 75 ppm for periods up to 15 minutes and a threshold limit value (TLV) of 50 ppm as a time weighted average (TWA) for a 8 h workday and a 40-hr workweek (ACGIH, 2000).

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for *o*-chlorostyrene (US Dept of Health and Human Service, 1995).

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) as a TWA for *o*-chlorostyrene of 50 ppm and 75 ppm as a STEL. NIOSH has not established an immediately dangerous to life or health (IDLH) value for *o*-chlorostyrene.

6. AUSTRALIAN PERSPECTIVES

6.1 Uses

Fifteen companies (48%) and 2 associations/unions who were sent the section 48 notice responded to the call for information. In addition to that 11 further companies responded directly to the section 48 call for information.

A major manufacturer of styrene monomer in Australia indicated that chlorostyrenes were not manufactured in Australia.

Data on imports and uses obtained in response to the NICNAS call for information are presented in Table 3. Data on importation were provided only for three of the PCSs. Quantities reported were for the period 1998 to early 2002.

Table 3: Uses and quantities of PCSs.

CAS Number	Chemical Name	Quantity (grams)	Use
2039-87-4	*o*-chlorostyrene	10	Scientific research
2039-85-2	*m*-chlorostyrene	10	Scientific research
	p-chlorostyrene	270	Scientific research

Further follow-up on the specific uses in scientific research indicated that they were identical for all three PCSs. These are:

- as a calibration standard; and
- used in reagent testing.

It is likely that PCSs are also being imported into Australia in products or incorporated into articles made of plastic, rubber or resins. Chlorostyrenes are expected to be bound in the matrix of these articles. However information on binding and mobility out of matrix is not known. Their inclusion into polychlorostyrene, polyester, plastic, rubber and resin matrix should prevent their environmental release, but this is dependent on the final disposal techniques of the incorporated matrix.

Small quantities of PCSs were imported in the past (>3 years) into Australia for use as flame retardants in engineering.

6.2 Emissions

Industries within Australia likely to produce octachlorostyrene as a by-product include aluminium and magnesium production facilities.

Australia currently has six aluminium smelters - two in Victoria, two in New South Wales, one in Tasmania and one in Queensland. Total production of aluminium from these smelters is approximately 2 million tonnes per year. The Australian Aluminium Council advised that chlorine degassing facilities are used in the casting and alloying areas of some Australian smelters. However, as there is no carbon present in the degassing process it is unlikely that octachlorostyrene is formed. The Council also advised that alumiuium smelting processes that have been identified as possible sources of octachlorostyrene (such as the "Alcoa Smelting Process" and the production of high-purity aluminium) are not used in Australian smelters. Currently, Australia does not produce magnesium metal. However in 1998, Australian Magnesium Corporation commenced operating a 1500 tonnes per year demonstration plant at Gladstone, Queensland. It plans to establish a commercial magnesium metal plant at Gladstone using the Australian Magnesium Process. It is expected to be in operation by 2002. The Australian Magnesium Process, developed in Australia, involves dissolving pure magnesite ore in hydrochloric acid to produce magnesium chloride via an electrolytic process. The chlorine gas released is recycled and combined with hydrogen, from natural gas, to produce hydrochloric acid for reuse in the process.

Implementation of an electrolytic magnesium production has been approved in Queensland. A series of development approval conditions were laid down for general development, air, water, stormwater, land and waste management aspects of the project. Other conditions include air emissions and ambient air quality monitoring and a reporting program that includes a specific report on chlorinated hydrocarbons. The definition of chlorinated hydrocarbons for this purpose is limited to the family of compounds made up of polychlorinated biphenyls, hexachlorobenzene, dioxin and furans only. Although the approval requirements do not specifically cover PCSs, their potential emissions should be covered inadvertently.

PCSs are released from similar processes as dioxins for which limited information exists in Australia.

6.3 Regulatory controls

The Australian Inventory of Chemical Substances (AICS) is an inventory of chemicals used within Australia. Two of the PCSs, octachlorostyrene and *p*-chlorostyrene are listed in the Inventory. Both of these chemicals were 'grandfathered' onto the AICS hence no assessment has been conducted by NICNAS (AICS, 1992). Although *m*-chlorostyrene is not listed in the AICS the chemical may be imported into Australia under an exempt category for research and development purposes. Octachlorostyrene, based on the supplied information, has not been imported into Australia since August 1999, but its listing in the AICS indicates it was either manufactured or imported into Australia during the period 1 January 1977 to February 1990 for commercial purposes.

No specific tariff code was identified under the Australian Customs Service tariff code system for these specific chemicals or the PCS group of chemicals.

o-Chlorostyrene is listed in the National Occupational Health and Safety Commission's (NOHSC) *List of Designated Hazardous Substances* (NOHSC, April 2002). The basis for inclusion in the List as a hazardous substance is that *o*-chlorostyrene has been assigned an exposure standard by NOHSC. The exposure standard is a TWA of 50 ppm or 283 mg/m^3 and a STEL of 75 ppm or 425 mg/m^3 (NOHSC, 1995). This standard has been adopted from the ACGIH.

PCSs are not specifically classified as dangerous goods in the Australian Code for the Transport of Dangerous Goods by Road or Rail (FORS, 1998).

PCSs are not specifically listed in the *Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP)* (NDPSC, 2001)

PCSs have not been considered to date by the Commonwealth Scheduled Waste Management Group in relation to the need for disposal of persistent organochlorine compounds. This indicates that little or no PCSs are stockpiled in Australia. However there are 8000 tonnes of hexachlorobenzene (HCB) awaiting disposal, mainly at Botany, NSW. The US EPA (2000) notes that octachlorostyrene is formed in many, if not all, circumstances where HCB is also formed, and it is likely that octachlorostyrene is also present in such HCB-containing wastes. However, similar to the international situation, there is no data on the likely levels of octachlorostyrene in the wastes stored at Botany.

PCSs are not listed in the Commonwealth National Pollution Inventory as requiring reporting.

7. CONCLUSIONS

m-, *p*- and *o*-Chlorostyrene

Small quantities of monochlorostyrene were identified as being imported into Australia mainly for scientific research. It is likely that these chemicals, as well as higher chlorinated styrenes, may be imported into Australia in products that are made up of polychlorostyrenes, polyesters, plastics, rubber and resins. Information regarding the binding to and mobility out of the product matrix is unknown. It is assumed that with the international reduction in PCSs production, their presence in Australia will also decline.

Monochlorostyrenes are not sufficiently persistent to be of concern particularly with the low levels currently introduced into Australia.

Octachlorostyrene

Little seems to be known internationally about the higher, potentially more persistent PCSs, penta to hexa, and octachlorostyrene, except their presence in environmental samples (US EPA, 2000).

Octachlorostyrene has been noted as being produced only as a by-product of circumstances that bring together carbon, chlorine and high temperatures and is often formed with hexachlorobenzene and dioxins/furans. Measures to manage these releases such as the Australia New Zealand Environment and Conservation Councils (1996) Hexachlorobenzene management plan should also reduce octachlorostyrene release.

No data was received for emissions of PCSs in Australia. Although various industries internationally such as the electrolytic production of magnesium; chlorination and distillation of niobium and tantalum; the production of steel; and chlorine fluxing of aluminium processes have been identified as producing PCS. The related Australian industries contacted either used a different process or had no monitoring data for these chemicals.

8. FOLLOW-UP ACTIONS

No information was provided for octachlorostyrene. It is likely that this chemical is not currently imported into or manufactured in Australia. Octachlorostyrene has been identified as a contaminant in HCB mixtures and is formed during the same processes. In addition octachlorostyrene has also been identified as being structurally similar to HCBs, dioxins and furans.

Given that 51% of companies identified as potential importers or manufacturers of octachlorostyrenes responded to the section 48 notice, NICNAS will explore options to track importation of octachlorostyrenes into Australia.

The release of octachlorostyrene as a by-product from mangnesium facilities has been identified as a potetial source of exposure in Australia to this chemical. Future licensing of magnesium smelters that use electrolytic extraction of magnesium should include as part of the environmental impact analysis release estimates for octachlorostyrene.

APPENDIX 1: List of Companies Contacted

Alcoa World Alumina Australia

Alpha Chemicals (Australia) Pty Ltd

AS Harrison & Co Pty Ltd

Australian Magnesium Corporation Ltd

Bostik Findlay Australia Pty Ltd

Bribros Australia Pty Ltd

Caltex Australia Limited

Chemlube Company Pty Ltd

Chem-Supply Pty Ltd

Ciba Specialty Chemicals Pty Ltd

Cognis Australia Pty Ltd

Dow Chemicals (Australia) Ltd

Du Pont (Australia) Ltd

Fuchs Australia Pty Ltd

HCA Colours Australia P/L

Houghton Australia Pty Ltd

Huntsman Corporation Australia Pty

International Chemicals Ltd

International Sales and Marketing

Lubrication Engineers Pty Ltd

Lubrizol Australia

Nufarm Coogee Pty Ltd

Oilchem Pty Ltd

Orica Australia Pty Ltd

Pennzoil Products Australia Company

Qenos Pty Ltd

Recochem Incorporated

Shoalhaven Mill

Sigma Aldrich Australia Pty Ltd

Sons of Gwalia

Swift and Company Limited

APPENDIX 2: List of Associations and Unions Contacted

Associations

AMIRA International Australian Mineral Industries Research Association Limited

Australian Aluminum Council

Australian Consumer and Specialty Products Association

Australian Mines and Metals Association

Institute of Electrical Inspectors

Minerals Council of Australia

NSW Minerals Council

PACIA – Plastics And Chemicals Industries Association

Waste Contractors & Recyclers Association, NSW

Unions

Australian Council of Trade Unions

Australian Manufacturing Workers Union

Communications Electrical and Plumbing Union - Electrical Division

Construction Forestry Mining Energy Union - Construction and General

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