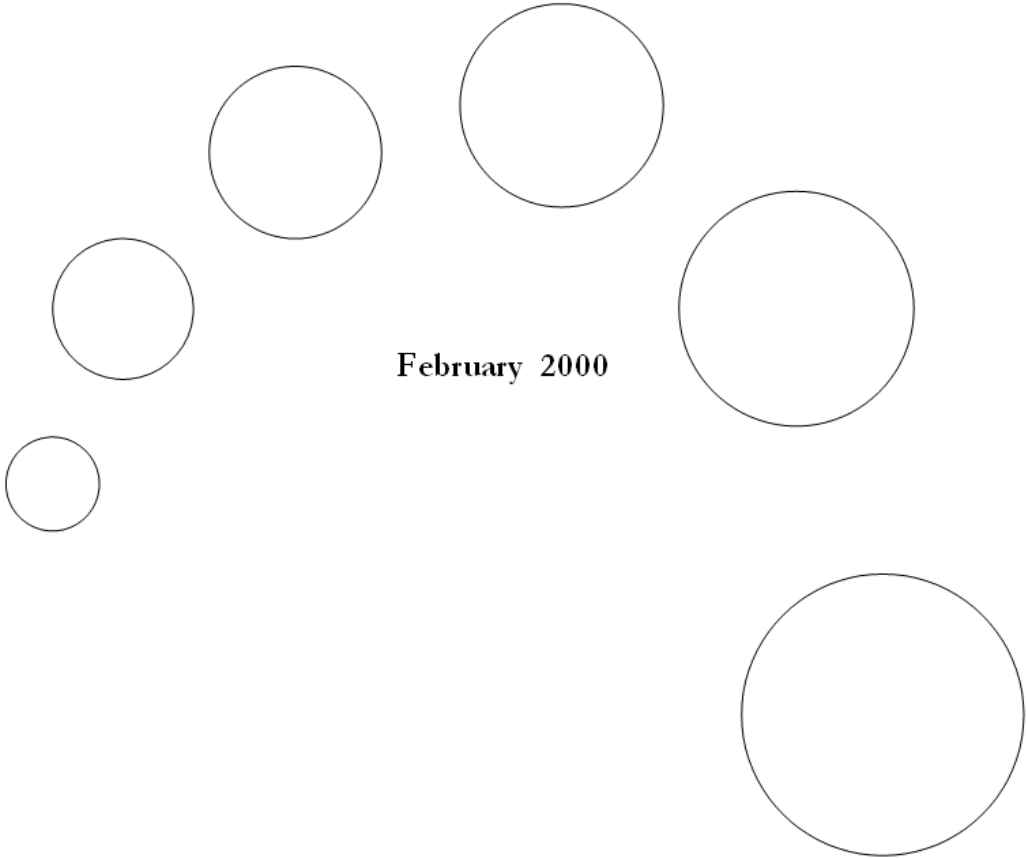


Sodium Ethyl Xanthate

Priority Existing Chemical Secondary Notification Assessment Report No.5S



February 2000

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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, by assessing the risks associated with the manufacture and use of such chemicals.

NICNAS is administered by the National Occupational Health & Safety Commission (NOHSC) and assessments are carried out in conjunction with Environment Australia (EA) and the Therapeutics Goods Administration (TGA), who carry out the environmental and public health assessments respectively. NICNAS has two major programs: one focusing on risks associated with *new chemicals*, prior to importation or manufacture and the other focussing on *existing chemicals* already in use in Australia.

As there are many thousands of existing industrial chemicals in use in Australia, NICNAS has an established mechanism for prioritising and assessing these chemicals. Such chemicals are referred to as Priority Existing Chemicals (PECs).

The scope of PEC assessments permits recommendations to be made which will assist in the management of workplace, public health and environmental risks. Recommendations may be directed to industry (employers and employees) and/or other Federal and State/Territory regulatory authorities. NICNAS cannot make regulatory decisions which fall within the responsibility of other regulatory authorities and as such, recommendations can only be given effect through consideration of risk management practices and processes by those agencies/authorities charged with regulatory decision making.

Where further information becomes available after publication of a PEC report and/or where certain prescribed circumstances occur, as stipulated under Section 64(2) of the Act, the Director (Chemicals Notification and Assessment) may require a reassessment of the hazards of the PEC under 'secondary notification provisions' (Division 6) of the Act. This Full Public Report has been prepared in accordance with these provisions.

Under Section 40 of the Act, a public comment process is also undertaken for secondary notification assessment reports.

For the purposes of Section 78(1) of the Act, copies of Full Public Reports for New and Existing Chemical assessments may be inspected by the public at the Library, NOHSC, Plaza level, Alan Woods Building, 25 Constitution Avenue, Canberra, ACT 2600 (between 9 am and 5 pm each weekday, except public holidays). Summary Reports are published in the *Commonwealth Chemical Gazette*, which is also available to the public at the above address.

Copies of this and other reports can be purchased from NICNAS either by using the prescribed application form at Appendix 6 of this report, or directly from the following address.

**334-336 Illawarra Road
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NSW 2204
AUSTRALIA**

Tel: +61 2 8577 8800

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Further information, available on request include:

- NICNAS Service Charter;
- information sheets on NICNAS Company Registration;
- information sheets on PEC and New Chemical assessment programs;
- application forms for New Chemical and PEC assessments;
- application form for the Australian Inventory of Chemical Substances (AICS)
- subscription details for the *Commonwealth Chemical Gazette*; and
- subscription details for the *NICNAS Handbook for Notifiers*.

PEC and New Chemical Summary Reports together with other information on NICNAS activities can be found on the NICNAS Web site at:

<http://www.nicnas.gov.au>

Overview

A Full Priority Existing Chemical report for sodium ethyl xanthate was published in May 1995. The reasons for the original declaration were (i) the large potential for occupational and environmental exposure due to its use in the Australian mining industry, (ii) the lack of information on its health and environmental effects and (iii) its potential to decompose to CS₂.

At the time of the PEC assessment, only *solid* sodium ethyl xanthate was being used in Australia, all of which was imported. In October 1998, notification was provided to the Director of Chemicals Notification and Assessment, that manufacture of liquid xanthates had begun in Australia. As such, this assessment, which focuses on the occupational, public health and environmental risks associated with the manufacture and use of *liquid* xanthates, was carried out under the 'secondary notification' provisions of the ICNA Act.

The only use identified for liquid sodium ethyl xanthate in Australia is as a flotation agent in mining applications. The production capability of a single plant in WA (the applicant for assessment) is currently around 5,000 tonnes per year, with a similar capability for a second plant planned in Queensland. The manufacture of liquid sodium ethyl xanthate essentially involves reaction of carbon disulfide (CS₂), sodium hydroxide and ethanol in a closed, batch type process.

Sodium ethyl xanthate exhibits moderate oral and dermal acute toxicity in animal studies and is an eye and skin irritant. Limited data on repeated dose toxicity are available. The main hazards from exposure to xanthates are considered to arise from CS₂, which is both a decomposition product of sodium ethyl xanthate during storage and use and a metabolite from xanthate biotransformation in animals and humans. Decomposition data provided by the applicant indicated that between 0.1 and 0.2% w/w CS₂ may be formed per day during transport/storage of liquid sodium ethyl xanthate.

Carbon disulfide exhibits low to moderate acute toxicity in animals and humans and is associated with a number of long-term effects which include cardiovascular, neurological and reproductive effects.

In Australia, exposure to sodium ethyl xanthate and CS₂ may occur during manufacture, transport and use of liquid sodium ethyl xanthates, mainly through skin contact of sodium ethyl xanthate and CS₂ or inhalation of CS₂.

The occupational risk assessment indicated a potential for acute health risks at manufacturing and end-use sites only in certain situations, such as maintenance and dilution/filling work, where adequate PPE may not be deployed. The lack of adequate dose-response data for repeated exposures, particularly at low level exposures, to either sodium ethyl xanthate or CS₂ precluded a formal risk characterisation, however, the available exposure data indicate the likelihood of chronic health risks to be low during manufacture, transport and end-use.

The WA manufacturing site has been assessed by the Department of Minerals and Energy (DME) and Department of the Environment in WA for compliance with the NOHSC Major Hazard Facilities standard and environmental emissions standards. Current control measures adopted at manufacturing and mining sites, particularly the control of plant

emissions and prevention of hazardous tailings discharge to waterways, would be expected to minimise potential health risks to the general public. As with any hazardous substance, acute health risks are possible from a transport accident in a populated area.

Sodium ethyl xanthate is very toxic to aquatic organisms and exhibits a high degree of mobility in soil. The environmental impact assessment indicated a potential for adverse environmental risks from spillage during manufacture and transport.

Recommendations

Based on the assessment findings, a number of recommendations were made, directed towards employers and employees involved in the manufacture, and handling of liquid sodium ethyl xanthate and to specific regulatory bodies involved in the protection of occupational, public and environmental health. The main recommendations are:

As 40% sodium ethyl xanthate aqueous solution has not been tested and classified *per se*, it should be classified as a hazardous substance in accordance with the *List of Designated Hazardous Substances* with the risk phrases: *Harmful in contact with skin and if swallowed* (R21/22) and *Irritating to eyes and skin* (R36/38). Solutions containing > 0.2% CS₂, should be classified accordingly.

Workers involved in the manufacture, transport and use of sodium ethyl xanthate also need to be trained in the safe handling of CS₂, particularly during manufacture, where CS₂, used as a production ingredient, is a potential health and fire hazard. In particular, for high risk activities all workers should be equipped with fully maintained and fitted full-face respirator (with suitable organic vapour cartridge) or self contained breathing apparatus (SCBA), impervious protective clothing and anti-static gloves and boots.

Due to the potential for adverse health and environmental effects from tanker spillage, it is recommended that adequate hazard communication in relation to emergency response/clean-up procedures be provided in the MSDS, emergency response/plant safety plan(s). In addition, it is recommended that for the purpose of transport a specific Emergency Procedures Guide (EPG) be developed for liquid xanthates for transport drivers. The availability of an appropriate EPG is considered particularly important in light of the fact that liquid xanthates are not currently classifiable under the ADG Code criteria. In this regard, the Advisory Committee for the Transport of Dangerous Goods (ACTDG) is supported in its proposal to the UN to classify xanthates with subsidiary risk 6.1 (*harmful/toxic substance*). In view of the potential environmental risks, it is also recommended that ACTDG consider classification of liquid xanthates under Class 9 as a *substance hazardous to the environment*.

Due to certain inadequacies with regard to current monitoring for CS₂ employed at both manufacturing and end use sites, it is recommended that appropriate air monitoring is carried out. Routine personal or, as a minimum, static monitoring should be carried out for all activities where potential exposure to CS₂ vapours exist. Monitoring should employ at least the minimum sampling times as recommended by NOHSC.

It is recommended that CS₂ exposure standard is maintained for review by NOHSC (NOHSC Guidance Note 1995), however the timing of such a review needs to take account of the quality of the human/animal database as currently it is considered that insufficient data exist to permit dose-response assessment for chronic effects, particularly at the lower levels that have been reported to be associated with adverse effects in some more recent epidemiological/clinical studies. In addition, it is recommended that when NOHSC review the exposure standard, that appropriate consideration is given to whether

sodium ethyl xanthate and CS₂ should be further considered within the 'health surveillance' framework, and in particular, the development of a biological exposure index (BEI) for CS₂.

Risks to the general public from manufacture and use of liquid xanthates were assessed as minimal. However, appropriate precautions should be taken to minimise release of hazardous degradation products, in particular, CS₂ and H₂S. In this regard, the DEP ambient air standard of <0.042 ppm (0.13 mg/m³) CS₂ should not be exceeded. Sodium ethyl xanthate should not be allowed to enter drains waterways or river systems and contaminated soil and spill absorbents should be disposed off as hazardous waste.

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Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
ACTDG	Advisory Committee for the Transport of Dangerous Goods
ADG Code	Australian Code for the Transport of Dangerous Goods by Road and Rail
AICS	Australian Inventory of Chemical Substances
AMIRA	Australian Mineral Industries Research Association
AS	Australian Standard
ATSDR	US Agency for Toxic Substances and Disease Registry
CAS	Chemical Abstract Service
CNS	central nervous system
CORK	Community of Rockingham and Kwinana
CS ₂	carbon disulfide
DCS	process logic control system
DEP	Department of Environment Protection
DFG	Deutsche Forschungsgemeinschaft
DME	Department of Minerals and Energy
EA	Environment Australia
EC	European Commission
EC ₅₀	Concentration at which 50% of the test population are affected EC ₉₅
	Concentration at which 95% of the test population are affected ERP
	emergency response plan
FORS	Federal Office of Road Safety
GGT	gamma glutamyltransferase
h	hour
HAZOP	hazard operation procedures
H ₂ S	hydrogen sulphide
HSE	Health and Safety Executive (UK)
IDLH	immediately dangerous to life and health
IRMS	integrated risk management system
ISO	International Standards Organization
JSOH	Japan Society for Occupational Health
KCAP	Kwinana Community Advisory Panel
KIMA	Kwinana Industries Mutual Aid Group
LC ₅₀	median lethal concentration
LOAEL	lowest observable adverse effect level
MCV	motor conduction velocity
MHF	Major Hazard Facility

MRL	minimum risk level
MSDS	Material Safety Data Sheet
NICNAS	National Industrial Chemicals Notification & Assessment Scheme
NOAEL	no-observable adverse effect level
NOHSC	National Occupational Health and Safety Commission
NSW	New South Wales
NZS	New Zealand Standard
OSHA	Occupational Safety and Health Administration (US)
PACIA	Plastics and Chemicals Industry Association
PEC	Priority Existing Chemical
PEC	predicted environmental concentration
PEL	permissible exposure level
PNEC	predicted no effect concentration
PPE	personal protective equipment
ppm	parts per million
PVC	polyvinyl chloride
QLD	Queensland
QRA	quantitative risk assessment
RTECS	Registry of Toxic Effects of Chemical Substances
SCBA	self contained breathing apparatus
SMR	safety management report
STEL	short term exposure limit
s.c.	sub-cutaneous
TGA	Therapeutic Goods Administration
TTCA	2-thiothiazolidine-4-carboxylic acid
TWA	time weighted average
WA	Western Australia

1. Introduction

1.1 History of xanthate use in Australia

Xanthates (usually, the sodium or potassium salts) are predominantly used in the mining industry as 'flotation' agents in the collection (recovery) of sulphide minerals, metallic elements (e.g., copper, nickel, silver, gold) and some oxidised minerals of lead and copper, from ore slurries. Examples are sodium and potassium ethyl xanthate, potassium amyl xanthate and sodium isopropyl and isobutyl xanthate. This use was first introduced by Keller in 1927.

Sodium ethyl xanthate is the shortest carbon chain xanthate and the most selective flotation agent. It is used mainly for the separation of copper, lead, gold, nickel and zinc ores. The amount of sodium ethyl xanthate used in this process is very small relative to the quantity of treated ore, being approximately 250 to 350 g (solid) per tonne of ore.

Overseas, sodium ethyl xanthate has also been used as a defoliant, herbicide and as an additive in the curing and vulcanisation of rubber and in high pressure lubricants. Cellulose xanthate is produced *in situ* as an intermediate in the production of viscose (Rayon) and cellophane. New uses of xanthates (unspecified) reported in the literature include inhibitors of fertiliser nitrogen transformation and colour developers for image-recording materials (ECT 1993).

In Australia, sodium ethyl xanthate, potassium amyl xanthate and sodium isobutyl xanthate have been widely used in the mining industry for the past 30 years. There is no evidence from State government records that xanthates have been used as pesticides in Australia.

Approximately 6000 tonnes of sodium ethyl xanthate (solid) are imported into Australia each year and between 3000-10,000 tonnes of aqueous liquid xanthates will be manufactured by Coogee Chemicals at plants in Western Australia and Queensland.

1.2 Declaration and assessment as a PEC

The chemical, sodium ethyl xanthate (CAS No. 140-90-9) was declared a Priority Existing Chemical (PEC) under the *Industrial Chemicals (Notification and Assessment) Act, 1989* (the Act) on 6 July 1993. The reasons for the declaration were (i) the large potential for occupational and environmental exposure due to its use as a flotation agent in the Australian mining industry, (ii) the lack of information on its health and environmental effects and (iii) its potential to decompose to CS₂.

Following the declaration of sodium ethyl xanthate as a PEC, six companies applied for assessment. At the time of the original PEC assessment, only *solid* xanthates were being used in Australia, all of which were imported. Industry sources indicate that the main source of imports of solid sodium ethyl xanthate is China.

The Full Public Report (PEC5) for sodium ethyl xanthate was published in May 1995 (NICNAS 1995) and the Summary Report in the *Chemical Gazette* of 2 May 1995.

The PEC report concluded that sodium ethyl xanthate should be classified as acutely 'harmful' by oral and dermal routes and as an eye and skin irritant. This classification has been adopted by NOHSC in the revised *List of Designated Hazardous Substances* (NOHSC 1999). The report also made a number of recommendations aimed at reducing the potential risks to human health and the environment, including the upgrading of MSDS and labels in line with NOHSC standards and the provision of adequate training to workers (particularly miners) on the fire hazards of *solid* xanthates. In particular, the report recommended that tests be commissioned by suppliers to further elucidate the factors involved in the self-combustion of sodium ethyl xanthate and that current packaging be assessed (in conjunction with relevant competent authorities) for adequacy and compliance with national regulations.

1.3 Secondary notification

Under section 64(2) of the Act, specific circumstances are prescribed where reassessment (secondary notification) of a PEC chemical may be warranted.

Section 64(2)(c) of the Act requires secondary notification of a chemical that has begun to be manufactured in Australia, where the chemical was not manufactured at the time of the PEC assessment. Sodium ethyl xanthate, in *solid* form, has previously been manufactured in Australia by Union Carbide at Botany, NSW, which ceased in the early 1980s.

In October 1998, Coogee Chemicals Pty Ltd notified the Director of NICNAS of their intention to manufacture *liquid* xanthates (including sodium ethyl xanthate) at a newly commissioned plant in Kwinana, Western Australia. In addition, Coogee Chemicals are currently planning to build a second liquid xanthate manufacturing plant in Queensland.

In accordance with the Act, the Director provided details of this secondary notification by way of notice in the *Chemical Gazette* of 1 December 1998, requiring assessment of sodium ethyl xanthate under section 65(2) of the Act. Only manufacturers or potential manufacturers of sodium ethyl xanthate were required to apply for assessment.

1.3.1 Scope and objectives

The main focus of this report was an assessment of the *manufacturing process* for *liquid* sodium ethyl xanthate at Coogee Chemicals, WA.

The objectives of this secondary notification assessment were:

- To assess health and environmental impacts from manufacture, transport and use of *liquid* sodium ethyl xanthate and the adequacy of current risk management measures;
- To assess any other data, that has been made available since the PEC5 report, of relevance to the assessment of health and environmental risks from exposure to sodium ethyl xanthate; and

- To make appropriate recommendations for further risk reduction measures where required.

In this report the term liquid xanthate(s) refers to aqueous solutions of xanthate(s). Unless otherwise specified, the term liquid sodium ethyl xanthate refers specifically to a 40% aqueous solution, as notified by the applicant. Where liquid or solid are not specified, it should be apparent which form of xanthate is being referred to, or if not previously qualified in the text, it should be assumed that the discussion is relevant to either form.

1.3.2 Sources of information/data

An important strategy for this assessment was to utilise other assessments recently carried out by other government departments, namely, the Department of Environmental Protection (DEP) and the Department of Minerals and Energy (DME) in Western Australia and the EPA in Queensland, in relation to licensing approvals for the Coogee Chemicals site(s), to avoid duplication of effort.

Information for this assessment was obtained in accordance with section 69 of the Act. In addition to a literature survey and site visit carried out by NICNAS and the information package submitted by the applicant (Coogee Chemicals), information was also provided by the following notifiers:

- DME, Western Australia
- WorkCover, New South Wales
- Ministry Environment & Energy, Toronto, Canada
- Cytec (Cyanamid) Aus. Ltd
- Redox Chemicals Pty Ltd
- Renison Ltd
- Tall Bennett Group

This report is an assessment of *liquid* xanthates and as such makes no attempt to update the original PEC5 report, apart from data relating to health hazards from sodium ethyl xanthate and CS₂. However, where relevant, reference has been made to the appropriate sections in PEC5 for further information.

For the purposes of environmental and public health risk assessments, this report considers new data in conjunction with that available for PEC5.

The recommendations to this report refer specifically to *liquid* sodium ethyl xanthate, but may also be relevant to solid sodium ethyl xanthate as well as other liquid xanthate products.

1.3.3 Peer review

During all stages of preparation, the report has been subject to internal peer review by NICNAS, EA and TGA. The report was also peer reviewed by the WA Department of Minerals and Energy (DME). In addition, specific sections of the report, relating to storage and transport of liquid sodium ethyl xanthate, were peer reviewed by WorkCover, NSW.

2. Applicant Details

In accordance with the *Industrial Chemicals Notification and Assessment Act, 1989* (the Act), the Director provided details of the secondary notification of sodium ethyl xanthate (PEC5) by way of notice in the *Chemical Gazette* of 1 December 1999, requiring assessment of sodium ethyl xanthate under section 65(2) of the Act. Only manufacturers or potential manufacturers of sodium ethyl xanthate were required to apply for assessment.

One application was received from:

Coogee Chemicals Pty Ltd
P.O. Box 5051
Rockingham Beach
Western Australia 6969

As required under the Act, the applicant supplied relevant information for this assessment, including process details and risk management initiatives for the manufacture and transport of liquid xanthates in Australia.

Information for the assessment was also provided by 7 notifiers (see Section 1.3.2), that is, companies that do not manufacture sodium ethyl xanthate, but hold information relevant to this assessment.

Under Section 36 of the Act, the applicant was provided with a draft copy of the report for correction of errors and variation of content.

3. Chemical Identity

3.1 Chemical name

Sodium ethyl xanthate is listed in the Australian Inventory of Chemical Substances (AICS) as:

Carbonodithioic acid, O-ethyl ester, sodium salt.

CAS number 140-90-9

EC number 205-440-9

EINECS number 203-207-6

3.2 Other names

Carbonic acid, dithio-, O-ethyl ester, sodium salt

Ethylxanthic acid, sodium salt

Sodium ethylxanthogenate Sodium-O-

ethyl carbonodithioate Sodium-O-ethyl

dithiocarbonate Sodium xanthogenate

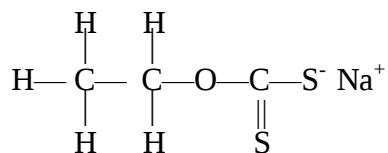
3.3 Trade names

Sodium ethyl xanthate

3.4 Molecular formula

C₃H₅OS₂Na

3.5 Structural formula



3.6 Molecular weight

144.14

3.7 Conversion factors

sodium ethyl xanthate:

$$1 \text{ mg/m}^3 = 0.169 \text{ ppm}$$

$$1 \text{ ppm} = 5.91 \text{ mg/m}^3$$

Carbon disulfide:

$$1 \text{ mg/m}^3 = 0.321 \text{ ppm}$$

$$1 \text{ ppm} = 3.11 \text{ mg/m}^3$$

4. Physicochemical Properties

Physical and chemical properties for *solid* sodium ethyl xanthate are presented in PEC5 (Section 4).

Limited physicochemical data were made available for assessment of *liquid* xanthates.

With regard to the 40% sodium ethyl xanthate solution, manufactured by Coogee Chemicals, neither the boiling point, freezing point, vapour pressure nor viscosity have been determined. The specific gravity was reported as 1.20 at 20°C. Sodium ethyl xanthate begins to crystallise from solution at -6°C.

Liquid sodium ethyl xanthate does not polymerise and is non-reactive in the presence of air/water.

4.1 Decomposition

The most important property of sodium ethyl xanthate (and xanthates in general) in relation to their hazard potential is their propensity to decompose.

On standing or when heated, xanthates may decompose to other products including, CS₂, H₂S and alcohols. Decomposition data for 10%, 25% and 40% solutions of sodium ethyl xanthate, at different temperatures, are provided in Table 1.

Table 1 – Percentage reduction in sodium ethyl xanthate content of various solutions at different temperatures

Concentration (%)*	Average daily loss (%)		
	20°C	30°C	40°C
10	1.1	2.7	4.6
25	0.7	2.0	4.3
40	0.5	na	na

*grams per 100 grams aqueous solution

na = not available

Source: Coogee Chemicals

Data in Table 1 indicate that the rate of decomposition of sodium ethyl xanthate decreases with increasing concentration and increases with increasing temperature. It should however be noted that this data does not appear to be consistent with that made available by the American Cyanamid Company for PEC5 for 10% and 25% solutions of sodium ethyl xanthate, where rates of decomposition were greater for a 25% solution at equivalent temperatures.

According to the data provided by Coogee Chemicals, decomposition on a w/w basis of 40% sodium ethyl xanthate solution (at 20°C) would give rise to an increase in CS₂ concentration of approximately 0.1% per day¹. This estimate assumes maximum conversion to CS₂, and does not account for other possible

¹ This calculation is consistent with the estimated (by the applicant) reduction in sodium ethyl xanthate concentration of 0.2% (w/w basis) per day.

decomposition pathways that do not lead to CS₂ formation. In addition, CS₂ may further react to form other decomposition compounds. Based on data for other sodium ethyl xanthate solutions an increased rate of decomposition would be expected at elevated temperatures.

Other factors e.g., pH, cations and anions, that affect the rate and pathways of decomposition for both solid and liquid sodium ethyl xanthate are discussed in PEC5 (Section 7).

5 Human Exposure Assessment

The potential exists for environmental, occupational and public exposure to sodium ethyl xanthate and decomposition products (e.g., mainly xanthic acid, CS₂ and hydrogen sulphide) from manufacture, transport and use as a flotation agent, of liquid sodium ethyl xanthate.

Environmental exposures from manufacture and use of sodium ethyl xanthate in Australia are discussed in Section 7.

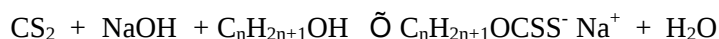
5.1 Occupational exposure

Occupational exposure to sodium ethyl xanthate and CS₂, as a reaction and/or decomposition product may occur during manufacture, transportation, storage and use of liquid sodium ethyl xanthate.

5.1.1 Manufacture of liquid xanthates

Currently, liquid sodium ethyl xanthate is being manufactured at one site in WA, with plans for another plant in Queensland.

Manufacture of xanthates at this plant is essentially a batch type process. The general chemical reaction for the process is as follows:



Where $n = 2, 3, 4$ or 5 (if potash used, $\text{Na} = \text{K}$)

It is anticipated that initially this plant will produce around 1500 liquid tonnes of sodium ethyl xanthate per annum, rising to a maximum of 5000 tonnes in the future.

Process description

The manufacturing process is an automated, computer controlled, 'closed' process. A flow diagram of the process is at Appendix 1.

For manufacture of sodium ethyl xanthate, the reactor is charged with a mixture of ethanol, aqueous sodium hydroxide and carbon disulfide. Manual sampling of the reaction mixture is undertaken to ensure maximum uptake of CS₂ prior to final dilution.

The resulting liquid xanthate solution is then diluted to 40-50% prior to automated transfer from reactor to bulk storage tanks (mild steel – each 25,000 L capacity).

The plant does not generate any solid or liquid effluent.

Potential exposure and numbers of workers involved

The manufacturing process is essentially a closed process, with potential exposures during normal operation limited to emissions from the stack and during process sampling and plant maintenance.

Currently, a total of 8 workers are trained in the operation of the plant of which, 2 operators plus 1 production supervisor are on site during each shift. Each shift consists of 8 h per day with the plant operating 24 h a day, 6 days a week.

The process is practically fully automated, controlled by a process logic system (DCS) operated from a plant control room, which is situated approximately 50 metres from the plant. The siting of the control room permits full view of the plant, including gantries.

Air Monitoring

During manufacture, no air monitoring is carried out for sodium ethyl xanthate directly, however, regular monitoring is performed for CS₂ at a number of key locations within the plant. Carbon disulfide concentrations are also monitored prior to maintenance activities in areas where exposure to CS₂ is most likely. Table 2 provides monitoring data carried out at Coogee Chemicals plant since xanthate manufacture commenced.

Table 2 - Carbon disulfide air monitoring data at liquid xanthate manufacturing plant

Location	Concentration of CS ₂ (ppm)
Plant (ground level)	<3
Scrubber (emission exhaust)	16 - >2000
Storage tank	During maintenance work >95 - 317
Road tanker	Top 30

Source: Coogee Chemicals (1999).

Note: monitoring was carried out using Drager tube (Accuro pump and short term test tubes) analyses. These tubes permit measurement of CS₂ in the ranges 3 to 95 ppm and 30 to 3,000 ppm respectively.

These data have been collected and provided by Coogee Chemicals Pty Ltd as back-up verification of their monitoring program.

Current monitoring at the Coogee plant is undertaken using Drager tube analyses. This method provides instantaneous 'grab' readings (1-2 minutes duration) and is used primarily as a method for 'spot checks'. Such monitoring is not suitable for detailed assessment of TWA exposure levels, which requires static or personal sampling over a minimum time period, usually 4 h.

Information provided by Coogee Chemicals indicates that the highest exposures to CS₂ are likely to be during plant maintenance. Limited data were available for maintenance work, apart from a 'one-off' procedure, involving the connection/disconnection of a CS₂ feed-line to install a flow meter, where levels of up to several hundred ppm were recorded. Coogee Chemicals reports that

pipelines supplying CS₂ to plant are designed to limit exposure to workers (see Section 8.1.3).

Where work is required on plant where exposure levels may be above the exposure standard, workers are required to wear breathing apparatus with portable air supply.

Occupational exposure limits/standards for CS₂ are discussed in Section 8.3.1.

5.1.2 Transport and storage

Information contained in this section was provided by the applicant.

Raw materials used in manufacture

Liquid CS₂ is imported by ship in dedicated 20 liquid tonne steel iso-tainers and transported by road on 'side-lifter' trucks. Iso-tainers received at the plant are loaded into a containment bund with capacity of 40,000 litres and connected directly to the xanthate plant ready for use. Empty iso-tainers are returned to overseas supplier for re-filling. No cleaning of iso-tainers is required.

Fifty per cent sodium hydroxide is received by road at the manufacturing plant in 16,000 litre tankers and transferred, using seal-less magnetic drive pump, to a bunded storage tank of 60,000 litres capacity.

Ethyl alcohol is also received by road at the manufacturing plant in 16 tonne steel iso-tainers and transferred, using seal-less magnetic drive pump, to a bunded storage tank of 60,000 litres capacity.

Amyl alcohol (for the production of sodium amyl xanthate) will either be received by iso-tainer or in 300 tonne bulk shipments. In the latter case, the alcohol will be transferred directly to the plant storage tank by existing pipeline from the Kwinana bulk cargo jetty.

Xanthate product(s)

Liquid xanthate from the manufacturing process is pumped from plant to two bulk storage tanks, each of 25,000 litres capacity. Dispatch tanker (mild steel - 25 or 50 tonnes capacity) loading is then carried out using a purpose built 'chiller dilution magnetic drive pump module' at the loading gantry which is situated approximately 50 metres from the plant.

Liquid xanthates are transported by road from the manufacturing plant for use in Western Australia. It is proposed that the Queensland plant will pump xanthates directly to end-use sites.

At the end-use site liquid xanthates are pumped from the road tanker using the purpose built 'chiller dilution module' (see above) into storage or stock tanks, which may range from 1000 to 100,000 litres capacity.

Potential exposure and numbers of workers involved

A maximum of 2 operators, including the tanker driver, are involved during filling/unloading operations.

Non-routine monitoring for CS₂ has been carried out in areas around road tankers, cargo trains and in holds of ships. A single air sample taken above a road tanker at Coogee Chemicals plant contained 30 ppm CS₂ (see Table 2). Coogee Chemicals report that potential exposure to CS₂ during pipeline connections from plant/end-use site to dispatch tankers is reduced by valve design and use of 'chiller dilution module'.

5.1.3 End use

For details of exposure scenarios for end-use of *solid* sodium ethyl xanthate in mining applications, the reader is referred to sections 10.1.1 to 10.1.3 of PEC5.

Occupational exposure scenarios are similar for both solid and liquid forms of sodium ethyl xanthate. However, the greatest risk to workers during use of solid sodium ethyl xanthate is at the mixing stage and this stage is not required with the liquid form. Dilution of liquid sodium ethyl xanthate to the required concentration does not involve manual handling of the liquid.

Xanthate unloading and storage

Aqueous sodium ethyl xanthate is pumped from the tanker to the storage/stock tank prior to end-use.

Xanthate solutions (35-40%) can be introduced 'neat' to the flotation circuit or may be further diluted to around 10% at the mine site to suit specific requirements. Dilution is achieved by the stoichiometric addition of water to a measured quantity of the concentrated solution (from stock tank) in a dilution tank (5,000 – 300,000 litres capacity).

At some mine sites xanthate solutions may be pumped from a holding tank over extended distances to the storage or stock tanks, which are located outdoors usually adjacent to the flotation area. The base of the stock tank may have a cone structure with a drainage point at the apex of the cone. Stock tanks are bunded to collect any spills, which are then pumped to the tailings systems. Potential for exposure during this process is therefore limited, however exposure could occur from pipeline leaks.

Flotation process

Sodium ethyl xanthate solution from the stock tank is pumped to a head tank. At some mine sites, transfer between the two tanks is automated by means of level sensors. The head tank at most sites is located above the flotation cell floor. Any overflow from the head tank is returned to the stock tank.

Remote controlled dosing pumps are used for the addition of liquid xanthates, which enter the flotation cell through closed pipes via the head tank. The solution is gravity fed from the head tank via control valves and flow meters to a series of dosage points. From these points there are a number of pipelines to addition points within the flotation cells. Addition of xanthates to the cell is via a continuous drip feed.

Although the process takes place in 'open' tanks/cells, the concentration of sodium ethyl xanthate in the tank is low and therefore release/exposure to CS₂ would be expected to be low. Atmospheric levels of CS₂ in flotation areas are

generally < 10 ppm (see PEC5). Workers involved in checking flows, the head tank or in adjusting and monitoring the pulp levels in the flotation process could be exposed to xanthate or CS₂.

Sampling

At some mine sites sodium ethyl xanthate solution from the head tank is bypassed through a parallel system into a collection cone for analysis. Dermal and inhalation exposure to sodium ethyl xanthate may occur to workers involved in the collection of samples or analysis of sodium ethyl xanthate.

Maintenance

Storage/stock tanks require periodic cleaning due to the build up of sludge. Precipitation of dissolved salts such as magnesium hydroxide and calcium carbonate and reaction of the heavy metal ions such as copper, lead, zinc and manganese with the sodium ethyl xanthate solution to form insoluble xanthates are responsible for sludge settling out in the tanks. The accumulated sludge contains trapped xanthate, which decomposes to CS₂ and alcohol. Stirring of the sludge with an air hose or 'sparger' volatilises the CS₂.

Cleaning of tanks involves complete emptying and thorough flushing with water. There is potential for worker exposure during maintenance, as sludge removal requires entry into the tank and manual removal. The frequency of cleaning storage tanks varies from once every three months to once or twice a year at different mines. In Australia around 20 workers are involved in general maintenance work for approximately 1 h per week (see PEC5).

Air monitoring

Atmospheric monitoring for sodium ethyl xanthate is not carried out at mine sites.

Random monitoring for CS₂ is undertaken at some sites, mainly using either Drager or Kitagawa detector tubes. Another reported method is charcoal tube/portable gas chromatography. Monitoring data for CS₂ at a number of end-use sites is summarised in section 10.1.3 of PEC5. The majority of analyses were below 5 ppm and although a number of readings were reported above this level, these were mainly associated with the mixing process for *solid* xanthates, which is not relevant for use of *liquid* xanthate products. No monitoring data were available for maintenance activities.

Detection tube analysis is used primarily as the method for 'spot checks'. This method provides short-term (1 -2 min duration) readings and as such is not suitable for assessment of TWA exposure levels, which requires sampling over a minimum time period, usually 4 h (NOHSC 1995).

5.2 Public exposure

Exposure to sodium ethyl xanthate and hazardous degradation products from spillage of liquid xanthates during transport may be significant due to the bulk quantities involved and the fact that containment is not as easy as for solid products. During the manufacture of sodium ethyl xanthate, the potential for exposure of the public to CS₂ vapour emissions is minimised through the use of a purpose designed caustic scrubber unit fitted to the plant stack. This unit will

remove any CS₂ vapours such that the maximum ground level concentration will not exceed the WA, DEP requirement of 42 ppb. Scrubber liquor will be returned to the process for conversion to xanthates. The plant will not generate any liquid or solid effluent. In addition, the buffer zone, between plant and residential areas, at the Coogee Chemicals site was assessed as adequate, based on potential CS₂ emissions from the plant stack.

As with solid sodium ethyl xanthate, the public is unlikely to be exposed to *liquid* sodium ethyl xanthate from its use in mining applications. Release of hazardous degradation products, including CS₂, hydrogen sulphide and ethanol, may result from residual sodium ethyl xanthate in the mineral bulk concentrate from the flotation process, which decomposes during the drying and/or smelting process. Exposure may also result from the decomposition of residual amounts of sodium ethyl xanthate remaining in the aqueous phase in tailings slurries, which are discharged into tailings dams, where the pH favours xanthate decomposition. However, tailings dams are usually situated in remote areas, with minimal risk of public exposure, either via ambient air or contamination of potable water.

6. Hazard Assessment and Risk Characterisation

Sodium ethyl xanthate decomposes on aging and is metabolised in animals and humans to CS₂. Therefore the hazards of CS₂ also need to be considered in hazard and risk assessments for sodium ethyl xanthate. In addition, CS₂ is used in the manufacture of xanthates.

6.1 Physicochemical hazards

Xanthates are classified in the ADG Code (FORS 1998) as ‘potential pyrophoric and self-heating substances’. This classification is appropriate for *solid* xanthates, which on contact with moisture/water are prone to self-combustion as a result of exothermic decomposition to CS₂ (see PEC5, Section 7), which is highly flammable.

Although *liquid* xanthates are not considered to present a hazard with respect to self-combustion, decomposition to CS₂ still occurs with an associated potential fire hazard (particularly from ‘aging’ of the product). However, due to the pH (range 7-11) of the liquid sodium ethyl xanthate product, decomposition to CS₂ is likely to be significantly slower than for *solid* xanthate products.

The recommended risk phrase for physicochemical effects for pure solid sodium ethyl xanthate, as listed in the NOHSC *List of Designated Hazardous Substances* (NOHSC 1999) is:

R15/29 Contact with water liberates highly flammable and toxic gas

Liquid xanthates do not exhibit the same hazards and the assignment of R15/29 (PEC5 Section 15.2.2) is not appropriate for 40% sodium ethyl xanthate solution (WorkCover 1999).

6.2 Fire/explosion risks

6.2.1 Manufacture

As for all plants using flammable materials, a potential fire risk exists for xanthate manufacture.

A detailed fire/explosion risk analysis was carried out for the Coogee Chemicals xanthate plant as part of the requirements for a ‘works approval’ by the Department of Environmental Protection, WA. This included a further analysis undertaken at the request of DME.

This assessment addressed the following potential risks:

- Flash fire/explosion from delivery, transfer or leakage of CS₂;

- Flash fire/explosion from CS₂ pipeline leak;
- Mixing tank explosion;
- CS₂ vapour cloud explosion;
- ‘knock-on’ effects of other plant fires to CS₂ and alcohol storage tanks; and
- Runaway reaction;

A number of different models and input parameters (e.g., failure frequencies) were used to quantify these risks. The overall level of risk i.e., chance of fatality due to process failure, at the boundary/off site was estimated to be between 10 - 20 x10⁻⁶, which is below the DEP criterion of 50 x 10⁻⁶.

During normal operation, levels of CS₂ measured at potential ‘hot spots’ around the plant are very low (all measurements below 8 ppm) and consequently, the risk of fire is also considered low.

6.2.2 Transport and end use

Although several incidents involving self combustion and adverse exposures have been reported during transport of *solid* xanthate products (mainly due to leakage of packaging), it is considered that, because the *liquid* products will be dispatched in dedicated, refrigerated, road tankers and because the levels of CS₂ vapour in tankers are likely to be low, the risk of fire should be significantly reduced.

No formal risk assessment was available for assessment of fire/explosion risks at mine sites, although it is considered that the risk of fires due to CS₂ should be significantly reduced from use of *liquid* xanthate products.

6.3 Health hazards

For a detailed hazard assessment for sodium ethyl xanthate and a review of the hazards and metabolism of CS₂, the reader is referred to Sections 8 and 9 of PEC5. This report only assesses new information and provides an overall summary of health hazards.

6.3.1 Sodium ethyl xanthate

Hazard Classification

The current recommended classification for sodium ethyl xanthate, as listed in the NOHSC *List of Designated Hazardous Substances* (NOHSC 1999) is ‘*Harmful*’ with the following risk phrases:

R21/22 Harmful in contact with skin and if swallowed

R36/38 Irritating to eyes and skin

In accordance with the List, the above hazard classification also applies to aqueous solutions of sodium ethyl xanthate above 20% (see Table 3), although the assignment of risk phrases R36/38 applies only above 25% in a mixture. This classification does not take into account decomposition products/impurities etc.

Table 3 – Health hazard classification of sodium ethyl xanthate mixtures/solutions

Concentration range/limit (% ^w / _w)	Risk phrase(s)	Overall hazard classification
≥ 25.0	R21/22, R36/38	Harmful (Xn)
≥ 20.0 - < 25.0	R36/38	Harmful (Xi)
< 20.0	not required	not hazardous

New data

A search of the literature on health effects of xanthates published since PEC5, revealed two studies which were considered appropriate for evaluation in the context of hazard and risk assessment.

Metabolism

No data were available on xanthate metabolism *per se* for assessment in PEC5.

It is known that sodium ethyl xanthate is metabolised to CS₂ due to the presence of the CS₂/cysteine (glutathione) conjugation product, 2-thiothiazolidine-4-carboxylic acid (TTCA) in urine of exposed workers.

A single metabolism study (in French) published by Merlevede and Peters (1965) was identified in the above literature search. In this study, humans and guinea pigs were dosed with various xanthate compounds, including sodium and potassium ethyl xanthate, and the amount of expired CS₂ monitored.

Following sub-cutaneous injection (70-200 mg/kg) of potassium ethyl xanthate in guinea pigs, up to 7% of the dose was expired as CS₂ after 8 h, with maximum elimination between 1 - 2 h in most animals. The rate of elimination was dose-related, however the total percentage recovered was independent of dose. A more rapid rate of elimination was seen following sub-cutaneous injection (50 and 100 mg/kg) of sodium ethyl xanthate, with CS₂ expiration complete after 6 h, with maximum elimination at 1 h (total recovery of CS₂ was not reported).

Following oral intake in human volunteers, of 150 and 250 mg sodium ethyl xanthate, a maximum rate (13 – 57 µg/m³/h) of CS₂ elimination in breath was seen between 1-2 h, with complete elimination by 6 h (total recovery of CS₂ was not reported).

The effect of alcohol on xanthate metabolism was also studied. In guinea pigs, concomitant sub-cutaneous injection of sodium diethyl xanthate and alcohol resulted in an increased rate of elimination, together with a greater total recovery of CS₂. These increases were directly related to the dose of alcohol.

An increased rate of elimination was also apparent in humans administered 250 mg sodium ethyl xanthate, following intake of 200 ml of alcohol (approximately 18% by volume), however, the lack of a suitable control group prevented quantitative assessment.

Case report

A single case report of a worker exposed to xanthate powder and solution (specific compound not specified) during the mixing process was reported by Donoghue (1998). Extensive skin contamination of the worker's chest area was evident (green staining) post exposure.

The worker developed an illness, consisting predominantly of gastrointestinal symptoms, which began 20 h after exposure and lasted for 3 days. Carbon disulfide body burden was confirmed by the detection of urinary TTCA (<4 mg/L measured approximately 68 h after exposure). Dräger tube testing, during subsequent mixing operations, recorded an airborne concentration of at least 60 ppm CS₂.

The worker was wearing cotton overalls, PVC gloves and an acid gas/particulate full-face respirator. It was not clear whether symptoms were the result of CS₂ inhalation or xanthate/CS₂ skin absorption as although the respirator did not include an organic vapour cartridge, the worker apparently did not experience any eye irritation, which suggests that the level of CS₂ within the respirator was not particularly high.

6.3.2 Carbon disulfide

The current recommended classification for CS₂ as listed in the NOHSC *List of Designated Hazardous Substances* (NOHSC 1999) is 'Toxic to Reproduction (Category 3)' with the following risk phrases:

R36/38	Irritating to eyes and skin
R48/23	Danger of serious damage to health by prolonged exposure through inhalation
R62	Possible risk of impaired fertility
R63	Possible risk of harm to the unborn child

There is no evidence from either animal or epidemiological studies to indicate a carcinogenic potential for CS₂.

In accordance with the List, the above hazard classification also applies to solutions containing CS₂ above 1% (see Table 4), although the assignment of risk phrases R36/38 applies only above 20% in a mixture. Solutions containing less than 1%, but greater than 0.2% CS₂ should be classified as 'Harmful'. This classification does not take into account other ingredients/impurities etc.

Table 4 – Health hazard classification of carbon disulfide mixtures/solutions

Concentration range/limit (% w/w)	Risk phrase(s)	Overall hazard classification
≥ 20	R48/23, R62, R63, R36/38	Toxic (T)
≥ 1.0 - < 20.0	R48/23, R62, R63	Toxic (T)
≥ 0.2 - < 1.0	R48/20	Harmful (Xn)
< 0.2	not required	not hazardous

Epidemiological data

A search of the literature on human health effects of CS₂ published since PEC5, revealed a number of epidemiological studies which were considered appropriate for inclusion in this report. These studies are summarised in Table 5. It should be emphasised that the evaluation of these studies is beyond the scope of this report and the following information is included for completeness of information.

Although a number of epidemiological studies indicate that some workers may have been exposed to levels of CS₂ lower than the current exposure standard (10 ppm / 31 mg/m³), it should be noted that the majority of these studies are retrospective in nature and as a consequence, do not provide adequate dose-response data for critical effects. Thus it is not currently possible to identify chronic NOAELs or LOAELs for such effects, as is required for the purpose of risk characterisation.

A similar conclusion was reached by US Department of Health & Human Services, in a recently published review of CS₂ (ATSDR 1996), where it is stated that “available epidemiological studies have the limitation of poor exposure measurements that are not individualised to the study participants. In addition, the exposures postulated to have occurred in these cohorts cover a wide range of levels, making extrapolations from one study to another difficult; many of these studies also document concomitant exposures to other chemicals, most notably H₂S.”

Despite the inherent problems with the available epidemiological database, ATSDR has derived an inhalation maximum risk level (MRL) of 0.3 ppm (0.9 mg/m³) for CS₂, primarily for the protection of public health. This value is based on peripheral neuropathy (minimal effects on nerve conduction velocities) in chronically exposed workers and was obtained by applying an uncertainty factor to the LOAEL of 7.6 ppm, determined in a well conducted clinical study by Johnson et al, 1983. The LOAEL represents the average exposure to CS₂, for individuals working 8 h per day, 5 days a week for a mean exposure period of 12 years.

In addition, ATSDR has derived an oral MRL of 0.01 mg/kg/d for acute exposure, based on a LOAEL of 3 mg/kg/d for early hepatic effects determined in a mouse study by Masuda et al, 1986 (ATSDR, 1996).

Table 5 – Summary of epidemiological studies/reviews on carbon disulfide available since PEC5

Industry (Country)	Number of exposed workers	Adverse health effect(s)/findings	CS ₂ monitoring	Reference
Viscose/rayon (Belgium)	120	Neurological effects (polyneuropathy)	3 - 147 mg/m ³ (1 – 47 ppm)	De Fruyt et al. (1998)
Occupational case studies (Korea)	34	Neurological effects (reduced cerebral blood flow)	Not stated	Lee and Kim (1998)
Rayon (Japan)	432	Neurological effects (reduced nerve conduction velocities)	No air sampling.	Omae et al. (1998); Takebayashi et al. (1998)
		Ophthalmological effects (microaneurysm) (>2:1 vs control)	25% urine samples > 5 mg/g TTCA*.	
		Endocrine effects (increased glycosylated haemoglobin)		
Viscose/ cellophane processing (Japan)	118	Cardiovascular effects (ECG abnormalities) (>4:1 vs control)	Up to 170 mg/m ³ (55 ppm)	Kuo et al. (1997)
Viscose/rayon (Poland)	188	Neurological effects (alpha rhythm frequency)	10-42 mg/m ³ (3 – 13 ppm) (mean annual data)	Sinczuk-Walczak & Szymczak (1997)
Xanthate mining workers (Australia)	200 (estimate)	Cardiovascular disease. Retrospective mortality study (based on data from Nurminen et al., 1982 for Finnish viscose workers). Estimated 1.28 extra deaths per year in mining workers due to CS ₂)	Not stated	Christophers and Zammit (1997)
Synthetic fibres (Poland)	119 (F)	Endocrine and reproductive effects (increased spontaneous abortion; decreased serum estradiol and progesterone and increased serum testosterone, prolactin & serotonin).	9 – 23 mg/m ³ (3 – 7 ppm)	Pieleszek (1997). Kuligowski (1996).
Viscose (Germany)	247 (M)	No adverse neurological or cardiovascular effects.	<0.2 – 65.7 ppm (0.6 - 204 mg/m ³) (median: 4 ppm/12 mg/m ³)	Reinhardt et al. (1997); Drexler et al. (1995a,1996)
Viscose/rayon (USA)	Historical data (NIOSH database)	Ischaemic heart disease. No excess risk of mortality below 20 ppm. Benchmark concentration of 16 - 18.5 ppm derived for early neurological effects (nerve MCV and amplitude ratio).	Historical data	Price et al (1996, 1997)

Table 5 – Summary of epidemiological studies/reviews on carbon disulfide available since PEC5 (Cont.)

Industry (Country)	Number of exposed workers	Adverse health effect(s)/findings	CS ₂ monitoring	Reference
Viscose/rayon (Belgium)	43-123	Hepatic effects (increased GGT) Cardiovascular effects (increased blood pressure); Neurological effects (polyneuropathy - significant < 10 ppm); Ophthalmological effects (microaneurysm - significant > 10 ppm); Reproductive effects (significant effects on libido/potency – no effects on fertility)	4 - 112 mg/m ³ (1 – 36 ppm)	Vanhoorne et al. (1992, 1994, 1995, 1996)
Not stated (Poland)	114	Neurological effects (CNS – cortical atrophy); Cardiovascular effects (increased cholesterol);	0-65 mg/m ³ (0 – 21 ppm)	Chrostek Maj & Czechtoko (1995)
Viscose/rayon (China)	163	Neurological effects (polyneuropathy in 13-53% workers)	40-67 ppm (124 – 208 mg/m ³)	Chu et al (1995)
Viscose/rayon (Italy)	493	Neurological effects (behavioral disturbance at levels <8 mg/m ³)	Historical data	Cassitto et al (1993)

* biological exposure index for CS₂ adopted by ACGIH

F= females

M = Males

6.3.3 Summary

Xanthates are metabolised in humans and animals to CS₂. Animal data for potassium ethyl xanthate indicate that up to 7% of dose may be eliminated as CS₂ in breath. The elimination vs time curves for sodium ethyl xanthate in humans and guinea pigs indicate that biotransformation to CS₂ is not saturated at doses studied (250 mg or 3.5 mg/kg in humans).

Alcohol increases the rate and extent of CS₂ elimination in breath in guinea pigs. Similarly, alcohol increases the rate of CS₂ elimination in humans, however, total recovery (extent) was not reported. Evidence also exists that CS₂ may bioaccumulate in animal and human tissues (ATSDR 1996; Cox et al., 1998).

The critical health effects from exposure to sodium ethyl xanthate in humans and animals are eye and skin irritation and possible neurological effects.

Acute effects, mainly gastrointestinal and CNS, were reported in one xanthate worker which were associated with possible inhalation and dermal exposure. Retrospective monitoring indicated that exposure to CS₂ levels may have been in excess of 60 ppm (187 mg/m³).

The available animal and human data do not permit the determination of a NOAEL for repeated/chronic exposure (oral or inhalation) to sodium ethyl xanthate.

In 30 day inhalation (aerosol) studies with potassium amyl xanthate (see PEC5, section 8.1.8), hepatotoxic effects were seen in dogs and mice at 23 mg/m³ (7.5 ppm), and nephrotoxic effects in rats at 252 mg/m³ (81.5 ppm). No long term (chronic) studies or studies for genotoxicity, sensitisation or reproductive effects were available for assessment of either sodium ethyl xanthate or analogues.

It is generally considered that adverse effects from exposure to xanthates (in humans and animals) are associated with CS₂ toxicity. It is not known what contribution to human toxicity is likely from inhalation/dermal absorption of CS₂ *per se*, as a xanthate decomposition product, and CS₂ as a xanthate metabolite. Effects due to the parent xanthate compound or other metabolites might also contribute to overall toxicity.

If metabolism to CS₂ is associated with critical effects, then the limited data available on xanthate metabolism indicates that similar toxicological profiles might be expected for animals and humans.

Animal and human studies indicate that the nervous system is the critical target organ for CS₂ from inhalation exposure. Apparently only one chronic inhalation study has been carried out in animals for CS₂ and there are no chronic animal or human data pertaining to neurological effects following dermal exposure (ATSDR 1996).

Notwithstanding the available epidemiological data, it has generally been considered that chronic adverse effects in humans from inhalation exposure to CS₂ are associated with levels in excess of 10 ppm², although further, more

² The NOHSC national exposure standard.

refined dose-response data is required in order to fully characterise chronic NOAELs or LOAELs.

6.4 Health Risk Characterisation

The characterisation of risks associated with exposure to solid or liquid sodium ethyl xanthate, is particularly difficult, due to the lack of adequate repeat dose toxicological and exposure data available for either sodium ethyl xanthate or analogues. Therefore, for the purposes of estimating potential health risks, it was considered appropriate to base estimates on available exposure data for CS₂.

As a full hazard assessment of CS₂ was outside the scope of this report and due to the fact that some epidemiological studies indicate that critical effects may occur at lower exposure levels than previously indicated, the following risk evaluations are of a qualitative nature. A major consideration in this assessment is that most epidemiological studies for CS₂ have been carried out on occupation populations exposed on a daily basis for many years, which is an unlikely scenario for workers involved in xanthate manufacture and use.

6.4.1 Occupational risks

Manufacture

Carbon disulfide monitoring data (see Table 2) are available for various sites/occupational scenarios during manufacture of sodium ethyl xanthate. It should be noted that these data are not representative of TWA exposures, which are generally required for assessment of chronic health risks.

The plant does not generate any solid or liquid effluent, although CS₂ emissions from the scrubber may be > 2000 ppm. However, ground level monitoring data during and after CS₂ addition to reactor, indicate that levels are below the limit of detection (<3 ppm). Given that workers are unlikely to be exposed for long time periods, even to these low levels, during normal plant operations, both acute and chronic risks are considered to be low.

Higher exposures, up to a few hundred parts per million, are likely during plant maintenance and during sampling of reactor product, although limited monitoring data were available for assessment. The wearing of personal protective equipment, particularly adequate respiratory equipment should eliminate chronic health risks from such exposures, however, the failure of such equipment may present an acute health risk.

No monitoring data were available for tanker filling activities. Although pipeline linkages from plant to dispatch tankers are designed to prevent leakage during connection/disconnection, CS₂ measurements around road tankers indicate that levels may be up to 30 ppm. As potentially exposed workers, including the tanker driver, do not wear respiratory protection during filling operations, it is considered that such operations may present an acute health risk. However, due to the relatively low level of exposure and the anticipated infrequency of filling operations, chronic health risks are considered unlikely.

Transport, storage and end use

For information on risks during transport, storage and use of solid sodium ethyl xanthate products, the reader is referred to sections 10.1.2 – 10.1.3 and 11.1.1 – 11.1.2 of PEC5. For details of additional incidents involving transport and use of xanthate products see Appendix 2.

Routine monitoring for CS₂ is not carried out during transport. However, as mentioned above, filling/unloading of tankers may be associated with exposures up to 30 ppm, with associated acute health risks.

Although air monitoring for CS₂ is carried out at end-use mining sites, the nature of the sampling is inadequate for the purpose of estimating TWA exposures (see Sections 5.1.1 & 5.1.3). In addition, there is a potential for dermal exposure to xanthates during operational procedures, which may increase body burden of CS₂.

Available air monitoring data for sites where *solid* xanthates are used indicate that atmospheric levels of CS₂ are generally below 10 ppm, including mixing areas and flotation tanks. However, the ‘open’ nature of these processes may lead to transient high levels, with concomitant acute health risks. Although levels of CS₂ in excess of 60 ppm were measured at one site in the vicinity of a mixing worker, this was associated with the use of solid xanthates. Such exposure levels are unlikely when handling liquid xanthate products and acute inhalation risks are considered to be significantly reduced when using *liquid* xanthate products.

Chronic risks to workers are more difficult to characterise due to the lack of TWA exposure data, however given that workers are unlikely to be exposed for long time periods during routine operations, risks are likely to be low. More refined monitoring data would assist firmer conclusions.

As with manufacture, workers considered to be at most risk are those involved in maintenance activities (e.g. cleaning of storage vessels and maintenance of feed systems to flotation cell), although wearing of appropriate personal protection should minimise these risks.

6.4.2 Public health risks

A quantitative risk assessment, relating to the Kwinana Tank Terminal, estimated the risk of fatality due to plant failure as 10×10^{-6} at the boundary of the facility. This is below the WA DEP guideline level of 50×10^{-6} .

Carbon disulfide emissions during the manufacture of sodium ethyl xanthate are not expected to result in ground level concentrations above 42 ppb, the odour threshold for CS₂. Human exposure occurs primarily through inhalation of CS₂ in air; however, no adverse health effects have been reported at air levels below 42 ppb, in spite of uptake of measurable levels of CS₂ (ATSDR, 1996).

Based on the available information and provided that appropriate occupational controls on release during transport and use (from plant and degradation products at mining sites) are in place, *liquid* sodium ethyl xanthate should not pose a risk to public health and is likely to present a lower risk than *solid* sodium ethyl xanthate.

If conditions of use are varied, greater exposure to the public may occur. In such circumstances, further information may be required to assess public health risks (see Section 11).

6.4.3 Uncertainties and assumptions in health risk estimates

An integral part of the risk characterisation process is an evaluation of the uncertainties and assumptions in the risk assessment process, the nature and significance of which, need to be taken into account in ensuing risk management initiatives.

The main uncertainties/assumptions inherent in the risk assessment/characterisation for sodium ethyl xanthate are as follows:

Inadequate data

- Lack of toxicity data, including human health effects, for sodium ethyl xanthate, particularly from chronic exposure;
- Lack of dose-response data in humans and animals, particularly for chronic low level inhalation and/or dermal exposure to CS₂;
- Lack of pharmacokinetic data for xanthate absorption and metabolism in both humans and animals;
- Lack of TWA exposure (for CS₂) data for routine activities;
- Lack of data on potential for dermal exposure, particularly during end-use processes.

Assumptions

- That the main health risk from xanthate handling and use is from exposure to CS₂;
- That inhalation is the main route of exposure i.e. that dermal exposure to CS₂ and CS₂ body burden from xanthate metabolism are negligible;
- That the available monitoring data for CS₂ are representative of actual TWA personal exposures;
- That the available monitoring data for CS₂ at plant and end-use locations is representative i.e., for other plants/sites where different conditions, such as weather conditions, scrubber efficiencies, exposure scenarios etc. may apply.

7. Environmental Assessment

7.1 Sources of environmental exposure

7.1.1 Manufacture

Release to the environment may occur from accidental spillage of the individual reactants used in the manufacture of sodium ethyl xanthate, or during manufacture, transfer and end use of the final product. Methods of transport and storage of the individual raw materials and final product are outlined in Section 5.1.2. All release estimates in this section assume maximum production of 5000 tonnes per annum of sodium ethyl xanthate, anticipated by the applicant.

Carbon disulfide (CS_2) is received in isotainers by road to the plant. The isotainers are connected directly to the xanthate plant ready for use. No cleaning of empty containers is required prior to return to supplier.

Sodium hydroxide and ethyl alcohol are pumped from delivery containers to bunded storage tanks. Any release from pipe connections during transfer is expected to be minimal.

The process of manufacture of liquid xanthates is outlined in Section 5.1.1. The system is fully closed and automated. The applicant states no solid or liquid effluent is generated and any unreacted or incomplete reaction products are recycled back into the process.

CS_2 is highly volatile. A purpose designed caustic scrubber unit will remove any CS_2 vapours. Scrubber liquor will be returned to the process for conversion to xanthates. Emissions from this source are expected to be negligible.

The plant has both primary and secondary containment measures. It is built on an impermeable concrete slab with appropriately sized bund walls. This will limit movement of any spills on site to groundwater, which is only 3-4 metres below the xanthate plant.

In the event of fire, firewater is to be retained within the confines of the plant and its associated storage area. Any firewater used in excess of the plant bunds retention capacity would be pumped via the underground sump to a remote holding tank outside the main plant area.

Accumulation or the rainwater within the plant area will be removed as necessary from the various sumps and pumped to the remote holding tank prior to testing before discharge to a soak well.

These factors indicate negligible release of the sodium ethyl xanthate during manufacture or storage at the manufacturing plant.

While some release may occur to the atmosphere through hose connections, the volatility of the aqueous salt solution will be relatively low, so atmospheric releases of sodium ethyl xanthate should not be significant. In addition, levels of CS_2 in xanthate solution at plant are likely to be very low (see section 4.1).

7.1.2 Transport

The initial assessment was for sodium ethyl xanthate being imported and transported in solid form. The risk of exposure to the environment in the case of accidental spillage is far less in this instance where solids are relatively easily recovered.

The manufacture of liquid sodium ethyl xanthate will lead to an increased risk of environmental exposure in the event of accidental spillage. Transport from the production site to areas of end use in Western Australia will be by road with tankers having a 25 tonne capacity. Where double road train configuration is used, up to 50 tonnes may be transported at a time. In the case of an accident, a maximum of 25 tonnes of 40% sodium ethyl xanthate solution could be released from a single point source. This scenario is discussed further below.

7.1.3 End use

Sodium ethyl xanthate is used as a collector during the processing of sulphide ores by flotation, a process that involves addition of the reagent to aqueous slurries of crushed and finely ground ore contained in flotation tanks. Air is blown through the slurry. In general, a series of such tanks is used. During the use of sodium ethyl xanthate in the flotation process the mineral particles become separated as a froth from the tailings, which settle at the bottom of the flotation tank.

The froth (float) is collected and dried at 600°C, while the tailings are conveyed as a slurry to a tailings dam where they settle, dry and consolidate. Spills and washings would also be directed to tailings dams. Tailings typically have a solids content of about 30%. In some operations, tailings may be intercepted in settling tanks so that wastewater containing low concentrations of xanthates can be recovered for reuse in flotation. Xanthates in the tailings are not monitored, but most would be expected to be retained in the froth. Drying at 600°C would destroy xanthates in the froth.

7.2 Environmental fate

It was calculated that at equilibrium, in the order of 99.95% of this chemical will partition to water, with only around 0.005% partitioning to air (Trent University, 1998). This assumed a vapour pressure of 1 Pa (indicative of moderate volatility), LogPow = 0, and a melting point of 0°C. While Kow and vapour pressure have not been tested, these values are considered conservative.

Hydrolysis will be a significant factor in determining the environmental fate of sodium ethyl xanthate. In neutral or mildly alkaline solutions, sodium ethyl xanthate decomposes to the alcohol, carbon disulfide, sodium carbonate and sodium trithiocarbonate, the two salts arising from neutralisation of carbon disulfide with the sodium hydroxide liberated. In more strongly alkaline media, hydrogen sulphide is liberated. However, strongly alkaline conditions are unlikely to be encountered under the conditions of use in the mining industry. The half-life at pH 7 at 25°C is reportedly about 260 h, increasing to over 500 h in the pH range 8 to 11 (Rao, 1971).

The IUCLID³ datasheet has provided an abiotic degradation half life of 3 days at 25°C and pH 8.5 for potassium isobutyl xanthate. No data are available on the test method. Other results from this reference indicate half lives around 13 days at 40°C and 100 days at 20°C, although no information is available on the pH of these solutions.

Sodium ethyl xanthate is hydrolytically unstable when exposed to acidic conditions, reverting rapidly to ethanol, carbon disulfide and caustic soda, and therefore will not persist in the acidic environment of tailings dams. If discharged to waterways, the chemical would be likely to persist for at least some days, hydrolysing only slowly in this more neutral environment. However, it is not expected to bioaccumulate in view of its ionic character.

The IUCLID datasheet describes an aerobic biodegradation test for potassium isobutyl xanthate following the OECD Guide-line 302B “Inherent biodegradability: Modified Zahn-Wellens Test”. The results showed degradation of 98% after 12 days, with approximately 30% after 3 h and 75% after 5 days. These results suggest that sodium ethyl xanthate will be inherently biodegradable and it is not expected to persist in the environment.

Sodium ethyl xanthate is not expected to contaminate the environment where ore tailings are confined to well constructed tailings dams. Modern tailings dams are sealed with special geo-textile lining fabric designed to prevent influx or efflux of water. Most will be retained on sulphide minerals and destroyed when they are dried after flotation. Minor residues that remain associated with tailings will be destroyed by hydrolysis in tailings dams.

Sodium ethyl xanthate in tailings have been discharged directly to waterways in exceptional circumstances. This practice was allowed to occur in Queenstown, Tasmania, which operated under ministerial exemption from State discharge requirements. Over 75 years of discharge the Queen and the King Rivers became devoid of aquatic life. Discharge from Mt Lyell copper mine ceased in 1995, when a new operator, Copper Mines of Tasmania (CMT) took over the lease. CMT restarted mining in December 1995 in accordance with the Copper Mines of Tasmania Pty Ltd Agreement Act, 1994. A tailings dam was constructed and tailings are no longer discharged to the rivers. The Australian Mining Industry Council advised the Environment Protection Agency in January 1995 that all Australian mines operating concentrators had tailings dams.

Releases of CS₂ to the wider environment as a result of industrial activity are expected to be primarily to the atmosphere, where it will be quickly dispersed. In the case of release to surface waters, CS₂ would be expected to move rapidly to the atmosphere, and the evaporation half life from a saturated solution has been estimated to be 11 min (ATSDR 1997). In the atmosphere, the half life of CS₂ through reaction with hydroxyl radicals is estimated at 1-10 wk and through atmospheric oxidation, the half life is estimated to be about 12 d (ATSDR 1997). This is not sufficient time to reach the stratosphere, although a significant degree of atmospheric transport can be expected in this time.

³ Results in the IUCLID data sheet (International Uniform Chemical Information Database – European Commission) are from non-confidential industry data and have not undergone any evaluation or validation by the European Commission.

7.3 Environmental effects

For details on environmental effects, the reader is referred to Section 12.3 and 12.4 of the PEC5 Report.

Information from the IUCLID data sheet for CS₂ indicates slight toxicity to fish, aquatic invertebrates and algae. The only significant exposure expected to the environment would be through the atmosphere, where CS₂ will be quickly dispersed. One test outlined in the IUCLID data sheet indicates low toxicity to terrestrial plants, although this test was based on the chemical in solution.

Further test results were obtained from the IUCLID data sheet for potassium isobutyl xanthate which may be used as a surrogate for sodium ethyl xanthate in the absence of other information. These studies have not undergone any evaluation or validation by the European Commission and were not available (being unpublished) for assessment, but the results reported may be used as a guide to the toxicity of sodium ethyl xanthate and are presented below. Results indicate that potassium isobutyl xanthate is slightly toxic to fish under acute exposure. A semistatic test on *Salmo salar* gave a 96 h LC₅₀ of 35-54 ppm, while a static 96 h test to *Brachydanio rerio* reported an LC₅₀ of 10-100 ppm.

Two 24 h *Daphnia magna* tests are reported, both following OECD Guide-line 202, part 1. The results indicate this chemical is moderately toxic to aquatic invertebrates with an EC₅₀ of 3.6 and an EC₉₅ of 11 ppm. A single 72 h test on the algae *Monoraphidium griffithii* demonstrated high toxicity with an EC₅₀ of 0.325 ppm. These figures are within the region of those reported in the initial assessment which also showed isobutyl salts to be less toxic than shorter chain xanthates.

A 14 day growth rate test on the aquatic plant *Lemna minor* is provided in the IUCLID datasheet. The results are presented in German. Interpretation of the results suggests that the radioactive half-life in the water is 2.57 days (initial concentration of 20 ppm). It appears that at a concentration of 10 ppm there was a reduction in root length around approx. 60%, and a reduction in leaf number of approx. 30%. These reductions in root length and leaf number increase to 85 and 75% when the concentration is increased to 20 ppm.

Toxicity of potassium isobutyl xanthate to bacteria is also covered in the IUCLID datasheet. 15 minute exposure to the bacteria *Photobacterium phosphoreum* showed high toxicity with an EC₅₀ = 0.65 ppm. However, when bacteria from a domestic water treatment plant were tested at 24 h exposure, it appears toxicity was not demonstrated in the range of 100-1000 ppm, although the end point reported was not a standard ecotoxicological hazard assessment assay.

To determine a predicted no effect concentration (PNEC) in water, an assessment factor of 10 is used. While there is a lack of chronic data available for liquid sodium ethyl xanthate, which may justify the use of a higher assessment factor (eg, 100), there are extensive results available for several xanthates including solid sodium ethyl xanthate, and results tend to be in agreement. The most sensitive species tested was the emerald shiner (*Notropis atherinoides*) with an LC₅₀ reported to be in the range of 0.01-0.1 ppm (see original report). Therefore, a PNEC of 1 µg/L is determined for the aquatic compartment.

7.4 Environmental risk

Xanthates have not been subjected to regulatory action in any other country. A Swedish proposal to select candidate substances for general restrictions on use identified a number of xanthates as being potentially dangerous for the environment (Lars Freij, 1993). However, no further investigations were conducted as several xanthates were no longer used in Sweden, and use of those that remained was not widespread, being confined to a few users in the mining industry.

7.4.1 Atmosphere

No experimental data on environmental organisms exposed to xanthates or CS₂ through the gas phase were available for assessment, so it is not possible to conduct a risk assessment for the atmosphere.

However, as calculated earlier, partitioning of xanthates to the atmosphere is expected to be negligible, so the potential for adverse impacts on the atmospheric compartment from the use or accidental spillage of this product is considered low.

Releases of CS₂ to the wider environment, as a result of industrial activity, are expected to be primarily to the atmosphere, where its half life through reaction with hydroxyl radicals and through atmospheric oxidation (ATSDR 1997) is not sufficient time to reach the stratosphere. However, a significant degree of atmospheric transport can be expected in this time.

7.4.2 Accidental spillage

The manufacture of liquid xanthates in Australia has implications for movement in the environment, particularly to the aquatic compartment, in the event of spillage.

The impact of an accidental spill can be illustrated. Flow rates in many Australian rivers can be negligible during the summer months. Therefore, a worst case spill will involve the chemical being released to a lentic body of water. The end product will be dispatched from the manufacturing plant to mining sites in road tankers with 25 tonne capacity. An accident involving rupturing the tank (worst case scenario) and resulting in only 10% (1000 kg product in a 40% solution) release to a standing body of water 15 cm deep with a surface area of 1 ha (1.5 ML of water) will lead to a concentration in the water of over 650 ppm (PEC – Predicted Environmental Concentration). In the event of a minor spill defined by the applicant to be 100 kg or less, the PEC could be as high as 65 ppm.

The PEC/PNEC is calculated to be 6.5×10^5 which indicates a risk that can not be mitigated. If this release were to enter a slow moving stream, it would require dilution in the order of 650000:1 before the potential hazard is considered acceptable. Even with a minor spill, the PEC/PNEC could be as high as 6.5×10^4 , still indicating a risk which can not be mitigated, and which would require dilution of 65000:1 to be at levels considered safe to aquatic organisms.

To truly determine the risk, the probability of such a spillage occurring needs to be considered. The calculation above shows that in the event of accidental spillage, the hazard to the environment is predicted to be very high when the aquatic compartment is exposed.

On the basis of the estimated number of journeys per year, the total distance traveled can be determined. This distance is then combined with the accident rate per km to give the annual accident rate for the transport of the chemical. An Environmental Impact Statement (EIS) for the Cowal Gold Project has conducted work on the likelihood of transport accidents including xanthates. Work performed by ANSTO Safety and Reliability, where available data on truck accident rates were reviewed, was used. On the basis of this review, an accident frequency of 1×10^{-5} per km was chosen for the EIS. It was further assumed that 30% of accidents result in spills (Resource Strategies, 1998).

The maximum annual production expected at the Kwinana site is 5000 tonnes. If it is assumed that the average distance between the manufacturing plant and end use site is 450 km, then between 45000 km (50 tonne road tankers) and 90000 km (25 tonne road tankers) will be traveled each year. It can be seen that if all journeys are conducted in 25 tonne tankers, the probability of an accident occurring in any one year is significant, and these calculations suggest that an accident during transport of sodium ethyl xanthate may be expected every one to two years, with a spill occurring every three to six years. This highlights the need for adequate instructions for control of spills and clean up in the event of an accident.

The applicant has advised that road tankers are specifically engineered and designed not to rupture or cause major spillages in the event of an accident, and in their 15 years of experience in the transport business, there have been no major tank ruptures or spillages. This may suggest the above calculations are conservative, but are considered necessary to try and quantify the risk involved, particularly to the aquatic environment. It has been demonstrated that even in the case of a minor spill to lentic or slow moving water bodies, the risk to aquatic life may be serious.

It was considered that the levels of CS₂ likely to be present during transport (see section 4.1) are insufficient to pose an environmental risk.

7.4.3 End use

Assuming a treatment rate of 500 g sodium ethyl xanthate per tonne of feed, 1% loss to tailings and 30% solids content in the tailings slurry, the concentration of sodium ethyl xanthate in the slurry will be in the order of 5 g in 3.3 tonnes, or about 1.5 ppm. These predictions are consistent with measured values in the range of 0.2 to 1.2 mg/L reported by Hawley (1977). Concentrations of sodium ethyl xanthate likely to found in the tailings slurry may be toxic to aquatic fauna. Such waste streams should therefore not be discharged to waterways.

As noted above, in well-managed mining operations, tailings from ore processing are excluded from waterways through retention in tailings dams, where any xanthates that they may contain decompose. Ore tailings in themselves can have severe detrimental impact on stream ecology, as exemplified by the deaths of the Queen and lower King Rivers in Tasmania.

When suitable precautions as outlined in the recommendations of the PEC5 report are taken to avoid entry of tailings to waterways, the environmental hazard of the end use of sodium ethyl xanthate can be described as minimal in view of the low environmental exposure and limited persistence.

Sodium ethyl xanthate is clearly a bioactive compound that should not be released to water. However, measures (on discharge of waste streams) currently employed in good mining practice are expected to minimise potential risks.

8. Occupational Risk Management

This section comprises mainly of an assessment of initiatives already implemented for controlling hazardous exposures to workers during manufacture, transport and end-use of liquid sodium ethyl xanthate. Certain of these initiatives will also reduce hazardous exposures to the public and the environment.

Where relevant, risk management measures have been assessed according to the NOHSC National Model Regulations for the Control of Workplace Hazardous Substances (NOHSC, 1994a). In addition, other Standards and Codes have been considered where relevant.

8.1 Workplace control measures

In general, the control of worker exposure to any hazardous substance should be achieved through the following hierarchy:

- elimination and substitution
- isolation
- engineering controls/equipment design
- safe work practices; and
- personal protective equipment

These measures are not mutually exclusive and effective control usually requires a combination of control strategies.

8.1.1 Elimination and substitution

The major hazard associated with sodium ethyl xanthate use, is CS₂, which is a degradation product of all xanthates. Because of the reduced propensity for degradation of liquid sodium ethyl xanthate, it is considered that the transport and use of liquid xanthate products is likely to lead to a reduction in potential health and fire risks that have been associated with the solid xanthate products.

Sodium ethyl xanthate has been substituted by some end-users, with other xanthate products that have lower self-heating and degradation potential. However, it is reported that particular xanthates are more specific for certain minerals in flotation applications and it is not known whether sodium ethyl xanthate could be substituted in all applications. In addition, it is not known whether other xanthates currently being used as substitutes, present a lower intrinsic health hazard than sodium ethyl xanthate.

8.1.2 Isolation

The overall production of sodium ethyl xanthate can be described as an isolated process as the charging of the mixing tank and reactor is an automated closed process.

Transportation of aqueous xanthate products by tanker provides a higher degree of isolation than for transport of solid xanthates in drums/bulker bags, with an associated reduction in risk of fire/leakage. However, an increased risk of environmental contamination from spillage would be expected.

8.1.3 Engineering controls

To minimise worker and environmental exposures to sodium ethyl xanthate, and other reaction materials, in particular CS₂, and the risk of fire/explosion, the following controls have been implemented at the Coogee Chemicals plant in WA:

- Storage tanks for liquid raw materials i.e., ethyl/amy alcohol and sodium/potassium hydroxide and alkaline xanthate product constructed (including bunding) in accordance with AS 3780;
- Storage tanks for alkaline xanthate product kept cool (below 18°C recommended) and vented to alkaline CS₂ scrubber;
- Carbon disulfide iso-tainers located in a purpose designed containment area, including fire wall and bunding with fixed water level (18 inches recommended), constructed in accordance with AS 3780;
- Transfer of ethyl or amy alcohol from storage tanks effected using a seal-less magnetic drive pump;
- Transfer of sodium hydroxide solution from storage tank effected using a centrifugal pump with bypass return line to storage tank;
- Transfer of CS₂ from iso-tainer controlled by multiple valve system with 'drive head' removal in the event of leak or when any part of the circuits breach programmed operating conditions;
- Nitrogen gas padding for all vessels, including CS₂ iso-tainers, where ignitable CS₂ vapour may be present;
- Automatic (heat activated - fusible loop tubing) deluge system for fire control, installed around CS₂ iso-tainers and alcohol storage vessels;
- Installation of 'sample return facility' in reactor;
- Reactor cooled by internal water cooled system to maintain reaction temperature < 30°C;
- Explosion vents on reactor;
- Caustic scrubber to remove CS₂ vapour emissions from reactor – scrubber liquor returned to process;
- Dry (butterfly) linkages in all pipelines to prevent leakage during connection/disconnection;
- Transfer of xanthates (at plant and end-use site) to and from dispatch tanker effected using a 'chiller dilution module' (P&ID) with seal-less magnetic drive pump;
- Grounding of all tanks and plant equipment to reduce fire hazard;
- Specialised electrical drives (TX6 rated) used in plant equipment to reduce heat/fire hazard;

- Process controlled by automated process logic control system located in the plant control room;
- Alarms programmed into process logic control system to warn of breaches in operation procedure, with automatic interlocks to interrupt production until correction effected; and
- Manual emergency response alarm, linked to site evacuation and fire warning systems (located in the plant control room).

8.1.4 Safe work practices

To minimise risks to workers involved in manufacture and transportation, the following safety measures have been implemented:

General measures

- Integrated Risk Management System (IRMS)⁴ to be designed and implemented to meet the requirements of the PACIA Responsible Care Program and the NOHSC Standard for Major Hazardous Facilities;
- HAZOP study undertaken for xanthate plant design;
- Emergency response plan (ERP) developed for xanthate plant;
- Regular auditing of safety plans and standard operating procedures (SOPs) in accordance with the provisions of ISO 9002:1994 (AS/NZS ISO 9002:1994);
- Plant personnel to work under safety conditions and procedures for plant maintenance (documented in SOPs); and
- Product stewardship arrangements with supplier of CS₂ - certification obtained for use.
- Appropriate handling of flammable and combustible liquids (AS1940).

Specific measures

- Access to plant compound restricted to authorised personnel only;
- Prohibition of all sources of ignition;
- Good personal hygiene practices;
- Plant to be made safe according to Zone 1 Class1 level, including static discharge provisions;
- Process alarm system tested at least once per week and verified in accordance with manufacturers recommendations;
- Vapour space of mixing vessel to be purged with nitrogen to maintain inert atmosphere in reactor throughout the manufacturing process with venting to the caustic scrubber;
- Tanks drained from lowest point to allow continuous drainage of any accumulated CS₂;

⁴ **Integrated Risk Management System (IRMS)** – is the comprehensive system for managing safety at a major hazard facility and which sets out: the safety objectives; the systems and procedures by which these are to be achieved; the performance standards which are to be met; and the means by which adherence to these standards is to be maintained.

- Regular inspection of CS₂ iso-tainers, including ESD valve and water layer depth in containment bund;
- Routine air monitoring for CS₂ carried out at various plant locations, including exposure 'hot spot' locations;
- Regular maintenance of all critical plant equipment and fittings (controlled by a computerised preventative maintenance program – IMPACT); and
- Regular inspection of fire fighting equipment;

8.1.5 Personal protective equipment

The appropriate Australian Standards used in the selection of personal protective equipment include: respiratory protection (AS 1319, 1715/1716), gloves (AS 2161), safety glasses (AS 1336/1337) and safety shoes (AS/NZS 2210).

Coogee Chemicals report that for general entry to plant, workers must wear:

- Full cover cotton shirt and trousers;
- Antistatic jackets;
- Antistatic boots;
- Antistatic gloves (if required); and
- Safety glasses.

For general entry into the plant, Coogee reported that workers are required to carry portable '5 min escape units', that supply fresh air in the event of an accident. If work is required on plant which may expose workers to high levels of CS₂ vapours, special breathing apparatus, which is hooked into a portable air supply line (located within plant) is required.

8.1.6 Other control measures

- Safety shower/eyewash installations in loading/unloading area and within plant;
- Fire hydrants with attendant equipment (situated within 50 metres of plant).

8.2 Hazard communication

8.2.1 Education and training

The following information, provided by Coogee Chemicals, relates to training and emergency response plans for workers involved in the manufacture and transport of liquid xanthates.

Plant operating procedures

Training in the safe and efficient operation of the plant is based on the standard operating procedures (SOPs) developed from the HAZOP evaluation.

Operating personnel are specifically trained in:

- Safe handling of CS₂, ethyl alcohol and liquid xanthates;
- First aid (in relation to the above chemicals); and

- Correct use of all safety equipment, including SCBA and all emergency response procedures.

Emergency response plan (ERP)

Coogee Chemical's existing Emergency Response Plan is currently being updated in line with its Integrated Risk Management System (IRMS) objectives, in particular to include procedures to address serious reagent (particularly CS₂) or xanthate release. These procedures are being developed under the following headings:

- Use of and raising alarms on site;
- Arranging and handling an evacuation;
- Selection and correct use of SCBA and PPE;
- Selected actions for the control and management of CS₂ leaks;
- Notification and reporting procedures in the event of a reagent or product leak; and
- Correct procedures in the event of a fire.

In the event of a spillage beyond the confines of the production plant, an ERP, including clean up, is being developed for the transport of both liquid xanthates and CS₂ and will be incorporated into the plant Safety Report (see Section 8.3.3).

Additional ERP measures include the availability of an on site 24 h emergency contact phone number and membership of the Kwinana Industries Mutual Aid (KIMA) group.

Public awareness

Public awareness has been proactively sought both prior to and following the commissioning of the Kwinana xanthate plant. This has been achieved by circulation of a Newsletter in 1996 to Kwinana residents and public meetings held in 1997, with the Kwinana Community Advisory Panel (KCAP), which comprises of representatives from the Community of Rockingham and Kwinana (CORK) and the Kwinana Watchdog. The Kwinana Town Council also advertised the plant proposal in the local community newspapers, with a formal offer by Coogee Chemicals to address any interested forum as requested by the Council.

8.2.2 Material Safety Data Sheets (MSDS)

MSDS are the primary source of information for workers involved in the handling of chemical substances. In accordance with NOHSC model regulations (NOHSC, 1994a) and State/Territory legislation, manufacturers/suppliers are required to provide MSDS to both workers and to customers.

MSDS for (i) sodium ethyl xanthate solution, (ii) sodium iso-butyl xanthate solution, and (iii) carbon disulfide were submitted for assessment by the applicant. For the purposes of this report, only the MSDS for sodium ethyl xanthate was evaluated. This MSDS was assessed against the NOHSC *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC, 1994b).

Adequate information was available in the MSDS on health hazards/first aid, precautions/procedures for use, storage and fire fighting and emergency contact details.

Incorrect data identified in the MSDS was the Dangerous Goods Class for solid xanthates (4.3 instead of 4.2).

Also, although not a requirement under the NOHSC Code of Practice, no reference was provided in the MSDS to relevant documentation developed by the manufacturer e.g. standard operating procedures (SOPs) or emergency response plans (ERP).

A suggested (sample) MSDS for sodium ethyl xanthate (40% solution), prepared from the existing MSDS provided by Coogee Chemicals and information made available for assessment, is presented at Appendix 4.

8.2.3 Labelling

Liquid sodium ethyl xanthate is currently distributed by road tanker directly from plant storage vessels to end-use holding tanks and hence, no product labelling is required under the NOHSC Model Regulations (NOHSC 1994a).

Should the current method of transport for liquid xanthates change or the product be decanted in the workplace, such that a potential for handling exists for workers, then labelling of containers according to the NOHSC *National Code of Practice for Labelling of Workplace Substances* (NOHSC 1994c) would be required. The requirements of this Code (which is adopted in State/Territory legislation), as they apply to liquid sodium ethyl xanthate, are presented in Appendix 3.

8.2.4 Placarding

Placarding of hazardous substances is required for *storage and transport* of hazardous substances and is covered by State/Territory placarding and dangerous goods legislation, respectively, and is needed to alert emergency services, workers and the general public to their hazardous nature.

The NOHSC *Guidance note for storage of chemicals* (NOHSC 1990) and draft *Standard for Storage and Handling of Dangerous Goods* (NOHSC 1998) default to the Federal Office of Road Safety Dangerous Goods Code (FORS 1998) for placarding requirements for *stored* chemicals.

Currently, the ADG Code only specifies a dangerous goods classification appropriate for *solid* xanthates i.e. Class 4.2 (Packing Group II) - substance liable to spontaneous combustion (FORS 1998).

The WA Department of Minerals and Energy (DME) and NSW WorkCover have advised that dangerous goods classification and placarding is inappropriate for a 40% ^{w/w} aqueous solution of sodium ethyl xanthate. As such, placarding of sodium ethyl xanthate storage vessels at Coogee Chemicals, WA site, is currently limited to the chemical identity. Placarding of transport tankers is currently in accordance with the generic⁵ requirements for both solid and liquid xanthates in the ADG Code, as follows:

⁵ Sodium ethyl xanthate is not listed specifically in the ADG Code.

- Shipping name – XANTHATES;
- United Nations (UN) number – UN 3342;
- Hazchem code – 1[Y];
- Emergency services contact details; and
- Specialist advice, including special provisions, Australian contact details and Emergency Procedure Guide.

Currently the minimum requirements are that site storage vessels should be placarded with UN 3342, Class 4.2.

In July 1995, representation was made by the Australian ACTDG to the UN Subcommittee of Experts on the Transport of Dangerous Goods (SETDG), proposing a change in classification for xanthates from the previous classification (Class 4.3) to Class 4.2, with a Subsidiary Risk Class 6.1 (toxic/harmful). Sodium ethyl xanthate meets the ADG Code ‘dermal criteria’ for classification under Class 6.1. The result of this proposal was the adoption of Class 4.2 and a note that resubmission may occur after further consultation with delegations from Canada and Germany, which apparently have more comprehensive information on the properties of xanthates in addition to experience with the transport of liquid xanthates.

8.3 Other regulatory controls

The following sections comprise standards/codes promulgated with the aim of protecting workers and in some cases the public from adverse exposures, including fire risks, to sodium ethyl xanthate and/or CS₂.

8.3.1 Occupational exposure standards

An occupational exposure standard for sodium ethyl xanthate has not been assigned by NOHSC or any other country. An ‘in-house’ exposure standard of 1 mg/m³ was set by Dow Chemicals in 1976, apparently based on the NOAEL for dogs exposed to the analogue, potassium amyl xanthate.

Atmospheric monitoring for sodium ethyl xanthate is not carried out at either the sites of manufacture or end-use. Monitoring is however carried out for CS₂, which is considered to be the major hazard during manufacture, storage and use of xanthates. This would appear justified, particularly for *liquid* xanthate use, not only with regard to the available toxicological database, but also on the grounds that sodium ethyl xanthate is not particularly volatile and hence inhalation exposure is unlikely to be a major source of exposure to free xanthate.

The NOHSC occupational exposure standard for CS₂ is 10 ppm (31 mg/m³) (time weighted average), with a skin notation (NOHSC 1995). This standard has been adopted from the US ACGIH TLV documentation, which is apparently based on “cardiovascular effects in workers exposed to air concentrations of between 10-40 ppm CS₂ and systemic effects observed following skin absorption” (ACGIH 1998).

This standard is listed in Appendix 3 (substances under review) of the NOHSC Guidance Note (NOHSC 1995) as requiring review due to ‘neurological and cardiovascular effects’.

Table 6 provides details of known national exposure standards adopted for CS₂.

Table 6 – National exposure standards for carbon disulfide

Country	Exposure limits				Skin notation
	TWA		STEL		
	ppm	mg/m ³	ppm	mg/m ³	
US NIOSH	1	3	10 ¹ (500) ²	30	yes
Hungary	2	5	3	10	yes
Czechoslovakia	3	10	6	20	
Denmark	5	15	-	-	yes
Sweden	5	16	8	25	yes
Poland	6	18	10	30	
Australia	10	31	-	-	yes
Finland	10	30	20	60	yes
France	10	30	25	75	
Germany (DFG)	10 ³	32	-	-	
Japan (JSOH) ⁴	10	31	-	-	yes
Netherlands ⁵	10	30	-	-	yes
Russia	10	30	-	-	
Switzerland	10	30	20	60	yes
United Kingdom (HSE)	10	32	-	-	yes
US ACGIH	10	31	-	-	yes
US OSHA ⁶	20	65	-	-	

N.B. Source: ACGIH (1998) – Standards current as at Jan 1993 unless otherwise indicated.

1 = 15-min ceiling concentration

2 = IDLH concentration

3 = Pregnancy Group B (probable risk of damage to developing embryo/foetus)

4 = 1996

5 = Oct 1997

6 = 1995

Currently, the highest TWA exposure limit for CS₂ (PEL: 20 ppm) is that set by the US OSHA -TWA (OSHA 1995). This exposure limit reflects the exposure limit that was in effect prior to the issuance of revised limits of 4 ppm (PEL), 12 ppm (STEL) and 500 ppm (IDLH) in January 1989, apparently established to “reduce substantially the significant risks of cardiovascular disease, neurological impairment, and adverse reproductive effects associated with exposures to CS₂” (OSHA 1989). These revised limits were voided by the US Eleventh Circuit Court of Appeals on 7 July 1992 (ATSDR 1996).

Ambient air quality at manufacturing site

With regard to ambient air quality, DEP, WA has recommended a design ground level concentration of < 0.042 ppm (0.13 mg/m³) CS₂ for the Coogee Chemical

xanthate plant. This value, which is apparently based on the odour threshold for CS₂, was adopted from the Victorian State EPA regulations (EPA 1970).

8.3.2 Health surveillance

Sodium ethyl xanthate is not listed in the NOHSC *Schedule of Substances Requiring Health Surveillance* (Schedule 3) in the Hazardous Substances Model Regulations. However, in accordance with the NOHSC Hazardous Substances Regulations, employers have a responsibility to provide health surveillance to those workers where exposure to a substance may lead to an identifiable substance related disease or adverse health effect.

Although adverse health effects have been reported in workers exposed to xanthate products, under current conditions of use, such reports are uncommon and symptomatology is diverse in nature.

Because adverse effects from xanthate exposure are generally considered to be associated with exposure to CS₂ vapours, the current method of choice for monitoring occupational exposure to xanthates is monitoring CS₂ in air (see Section 8.3.1).

Studies on viscose and rubber workers have demonstrated that urinary 2-thiothiazolidine-4-carboxylic acid (TTCA) levels correlate well with airborne levels of CS₂ even at low exposure levels (Krstev et al., 1993; Drexler et al 1995b; Cox et al., 1998). Of interest in a study by Cox et al., (1998) was that low level exposure, below the detection limit (<0.5 ppm CS₂) was associated with increasing levels of TTCA during the work shift and that these levels did not return to normal pre-shift levels (0.3 mg/g TTCA in creatinine) before the start of the next shift. This indicates that accumulation of CS₂ in body tissues may occur. Studies in rats and guinea pigs indicate that CS₂ is initially accumulated in liver, brain, blood and adrenals (see PEC5).

Significantly increased TTCA excretion has been seen in viscose workers undertaking heavy physical work and in workers with increased potential skin contact (Drexler et al 1995b). A further issue in this regard is the potential contribution to CS₂ body burden from dermal exposure to xanthates, the magnitude of which has not been determined.

If bioaccumulation and/or dermal absorption are significant for CS₂ and/or sodium ethyl xanthate, then air monitoring may not be an adequate predictor of chronic hazardous exposure to xanthates.

ACGIH has adopted a health-based biological exposure standard (BEI) for CS₂, of 5 mg/g TTCA in creatinine (ACGIH, 1994).

8.3.3 Standard for Major Hazard Facilities

The Coogee Chemicals manufacturing site in WA meets the criteria for classification as a Major Hazardous Facility (MHF) under Schedule 1 of the NOHSC *National Standard for the Control of Major Hazard Facilities* (NOHSC 1996).

The objective of the MHF Standard is to prevent major accidents and near misses, and to minimise the effects of any major accidents by requiring operators to:

- Identify and assess all hazards and implement control measures to reduce the likelihood and effects of a major accident;
- Provide information to the relevant public authority and the community, including other closely located facilities, regarding the nature of the hazards at a major hazard facility and emergency procedures in the event of a major accident;
- Report and investigate major accidents and near misses and take appropriate corrective action; and
- Record and discuss the lessons learnt and the analysis of major accidents and near misses with employees and employee representatives.

The MHF Standard is designed to be implemented by a single public authority (known as the Relevant Public Authority) and is intended to enable a Safety Report⁶ to be produced that fulfills the requirements of any public authority involved. The NOHSC *Code of Practice for the Control of Major Hazard Facilities* (NOHSC 1996), provides practical guidance on how to meet these requirements. A summary diagram for the implementation and administration of the MHF Standard can be found in Appendix 5.

In WA, existing facilities/plants were required to develop/update⁷ Safety Reports in accordance with the MHF Standard, following regulatory implementation on 30 September 1997. As of this date, any new/proposed plant/facility meeting the MHF Standard (Schedule 1 criteria), has to comply with this Standard prior to obtaining a license for the storage of dangerous goods. At the time of preparing this report, Coogee Chemicals had completed development of their Integrated Risk Management System to meet the MHF Standard and submitted their Safety Report to the Department of Minerals and Energy (the Relevant Public Authority in WA) for approval.

⁶ **Safety Report** – also referred to as a Safety Management Report, is a written presentation of the technical, management and operational information covering the hazards and risks of a major hazard facility and their control, and which provides justification for the measures taken to ensure the safe operation of the facility.

⁷ Within a timeframe agreed between the Operator and the Relevant Public Authority.

9. Summary and Conclusions

9.1 Background and scope

A full PEC report for *solid* sodium ethyl xanthate was published in May 1995. At the time of the PEC assessment, only *solid* sodium ethyl xanthate was being used in Australia, all of which was imported.

In October 1998, Coogee Chemicals Plc Ltd provided secondary notification to the Director of Chemicals Notification and Assessment, that it had begun manufacturing *liquid* xanthates (mainly sodium ethyl xanthate) at its plant in Western Australia, with a proposed additional manufacturing plant in Queensland.

This secondary notification assessment report has focused on the occupational, public health and environmental risks associated with the manufacture and use of *liquid* xanthates in Australia.

The only use identified for both liquid and solid xanthates in Australia is as a 'flotation agent' in mining applications. Currently, around 6000 tonnes of *solid* sodium ethyl xanthate are imported into Australia per annum. The combined annual production capability of Coogee Chemicals xanthate plants is 10,000 tonnes of *liquid* sodium ethyl xanthate.

9.2 Health hazards

Sodium ethyl xanthate exhibits moderate dermal and oral acute toxicity in animal studies and is an eye and skin irritant. Limited animal data exist for chronic exposure to xanthates. Adverse health effects are documented only for acute exposures to xanthates in humans.

The main health hazards from exposure to xanthates are considered to arise from CS₂, which is both a decomposition product and metabolite of sodium ethyl xanthate. Carbon disulfide is also a starting reagent in liquid xanthate manufacture. Carbon disulfide exhibits low to moderate acute toxicity in animals and humans and is associated with a number long-term effects, including cardiovascular, neurological and reproductive effects in animals and humans.

Both sodium ethyl xanthate and CS₂ are listed in the NOHSC *List of Designated Hazardous Substances*.

In addition to its health hazards, CS₂ is extremely flammable and a number of fire incidents have been reported during transport and storage of *solid* xanthate products.

9.3 Exposures and risks associated with liquid xanthates

Health risks to workers and the public may arise from manufacture, transport and end-use of sodium ethyl xanthate, although available pharmacokinetic, toxicological and epidemiological data for both sodium ethyl xanthate and/or CS₂

are currently insufficient to fully characterise dose response relationships for critical effects.

Despite the lack of data, health risks were assessed in this report utilising available data on CS₂ exposures.

9.3.1 Manufacture

Fire/explosion risks due to process failure at the Coogee Chemicals site have been assessed by WA Department of the Environment (DEP) and Department of Minerals and Energy (DME) as below the acceptable risk level. Risks of fire during normal operation were also considered to be low due to the low levels of CS₂ at potential 'hot spots'.

In the assessment of health risks from liquid xanthate manufacture, available monitoring data indicate that ambient site levels of CS₂ are below 3 ppm, and chronic health risks were considered low. High exposures of up to several hundred ppm are likely during certain maintenance activities. Acute risks are however likely to be low, due to the exposure reduction measures employed at the Coogee Chemicals plant, in particular the wearing of appropriate respiratory equipment. Similarly, chronic risks were considered low due to the infrequency of high exposure operations.

9.3.2 Transport and end-use

Limited air monitoring data were available for the assessment of occupational risks from transport and end use of liquid xanthates.

Available data indicate that levels around road tankers during filling procedures may be up to 30 ppm, however, due to the anticipated infrequency of exposure, chronic risks to workers are considered low. A potential exists for acute risks, in particular, workers dealing with spills and risk reduction measures beyond those currently employed are considered necessary for potentially exposed workers.

Available monitoring data (instantaneous) for xanthate 'mixing' and 'flotation' activities indicate that CS₂ levels are generally below 5 ppm (16 mg/m³), although CS₂ levels in excess of 60 ppm (187mg/m³) were monitored at one site, where a xanthate worker experienced adverse effects during the mixing process. However, this process is not undertaken with liquid xanthates and potential acute inhalation exposures during end-use are therefore likely to be significantly reduced. It is therefore considered that provided adequate personal protective equipment (see Section 9.4.1) is worn during potential high exposure activities, e.g., maintenance procedures, sampling activities and mixing/dilution operations, acute and chronic risks to end-use workers are likely to be low.

9.3.3 Public

The manufacture, transport and current end-use of liquid sodium ethyl xanthate is not considered to pose a significant risk to the general public provided that precautions are taken to ensure that the amounts of sodium ethyl xanthate released into tailings dams do not give rise to levels of hazardous degradation products and that emergency procedures for the containment and clean up of accidental spills are made available and followed.

9.3.4 Environment

Sodium ethyl xanthate is very toxic to aquatic organisms and exhibits a high degree of mobility in soil. In the assessment of environmental risks from manufacture and transport, the main concern is the potential for environmental impact in the event of accidental spillage. The PEC/PNEC ratio for spillage during transportation indicates a high potential risk. This highlights the need for adequate hazard communication (see Section 9.4.4), particularly for the control of spills and clean up.

9.4 Current regulation and risk management

9.4.1 Control measures

Important health and fire risk reduction measures currently employed by Coogee Chemicals at their xanthate manufacturing plant in WA, include:

- regular monitoring carried out for CS₂;
- use of respirators with suitable gas filter where exposure to CS₂ in excess of the exposure standard is possible. Ancillary air supply used for high exposure work e.g., maintenance.
- use of impervious, anti-static gloves and protective clothing during handling of CS₂;
- optimisation of storage/transport conditions to favour reduced xanthate decomposition;
- xanthate storage tanks ventilated and drained from lowest point, to allow continuous removal of accumulated CS₂;
- carbon disulfide containers stored over water bunding and fitted with deluge system;
- grounding of all tanks and plant equipment according to Zone 1 Class1 static discharge provisions, to reduce fire hazard;
- regular maintenance of all critical plant equipment and fittings;
- development of a plant management safety plan according to the NOHSC Standard for Major Hazard Facilities.

A single case report of a xanthate end-use worker experiencing adverse effects from exposure to xanthate powder and solution (unspecified) serves to highlight the importance of adequate personal protective equipment. The worker was wearing cotton overalls, PVC gloves and an acid gas/particulate full-face respirator. Dermal exposure was evident and inhalation exposure was also possible as the respirator did not include an organic vapour cartridge.

9.4.2 Exposure monitoring

Although regular air monitoring of CS₂ is carried out during manufacture, such monitoring does not appear to be undertaken on a routine basis at mining sites. Such monitoring is generally undertaken by random 'grab' sampling techniques e.g., Drager tubes, which prevent detailed assessment of TWA exposures. Such data are insufficient to fully characterise risks to potentially exposed workers. In

addition, the limit of detection for this air monitoring method is insufficient to ascertain compliance⁸ with the DEP recommended design ground level concentration (see Section 9.4.2).

Personal sampling is the preferred method for obtaining individual work profile data. For example, TWA CS₂ exposures determined for viscose workers with personal samplers were up to twice those measured by static sampling (Krstev et al., 1993).

9.4.3 Health surveillance and exposure standards

Although routine health surveillance for workers exposed to liquid xanthates is not currently indicated, recent studies provide evidence that biological monitoring of the urinary metabolite of both sodium ethyl xanthate and CS₂, TTCA, may be a more accurate predictor of hazardous exposures, particularly where dermal exposure occurs⁹. In this regard ACGIH has adopted a BEI for CS₂.

Although there are epidemiological data, mainly for the rayon/viscose industry, that indicate that critical effects may occur at exposure levels lower than 10 ppm (31 mg/m³) CS₂ (the national exposure standard) these studies are retrospective in nature and as such do not permit definitive exposure/effect associations at the lower end of the exposure ranges monitored.

NOHSC has listed the current exposure standard for CS₂ for review, however, it is considered that the available epidemiological and animal data are inadequate to recommend that this review be expedited.

With regard to ambient air quality the DEP, WA have recommended a design ground level concentration at the xanthate plant of < 0.042 ppm (0.13 mg/m³) CS₂.

9.4.4 Hazard communication

Currently, liquid sodium ethyl xanthate is distributed directly from the manufacturing plant to end-use storage tanks by road tanker. As such, product labelling and placarding requirements for storage and transport are regulated under the ADG Code.

Although xanthates are regulated by the ADG Code, the current listed classification is relevant for *solid* products only. Although it is considered that health/fire risks from transport and storage of solid xanthate products are likely to be significantly decreased for liquid xanthates, it is considered that current placarding of sodium ethyl xanthate may be inadequate for the purpose of alerting workers and emergency services to the potential health and environmental risks from exposure to liquid sodium ethyl xanthate.

⁸ 'worse-case' modelling data indicate that the ground level concentration for CS₂ is well below the DEP design ground level concentration.

⁹ It is considered that inhalation of CS₂ is likely to be significantly reduced from use to liquid xanthates, however, dermal exposure to both xanthate and CS₂ might be of greater significance for liquid xanthate products.

As 40% liquid sodium ethyl xanthate meets the criteria for classification as a hazardous substance according to NOHSC criteria, should liquid sodium ethyl xanthate be transported/packaged by alternative methods, such that they require direct handling in the workplace (e.g., decanting), then the NOHSC requirements for labelling of workplace substances would have to be met.

9.5 Data gaps

A number of important data gaps were identified in this report, some of which have been identified and/or discussed in the preceding text. Other important gaps are as follows:

Decomposition/degradation of sodium ethyl xanthate solutions.

Data provided for assessment were inconsistent. Quantitative data on CS₂ formation from decomposition of sodium ethyl xanthate solution(s) is required for the purposes of health hazard classification and labelling. In addition, such data would shed more light on issues associated with potential hazards from exposure to CS₂.

Note: It is understood that work on the ‘degradation and of flotation agents’, including sodium ethyl xanthate is currently being carried out by the University of Western Sydney in collaboration with the Australian Mineral Industries Research Association (AMIRA).

Toxicological/epidemiological data

Although solid sodium ethyl xanthate is harmful by oral and dermal routes and has been associated with acute effects in humans, no data were available on the acute toxicity of sodium ethyl xanthate (40% solution) in humans or animals. Although 40% sodium ethyl xanthate solution is classified as hazardous under NOHSC criteria, information on acute dermal toxicity of the 40% solution *per se* would be required for the purpose of ADG Code classification.

Pharmacodynamic data on the effects of chronic *low level* exposure to CS₂ following inhalation, is needed to establish dose-response relationships for critical effects. Available epidemiological and animal data are considered inadequate for the purpose of determining NOAELs for critical effects.

Note: Carbon disulfide is on the US EPA HPV Challenge Program List and is currently being assessed in the OECD SIDS program.

Pharmacokinetic data

It is known that xanthates are metabolised in animals and humans to CS₂ and that xanthates may be absorbed by inhalation and dermal exposure. For the purpose of fully evaluating hazardous exposures to liquid sodium ethyl xanthate, further pharmacokinetic data are needed on dermal absorption, biotransformation and distribution/body burden of both xanthates and CS₂.

This data would also assist considerations relating to the need for a biological exposure standard for sodium ethyl xanthate.

10. Recommendations

This section provides recommendations arising from the secondary notification assessment of liquid sodium ethyl xanthate. In general these recommendations have been formulated for *liquid* sodium ethyl xanthate and specifically for manufacture and end-use in mining applications. However, manufacture, transport and use scenarios in Australia are likely to be similar for other liquid xanthates. Similarly, all xanthates release CS₂. As such, the recommendations arising from this report are likely to be relevant for other liquid xanthate products.

The following recommendations are directed towards employers and employees involved in the manufacture and handling of liquid sodium ethyl xanthate and to specific regulatory bodies involved in the protection of occupational, public and environmental health.

10.1 Hazard classification

In accordance with the NOHSC *List of Designated Hazardous Substances (1999)*, the recommended hazard classification for sodium ethyl xanthate is:

- **HARMFUL IN CONTACT WITH SKIN AND IF SWALLOWED**
- **IRRITATING TO EYES AND SKIN**

Products or preparations containing > 20% sodium ethyl xanthate should also be classified as 'Hazardous' or 'Harmful'. However, products containing other hazardous substances (e.g. decomposition products) should be classified accordingly.

10.1.1 Consideration of hazardous impurities

It should be noted that decomposition data for 40% sodium ethyl xanthate solution, indicate that at 20°C, CS₂ content may increase in concentration (^w/_w) by up to 0.1% per day. From the available data (see Table 1, Section 4.1), this rate of decomposition would be expected to be significantly greater at higher temperatures, e.g., up to two fold increase at temperatures experienced at mine sites. In this regard:

Sodium ethyl xanthate solutions containing >0.2% CS₂, should be classified as:

- **HARMFUL TO HEALTH BY PROLONGED EXPOSURE**

and, sodium ethyl xanthate solutions containing >1% CS₂, should be classified as:

- **TOXIC TO HEALTH BY PROLONGED EXPOSURE**
- **TOXIC TO REPRODUCTION (CATEGORY 3)**

10.2 Hazard communication

As liquid sodium ethyl xanthate, above 20% w/w, is classified as a hazardous substance, employers and suppliers should be aware of their obligations to provide adequate information about the hazards of the chemical. Details of these obligations, consistent with employers' general duty of care, are provided in the NOHSC *National Model Regulations for the Control of Workplace Hazardous Substances* (NOHSC 1994a).

10.2.1 Material Safety Data Sheets

The NOHSC National Code of Practice for the Preparation of Material Safety Data Sheets (NOHSC 1994b) provides guidance for the preparation of MSDS.

It is recommended that MSDS be upgraded in line with the sample MSDS for sodium ethyl xanthate (40% w/w solution) provided at Appendix 4. With the exception of certain physicochemical properties, it is considered that this MSDS would also be appropriate for other aqueous solutions of sodium ethyl xanthate above 20% w/w.

MSDS should be made available to all workers involved in manufacture and end-use of sodium ethyl xanthate solutions.

10.2.2 Transport and storage

Currently, the ADG Code (FORS 1998) only specifies a dangerous goods classification appropriate for *solid* xanthates i.e., Class 4.2.

Solid sodium ethyl xanthate meets the ADG Code criteria for classification under 6.1 with regard to dermal toxicity and acute toxicity has been reported in humans exposed from dermal exposure to xanthates. Therefore the Advisory Committee for the Transport of Dangerous Goods (ACTDG) is supported in its proposal to the UN to classify *solid* xanthates with subsidiary risk 6.1.

It is further recommended that ACTDG considers the case of *liquid* xanthates in any further representation to the UN for dangerous goods classification, particularly for classification under Class 6.1 (toxic/harmful) and/or 9 (hazardous to the environment). However, currently the minimum requirements are that site storage vessels at either end of the transport activity should be placarded as dangerous goods with UN 3342, Class 4.2.

It is also recommended that an appropriate Emergency Procedure Guide (EPG) is developed for *liquid* xanthates in order that potential risks are conveyed to tanker drivers and emergency services.

With regard to spills, the following statements should be included in the MSDS and reflected in any EPG for *liquid* xanthates.

THIS PRODUCT IS HIGHLY TOXIC TO AQUATIC ORGANISMS. DO NOT ALLOW THE CHEMICAL TO ENTER DRAINS, WATERWAYS OR RIVER SYSTEMS.

It is recommended that any instruction to clean-up spills with large amounts of water be amended to:

**CLEAN SPILL WITH MINIMAL AMOUNTS OF WATER,
COLLECTING CONTAMINATED WATER WHERE POSSIBLE AND
DISPOSED OF AS LIQUID WASTE.**

In view of the soil mobility of sodium ethyl xanthate and its aquatic toxicity, it is recommended that the following statement is included:

**IN THE EVENT OF A ROADSIDE SPILL, CONTAMINATED SOIL
SHOULD BE COLLECTED WHERE POSSIBLE AND DISPOSED OF IN
ACCORDANCE WITH LOCAL GOVERNMENT REGULATIONS.**

10.2.3 Training and education

Workers involved in xanthate manufacture and end-use should be familiar with relevant risk management initiatives, such as Training & Operating Handbooks; Standard Operating Procedures (SOPs) and/or Emergency Response Plans (ERP).

Workers involved in the manufacture, transport and end-use of sodium ethyl xanthate need to be trained in the safe handling of both xanthates and CS₂.

Manufacturing plant operations personnel should be specifically trained in:

- Safe handling of raw materials (particularly CS₂) used in the manufacture of liquid xanthates;
- Safe handling of liquid xanthate products;
- First aid and fire fighting measures (in relation to the above chemicals);
- Correct use of all safety equipment, including SCBA;
- Emergency response procedures;
- Selected actions for the control and management of CS₂ leaks/spills; and
- Notification and reporting procedures in the event of a reagent or product leak.

Transport personnel should be specifically trained in:

- Safe handling of liquid xanthates and hazardous reactants (particularly CS₂);
- First aid and fire fighting measures (in relation to the above chemicals); and
- Procedures for dealing with liquid xanthate spills (beyond the confines of the production plant).

Workers involved in reagent *mixing/dilution* and *flotation* operations should be specifically trained in:

- Safe handling of liquid xanthates;
- Hazards of xanthate decomposition products, particularly CS₂;
- Correct use of all safety equipment, including SCBA;

- First aid and fire fighting measures (in relation to the above chemicals);
- Standard operating and emergency response procedures; and
- Safe disposal procedures.

Training provided at induction should be reinforced at regular intervals, especially in relation to emergency procedures.

10.3 Occupational control measures

In general, it is considered that current control measures employed during manufacture and end-use are adequate with respect to minimising risks from adverse exposures to sodium ethyl xanthate or CS₂.

However, because personal protective equipment worn by a xanthate mining worker proved insufficient in preventing acute effects in a recent incident (see Appendix 2), it is recommended that for high risk activities,

where:

- dermal exposure to liquid xanthates is possible;
- levels of CS₂ vapour may be above the exposure standard; and
- where such exposures are not fully characterised either in terms of duration and acute or chronic exposure,

that all workers are equipped with the following:

- fully maintained and fitted full-face respirator with suitable organic vapour cartridge or SCBA;
- impervious, antistatic gloves and protective clothing; and
- antistatic boots.

10.4 Occupational monitoring and exposure standards

10.4.1 Air monitoring

Routine air monitoring for CS₂ is recommended at xanthate manufacturing plants and end-use facilities, particularly in areas where CS₂ levels may exceed the exposure standard. In particular, static monitoring should be carried out prior to maintenance activities to ascertain CS₂ exposure levels, in order to determine the type of personal protective equipment deployed.

Personal, or as a minimum, static monitoring should be carried out for all routine activities where potential exposure to CS₂ vapours exist, particularly workers involved in mixing and flotation processes at mine sites. For estimating TWA exposures, it is recommended that such monitoring should employ at least, the minimum sampling times as recommended by NOHSC (NOHSC, 1995).

The frequency of routine TWA monitoring will depend on the results obtained and can be reduced once it has been established that control measures are effective and that levels do not exceed the exposure standard for CS₂.

10.4.2 Exposure standards

The current NOHSC standard for carbon disulfide (TWA: 10 ppm) is adopted from ACGIH.

This exposure standard is listed in Appendix 3 (substances under review) of the NOHSC Guidance Note (NOHSC 1995) as requiring review due to 'neurological and cardiovascular effects'.

It is recommended that carbon disulfide is maintained as a substance for review by NOHSC. The timing of this review needs to take into account the availability of human and/or animal data (hitherto unavailable), that will permit dose-response assessment for chronic exposures, particularly at the lower levels reportedly associated with adverse effects in some more recent epidemiological/clinical studies (see Section 6.3.2).

When reviewing the airborne exposure standard for CS₂, NOHSC should consider the issues discussed in Section 8.3.2 of relevance to a health-based biological exposure standard (BEI) for CS₂ and decide whether xanthates warrant further consideration within the 'health surveillance' framework.

10.5 Public health protection

Appropriate precautions should be taken to minimise release of the hazardous degradation products of sodium ethyl xanthate, in particular CS₂ and H₂S. Such engineering controls may include the use of suitable scrubbers and/or afterburners to limit their release into the environment. The ambient air standard of <0.042 ppm (0.13 mg/m³) CS₂, recommended by the DEP, WA and based on the odour threshold for CS₂ should not be exceeded.

Precautions should be taken to ensure that the amounts of sodium ethyl xanthate released into tailings dams do not give rise to levels of hazardous degradation products which may represent a hazard to public health.

Emergency procedures for the containment and clean up of accidental spills are available and should be followed. Spills should be contained by diking, the material removed and reclaimed by mechanical means, contaminated soil and absorbents disposed of as hazardous waste (see recommendation 10.2.2), and the area cleaned with minimal amounts of water.

11. Secondary Notification

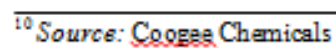
Under Section 65 of the *Industrial Chemicals (Notification and Assessment) Act, 1989*, (the Act), renewed secondary notification of sodium ethyl xanthate may be required, where a manufacturer or importer of sodium ethyl xanthate becomes aware of any circumstances which may warrant a reassessment of its hazards and risks. Specified circumstances include:

- The function or use of sodium ethyl xanthate has changed, or is likely to change, significantly;
- The amount of sodium ethyl xanthate manufactured or introduced into Australia has increased, or is likely to increase, significantly;
- Additional information has become available to introducer(s) on adverse health and environmental effects of liquid or solid sodium ethyl xanthate;
- Any incidents/accidents involving adverse health or environmental effects occur from manufacture, transport and use of liquid sodium ethyl xanthate;
- The mode of distribution/supply of liquid xanthates has changed (e.g., from tanker to drums); and
- Manufacture of solid sodium ethyl xanthate (or other solid xanthates) has begun in Australia.

In addition, where data becomes available to fill the gaps identified in Section 9.5, this may also require secondary notification.

The Director (Chemicals Notification and Assessment) must be notified within 28 days of the manufacturer/importer becoming aware of any of the above or other circumstances prescribed under section 65 of the Act.

Process Flow Diagram for Sodium Ethyl Xanthate Manufacture¹⁰



Appendix 2

Incident Reports for Xanthate Products

A number of incidents have occurred from the transport and use of *solid* xanthate products. The reader is referred to PEC5 for a summary of incidents reported from 1984 – 1994. The following comprises a summary of incidents made available to NICNAS since the publication of the PEC5 report.

Transport incident – 1993

An incident in 1993, involving the transport of solid sodium ethyl xanthate, was investigated by the WA Department of Minerals and Energy (DME, 1993).

A ‘traytop’ vehicle transporting a mixed load of dangerous goods (comprising 8200 kg solid sodium ethyl xanthate; 205 L of sodium hypochlorite and 50 L of compressed oxygen) on the Brookton highway, WA, rolled onto its side, spilling part of its load.

Approximately 1800 kg of spilt sodium ethyl xanthate was repackaged into its consignment drums by the fire brigade. No adverse health effects were reported.

Transport incident – 1995

In October 1995, a shipment (from China) of several tonnes of solid sodium isopropyl xanthate at Port Botany container terminal in Sydney had apparently started to undergo self-combustion with resultant decomposition to CS₂. Emergency services, including the Fire Brigade attended the scene and appropriate action was taken to contain the fire and evacuate nearby areas. Monitoring for CS₂ was also carried out (**results?**) once the contents of the container had been identified (no hazard labelling appeared on the container).

NICNAS was requested to carry out an inspection of the container. Defective packaging (bulker bags) was identified as the probable cause. No adverse health effects were reported.

Occupational incident - 1998

Donoghue (1998) reported an incident where a worker involved in the xanthate mixing process at a Queensland gold mine site was exposed to xanthate powder (specific compound not specified) and solution. The worker was wearing cotton overalls, PVC gloves and an acid gas/particulate full-face respirator. Extensive skin contamination of the worker’s chest area was evident (green staining) on showering.

The exposed worker developed an illness (which began 20 h after exposure and lasted for 3 days), which consisted of predominantly gastrointestinal symptoms.

Carbon disulfide body burden¹¹ was confirmed by the detection of urinary 2-thiothiazolidine-4-carboxylic acid (TTCA) (<4 mg/L measured approximately 68 h after exposure).

¹⁰ Carbon disulfide is readily absorbed dermally, however CS₂ is also a human metabolite of xanthates.

Drager tube testing, during subsequent mixing, recorded a maximum concentration of at least 60 ppm CS₂. It was not clear whether symptoms were the result of CS₂ inhalation¹² or xanthate/CS₂ skin absorption.

¹¹ Although respiratory protection did not include an organic vapour cartridge, the worker did not experience any eye irritation, which suggests that the level of CS₂ within his full-face respirator was not high.

Appendix 3

Labelling of Sodium Ethyl Xanthate Solutions according to NOHSC Model Regulations¹³

Ingredient disclosure

Under the NOHSC Labelling Code, sodium ethyl xanthate is classified as a ‘Type II’ substance i.e., a generic name may be used¹⁴, when present in a mixture/solution above >20% w/w.

Signal word

In accordance with the NOHSC Labelling Code, a ‘signal word’ should be used in the labelling of all hazardous substances. For sodium ethyl xanthate, (present in a mixture/solution above >20% w/w), the signal word ‘HARMFUL’ or ‘HAZARDOUS’ is appropriate.

Risk phrases

According to the NOHSC *List of Designated Hazardous Substances* (1999), the following risk phrases are recommended for labelling of pure sodium ethyl xanthate:

R15/29*	Contact with water liberates highly flammable and toxic gas
R21/22	Harmful in contact with skin and if swallowed
R36/38	Irritating to eyes and skin

[may be of limited relevance for sodium ethyl xanthate solutions]*

Mixtures (none reported for assessment) or solutions of sodium ethyl xanthate should be labeled according to all ingredients. In particular, where levels of decomposition products are known or can be predicted to occur in sodium ethyl xanthate solutions, the relevant risk phrases for such ingredients should also be included, where above the minimum concentration cut-off level(s). For example, risk phrases R48/20 would apply to xanthate solutions containing >0.2% *carbon disulfide* and R62/63 would apply to solutions containing >1% *carbon disulfide* (see Section 6 for details of concentration cut-off levels for sodium ethyl xanthate and carbon disulfide).

Safety phrases

The recommended safety phrases for sodium ethyl xanthate solutions should be selected from the following:

*Where levels of **carbon disulfide** (decomposition product) are likely to be **low**:*

S3/9	Keep in a cool, well ventilated place
S35	This material and its container must be disposed of in a safe way
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection

¹² NOHSC *National Code of Practice for Labelling of Workplace Substances* (NOHSC 1994).

¹³ Provided it is notified to NOHSC.

Where levels of **carbon disulfide** (decomposition product) are likely to be **high**:

S16 Keep away from sources of ignition – no smoking

S23 Do not breathe vapour

S35 This material and its container must be disposed of in a safe way **S36/37/39**

S38 Wear suitable protective clothing, gloves and eye/face protection **S38** In
case of insufficient ventilation wear suitable respiratory
equipment

S51 Use only in well ventilated area

Sample Material Safety Data Sheet for Sodium Ethyl Xanthate (40% solution)

Date of issue	11 April 2000
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Aqueous sodium ethyl xanthate (40% w/w) is classified as 'hazardous' according to the National Occupational Health and Safety Commission's *Approved Criteria for Classifying Hazardous Substances* [NOHSC:1008(1994)] .

Company details

Company name	
Address	
State	Postcode
Telephone number	Emergency telephone number
Facsimile number	Telex number



Identification

Product name
Sodium ethyl xanthate (aqueous solution)
Other names
Carbonodithioic acid O-ethyl ester, sodium salt; ethylxanthic acid, sodium salt; sodium ethyl xanthogenate; sodium xanthogenate; sodium O-ethyl dithiocarbonate; sodium O-ethyl carbonodithioate
Manufacturer's product code
UN number
3342
Dangerous goods class and subsidiary risk
Under consideration
Hazard code
1[Y]
Poisons Schedule number
Not scheduled
Use
Mining applications (flotation/collection agent)



Physical description and properties		
Appearance Clear orange liquid (at 25°C)		
Boiling point >100°C	Freezing point -6°C	
Vapour pressure No data. Decomposes to volatile compounds		
Specific gravity 1.20 (at 20°C)		
Flashpoint Not relevant		
Flammability limits For carbon disulfide: 1.3% (lower) to 50.0% (upper) v/v in air		
Solubility in water Miscible in all proportions		
Other properties		
<u>Odour</u> : Unpleasant, typical of <u>sulphurated organics</u>		
<u>Odour threshold</u> :		
Detection Threshold:		ppm
Identification Threshold:		ppm
Reactivity: Does not <u>polymerise</u> . Non-reactive in the presence of air/water, but will release alcohol and carbon disulfide on standing and when heated. Decomposition accelerated at low <u>pH</u> .		
Ingredients/impurities		
Chemical entity Sodium ethyl xanthate	CAS Number 140-90-9	Proportion 40% w/w
Water		60% w/w
Free alkalis		
Ethanol		
Carbon disulfide		<2% w/w

Health hazard information

HEALTH EFFECTS

Acute

Inhalation: DO NOT BREATHE VAPOUR. Due to release of carbon disulfide vapours, acute exposure to xanthates may cause CNS and respiratory depression, convulsions, unconsciousness, epigastric pain/vomiting, blurred vision, headaches and nausea.

Human fatalities have occurred following acute exposure (>3000 ppm) to carbon disulfide.

Skin: HARMFUL AND IRRITATING IN CONTACT WITH SKIN. May cause moderate skin irritation. May cause systemic effects via dermal absorption.

Carbon disulfide is a severe skin irritant and may cause systemic effects via dermal absorption.

Eye: IRRITATING TO EYES. May also cause light sensitivity.

Swallowed: HARMFUL IF SWALLOWED. May cause vomiting, convulsions, unconsciousness.

Chronic

Inhalation: No human evidence available for xanthates. In animals, repeated or prolonged exposure to xanthates has been associated with effects on liver, spleen, kidney and CNS.

In humans, long term exposure to carbon disulfide (<30 ppm) has been associated with serious adverse effects (e.g. cardiovascular effects, neurological effects, retinal damage, hearing defects and effects on the reproductive system).

Eye: See above.

Skin: No human or animal evidence available. May be absorbed through skin with similar effects as for inhalation (see above).

FIRST AID

Inhalation: Remove from exposure. Keep warm and at rest until fully recovered. Apply artificial respiration if breathing stopped. Begin CPR if heart action stopped. Call a doctor.

Skin: Remove contaminated clothing. Wash immediately with copious quantities of water. Call a doctor.

Eye: Irrigate immediately with copious quantities of water for at least 15 minutes. Call a doctor if irritation persists.

Swallowed: Rinse mouth with water. Give plenty of water to drink. Do not give anything by mouth if person is losing consciousness. Call a doctor. Do not induce vomiting.

First aid facilities

[Contact details of nearest hospital and/or site occupational health physician]

[Telephone number of relevant Poisons Information Centre]

Contraindications

Alcohol consumption may increase harmful effects of absorbed sodium ethyl xanthate.

Pre-existing conditions which may be aggravated by exposure to carbon disulfide vapour include asthma or other respiratory disease, cardiovascular and neuropsychic disorders and vitamin B6 deficiency.

Avoid exposure to carbon disulfide during pregnancy.

ADVICE TO DOCTOR

Treat symptomatically. No specific antidote.

Treatments that have been used in acute carbon disulfide poisoning include: activated charcoal, sodium bicarbonate solution and gastric lavage. Intravenous administration of urea and vitamin B6 have also been recommended.

Precautions for use

EXPOSURE STANDARDS

No Australian Exposure Standard for sodium ethyl xanthate.

Regular monitoring for *carbon disulfide* should be carried out at 'hot spots' at manufacturing plants and end-use sites.

Australian exposure standard for *carbon disulfide*: 10 ppm (31 mg/m³)TWA, with 'skin notation' (sk).

[The skin notation indicates that dermal absorption may be a significant source of exposure].

DEP, WA has recommended a design ground level concentration (GLC) of < 0.042 ppm (0.13 mg/m³) CS₂ for xanthate manufacturing sites.

ENGINEERING CONTROLS

USE ONLY IN WELL VENTILATED AREA. Local exhaust ventilation may be necessary for some operations. Control airborne vapour concentration of carbon disulfide below the exposure standard.

Carbon disulfide formation during manufacture, storage and use of sodium ethyl xanthate may be reduced by keeping solution at alkaline pH (>10 recommended) and cool (<18°C recommended).

Tanks and bunding should be constructed in accordance with AS 3780.

All tanks and equipment to be grounded.

PERSONAL PROTECTION

WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES, EYE/FACE PROTECTION AND RESPIRATORY EQUIPMENT.

Where exposure to carbon disulfide vapour is likely, a respirator fitted with a suitable gas filter (type A or AX) should be worn. SCBA used when working in areas where CS₂ exposures are likely to be high. Respiratory protective equipment should conform to AS 1716.

Impervious, antistatic gloves conforming to AS 2161 should be used when handling xanthate solutions.

Chemical safety goggles/face shield conforming to AS 1337 should be used when handling xanthate solutions.

Protective (impervious) clothing conforming to AS 3765 should be used when handling xanthate solutions.

FLAMMABILITY

Although xanthate solutions are not flammable substances, they decompose to flammable compounds such as alcohol and carbon disulfide.

KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING. Storage tanks (manufacture and use) and plant reactor to be grounded (manufacture).

Deluge system to be installed for carbon disulfide containers (manufacture).

Fire hydrants with attendant equipment situated in close proximity (within 50 metres recommended) of plant (manufacture).

Safe handling information

STORAGE and TRANSPORT

Should not be transported or stored with incompatible substances (ADG Class 1; 2.1; 3; 5; 8 (acids)) or foodstuffs.

KEEP IN A COOL, WELL VENTILATED PLACE. To reduce build-up of carbon disulfide during transport and storage sodium ethyl xanthate solution should be kept below 18°C. Tanks should be well ventilated and drained from lowest point to allow continuous removal of any accumulated carbon disulfide.

Water layer to be maintained (18 inches recommended) in carbon disulfide storage bund (manufacture).

Should be stored and transported in accordance with the ADG Code requirements:

Correct shipping name: XANTHATES

Packing group: II or III (solid only)

Special provision: SP184

Emergency Procedure Guide: 4B3 (solid only)

SPILLS and DISPOSAL

This product is highly toxic to aquatic organisms. DO NOT ALLOW THE CHEMICAL TO ENTER DRAINS, WATERWAYS OR RIVER SYSTEMS.

AVOID SKIN/EYE CONTACT OR INHALATION. Personal protective equipment (as noted in the appropriate section above) should be worn. In a minor spill situation use a respirator with an organic vapour cartridge. For major spills use SCBA.

Spills should be contained by diking. Removed material reclaimed by mechanical means and contaminated soil and absorbents disposed of in accordance with local government regulations.

In the event of a roadside spill, contaminated soil should be collected where possible and disposed of in accordance with local government regulations.

Clean spills with minimal amounts of water, collecting contaminated water where possible and dispose of as liquid waste.

FIRE/EXPLOSION HAZARD

LIBERATES HIGHLY FLAMMABLE AND TOXIC GAS - DO NOT BREATHE VAPOUR. Although xanthate solutions are not flammable substances, they may decompose on standing/heating to toxic and highly flammable compounds such as carbon disulfide and alcohol. Combustion products may also include carbon monoxide and sulphur oxides.

Special precautions should be observed during (i) pumping xanthate solutions; (ii) draining and cleaning tanks; (iii) performing maintenance work on tanks and pipelines.

Fire fighting: wear self-contained breathing apparatus & complete protective clothing. Use appropriate media for surrounding fire (Do not use carbon dioxide).

TRAINING MATERIAL

Workers involved in xanthate *manufacture* should be familiar with the relevant risk management initiatives, such as Risk Management Systems (IRMS); Emergency Response Plans (ERP) and Standard Operating Procedures (SOPs).

Workers involved in *mining applications* involving xanthates, should be familiar with SOPs. The following publications may be useful where suitable 'in-house' documentation is not available:

Training & Operating Handbook (1990) for Reagent Mixers
[prepared by Mt Isa Mines]

Training Module (1993) for Concentrators (Flotation Operators)
[prepared by Mt Isa Mines]

Relevant publications

National Industrial Chemicals Notification & Assessment Scheme, Full Public Report - Priority Existing Chemical No. 5 - Sodium Ethyl Xanthate, NICNAS, 1995.

Australian Dangerous Goods (ADG) Code, FORS, 1998.

Other information

Toxicological data

Acute *oral* LD₅₀ (mouse)= 730 mg/kg (10% aqueous solution of sodium ethyl xanthate)

Acute *dermal* LD₅₀ (rabbit) <1000 mg/kg (sodium ethyl xanthate).

Repeat dose (30 d) *inhalation* (mouse & dog)- 100 mg/m³ (*potassium amyl xanthate*) elicited hepatotoxic and CNS effects.

Repeat dose (90 d) *oral* (rat)- 10 mg/kg (*potassium butyl xanthate*) elicited effects in CNS, liver and spleen.

Environmental data

Sodium ethyl xanthate emissions will partition to water, but are of limited persistence.

Sodium ethyl xanthate is toxic (moderate to high) to aquatic fauna (invertebrates and fish). Predicted LC₅₀s for aquatic fauna are above 2 ppm and chronic end-points above 0.2 ppm. Effects on algal growth are predicted below 1 ppm.

Contact point

Contact name

Telephone number

Position title

Address

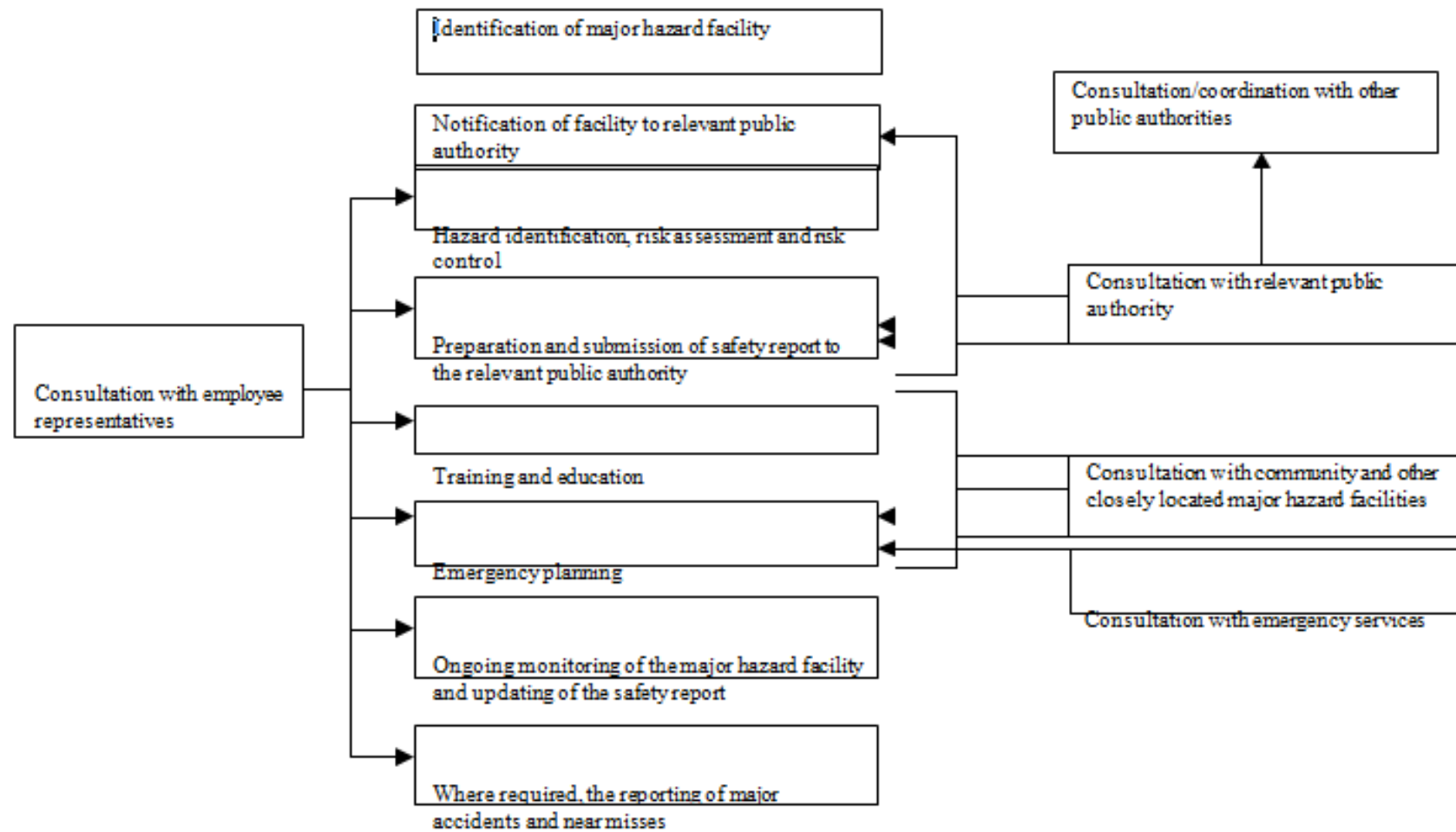
State

Postcode

Country

Australia

IMPLEMENTATION AND ADMINISTRATION OF THE NATIONAL STANDARD FOR THE CONTROL OF MAJOR HAZARD FACILITIES



1. NOTES

1. The safety report submitted to the relevant public authority shall:

- (a) identify the nature and scale of the use of any materials listed in Schedule 1: *The Identification of a Major Hazard Facility*;
- (b) identify the type, relative likelihood and consequences of major accidents that might occur;
- (c) give details of the Safety Management System for the major hazard facility, including the arrangements:
 - (i) for the safe operation of the major hazard facility, including the control of serious deviations that could lead to a major accident and emergency procedures at the site,
 - (ii) made to ensure that the means for the safe operation of the major hazard facility are properly designed, constructed, tested, operated, inspected and maintained, and
 - (iii) for providing assurance, in accordance with sub-section 7.10 of the national standard; and
- (d) provide justification as to the adequacy of the measures taken to ensure the safety of the facility.

2. Consultation with employees and employee representatives occurs at the following stages:

- (a) hazard identification, risk assessment and risk control, including the updating of risk assessments and risk controls;
- (b) the establishment, implementation and maintenance of the Safety Management System;
- (c) preparation and updating of safety reports and emergency plans;
- (d) preparation of reports on major accidents and near misses; and
- (e) induction, and the provision and updating of training and education.

Source: NOHSC (1996)

Appendix 6

ORDER FORM FOR NICNAS PRODUCTS

<i>I wish to purchase:</i>	<i>Quantity</i>
NICNAS "Handbook for Notifiers" @ AUD \$95.00 each	
Australian Inventory of Chemical Substances (AICS) CD ROM @ \$180.00 annual subscription (free six monthly update) within Australia only	
Copy/s of Full Public Report/s for the following new chemical assessment/s: Include NICNAS reference number (no charge):	
Copy/s of Full Public Report/s for the following priority existing chemical (PEC) assessment/s (no charge):	
PEC/4S - HCFC-123 (Secondary Notification)	 PEC/5S
– Sodium ethyl xanthate (Secondary Notification)	 PEC/7 - 1,4-
Dioxane	
PEC/9 - Chrysotile asbestos	
PEC/10 – Acrylonitrile	

All prices include postage and packaging within Australia and by SEAMAIL overseas. For AIRMAIL please include an additional \$50.00 for each Handbook and \$10.00 for each other NICNAS product.

Overseas only: Please send by AIRMAIL. YES / NO

ALL ORDERS MUST BE ACCOMPANIED BY PREPAYMENT IN AUSTRALIAN DOLLARS PURCHASE ORDERS NOT ACCEPTED

I enclose \$..... cheque/money order payable to National
Occupational Health & Safety Commission drawn on an Australian bank in
Australian dollars

OR Bankcard [☐] Visacard [☐] Mastercard [☐]

Card Number: _____ Expiry Date: _____

Card Holder: _____ Signature: _____

Name of _____

Recipient: _____

Position: _____

Company: _____

Address: _____

Postcode _____

Telephone: (____) _____ Fax: (____) _____

Send this order to : **National Occupational Health & Safety Commission
Finance Section
GPO Box 58
Sydney NSW 2001
Australia**

References

- ACGIH (1994) TLV-Threshold limit values and biological exposure indices for 1994-1995. Cincinnati, OH, American Conference of Governmental Industrial Hygienists.
- ACGIH (1998) Documentation of the threshold limit values and biological exposure indices. Cincinnati, OH, American Conference of Governmental Industrial Hygienists.
- AS/NZS ISO 9002 (1994) Quality systems – Model for quality assurance in production, installation and servicing.
- ATSDR (1996) Agency for Toxic Substances and Disease Registry: Toxicological profile for carbon disulfide. Atlanta, GA, US Department of Health and Human Services, Research Triangle Institute Contract No. 205-93-0606.
- ATSDR (1997) Agency for Toxic Substances and Disease Registry: Carbon disulfide (update). Atlanta, GA, US Department of Health and Human Services, Document No. PB/97/121073/AS.
- Beauchamp, R.D, Bus, J.S, Popp, J.A, et al. (1983) A critical review of the literature on carbon disulfide toxicity. *CRC Crit Rev Toxicol*, **11**:169-278.
- Cassitto MG, Camerino D, Imbriani M et al (1993) Carbon disulfide and the central nervous system: a 15-year neurobehavioural surveillance of an exposed population. *Environ Res*, **63**(2):252-263.
- Christophers A and Zammit M (1997) Critique of the Kerr Report: Best estimate of the magnitude of health effects of occupational exposure to hazardous substances. *J Occup Health Safety - Aust/NZ*, **13**(4):331-339.
- Chrostek, Maj and Czeczotko (1995) The evaluation of the health status of workers occupationally exposed to low concentrations of carbon disulphide. *Przegl Lek*, **52**(5). 249-256.
- Chu CC, et al (1995) Polyneuropathy induced by carbon disulphide in viscose rayon workers. *Occup Environ Med*, **52**(6): 404-7.
- Cox C, Hee SS and Tolos WP (1998) Biological monitoring of workers exposed to carbon disulfide. *Am J Ind Med*, **33**(1):48-54.
- De Fruyt, F Thierry, E, De Bacquer, D et al. (1998) Neuropsychological effects of occupational exposures to carbon disulfide and hydrogen sulfide. *Int J Occup Environ Health*, **4**(3):139-146.
- Donoghue AM (1998) Case report - carbon disulphide absorption during xanthate reagent mixing in a gold mine concentrator. *Occup Med*, **48**(7):469-470.

- DME (1993) Dangerous Goods Transport Accident Report - Summary of Accident Reports, WA Department of Minerals and Energy. File No. 233/93.
- DME (1997), WA Dept of Minerals and Energy, Explosives and Dangerous Goods Division. Personal Communication – letter to Coogee Chemicals (Oct 1997).
- Drexler H, Ulm K, Hubmann M et al (1995a) Carbon disulphide III. Risk factors for coronary heart disease in workers in the viscose industry. *Int Arch Occup Environ Health*, **67**(4) 243-252.
- Drexler H, Goen T, Angerer J (1995b) Carbon disulphide II. Investigations on the uptake of CS₂ and the excretion of its metabolite 2-thiothiazolidine-4-carboxylic acid after occupational exposure. *Int Arch Occup Environ Health*, **67**(1) 5-10.
- Drexler H, Ulm K, Hardt R et al (1996) Carbon disulphide IV. Cardiovascular function in workers in the viscose industry. *Int Arch Occup Environ Health*, **6**(1) 27-32.
- EPA (1970) *Victorian Environmental Protection Act 1970*, State Environmental Protection Policy (The Air Environment).
- FORS (1998) Australian Code for the Transport of Dangerous Goods by Road and Rail (ADG Code), 6th ed. Canberra, Federal Office of Road Safety.
- Hawley, JR (1977) The use, characteristics and toxicity of mine-mill reagents in the province of Ontario. Ontario, Canada, Ministry of the Environment.
- Johnson BL, Boyd J, Burg JR et al (1983) Effects on the peripheral nervous system of workers' exposure to carbon disulfide. *Neurotoxicity*, **4**:53-65.
- Kroschwitz JI (Exec. Editor) (1998) *Kirk-Othmer encyclopedia of chemical technology* (4th ed.), Vol 25. NY, John Wiley & Sons, pp 713- 734.
- Krstev S, Perunovic B, Farkic B et al (1993) Environmental and biological monitoring in carbon disulfide exposure assessment. *Med Lav*, **84**(3):473-481.
- Kuligowski (1996) The influence of chronic exposure to carbon disulfide on metabolism of catecholamines and serotonin in women. *Ann Acad Med Stetin*, **42**:139-156.
- Kuo HW, Lai JS, Lin M et al (1997) Effects of exposure to carbon disulfide (CS₂) on electrocardiographic features of ischemic heart disease among viscose rayon factory workers. *Int Arch Occup Environ Health*, **70**(1):61-66.
- Lars Freij (ed) (1993) A pilot procedure to select candidate substances for general restrictions on use. Stockholm, Swedish National Chemicals Inspectorate.
- Lee E and Kim MH (1998) Cerebral vasoreactivity by transcranial Doppler in carbon disulfide poisoning cases in Korea. *J Korean Med Sci*, **13**(6):645-651.
- Masuda Y, Yasoshima M and Nakayama N (1986) Early, selective and reversible suppression of cytochrome P-450 in liver microsomes, following administration of carbon disulphide in C57BL/6CR mice. *Biochem Pharmacol*, **37**:2363-2371.

- Merlevede E and Peters J (1965) Metabolism of xanthates in man and guinea pig (in French). Archives of the Belgian Medical Society, **23**(8): 513-551.
- NICNAS (1995) Full Public Report: Sodium Ethyl Xanthate: Priority Existing Chemical No. 5. Canberra., AGPS.
- NOHSC (1990) Storage of chemicals - guidance note for placarding stores for dangerous goods and specified hazardous substances: guidance note for emergency services manifests. Canberra., AGPS.
- NOHSC (1994a) National model regulations and code of practice for the control of workplace hazardous substances. Canberra, AGPS.
- NOHSC (1994b) National code of practice for the labelling of workplace substances. Canberra, AGPS.
- NOHSC (1994c) National code of practice for the preparation of material safety data sheets. Canberra, AGPS.
- NOHSC (1995) Exposure standards for atmospheric contaminants in the occupational environment and national code of practice. Canberra, AGPS.
- NOHSC (1996) National standard and code of practice for the control of major hazard facilities. Canberra, AGPS.
- NOHSC (1998) Draft standard for storage and handling of dangerous goods. Canberra, AGPS.
- NOHSC (1999) List of designated hazardous substances [NOHSC:10005(1999)]. Sydney, National Occupational Health and Safety Commission.
- Omae K, Takebayashi T, Nomiyami T et al. (1998) Cross sectional study of the effects of carbon disulphide on arteriosclerosis in rayon manufacturing workers. Occup Environ Med, **55**(7):468-472.
- OSHA (1989) US Department of Labour, Occupational Safety and Health Administration: 29 CFR Part 1910, Air Contaminants; Final Rule. Fed. Reg.54(12):2535-2538 (Jan 19, 1989).
- Pieleszek A (1997) The effect of carbon disulphide on menopause, concentration of monoamines, gonadotropins, estrogens and androgens in women (in Polish). Ann Acad Med Stetin, **43**:255-267.
- Price B, Berner T, Henrich RT et al (1996) A benchmark concentration for carbon disulfide: analysis of the NIOSH carbon disulfide database. Regul Toxicol Pharmacol, **24**(2):171-176.
- Price B, Bergmann TS, Rodriguez M et al (1997) A review of carbon disulfide exposure data and the association between carbon disulfide exposure and ischemic heart disease. Regul Toxicol Pharmacol, **26**(1):119-128.
- Rao RS (1971) Xanthates and related compounds. New York, Marcel Dekker.
- Reinhardt F, Drexler H, Bickel A et al (1997). Electrophysiological investigation of central, peripheral and autonomic nerve function in workers with ;long-term low-

level exposure to carbon disulphide in the viscose industry. *Int Arch Occup Environ Health*, **70**(4):249-256.

Resource Strategies (1998) Environmental Impact Statement: Cowal Gold Project: Risk and Hazard Assessment. 13 March, 1998.

Sinczuk-Walczak H and Szymczak (1997) Rhythm patterns of basic brain bioelectric activity in workers chronically exposed to carbon disulfide. *Int J Occup Med Environ Health*, **10**(4):429-440.

Standards Australia (1993) Australian Standard 1940: The storage and handling of flammable and combustible liquids. Homebush, NSW, Standards Australia.

Takebayashi T, Omae K, Ishizuka C et al. (1998) Cross sectional observation of the effects of carbon disulphide on the nervous system, endocrine system and subjective symptoms in rayon manufacturing workers. *Occup Environ Med*, **55**(7):473-479

Trent University (1998) Level 1 Fugacity Based Environmental Equilibrium Partitioning Model, Version 2.1. Ontario, Canada, Trent University, Environmental Modelling Centre.

Vanhoorne M, De Bacquer D and Barbier F (1992) Epidemiological study of the cardiovascular and liver effects of carbon disulfide. *Int Arch Occup Health*, **63**(8): 517-523.

Vanhoorne M, Comhaire F and De Bacquer D (1994) Epidemiological study of the effects of carbon disulfide on male sexuality and reproduction. *Arch Environ Health*, **49**(4): 273-278.

Vanhoorne M, Ceulemans L, De Bacquer et al (1995) An epidemiologic study of the effects of carbon disulfide on the peripheral nerves. *Int J Occup Environ Health*, **1**(4):295-302.

Vanhoorne M, De Rouck A and De Bacquer (1996) Epidemiological study of the systemic ophthalmological effects of carbon disulfide. *Arch Environ Health*, **51**(3):181-188.

Verscheuren K (1983) Handbook of environmental data on organic chemicals (2nd ed.), Van Nostrand Reinhold.

WorkCover (1999) Personal Communication 25 August 1999. Chemical Safety Unit, WorkCover Authority, New South Wales.