

FULL PUBLIC REPORT

Sodium Ethyl Xanthate

**PRIORITY
EXISTING
CHEMICAL
NO. 5**

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Preface

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

The principal aim of NICNAS is to help protect people and the environment from the harmful effects of industrial chemicals by finding out the risks to occupational health and safety, to public health and the environment.

NICNAS has two major parts: one focussing on the risks associated with new chemicals before importation or manufacture; and another focussing on existing industrial chemicals already in use in Australia. As there are many thousands of existing industrial chemicals in Australia, NICNAS has a mechanism of prioritising assessments by declaring certain existing chemicals to be Priority Existing Chemicals (PECs). This report provides the full public report of a PEC assessment. A summary report is also publicly available and has been published in the *Commonwealth Chemical Gazette*.

NICNAS is administered by Worksafe Australia. Assessments under NICNAS are done in conjunction with the Commonwealth Environment Protection Agency and Department of Human Services and Health.

This assessment report has been prepared by the Director Chemicals Notification and Assessment in accordance with the Act. This report has not been subject to tripartite consultation or endorsement by the National Occupational Health and Safety Commission.

Copies of the full public report can be purchased from Commonwealth Government Bookshops.

In accordance with Section 40 of the Act, a person may apply to the Director for variation of this full public report using the approved form by 30 May 1995. A fee must be paid with the application.

On publication of the Summary Report in the *Chemical Gazette* of 2 May 1995, the chemical will no longer be a Priority Existing Chemical in accord with Section 62 of the Act.

For the purposes of subsection 78(1) of the Act, copies of full public reports may be inspected by the public at the Library, Worksafe Australia, 92-94 Parramatta Road, Camperdown, NSW 2050, between 10 a.m. and 12 noon and 2 p.m. and 4 p.m. each weekday except on public holidays.

A pamphlet giving further details of the PEC program and approved forms to apply for variation of this report are available from Worksafe Australia. Please contact the Chemical Assessment Division at:

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Contents

Preface	iii
1. Introduction	1
1.1 Declaration	1
1.2 Data collection	1
1.3 History of xanthate use	2
2. Applicants	3
3. Chemical identity	4
3.1 Chemical name	4
3.2 Chemical Abstracts Service (CAS) Registry Number	4
3.3 Other names	4
3.4 Trade names	4
3.5 Molecular formula	4
3.6 Structural formula	4
3.7 Molecular weight	4
4. Physical and chemical properties	5
4.1 Sodium ethyl xanthate	5
4.1.1 Appearance	5
4.1.2 Odour	5
4.1.3 Melting point	5
4.1.4 Boiling point	5
4.1.5 Specific gravity	5
4.1.6 Vapour pressure	5
4.1.7 Water solubility	5
4.1.8 Partition co-efficient	5
4.1.9 Hydrolysis as a function of pH	5
4.1.10 Adsorption/desorption	5
4.1.11 Dissociation constant	5
4.1.12 Flammability	5
4.1.13 Combustion products	6
4.1.14 Decomposition temperature	6
4.1.15 Decomposition products	6
4.1.16 Autoignition temperature	6
4.1.17 Reactivity	6
4.1.18 Particle size distribution	6
4.1.19 Composition of commercial product	6

4.2	Carbon disulphide	6
4.2.1	Molecular weight	7
4.2.2	Appearance	7
4.2.3	Odour	7
4.2.4	Odour threshold	7
4.2.5	Freezing point	7
4.2.6	Boiling point	7
4.2.7	Specific gravity	7
4.2.8	Vapour pressure	7
4.2.9	Relative vapour density	7
4.2.10	Water solubility	7
4.2.11	Flash point	7
4.2.12	Autoignition temperature	7
4.2.13	Explosive properties	7
4.2.14	Reactivity/stability	7
4.2.15	Conversion factors	7
5.	Methods of detection and analysis	8
5.1	Structural analysis	8
5.1.1	Spectral data	8
5.2	Analytical methods for sodium ethyl xanthate	8
5.2.1	Chemical methods	8
5.2.2	Gravimetric method	9
5.2.3	Electrometric methods	9
5.2.4	Radio tracer method	10
5.3	Analytical determination of carbon disulphide	10
5.3.1	Air sampling methods	10
5.3.2	Analytical methods	11
5.3.3	Biological monitoring	11
6.	Use	13
7.	Decomposition	14
7.1	Solid	14
7.2	Aqueous solution	14
7.3	Factors affecting decomposition	14
7.3.1	Concentration	15
7.3.2	Temperature	16
7.3.3	pH	16
7.3.4	Aging of the solution	16
7.3.5	Metal salts	16

8.	Hazard assessment	17
8.1	Animal toxicological data	17
8.1.1	Acute toxicity	17
8.1.2	Oral toxicity	17
8.1.3	Acute dermal irritation/toxicity	18
8.1.4	Acute eye irritation	19
8.1.5	Skin sensitisation	20
8.1.6	Genotoxicity	20
8.1.7	Carcinogenicity	20
8.1.8	Repeated-dose toxicity	20
8.1.9	Overall assessment of toxicological data	25
8.2	Human health effects	26
8.3	Classification of sodium ethyl xanthate	26
9.	Carbon disulphide	27
9.1	Introduction	27
9.2	Physical hazards	27
9.3	Metabolism	27
9.4	Health effects	27
9.4.1	Human health effects	27
9.5	Summary	29
9.6	Hazard classification	29
10.	Exposure assessment	30
10.1	Occupational exposure	30
10.1.1	Exposure	30
10.1.2	Incident reports	32
10.1.3	Atmospheric monitoring	34
10.2	Public exposure	36
10.3	Handling of sodium ethyl xanthate at mine sites	37
10.3.1	Mixing area	37
10.3.2	Flotation area	39
11.	Assessment of risk to human health	40
11.1	Occupational health and safety	40
11.1.1	Health and safety hazards	40
11.1.2	Occupational risk	41
11.2	Public health risk	42

12. Environmental assessment	43
12.1 Environmental exposure	43
12.2 Environmental fate	43
12.3 Environmental effects	44
12.3.1 Terrestrial toxicity	44
12.3.2 Aquatic toxicity	44
12.3.3 Conclusion	45
12.4 Environmental risk	46
13. Risk management	47
13.1 Hazard communication	47
13.1.1 Material Safety Data Sheet	47
13.1.2 Labels	47
13.1.3 Education and training	48
13.2 Control measures	48
13.2.1 Elimination and substitution	48
13.2.2 Isolation	49
13.2.3 Engineering controls	49
13.2.4 Safe work practices	49
13.2.5 Personal protective equipment	50
13.2.6 Emergency procedures	51
13.3 Packaging	51
13.4 Regulatory controls	51
13.4.1 Exposure standard	51
13.4.2 Health surveillance	52
14. Conclusion	53
15. Recommendations	54
15.1 Classification	54
15.2 Provision of information	54
15.2.1 Material Safety Data Sheets	54
15.2.2 Labels	54
15.2.3 Training and education	55
15.3 Packaging	55
15.4 Exposure standard and atmospheric monitoring	56
15.5 Health surveillance	56
15.6 Environmental protection	56
15.7 Incidents	56
15.8 Other xanthates	56

16. Requirements for secondary notification	57
Appendix	
1. Sample Material Safety Data Sheet for sodium ethyl xanthate	57
References	64

1. Introduction

1.1 Declaration

The chemical, sodium ethyl xanthate (CAS No 140–90–9) was declared a Priority Existing Chemical under the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), by the Minister of Industrial Relations, by notice in the *Chemical Gazette* of 6 July 1993.

Section 48 of the Act states that a chemical may be declared a priority existing chemical if there are reasonable grounds for believing that the manufacture, handling, storage, use or disposal of an industrial chemical gives or may give rise to a risk of adverse health effects or adverse environmental effects.

For sodium ethyl xanthate these grounds were:

- the large potential for occupational and environmental exposure due to widespread use as a flotation agent in the mining industry;
- the lack of information on the health and environmental effects of sodium ethyl xanthate which is of concern in view of the high volume use and potential exposure; and
- sodium ethyl xanthate decomposes to the toxic and flammable gas, carbon disulphide.

At the time of the declaration two incidents involving sodium ethyl xanthate highlighted the problems that could arise during transport and use of the chemical. An incident in Alice Springs involved a chemical leak at the railway station leading to the evacuation of about 100 people and hospitalisation of six railway workers after inhaling fumes. In the second incident at Stawell, residents in the vicinity of a mine using sodium ethyl xanthate complained of foul odour, headache, dizziness and nausea.

In accordance with Section 55 of the Act, those introducing sodium ethyl xanthate into Australia applied for assessment of the chemical as a priority existing chemical (PEC). As sodium ethyl xanthate is not manufactured in Australia, applications were limited to importers.

1.2 Data collection

Information for assessment, both toxicological data and information on exposure, was supplied by importers and end-users, such as mining companies. Toxicological data was also obtained from past manufacturers of sodium ethyl xanthate.

While sodium ethyl xanthate is the subject of the assessment, information on other xanthates used for similar purposes was included for completeness.

Overseas organisations such as the Swedish National Chemicals Inspectorate, the U.S. Environmental Protection Agency, Environment Canada, Health Canada and the International Register of Potentially Toxic Chemicals, which is a part of the United Nations Environment Programme, were contacted. A comprehensive search of databases and the literature was carried out for information to assist in the assessment.

The literature search revealed that there was very little published data on the toxicity of sodium ethyl xanthate or any of the other xanthates. The few studies

that were obtained were unpublished and carried out by past manufacturers in the 1950s.

Site visits to Mount Isa Mines Ltd, Queensland, and Woodlawn Mines, Tarago, New South Wales (which uses sodium iso butyl xanthate), were also carried out to assist in the assessment of sodium ethyl xanthate.

Published data on the hazards of carbon disulphide were also considered in this assessment as it is the major decomposition product of sodium ethyl xanthate.

1.3 History of xanthate use

The primary use of xanthates of the alkali metals, sodium and potassium, is as mineral collectors. This use was introduced by Keller in 1925.¹ Mineral collectors are organic substances used for the recovery of metal sulphides from ore slurries. Sodium ethyl xanthate was also used overseas as a defoliant, herbicide and as an additive in rubber to protect against atmospheric gases, especially oxygen and ozone.

In Australia, sodium ethyl xanthate has been used widely in the mining industry for over 30 years. It is one of a number of xanthates used as a flotation agent for mineral collection, for example sodium isobutyl xanthate and potassium amyl xanthate are also commonly used. There is no evidence in any State government records of sodium ethyl xanthate being used as a pesticide in Australia.

2. Applicants

ICI Australia Pty Ltd

1 Nicholson Street
Melbourne VIC 3000

Mineral and Chemical Traders Pty Ltd

59 Parraween Street
Cremorne NSW 2090

Mintrade Pty Ltd

Level 1, 14 Edmonstone Street,
South Brisbane QLD 4101

Quantum Chemicals Pty Ltd

Suite 4
21 Kitchener Parade
Bankstown NSW 2200

Redox Chemicals Pty Ltd

30-32 Redfern Street
Wetherill Park NSW 2164

Renison Limited

Renison Tin Division
P O Box 20
Zeehan TAS 7469

3. Chemical identity

3.1 Chemical name

- Sodium ethyl xanthate

3.2 Chemical Abstracts Service (CAS) Registry Number

- 140-90-9

3.3 Other names

- Carbonic acid, dithio-, O-ethyl ester, sodium salt
- Carbonodithioic acid, O-ethyl ester, sodium salt
- Sodium ethylxanthogenate
- Sodium-O-ethyl carbonodithioate
- Sodium-O-ethyl dithiocarbonate

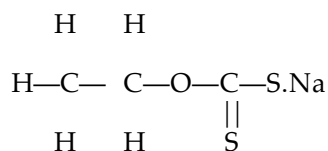
3.4 Trade names

- Aero Xanthate 325
- Z4

3.5 Molecular formula

- C₃-H₅-Na-O-S₂

3.6 Structural formula



3.7 Molecular weight

- 144.14

4. Physical and chemical properties

4.1 Sodium ethyl xanthate

4.1.1 Appearance

Pale yellow, amorphous, powder.

4.1.2 Odour

Disagreeable odour due to the presence of carbon disulphide.

4.1.3 Melting point

182–256°C

4.1.4 Boiling point

Not applicable as it decomposes on heating.

4.1.5 Specific gravity

1.263

4.1.6 Vapour pressure

Non-volatile solid at 25°C. However, it decomposes to volatile compounds.

4.1.7 Water solubility

450 g/L at 10°C

4.1.8 Partition co-efficient

This parameter, $\log P_{ow}$, is not applicable to substances that dissociate in aqueous solution.

4.1.9 Hydrolysis as a function of pH

Xanthates are known to hydrolyse very rapidly under acidic conditions, and to be stabilised by high pH conditions. Below pH 9 at 25°C sodium ethyl xanthate almost totally dissociates.

4.1.10 Adsorption/desorption

Sodium ethyl xanthate adsorbs strongly to sulphide minerals but has less affinity for surfaces in general.

4.1.11 Dissociation constant

The high water solubility and ionic character identify sodium ethyl xanthate as a dissociable compound. Ethyl xanthic acid is a moderately strong acid with a reported pK_a of about 1.6 from which a pK_b of 12.4 may be estimated for its conjugate base. Aqueous solutions of xanthates are alkaline, reflecting the hydrolytic formation of caustic soda.

4.1.12 Flammability

Flammable (solid).

4.1.13 Combustion products

Sodium sulphide, sulphur dioxide, carbon dioxide and water are combustion products through flammable intermediary decomposition products such as ethyl alcohol and carbon disulphide. The hazardous total combustion products are sodium sulphide and sulphur dioxide. Incomplete combustion can result in thio ethers and carbonyl sulphide.

4.1.14 Decomposition temperature

> 25°C

4.1.15 Decomposition products

Sodium ethyl xanthate in the presence of moisture decomposes to carbon disulphide, ethyl alcohol, sodium carbonate and trithiocarbonate.

4.1.16 Autoignition temperature

250°C

4.1.17 Reactivity

Hygroscopic and reacts with water to form ethyl alcohol, sodium carbonate, trithiocarbonate and carbon disulphide. Susceptible to oxidation and reacts with oxidising agents to form dioxanthogens.

4.1.18 Particle size distribution

Pelletised form	width	5 to 6 mm
	length	5 to 15 mm
Powder	range	1 to 10µm
	mean	5µm

4.1.19 Composition of commercial product

Composition varies depending on the source of import. The specifications were supplied by three applicants and are given below.

Purity of the chemical	90% minimum
Moisture	3–7% maximum
Free alkalies	0.2% maximum
Sodium thiosulphate	2% maximum
Sodium sulphide and sodium thiocarbonate	Trace
Sodium sulphate and other inorganic salt	Trace to 7%
Other volatiles	Approx 2%

4.2 Carbon disulphide

Sodium ethyl xanthate in the presence of moisture and/or heat decomposes. Carbon disulphide (CAS number 75–15–0) is the major decomposition product and has a low autoignition point and is highly flammable. The pertinent characteristics of carbon disulphide are:

4.2.1 Molecular weight

76.14

4.2.2 Appearance

Clear, colourless or faintly yellow liquid at 20°C and 101.3 kPa

4.2.3 Odour

Sweet ethereal odour when pure. However carbon disulphide is usually foul smelling and rarely encountered in the pure form.

4.2.4 Odour threshold²

0.1 ppm (response in 100% of subjects)

0.2 ppm (response in 50% of subjects)

0.02 ppm (perception in humans).

4.2.5 Freezing point

-111.5°C

4.2.6 Boiling point

46.5°C at 760 mm Hg

4.2.7 Specific gravity

1.263 at 20°C

4.2.8 Vapour pressure

40 kPa at 20°C

4.2.9 Relative vapour density

2.67 (air=1)

4.2.10 Water solubility

2.1 g/L at 20°C

4.2.11 Flash point

-30°C (closed cup)

4.2.12 Autoignition temperature

99°C

4.2.13 Explosive properties

1.3–50% (v/v) in air

4.2.14 Reactivity/stability

Reacts vigorously with oxidising agents

4.2.15 Conversion factors

1 mg/m³ = 0.321 ppm

1 ppm = 3.11 mg/m³

5. Methods of detection and analysis

5.1 Structural analysis

Sodium ethyl xanthate can be characterised by:

- Infra-red spectroscopy;
- Ultra-violet spectroscopy; and
- X-ray crystallography.

5.1.1 Spectral data*

Ultra violet spectrum 301 nm

Infra-red spectrum 1179, 1160, 1115, 1085 cm⁻¹

5.2 Analytical methods for sodium ethyl xanthate

Atmospheric monitoring of sodium ethyl xanthate is not done routinely in Australian workplaces. There is no recognised methodology specific to sodium ethyl xanthate.

Quantitative analysis of xanthate solutions may be carried out in flotation plants to check strength of solution. The methods of analysis for sodium ethyl xanthate have been described in detail in Rao, 1971.³ Instrumental or chemical methods may be used in the analysis.

The ultra-violet spectrophotometric method is superior to chemical methods as the presence of small amounts of sulphur compounds, present as by-products of dissociation, may interfere with analysis by chemical methods. The spectrophotometric method is useful for xanthate analysis in flotation plants, in research laboratories and for automatic reagent regulation systems. The presence of reducing ions and dixanthogens do not affect light absorption.

5.2.1 Chemical methods

Chemical methods available for analysis of xanthates are the:

- Iodometric method;
- Precipitation as a copper salt;
- Acid-base method;
- Argentometric method;
- Mercurimetric method; and
- Perchloric acid method.

Iodometric method

This method is based on the oxidation of xanthate to dixanthogen by iodine. Dilute iodine in aqueous solution (0.001N) is used and the end-point is detected using starch as indicator. An accuracy within 1% can be obtained by this method. As the analysis is prone to interference from other reductants such as sulphide, sulphite,

* Type of spectrum and major identification peaks.

thiosulphate and lead, the method is recommended as a rough guide only to xanthate concentration, for example in flotation liquors and fresh xanthate solutions.

Precipitation of Xanthate as a copper salt

Xanthate in a cold aqueous solution is precipitated as the copper salt using a copper sulphate/tartrate reagent. The filtered copper xanthate is dissolved in 10 M nitric acid and the free copper ion determined iodometrically. Impurities such as sulphite, thiosulphate and carbonate do not interfere but sulphides and thiocarbonates lead to high results.

Acid-base method

This method is accurate within 1% and is useful for analysis in chemical laboratories. A dilute aqueous xanthate solution is acidified with an excess of 0.01M hydrochloric acid to produce neutral carbon disulphide and alcohol. The excess acid is back-titrated with standard 0.1M alkali using methyl red as indicator. The presence of hydroxide in the sample can be corrected for by separately titrating with 0.1M acid to a phenolphthalein end-point. Carbonates and sulphates can be removed before titration as barium salts.

Argentometric method

Silver xanthate is precipitated from dilute xanthate solution by silver nitrate, followed by the addition of excess standard thiocyanate solution using 10% ferric nitrate as indicator. Excess thiocyanate is back-titrated with silver nitrate. A serious disadvantage of the method is the blackening of the yellow silver xanthate precipitate in the presence of an excess of silver nitrate.

Mercurimetric method

The Mercurimetric method has an accuracy within 1%. Xanthate is dissolved in 40% aqueous dimethylamine, heated and then titrated with 0.05 N O-hydroxymercuribenzoate (HMB) using thiofluorescein as indicator.

Perchloric acid method

Xanthate is dissolved in glacial acetic acid, followed by titration with 0.1N perchloric acid using crystal violet as indicator.

5.2.2 Gravimetric method

The Gravimetric method converts the xanthate solution to lead xanthate by the addition of 10% lead nitrate. Lead xanthate is separated out by dissolving in benzene. Benzene is evaporated from the separated benzene layer. The amount of xanthate present in the solution can be calculated from the weight of lead xanthate precipitate. A correction factor to allow for the slight solubility of xanthate in water can be applied to improve the reliability of the method.

5.2.3 Electrometric methods

The Electrometric methods of analysis measure the current, voltage or resistance in relation to the concentration of the chemical in solution. The methods available for analysis of xanthates are the Potentiometric method and Polarographic method.

Potentiometric method

The argentometric method described above can be carried out potentiometrically using a silver electrode. Interference from strong alkalis in solution can be avoided by buffering with boric acid. Xanthates can also be determined potentiometrically by

titration with 0.02N copper sulphate or 0.05N copper nitrate solution using a copper electrode. Interference from sulphide can be avoided by precipitation with a zinc carbonate suspension and carbonates and thiocarbonates are removed from solution by adding 20% barium chloride. The accuracy of this method is within 0.5%.

Polarographic method

Xanthate in flotation liquors can be determined by obtaining a polarogram anodically over the range 0.1 to 0.7V vs saturated calomel electrode (SCE). The sodium should contain 0.05 to 2.5 mmoles of xanthate/L, 0.1N potassium chloride (as supporting electrolyte), 0.05N sodium hydroxide (pH regulator) and 0.001M eosin (to prevent the formation of an adsorbed film of xanthate). Impurities such as sulphide, sulphite, sulphate, carbonate and thiosulphate do not interfere.

5.2.4 Radio tracer method

The Radio tracer method has an accuracy of $\pm 0.6\%$. It is used extensively for determining xanthate content in the adsorbed layers on mineral surfaces.

Xanthate in solution is oxidised with alkaline permanganate to sulphate, which can be precipitated as barium sulphate. The radioactivity of the dried precipitate can be measured.³⁵S, which is a low-energy beta emitter with a half life of 87.1 days, is used.

5.3 Analytical determination of carbon disulphide

Atmospheric monitoring of carbon disulphide is carried out at some mine sites as carbon disulphide is evolved during storage and use of sodium ethyl xanthate. Sampling for carbon disulphide may be carried out at fixed sites or by personal monitoring. A number of air sampling and analytical methods are available for the determination of carbon disulphide in air.

Estimation of the concentration of carbon disulphide metabolites in blood or urine can be used as a measure of exposure.

5.3.1 Air sampling methods

Activated charcoal tube method

The activated charcoal tube method is used for personal monitoring. This method consists of a measured volume of air being drawn through a glass or metal tube packed with activated charcoal. The carbon disulphide is adsorbed on the charcoal and removed from the flowing air stream. The collected air vapours are desorbed by a suitable solvent and the solution is analysed.⁴

This method is suitable for the measurement of carbon disulphide in a concentration range of about 3 to 25 ppm for samples of 10 litres of air. The method may be used for sampling over periods in the range of 10 mins to 8 hrs.

No interference occurs from hydrogen sulphide.⁵ High humidity can interfere with the collection as carbon disulphide cannot be collected efficiently when condensation occurs in the tube.

Liquid absorption method

The liquid absorption method is useful for the determination of carbon disulphide concentrations at fixed sites. In this method air is drawn through an ethanolic solution of copper salt and diethylamine. The carbon disulphide in the air reacts with the liquid. Hydrogen sulphide present in the air must be removed on lead acetate treated cotton wool before the air enters the absorption solution.⁶

5.3.2 Analytical methods

Gas chromatography

A gas chromatograph fitted with a flame photometric detector and a sulphur filter is useful for the determination of carbon disulphide.⁷ This method is used in combination with the activated charcoal sampling method. The method is very sensitive and can detect 1 μg of carbon disulphide in a charcoal tube. The accuracy of the method is reported to be 6%. It is used widely for the determination of personal exposure to carbon disulphide.

Photometric determination

This method is based on the reaction of carbon disulphide in an ethanolic solution with diethylamine and a copper salt. This results in a yellow brown metallic complex of diethyldithiocarbamate. The concentration of carbon disulphide is directly proportional to the colour of the solution. The concentration in the sample can be determined using a UV visible spectrophotometer at 420 nm. Hydrogen sulphide causes interference with the determination of carbon disulphide by this method. This method is not sensitive enough to monitor carbon disulphide concentrations below 1 ppm.

Direct measurement using gas detector tubes

This is a simple and inexpensive method of measuring the atmospheric carbon disulphide concentration. This method, though, gives only approximate results and if the levels are exceeded, more accurate methods should be used. In this method a known volume of air is drawn through the detector tube. The carbon disulphide in the air reacts with the reagent in the tube, forming a complex such as copper-dialkylaminodithiocarbamate. The concentration of carbon disulphide is estimated by the length of the coloured zone.

Gas analysers

Gas analysers may be used for continuous environmental monitoring of atmospheric carbon disulphide.

Analysers used for continuous monitoring may be based on:

- Electrical conductivity. Air is drawn through an absorbing solution and the reaction of the gas with the solution changes the electrical conductivity according to the concentration of the gas.
- Light absorption in the infrared region.

Carbon disulphide has to be oxidised in a combustion oven to eliminate any interferences and increase the sensitivity.⁶

5.3.3 Biological monitoring

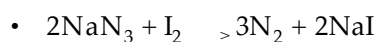
Determination of carbon disulphide concentrations in blood or urine is not useful as a measure of exposure, as only 1% of the absorbed carbon disulphide is excreted unchanged in the urine. Estimation of the concentration of the metabolites of carbon disulphide can be used as a measure of exposure.

Iodine-azide test

The iodine-azide test is based on the capacity of a metabolite of carbon disulphide to catalyse the iodine-azide reaction. The time required for decolourisation of iodine after addition of the iodine-azide reagent to the urine is an indication of the amount of carbon disulphide metabolite in the urine. The time is inversely and exponentially related to the concentration of the metabolite. The time is corrected

according to the creatinine concentration to avoid collection of 24 hr urine samples. An exposure coefficient can be calculated from the creatinine concentration.

The iodine-azide reaction catalysed by the metabolite probably a thiazolidine is:



This method is sensitive to atmospheric concentrations of 16 ppm and above of carbon disulphide. Exposure is considered to be negligible if decolourisation does not occur within 3 hrs. This method is not a precise method of monitoring and only indicates overexposure.⁸

This method has been modified by Jakubowski⁹ and is based on measurement of the amount of iodine used for titration of the carbon disulphide metabolites that catalyse the iodine-azide reaction. This method can be used to assess exposure to carbon disulphide levels as low as 3 ppm.

Determination of thio compounds

Estimation of urinary thio-thiazolidine-4-carboxylic acid (TTCA) concentration by high performance liquid chromatography may be used to monitor carbon disulphide exposure.⁸ TTCA is formed in the body by the reaction between carbon disulphide and glutathione. Excretion of TTCA may reflect the rate of metabolism of carbon disulphide rather than exposure.

6. Use

Xanthates are used in the mining industry as flotation agents in the recovery of metal sulphides. The efficiency of xanthates as mineral collectors increases with the length of the carbon chain but this results in a decrease in the selectivity. Xanthates have a heteropolar molecular structure with a nonpolar hydrocarbon group and a polar sulphide group. A surface chemical reaction occurs between the sulphide ores and the polar group. This reaction forms a water repellent film on the mineral surface and this allows the mineral particles to be carried by air bubbles to the surface. The amount of xanthate used is very small relative to the quantity of ore treated, being approximately 250 to 350 g/tonne of ore.

Sodium ethyl xanthate is the shortest carbon chain xanthate and is the weakest and most selective mineral collector. It is used mainly for the separation of copper, nickel, lead, gold and zinc at several mining sites in Australia.

Sodium ethyl xanthate is not manufactured in Australia. The chemical is manufactured in China and imported into Australia in powder or pellet form, generally in steel drums and, more recently, in bulker bags. The annual consumption of sodium ethyl xanthate in Australia is approximately 2500 tonnes.

During use, the solid sodium ethyl xanthate is mixed with water to form a dilute aqueous solution and typically concentrations in the order of 10% are used. The pH of the solution ranges from 7 to 11.

7. Decomposition

Xanthates decompose in the presence of water. Sodium ethyl xanthate may come into contact with water as a powder or pellet and is used as an aqueous solution in mining processes.

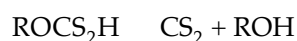
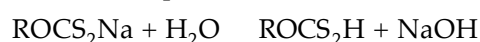
7.1 Solid

Sodium ethyl xanthate is transported and stored as a solid. Sodium ethyl xanthate powder and pellets are stable if stored under dry, cool conditions. However, it is hygroscopic and when exposed to moisture in air it decomposes, releasing carbon disulphide.

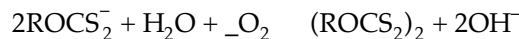
7.2 Aqueous solution

There are three decomposition pathways of xanthates in aqueous solution:

- A. Xanthates dissociate forming alkali metal cations and xanthate anions. The solution undergoes further hydrolysis to xanthic acid which decomposes into carbon disulphide and alcohol.



- B. Xanthate is oxidised to dixanthogen. The extent of this reaction is very small and dependent on the pH. Equilibrium is reached after about 5–10% of the xanthate is oxidised, and the reaction increases with a fall in the pH.



- C. In neutral and alkaline media, xanthates decompose by hydrolytic decomposition.



Further hydrolysis of sodium trithiocarbonate to sodium carbonate and hydrogen sulphide and carbon disulphide to carbon dioxide and hydrogen sulphide may occur. The reaction is catalysed by the alcohol formed from the xanthic acid and is self accelerating.

Reaction C is the main reaction in alkaline solution while A and B occur in acidic solutions. During use in mining processes, reaction C is the principal decomposition pathway and carbon disulphide the principal decomposition product. Part of the carbon disulphide formed may decompose further to carbonate and thiocarbonate salts, some of it may evaporate and some may build up in the xanthate solution. Once the solubility of carbon disulphide is exceeded it forms a separate layer below the sodium ethyl xanthate solution.¹⁰

Some of the decomposition products are also effective as flotation agents and are known as active impurities. These are hydro-sulphide (HS^-) and trithiocarbonate (CO_3^{2-}) ions.¹¹

7.3 Factors affecting decomposition

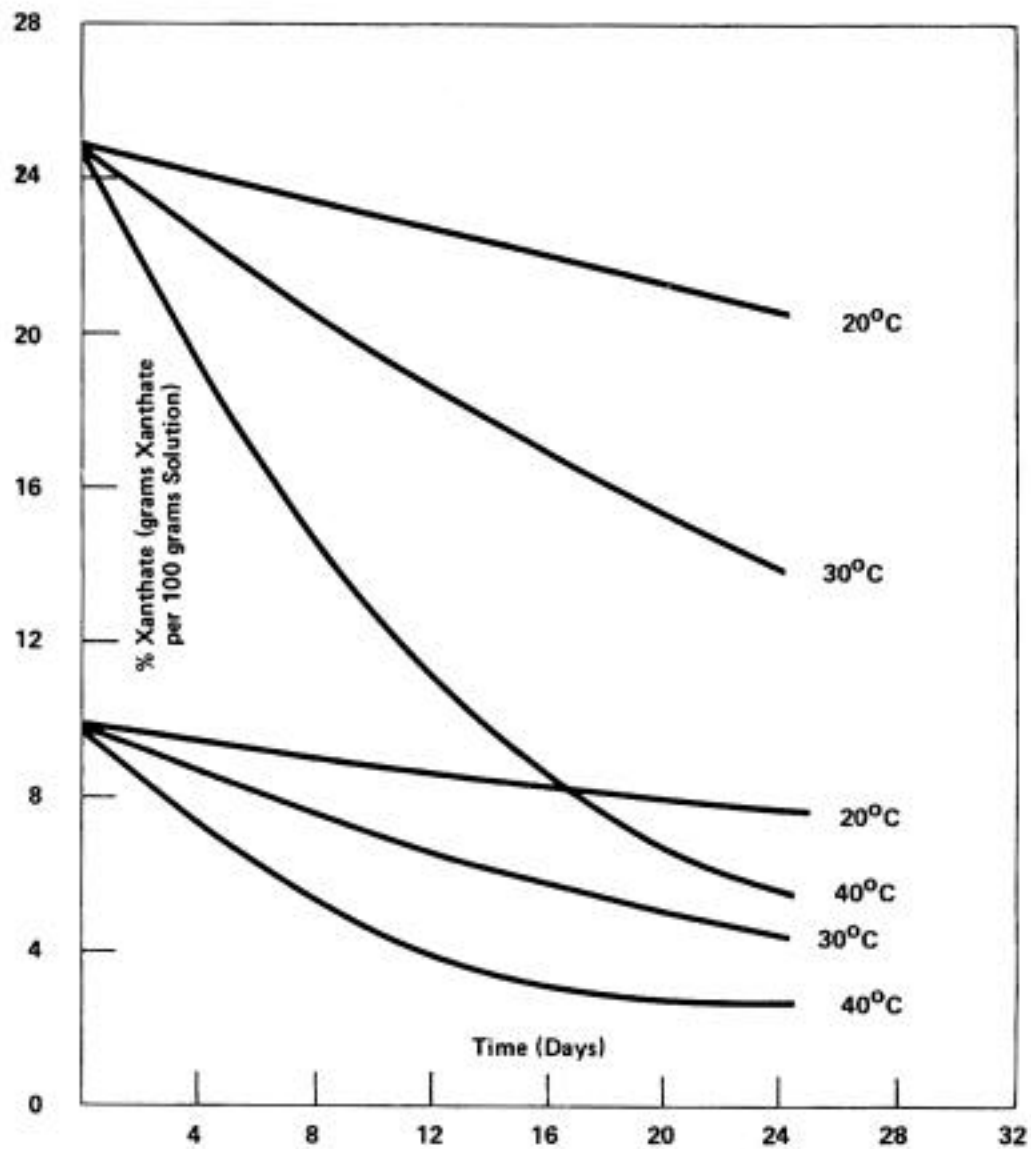
The rate of decomposition of sodium ethyl xanthate is dependent on several factors, the most important being concentration, pH of the solution and temperature. Other factors which affect rate of decomposition include aging of the solution and presence of metal salts.

7.3.1 Concentration

Decomposition rate is accelerated at high concentrations.

Figure 1 shows the decomposition rates of 25% and 10% solutions of sodium ethyl xanthate.¹⁰

Figure 1: Decomposition of Aero 325 xanthate solutions
(American Cyanamid Company, 1972)



7.3.2 Temperature

Decomposition rate increases with increase in temperature.

Table 1: Effect of temperature on the decomposition rate of 10% solution of sodium ethyl xanthate at pH 10 (From: Crozier et al, 1984)¹²

<i>Temperature</i>	<i>Decomposition/day</i>
20°C	1.1%
30°C	2.7%
40°C	4.6%

Table 1 and Figure 1 indicate that the decomposition rate increases with increase in temperature. The temperature at most mining sites is > 30° C and is conducive to decomposition of xanthates.

7.3.3 pH

Decomposition is rapid at pH below 7 and decreases as the pH increases.

The rate of decomposition at pH 6 is about double the rate at pH 8. At pH 6.5 the decomposition rate is 16% per day.¹³ As shown in Table 1 above, sodium ethyl xanthate at pH 10 and 30°C decomposes slowly (2.7% per day). In the mining process, sodium ethyl xanthate is used as an aqueous solution with a pH of 7 to 11.

Alkalies are often used to stabilise xanthate solutions and can be added during the manufacture of solid sodium ethyl xanthate or at mining sites during preparation of aqueous solutions.

7.3.4 Aging of the solution

The rate of decomposition decreases with the age of the solution.

Decomposition is greatest during the first hour and then the rate decreases. The decrease in the rate of decomposition is due to the accumulation of reaction products which inhibit further decomposition. At mining sites, xanthate solutions are generally stored for one day.

7.3.5 Metal salts

Decomposition is accelerated by the presence of metal salts, such as copper, iron, lead and zinc.

Metal salts are often present in flotation tanks when xanthates are used.

8. Hazard assessment

8.1 Animal toxicological data

8.1.1 Acute toxicity

There is very little published and unpublished data available on the adverse health effects of xanthates in general and sodium ethyl xanthate in particular. Toxicological data for other xanthates were also assessed where available, as the adverse effects of the various xanthates are similar.

8.1.2 Oral toxicity

Oral toxicity of Sodium Ethyl Xanthate¹⁴

The study was carried out in 1951 and complies generally with current test protocols such as the Organisation for Economic Cooperation and Development (OECD) guidelines for testing of chemicals No. 401.¹⁵ This study predates the requirements for good laboratory practice, however the study was considered adequate for this assessment. A 10% aqueous solution of sodium ethyl xanthate was administered orally by gavage. The pH of the solution was approximately 10.5 to 11. The animals were observed for signs of gross toxicological effects for seven days.

Table 2: Acute oral toxicity in male albino mice administered 10% aqueous solution of sodium ethyl xanthate

<i>Dosage (mg/kg)</i>	<i>Mortality</i>	<i>Clinical observations</i>	<i>Gross pathology</i>
500	0/13	Depression followed by hyperexcitability, tremors, paralysis, exophthalmia and clonic followed by tonic convulsions.	Consolidated lungs, pale granular livers, unusually small spleens and atonic intestines.
600	0/13		
750	7/13		
900	8/13		
1000	9/13	Pinkness of feet and nose, preening and salivation.	Surviving animals showed no abnormalities.
1500	12/13		
2000	13/13		
5000	2/2		

The majority of deaths occurred on the first day and the animals that survived appeared normal within two days. The study does not indicate how many animals developed the symptoms, at what doses and the day of development of the symptoms.

The results of this study indicate that a 10% aqueous solution of sodium ethyl xanthate has an oral LD₅₀ of 730 mg/kg in male mice. The target organs for oral toxicity of sodium ethyl xanthate were the central nervous system, liver and spleen.

Oral toxicity of other xanthates

Table 3 summarises oral toxicity data, published in the literature, for other xanthates that are used in the mining industry.

Table 3: Oral toxicity of xanthates (from: Kirk-Othmer, 1984)¹⁶

<i>Xanthate</i>	<i>Species</i>	<i>LD₀ (mg/kg)</i>	<i>LD₅₀ (mg/kg)</i>	<i>References</i>
Sodium ethyl	rat	500	—	17
Potassium ethyl	rat mouse	500	1700 583	17, 18
Sodium isopropyl	rat	250	—	17
Potassium isopropyl	rat mouse	— —	1700 583	18 —
Potassium <i>n</i>-butyl	mouse	—	411 465	19,20
Sodium isobutyl	rat	500	—	17
Potassium isobutyl	rat mouse	— —	1290 480	18 18
Sodium <i>sec</i>-butyl	rat	—	>2000	17
Potassium amyl (mixed)	rat	1000	1000–2000	17, 21
Potassium iso amyl	rat mouse	— —	765 470	18 18
C₅-C₆ mixture	rat	—	1500	22

The data in Table 3 indicate that xanthates are harmful by the oral route both in rats and mice. The LD₅₀ of the various xanthates are similar, ranging from 411 to 583 mg/kg in mice and from 1000 to >2000 mg/kg in rats.

The acute oral toxic effects of one xanthate, potassium butyl xanthate, are provided in two summaries in Chemical Abstracts.^{23,24} Similar symptoms and pathology findings were seen in these studies carried out by Babayan.^{19,20}

For example, in the first study¹⁹ oral administration of potassium butyl xanthate to rats produced increased motor activity, cyanosis, irritability, increased respiration and convulsions with death occurring 1 to 2 hours after administration. The LD₅₀ was 411 mg/kg. Autopsy showed perivascular and pericellular oedema, multiple haemorrhages in the lungs, perivascular subarachnoid haemorrhages and acute swelling of the cells of the cortex, subcortical ganglia and the brain stem. Fatty dystrophy of the liver and protein dystrophy of the twisted canaliculi of the kidneys were observed. It is not clear from the summary, if potassium butyl xanthate was administered as a solid or in solution.

The findings of these studies indicate that potassium butyl xanthate produces adverse effects on the central nervous system, liver and kidneys.

8.1.3 Acute dermal irritation/toxicity^{14, 25}

This study was conducted in 1951 and was repeated later in the same year. Exposure in both studies was for 18 hrs and was not according to the OECD Guidelines for acute dermal irritation (4 hrs)²⁶ or for dermal toxicity (24 hrs).²⁷ The initial study was performed to assess dermal irritation but deaths during the study led to further studies. Sodium ethyl xanthate was administered by occlusive application to the shaved abdomen of the rabbits either as 1.0 ml/kg of a 10% aqueous solution or as 1 gm/kg of the 100% dry material in a paste formed with water. The animals were observed for 12 days.

Results of the dermal application studies are summarised in Table 4.

Table 4: Effects of sodium ethyl xanthate following dermal application

<i>Animals</i>	<i>Dose</i>	<i>Clinical Observations</i>	<i>Gross pathology</i>
3 rabbits	1 ml/kg, as 10% solution	No skin irritation.	No substance related changes.
3 rabbits	1 gm/kg, as a paste	2/3 died; surviving animal had moderate irritation with oedema and pigmentation of the skin.	Moderate amount of peritoneal fluid, visceral organs were normal.
5 male rabbits	1 gm/kg, as a paste	5/5 died following overnight exposure; oedema of the skin with pigmentation.	Haemorrhagic lungs and peritoneal and pleural fluid. Other changes were markedly cyanotic ears (2/5), haemorrhagic conditions (2/5) and evidence of diarrhoea (3/5).
1 male rabbit	1 gm/kg, as a more liquid paste than above	Moderate oedema and pigmentation of the skin.	No substance related changes.
3 rabbits	1 gm/kg as a paste	All 3 animals died within 24 hrs; retropulsion, salivation, loss of righting reflex and haemorrhagic and oedematous areas of the skin were noted.	The liver appeared dark and mottled and the kidneys showed spotty haemorrhages.

Under the conditions of the study, application of 10% solution of sodium ethyl xanthate (pH 10.5 to 11) for 18 hrs did not cause skin irritation in rabbits. Similar application of 1 gm/kg of sodium ethyl xanthate in the form of a paste resulted in the death of ten out of twelve animals within 24 hrs. The surviving animals developed irritant effects including oedema and pigmentation of the skin. The sulphide odour noted during the study suggests that decomposition of sodium ethyl xanthate occurred. The dermal LD₅₀ was < 1000 mg/kg.

8.1.4 Acute eye irritation¹⁴

The study was done in 1951 using sodium ethyl xanthate as a 10% solution at pH 10.5 to 11 and as a fine powder. Two groups of three albino rabbits each were used in this study.

A 0.05 ml aliquot of 10% aqueous solution of sodium ethyl xanthate was instilled into the conjunctival sacs of the left eyes of albino rabbits of one group. The eyes were held closed for one minute, observed immediately for reaction 1 hr and 4 hrs later and then daily for 9 days. Mild irritation was observed immediately after instillation but the eyes appeared normal one hour later. One animal showed slight irritation at 4 hrs but was normal on the second day. There were no signs of oedema or necrosis. Autopsy on day 9 did not reveal any gross pathology.

Approximately 30 mg of sodium ethyl xanthate powder was applied to the conjunctival sacs of the second group of rabbits. All three animals showed immediate marked irritation, scrambling, excitement and evidence of pain. There was lacrimation in one animal and phonation in another. Moderate irritation and oedema of the lids was observed in all the animals at the end of 1 hr. The same observations were noted at 4 hrs with one animal showing exudate. Mild irritation was seen after 24 hrs and two rabbits appeared normal after three days. One rabbit showed slight irritation until day 5. There were no signs of opacity or necrosis. The symptoms seen in the animals could be due to the physical irritation caused by solid particles in the eye. The animals were sacrificed on day 9 when no gross pathology was observed at autopsy.

The results of this study indicate that the powder is a moderate irritant to rabbit eyes while the 10% aqueous solution of sodium ethyl xanthate is mildly irritating. The irritant effects of the solution disappeared 1 hr after instillation. The eye effects produced by the powder were reversible, persisting for 24 hrs in all the animals with the effects lasting for up to 4 days in one animal.

8.1.5 Skin sensitisation

No studies were available for assessing the skin sensitisation potential of sodium ethyl xanthate or other xanthates.

8.1.6 Genotoxicity

No studies were available for assessing the genotoxicity of sodium ethyl xanthate or other xanthates.

8.1.7 Carcinogenicity

No studies were available for assessing the carcinogenicity of sodium ethyl xanthate or other xanthates.

8.1.8 Repeated-dose toxicity

Four-month oral toxicity study of potassium butyl xanthate

Two sub-chronic oral studies^{19, 20} of the toxic effects of potassium butyl xanthate are summarised in Chemical Abstracts.^{23, 24} Findings were similar in both studies and included central nervous system, liver and spleen effects.

For example, in one study, potassium butyl xanthate was administered orally (10 mg/kg) or as air dust to rats, rabbits and dogs for 4 months. During administration effects observed from week 6 to week 7 of treatment were tachypnoea, cyanosis, loss of hair and dermatitis. Loss of weight and increase in blood sugar and cholesterol were observed later. Convulsions and paralysis of the extremities were observed in some animals from week 9 of administration. Some animals died during the administration.²⁰

Thirty-day inhalation toxicity study with potassium amyl xanthate²⁸

A 30-day repeated inhalation study for potassium amyl xanthate was conducted in 1976.

Animals were exposed to potassium amyl xanthate as an aqueous aerosol. Attempts at dust exposure were unsuccessful as potassium amyl xanthate is hygroscopic. Animals were exposed to concentrations of 0, 100 and 800 mg/m³ of potassium amyl xanthate. These concentrations were equivalent to actual doses of 0, 23 and 252 mg/m³. Analysis of the particle size indicated that all the particles at the lower dose of 100 mg/m³ were less than 10µm in diameter while approximately 80% of the particles had a diameter of 10µm or less at a dose of 800 mg/m³. It is not possible to state from the description of the exposure method whether air flow was dynamic or static.

Exposure levels for the study were established by a preliminary experiment. In the preliminary experiment, three groups of 10 male Sprague-Dawley rats were exposed to concentrations of 0, 200 or 800 mg/m³ of potassium amyl xanthate, 6 hrs daily for 10 exposures in 2 weeks. No signs of toxicity were observed in animals exposed to a concentration of 200 mg/m³. Rats exposed to a concentration of 800 mg/m³ showed a statistically significant decrease in body weight after the fifth exposure. Recovery of the body weight occurred within 4 days and may not have been exposure related. The only substance related adverse effect observed was a yellow-brown staining of

the hair coat of the rats. Overexposure of the animals exposed to a concentration of 800 mg/m³ occurred because of a technical problem in the aerosol generating apparatus.

In the 30-day study, three groups of animals, each consisting of 10 male Swiss-Webster mice, 10 male Sprague-Dawley rats, 4 male New Zealand White rabbits and 2 male beagle dogs were exposed to either filtered room air or to concentrations of 100 or 800 mg/m³ of potassium amyl xanthate. Whole body exposure was for 6 hrs daily, 5 days a week for a total of 20 exposures in 1 month. Ten mice of the 800 mg/m³ group died along with 5/6 replacement mice.

The animals were observed during the exposures and body weights were recorded three times a week throughout the experiment. Body weight data, organ to body weight ratios and clinical laboratory parameters were analysed statistically using analysis of variance and Dunnett's test.

Most of the mice died when exposed to 800 mg/m³. Five of the 16 mice that died showed convulsions and hyperactivity prior to death. The adverse effects produced by the two doses of potassium amyl xanthate are shown in Table 5.

The results of this study indicate that potassium amyl xanthate has an adverse effect on the central nervous system and liver in mice, the liver and kidneys in rats and the liver in dogs. There were no treatment-related changes in the haematological or urinalysis values in any of the animals.

Table 5: Results of repeated inhalation study with potassium amyI xanthate in laboratory animals²⁸

	Dogs (2 animals)	Rabbits (4 animals)	Rats (10 animals)	Mice (10, 6 animals)
100 mg/m ³				
Eyes	No irritation	No irritation	No irritation	No irritation
Nasal effects	No effects	No effects	No effects	No effects
Hair coat	Yellow brown staining.	Progressive yellow brown staining	Yellow brown staining	No staining
Other effects	Staining of the appendages and scrotum; ulceration of the skin in the scrotal region.	None	None	None
Body weight	No change	No change	No change	No change
Organ weight	No change	No change	No change	Higher liver to body weight ratio than controls
Liver enzyme changes	Marked elevation of serum alanine aminotransferase and alkaline phosphatase activities	No change	No change	No change
Histopathology changes	Hepatocellular degeneration, necrosis and inflammation	No treatment related change	No treatment related change	No treatment related change
Deaths	None	None	None	None

Table 5 cont...

	Dogs	Rabbits	Rats	Mice
800 mg/m³				
Eye changes	Excessive lacrimation due to	Conjunctival redness during the	No irritation	No changes
Nasal effects	None	None	Reddish nasal discharge	None
Hair coat	Yellow brown staining of the	A more intense yellow brown	Yellow brown staining of the	No effects
Skin	Ulceration of the skin in the	No effect	No effect	No effect
Body weight	No change	No change	No change	No change
Organ weight	No change	No change	Higher liver to body weight ratio than controls	Higher liver to body weight ratio than controls
Liver enzyme changes	Marked elevations of serum alanine aminotransferase and alkaline phosphatase activities.	No changes	Males had high absolute kidney weight and kidney/body weight ratios	Higher absolute liver weight
Histopathology changes	Slight elevation of serum aspartate-aminotransferase activity	No changes	High serum alanine aminotransferase activity	No changes
Deaths	Hepatocellular degeneration, necrosis and inflammation	No changes	Microscopically visible granular degeneration of the	No changes
	None	None	One, but not related to exposure	10 from the original group and 5/6 replacement animals died. Convulsions hyperactivity in 5/16 prior to death.

8.1.9 Overall assessment of toxicological data

Table 6: Summary of toxicity tests for xanthates

<i>Toxicological endpoint</i>	<i>Chemical</i>	<i>Species</i>	<i>Result</i>	<i>Section</i>	
Acute oral	Sodium ethyl xanthate (10% solution)	Mice (male)	LD ₅₀ 730 mg/kg	8.1.2	
	Other xanthates	Mice Rats	LD ₅₀ 411-583 mg/kg LD ₅₀ 1000-2000 mg/kg	8.1.2	
Acute dermal irritation/ toxicity	Sodium ethyl xanthate			8.1.3	
	– 10% solution – 1 gm/kg as paste	Rabbits Rabbits	Non irritant LD ₅₀ <1000 mg/kg		
Acute eye irritation	Sodium ethyl xanthate			8.1.4	
	– 10% solution – 30 mg powder	Rabbits Rabbits	Non-irritant Marked irritation immediately, moderate irritation up to 4 hrs, mild irritation at 24 hrs		
Repeated dose toxicity					
• 4 month oral	Potassium butyl xanthate (10 mg/kg)	Rats	Changes in the central nervous system, liver and spleen	8.1.8	
• 30 day inhalation	Potassium amyl xanthate	– 100 mg/m ³	Dogs	Hepatotoxic effects	8.1.8
			Rabbits Rats	No adverse effects No adverse effects	
		Mice	Higher liver/body weight ratio		
	– 800 mg/m ³	Dogs	Hepatotoxic effects	8.1.8	
		Rabbits Rats Mice	No adverse effects Nephrotoxic effects 15/16 died, 5/15 showed hyperactivity and convulsions prior to death		

The acute oral toxicity study indicates that sodium ethyl xanthate as a 10% solution at a pH of 10.5 to 11 has an LD₅₀ of 730 mg/kg in mice. The target sites are the central nervous system, liver and the spleen. The oral LD₅₀ for other xanthates in mice ranges from 411 to 583 mg/kg and in rats from 1000 to 2000 mg/kg.

The target sites for the adverse effects of potassium butyl xanthate both after single and repeated oral administration were the central nervous system, liver and kidneys, as with sodium ethyl xanthate, indicating similar target organs for the various xanthates.

The dermal irritation/toxicity study in rabbits indicates that sodium ethyl xanthate powder has an LD₅₀ of <1000 mg/kg and is a moderate irritant while the 10% solution is non irritating to the skin.

The acute eye irritation study indicates that sodium ethyl xanthate as a powder caused mild to moderate irritation, while it is not an irritant in the diluted form (10% solution).

Inhalation of potassium amyl xanthate produces adverse effects in the livers of dogs, rats and mice. The other affected organs are the kidneys in rats and the central nervous system in mice.

The target sites for sodium ethyl xanthate, and other xanthates are the central nervous system, liver and kidneys. The adverse effects seen in the toxicity studies could be due to the xanthates (such as sodium ethyl xanthate), their decomposition products or a combination of both.

8.2 Human health effects

No human studies were available for assessment.

There is only one report of human health effects in the published literature. The Canadian Centre for Occupational Health and Safety (1994)²⁹ has summarised a report by Rakhimova (1973)³⁰ of acute exposure of a worker who opened a tank containing sodium ethyl xanthate. The worker lost consciousness and was removed from the work site. On revival he was restless, vomited and had convulsive twitching of muscles in his arms and legs. He complained of difficult breathing, teary eyes and hoarseness and later developed light sensitivity and fluid accumulation in the eyelids and eye discharge.

Limited unpublished health effects information was available for assessment. Contract workers at one mining site (Kalgoorlie Consolidated Gold Mines Pty Ltd) reported nausea and, complaints of headache, dizziness, nausea and foul odour from residents in the vicinity of a mine using sodium ethyl xanthate (Section 10.1.2) have been reported.

Inhalation of fumes following a chemical leak at the railway station in Alice Springs in May 1993 led to the hospitalisation of six railway workers. The workers were involved in transshipping cargo from a train to road transport (Section 10.1.2).

8.3 Classification of sodium ethyl xanthate

In accordance with the health effects criteria detailed in the National Commission's *Approved Criteria for Classifying Hazardous Substances*³¹ sodium ethyl xanthate is classified as harmful by the oral and dermal routes and is an eye and skin irritant. The 10% solution of sodium ethyl xanthate is classified as harmful by the oral route and is not a skin and eye irritant. Based on the classification of its health effects and in accordance with the *Approved Criteria*³¹ sodium ethyl xanthate is considered to be a hazardous substance.

The above classification is based on the limited toxicity data available for sodium ethyl xanthate at the time of assessment. No human health effects data were available. The data were insufficient to classify sodium ethyl xanthate for other health hazards such as chronic effects, acute inhalational effects, carcinogenicity and mutagenicity.

According to the *Australian Code for the Transport of Dangerous Goods by Road and Rail* (ADG Code)³² sodium ethyl xanthate is classified as a dangerous good, Class 4.3, that is, substances which in contact with water emit flammable gases.

9. Carbon disulphide

9.1 Introduction

Sodium ethyl xanthate readily decomposes to carbon disulphide, especially in the presence of moisture. Therefore, the hazards of carbon disulphide (CS₂) need to be considered in the assessment of sodium ethyl xanthate.

9.2 Physical hazards

Carbon disulphide has a low flash point and autoignition temperature and is therefore a potential fire and explosion hazard. The chemical is 2.6 times heavier than air and may accumulate in low lying areas.

9.3 Metabolism

Carbon disulphide is readily absorbed by inhalation.⁶ Studies also indicate that carbon disulphide as a liquid, such as a solvent or aqueous solution, is absorbed through the skin.

Studies in humans have shown that approximately 70–90% of carbon disulphide absorbed into the body is metabolised, with 1% excreted unchanged and the remainder exhaled.⁶ Due to its affinity for lipid-rich tissues and organs, carbon disulphide rapidly disappears from the bloodstream. In humans, carbon disulphide is metabolised to give organo-sulphur compounds such as thiourea in the urine. Studies in rats and guinea pigs have indicated that carbon disulphide is initially accumulated in the liver, brain, blood and adrenals.

9.4 Health effects

As there is a great deal of published literature available on the human health effects of carbon disulphide, animal data has not been independently considered for this report. However, it is important to note that data from animal studies are consistent with observed human health effects.

9.4.1 Human health effects

Acute effects

Signs of toxicity after acute poisoning include tremor, prostration, dyspnea, cyanosis and vascular collapse. In severe cases, coma and death due to central nervous system depression and respiratory paralysis have resulted.³³ Exposure to concentrations of 3000 ppm or more for short periods has resulted in death.

Skin contact with carbon disulphide has resulted in serious blisters in the hands and fingers.²

Nervous system effects

Central nervous system (CNS) and peripheral nervous system effects have been frequently observed in workers exposed to carbon disulphide, particularly viscose rayon workers. Effects of carbon disulphide poisoning in early reports included polyneuritis (consisting of weakness in the legs and knees), headaches and irritability.

The main symptoms of toxicity revealed in a detailed study of Finnish viscose rayon workers were fatigue, insomnia, paraesthesia and headaches, with sensory or motor

in 26 of 36 workers. Behavioural tests on workers at the plant revealed intelligence reduction, slower response and loss of manual dexterity.³³

In a later study of rayon plant workers exposed to carbon disulphide no behavioural changes were identified at carbon disulphide concentrations below 20 ppm.²

Cardiovascular effects

Atherosclerosis of the cerebral and peripheral arteries has been observed in several cases of workers exposed to carbon disulphide.

An increase in the serum cholesterol concentration has been observed in workers repeatedly exposed to approximately 20 to 60 ppm carbon disulphide, but not in workers exposed to carbon disulphide concentrations below 20 ppm.

An increased incidence of heart disease has been reported in workers exposed to carbon disulphide.³³ In a mortality study of workers at an English viscose rayon factory, an increased coronary heart disease death rate of 2.5 times the expected rate was observed for workers in the viscose spinning area of the plant, where exposure to carbon disulphide was greatest (above 20 ppm). In a study of Finnish viscose rayon workers exposed to approximately 10 to 30 ppm, a mortality study revealed a similar increased risk of coronary heart disease. A detailed health survey of the surviving workers in this study showed an increased incidence of angina and high blood pressure, but a similar survey by the same authors of Japanese workers exposed to similar carbon disulphide levels revealed no effects on blood pressure or angina incidence.

Eye effects

A number of adverse eye effects have been noted in workers exposed to carbon disulphide vapours. In a study³³ of Finnish viscose rayon workers exposed over long periods to approximately 10 to 30 ppm, disturbances in the microcirculation of the ocular fundus were detected by observing delayed filling of the choroid in the peripapillary region using a fluorescein angiographic technique. An increased width of the retinal arterioles was also noted.

A study³³ of Japanese viscose rayon workers exposed over prolonged periods to 5 to 20 ppm carbon disulphide revealed a high incidence of small (dot) retinal haemorrhages and/or microaneurysms, with the incidence directly proportional to the length of exposure. The effect was confirmed in a larger study of Japanese workers, but a similar study in Finnish workers did not reveal this effect.

Reproductive effects

Studies of female viscose rayon workers in Russia and Germany have indicated that menstrual disorders or spontaneous abortion occurred after exposure to around 10 ppm of carbon disulphide. However, the reports were considered of poor quality.³³ Spontaneous abortion has not been confirmed by other studies. Menstrual disorders have been observed in recent studies, such as by Zhou et al (1988)³⁴ in female workers exposed to carbon disulphide levels below 3 ppm for 3 years.

Studies in male workers have also revealed adverse effects on the reproductive system after exposure to carbon disulphide. Decreased libido was observed in workers in the 1940s who were exposed to high carbon disulphide concentrations. A later study of male Romanian viscose rayon workers revealed changes in sperm cell morphology—including hypospermia, teratospermia and asthenospermia—where carbon disulphide levels were believed to be about 13–26 ppm but with excursions up to 250 ppm.

Other effects

Hearing defects have been observed in workers exposed to carbon disulphide. Audiometric tests on a group of Polish viscose rayon workers revealed that 97% of the workers suffered hearing defects, including a poorer sound perception near the normal threshold. This indicated damage near the central supracochlear region of the ear. A study of German workers exposed to 12 to 93 ppm carbon disulphide revealed a hearing loss of high frequency sound, and a high incidence of dry mucosa in the nose. A study of rayon workers in Brazil exposed to approximately 29 ppm carbon disulphide and 86 to 89 dB noise, 60% of the workers suffered hearing loss.²

9.5 Summary

Carbon disulphide is a dangerous fire and explosion hazard.

Carbon disulphide can be absorbed by inhalation, through the skin and by the oral route. Acute exposure to high concentrations (500 to 1000 ppm) may result in psychosis and narcosis. Carbon disulphide vapour is a severe irritant to the eyes, skin and respiratory system, and the liquid may cause burns.

Repeated exposure to carbon disulphide vapour can adversely affect the central and peripheral nervous systems, including weakening of the muscles of the legs and damage to the peripheral and cerebral arteries. Carbon disulphide has been shown to contribute towards coronary heart disease in exposed workers, and severe effects on the retina of the eye have been observed. Hearing defects in workers exposed to carbon disulphide have also been reported.

Adverse effects on the reproductive system of workers have been noted, including menstrual abnormalities in females and decreased libido and changes in sperm morphology in males.

9.6 Hazard classification

Carbon disulphide is on the National Commission's *List of Designated Hazardous Substances*³⁵ and is classified as:

- R23 Toxic by inhalation.
- R36/38 Irritating to eyes and skin.
- R47 May cause birth defects.
- R48 Danger of serious damage to health by prolonged exposure.
- R11 Highly flammable.

10. Exposure assessment

10.1 Occupational exposure

10.1.1 Exposure

Sodium ethyl xanthate is not manufactured in Australia and hence occupational exposure to sodium ethyl xanthate is limited to workers involved in the transport, use and storage of the chemical. A number of mines in Australia use sodium ethyl xanthate or one of the other alkyl xanthates. A range of measures have been implemented by users to control worker exposure and include isolation, engineering controls, administrative controls, safe work practices and personal protective equipment.

Transport and storage

Sodium ethyl xanthate in pellet or powder form is imported in 110–120 kg steel drums with an inner polyethylene liner. The inner lining is tied off while the drum lids are secured by ring clamps. The quality of the packaging of the chemical varies from batch to batch. The drums are imported by ship in sealed containers. The containers are transported to the use site by road or rail and the drums unloaded and stored upon arrival.

Recently, bulk packaging of sodium ethyl xanthate, in plastic bulker bags containing 500–700 kg, has been introduced. The packaging consists of a polyethylene inner bag containing the xanthate enclosed in an outer hessian bag. The inner bag is manually tied. The hessian bag is a support for the inner bag and has lifting straps for transport. The hessian bag is not sealed. Recently some bulker bags have been modified to include a double lined inner plastic bag enclosed in an outer polyethylene bag and the inner bag is heat sealed.

Conditions of storage vary at different mine sites ranging from a fully enclosed area to a large storage shed with only three walls, to a covered area with only a roof and no walls.

There is the greatest potential for worker exposure to xanthate powder or pellets and carbon disulphide vapour during transport and storage if the drums or bulker bags are damaged or not adequately sealed. Sodium ethyl xanthate in contact with moisture produces carbon disulphide. One or two workers are involved in the handling and storage of the drums or bulker bags at each mining site.

Mixing process

Xanthate drums are transported from the storage area to the mixing area by fork-lift. Batches of sodium ethyl xanthate solutions are prepared daily or once or twice a week depending on the extent of use. Two workers are involved in the mixing process at most mining sites for about 4 hours per batch.

Before the mixing process at some mines, xanthate drums are opened to the atmosphere for a short time to allow dissipation of any vapours that may have formed during storage.

Workers involved in the mixing process open the drums containing the chemical and tie back the polyethylene lining. The drums are tipped into the mixing tank, containing water, through chutes and are then washed and stored for disposal. At some sites, the drums are lifted into the chutes with a fork-lift or overhead crane and the driver remains in the cabin of the fork-lift. At other sites the drums are

lifted on to a roller and transported on the roller into a hopper which inverts the drum into the mixing tank. Bulker bags are emptied by lifting into a hopper containing spikes which puncture the bags and empty the contents into the mixing tank.

At some sites, jets of water are used to empty the drums and minimise dust generation. Adding water rapidly can also avoid build up of heat that occurs when sodium xanthates are exposed to small quantities of water. Extraction ventilation systems operate above the area where the drum contents are discharged into the mixing tank.

The sodium ethyl xanthate is automatically mixed with water, in an enclosed tank, using a rotating paddle type system or mechanical drum rotation device. During the mixing operation, the roller door to the mixing vessel is kept closed. Ventilation of the mixing tank is generally by local exhaust ventilation. Some mine sites have in addition a water scrubber-cyclone system which absorbs both dust and soluble gases. The area around the mixing tank is generally bunded to contain 100% of tank volume.

The empty drums are flushed, crushed and transported for burial either at a licensed landfill or in the tailings dam.

There is a high potential for worker exposure to sodium ethyl xanthate and carbon disulphide during the mixing process, depending on the degree of automation. During tipping of the drums there is a likelihood of dust generation and hence exposure to the worker. Spills of the powder or pellets during emptying of the drums could also lead to exposure.

Storage of the solution

Sodium ethyl xanthate aqueous solution is pumped from the mixing tank to a holding tank through pipes. At some mine sites the solution may be pumped over extended distances to the storage tank. The storage or stock tanks 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. The stock tanks are bunded to collect any spills from the tanks. Spills are pumped to the tailings systems. Potential for exposure during this process is therefore limited. Inhalation exposure could occur due to leaks in the pipes.

Flotation process

Sodium ethyl xanthate from the stock tank is automatically pumped to a head tank. The head tank at most sites is located above the flotation floor. It is fitted with level sensors at some mine sites to automate transfer between the two tanks. Any overflow from the head tank goes back to the stock tank.

Remote controlled dosing pumps are used for the addition of the solution to the flotation cell. Sodium ethyl xanthate solution enters the flotation cells through closed pipes via a 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 lines to addition points within the flotation cells. Addition of xanthates to the float tanks is via a continuous drip feed.

Workers involved in checking flows, the head tank or in adjusting and monitoring the pulp levels in the flotation process could be exposed to the chemical or carbon disulphide.

Maintenance

Storage tanks must be cleaned regularly due to the build up of sludge. Impurities in the water used for dissolving sodium ethyl xanthate result in sludge formation. 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 the sludge settling out in the tanks. The accumulated sludge contains trapped xanthate which decomposes to carbon disulphide and alcohol. Stirring of the sludge with an air hose or sparger volatilises the carbon disulphide.

Cleaning the tanks involves complete emptying and thorough flushing of the tank with water. There is potential for worker exposure during maintenance as build up of sludge requires entry into the tank and manual removal by a person. The frequency of cleaning storage tanks varies from once every three months to once or twice a year at different mines.

Sampling procedure

At some mine sites sodium ethyl xanthate solution from the head tank is bypassed through a parallel system into a collection cone for measurement of the chemical added to the flotation cell. A timed sample of xanthate is collected in a plastic cylinder and measurement is performed. Dermal and inhalation exposure to sodium ethyl xanthate may occur to personnel involved in the collection of samples or analysis of sodium ethyl xanthate.

Summary

Sodium ethyl xanthate is not manufactured in Australia and hence occupational exposure to sodium ethyl xanthate is limited to workers involved in the transport, use and storage of the chemical. Exposure to sodium ethyl xanthate powder or pellets as well as to carbon disulphide vapour could occur.

Damage to the packaging can lead to release of solid xanthate and to moisture absorption and formation of carbon disulphide. There is a high potential for worker exposure both to sodium ethyl xanthate and carbon disulphide vapour during the mixing process. Spills and dust generation during emptying of drums into the mixing tank can lead to exposure to solid sodium ethyl xanthate. Maintenance workers involved in cleaning tanks or personnel involved in the collection of samples may be exposed to sodium ethyl xanthate solution and to carbon disulphide.

Potential for exposure during transfer of the sodium ethyl xanthate solution from the mixing to the storage tank, during storage of the solution and the flotation process is low.

10.1.2 Incident reports

Transport incident—Alice Springs, 1993

An incident in Alice Springs in May 1993 involved a chemical leak at the railway station leading to the evacuation of about 100 people. Six railway workers involved in transshipping cargo from a train to road transport had to be taken to hospital for treatment after inhaling fumes. The cargo consisted of 56 drums of sodium ethyl xanthate. Investigation of the incident revealed that several drums had lost their lids and the inner plastic liners were ripped causing leakage of toxic fumes. The clamps holding down the lids had worked loose due to the vibration induced by the journey. The recommendations by the Work Health Authority following the investigation were that suppliers should be made aware of the problems of inferior quality packaging and that shipments carrying drums should be secured to minimise vibration and reduce the chances of mechanical damage.

Transport incident—Alice Springs, 1984

A transport incident in 1984 involving sodium ethyl xanthate was investigated by the Dangerous Goods Section of the Northern Territory Department of Mines and

Energy. Approximately 20 steel drums of sodium ethyl xanthate had been loaded into a freight container together with medical equipment and supplies. On arrival of the container at its destination in Alice Springs it was found that a considerable quantity of the sodium ethyl xanthate dust had escaped from the drums and had permeated the medical equipment and supplies. A large quantity of medical supplies, which had been contaminated, had to be destroyed.

Investigation revealed that the causes of the leaking drums were that:

- some of the drums were rusty and split as a result of vibration during transport from original port of arrival in Sydney;
- some drum lids had become loose and had partly opened during transport; and
- a small hole had been drilled in the side of each drum close to their top to relieve pressure build-up from production of carbon disulphide. This small hole was then sealed with a self tap screw prior to the shipment. Some of these screws had fallen out contributing to the leaking of the drums. This practice for providing pressure relief has been discontinued.

Fire incident—Mt Isa, Queensland

In January 1994 a trial shipment of sodium ethyl xanthate packaged in 700 kg plastic bulker bags caught fire in the storage area at a mining site. The fire spread rapidly and three operations personnel and one fireman were affected by fume inhalation and hospitalised overnight.

Bulker bags consisting of an inner polyethylene bag tied off manually and enclosed in a hessian bag were involved in the incident. On arrival at the port, although the bags appeared in good condition a smell problem was reported. The fire occurred just two weeks after arriving at the port and less than one week after unloading at the mining site. The maximum temperature at the mine site during storage ranged from 29°C to 40°C. On the day of the fire temperatures ranged from 25°C (minimum) to 37°C (maximum).

Most of the bulk sodium ethyl xanthate was severely affected by fire. The fire was observed to spread quickly from bag to bag, whereas only one drum containing sodium ethyl xanthate in the area caught fire. This highlights a major problem with the use of bulker bags in contrast to drums. The material continued to reignite and was disposed of immediately.

An extensive investigation of the incident was undertaken by the mining company and trading company. The manufacturer and other mine sites using similarly packaged xanthates were contacted. The manufacturer stated that the moisture content of the sodium ethyl xanthate at the time of manufacture was 3% to 6%. The other users of bulker bags indicated that they had not experienced any fires. This could possibly be due to cooler climates or the use of a more stable xanthate resulting in lower emissions of carbon disulphide.

The mining company proposed several possibilities concerning release of carbon disulphide, including:

- puncturing of the bag during packaging;
- inadequate sealing of the bag; and
- penetration of the gas through the bag.

They concluded that the most likely cause was ineffective sealing of the inner plastic bag due to manual tying leading to the escape of carbon disulphide. The investigators also concluded that spontaneous combustion of sodium ethyl xanthate was unlikely and

that the likely cause of ignition was a spark associated with a forklift unloading steel drums. However, the possibility of spontaneous combustion cannot be ruled out.

The mining company decided not to continue the use of bulker bags at Mt Isa until adequate solutions to the packaging problem were found.

During the investigation several recommendations for changes to packaging were made, including heat sealing the plastic bulker bags, using multiple layers of plastic bags and transporting in an outer wooden box.

The mining company was also concerned over the response to the emergency and in particular the entry of unauthorised personnel into the fire area without any respiratory protection.

Fire incident—O'Connor, WA

In November 1994, a shipment of 80 bulker bags each containing 700 kg of potassium amyl xanthate was unloaded for testing at Fremantle, the first port of call, following the issue of a product alert by the manufacturer. The containers were being shipped from South Africa to Papua New Guinea and the product alert was issued following a fire involving potassium amyl xanthate at the manufacturing plant in South Africa.

The containers were taken by road to a transport yard at O'Connor after two days at the port to facilitate product testing (temperature measurement). Two of the bulker bags were found to be "smoking" when examined at the yard. The two bags and another that was found to be unstable were placed in an empty freight container and isolated. The potassium amyl xanthate was allowed to burn under controlled conditions. A 500 metre exclusion zone was established by evacuating about 100 homes in the downwind direction. The cause of the spontaneous ignition of this batch of potassium amyl xanthate is being investigated by the manufacturers.

The remaining 77 bulker bags were relocated to a remote location and were subsequently transported by road to a mine site for use in the processing plant.

There was an inconsistency in the dangerous goods classification of potassium amyl xanthate between the ship's manifest, markings on the containers, the safety information sheet supplied by the manufacturer, the labels on the bulker bags and the Material Safety Data Sheet (MSDS) supplied by the local agent.

Public exposure—Stawell, Victoria

In January 1993 residents in the vicinity of a mine using sodium ethyl xanthate complained of headache, dizziness, nausea and foul odour. Other symptoms reported were eye irritation, sore throat and impaired breathing. The ill-effects were reported up to three kilometers from the mine site. The increased odour emissions followed alterations to the metal extraction process and the use of sodium ethyl xanthate. The situation was thought to have been aggravated by the weather conditions. Atmospheric monitoring for carbon disulphide in the mixing area showed that the levels were below 10 ppm.

Use of sodium ethyl xanthate was discontinued until engineering controls had been improved. The company installed controls which included:

- an 800°C afterburner on the carbon regeneration kiln to destroy odours; and
- a caustic scrubber installed at the mixing tank and elution circuit to capture carbon disulphide.

The company have stated that "subsequent engineering controls applied to the areas of fugitive odour escape appear to have cured the problem as no complaints were registered with the latest operation of the flotation circuit". The use of sodium ethyl xanthate was subsequently curtailed at this mining site for economic and efficiency reasons.

10.1.3 Atmospheric monitoring

Atmospheric monitoring for sodium ethyl xanthate is not carried out at the mine sites where it is used. Random instantaneous sampling for carbon disulphide is undertaken at some mine sites and in holds of ships, however, very limited monitoring data were available for assessment. Monitoring for carbon disulphide at most mine sites was carried out using detector tubes either Drager or Kitagawa “length of stain” tubes. Other collection devices used include activated charcoal tubes and portable gas chromatography.

In some States the rail authorities have carried out random monitoring for carbon disulphide before unloading sodium ethyl xanthate.

Western Mining Corporation

Western Mining Corporation submitted data from a review undertaken by Industrial Risk Management Pty Ltd ³⁶ of more than 400 atmospheric samples reported to the Department of Mines. The samples measured carbon disulphide levels at their various mining operations and the results showed that:

- the maximum carbon disulphide level measured was 15 ppm in the mixing section;
- only two readings were above 10 ppm;
- only 20 readings were at or above 5 ppm and most of these were recorded as being in the “mixing section”; and
- the average concentration of atmospheric carbon disulphide from 133 samples taken in the mixing section was less than 2.5 ppm.

Western Mining also submitted atmospheric monitoring data from Olympic Dam Operations as shown in Table 7. No information was supplied on the number of samples. All samples were instantaneous readings.

Table 7: Carbon disulphide levels (instantaneous) at Olympic Dam Operations, Western Mining Corporation Ltd

<i>Location</i>	<i>Average CS₂ (ppm)</i>	<i>Maximum CS₂ (ppm)</i>
Xanthate mixing area	5	15
Flotation area	2	7

Mt Isa Mines Limited

Atmospheric monitoring of carbon disulphide at Mt Isa Mines Ltd was undertaken using Kitagawa “length-of-stain” detector tubes. The carbon disulphide levels measured at the various sites in the mine are provided in Table 8.

Table 8: Carbon disulphide levels (instantaneous) at Mt Isa Mines Ltd

<i>Area</i>	<i>Activity description</i>	<i>CS₂ level (ppm)</i>
Reagent Mixing Plant	Between storage shed and tanks with sodium ethyl xanthate drums opened for 1 hr in full sun	2
	Walkway over spillage pump	< 0.3
	Drum crushing area	< 0.3
	Walkway above stock tanks, downward of tanks	< 0.3
Flotation area	Area between cell banks, between two cell sodium ethyl xanthate addition points	1
	Raised aisle between xanthate distributors	5

Pasminco Mining, Broken Hill

Routine atmospheric monitoring for carbon disulphide is not performed by Pasminco Mining at Broken Hill. However, carbon disulphide levels as high as 16 ppm have been detected a few metres from the mixing station using a Drager tube.

Government authorities

In some States the rail authorities carry out random monitoring for carbon disulphide at the time of arrival of sodium ethyl xanthate before transferring the load from the ship on to trains. Queensland authorities have reported carbon disulphide levels as high as 20 ppm in containers with the door slightly open, when some of the drum lids were observed to be loose.

Summary

The exposure standard recommended by the National Commission for carbon disulphide is a TWA of 10 ppm.³⁷ From the limited data submitted for assessment it appears that, generally, carbon disulphide levels at the mine sites are below the TWA. However, instantaneous sampling using detector tubes indicated that, at times, short-term excursions above 10 ppm occurred in the mixing area during mixing activity at some user sites. High levels were also recorded in containers in ship holds on arrival of sodium ethyl xanthate at the ports.

The monitoring data indicate that there is the potential for exposure to high levels of carbon disulphide during mixing and transport. However, the data were inadequate to demonstrate how widespread this problem is and whether there is the potential for exposure in other areas or activities.

10.2 Public exposure

The public is unlikely to be exposed to sodium ethyl xanthate through its use as a flotation agent in the mining industry. An 8–13.5% aqueous solution of sodium ethyl xanthate is made up on site.

Since the compound decomposes and the major product is carbon disulphide, there exists some potential for the contamination of the immediate atmosphere which may impact on public health. This risk is minimised by the use of adequate transport and engineering controls. Release of the hazardous degradation products may also result from the decomposition of residual amounts of sodium ethyl xanthate which remain in the aqueous phase in the tailings slurry, which is discharged to a tailings dam. However, such dams are typically located on remote sites and the residual concentrations of sodium ethyl xanthate are expected to be low.

Two incidents have been reported where possible public health concerns have been raised, one at Stawell, Victoria and the other at Alice Springs (see Section 10.1.2).

10.3 Handling of sodium ethyl xanthate at mine sites

10.3.1 Mixing area

Photograph 1



Ground level view showing mixing tank and drum storage area. Personal protective equipment stored in white box at left of picture.

Photo: Western Mining Corp. Ltd

Photograph 2



Door and rollers used for the emptying of drums into the mixing tank.

Photo: Western Mining Corp. Ltd

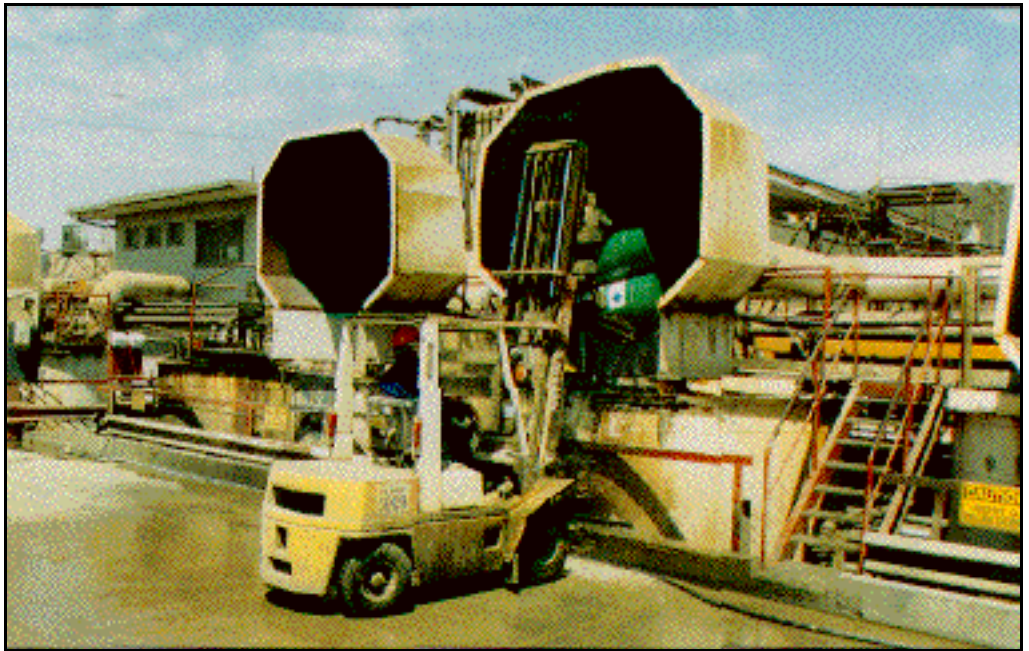
Photograph 3



Drums on mixing floor. Note rollers on floor.

Photo: Western Mining Corp. Ltd

Photograph 4

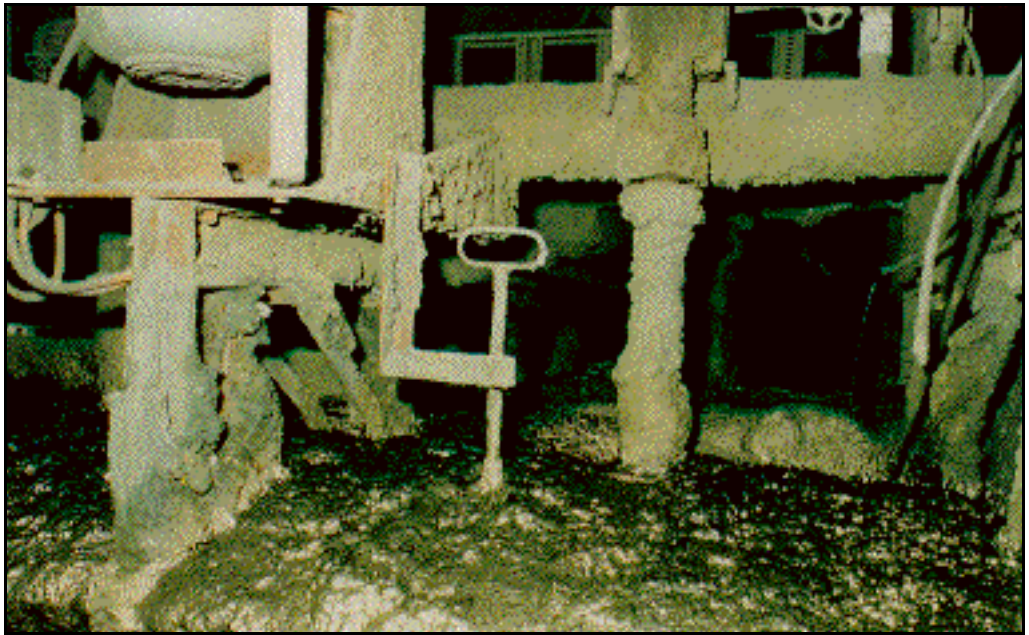


Mixing area showing the emptying of drums containing sodium ethyl xanthate.

Photo: Mt. Isa Mines Ltd

10.3.2 Flotation area

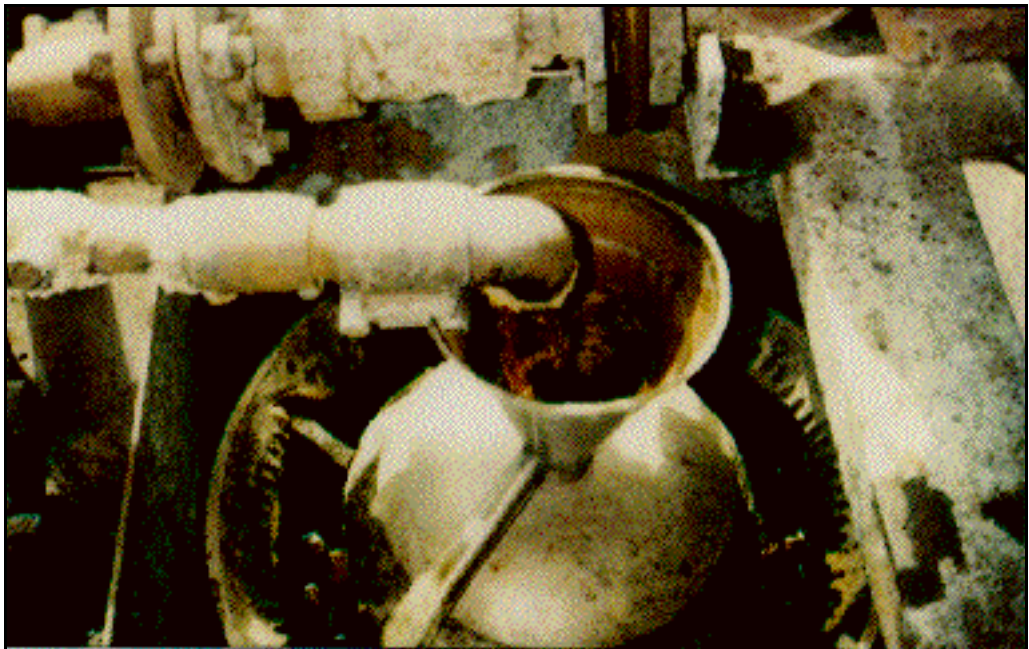
Photograph 5



Flotation cell showing sodium ethyl xanthate addition point at right of centre.

Photo: Mt. Isa Mines Ltd

Photograph 6



Distribution cup used to distribute sodium ethyl xanthate evenly through flotation tanks.

Photo: Western Mining Corp. Ltd

11. Assessment of risk to human health

11.1 Occupational health and safety

11.1.1 Health and safety hazards

Animal studies have shown that solid sodium ethyl xanthate is a skin and eye irritant. Studies with 10% aqueous solution of sodium ethyl xanthate show that it is not a skin and eye irritant. Acute oral and dermal toxicity studies show that 10% aqueous sodium ethyl xanthate is harmful by the oral and dermal routes and the target sites are the central nervous system, liver and kidneys. No inhalational or chronic data were available for sodium ethyl xanthate.

There is very little information available on human health effects of sodium ethyl xanthate. One published case report indicated eye, respiratory and CNS effects as a result of acute exposure. Other reports include complaints of nausea from contract workers at a mine site and complaints of headache, dizziness, nausea and foul odour from residents in the vicinity of a mine using sodium ethyl xanthate. Acute effects, such as loss of consciousness, have been reported in incidents where workers have been exposed to fumes given off by sodium ethyl xanthate.

Situations which are likely to present the greatest risk to workers handling or using sodium ethyl xanthate are:

- direct skin contact with sodium ethyl xanthate powder or pellets;
- inhalational exposure to sodium ethyl xanthate dust;
- direct skin contact with carbon disulphide;
- inhalational exposure to carbon disulphide vapour; and
- conditions which are conducive to carbon disulphide formation and its flammability such as low pH, moisture and heat.

Health effects data indicate that dermal exposure to sodium ethyl xanthate should be avoided and hence the generation of dust should be minimised. Mechanical and physical damage to the pellets such as sweeping should be avoided to minimise dust generation. The particle size of sodium ethyl xanthate powder is in the range of 1 to 10 μm (mean 5 μm) and pellet size ranges from 5 to 6 mm. The powder is well within the inspirable range ($< 185 \mu\text{m}$) and the majority is within the respirable range ($< 7 \mu\text{m}$). Therefore, there is a greater risk to workers when handling the powder.

Under the conditions of use, carbon disulphide is the major decomposition product of sodium ethyl xanthate and it is therefore important to also consider the health and safety hazards of this substance. Carbon disulphide is readily given off when sodium ethyl xanthate comes into contact with water. Carbon disulphide is very volatile and poses a fire hazard because of its low auto ignition point and high flammability. Carbon disulphide causes acute effects such as severe irritation to the skin and eyes and respiratory system and is toxic by inhalation. Repeated exposure to carbon disulphide may cause long-term effects such as reproductive and CNS effects. Health effects data indicate that dermal and inhalational exposure to carbon disulphide should be minimised.

11.1.2 Occupational risk

Transport and storage

During transport and storage of sodium ethyl xanthate the major risk is release of carbon disulphide vapour from solid sodium ethyl xanthate. Inhalational and dermal exposure to carbon disulphide vapour can cause adverse health effects. This has been demonstrated in the incident at Alice Springs (1993) where workers were taken to hospital suffering acute effects of exposure to carbon disulphide vapour released from steel drums due to the lids working loose during transport.

One of the factors involved in the formation of carbon disulphide is the moisture content of the product. Sodium ethyl xanthate powder and pellets contain up to 7% moisture. Damage to the packaging or inadequate packaging can lead to absorption of additional moisture and release of carbon disulphide. Defective packaging has resulted in damage to the drums and the lids working loose during transport. Bulker bags are more prone to puncture during transport and also during filling of the bags at the manufacturing site. In addition, both drum liners and inner bulker bags are usually manually tied and not sealed.

Another significant risk during transport and storage is the potential of spontaneous combustion. Spontaneous combustion depends on the heat of the reaction involved, moisture content, ambient temperature and the size of the packaging. The larger the packaging size is the greater the risk of spontaneous combustion, hence bulker bags present a greater risk than steel drums. The risk is also increased due to the conditions in which the sodium ethyl xanthate is stored. High temperatures in the holds of ships and storage areas in mining sites in the hotter districts of Australia can lead to increased release of carbon disulphide. Two incidents, at Mt Isa (1994) and O'Connor (1994), highlight the very dangerous situation where sodium ethyl xanthate can catch fire during storage.

There is also the potential for skin contact and inhalation of sodium ethyl xanthate during clean up of spills. Safe work practices and personal protective equipment, such as gloves, should minimise this risk.

Mixing process

The greatest risk to workers in this process is during the opening of the packaging and transfer of the chemical into the mixing tank. The process can lead to spills of powder and pellets during transfer and release of carbon disulphide upon opening the drums. Due to the small particle size of sodium ethyl xanthate, there is a greater potential for inhalation. The drums are moved by fork-lift or overhead crane. At some sites the operator is enclosed in the cabin. The number of workers involved is small with only one or two workers required during this stage.

Sodium ethyl xanthate solutions are made on a batch basis from one to several times per week. The mixing process is automated at most mine sites and ventilation of the mixing tank is provided by local exhaust ventilation. At some mine sites ventilation is via a wet scrubber or short stack. Air monitoring data were limited and of poor quality and considered inadequate to assess controls. However, the monitoring data did indicate that in the mixing area, some short-term excursions of the atmospheric levels of carbon disulphide above 10 ppm occur. During mixing there is a potential for exposure to high levels of carbon disulphide for short periods. The level of exposure of workers to carbon disulphide will be dependent on the quality of ventilation. In the absence of adequate ventilation risk to workers would be higher.

Transport and storage of solution

Sodium ethyl xanthate solution is not irritating to skin and eyes. In addition, as the pH of the solution is in the range 7 to 10, decomposition of sodium ethyl xanthate to carbon disulphide would be slow. The solution is automatically transferred and generally stored in closed systems. Therefore risk to workers during transport and storage of the 10% aqueous solution of sodium ethyl xanthate would be minimal. Overflow of the tanks is unlikely if they are fitted with level sensors.

Flotation process

The flotation process is fully automated. The process takes place in open tanks and there is the potential for formation of carbon disulphide vapour. However, the concentration of sodium ethyl xanthate in the flotation tank is low and, therefore, the release of carbon disulphide would be expected to be low. Air monitoring data, although limited and of poor quality, indicate that the atmospheric levels of carbon disulphide are below 10 ppm in the flotation areas. The risk to workers during the flotation process is considered to be low.

Maintenance and sampling

There is a high potential for dermal and inhalation exposure to sodium ethyl xanthate solution and carbon disulphide during the cleaning of the tanks. Each storage tank needs to be cleaned one to four times per year. During cleaning the tanks are flushed with water. If workers need to enter the tank potential for exposure is high. However, where workers at mines sites follow standard operating procedures for working in a confined space,³⁸ including personal protective equipment, the risk to workers is low.

Potential for exposure is limited but could occur due to leaks in the plumbing system, during repair or replacement of plumbing systems, or during removal of samples for quality control purposes. Around twenty personnel are involved in general maintenance work for approximately 1 hour per week. Risk to workers is considered low where maintenance operations are planned, conducted by trained personnel and appropriate protective clothing is worn.

11.2 Public health risk

When used as a flotation agent in the mining industry, the potential for public exposure to sodium ethyl xanthate is low. However, since the compound readily decomposes, releasing carbon disulphide, there may be some public exposure to carbon disulphide, particularly in the case of accidental spillage during transport. To minimise exposure to the public emergency procedures for the containment and clean-up of accidental spills should be followed.

Based on the available information and provided that appropriate controls on release are in place and transport packaging is adequate, sodium ethyl xanthate should not present a significant risk to public health.

12. Environmental assessment

12.1 Environmental exposure

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, either in air under ambient conditions or at elevated temperatures in an oven,* 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. Xanthate residues in the ore concentrate are expected to decompose during drying or smelting.

12.2 Environmental fate

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 disulphide, sodium carbonate and sodium trithiocarbonate, the two salts arising from neutralisation of carbon disulphide 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 hours, increasing to over 500 hours in the pH range 8 to 11.³

Sodium ethyl xanthate is hydrolytically unstable when exposed to acidic conditions, reverting rapidly to ethanol, carbon disulphide 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.

Sodium ethyl xanthate is not expected to contaminate the environment where ore tailings are confined to well constructed tailings dams. 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 residues in tailings have been discharged directly to waterways in exceptional circumstances. Until recently (1994), this practice was allowed to occur at the Mt Lyell copper mine in Queenstown, Tasmania, which operated under a ministerial exemption from State discharge requirements. Although currently closed, indications are that the Mt Lyell copper mine may be reopened by December 1995. Any resummptions in

* For example, Mt Isa Mines Ltd reports that lead concentrates are sintered and smeltered at 300°C.

operations will require the construction of a tailings dam as the Tasmanian Department of Land and Environment has indicated that exemptions allowing discharge to rivers will not be issued. The Queen River into which discharges occur, and the King River between Macquarie Harbour and its junction with the Queen, no longer support aquatic life. The Australian Mining Industry Council advised the Environment Protection Agency in January 1995 that all Australian mines currently operating concentrators have tailings dams.

12.3 Environmental effects

12.3.1 Terrestrial toxicity

Mount Isa Mines Limited reports that some potential exists for avian exposure to xanthate residues in tailings and concentrate dams. Little appears to be known on the avian toxicity of xanthates.

Antimicrobial activity is evident from the median inhibitory limit on ammonia oxidation in *Nitrosomonas* of 12 ppm.³⁹ Potassium ethyl xanthate is a nitrification inhibitor that has also been observed to inhibit soil denitrification at concentrations around 50 ppm, but only in soils previously amended with mannitol to stimulate denitrifying activity.⁴⁰

12.3.2 Aquatic toxicity

Sodium ethyl xanthate has been used as a pesticide overseas. US EPA predictions⁴¹ indicate that sodium ethyl xanthate is likely to have herbicidal, microbicidal and insecticidal activity. Predicted LC₅₀s for aquatic fauna are above 2 ppm, and chronic end-points above 0.2 ppm. Effects on algal growth are predicted at concentrations below 1 ppm.

Fish

Formal test reports were only provided for potassium amyl xanthate. When tested under static conditions at nominal concentrations between 6 and 100 ppm, the 96 h LC₅₀ to rainbow trout was 12 ppm.⁴² No deaths were recorded to 48 hours at this concentration, but 50% mortality occurred within 24 hours at a nominal concentration of 25 ppm, increasing to 100% by 48 hours. The nominal 24 and 48 hours LC₅₀s were 25 and 18 ppm respectively, and the no effect level was 6 ppm.

Static toxicity testing of sodium ethyl xanthate with rainbow trout is reported in the literature.⁴³ The nominal 96-hour LC₅₀ at 12°C for two commercially available products was about 14 ppm, little different from the 24 hours end-point of 17 ppm. The LC₅₀ for the potassium salt (both pure and as commercial product) was of similar magnitude. Toxicity of pure potassium ethyl xanthate increased sharply at higher temperatures, with nominal LC₅₀s falling to between 1.5 and 2.0 ppm at 16 and 20°C.

A great disparity in the toxicity of sodium ethyl xanthate towards rainbow trout was apparent from 96-hour static and 28-day flow-through testing.⁴⁴ Again, concentrations are nominal, but continuous introduction of the toxicant in the flow-through tests should mean that the flow-through data reflect actual concentrations. The LC₅₀ for two commercial forms of sodium ethyl xanthate was between 10 and 50 ppm, with a concentration of 56 ppm killing all fish exposed under static conditions within 4 days. Under flow-through conditions, a concentration of 1 ppm killed all exposed fish within 8 days.

A review⁴⁵ conducted for the Ontario Ministry of the Environment reported acute aquatic toxicity data for a selection of xanthates (Table 9). The author advises that 96 h LC₅₀ data were obtained under static conditions and are expressed as measured concentrations. The concentrations were measured at the beginning of the study. However formal test reports were not available.

Table 9: Acute aquatic toxicity of xanthates (Hawley, 1977)⁴⁵

Xanthate	Test organism	Toxicity range (ppm)		Toxicity rating*
		Product A	Product B	
Sodium ethyl	<i>D. magna</i>	0.1–1.0	—	2
	<i>N. atherinoides</i>	0.01–0.1	—	1
	<i>P. promelas</i>	0.32–3.2	0.18–1.8	2–3
Potassium ethyl	<i>D. magna</i>	0.1–1.0	—	2
	<i>N. atherinoides</i>	0.01–0.1	—	1
	<i>P. promelas</i>	0.1–1.0	0.56–5.6	2, 2–3
Potassium amyl	<i>D. magna</i>	0.1–1.0	—	2
	<i>N. atherinoides</i>	10–100.1	—	4
	<i>P. promelas</i>	1.8–18	18–180	3–4, 4–5
Potassium isopropyl	<i>D. magna</i>	—	—	—
	<i>N. atherinoides</i>	—	—	—
	<i>P. promelas</i>	3.2–32	—	3–4
Potassium hexyl	<i>D. magna</i>	—	—	—
	<i>N. atherinoides</i>	—	—	—
	<i>P. promelas</i>	100–1000	—	5
Sodium sec-butyl	<i>D. magna</i>	—	0.56–10	2–3
	<i>N. atherinoides</i>	—	1.0–10	3
	<i>P. promelas</i>	32–320	3.2–56	4–5, 3–4
Sodium isobutyl	<i>D. magna</i>	0.56–10	—	2–3
	<i>N. atherinoides</i>	10–100	—	4
	<i>P. promelas</i>	32–320	56–560	4–5, 4–5
Sodium isopropyl	<i>D. magna</i>	0.1–1.0	—	2
	<i>N. atherinoides</i>	0.01–0.1	—	1
	<i>P. promelas</i>	0.32–5.6	0.18–1.8	2–3, 2–3
* Rating	Category description	LC₅₀ (ppm)		
1	very highly toxic	< 0.1		
2	highly toxic	0.1–1		
3	moderately toxic	> 1–10		
4	slightly toxic	> 10–100		
5	practically non-toxic	> 100		

Two species were tested: the emerald shiner (*Notropis atherinoides*); and fathead minnow (*Pimephales promelas*). The LC₅₀ value for the former is reportedly between 0.01 and 0.1 ppm, and for the latter between 0.18 and 1.8 or 0.32 and 3.2 ppm in separate studies on different commercial products (Product A and B) of sodium ethyl xanthate. Sodium isopropyl xanthate exhibited similarly high toxicity but the isobutyl compound was no more than slightly toxic to both species.

Daphnia

The nominal 48 h LC₅₀ to *Daphnia magna* tested under static conditions was 3.9 ppm with a no effect level, based on surfacing and clumping, below 1 ppm.⁴⁶

The review by Hawley (1977)⁴⁵ cites an LC₅₀ between 0.1 and 1 ppm. Similar end-points (0.1–10 ppm) were returned by all xanthates tested.

12.3.3 Conclusion

Little is known of the avian toxicity of xanthates, but avian exposure to residues in tailings dams is not expected to elicit adverse effects as residues are low (in the order of 1 ppm) and no effect levels in rodents are two orders of magnitude higher.

Sodium ethyl xanthate must be regarded as highly toxic to aquatic fauna, but the variability in aquatic toxicity data merits comment. Static testing, which would

simulate a spill situation, indicates moderate toxicity to invertebrates and slight toxicity to fish, based on nominal concentrations. Flow-through tests, which more closely reflect continuous input via effluent discharge rather than spills, indicate high toxicity to fish. Static test results reported by Canada indicate sodium ethyl xanthate to be very highly toxic to fish and invertebrates, based on measured concentrations, in contrast to the nominal data. Other xanthates range from practically non-toxic to fish to very highly toxic.

Xanthates are unstable compounds, and the apparent toxicity may reflect the action of impurities or degradation products. Data to indicate rates of degradation under the test conditions and the products formed are not available. However, it may be noted that hydrogen sulphide is extremely toxic to fathead minnows exposed in flow through bioassays, with 96-hour end points varying between 7 ppb and 550 ppb over the temperature range 6–24°C.³⁹

12.4 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 use⁴⁷ identified a number of xanthates as being potentially dangerous for the environment. However no further investigations were conducted as several xanthates were no longer used in Sweden. Use of those that remained was not widespread, being confined to a few users in the mining industry.

Assuming a treatment rate of 500 gms 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 gms 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.⁴⁵ Concentrations of sodium ethyl xanthate likely to be found in the tailings slurry may be toxic to aquatic fauna. Such waste streams should therefore not be discharged to waterways.

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 are taken to avoid entry of tailings to waterways, the environmental risk of sodium ethyl xanthate can be described as minimal in view of the low environmental exposure and limited persistence.

13. Risk management

13.1 Hazard communication

13.1.1 Material Safety Data Sheet

Material Safety Data Sheets (MSDS) provide information to workers to allow the safe handling of chemicals. Seven MSDS for sodium ethyl xanthate were provided as part of the information package for assessment. Six MSDS for other xanthates were also provided.

MSDS for sodium ethyl xanthate were assessed and some were found to be below the standard considered appropriate. Five out of the seven MSDS were written in accordance with the National Commission's *National Code of Practice for the Preparation of Material Safety Data Sheets*.⁴⁶

The data found to be inadequate in some of the MSDS were:

- no name of the Australian importer with an Australian address (1/7);
- no Australian telephone number for information in case of an emergency (1/7);
- inconsistency in the UN number. According to the ADG Code, the UN number for sodium ethyl xanthate is 2813, but some states such as Queensland believe that 3134 would be more appropriate;
- an incorrect UN number of 3130 (1/7);
- the chemical composition of the substance with a list of the ingredients, CAS numbers and the proportions was not stated (5/7);
- no use information of the chemical (2/7);
- summary of the health effects of sodium ethyl xanthate had general statements on health effects with no supporting data. The summary did not specify if the effects were based on human or animal data (5/7);
- exposure standard for carbon disulphide was expressed as a threshold limit value (TLV) of ACGIH instead of a TWA (3/7); and
- control measures were described by standard phrases, such as adequate ventilation, instead of more specific guidance such as local exhaust ventilation during the mixing process (6/7).

The sections in the MSDS on first aid and safe handling were satisfactory with sufficient information being provided for storage and transport, disposal, spills and firefighting.

13.1.2 Labels

The label is the initial source of information for an employee handling a hazardous substance. In accordance with the National Commission's *National Model Regulations for the Control of Workplace Hazardous Substances*,⁴⁹ all containers of hazardous substances supplied to, used or handled in the workplace should be appropriately labelled. Appropriate labelling for hazardous substances is detailed in the National Commission's *National Code of Practice for the Labelling of Workplace Substances*.⁵⁰

Sodium ethyl xanthate is classified as a dangerous good according to the ADG Code.³² It belongs to Class 4.3, that is, substances which in contact with water emit

flammable gases, and therefore has to comply with the labelling requirements of the ADG Code.³²

The labels provided in the assessment package complied with the requirements of the ADG Code.³² However, when assessed against the *National Code of Practice for the Labelling of Workplace Substances*⁴⁸ all the labels were considered inadequate and lacked:

- risk or safety phrases;
- first aid procedures;
- emergency procedures; or
- reference to the MSDS.

The risk and safety phrases considered appropriate for sodium ethyl xanthate are listed in Chapter 15.

13.1.3 Education and training

Besides MSDS and labels, the assessment package showed that information to workers on the safe handling of chemicals is provided at induction through competency based training programs. The training programs include information on the adverse health effects of chemicals, safe handling procedures appropriate for the area of work, interpretation of air monitoring results and MSDS and selection, use and maintenance of personal protective equipment. Operators using sodium ethyl xanthate are advised of the flammable nature of the chemical and safe work practices to be followed for the chemical.

Some mine sites supply workers with written instructions on operating safely with reagents. Manuals on operating safely with reagents were provided in the assessment package by BHP Minerals Ltd and Mt Isa Mines Ltd. These outlined the hazard of the chemical, safe work practices to be followed in the mixing area, first aid and firefighting measures.

13.2 Control measures

For hazardous substances, such as sodium ethyl xanthate and carbon disulphide, effective control measures should be in place to reduce exposure and minimise the risks to health and safety. Control measures should be achieved by the following hierarchy:

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

In relation to sodium ethyl xanthate and carbon disulphide, controls should be in place to minimise dermal and inhalational exposure. Workplaces have implemented various safe work practices and engineering controls to reduce worker exposure and these are described below.

13.2.1 Elimination and substitution

Sodium ethyl xanthate readily decomposes in the presence of moisture and heat to evolve carbon disulphide. Some mining sites have used other xanthates that are more stable and resistant to heat and moisture. However, due to their structural

similarity, it is expected that all xanthates would have similar health effects either due to the xanthate or carbon disulphide.

13.2.2 Isolation

Isolation is the separation of the process from people by distance or the use of barriers to prevent exposure. At mining sites the mixing process is segregated from other workplace activities and sodium ethyl xanthate is stored in a separate area.

13.2.3 Engineering controls

Engineering controls are plant or processes which minimise the generation of hazardous substances, suppress or contain hazardous substances, or which limit the area of contamination in the event of spills or leaks.

Engineering controls which have been generally implemented at mining sites include:

- enclosure and automation of the transfer and mixing process;
- enclosure of the cabin of the fork-lift or crane used for drum tipping;
- extraction ventilation systems above the area where drum contents are discharged into the mixing tank;
- local exhaust ventilation system with a water scrubber system above the mixing tank to absorb dust and gases or exhaust vents to the atmosphere via a short stack;
- bunding the area around the mixing tank so as to contain 100% of the tank volume;
- remote controlled dosing pumps;
- good general ventilation of the plant; and
- storage of solid sodium ethyl xanthate in well ventilated areas.

The engineering controls vary at the different mine sites and all the listed controls are not present at all the sites.

At the Stawell mining site, an 800°C afterburner on the carbon regeneration kiln to destroy odours and caustic scrubbers were introduced. This was carried out in response to public complaints of symptoms which developed after the introduction of sodium ethyl xanthate in a gold mining process. The company reported that no more complaints were received after these control measures were introduced.

13.2.4 Safe work practices

Safe work practices are administrative practices which require people to work in safer ways.

Safe work practices introduced at mining sites for storage, use and transport of sodium ethyl xanthate include:

- Restricted access to the working area.
- Storage of solid sodium ethyl xanthate in a cool, dry place.
- Avoidance of dust generation.
- Prohibition of all ignition sources.
- Closure of the roller door to the automatic mixing vessel during the mixing operation.
- Prompt cleaning up of spills.
- Maintenance of good housekeeping in the storage facility and around the mixing area.

- Regular and frequent cleaning of the storage tanks with observance of the standard procedures for safe working in a confined space.
- Good personal hygiene practices.

As variables such as moisture content of sodium ethyl xanthate and storage temperature are particularly important for preventing incidents with sodium ethyl xanthate it is important that further information be provided by manufacturers and users about the range of conditions suitable for transport and storage. Preventive action such as evidence of good manufacturing practice including quality control procedures that control moisture content of products and assure quality of packaging would also be important.

13.2.5 Personal protective equipment

Personal protective equipment (PPE) is used as a control measure where other control measures are not practicable or in conjunction with the other control measures to increase worker protection.

During the use of sodium ethyl xanthate, the following personal protective equipment is generally used at mining sites:

- | | |
|--------------------------|---|
| • Reagent operators | Chemically impervious protective overalls, long sleeve gloves, full face respirators with organic filter. |
| • Flotation operators | Long sleeve chemically impervious gloves when measuring flows, protective overalls. |
| • Maintenance workers | Long sleeve chemically impervious gloves, face and eye protection and protective overalls. |
| • Workers entering tanks | Appropriate PPE for working in a confined space |

Personal protective equipment should be selected and used in accordance with the relevant Australian Standards.

Suitable PPE and when it should be used include:

- chemically impervious protective clothing in accordance with AS 3765⁵¹ when direct skin contact may occur (such as cleaning spills and tanks, sampling and transferring solid xanthate to the mixing tanks);
- long sleeve gloves of impervious material in accordance with AS 2161⁵² when direct skin contact may occur (such as cleaning spills and tanks, sampling and transferring solid xanthate to the mixing tanks);
- face and eye protection should comply with AS 1337⁵³ and used in accordance with AS 1336⁵⁴ when direct contact with the face may occur (such as during maintenance); and
- a combination particulate and gas filter with a minimum class P2 particulate filter and a gas filter which can adsorb carbon disulphide such as type A or AX. The respiratory protective equipment should be in accordance with AS 1716⁵⁵ and used when inhalation exposure to xanthate dust or carbon disulphide vapour may occur, such as, when opening containers, drums or bulker bags, during accidents and emergencies and when entering storage tanks. During cleaning of storage tanks, a self-contained breathing apparatus or an air-line respirator may be required.

13.2.6 Emergency procedures

As for any hazardous substance, an emergency response plan is essential for those workplaces handling sodium ethyl xanthate, especially during the transport and storage of the chemical in powder or pellet form. In the event of a leak, spill or fire, a written response is necessary for workers in the area and for emergency services who may be required to deal with the release. It is also essential that the workers are familiarised with the procedures during their education and training.

Most applicants provided information indicating that emergency procedures were clearly written down and some companies indicated that this information was included in the training package for personnel. However, the fire incident at a Mt Isa mining site (section 10.1.2) highlights not only the need for such procedures but also the need to educate and train the worker. Though the company has written emergency procedures and workers are provided with training at induction, the incident highlighted the failure to implement these procedures at the time of the incident.

13.3 Packaging

According to the ADG Code,³² xanthates are assigned to Class 4.3, that is, substances which in contact with water emit flammable gases, and Packaging Group II. Under the ADG Code³² class 4 substances may be packaged by any suitable method, provided that the requirements of sub-paragraph 5.9.4 are met. According to sub-paragraph 5.9.4, if packed in drums, then the removable head type may be used and the chemical should be packaged under an inert dry gas in a hermetically sealed container.

At least four of the incidents reported over the last two years have revealed deficiencies in packaging. Specific problems which have been encountered with the packaging are:

- the lids of drums working loose during transportation and carbon disulphide given off; and
- carbon disulphide release from bulker bags during transportation and storage.

These packaging problems led to the hospitalisation of several workers and in one incident the serious threat of fire to persons and property. The incidents highlight the need for a thorough investigation of packaging and in particular whether packaging meets the requirements of the ADG Code³² and, if so, whether there is need for change in the requirements.

13.4 Regulatory controls

13.4.1 Exposure standard

An exposure standard for sodium ethyl xanthate has not been assigned by the National Commission, or any other country. Atmospheric monitoring is not carried out at the mining sites where it is used. It is not recommended that an exposure standard for sodium ethyl xanthate be developed by the National Commission.

An inhalation study with potassium amyl xanthate was conducted by Dow Chemicals which showed that the chemical had an adverse effect on the central nervous system, liver and kidney. A no-effect level for hepatotoxicity in dogs could not be demonstrated in this study. On the basis of this study, in 1976 Dow Chemicals recommended reduction of in-house exposure levels to 1 mg/m³. This level is ten

times lower than the nuisance dust level generally used and emphasises the need to maintain low dust levels during use of sodium ethyl xanthate.

Xanthates in the presence of heat/moisture decompose and under the conditions of storage and use the major decomposition product is carbon disulphide. The National Occupational Exposure Standard for carbon disulphide in Australia is a TWA of 10 ppm with a skin notation which indicates that significant absorption occurs through the skin.³⁷

Several mining sites randomly measure atmospheric levels of carbon disulphide. The limited monitoring data indicates that there were some excursions over 10 ppm on a few occasions in the mixing areas. Monitoring at all mining sites was by random instantaneous sampling and an adequate and detailed assessment of exposure could not be made on the information provided. Detailed monitoring data around high risk areas such as transport and storage, mixing areas and in tank cleaning operations would be necessary to better define and control risks from carbon disulphide.

13.4.2 Health surveillance

Currently the extent of health care provided to the workers in Australian mines differs at the various mines. Most mine sites have a medical unit with an occupational nurse carrying out routine health checks. Smaller mine sites have an occupational physician visiting on a monthly basis to talk with the workers while larger mines like Mt. Isa Mines Ltd have resident physicians. Most mine sites have no formal health surveillance programs for workers exposed to sodium ethyl xanthate and other xanthates. At some mines, workers undergo health checks on a six- to 12-monthly basis, which include a physical examination and routine investigations, such as blood and urine tests.

No adverse health effects have been reported in workers in the data submitted for assessment except at one mine site where some contract workers complained of nausea probably due to the odour of the decomposition products.

It is recommended that sodium ethyl xanthate not be considered for addition to schedule 3 of the National Commission's *National Model Regulations for the Control of Workplace Hazardous Substances*⁴⁹ as adverse health effects are not expected under the current conditions of use. However, under these regulations, employers will need to provide health surveillance in workplaces where assessment shows that exposure to sodium ethyl xanthate may result in a substance-related health effect.

14. Conclusion

Sodium ethyl xanthate is used widely in the mining industry in Australia as a flotation agent. The toxicological data available on xanthates, including sodium ethyl xanthate, is limited. The main health hazards of sodium ethyl xanthate are irritation of the skin and eyes and dermal toxicity. In acute oral and dermal studies the chemical causes adverse effects on the central nervous system, liver and kidneys.

Sodium ethyl xanthate readily decomposes at high temperatures and in the presence of moisture to evolve carbon disulphide. Carbon disulphide has a low autoignition temperature and is highly flammable and explosive. Carbon disulphide also produces adverse health effects.

Packaging of solid sodium ethyl xanthate presents a major risk to workers during transport and storage. To minimise carbon disulphide production, it is important to ensure that packaging minimises exposure to heat as well as moisture. Defective packaging, such as loose lids on steel drums and loosely tied or damaged bulker bags can lead to exposure to solid xanthate and increased production of carbon disulphide. In addition, transporting the chemical in large packages, such as bulker bags, increases the risk of autoignition and flammability. Several incidents have highlighted these packaging problems. Improvements to packaging should be investigated, particularly in the use of bulker bags.

Occupational exposure during use to solid sodium ethyl xanthate and carbon disulphide is expected to be low as the process is generally isolated and automated and the chemical is used in low concentrations. The most likely areas for exposure are during the mixing process and during cleaning of storage tanks and other maintenance work. A range of control measures have been implemented to minimise exposure at the different mine sites. The atmospheric monitoring data submitted were of poor quality making it difficult to assess the adequacy of controls.

Sodium ethyl xanthate is unlikely to present a risk to the public.

Sodium ethyl xanthate is highly toxic to aquatic fauna. Ore tailings containing xanthate residues should therefore not be discharged to waterways.

Sodium ethyl xanthate is currently unlikely to present a risk to the environment as Australian mines do not discharge ore tailings directly into waterways because of the severe detrimental consequences of such practices on stream ecology, irrespective of content.

15. Recommendations

15.1 Classification

In accordance with the health effects criteria detailed in the National Commission's Approved Criteria³¹ and based on the information available, sodium ethyl xanthate should be classified by manufacturers and importers as 'harmful' by the oral and dermal routes and as an eye and skin irritant. Based on the classification of its health effects and in accordance with the Approved Criteria,³¹ sodium ethyl xanthate is considered to be a hazardous substance.

Based on animal studies, 10% solution of sodium ethyl xanthate is classified as harmful by the oral route but not a skin and eye irritant.

According to the ADG Code³² sodium ethyl xanthate should be classified as a dangerous good, Class 4.3, that is, substances which in contact with water emit flammable gases.

15.2 Provision of information

As sodium ethyl xanthate is a hazardous substance, employers and suppliers should be aware of their obligations to provide information, such as MSDS and labels, about the hazards of sodium ethyl xanthate. Details of these obligations, consistent with employers general duty of care, are provided in the *National Model Regulations to Control Workplace Hazardous Substances*.⁴⁹

15.2.1 Material Safety Data Sheets

The National Commission's *National Code of Practice for the Preparation of Material Safety Data Sheets*⁴⁸ provides appropriate guidance to prepare MSDS.

A survey of the MSDS for sodium ethyl xanthate indicated that some were below the standard considered appropriate under this code of practice. It is recommended that manufacturers and importers review and upgrade MSDS in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets*,⁴⁸ and in particular ensure that the:

- correct UN number is included in the MSDS;
- information on the use of the chemical is provided;
- hazardous ingredients and their proportions are listed, even if present as impurities;
- supporting data for the health effects are stated. If no human data are available it should be stated. Animal data should be summarised and the species and route of exposure stated; and
- summary of health effects of carbon disulphide is included as exposure is possible during use of xanthates.

15.2.2 Labels

The *National Code of Practice for the Labelling of Workplace Substances*⁵⁰ provides standards for the labelling of workplace hazardous substances.

As all labels were found inadequate, it is recommended that labels be reviewed, upgraded and, in addition to the requirements of the ADG Code,³² should include the risk and safety phrases, first aid procedures, emergency procedures and reference to the MSDS in accordance with the *National Code of Practice for the Labelling of*

Workplace Substances.⁵⁰ Consistent with the classification the following risk and safety phrases are recommended:

Risk phrases

R21/22	Harmful in contact with skin and if swallowed
R36	Irritating to eyes
R38	Irritating to skin
R15, 29	Contact with water liberates highly flammable and toxic gases.

Safety phrases

S24/25	Avoid contact with skin and eyes.
S36, 37, 39	Wear suitable protective clothing, gloves and eye/face protection.
S3/9	Keep in a cool well ventilated place.

15.2.3 Training and education

Workers potentially exposed to sodium ethyl xanthate need to be trained in safe work practices to be followed in the handling, storage and transportation of the chemical. The workers should be trained in the procedures to be followed in the case of an emergency, as experience in fires in mines using sodium ethyl xanthate have shown that the fire spreads rapidly, especially when bulker bags are present. Training provided at induction should be reinforced at regular intervals, especially the emergency procedures so that workers are familiar with the procedures and can act quickly in an emergency situation.

15.3 Packaging

The most significant risk to workers and the public is through ineffective or inappropriate packaging of solid sodium ethyl xanthate, in both drums and bulker bags. Problems in packaging have led to the formation and release of carbon disulphide, causing fires and adverse health effects in humans.

Data on the self combustion of sodium ethyl xanthate—particularly on the interaction of parameters such as temperature, humidity, moisture content and package size—is not available. Therefore, it is difficult to predict situations where self-combustion may occur. It is recommended that factors affecting self-combustion should be accurately assessed by appropriate scale-down tests. These tests should be carried out by manufacturers and importers and a testing plan be provided to the Director Chemical Assessment within six months of publication of this report.

The release of carbon disulphide from packages of sodium ethyl xanthate should be eliminated as far as possible. It is recommended that monitoring for carbon disulphide by the manufacturer before dispatch and by the importer on receipt of the consignment be undertaken routinely. Monitoring of carbon disulphide should be introduced as soon as possible and the results of this monitoring should be available for inspection on request. A report on implementation of this recommendation should be provided by manufacturers and importers to the Director Chemical Assessment within 12 months of publication of this report. It is recommended that the moisture content of packaged sodium ethyl xanthate is kept to a minimum. Specifications for the moisture content for each batch should be supplied by the manufacturer.

Packaging should ensure that damage does not occur under normal transport conditions and that carbon disulphide is not released during transport and storage. It is recommended that manufacturers and importers arrange with the relevant competent authority, or suitable competent person, to carry out random inspections of packaging of sodium ethyl xanthate to assess its adequacy and whether it meets the current packaging requirements of the ADG Code.³²

15.4 Exposure standard and atmospheric monitoring

An exposure standard for sodium ethyl xanthate has not been assigned by the National Commission. It is not recommended that an exposure standard for sodium ethyl xanthate be developed by the National Commission. It is recommended that dust levels should be maintained as low as possible in view of the dermal toxicity of sodium ethyl xanthate and the likelihood of carbon disulphide formation. A level of 1 mg/m³ as used by Dow Chemicals is considered appropriate as an operational level.

As atmospheric monitoring of carbon disulphide is currently only undertaken randomly at mining sites it is recommended that more routine procedures be carried out particularly in those areas where exposure is likely to occur such as the mixing area, storage areas, around the stock tanks and around the flotation cells. The frequency of monitoring will depend on the results obtained and can be reduced once it is established that control measures are effective and levels do not exceed the current exposure standard for carbon disulphide (10 ppm TWA).

15.5 Health surveillance

Sodium ethyl xanthate is widely used in Australia and is hazardous to health. However, it is considered that the chemical does not adversely affect the health of workers under the present conditions of use.

It is recommended that sodium ethyl xanthate not be considered for addition to schedule 3 of the National Commission's *National Model Regulations for the Control of Workplace Hazardous Substances*.⁴⁹ Under regulations introduced in Commonwealth, State or Territory government jurisdictions in accordance with these model regulations, employers will need to provide health surveillance in workplaces where assessment shows that exposure to sodium ethyl xanthate may result in a substance-related health effect.

15.6 Environmental protection

To ensure that risk remains low, xanthate use should be restricted to well managed mining operations using tailings dams of appropriate size to prevent entry of flotation effluents to waterways. Direct discharge of xanthates or effluents containing them to waterways is unacceptable.

15.7 Incidents

It is recommended that any further incidents involving sodium ethyl xanthate be notified to the Director Chemical Assessment.

15.8 Other xanthates

The uses, adverse health effects and release of carbon disulphide and its associated hazards are similar to all xanthates. The recommendations arising from the assessment of sodium ethyl xanthate would therefore be appropriate to all xanthates.

16. Requirements for secondary notification

Under the Act, secondary notification of sodium ethyl xanthate shall be required if any of the circumstances stipulated under Subsection 64(2) of the Act arise.

Sample Material Safety Data Sheet for sodium ethyl xanthate

Date of issue 11 April 2000

Page 1 of Total 2

**SODIUM ETHYL XANTHATE is considered hazardous
according to the criteria of Worksafe Australia**

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

Identification	
Chemical name	Sodium ethyl xanthate
Other names	Sodium xanthogenate, Sodium ethyl dithiocarbonate
Shipping name	Substances which in contact with water emit flammable gases
Manufacturers product code	
UN Number	3134 - Water reactive solid, Poisonous, N.O.S.
Dangerous goods class	4.3 - Substances which in contact with water emit flammable gases
Subsidiary risk	6.1(a)
Hazchem code	4WE
Poisons Schedule number	None allocated
Packaging group	II
Use	Flotation agent used in the separation of ores

Physical description and properties

Appearance

Pale yellow amorphous powder

Vapour pressure

Non volatile solid. Decomposes to volatile compounds

Specific Gravity

1.263

Melting point

182 - 256°C

Flashpoint

Not relevant

Flammability limits

Carbon disulphide - 1.3 to 50% (v/v) in air

Solubility in water

450 g/L at 10°C

Other properties

Reactivity: Hygroscopic and reacts with water to form carbon disulphide, ethyl alcohol, sodium carbonate and trithiocarbonate. Reacts with oxidising agents to form dixanthogens.

Autoignition Temperature: 250°C

Generates heat on contact with water, and this accelerates decomposition. Decomposition is also accelerated by low pH

Ingredients

Chemical entity	CAS Number	Proportion
Sodium ethyl xanthate	140-90-9	
Moisture		
Free alkalis		

Health hazard information

HEALTH EFFECTS

Sodium ethyl xanthate reacts with water to form carbon disulphide and therefore the health effects of carbon disulphide must also be considered

Acute

Inhalation: Due to release of carbon disulphide, acute exposure may cause loss of consciousness, tremors, difficulty in breathing, vascular collapse and possible death

Swallowed: Oral LD₅₀ of 730 mg/kg (mice) for a 10% aqueous solution of sodium ethyl xanthate.

Eye: Sodium ethyl xanthate is a mild to moderate eye irritant (rabbit). Carbon disulphide vapour is a severe eye irritant.

Skin: Sodium ethyl xanthate has a dermal LD₅₀ of < 1000 mg/kg (rat) and is a moderate skin irritant (rabbit). Carbon disulphide is a severe skin irritant and can cause serious blisters on contact.

Chronic

No human evidence is available and no animal studies have been conducted for long term effects of sodium ethyl xanthate. Prolonged exposure to other xanthates produces adverse effects on the central nervous system in mice while toxic effects were seen in kidneys and liver in dogs and rats.

Repeated exposure to carbon disulphide vapour can adversely affect the central and peripheral nervous systems, causing weakening of the muscles of the legs, fatigue, sleeplessness and irritability. Carbon disulphide has been shown to contribute towards coronary heart disease in exposed workers, and severe effects on the retina of the eye have been observed. Hearing defects in workers exposed to carbon disulphide have also been reported.

Adverse effects on the reproductive system of workers has been noted, including decreased libido and changes in sperm morphology in males and menstrual abnormalities in females.

FIRST AID

Inhaled: Remove person from exposure - avoid becoming a casualty. Remove contaminated clothing and loosen remaining clothing. Allow patient to assume most comfortable position and keep warm. If breathing stops artificial respiration to be given by trained personnel. Keep at rest until fully recovered. Seek medical advice.

Eye: Immediately irrigate with copious quantities of water for at least 15 minutes. Eyelids to be held open. Seek immediate medical assistance.

Skin: Flush contaminated skin with plenty of water. Remove contaminated clothing and wash before re-use. Seek medical assistance if irritation persists.

Swallowed: Rinse mouth with water. Give plenty of water to drink. If person is losing consciousness do not give anything by mouth. Seek immediate medical assistance.

Health hazard information

ADVICE TO DOCTOR

Treat symptomatically

Precautions for use**EXPOSURE STANDARDS**

No exposure standard has been allocated for sodium ethyl xanthate by the National Occupational Health and Safety Commission.

Exposure standard for the major decomposition product carbon disulphide is 10 ppm TWA with a skin notation (i.e., absorption through the skin may be a significant source of exposure).

ENGINEERING CONTROLS

The mixing area (for the preparation of sodium ethyl xanthate solution) should be segregated from non-involved personnel and the mixing process should be automated. Use local exhaust ventilation in mixing area. Avoid generating and inhaling dust.

PERSONAL PROTECTION

A combination respirator fitted with a particulate filter and a gas filter which can adsorb carbon disulphide, such as type A or AX should be worn during the mixing process. The respiratory protective equipment should be in accordance with AS 1716.

Impervious gloves conforming to Australian Standard AS 2161-1978 should be worn. Protective clothing conforming to Australian Standard AS 3765.1-1990 should be worn.

Eye protection conforming to Australian Standard AS 1337 - 1984 should be worn.

FLAMMABILITY

Sodium ethyl xanthate in contact with water will emit carbon disulphide which is highly flammable. The dry powder or pellet form may also be flammable because of the presence of moisture in the product.

Safe handling information**STORAGE AND TRANSPORT**

Storage should be in a restricted area. Store in a cool, dry, well ventilated area away from any ignition sources. Containers may be earthed to reduce the possibility of sparks from static electricity.

During handling of sodium ethyl xanthate avoid generation of dust.

UN No: 3134

Packaging Group II

ADG Code: Classified as a dangerous good, Class 4.3; substances which in contact with water emit flammable gases.

Should not be transported or stored with Explosives (Class 1), Flammable gases (Class 2.1), Flammable liquids (Class 3), Oxidising agents (Class 5), Corrosives (Class 8) or foodstuffs.

SPILLS AND DISPOSAL

Care should be taken not to puncture containers when moving with forklift. In the event of a spill do not wash material into drain or sewer. Vacuuming of solid spills is recommended. Collect in properly labelled containers for disposal. Dispose in accordance with local and state regulations. Personal protective equipment as noted in the appropriate section above should be worn.

FIRE/EXPLOSION HAZARD

Combustible. Evolves highly flammable, toxic carbon disulphide vapours.

Fire fighters should wear full protective equipment including self contained breathing apparatus. Evacuation of the people from the neighbourhood should be considered if necessary. For fighting fires use CO₂, dry chemical, sand or soil. With large fires flooding with water may be appropriate.

Other information

ECOLOGICAL INFORMATION

Sodium ethyl xanthate is highly toxic to aquatic fauna and fish.

Avoid disposing to waterways.

Contact point

Title

Telephone number

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