

## NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

### FULL PUBLIC REPORT

#### Potassium Ferrite ( $K_2Fe_{22}O_{34}$ )

Under subsection 38(5) of the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), the Director of Chemicals Notification and Assessment publishes this assessment report by giving a copy of it to:

- the Chief Executive Officer of the National Occupational Health and Safety Commission (Worksafe Australia);
- the Secretary of the Department of the Environment;
- the Secretary of the Department of Health and Family Services; and
- the Department of Occupational Health, Safety and Welfare (Western Australia).

This assessment report will be available for inspection by the public.

Director  
Chemicals Notification and Assessment

April 1998

## Potassium Ferrite ( $K_2Fe_{22}O_{34}$ )

### 1. APPLICANT

The Shell Company of Australia Limited of 1 Spring Street MELBOURNE VIC 3001 has submitted a standard notification statement in support of their application for an assessment certificate for Potassium Ferrite ( $K_2Fe_{22}O_{34}$ ).

### 2. IDENTITY OF THE CHEMICAL

**Chemical Name:** potassium ferrite

**Chemical Abstracts Service (CAS) Registry No.:** 12160-44-0

**Trade Name:** potassium ferrite

**Molecular Formula:**  $K_2Fe_{22}O_{34}$

**Structural Formula:** not applicable

**Molecular Weight:** 1850.8, see comments below

#### Comments on Chemical Identity

The notified chemical is a solid formulation based on iron oxides and contains ferrite type compounds as well as some alkaline hydroxides. It is formally a mixture of ferric oxide and potassium oxide, the molecular formula of which could be written as  $K_2O(FeO_3)_{11}$ . However, ferrite type compounds are produced through solid state fusion reactions at elevated temperatures between ferric oxide and alkali metal carbonates or hydroxides and are usually understood to contain the  $(Fe^{III}_2O_4)^{2-}$  moiety (1). The formation reaction involves the elimination of water and in the case of the present chemical, could be written as:



or



However, such solid state reactions are often far more complex than such simple equations imply, and may involve significant non-stoichiometry and the formation of solid state structures containing transition metal atoms (in this case iron) in mixed valence states. The importance of these issues to the catalytic activity of the ferrite materials were alluded to in a copy of research paper provided in the notification (2).

The notified chemical ( $K_2Fe_{22}O_{34}$ ) will not be imported in isolation, but as an inseparable component (less than 10%) of an imported catalyst - called Criterion 035 Catalyst. The Material Safety Data Sheet (MSDS) for the Criterion 035 Catalyst supplied with the notification indicates that this material contains iron oxide ( $Fe_2O_3$ ), potassium oxide, potassium molybdate, potassium carbonate, cerium oxide and calcium oxide in addition to two different ferrite compounds.

The notifier indicated that, in addition to the notified chemical discussed here (ie that with formal formula  $K_2Fe_{22}O_{34}$ ), the imported material also contains a second ferrite compound with formula  $K_2Fe_{10}O_{16}$  together with 10% of residual potassium carbonate. The second ferrite compound has also been submitted to NICNAS, and is assessed as NA/597. Both these ferrite compounds appear to be constituents of a material known as Mapico CG-20X which in turn is a component of the new imported catalyst. An analysis of the Mapico CG-20X ferrite containing material has been provided, and is as follows:

#### Mapico CG-20X

Component	Percentage	CAS No
potassium ferrite $K_2Fe_{22}O_{34}$	83.8	12160-44-0
potassium ferrite $K_2Fe_{10}O_{16}$	6.2	12160-30-4
potassium carbonate $K_2CO_3 \cdot 1.5H_2O$	10.0	584-08-7

X-ray diffraction data for the Mapico CG-20X material was submitted with the notification which serves to identify the principal mineral constituents in the new ferrite containing material, i.e.  $K_2Fe_{22}O_{34}$ ,  $K_2Fe_{10}O_{16}$  and  $K_2CO_3$ , and to quantify their relative proportions.

### 3. PHYSICAL AND CHEMICAL PROPERTIES

The following listed properties are for Mapico CG-20X

<b>Appearance at 20°C and 101.3 kPa:</b>	fine reddish brown powder
<b>Melting Point:</b>	> 1 500°C
<b>Density:</b>	3 770 kg.m <sup>-3</sup>
<b>Vapour Pressure:</b>	not determined
<b>Water Solubility:</b>	< 1 mg.L <sup>-1</sup> at 25°C, see comments below
<b>Partition Co-efficient (n-octanol/water):</b>	not determined, see comments below
<b>Hydrolysis as a Function of pH:</b>	not determined, see comments below
<b>Adsorption/Desorption:</b>	not determined, see comments below
<b>Dissociation Constant:</b>	not determined, see comments below

#### Comments on Physico-Chemical Properties

Samples of Mapico CG-20X (10 or 100 mg, six of each) were weighed into flasks, mixed with water and stirred. At 24, 48 and 144 hours, the stirring was stopped for one pair of flasks for each loading rate and stored for 24 hours to allow settling. Aliquots of the 'supernatants' were then removed, centrifuged, and filtered (0.22 µm filter). The filtrates and filters were then analysed for iron content using Inductively Coupled Plasma - Atomic Emission Spectrometry. The water solubility of Mapico CG-20X was determined as less than 1 mg.L<sup>-1</sup>, which is to be expected for materials of this nature. Further tests indicated that there was no relationship between the loading rates of potassium ferrite and the amount of iron found in the solution.

The water solubility test report indicated that some potassium is leached from the ferrite material, which is also expected given that the material contains (soluble) potassium carbonate - see above. However, it should also be realised that the notified chemical is never isolated from Mapico CG-20X of which it is an important component, and other chemical constituents of the Criterion 035 Catalyst may be appreciably water soluble.

The notified chemical (K<sub>2</sub>Fe<sub>22</sub>O<sub>34</sub>), is formed by the fusion of Fe<sub>2</sub>O<sub>3</sub> and alkali

of water - see discussion on 'Chemical Identity' above. At ambient temperatures when exposed to water these reactions could theoretically be reversed leading to decomposition of the ferrite materials to  $\text{Fe}_2\text{O}_3$  and alkali metal hydroxides. However, a study conducted using infrared spectroscopy failed to detect any  $\text{Fe}_2\text{O}_3$  in the product after 144 hours exposure to water, indicating that this reaction was not a significant breakdown pathway for the new chemical. However, Mapico CG-20X does contain approximately 10% of  $\text{K}_2\text{CO}_3$ , which would leach out of the material giving it highly alkaline properties.

Mapico CG-20X, (containing the notified chemical) contains no organic groups and has no tendency to dissolve in oils or fats, and consequently partition coefficient and adsorption/desorption coefficient have little relevance for this material. However, test reports on the determination of these properties were provided in the notification. The solubility of the Mapico CG-20X in n-octanol was determined as less than  $0.1 \text{ mg.L}^{-1}$  (detection limit for iron of the analytical instruments employed), and as a consequence of this low solubility it was not practicable to determine the n-octanol/water partition coefficient. However, under realistic conditions Mapico CG-20X will have very little tendency to accumulate in either aqueous or the organic environment, and will remain primarily in the solid phase. The material will have very little potential to bioaccumulate.

The nature of the material, particularly its low solubility in both water and in organic solvents, together with other experimental limitations makes it very difficult or impossible to determine  $K_{OC}$  directly. Nor is it possible to estimate this parameter from other properties such as  $P_{OW}$ . However, the notifier indicates that if released into the environment the ferrite material would very likely adsorb to and become strongly associated with soil particles, although it would not necessarily become associated with sewage sludge.

The notifier also supplied reports on the determination of the surface tension of aqueous "solutions" of Mapico CG-20X, and also its solubility in a variety of organic solvents (apart from n-octanol). The material had little effect on the surface tension of water, and for a (nominally) 90% saturated solution at  $20^\circ\text{C}$ , lowered this parameter from  $73.1 \text{ mN.m}^{-1}$  to a mean of  $70.5 \text{ mN.m}^{-1}$ , and is consequently not surface active (3).

The solubility of Mapico CG-20X in hexane, cyclohexane, dichloromethane, acetonitrile, acetone, propan-2-ol and methanol was determined to be less than  $10 \text{ mg.L}^{-1}$  in all cases.

As mentioned above, Mapico CG-20X reacts with moisture or water, producing potassium hydroxide, and consequently the notified chemical is effectively a strong base and would be caustic if exposed to water.

#### 4. PURITY OF THE CHEMICAL

**Degree of Purity:** 83.8%  $\text{K}_2\text{Fe}_{22}\text{O}_{34}$  (potassium ferrite)

**Toxic or Hazardous Impurities:** 6.2%  $\text{K}_2\text{Fe}_{10}\text{O}_{16}$  (potassium ferrite)

**Non-hazardous impurities (>1% by weight):** potassium carbonate

**Additives/Adjuvants:** none

#### 5. USE, VOLUME AND FORMULATION

The notified chemical will not be manufactured in Australia but will be imported from the USA as a component (less than 10%) of a solid known as Criterion 035 Catalyst. Details of the composition of the catalyst are described in the notifier's MSDS for this product. It is anticipated that up to 100 tonnes of the new catalyst will be imported annually over the next five years, and consequently annual imports of the new ferrite material will be approximately 10 tonnes. The catalyst is supplied as pellets (approximately 5 mm in diameter) and will be imported in 1 500 kg woven polypropylene "super sacks" with inner polypropylene liners to prevent exposure to moisture. The exterior of the super sack is further protected by a layer of polyethylene shrink wrap. Contact with moisture has a detrimental effect on the catalyst which leaches strongly basic (pH > 12) potassium hydroxide solution.

The notified chemical is a component of a pelletised solid catalyst (Criterion 035 Catalyst) intended for use in the petro-chemical industry for conversion of ethylbenzene to styrene. Ferrite compounds similar to the notified chemical have been used for many years as catalysts for the conversion (by dehydrogenation) of ethylbenzene to the industrially important styrene.

#### 6. OCCUPATIONAL EXPOSURE

The catalyst will arrive by sea and be transported from the dock to the customer's site by truck in 1 500 kg polypropylene super sacks. Transport and storage workers handling sacks of the notified chemical will not be exposed under normal circumstances.

The notifier anticipates that for economic reasons it is unlikely that quantities of the catalyst will be stored for lengthy periods at customer sites prior to being added into the reactors.

At the customer site during styrene manufacture, the catalyst is contained in an enclosed reactor. The notifier does not anticipate worker exposure to the notified chemical during normal operation.

The catalyst containing the notified chemical is in pelletised form. The catalyst is handled when spent catalyst is removed and fresh catalyst is added. This process occurs about every two years, and can take two days to complete. The styrene plant is shut down to allow for changeover.

Catalyst changeover is the process whereby spent catalyst is unloaded from the reactor and replaced with fresh catalyst. The unloading process involves steaming the spent catalyst for two days to remove excessive hydrocarbon. The reactor is then purged with nitrogen for another day to further reduce the residual hydrocarbon content to less than 1% coke. Some styrene plants introduce diluted air to burn any residual coke and to oxidise the catalyst to prevent fire hazards during catalyst unloading. The spent catalyst is removed under vacuum unloading.

The changeover process involves loading the catalyst into a two-stage radial flow reactor, which is operated under slight vacuum (9 psia) and at temperatures of 600 to 650°C and in the presence of steam (which apparently assists in keeping the catalyst active). Loading of the catalyst into the reactor is conducted either in an air or inert environment. The catalyst is transferred manually from the super sacks to the loading hopper, then to the catalyst bed located in the reactor vessel, using a nylon (or equivalent) sock extending from the bottom of the loading hopper to the catalyst level in the bed.

The loading and unloading operation occurs under the supervision of trained technical personnel and requires one worker inside the reactor, and two to four workers outside for top loading. The notifier advises that all workers involved in these activities are required to wear personal protective equipment, including a supply of fresh breathing air, or a respirator for the worker inside the reactor. The changeover process is subject to local exhaust ventilation.

There is the potential for dermal, ocular and inhalation exposure to occur when the catalyst is transferred from the original sacks to the loading hopper, during disconnection of the nylon 'sock' or in the case of a spillage. Moreover, the notifier indicates there is possible overexposure to dusts, including respirable sizes (iron oxide, potassium oxide, potassium molybdate, molybdenum oxide, potassium carbonate, cerium oxide and calcium oxide), and caustic or corrosive liquids during the unloading process.

Spent catalyst is dumped either wet or dry in drums at a disposal site. The notifier indicates that toxic dusts, benzene, volatile organic chemical fumes, and gases such as carbon monoxide are associated with dry dumping. In addition, with a dry dump the catalyst is in a pyrophoric state (i.e. may spontaneously combust on exposure to air). Dermal, ocular and inhalation exposure is likely as the drums are manually filled with spent catalyst.

## **7. PUBLIC EXPOSURE**

The notifier does not anticipate public exposure to the notified chemical during normal operation in the enclosed reactor.

During use of the notified chemical, some potassium leaves the reactor as potassium hydroxide and potassium carbonate. These potassium compounds deposit out in downstream equipment as the temperature is reduced and can be found at low levels in the condensed process water (ie, heat/exchange/cooling system, steam systems). The loss averages approximately 3% in the catalyst bed, and as high as 8% in the individual catalyst pills. Catalyst loss in the form of dust inside the reactors is negligible. Catalysts can be dumped either wet or dry by contractors at an approved disposal site. The same procedure will be followed with any material spilled in a transport accident. Prior to dumping styrene catalyst, the spent catalyst is steamed for approximately 2 days to remove excessive hydrocarbon. The reactor is then purged with nitrogen for another day to further reduce the residual hydrocarbon content to less than 1% coke.

## **8. ENVIRONMENTAL EXPOSURE**

### **Release**

During charging of the reactors with fresh pellets of catalyst, the fresh material is removed from the packaging used for transport (see above) into a hopper on top of the reactor, and then discharged to the bottom in a controlled manner (to assure correct distribution) via a nylon sock. Although some fugitive dust emission could occur under certain circumstances during the charging operations, little release to the environment is anticipated during this operation.

During operation of the reactors there is apparently no loss of the ferrite component, although considerable loss of potassium hydroxide and potassium carbonate is usual, and may amount to 8% of the catalyst bed. These compounds are removed through entrainment in the product streams (probably in association with steam), and are removed during downstream processes.

Removal and disposal of spent catalyst from the reactors is more troublesome, and the notifier indicates in the MSDS supplied with the notification that the spent material is pyrophoric. Consequently, before the discharge operation is undertaken it is usual to purge the reactors with steam for two days to remove entrained hydrocarbons and then to destroy coke and other flammable material by purging with air. The most effective method for removal of the spent catalyst from the reactors is through the use of vacuum discharge equipment. These measures will minimise release of the spent catalyst and associated hydrocarbon impurities during catalyst unloading operations, but as with the loading operations it is possible that small emissions of dust containing the new ferrite chemical may occur.



## Fate

After unloading from the reactors, the spent catalyst, containing the notified chemical, is disposed of. Due to the caustic nature of certain soluble components (i.e. potassium hydroxide and potassium carbonate), the notifier indicates that the preferred method for disposal is recycling to cement and brick kilns for incorporation into such products. This method is employed in the United States. However, in Australia, spent catalyst will be disposed of in covered drums at prescribed waste disposal sites, where the notified chemical will be contained.

## 9. EVALUATION OF TOXICOLOGICAL DATA

The test material, in sections 9.1 to 9.3, refers to the material (Mapico CG-20X) comprising:  $K_2Fe_{22}O_{34}$  (83.8%);  $K_2Fe_{10}O_{16}$  (6.2%); and  $K_2CO_3 \cdot 1.5H_2O$  (10%).

The notifier indicates that the second potassium ferrite species,  $K_2Fe_{10}O_{16}$ , shares a close chemical structure to  $K_2Fe_{22}O_{34}$  and is anticipated to demonstrate very similar toxicology. The second species has also been submitted to NICNAS and is assessed as NA/597.

### 9.1 Acute Toxicity

#### Summary of the acute toxicity of Potassium Ferrite

<i>Test</i>	<i>Species</i>	<i>Outcome</i>	<i>Reference</i>
acute oral toxicity	rat	$LD_{50} > 2\,000\text{ mg.kg}^{-1}$	(4)
acute dermal toxicity	rat	$LD_{50} > 2\,000\text{ mg.kg}^{-1}$	(5)
skin irritation	rabbit	not determined	-
eye irritation	rabbit	not determined	-
skin sensitisation	guinea pig	skin sensitiser	(6)

#### 9.1.1 Oral Toxicity (4)

<i>Species/strain:</i>	rat/Sprague-Dawley
<i>Number/sex of animals:</i>	5/sex
<i>Dose:</i>	$2\,000\text{ mg.kg}^{-1}$ in corn oil
<i>Observation period:</i>	15 days

<i>Method of administration:</i>	gavage, 10 mL.kg <sup>-1</sup> bodyweight
<i>Clinical observations:</i>	piloerection, hunched posture in all rats, soft to liquid faeces in females only; recovery complete in all rats by day 5
<i>Mortality:</i>	nil
<i>Morphological findings:</i>	no abnormalities recorded at day 15
<i>Test method:</i>	similar to OECD guidelines (7)
<i>LD<sub>50</sub>:</i>	> 2 000 mg. kg <sup>-1</sup>
<i>Result:</i>	the notified chemical was of low acute oral toxicity in rats

#### 9.1.2 Dermal Toxicity (5)

<i>Species/strain:</i>	rat/Sprague-Dawley
<i>Number/sex of animals:</i>	only one animal used because of irritant nature of test substance
<i>Dose:</i>	2 000 mg.kg <sup>-1</sup> in corn oil
<i>Observation period:</i>	15 days
<i>Method of administration:</i>	2.4 mL. kg <sup>-1</sup> of notified chemical applied to a shaved area of the dorso-lumbar region, under occlusive dressing for 24 hours.
<i>Clinical observations:</i>	severe dermal response, necrosis/whitening of the epidermis and moderate oedema for duration of test
<i>Mortality:</i>	nil
<i>Morphological findings:</i>	no abnormalities recorded at Day 15
<i>Test method:</i>	according to OECD guidelines (7)
<i>LD<sub>50</sub>:</i>	> 2 000 mg. kg <sup>-1</sup>
<i>Result:</i>	the notified chemical was of low dermal toxicity in rats

### 9.1.3 Inhalation Toxicity, Skin and Eye Irritation

In accord with UK animal welfare considerations and in compliance with OECD test guidelines (7), inhalation and skin and eye irritant studies were not conducted on the basis that potassium ferrite was expected to be corrosive (indicated by a pH of 12.9 which was measured using a 10% w/v solution in distilled water) and caused skin tissue necrosis as observed in the acute dermal toxicity study.

### 9.1.4 Skin Sensitisation (6)

<i>Species/strain:</i>	guinea pig/Dunkin-Hartley
<i>Number of animals:</i>	20 test males; 10 control males
<i>Induction procedure:</i>	<p>day 1: three pairs of intradermal injection to clipped scapular region:</p> <p>0.1 mL of Freund's Complete Adjuvant (FCA) and 50:50 with water for irrigation;</p> <p>0.1 mL of 0.25% w/v notified chemical in water for irrigation;</p> <p>0.1 mL of 0.25% w/v notified chemical in 50:50 mix of FCA and water for irrigation.</p> <p>day 7: occluded application, to clipped scapular region, 7.5% w/v of the notified chemical (0.4mL of test material), in distilled water, for 48 hours.</p>
<i>Challenge procedure:</i>	<p>day 21: occluded application of notified chemical (0.2 mL of 7.5% w/v and 3.5% w/v of test material in distilled water, to the clipped posterior and anterior flank, respectively), for 24 hours.</p>

Challenge outcome:

<b>Challenge concentration</b>	<b>Test animals</b>		<b>Control animals</b>	
	<b>24 hours*</b>	<b>48 hours*</b>	<b>24 hours</b>	<b>48 hours</b>
3.5%	7/20**	8/20**	0/10	0/10
7.5%	5/20**	5/20**	0/10	0/10

\* time after patch removal

\*\* number of animals exhibiting positive response

*Test method:* similar to OECD guidelines (7)

*Comments:* nine animals showed evidence of sensitisation, eight gave negative responses and the remaining three gave inconclusive responses

*Result:* the notified chemical was sensitising to the skin of guinea pigs.

## 9.2 Repeated Dose Toxicity (8)

*Species/strain:* rat/CD

*Number/sex of animals:* 5/sex/group

*Method of administration:* gavage

*Dose/Study duration::* the test material was administered daily for 28 days as follows:

control: 0 mg.kg<sup>-1</sup>.day<sup>-1</sup>

low dose: 15 mg.kg<sup>-1</sup>.day<sup>-1</sup>

mid dose: 150 mg.kg<sup>-1</sup>.day<sup>-1</sup>

high dose: 500 mg.kg<sup>-1</sup>.day<sup>-1</sup>

*Clinical observations:* slight to moderate gait abnormalities were observed in 2 females of the high dose group during weeks 2, 3 and 4 of treatment; blood-stained faeces were observed in one male of the low dose group during weeks 3 and 4

*Clinical  
chemistry/Haematology*

males of the high dose group had significantly higher total protein levels compared to the control animals; no treatment related changes in haematological parameters were reported; NB: no historical control reference values were provided for either clinical chemistry or haematological parameters

*Histopathology:*

macroscopic: gross examination revealed depressed areas in the stomach of two males of the high dose group and a thickened stomach wall in one male in the mid dose group; abnormal dark contents in the gastro-intestinal tract were observed in two females of the high dose group; a moderate proteinaceous plug was observed in the urinary bladder of three males of the high dose group.

microscopic: minimal keratosis of the stomach mucosa was observed in one male of the high dose group; mucosal oedema was observed in animals of the mid and high dose groups

minimal to moderate cortico-medullary mineralisation of the kidneys was observed in females of both control and treated groups

*Test method:*

similar to OECD guidelines (7)

*Result:*

no signs of systemic toxicity were observed; treatment-related effects were limited to stomach lesions at dose levels of 150 and 500 mg.kg<sup>-1</sup>.day<sup>-1</sup>

### 9.3 Genotoxicity

#### 9.3.1 *Salmonella typhimurium* Reverse Mutation Assay (9)

<i>Strains:</i>	TA98, TA100, TA1535, TA1537 and CM891
<i>Concentration range:</i>	5 to 5 000 $\mu\text{g}.\text{plate}^{-1}$
<i>Test method:</i>	similar to OECD guidelines (7)
<i>Result:</i>	the notified chemical was not considered to be mutagenic in the bacterial strains tested in the absence or presence of metabolic activation provided by rat liver S9 fraction

#### 9.3.2 Micronucleus Assay in the Bone Marrow Cells of the Mouse (10)

<i>Strain:</i>	mouse/CD-1
<i>Number and sex of animals:</i>	5/sex/dose
<i>Doses:</i>	0, 126, 252, 252 and 504 $\text{mg}.\text{kg}^{-1}$
<i>Method of administration:</i>	notified chemical via intraperitoneal injection; positive control (mitomycin C) via intragastric gavage.
<i>Test method:</i>	similar to OECD guidelines (7)
<i>Result:</i>	the notified chemical was not clastogenic in bone marrow cells of the mouse, <i>in vivo</i>

#### 9.3.3 Lymphocyte Cytogenetic Study (11)

<i>Cell type:</i>	lymphocytes, human, male
<i>Doses:</i>	0, 8, 40, 200, 1 000 & 5 000 $\mu\text{g}.\text{mL}^{-1}.\text{culture}^{-1}$
<i>Test method:</i>	similar to OECD guidelines (7)
<i>Comment:</i>	a dose related increase in aberrant chromosomes in the absence of metabolic activation provided by rat liver S9 fraction. The aberration types comprised mainly chromatid breaks and chromosome fragments
<i>Result:</i>	the test material was considered to be clastogenic under the conditions of this

chromosomal aberration test in the absence  
of rat liver S9 fraction

#### 9.4 Overall Assessment of Toxicological Data

The notified chemical was of low acute oral and dermal toxicity in rats (both oral and dermal LD<sub>50</sub>s exceeding 2 000 mg.kg<sup>-1</sup>).

Repeat dose oral toxicity studies at doses up to 500 mg.kg<sup>-1</sup> for 28 days did not result in any animal deaths. However, stomach lesions, presumably due to the irritant nature of the notified chemical were noted. Gait abnormalities were observed in females at dose levels of 500 mg.kg<sup>-1</sup>. The relevance of this finding is not apparent, as the other reported neurological findings were unremarkable.

The notified chemical is corrosive; it has a high pH (12.9) and caused skin tissue necrosis as reported in the acute dermal toxicity test. Consistent with animal welfare considerations and OECD test guidelines (7), inhalation and eye and dermal irritation studies were not performed.

The notified chemical is a moderate skin sensitiser in guinea pigs.

The notified chemical was not found to be mutagenic in bacteria and did not induce an increase in micronuclei in an *in vivo* mouse micronucleus assay. Clastogenic effects (chromatid breaks and chromosome fragments) were observed, however, in an *in vitro* human lymphocyte cytogenetic assay. The clastogenic effects were limited. The biological significance of these effects is open to interpretation. From the information supplied, and given that the test material has a high pH (12.9 for a 10% w/v solution) it cannot be excluded that a non-physiological pH may have been achieved at the concentrations tested and these in turn may have generated a false positive response which is reported to occur according to Morita et al 1989 (12). In addition, chromatid breaks, unlike chromosomal breaks, have a higher probability of undergoing repair. However, to fully evaluate the significance of chromosomal aberrations in the lymphocyte cytogenetic test seen with this notified chemical, confirmatory tests, such as an *in vitro* micronucleus assay and an *in vivo* cytogenetic assay would be required.

Based on its dermal sensitising potential and corrosive nature (related to the high pH) the notified chemical would be classified as hazardous according to the National Occupational Health and Safety Commission's *Approved Criteria for Classifying Hazardous Substances* (13).

## 10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

The notifier provided a test report detailing ecotoxicity tests for the ferrite containing material Mapico CG-20X against rainbow trout, Daphnia and green algae. These tests were conducted in accordance with OECD test guidelines.

Due to the insolubility of the test material, all tests were performed with Water Accommodation Fractions (WAFs) of the ferrite. The WAFs were prepared by stirring weighed quantities of the test material (i.e. Mapico CG-20X) into the appropriate volume of water for a period of approximately 24 hours, allowing the suspended solid material to settle for 24 hours, and the aqueous WAFs drawn off for use in the tests. The control media were subject to the same preparation regime, except that no ferrite containing material was added.

The test on rainbow trout was conducted using a semi static procedure over a 96 hour period at one nominal WAF loading, i.e.  $1\,000\text{ mg.L}^{-1}$ , with daily replenishment of the WAF containing water. Seven rainbow trout fingerlings were introduced into the 10 L vessel of the WAF, and their condition monitored daily. Analysis of the water for iron content throughout the test indicated this was present in the WAF at low concentration only, and the maximum analytical result was  $2.3\text{ mg.L}^{-1}$  (48-hour sample).

No fish mortality was observed over the 96-hour duration of the test, although one fish displayed minor toxic symptoms (not specified) for the first 72 hours of the test but had apparently recovered by the end of the test. No adverse effects on the fish in the control water were noted over the test period.

The test on Daphnia was also performed with a single WAF of  $1\,000\text{ mg.L}^{-1}$  loading of ferrite using a static method together with a control water over a 48 hour test period. Ten daphnids were added to the test vessel and that containing the control water. No dissolved iron was detected in test media throughout the study (limit of detection  $0.1\text{ mg.L}^{-1}$ ). However, approx.  $0.4\text{ mg.L}^{-1}$  of iron in suspension was found both at the start and end of the study. There were no recorded deaths (immobilisation) of daphnids.

The algal growth inhibition tests were performed with WAFs containing 0 (control), 46, 100, 220, 460 and  $1\,000\text{ mg.L}^{-1}$  loadings of the ferrite, and inhibition of the algal growth rates was determined using both the area under the growth curve (b) and determination of the average specific growth rates (r). The tests were conducted using WAF solutions as prepared as described above. At four of the loading rates the test medium was significantly more alkaline than the control medium. Therefore, the test was conducted with and without pH adjustment. For the set requiring pH adjustment, sulfuric acid (0.1 M) was used to adjust the WAFs to within 0.3 (pH value) of the control medium, except for the lowest loading rate which was within range.

No dissolved iron was detected in test media throughout the study (limit of detection  $0.1\text{ mg.L}^{-1}$ ), except for one value ( $0.1\text{ mg.L}^{-1}$ ) for a freshly prepared medium from the highest loading ( $1\,000\text{ mg.L}^{-1}$ ) which involved pH adjustment.



The concentrations of iron in suspension were essentially dose-related ranging from 0.2 mg.L<sup>-1</sup> (loading rate of 46 mg.L<sup>-1</sup>) to approximately 1 mg.L<sup>-1</sup> (loading rate of 1 000 mg.L<sup>-1</sup>). Little decrease in suspended material, probably as a result of the constant agitation, was evident over the 72 hours.

The respiration inhibition tests were conducted with activated sludge over a three hour period using WAFs prepared with nominal ferrite material loadings of 0 (control), 1, 10, 100 and 1 000 mg.L<sup>-1</sup>. Although the prepared WAF solutions had alkaline pH (due to the presence of KOH), this was buffered by the bicarbonate alkalinity to values between 8.1 and 8.4, and the temperature was always between 18.8 and 20°C. For the WAF solutions containing 1, 10 and 100 mg.L<sup>-1</sup> loading of ferrite the inhibition of respiration after 3 hours was less than 10%, but for the 1 000 mg.L<sup>-1</sup> preparation this had increased to 24%.

The ecotoxicity data presented indicate that the new ferrite chemical is not toxic to either rainbow trout or to *Daphnia* up to the limit of its water solubility, and the WAF solutions show slight toxicity to green algae and to aerobic bacteria.

<i>Test</i>	<i>Species</i>	<i>Results</i>	<i>Reference</i>
acute toxicity 96 hours Semi-static OECD TG 203	rainbow trout ( <i>Oncorhynchus mykiss</i> )	LL <sub>50</sub> > 1 000 mg.L <sup>-1</sup> NOEL = 1 000 mg.L <sup>-1</sup>	(14)
acute immobilisation 48 hours static OECD TG 202	water flea ( <i>Daphnia magna</i> )	EL <sub>50</sub> > 1 000 mg.L <sup>-1</sup> NOEL = 1 000 mg.L <sup>-1</sup>	(14)
growth inhibition 72 hours static OECD TG 201	algae ( <i>Raphidocelis subcapitata</i> )	<u>Without pH adjustment</u> E <sub>b</sub> L <sub>50</sub> = 46 - 100 mg.L <sup>-1</sup> E <sub>r</sub> L <sub>50</sub> = 460 - 1 000 mg.L <sup>-1</sup> 1	(14)
		<u>With pH adjustment</u> E <sub>b</sub> L <sub>50</sub> = 100 - 220 mg.L <sup>-1</sup> E <sub>r</sub> L <sub>50</sub> > 1 000 mg.L <sup>-1</sup>	
respiration inhibition OECD TG 209	aerobic waste water bacteria	EL <sub>50</sub> > 1 000 mg.L <sup>-1</sup>	(15)

## **11. ASSESSMENT OF ENVIRONMENTAL HAZARD**

When used in the manner indicated by the notifier, the environmental hazard from the notified chemical is low. However, the spent catalyst material is pyrophoric and there is consequently a possible environmental hazard from fire. The possibility of this occurrence will be reduced through the purging of the reactors of combustible materials, and the employment of properly trained personnel in the performance of this operation.

The notified chemical is not toxic to fish and *Daphnia* up to the limit of its water solubility, but shows slight toxicity to green algae and to aerobic wastewater bacteria. Although transitory release of small quantities of dust containing the notified chemical may occur during charging and discharging the reactors, this is unlikely to present any environmental hazard. However, the catalyst containing the notified chemical also contains soluble caustic alkalis which would lead to significant increase in pH of water bodies with which it comes into contact, and consequently release into the water compartment may cause a transitory hazard, particularly if released to confined water bodies or slowly flowing streams. Precautions for prevention of any release to the water compartment should be observed in transportation and general handling of the catalysts containing the new material - either fresh or spent material.

## **12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS**

The notified chemical is a moderate skin sensitiser in guinea pigs and is corrosive (related to the high pH of 12.9). Therefore, the notified chemical would be classified as hazardous according to the National Occupational Health and Safety Commission's *Approved Criteria for Classifying Hazardous Substances* (13).

The notified chemical will be imported as a component (less than 10%) of a catalyst in 1 500 kg sealed woven polypropylene sealed super sacks. Exposure of transport workers and storage workers is unlikely except in the event of an accident. Hence the risk of adverse health effects to these workers from the notified chemical is expected to be minimal. Because of the corrosive properties of the notified chemical and the other components of the catalyst, the catalyst itself is classified as a Dangerous Good (Class 8) according to the *Australian Code for the Transport of Dangerous Goods by Road and Rail* (16) and appropriate precautions should be taken during transport, storage and handling (see notifier's MSDS).

Once the catalyst is within the reactor, worker exposure to the notified chemical is not likely. Therefore, the risk during normal operation of the reactor is negligible. The main concern for worker health involves the manual loading and unloading of catalyst into the reactor, a process which occurs about every two years, over a period of about two days. There is potential for dermal, ocular and inhalation exposure to the notified chemical during these activities. This process occurs skin, eye and respiratory effects. Nevertheless, personal protective equipment as described below should be worn during catalyst changeover, particularly as the catalyst contains a respirable component.

Although the catalyst contains less than 10% of the notified chemical, other components are present in the catalyst that would be classified as hazardous according to the Approved Criteria (13) because of their corrosive properties and concentration in the final catalyst product. Therefore, the effects identified above for the notified chemical are also relevant to the catalyst.

The catalyst containing the notified chemical also contains iron oxide. Cumulative inhalatory exposure to iron oxide causes a benign condition of the lung known as siderosis which may result in the development of mild lung impairment. As mentioned above local exhaust ventilation will control exposure and reduce the risk of this health effect occurring. In addition, the long time intervals between catalyst changeover suggest that significant cumulative exposure will not occur.

Carbon monoxide, benzene and volatile organic chemical vapours are released when the spent catalyst is dry dumped. Carbon monoxide is a chemical asphyxiant. Benzene is classified as a carcinogen category 1 according to the National Commission's *List of Designated Hazardous Substances* (17).

The notified chemical is an industrial specialty product and there is negligible potential for public exposure arising from its use in styrene production under normal conditions. Minimal exposure may occur as a result of accidental spillage during transport or during disposal.

### **13. RECOMMENDATIONS**

To minimise occupational exposure to potassium ferrite the following guidelines and precautions should be observed:

- Safety goggles should be selected and fitted in accordance with Australian Standard (AS) 1336 -1994 (18) to comply with Australian/New Zealand Standard (AS/NZS) 1337-1992 (19);
- Respirators should be selected and fitted in accordance with Australia/New Zealand Standard 1715 -1994: *Use and Maintenance and Respiratory Protective Devices* (20) and Australian/New Zealand Standard 1716 -1991 *Respiratory Protective Devices* (21);
- Industrial clothing should conform to the specifications detailed in AS 2919 (22) and AS 3765.1 (23);
- Impermeable gloves or mittens should conform to AS 2161 (24);
- All occupational footwear should conform to AS/NZS 2210 (25);

- Spillage of the notified chemical should be avoided, spillages should be cleaned up promptly which should then be put into containers for disposal;
- Good personal hygiene should be practised to minimise the potential for ingestion; and
- A copy of the MSDS should be easily accessible to employees.

Care should be taken to avoid generation of dust, release of gases and vapours and contact with caustic liquids when handling the product containing the notified chemical. Engineering controls to limit exposure levels to dust and vapours are required and air monitoring should be conducted during catalyst change over to ensure control measures are adequate. The following National Occupational Health and Safety Commission Exposure Standards for Atmospheric Contaminants in the Occupational Environment (26) should be used as a guide in the control of workplace exposure to potentially hazardous components of the end use product, Criterion Catalyst 035: iron oxide, 5 mg/m<sup>3</sup> (TWA); calcium oxide, 2 mg/m<sup>3</sup> (TWA); molybdenum, soluble compounds (as Mo), 5 mg/m<sup>3</sup> (TWA); molybdenum, insoluble compounds (as Mo), 10 mg/m<sup>3</sup> (TWA); benzene, 5 ppm (TWA); carbon monoxide, 30 ppm (TWA); and dusts not otherwise specified, 10 mg/m<sup>3</sup> (TWA). Workers should be advised of the pyrophoric nature of the spent catalyst.

#### **14. MATERIAL SAFETY DATA SHEET**

The MSDS for the product Criterion Catalyst 035 containing the notified chemical was provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (27).

This MSDS was provided by the applicant as part of the notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of the applicant.

#### **15. REQUIREMENTS FOR SECONDARY NOTIFICATION**

Under the Act, secondary notification of the notified chemical shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

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