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**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME**

**FULL PUBLIC REPORT**

# TRIPOTASSIUM VANADATE

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Director
Chemicals Notification and Assessment

# FULL PUBLIC REPORT

# TRIPOTASSIUM VANADATE

## 1. APPLICANT

Nalco Australia Pty Ltd, 2 Anderson Street, Botany, NSW 2219.

## 2. IDENTITY OF THE CHEMICAL

**Chemical name:** Tripotassium vanadate

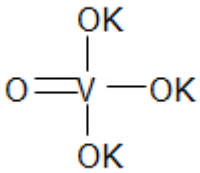
**Chemical Abstracts Service (CAS) Registry No.:** 14293-78-8

**Other name(s):** Vanidic acid, Tripotassium salt,
and tripotassium *ortho*vanadate

**Trade Name(s):** PR-4391 (23 % aqueous solution)

**Molecular formula:** $K_3VO_4$

**Structural formula:**




**Molecular weight:** 183.91 g/mol

**Method of detection and determination:**

Atomic Absorption Spectroscopy or colourimetric analysis.

## 3. PHYSICAL AND CHEMICAL PROPERTIES

**Appearance at 20°C and 101.3 kPa:** Colourless liquid (23% aqueous solution)

**Odour:** Odourless (23% aqueous solution)

**Melting Point:** Not available

**Specific Gravity:** 1.24 - 1.28 kg/L at 25°C (23% aqueous solution)

**Vapour Pressure:** Not available

**Water Solubility:** Completely soluble at 23 g/100 mL. Saturation point not determined.

**Adsorption/Desorption:** Not available

**Dissociation Constant:** Completely dissociates in aqueous solution.

**Decomposition Temperature:** Not available

**Decomposition Products:** Oxides of vanadium

**Autoignition Temperature:** Not available

**Explosive Properties:** Not available

**Particle size distribution:** Not relevant

**Hydrolytic stability as a function of pH:**

At high pH solutions contain colourless mononuclear vanadate ions ($VO_4^{3-}$). Solutions become yellow and then orange due to the formation of di- and tri-nuclear species, as pH is lowered. Below pH 6.8, hydrated vanadium pentoxide precipitates. Even at higher pHs, crystalline "vanadates"

of variable composition and unknown structure can precipitate from solution (1).

## 4. PURITY OF THE CHEMICAL

**Degree of purity:**

Tripotassium vanadate is manufactured by reacting vanadium pentoxide with excess potassium hydroxide in solution and is not isolated. The reaction is complete as indicated by the solution becoming colourless.

**Toxic or hazardous impurity:** Potassium hydroxide (8.5% excess). This substance is corrosive to skin and eyes.

**Additive(s)/Adjuvant(s):** None

## 5. INDUSTRIAL USE

Tripotassium vanadate is to be used as a tracer in Watergy 999, which will be used as a corrosion inhibitor. The corrosion inhibitor will be used in water cooling towers of air conditioning systems which use evaporative cooling. The notified chemical will replace the use of chromium compounds.

The estimated quantity of tripotassium vanadate is 4 tonnes per year.

## 6. OCCUPATIONAL EXPOSURE

### 6.1 During Manufacturing Process

PR4391

Tripotassium vanadate will be manufactured on one site from vanadium pentoxide and potassium hydroxide. Water is added to a 2 tonne, stainless steel blender and potassium hydroxide (49% solution) is pumped into the blender. The vanadium pentoxide powder is then manually added into the blender through the hatch

by one trained operator. During the addition of the vanadium pentoxide heat is generated, but the temperature within the blender is maintained at 70 - 80°C via cooling coils. The reaction mixture is maintained at this temperature until it becomes colourless, which takes approximately 2 hours. The mixture is then checked by the quality control laboratory. Once the reaction is complete, the 23% solution of potassium vanadate is cooled to 20 - 30°C and is transferred to lined, 200 L steel drums by gravity feed. PR4391 is stored in these drums on site until it is needed for the manufacture of Watergy 999.

This operation will take place a maximum of 11 times per year (based on the maximum estimated manufacturing volume of potassium vanadate of 4 tonnes per year).

The blender is fitted with a fume extractor connected to a wet scrubber.

Since vanadium pentoxide dust is a hazardous material, the operator will be wearing an air breather, PVC gloves, impervious apron and boots during the manual addition of the vanadium pentoxide.

Watergy 999

Potassium vanadate (PR4391) is pumped directly from the 200 L steel drums to a 10 tonne stainless steel blender containing the other ingredients in Watergy 999. Watergy 999 contains 6% of PR4391. Once blended Watergy 999 is transferred to 20 L plastic containers, 200 L drums or 1,000 L intermediate bulk containers by gravity feed and transported in these containers. One operator will be involved in this operation which will take place a maximum of 7 times per year (based on the maximum estimated manufacturing volume of potassium vanadate of 4 tonnes per year). Four workers will be involved in storage and handling on site and approximately 50 truck drivers, who will transport Watergy 999 to air conditioning/cooling tower management and service companies.

## 6.2 During Dosing of Cooling Towers

Worker exposure to Watergy 999 during dosing of cooling towers is expected to be low since dosing is carried out using dosing

pumps. There will be a limited number of sites where Watergy 999 is dosed manually. However, the quantity of Watergy 999 used at these sites will be less than 1 L per tower. The number of workers who will be involved in the dosing operation is estimated to be 500 and will be made up of trained Nalco technical sales staff and employees of air conditioning maintenance companies.

## 7. PUBLIC EXPOSURE

The public will not be exposed to the chemical during its manufacture and application. The chemical will be added to a product used for corrosion and scale inhibition in evaporative recirculating cooling towers. Dosing of cooling systems with the product would only be performed by company sales representatives, and employees of building maintenance and air conditioning/cooling tower management and service companies.

An amount of approximately 0.01% or less of the recirculating volume is discharged as small water droplets (drift) to which the public might be exposed. Liquid may be discharged from cooling towers to sewers, internal effluent treatment plants, or stormwater drainage. Plumbing connections between cooling systems and potable water systems are illegal and public exposure to water contaminated by cooling tower chemicals is therefore very unlikely.

## 8. ENVIRONMENTAL EXPOSURE

### . Release

Watergy 999, containing 1.38% tripotassium vanadate ($K_3VO_4$), is typically dosed to cooling towers at 100 ppm, which equates to around 1.4 ppm of the notified substance, or 0.4 ppm as vanadium. Release of cooling water containing the notified substance may occur via drift (small droplets entrained in cooled air), leaks, or blowdown (removal of liquid to avoid excessive build up of naturally occurring salts in cooling water). Total annual release of cooling water from cooling towers around Australia is estimated at 20 million tonnes (10% as drift and the remainder as blowdown) of which less than 5% is expected to be treated with vanadate traced products. Liquid effluents are expected to be contained on-site before discharge to sewer (80%) or stormwater. City buildings are required to connect to sewer for such

discharge, but some are still being converted from stormwater. Based on the above figures, annual release of tripotassium vanadate will amount to around a tonne (280 kg V), or 25% of annual production.

### . Fate

The notified substance will be discharged at a concentration in the order of 1 ppm (0.4 ppm V) in aqueous effluent from cooling towers. In the absence of direct information on tripotassium vanadate, a general outline of the fate of vanadium in the environment (2) will be presented.

Average background levels of vanadium in river water from Japan and the USA are in the order of 1 ppb. In the oceans, levels do not exceed 3 ppb. Levels are low because sorptive and biochemical processes remove vanadium from the water column, with the bulk being bound to and precipitated with silt, particularly ferric hydroxides and organic matter. Some is also assimilated by organisms, such as marine algae. Tripotassium vanadate discharged to the aquatic environment can be expected to undergo dilution, sorption, and precipitation in sediment.

## 9. EVALUATION OF TOXICOLOGICAL DATA

No toxicity data were submitted for tripotassium vanadate. This compound is expected to have a similar toxicological profile to other compounds containing vanadium in the oxidation state of V. Trisodium vanadate ($Na_3VO_4$), vanadium pentoxide ($V_2O_5$) and sodium vanadate ($NaVO_3$) are such compounds. Toxicity data on these analogous compounds will be discussed below.

### 9.1 Human Data

The majority of data on the occupational health effects of vanadium compounds is based on experience with vanadium pentoxide ($V_2O_5$)(3).

Vanadium pentoxide is used in welding electrode coatings; as an additive to steels; and as a catalyst in glass and ceramic glazes, and oxidation of sulphur dioxide.

Acute vanadium pentoxide intoxication was observed in 16 workers, who were exposed to respirable vanadium pentoxide dust particles in excess of 0.5 $mg/m^3$. Symptoms were indicative of ocular and respiratory tract irritation and included conjunctivitis, nasopharyngitis, hacking cough, fine rales, and wheezing.

Workers exposed to a mixture of vanadium pentoxide and sodium vanadate ($NaVO_3$) dust at concentrations of 0.25 $mg/m^3$ developed green tongue, metallic taste, throat irritation, and cough.

Chronic exposure to vanadium pentoxide has been suggested to increase the incidence of asthma.

An allergic type of eczema has been reported in humans patch tested with sodium vanadate.

Worksafe Australia has set an exposure standard for vanadium pentoxide dust and fumes of 0.5 $mg/m^3$ (TWA) (4).

## 9.2 Animal Data

### 9.2.1 Acute Toxicity

#### 9.2.1.1 Death

$LD_{50}$ values for some vanadium compounds are presented in Table 1. The $LD_{50}$ values show vanadium compounds to possess moderate to high acute toxicity.

**Table 1:** $LD_{50}$ values of vanadium compounds (5)

| **Compound** | **Route** | **Species** | **$LD_{50}$** |
|---|---|---|---|
| $Na_3VO_4$ | Oral | Rabbit | 100 mg/kg |
| $Na_3VO_4$ | IP | Mouse | 36 mg/kg |
| $NaVO_3$ | Oral | Mouse | 75 mg/kg |
| $NaVO_3$ | IP | Mouse | 36 mg/kg |
| $V_2O_5$ | Oral | Rat | 10 mg/kg |
| $V_2O_5$ | Oral | Mouse | 23 mg/kg |
| $V_2O_5$ | IP | Rat | 12 mg/kg |

IP = intraperitoneal

#### 9.2.1.2 Respiratory Irritation

Monkeys which were exposed to 2.8 mg vanadium/$m^3$ as vanadium pentoxide ($V_2O_5$) by inhalation for 6 hours showed increased pulmonary resistance 24 h after exposure (6). There was also an increase in polymorphonuclear leucocytes in bronchoalveolar lavage. These effects were not seen at 0.3 mg vanadium/$m^3$.

Rabbits exposed to vanadium pentoxide dust at 205 mg/$m^3$ for 7 hrs showed tracheitis, pulmonary oedema, and bronchopneumonia (7). With chronic exposure at 20-40 mg/$m^3$ for 1 hr/day for several months rabbits showed chronic rhinitis, tracheitis, emphysema, atelectasis and bronchopneumonia (7).

These studies show that vanadium as vanadium pentoxide is a respiratory irritant.

#### 9.2.1.3 Skin Irritation

No data.

#### 9.2.1.4 Eye Irritation

Rabbits exposed to vanadium pentoxide dust showed conjunctivitis from acute (205 mg/$m^3$ for 7 hrs) or chronic (20-40 mg/$m^3$ for 1 hr/day for several months) exposures (7).

Vanadium as vanadium pentoxide is an eye irritant.

#### 9.2.1.5 Skin Sensitisation

No data.

### 9.2.2 Repeated Dose Toxicity

Rats receiving sodium vanadate ($NaVO_3$) in drinking water at a concentration of 50 ppm for 3 months had mononuclear cell infiltration (mostly perivasular) in the lungs (8). There was hypertrophy and hyperplasy in the white pulp of the spleen and microhaemorrhagic foci in the corticomedullary region of the kidneys. An increase in plasma urea levels was also observed.

Rats that breathed bismuth orthovanadate ($BiVO_4$) for 6 hrs/day for 2 weeks showed increase in lung weight, and alveolar proteinosis as shown by an increased accumulation of alveolar macrophages, lung lipids and Type II pneumocytes (9).

These studies indicate that the target organ for repeated-dose toxicity of vanadium compounds is the respiratory system.

### 9.2.3 Genotoxicity

Vanadium pentoxide ($V_2O_5$) was found to be positive, without metabolic activation, in causing gene mutations in *Escherichia coli*, but negative in *Salmonella typhimurium* (10).

Trisodium vanadate ($Na_3VO_4$) at 10-100 µM was shown to reversibly inhibit anaphase movement of chromosomes and spindle elongation in lysed mitotic $PtK_1$ cells. This was suggested to result from

the inhibition of dynein ATPase activity by the vanadate anion (11).

Vanadate has been shown to cause strand breaks in chromosomes in an *in vitro* human lymphocyte assay (12).

These *in vitro* studies indicate that vanadium compounds have the potential to be genotoxic.

### 9.2.4 Mechanistic Studies

The effects of vanadium compounds on the respiratory system have been shown to be mediated by damage to alveolar macrophages (13). Vanadium compounds decrease macrophage membrane integrity and impair phagocytotic activity and viability. Without macrophages, the respiratory system is unable to clear foreign particles.

The vanadate anion has been shown to inhibit ouabain-sensitive $Na^+/K^+$ ATPase activity with an $IC_{50}$ of 40 nM (14). The $Ca^{2+}$ ATPase activity is also inhibited (15). These ATPase pumps are necessary for active transport of material across cell membranes.

## 9.3 Overall Assessment of Toxicological Data

There are no data available on the toxicity of tripotassium vanadate. However, considerable human and animal data are available on the effects of vanadium, as vanadium pentoxide ($V_2O_5$), after inhalational exposure. Limited data are also available for some other vanadium(V) compounds such as sodium vanadate ($NaVO_3$), trisodium vanadate ($Na_3VO_4$).

$LD_{50}$ values for vanadium(V) compounds presented in Table 1 are in the range of 10 - 100 mg/kg by the oral route, indicating that these compounds have moderate to high acute toxicity.

Inhalational exposure to vanadium, as vanadium pentoxide, has been shown to cause respiratory and ocular irritation in humans and animals. When vanadium compounds are administered by the oral route, the respiratory system is again the target organ for toxicity. The decrease in macrophage activity has been suggested to be the basis for the respiratory effects of vanadium

compounds. The respiratory effects are observed both after acute and chronic exposure to vanadium compounds.

There are no animal studies on the potential of vanadium compounds to cause skin irritation. However, sodium vanadate has been shown to cause an allergic type of eczema in humans using patch tests.

*In vitro* genotoxicity data indicate that vanadium compounds have the potential to cause gene mutations and chromosomal damage, and interfere with spindle formation.

Mechanistic studies show that vanadium(V) compounds inhibit $Na^+/K^+$ ATPase and $Ca^{2+}$ ATPase activity, and therefore, inhibit active transport across the cell membrane. This may be the basis of some of the toxicity of vanadium compounds.

## 10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

In absence of direct information on tripotassium vanadate ($K_3VO_4$), data for vanadium compounds (2) will be used for guidance. The fish data listed below used vanadium pentoxide as toxicant, while the marine invertebrates and alga were exposed to sodium *meta*vanadate ($NaVO_3$). Results are expressed as concentration of vanadium.

The daphnid study (16) used production of ephippial eggs as a sensitive indicator of effect. Egg production was stimulated at low vanadium concentrations.

| Test | Species | Result |
|---|---|---|
| 7 d acute | Rainbow trout | $LC_{50}$ = 2.4-6.5 mg.$L^{-1}$ |
| 96 h acute | Rainbow trout fingerlings | $LC_{50}$ = 6-22 mg.$L^{-1}$ |
| 9 d acute | Worm (*Nereis diversicolor*) | $LC_{50}$ = 10 mg.$L^{-1}$ |
| 9 d acute | Mussel (*Mytilus galloprovincialis)*) | $LC_{50}$ = 35 mg.$L^{-1}$ |
| 9 d acute | Crab (*Carcinas maenas*) | $LC_{50}$ = 65 mg.$L^{-1}$ |
| 15 d acute | Alga (*Dunaliella marina*) | $LC_{50}$ = 0.5 mg.$L^{-1}$ |
| 98 d chronic | *Daphnia magna* | NOEC = 0.56 mg.$L^{-1}$ |

The acute results listed above indicate that vanadium is slightly to moderately toxic to aquatic fauna and highly toxic to algae.

## 11. ASSESSMENT OF ENVIRONMENTAL HAZARD

Concentrations discharged in blowdown effluent are expected to be in the order of 0.4 ppm V, or slightly below levels that were toxic to algae in 15 d tests. However, vanadium concentrations are expected to be reduced by dilution to non-toxic levels before entering the environment. The estimated annual discharge of 280 kg V equates to around 800 g per day across Australia, or around 200 g daily for the city of Melbourne. Dilution in the average daily flow (500 ML) through Werribee treatment complex would leave a vanadium concentration of 0.4 ppb, which is below natural background levels and three orders of magnitude below acutely toxic levels. Therefore, environmental hazard would appear minimal.

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

Despite the lack of toxicity data on the notified chemical, tripotassium vanadate, data on analogous compounds show that vanadium compounds have moderate to high acute toxicity. These compounds are ocular irritants and cause toxicity in the respiratory system following inhalational exposure. Adverse respiratory effects are also observed with oral exposure to vanadium compounds. Dermal exposure to sodium vanadate has been shown to cause an allergic type of eczema. In addition, data shows that vanadium compounds have a potential for genotoxic effects. Therefore, inhalational, oral and dermal exposure of workers and the public to vanadium compounds should be minimised.

The proposed manufacturing process and pattern of use for tripotassium vanadate indicates that occupational and public exposure to this chemical will be minimal and the risk with respect to its use will be low.

## 13. RECOMMENDATIONS

To minimise occupational exposure to tripotassium vanadate, the following guidelines and precautions should be observed:

. good work practices should be employed to avoid splashings or spillages, or the generation of aerosols;

. if engineering controls and work practices do not reduce exposure to a safe level, then the following personal protective equipment should be used:

- splash-proof goggles or face shield, as appropriate (AS1336, AS 1337) (17, 18);

- impervious elbow length gloves (AS 2161) (19);

- impervious protective clothing (AS 3765.1, AS3765.2) (20, 21);

- any accidental spillages should be cleaned up immediately;

- good personal hygiene should be observed at all times;

and

- a copy of the Material Safety data sheet should be made easily accessible to workers.

## 14. MATERIAL SAFETY DATA SHEET

The Material Safety Data Sheet (MSDS) for tripotassium vanadate (Attachment 1) was provided in Worksafe Australia format (22). This MSDS was provided by Nalco Australia Pty Ltd as part of their notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of Nalco Australia.

## 15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), secondary notification of tripotassium vanadate shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

## 16. REFERENCES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