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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME (NICNAS)

FULL PUBLIC REPORT

Hexafluorotitanic acid

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Director
Chemicals Notification and Assessment

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1. APPLICANT AND NOTIFICATION DETAILS

APPLICANT(S)
Henkel Australia Pty Ltd (ABN 82 001 302 996)
135-141 Canterbury Road
KILSYTH VIC 3137

NOTIFICATION CATEGORY
Standard: Chemical other than polymer (more than 1 tonne per year)

EXEMPT INFORMATION (SECTION 75 OF THE ACT)
Data items and details claimed exempt from publication:

Spectral Data, Purity, Identity and Weight Percent of Toxic or Hazardous Impurities, Non-Hazardous Impurities and Identity and Weight Percent of Toxic or Hazardous Impurities, Details of Formulations, Estimated Manufacture and Import Volumes, Customer Identity, % Percentage of the Notified Chemical in Formulations and Methods of Determination.

VARIATION OF DATA REQUIREMENTS (SECTION 24 OF THE ACT)
Variation to the schedule of data requirements is claimed as follows:

Use of analogue data throughout Physicochemical Properties, Toxicological Investigations and Environment sections.

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT(S)
CEC/633 (27 August 2004)

NOTIFICATION IN OTHER COUNTRIES
None known

2. IDENTITY OF CHEMICAL

CHEMICAL NAME
Titanate(2-), hexafluoro-, dihydrogen

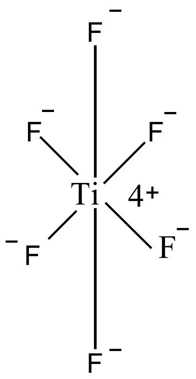
OTHER NAME(S)
Hexafluorotitanic acid
Fluorotitanic acid
Hydrogen titanium fluoride

MARKETING NAME(S)
Hexafluorotitanium acid 50%

CAS NUMBER
17439-11-1

MOLECULAR FORMULA
$F_6Ti.2H$

STRUCTURAL FORMULA



$\bullet\ 2\ H^{+}$

MOLECULAR WEIGHT
163.91

3. COMPOSITION

DEGREE OF PURITY
Medium

ADDITIVES/ADJUVANTS

Chemical Name	Hydrofluoric acid		
CAS No.	7664-39-3	*Weight %*	0.5-1
Hazardous Properties	At Concentrations equal to or more than 7%: Very Toxic (T+): R26/27/28 - Very toxic by inhalation, in contact with skin and if swallowed; R35 - Causes severe burns. At Concentrations equal to or more than 1% and less than 7%: Toxic (T): R23/24/25 - Toxic by inhalation, in contact with skin and if swallowed; R34 - Causes burns. At Concentrations equal to or more than 0.1% and less than 1%: Harmful (Xn): R20/21/22 - Harmful by inhalation, in contact with skin and if swallowed; R36 - Irritating to eyes. (NOHSC 1999)		

Chemical Name	Water		
CAS No.	7732-18-5	*Weight %*	48.8

4. INTRODUCTION AND USE INFORMATION

MODE OF INTRODUCTION OF NOTIFIED CHEMICAL (100%) OVER NEXT 5 YEARS
Imported as a 50% concentrate.

MAXIMUM INTRODUCTION VOLUME OF NOTIFIED CHEMICAL (100%) OVER NEXT 5 YEARS

Year	*1*	*2*	*3*	*4*	*5*
Tonnes	3-10	10-30	10-30	10-30	10-30

USE
As a corrosion inhibitor for use in metal surface treatments such as in the coil coating industry.

5. PROCESS AND RELEASE INFORMATION

5.1. Distribution, transport and storage

PORT OF ENTRY
Melbourne

IDENTITY OF MANUFACTURER/RECIPIENTS
Henkel Australia Pty Ltd

TRANSPORTATION AND PACKAGING
The imported hexafluorotitanium acid 50% will be shipped and transported by road in 25 L, 40 L, and 200 L polylined steel drums directly from dockside to the notifier's reformulation plant. The formulated product containing <10% hexafluorotitanium acid will be filled in 1000 L IBC's with tamper proof caps or 200 L polylined steel drums, and then transported by truck or rail to end users in the coil coating industry.

5.2. Operation description

The notified chemical will not be manufactured in Australia but will be imported as a 50% aqueous solution. At the notifier's reformulation plant, this acid concentrate will be blended with water and other ingredients to produce a corrosion inhibitor product, typically in batches of 200-1000 L. Laboratory technicians will perform testing and adjustment to the formulation specifications if necessary. The blending and transfer of the reformulated corrosion inhibitor solution components into a mixing tank will occur in a fully enclosed automated and controlled environment. Workers will only be involved in connecting and disconnecting pipelines and transfer hoses, and operation of valves and pumps via automated equipment. Packaging of the finished product into 200 L drums or 1000 L tanks will also use automated filling lines.

On completion of the blending process, it is indicated that residues of the notified chemical will be flushed through containers, pipelines and transfer hoses to effluent after precipitating fluorides with calcium salts and filter press in a wastewater treatment plant of the facility.

During end use in surface treatment for aluminium, zinc and zinc aluminised coated steel coils, the reformulated corrosion inhibitor solution will be diluted with water and other additives to a concentration of 0.01% using a metered pump system. The applied coating is not rinsed off but dried in place to allow at least 90% transfer efficiency. Chemicals not transferred onto coils from the solution are recycled and reused. After drying to evaporate residual water, layers of paint are applied to the coated strip which is cured by baking in an oven. The coil coating process is expected to occur in an effective filtered exhaust system.

5.3. Occupational exposure

Number and Category of Workers

Category of Worker	*Number*	*Exposure Duration (hours/day)*	*Exposure Frequency (days/year)*
Transport and Warehousing	**10**	**4**	**220**
Reformulation			
Make up	2	2	10
QC testing	1	1.25	10
Filling	2	2	10
Cleaning and Maintenance	2	2	10
Coil Coating	**30**	**4**	**220**

Exposure Details

Transport and Warehousing of the notified chemical as imported.

The drums will be transported from the dockside to the reformulation site in Kilsyth, Victoria where it will be stored. Exposure during transport and storage is not expected, except in the event of an accident where the drums are pierced or dropped. Workers are expected to wear coveralls, long sleeved clothing and impervious gloves. In the event of an accident, workers will wear impervious gloves, rubber apron and shoes, coveralls, goggles and organic vapour respirators to control exposure.

Reformulation.
Make up
The notified chemical will be transferred from the drums to mixers by automated transfer pumps. Dermal and to a lesser extent ocular exposure to the notified chemical may occur as result of drips and spills during connecting and disconnecting pipelines and transfer hoses. Exhaust ventilation will be employed in the make up area. Workers involved in the make up process will wear impervious gloves, rubber apron and shoes, coveralls, goggles and organic vapour respirator.

Exposure to HF during the reformulation process is possible due to the low pH and fluoride content of the imported aqueous solution.

Quality control testing
Samples for QC testing are taken before filling. These samples are collected using a sampling cup with an extension handle and then transferred to sealed plastic bottles. The samples are tested in the laboratory under local exhaust ventilation. Dermal and to a lesser extent ocular exposure to the notified chemical may occur as result of drips and spills during the sampling and testing process. Workers involved in quality testing will wear impervious gloves, rubber apron and shoes, coveralls, goggles and an organic vapour respirator.

Filling.
Once a batch is approved, the finished product containing <10% notified chemical is filtered and filled into 1000 L IBCs or 200 L polylined drums via enclosed lines. Dermal and to a lesser extent ocular exposure to the notified chemical may occur as result of drips and spills during the connection and disconnection of filling lines.

Maintenance and Cleaning
Periodic maintenance and cleaning of the reformulation equipment will occur. During cleaning, water is pumped through the lines to the mixing tank disposed of to sewer following pre treatment in the on site water treatment facility. Workers involved in maintenance and cleaning will wear impervious gloves, rubber aprons, and shoes, coveralls, goggles. Use of organic vapour respirators is recommended.

Transport and warehousing of finished product containing notified chemical.
Dermal and ocular exposure to the notified chemical in the finished product may occur during transport and warehousing if the packaging breached but will be limited to a concentration of <10%.

Coil Coating
The finished product is mixed with other additives and water in an enclosed bath after being introduced into the bath using a metered pump system. The final concentration of the notified chemical in the bath will be less than 1%. Dermal exposure through drips and spill may occur during the connection and disconnection of lines to the pump. Once it is added to the bath exposure to the notified chemical should not occur. The coil coating area is fitted with a filtered exhaust system. The metal for coating is attached to conveyor system and is cleaned and rinsed prior to being immersed in the bath containing the notified chemical. The applied coating is not rinsed but dried in place once the metal is removed from the bath. Workers involved in the process will wear coveralls, long sleeve clothing, goggles, and imprevious gloves. In case of spills, rubber shoes and aprons, and organic vapour respirators will be used.

Exposure to HF during treatment is possible due to the low pH and fluoride content of the product containing the notified chemical.

5.4. Release

RELEASE OF CHEMICAL AT SITE
Any spillages of the imported solution containing the notified chemical would be contained to the plant through existing bunding and neutralised with lime slurry. From reformulation of the imported

solution it is estimated that waste of up to 120 kg of the notified chemical per annum will be generated by cleaning up minor spills and equipment and rinsing drums. The residues are washed into the waste water treatment facility. The water waste will be disposed of to sewer after pre-treatment in the waste treatment plant through precipitation with calcium salts and filter pressing and disposed of to landfill via a licensed waste contractor. Only a small portion (1%) of the notified chemical present in the waste water will be released in effluent approximating 1.2 kg per annum.

RELEASE OF CHEMICAL FROM USE

Coil coating in Australia occurs at approximately 7 industrial facilities. The product is applied to the coils as a solution containing less than 1% of a salt of the acid. The applied coating is not subsequently rinsed off but dried in place giving greater than 90% transfer to the coated metal. The notified chemical remains unchanged throughout the application process and any material not transferred is recycled back into the coil coating solution and re-used. There is no release of the notified chemical into the aquatic environment during the coil coating process. All solution lines are periodically cleaned and this rinsate is utilised as a diluent for the coil coating solution, such that it is recycled back into the process and re-used. Drums or IBCs containing residual reformulated corrosion inhibitor solution are transported back to the manufacturing site for cleaning and recycling.

5.5. Disposal

The empty containers will be recycled and any residual product or discharge water at the notifier's site will be disposed of to the waste treatment plant and ultimately to landfill.

5.6. Public exposure

The notified chemical is intended for use in the coil coating industry only. After application and once dried, the notified chemical is cured into an inert matrix and hence is unavailable for exposure. Public exposure to the notified chemical therefore will only occur in the event of a transport accident or spillage.

6. PHYSICAL AND CHEMICAL PROPERTIES

The physicochemical properties of the notified chemical relate to its being a strong acid. Meshri (1994) notes that hexafluoroanions of Group 4 (IVB) are octahedral complexes, which are quite stable in acidic media. Solutions having pH > 4 tend to hydrolyse forming the metal dioxides. The acid exists in the presence of excess HF (0.5%) at a maximum concentration of 63%.

The following physico-chemical properties have been derived from the MSDS for the 50% aqueous solution of hexaflurotitanic acid.

Appearance at 20°C and 101.3 kPa Colourless fuming liquid with pungent odour

Melting Point <0°C

Remarks Test report not provided.

Boiling Point >100°C

Remarks Test report not provided.

Density 1500 kg/m^3 at 20°C

Remarks Test report not provided.

Vapour Pressure 1.01 kPa at 20°C

Remarks Test report not provided, but may reflect the water content of the material.

Water Solubility Not determined

Remarks Hexafluorotitanic acid is soluble to 63% (w/v) in water (Meshri 1994).

Hydrolysis as a Function of pH Not determined

Remarks Hexafluorotitanic acid hydrolyses rapidly to TiO_2 and F^- in dilute solution at neutral and basic pH.

Partition Coefficient (n-octanol/water) Not determined

Remarks Hexafluorotitanic acid is expected to partition predominantly to water based on its ionic nature.

Adsorption/Desorption Not determined

Remarks The notified chemical is freely soluble in aqueous systems. It is not expected to adsorb to solids, sediments or organic matter.

Dissociation Constant $pK_1 = 4\text{-}8$

Remarks Henkel Surface Technologies have indicated that the Ka1 lies between 1×10^{-4} and 1×10^{-8}. Commercial fluorotitanic acid also typically contains 0.1–0.5% free hydrofluoric acid which has a Ka of 7.2×10^{-3}. The pH of the concentrate is approximately 2.2 to 2.4 because of the large amount of proton consumption due to water formation with the oxygen in the manganese oxide.

Particle Size Not determined

Remarks The notified chemical will be imported as an aqueous solution.

Flash Point Not determined.

Remarks The notified chemical will be imported as an aqueous solution.

Flammability Limits Not determined

Remarks The notified chemical will be imported as an aqueous solution.

Autoignition Temperature Not determined

Remarks The notified chemical will be imported as an aqueous solution.

Explosive Properties Not determined

Remarks The notified chemical is not expected to have explosive properties based on its molecular structure.

Reactivity

Remarks In the vapour phase, hexafluorosilicic acid dissociates to HF and silicon tetrafluoride. Hexafluorosilicic acid is not stable as pure and can be handled only as aqueous solution. Similar behaviour is expected of hexafluorotitanic acid.

Hexafluorotitianic acid solution in water is incompatible with strong bases and alkali metals.

7. TOXICOLOGICAL INVESTIGATIONS

There are no toxicological data available for the notified chemical. Hexafluorosilicic acid can be considered as an analogue for the notified chemical. Both silicon and titanium dioxides react with aqueous HF to give the corresponding isostructural hexafluoroacids in solution. Hexafluoroacids, in general, can be regarded as being sources of HF. In this respect, hexafluorosilicic acid and hexafluorotitanic acids would be expected to have very similar toxicological properties which are also similar to those of aqueous HF

In the absence of toxicology information for hexafluorotitanic acid, the notifier submitted information of studies conducted on various inorganic complex fluorides and aqueous HF. These studies were accepted in support of claims for variation to the toxicity information, and as read across data for the assessment of potential health effects of hexafluorotitanic acid. Other toxicological properties for the notified chemical relate to its being a strong acid. In order to determine the possible chronic effects of hexafluorotitanic acid, information on titanium and its compounds have also been included in the toxicological investigations.

A toxicity profile for hexafluorosilicic acid was obtained from IUCLID, which is published by the European Chemicals Bureau (European Chemicals Bureau, 2003). The report contained toxicity information on hexafluorosilicic acid compounds, as well as hydrogen fluoride (HF). The toxicity endpoints are tabulated below:

Endpoint and Result	*Assessment Conclusion*
Rat, acute oral LD50 125 mg/kg bw (disodium salt)	toxic
Mouse, acute oral LD50 220 mg/kg bw (disodium salt)	harmful
Rabbit, acute oral LD50 125 mg/kg bw (disodium salt)	low toxicity
Guinea pig, acute oral LD50 500 mg/kg bw (dipotassium salt)	low toxicity
Rat, acute inhalation LC50 1.11 mg/L/1 hour (hydrogen fluoride)	toxic
Rat, acute inhalation LC50 3.3 mg/L/1 hour (silicon tetrafluoride)	harmful
Mouse, acute inhalation LC50 0.436 mg/L/1 hour (hydrogen fluoride)	low toxicity
Monkey, acute inhalation LC50 1.543 mg/L/1 hour (hydrogen fluoride)	low toxicity
Rabbit, skin irritation (fluorosilicates)	slightly irritating (weak hyperemia after skin contact)
Rabbit, eye irritation (fluorosilicates)	severely irritating (severe corneal damage)
Genotoxicity – bacterial (*S. typhimurium*) reverse mutation	non mutagenic
Genotoxicity – bacterial (*E. coli*) gene mutation	non-mutagenic

The toxic properties of various fluorocompounds were also sourced from the Hazardous Substance Data Bank (HSDB), which states that hexafluorosilicic acid corrodes glass and stoneware. It is toxic by inhalation, ingestion or skin contact, and may cause severe injury or death. The chemical is corrosive by skin contact and inhalation. Hexafluorosilicic acid at concentrations not causing damage to intact skin caused necrosis in injured skin spreading to the deeper regions (cited in HSDB, 2003).

Fluorosis in 50 workers working with phosphate fertilizers for 30 years was reported. These workers were exposed to gaseous fluoride in the form of SiF_4 and H_2SiF_6 from 0.04 to 0.17 mg/m^3. Nine workers showed increased bone density but no signs of disability. Chronic exposure to excess fluoride causes increased osteoblastic activity, increased density and calcification of bone, ligaments, tendons and muscle attachments. Severe effects included disablement and crippling in chronic poisoning (Goodman and Gilman, 1996, cited in HSDB, 2004).

HF and fluoride compounds

According to Meshri (1994) hexafluoroacids, such as hexafluorotitanic acid, hexafluorozirconic acid and hexafluorohafnic acid, exist only in aqueous media in the presence of excess HF. Inhaled HF is completely absorbed in the upper respiratory tract and distributed rapidly to the blood. When in contact with skin, the extent of absorption varies depending on the time of exposure, concentration and corrosive effects on the skin (ATSDR, 1993, cited in NICNAS, 2001). Once in the body, HF ionises to fluoride and its effects are the same as other sources of fluoride. After uptake fluoride distributes through all soft tissues and may also cross the placenta during pregnancy. About half of the absorbed fluoride is sequestered in bone and teeth (NICNAS, 2001). Fluoride exchanges with hydroxyl radicals of hydroxyapatite (the inorganic constituent of bone) to form fluorohydroxyapatite. Fluoride that is not retained is excreted rapidly in urine. Under certain conditions perspiration may be an important route of fluoride excretion. The concentration of fluoride retained in bones and teeth is a function of both the concentration of fluoride intake and the duration of exposure. Periods of excessive fluoride exposure will result in increased retention in the bone. However, when the excessive exposure is eliminated, the bone fluoride concentration will decrease to a concentration that is again reflective of intake (USEPA Office of Drinking Water; Criteria Document (Draft): Fluoride p. III-19 (1985)).

The ACGIH (1992) states in their supporting documentation for setting exposure standards for various fluoride compounds of 2.5 mg/m^3 (TLV) that the toxic effects of inorganic fluoride compounds are nearly always due to the fluoride content. The TLV is based on a study in which a minimum increase in bone density occurred at 3.38 mg F/m^3. In the ACGIH supporting documentation it was noted that sodium fluoride is negative in the Ames test and positive in the mouse lymphoma test. In two tests for the induction of chromosomal aberrations and (Sister Chromatid Exchanges) SCEs in CHO cells contradictory results were obtained for each of the toxicological endpoints.

HF is both corrosive and toxic, with higher concentrations causing greater harm. Acute toxicity is a major hazard of HF relevant to accidental exposure. Fatalities from accidental exposure to HF have occurred through inhalation and also via the dermal route (Muriale et al, 1996; Tepperman, 1980, cited in NICNAS, 2001). Acute exposure results in burns and respiratory damage, and in systemic effects that can be fatal. Systemic effects of HF include disturbance of plasma calcium levels and other electrolyte balance. Hypocalcemia can produce ventricular fibrillation and death. Human dermal contact with HF causes painful second and third degree skin burns that heal very slowly. Lower concentrations of HF (0.1%) can cause delayed burns if not treated promptly (Perry et al, 1994 cited in NICNAS, 2001).

Inhalation of low concentrations of HF (1 to 2 mg/m^3) caused upper airway and eye/skin irritation in volunteers. The no observed adverse effect level (NOAEL) in animals is 0.72 mg/m^3 (NICNAS, 2001).

Chronic exposure to HF may cause skeletal fluorosis. In humans, this is a known effect of prolonged exposure to fluoride through inhalation or oral routes. HF is not believed to be a sensitiser or to be genotoxic or carcinogenic. Human data on reproductive toxicity of fluoride are inconclusive (NICNAS, 2001).

Symptoms following ingestion of soluble fluoride salts were described as follows: large doses lead promptly to burning or crampy abdominal pain, intense vomiting and diarrhoea, often with haematemesis and melena. Dehydration and thirst occur. Muscle weakness, tremors and rarely epileptiform convulsions, preceded or followed by progressive central nervous system depression (lethargy, coma and respiratory arrest, even in the absence of circulatory failure). Shock characterised by pallor, weak and thready pulse (sometimes irregular), shallow unlaboured respiration, weak heart sounds, wet cold skin, cyanosis, anuria, dilated pupils followed almost invariably by death in 2 to 4 hours. Even in the absence of shock, arrhythmias may occur, especially multiple episodes of ventricular fibrillation leading eventually to cardiac arrest. If the victim survives a few hours, paralysis of the muscles of deglutition, carpopedal spasm and painful spasms of the extremities occur. Occasionally localized or generalized urticaria is observed. The above symptoms are related to a variety of metabolic disorders that may occur in acute fluoride poisoning including hypocalcemia, hypomagnesemia, metabolic and/or respiratory acidosis and sometimes hyperkalemia (Gosselin et al, 1984).

In experimental animals, the fluorosilicates appear to be as toxic as the corresponding fluorides. If sufficient fluoride is absorbed, fluoride ion increases capillary permeability and also produces a coagulation defect. These actions lead to haemorrhagic gastroenteritis and haemorrhages, congestion and oedema in various organs including the brain. Clinical manifestations include excitability, muscle tremors, weakness, urination, defecation, salivation, emesis, sudden collapse, clonic convulsions, coma and death due to respiratory and cardiac failure (Gosselin et al, 1984).

Titanium and titanium compounds

Titanium and its compounds are ubiquitous in the environment. Exposure to titanium is mainly associated with titanium dioxide, titanium carbide or titanium tetrachloride. Titanium dioxide is the most widely used titanium compound. Exposure is usually in the form of dust but exposure to fumes and vapours could occur during handling of titanium tetrachloride (RTECS, 2004). Approximately 3% of an oral dose of titanium is absorbed and the majority of that absorbed is excreted in the urine (Goyer RA, 1996). The estimated body burden is approximately 15 mg and most is found in the lungs, probably as a result of inhalation exposure. Titanium dioxide has the ability to dry and defat the skin by adsorption. Animal studies showed that titanium dioxide is not carcinogenic by the oral route whereas inhalation studies demonstrated that an excess of tumours is formed in rats exposed to a high dose. This observation was not observed in mice and it is believed to be associated with lung overload effects with insoluble, low toxicity dust, which is rat specific (Egerton TA, 1997). This observation was supported by the fact that an epidemiological study of pigment production workers exposed to titanium dioxide did not demonstrate any excess of tumours (Chen JL et al, 1988, cited in Egerton TA, 1997).

8. ENVIRONMENT

8.1. Environmental fate

No environmental fate data were submitted. As an inorganic complex the notified chemical will not undergo microbial degradation, though it is unstable under neutral to alkaline conditions in solution, and the end products are expected to be fluoride ions and titanium dioxide.

8.2. Ecotoxicological investigations

No ecotoxicity data were submitted. Considering the insolubility of the notified chemical under neutral to alkaline conditions, it is unclear what the relevant species would be for testing of the aquatic toxicity.

The most common oxidation state of titanium is IV. It forms a stable and non-toxic dioxide, which occurs naturally in the earth’s crust.

Hexafluoroacids in general can be regarded as being sources of HF and in this respect, hexafluorotitanic acid would be expected to have similar toxicological properties to those of aqueous HF. The notified chemical, although a source of aqueous HF, contains very little free, or uncomplexed fluoride in solution due to the capacity of titanium (IV) to complex fluoride. Therefore the solution will contain various fluoro or oxofluoro species of titanium (IV), having a fluoride to titanium ratio of less than six as shown in the following equation:

$[TiF_6]^{2-} + nH_2O \leftrightarrows [TiF_{(6-n)}(OH)_n]^{2-} + nHF$ (Schmitt et al 1960)

The notifier has provided the toxicity of HF to aquatic organisms based on the NICNAS Priority Existing Chemical Assessment Report (NICNAS, 2001). The results indicate that following the guidelines of Mensink *et al.* (1995), HF can be considered to be slightly to very slightly toxic to fish based on the validated results. Similarly for invertebrates, all test results are indicative of slight to very slight toxicity. Chronic results for invertebrates are suggestive of very slight toxicity with NOECs all reported to be >1 ppm.. The toxicity of fluoride to algae and aquatic plants can be described as slight to very slight. These results indicate that HF is of low toxicity to the aquatic organisms.

The following results are derived from a literature report (http://www.scientificjournals.com/sj/espr_special/Pdf/aId/3643) on the toxicity of titanium fluoride to fresh water fish, the guppy (*Poecilia reticulata*), *Daphnia magna* and algae (*Chlorella vulgaris*). Conventional acute bioassays as well as in vitro toxicity tests based on the activity of the enzymes lactate dehydrogenase (LDH) (Diamantino *et al,* 2001) and acetycholinesterase (AchE) (Guilhermino *et al,* 1996) were performed. Growth inhibition tests and acute immobilisation bioassays were performed on *Chlorella vulgaris* and *Daphnia magna*, respectively. The in vitro toxicity tests were performed on *Poecilia reticulata*. However, details of the tests were not available and the identity of the test substance is not specified clearly.

8.2.1. Acute toxicity to fish

TEST SUBSTANCE	Titanium fluoride
METHOD	Guilhermino *et al* (1996) and Diamantino *et al* (2000)
Species	*Poecilia reticulata*
Exposure Period	Unknown.
Auxiliary Solvent	Unknown
Water Hardness	Unknown
Analytical Monitoring	Unknown

Remarks – Method	The *in vitro* toxicity tests are based on the activity of the enzymes LDH and AChE

RESULTS

Remarks – Results	Titanium fluoride inhibited the activity of *Poecilia reticulata* AchE at concentrations equal or higher than 25 mg/L. No significant alterations were found on LDH activity. It is noted that the 96 h LC50 (28.7 – 190 mg/L) of the analogue hexafluorosilicic acid to fish is comparable to the toxic concentration (≥ 25 mg/L) of titanium fluoride but the former is a sub-lethal effect.
CONCLUSION	Titanium fluoride induced toxic effects on *Poecilia reticulata* at ≥ 25 mg/L

8.2.2. Acute/chronic toxicity to aquatic invertebrates

TEST SUBSTANCE	Titanium fluoride
METHOD	
Species	*Daphnia magna*
Auxiliary Solvent	Unknown.
Water Hardness	Unknown.
Analytical Monitoring	Unknown.
Remarks - Method	This is based on the OECD acute immobilisation bioassay
RESULTS	
Remarks - Results	Mortality of *Daphnia magna* was observed at concentrations equal to or higher than 66.7 mg/L.
CONCLUSION	Titanium fluoride induced toxic effects on *Daphnia magna* at ≥66.7 mg/L

8.2.3. Algal growth inhibition test

TEST SUBSTANCE	Titanium fluoride
METHOD	OECD 1995
Species	*Chlorella vulgaris*
Exposure Period	Unknown.
Auxiliary Solvent	Unknown.
Water Hardness	Unknown.
Analytical Monitoring	Unknown
Remarks - Method	This is based on the OECD growth inhibition test
RESULTS	
Remarks - Results	Titanium fluoride inhibited the growth of *Chlorella vulgaris* at concentrations equal or higher than 40 mg/L. It is noted that the reported 96 h LC50 of 10 mg/L of the analogue hexafluorosilicic acid is lower than that of the titanium fluoride.
CONCLUSION	Titanium fluoride induced toxic effects on *Chlorella vulgaris* at ≥40 mg/L

SUMMARY

Titanium fluoride induced toxic effects on all the organisms at the concentrations tested (sublethal on *Poecilia reticulata* at ≥ 25 mg/L; mortality to *Daphnia magna* at ≥66.7 mg/L and *Chlorella vulgaris* at ≥40 mg/L). The abstract concludes that the results indicate that titanium fluoride is less toxic than chromium compounds actually used in the metal finishing industry.

It is apparent that the toxicity of titanium fluoride to the aquatic organisms is comparable, if not more toxic to that of HF. Therefore, in the risk assessment, the toxicological end point will be based on the toxicity of titanium fluoride to the aquatic organisms.

9. RISK ASSESSMENT

9.1. Environment

9.1.1. Environment – exposure assessment

Waste water discharge from the reformulation site from cleaning the manufacturing equipment, drum rinsing for recycling and cleaning up spills will be pre-treated in the waste water treatment plant prior to discharge to sewer. In the treatment plant fluorides are precipitated with calcium salts and filter pressed. Almost 99% of the notified chemical will be precipitated, approximating 120 kg per annum. Under these conditions the notified chemical is expected to end up in the sludge. The ultimate fate of the sludge is likely to be landfill. Only a small proportion of the notified chemical ie up to 1.2 kg per annum will be released in the effluent.

The notifier indicates that during the coil coating process the notified chemical has a transfer efficiency of >90% and any material not transferred is recycled back into the coil coating solution and re-used. There is no release of the notified chemical into the aquatic environment during the coil coating process.

Given that there is very little release of the notified chemical into the effluent from the reformulation process, a PEC calculation is not relevant in this case.

9.1.2. Environment – effects assessment

The aquatic toxicity data of titanium fluoride indicate that the most sensitive toxicological end-point is the sub-lethal toxic effect at ≥25 mg/L on fish. Therefore, the Predicted No Effect Concentration (PNEC) is 25 µg/L, using a conservative safety factor of 1000 (because of the lack of test details).

9.1.3. Environment – risk characterisation

A PEC calculation has not been preformed but considering the limited release to water it is likely to result in a significantly lower concentration than the PNEC of 25 µg/L. Therefore there is unlikely to be an environmental risk to aquatic organisms.

It is expected that waste generated will ultimately be disposed of to landfill. In landfill the notified chemical is likely to be exist as the inert titanium oxide from the sludge after the on-site waste water treatment. Thus the titanium oxide is not expected to be mobile or leach from the soil into ground or surface water.

9.2. Human health

9.2.1. Occupational health and safety – exposure assessment

The reformulation of the notified chemical into products and preparatory processes for metal treatment are for the most part described as automated and enclosed. Because of the excess HF content in the product, workers will not only be exposed to the notified chemical but also to HF during reformulation of the notified chemical and metal treatment. The common potential sources of exposure during reformulation occur during the make up stage, QC testing and filling of drums and IBCs. Worker exposure during metal treatment will be restricted to the charging of the coating baths. Dermal, ocular and inhalation exposure may occur during the above activities.

Chronic exposure through dermal and inhalation routes is likely to occur from exposure to low concentrations of HF during metal treatment. NICNAS conducted exposure modelling (EASE) to estimate chronic exposure to HF during metal treatment using two exposure scenarios, semi-closed and open processes. EASE estimations were carried out with metal treatment products containing 8 to 10% HF (NICNAS, 2001). For a non-dispersive use with local exhaust ventilation, air concentrations of 0.5 to 1 ppm and inhalation intake of 0.06 to 0.12 mg/kg/day were predicted. For a wide dispersive use, direct handling and dilution ventilation, air concentrations of 100 to 140 ppm and inhalation intake of 12 to 16.8 mg/kg/day were predicted. The use of the notified chemical involves much lower HF levels and will accordingly result in lower exposure.

During reformulation and metal treatment the use of personal protective equipment is mandatory to prevent exposure to the notified chemical and to HF. Where possible, automation and enclosed processes are preferred when handling and using the product. There are a number of regulatory controls for HF in place in Australia and these should be implemented during use of the notified chemical in forms containing free HF. The controls implemented as described in the submission are adequate to mitigate occupational exposure to the notified chemical and exposure to low levels of HF.

Exposure to waterside, warehouse and transport workers is low considering the handling of sealed packages containing the notified chemical.

9.2.2. Public health – exposure assessment

The notified chemical and the products containing it are intended for industrial use only. Public exposure to the notified chemical may occur in the unlikely event of a transport accident. Dermal contact to metals treated with the notified chemical is possible; however, at this stage the notified chemical will form part of the treated metals and is not available for separate exposure.

9.2.3. Human health – effects assessment

There are no toxicological data available for the notified chemical. Information on hexafluorosilicic acid (isostructural analogue), HF and fluoride compounds, and titanium and titanium compounds were used as read across data for assessing the possible health effects of the notified chemical.

The major health effect of the notified chemical is likely to be its corrosive properties. By analogy, the notified chemical is very toxic by inhalation, ingestion or skin contact. There are no studies available to investigate sensitisation potential either in animals or in humans. The notified chemical is not expected to be genotoxic or carcinogenic.

The notified chemical is known as a source of aqueous HF and fluoride ions, and chronic exposure to the notified chemical by inhalation or oral routes may cause skeletal fluorosis. Reproductive studies conducted on fluoride gave inconsistent results.

There is no exposure standard set for the notified chemical. However, there is a NOHSC exposure standard of 2.5 mg/m^3 time-weighted-average (TWA) for fluorides (as F) and 3 ppm or 2.6 mg/m^3 (TWA) for HF (as F) (NOHSC, 1995).

On the basis of the data supplied, the notified chemical would be classified as hazardous substance in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2002). The notified chemical has a low pH and the fact that HF is present and active at a low pH indicates it would be appropriate to classify the notified chemical with the following risk phrases: R26/27/28 – Very toxic by inhalation, in contact with skin and if swallowed; and R35 – Causes severe burns.

9.2.4. Occupational health and safety – risk characterisation

The notified chemical will be introduced as an aqueous solution containing 50% hexafluorotitanic acid and will be reformulated into a product containing less than 10% hexafluorotitanic acid for use in metal treatment. The major OHS concern when handling the notified chemical is its corrosive properties and toxic effects by all routes of exposure. Based on the NICNAS PEC report, inhalation exposure to HF during metal treatment may be increased in wide dispersive use, which is similar to an open cleaning process with direct handling and dilution ventilation.

Exposure to the notified chemical and HF during reformulation and the preparation of acid baths may occur; however, the both processes will be mostly automated.

The notified chemical consists of titanium in oxidation state IV, which is the most stable and common oxidation state of this element. Hence during use, it is unlikely that that the chemical will form unstable titanium species. Also, hexafluorotitanic acid, although a source of HF, contains very little free or uncomplexed fluoride in solution due to the capacity of titanium (IV) to complex fluoride. However, in the case of chronic effects of fluoride intake, the risk from fluoride exposure is determined by the amount of total fluoride ingested. Overall, occupational exposure to fluorides when used as described in this notification is expected to be low.

The concentration of HF in the imported solution is expected to be <1%. The excess HF will be present in the reformulated corrosion inhibitor solution, would be expected to be <0.1%.

The concentration of the notified chemical and HF in the imported aqueous solution is sufficient to classify it as very toxic by inhalation, in contact with skin and if swallowed. However the control measures (use of PPE and engineering controls) employed during handling and reformulation will ensure adequate protection and low exposure. Hence the OHS risk posed to workers is low provided the controls are maintained.

Based on the low concentration of notified chemical and HF in the reformulated corrosion inhibitor solution, and the expected low exposures during use, the risk posed by the notified chemical to OHS is low. In addition, the control measures (use of PPE and engineering controls) during handling and use of the notified chemical will ensure sufficient protection against the notified chemical.

9.2.5. Public health – risk characterisation

Public contact to the notified chemical will only occur following accidental exposure from a spill and from touching treated metals. However, public exposure is assessed as negligible because the notified chemical will form part of the metal after metal treatment and in most cases will be coated with paint when the material reaches the public domain. In this form, the notified chemical is not expected to leach from the metal and be dermally absorbed. The potential for public exposure to the notified chemical during all phases of its life cycle is considered to be negligible.

Overall, the risk from public exposure to the notified chemical is considered to be negligible

10. CONCLUSIONS – ASSESSMENT LEVEL OF CONCERN FOR THE ENVIRONMENT AND HUMANS

10.1. Hazard classification

Based on the available data the notified chemical is classified as hazardous under the NOHSC *Approved Criteria for Classifying Hazardous Substances*. The classification and labelling details are:

R26/27/28 – Very toxic by inhalation, in contact with skin and if swallowed; and
R35 – Causes severe burns.

and

As a comparison only, the classification of notified chemical using the Globally Harmonised System for the Classification and Labelling of Chemicals (GHS) (United Nations, 2003) is presented below. This system is not mandated in Australia and carries no legal status but is presented for information purposes.

Acute Toxicity Category 1:
Symbol: Skull and crossbones
Signal Word: Danger
Hazard statement: Toxic if swallowed; Toxic in contact with skin; and Toxic if inhaled.

Skin corrosion/irritation Category 1:
Symbol: Corrosion
Signal Word: Danger

Hazard Statement: Causes severe skin burns and eye damage

10.2. Environmental risk assessment

The chemical is not considered to pose a risk to the environment based on its reported use pattern.

10.3. Human health risk assessment

10.3.1. Occupational health and safety

There is Low Concern to occupational health and safety under the conditions of the occupational settings described.

10.3.2. Public health

There is Negligible Concern to public health when used as described in the notification.

11. MATERIAL SAFETY DATA SHEET

11.1. Material Safety Data Sheet

The MSDS of the notified chemical provided by the notifier was in accordance with the NOHSC *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC 2003). It is published here as a matter of public record. The accuracy of the information on the MSDS remains the responsibility of the applicant.

11.2. Label

The label for the notified chemical provided by the notifier was in accordance with the NOHSC *National Code of Practice for the Labelling of Workplace Substances* (NOHSC 1994). The accuracy of the information on the label remains the responsibility of the applicant.

12. RECOMMENDATIONS

REGULATORY CONTROLS

Hazard Classification and Labelling

- The NOHSC Chemicals Standards Sub-committee should consider the following health hazard classification for the notified chemical:

  - R26/27/28 – Very toxic by inhalation, in contact with skin and if swallowed; and
  - R35 – Causes severe burns.

- Use the following risk phrases for products/mixtures containing the notified chemical:
  - ≥10%: R26/27/28 – Very toxic by inhalation, in contact with skin and if swallowed; R35 – Causes severe burns.
  - ≥7%conc<10%: R26/27/28 – Very toxic by inhalation, in contact with skin and if swallowed; R34 – Causes burns.
  - ≥5%conc<7%: R23/24/25 – Toxic by inhalation, in contact with skin and if swallowed; R34 – Causes burns.
  - ≥1%conc<5%: R23/24/25 – Toxic by inhalation, in contact with skin and if swallowed; R36/38 – Irritating eyes and skin.
  - 0.1%conc<1%: R20/21/22 – Harmful by inhalation, in contact with skin and if swallowed.

- The notified chemical should be classified as follows under the ADG Code:
  - Class 8 – Corrosive
  - Packaging Group II

- Suppliers should label the notified chemical as a Class 8 dangerous good with the signal word Corrosive and the risk and safety phrases listed above.

Exposure Standard

- The NOHSC exposure standards for hydrogen fluoride (as F) of 3 ppm or 2.6 mg/m^3 (TWA), and fluoride (as F) of 2.5 mg/m^3 should be observed during handling and use of the notified chemical.

CONTROL MEASURES
Occupational Health and Safety

- Employers should implement the following engineering controls to minimise occupational exposure to the notified chemical as introduced:
  - Exhaust ventilation when diluting the chemical prior to use and during transfer of diluted preparation into acid treatment baths.
  - Enclosed and automated metal treatment process

- Employers should implement the following safe work practices to minimise occupational exposure during handling of the notified chemical as introduced:
  - When diluting chemical solution and during transfer operations, avoid spills and splashing.

- Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified chemical as introduced:
  - Neoprene or PVC gloves;
  - Goggles or faceshield;
  - Acid resistant clothing which protects the body, arms and legs; and
  - Respiratory protection.

  Guidance in selection of personal protective equipment can be obtained from Australian, Australian/New Zealand or other approved standards.

- Atmospheric monitoring should be conducted to measure workplace concentrations during formulation and use of the notified chemical.

- A copy of the MSDS should be easily accessible to employees.

- If products and mixtures containing the notified chemical are classified as hazardous to health in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances*, workplace practices and control procedures consistent with provisions of State and Territory hazardous substances legislation must be in operation.

Environment

Disposal

- The notified chemical should be disposed of by landfill.

Emergency procedures

- Contain and collect spillage with absorbent materials (eg sand earth, vermiculite). Transfer to sealed containers suitable for storing spilled material. Clean and flush areas in contact with spilled material with adequate water to render the area safe for human contact.

12.1. Secondary notification

The Director of Chemicals Notification and Assessment must be notified in writing within 28 days by the notifier, other importer or manufacturer:

(1) Under Section 64(1) of the Act; if
    - information on toxicity and ecotoxicity studies conducted on the notified chemical becomes available

or

(2) Under Section 64(2) of the Act:
    - if any of the circumstances listed in the subsection arise.

The Director will then decide whether secondary notification is required.

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