File No: LTD/1313

March 2007

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME (NICNAS)

FULL PUBLIC REPORT

Hexafluorotitanic acid

This Assessment has been compiled in accordance with the provisions of the *Industrial Chemicals (Notification and Assessment) Act 1989* (Cwlth) (the Act) and Regulations. This legislation is an Act of the Commonwealth of Australia. The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) is administered by the Department of Health and Ageing, and conducts the risk assessment for public health and occupational health and safety. The assessment of environmental risk is conducted by the Department of the Environment and Water Resources.

For the purposes of subsection 78(1) of the Act, this Full Public Report may be inspected at:

Library
Australian Safety and Compensation Council
25 Constitution Avenue
CANBERRA ACT 2600
AUSTRALIA

To arrange an appointment contact the Librarian on TEL + 61 2 6279 1162 or email ascc.library@dewr.gov.au

This Full Public Report is available for viewing and downloading from the NICNAS website or available on request, free of charge, by contacting NICNAS. For requests and enquiries please contact the NICNAS Administration Coordinator at:

Street Address: 334 - 336 Illawarra Road MARRICKVILLE NSW 2204, AUSTRALIA.
Postal Address: GPO Box 58, SYDNEY NSW 2001, AUSTRALIA.
TEL: + 61 2 8577 8800
FAX + 61 2 8577 8888
Website: www.nicnas.gov.au

Director
NICNAS

TABLE OF CONTENTS

FULL PUBLIC REPORT

Hexafluorotitanic acid

1. APPLICANT AND NOTIFICATION DETAILS

APPLICANT(S)
Chemetall (Australasia) Pty Ltd (ABN 25 074 869 015) of 17 Turbo Drive, Bayswater North VIC 3153

NOTIFICATION CATEGORY
Limited-small volume: Chemical other than polymer (1 tonne or less per year).

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

> Spectral Data, Methods of Determination, Purity, Identity and Weight Percent of Toxic or Hazardous Impurities, Non-Hazardous Impurities, Details of Formulations, Estimated Manufacture and Import Volumes, and Customer Identity.

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

> Melting Point/Boiling Point, Specific Gravity/Density, Vapour Pressure, Water Solubility, Hydrolysis as a Function of pH, Partition Co-efficient, Absorption/Desorption, Dissociation Constant, Particle Size, Flash Point, Flammability Limits, Autoignition Temperature, Explosive Properties and Reactivity.

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT(S)
None

NOTIFICATION IN OTHER COUNTRIES
None

2. IDENTITY OF CHEMICAL

CHEMICAL NAME
Titanate(2-), hexafluoro-, dihydrogen, (*OC*-6-11)-

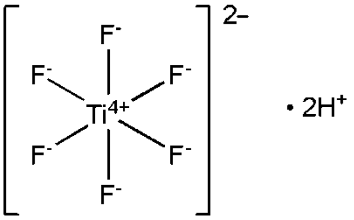
OTHER NAME(S)
Fluotitanic(IV) acid
Hydrogen hexafluorotitanate
Dihydrogen hexafluorotitanate
Fluorotitanic acid
Hexafluorotitanic acid
Hydrogen titanium fluoride
Hexafluorotitanium acid
Titanate(2-), hexafluoro-, dihydrogen

MARKETING NAME(S)
Hexafluorotitanic acid
Gardobond X4707 A
Gardobond X4747
Gardobond X4707
Gardobond X4747E
Oxsilan Additive 9925
Oxsilan AL0500B
Hexafluorotitanic acid 50% concentrate

CAS NUMBER
17439-11-1

MOLECULAR FORMULA
$F_6Ti.2H$

STRUCTURAL FORMULA



MOLECULAR WEIGHT
163.9 g.mol^{-1}

METHODS OF DETECTION AND DETERMINATION

METHOD	Infrared spectroscopy

3. COMPOSITION

DEGREE OF PURITY
>95%

HAZARDOUS IMPURITIES/RESIDUAL MONOMERS

Chemical Name	Hydrofluoric acid		
CAS No.	7664-39-3	*Weight %*	<1%
Hazardous Properties	At concentrations greater than or equal to 0.1% and less than 1% (HSIS, 2006): • Harmful (Xn): R20/21/22: Harmful by inhalation, in contact with skin and if swallowed. • R36: Irritating to eyes.		

NON HAZARDOUS IMPURITIES/RESIDUAL MONOMERS (> 1% by weight)
None

4. INTRODUCTION AND USE INFORMATION

MODE OF INTRODUCTION OF NOTIFIED CHEMICAL (100%) OVER NEXT 5 YEARS
The notified chemical will be imported as a <10% component of finished products in 25 kg poly drums. It will also be imported as a 50% concentrate in 250 kg poly drums.

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

Year	*1*	*2*	*3*	*4*	*5*
Volume	<200 kg	<300 kg	<500 kg	<700 kg	<1,000 kg

USE
The notified chemical will be used in metal coating formulations, which will be used by the metal manufacturing industry for preparation of metal surfaces prior to painting. The coating will serve to protect metal surfaces against corrosion.

5. PROCESS AND RELEASE INFORMATION

5.1. Distribution, transport and storage

PORT OF ENTRY
The notified chemical will be imported through Melbourne, by wharf.

IDENTITY OF MANUFACTURER/RECIPIENTS
Various companies in the automotive and automotive component industries, coil coating applications, as well as industrial paint and powder coat applicators.

TRANSPORTATION AND PACKAGING
The imported formulated coating products containing <10% notified chemical will be shipped and transported by road directly from dockside to the notifier's site for warehousing. The finished products will then be transported by truck or rail to end-users.

The imported 50% concentrate of the notified chemical will be shipped and transported by road directly from the dockside to the notifier's reformulation plant, where it will be used to formulate coating products. The formulated products will be filled into 25 L and 200 L poly drums, and these will be transported by truck or rail to end users.

5.2. Operation description

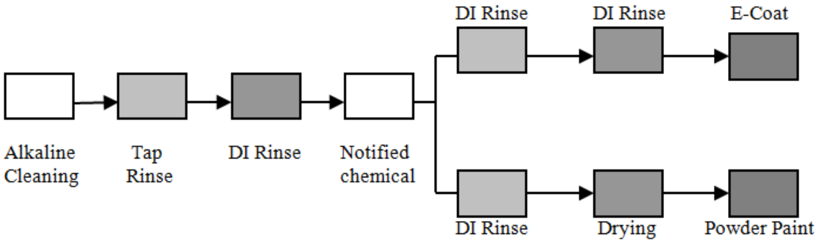
Reformulation of products in Australia
The notified chemical will also be imported as a 50% concentrated aqueous solution. At the notifier's reformulation plant, this acid concentrate will be blended with water and other ingredients to produce formulated coating products (containing <10% notified chemical), typically in batches of 200-8,000 L.

The blending and transfer of the reformulated product 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. Laboratory technicians will perform testing and adjustment to the formulation specifications where necessary. Packaging of the finished coating products into 25 L drums or 200 L poly drums will use automated filling lines.

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

Metal treatment
The imported formulated products, Oxsilan Additive 9925, Oxsilan AL0500B, Gardobond X4707A, Gardobond X4747A, Gardobond X4707E and Gardobond X4747E (containing <10% notified chemical) will be transported by road to the notifier's warehouse, where they may be repackaged and/or relabelled prior to delivery to customers. These products may also be produced by the reformulation process described above.

At customer sites, the solution product containing the notified chemical will be introduced into the enclosed bath or spray tank to <0.2%, using a metered pump system. There, it will be mixed with other additives and water. The metal substrates will be treated by a process resembling that shown in the following diagram:



These stages will be:

1. All substrate metal surfaces will be cleaned to remove grease, oil and other contaminants.
2. The metal substrate will be rinsed with tap water.

3. The metal substrate will be rinsed with deionised (DI) water.
4. The metal substrate will be treated with a solution of the notified chemical (<0.2%), along with other components including inorganic acids, silanes, zirconium, nickel and manganese salts and polyacrylic acid, depending on the metals being treated. These solutions will be applied either by spray or by immersion in tanks of 500-10,000 L capacity, in enclosed, conveyed processing lines. The metal is treated for a period of 0.5 to 5 minutes.
5. The metal substrate will be rinsed with deionised (DI) water.
6. The metal substrate will be dried in an oven, with drying temperatures in the range of 60-120ºC (optimally ~80ºC).
7. Finally, the metal substrate will be painted.

5.3. Occupational exposure

Number and Category of Workers

Category of Worker	*Number*	*Exposure Duration*	*Exposure Frequency*
Waterside and transport	3-6	2-3	20-30
Warehouse	2-3	2-3	20-30
Reformulation of products in Australia containing the notified chemical			
Make-up	2	2	10
Quality control testing	1	1.25	10
Filling	2	2	
Cleaning and maintenance	2	2	10
End-Use: Metal treatment for various industries			
Plant operators	<100	8	20-30

Exposure Details

Transport and Warehousing
The imported drums of the formulated notified chemical solutions will be transported from the dockside to the notifier's warehouse, where they 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. In this event, dermal and ocular exposure to the notified chemical in the finished product may occur, but this exposure would be limited to a <10% concentration.

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
At the notifier's site, 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 concentrated (50%) solution of the notified chemical could potentially occur from 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 an 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.

Reformulation: Quality control testing
Samples for QC testing are taken before filling. These samples will be collected using a sampling cup with an extension handle and then transferred to sealed plastic bottles. The samples will be 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 acid vapour respirator.

Reformulation: Filling
Once a batch is approved, the finished product containing <10% notified chemical will be filtered and filled into 25 L and 200 L poly 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.

Reformulation: Maintenance and Cleaning

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

End-Use: Metal cleaning and painting
The formulated product will be 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 0.2%. Dermal exposure through drips and spill may occur during the connection and disconnection of lines to the pump. Workers involved in the process will wear coveralls, long sleeve clothing, goggles, and impervious gloves. In case of spills, rubber shoes and aprons, and acid vapour respirators will be used.

Once the notified chemical has been added to the bath, exposure of workers should not occur, as it will be contained within an automated, enclosed system. The metal substrates for coating will be attached to a conveyor system and it will be cleaned and rinsed before and after being immersed in the bath containing the notified chemical. The applied coating is then dried in an oven before being painted.

No exposure of workers to the notified chemical should occur from finished metal substrates, as the notified chemical will react with the surface of the metal, and the excess will be removed. In addition, the metal objects are expected to be coated with paint, which forms a physical barrier on top of the treated metal surface.

Exposure of workers to HF during treatment is possible due to the low pH and fluoride content of the product containing the notified chemical. The area is fitted with a filtered exhaust system.

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 20 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 wastewater treatment facility.

Wastewater 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 wastewater is expected to be released in effluent approximating <10 kg per annum.

The imported drums will be disposed of to landfill.

RELEASE OF CHEMICAL FROM USE
In the systems using bath immersion and spray, losses will occur as the notified chemical is consumed. Sensors in the bath automatically monitor the active strength of the bath solution. The bath volume will be replenished with deionised water, and the addition of product will maintain the active strength of the bath. With time, contaminants are expected to a build up in the bath (oxides, dirt etc.) that will limit the life of the bath to approximately 6 months. The bath will be emptied and cleaned with deionised water. The bath waste and the deionised water used for cleaning will be sent to the on-site waste treatment plant, where they will be treated for disposal to sewer and solids to landfill.

5.5. Disposal

The empty containers from end-use products will be disposed of to landfill 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 industrial processes only, and will not be sold for use to the public. Public exposure to the notified chemical therefore will only occur in the event of a transport accident or spillage.

Members of the public will be exposed to metal objects that have been treated with solutions containing the notified chemical. However, after application of these solutions and drying on the surface of an object, it will form part of an inert matrix and will be unavailable to cause exposure.

6. PHYSICAL AND CHEMICAL PROPERTIES

The physicochemical properties of the notified chemical relate to its being a strong acid. The hexafluoroanions of Group 4 (IVB) are stable octahedral complexes in acidic media, but these rapidly hydrolyse at pH >4.

Several of the following physicochemical properties have been derived from the Honeywell MSDS for "hexafluorotitanium acid 50% concentrate".

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

Melting Point/Freezing Point <0°C

Remarks	Test report not available. Melting point estimated, based on the water content.

Boiling Point >100°C at 101.3 kPa

Remarks	Test report not available. Information cited in Honeywell MSDS for "hexafluorotitanium acid 50% concentrate".

Density 1,500 kg/m^3 at 20°C

Remarks	Test report not available. Information cited in Honeywell MSDS for "hexafluorotitanium acid 50% concentrate".

Vapour Pressure 1.01 kPa at 20°C

Remarks	Test report not available, but the value above may reflect water content of the material.

Water Solubility >500 g/L (expected)

Remarks	The notified chemical is soluble to 50% (w/v) in water, on the basis that the 50% solution is completely miscible. Information cited in Honeywell MSDS for "Hexafluorotitanium acid 50% concentrate". The notified chemical has a maximum concentration of 63% in the presence of excess (0.5%) HF (Meshri DT, 1994).

Hydrolysis as a Function of pH Not determined

Remarks	In dilute solution at neutral and basic pH, the notified chemical hydrolyses rapidly to TiO_2 and F^-. In acidic solution, the notified chemical forms a stable octahedral complex (Meshri DT, 1994).

Partition Coefficient (n-octanol/water) Not determined

Remarks	The notified chemical 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 $pKa_2 = 4.20$ (notified chemical)
$pKa_1 < 0.52$; $pKa_2 \sim 4.8$ (fluorophosphate)

Remarks The pKa_2 for the notified chemical has been determined to be 4.2, by conductometric and thermometric titration (Sengupta and Dasgupta, 1978). In this study, its pKa_1 could not be determined.

An analogous chemical, fluorophosphate, has a pKa_1 of 0.52 and pKa_2 of 4.8 (ACD/pKa DB). Another analogue, hexafluorosilicic acid, dissociates in water to protons and SiF_6-anions. In buffered systems the corresponding salt is formed. A 4% aqueous solution of hexafluorosilicic acid has a pH of ~ 2.

Particle Size Not determined

Remarks The notified chemical will be imported as a 50% concentrated aqueous solution and in liquid form in finished products.

Flash Point Not determined

Remarks The notified chemical will be imported as a 50% concentrated aqueous solution and in liquid form in finished products.

Flammability Limits Not determined

Remarks The notified chemical will be imported as a 50% concentrated aqueous solution and in liquid form in finished products.

Autoignition Temperature Not determined

Remarks The notified chemical will be imported as a 50% concentrated aqueous solution and in liquid form in finished products.

Explosive Properties

Remarks The notified chemical will be imported as a 50% concentrated aqueous solution and in liquid form in finished products. The notified chemical is not expected to have explosive properties based on its molecular structure.

Reactivity

Remarks Stable under normal condition of use.
Hazardous polymerisation will not occur. Avoid contact with strong alkalis and oxidising agents. The notified chemical emits acrid smoke and fumes when heated to decomposition.

7. TOXICOLOGICAL INVESTIGATIONS

No toxicity data were submitted.

8. ENVIRONMENT

8.1. Environmental fate

No environmental fate data were submitted.

8.2. Ecotoxicological investigations

No ecotoxicity data were submitted

9. RISK ASSESSMENT

9.1. Environment

9.1.1. Environment – exposure assessment

The notified chemical will be imported in finished products in 25 kg poly drums at a concentration ranging from <10%. The notified chemical will also be imported as a 50% concentrate in 250 kg poly drums.

Waste water discharge from the reformulation site from cleaning the manufacturing equipment, drum rinsing and cleaning up spills will be pre-treated in the waste water treatment plant prior to discharge. The life of the bath is expected to be approximately 6 months. The bath will be emptied and cleaned with deionised water. The bath waste and the deionised water used for cleaning will be sent to the on-site waste treatment plant and treated for disposal to sewer and solids to landfill. The complex will hydrolyse in the treatment plant and fluorides will be precipitated with calcium salts and filter pressed. Almost 99% of the notified chemical will be precipitated. 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 is expected to be released in the effluent. There is no release of the notified chemical into the aquatic environment during the metal treatment process.

It is expected that waste generated will ultimately be disposed of to landfill. In landfill, the notified chemical is likely to yield inert titanium dioxide from the sludge after onsite wastewater treatment. Thus, the titanium oxide is not expected to be mobile or leach from the soil into ground or surface water.

9.1.2. Environment – effects assessment

As no ecotoxicity data were submitted, no PNEC value could be calculated, and the potential effect of the notified chemical on the environment cannot be predicted.

However, due to the intended end use of the notified chemical and the fate of treated articles, it is unlikely that a significant amount will be released into the sewer. It is expected that the majority of the waste will be pre-treated in the waste water treatment plant prior to being disposed of in approved landfills as inert solid waste. In landfill, the solid wastes should be contained and should not escape into the environment to cause any effects.

9.1.3. Environment – risk characterisation

No aquatic exposure is anticipated during normal use of the notified chemical. During application of the anticorrosion coating, notified chemical wastes could be generated. It is expected that the majority of this waste will be will be pre-treated in the waste water treatment plant prior to disposal in approved landfills as inert solid waste. In landfill, the solid wastes should be contained and should not pose a significant risk to the environment.

The majority of the notified chemical will be incorporated into coatings that will be applied to surfaces and painted over. As such, it will share the fate of the surfaces to which it has been applied at the end of their useful life (5-20 years). Hence, it will either be disposed of to landfill or destroyed by during recycling of the metal surfaces to which it is applied.

9.2. Human health

9.2.1. Occupational health and safety – exposure assessment

Workers will be exposed to the notified chemical during metal treatment and during reformulation of the concentrated solution (50% notified chemical). Dermal, ocular and inhalation exposure are possible. During both metal treatment and reformulation, personal protective equipment will be used to prevent worker exposure to the notified chemical.

The preparatory process for the treatment of metal substrates may involve some manual operations, such the connection and disconnection of hoses and valves during the charging of the coating baths or spray tank. Therefore, exposure to significant levels of the notified chemical (at <10%) could occur during these processes. The actual treatment of metal substrates with the notified chemical is both an automated and enclosed process, and workers will not be exposed to the notified chemical during metal treatment under normal circumstances.

The potential sources of exposure during the reformulation process are likely to occur during the make up stage, QC testing and during the filling of drums. Exposure during this process would be to the concentrated solution of the notified chemical (50%).

The potential for waterside, warehouse and transport workers to be exposed to the notified chemical is low, as they will only handle sealed drums and containers. Exposure may occur in the event of a transport accident. As it is a dangerous good, the workers handling it should be trained in the appropriate procedures to minimise their exposure in such a circumstance.

Because of the excess HF content in the product, workers will not only be exposed to the notified chemical but also to HF during metal treatment. The common potential sources of exposure in metal processing activities include transfer from storage site to activity site, repackaging, dilution prior to use, transfer of solutions from original containers or diluted solutions into acid bath tanks, immersion of metals in a bath, and spraying metals with solutions containing the notified chemical. Dermal, ocular and inhalation exposure may occur during the above activities.

During use, personal protective equipment is mandatory to prevent exposure of workers to the notified chemical and to HF. Where possible, automation and enclosed processes are preferred when handling and using products containing the notified chemical. The controls implemented as described in the submission are adequate to mitigate occupational exposure to the notified chemical and to low levels of HF.

9.2.2. Public health – exposure assessment

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. Additionally, in most cases surfaces 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 surface of the metal to be absorbed by any route. The potential for public exposure to the notified chemical during all phases of its life cycle is considered negligible.

9.2.3. Human health – effects assessment

There are no toxicological data available for the notified chemical, so its possible health effects have been assessed from its known properties and the toxicity of analogous chemicals.

According to Meshri (1994), hexafluoroacids such as hexafluorotitanic acid, hexafluorozirconic acid and hexafluorohafnic acid exist only in aqueous media in the presence of excess hydrofluoric acid (HF). Therefore, the notified chemical could be regarded as being a source of HF. In this respect, the notified chemical, hexafluorosilicic acid (a structurally analogous hexafluoroacid), and aqueous HF are expected to have very similar toxicological properties. Other toxicological properties for the notified chemical may result from it being a strong acid. The possible chronic effects of titanium and its compounds have also been considered.

Hexafluorosilicic acid:
A toxicity profile for hexafluorosilicic acid (CAS 16961-83-4) was obtained from IUCLID, which is published by the European Chemicals Bureau (ECB, 2003):

Endpoint and Result		*Conclusion*
Rat, acute oral	LD_{50} 125 mg/kg bw (disodium salt)	toxic
Mouse, acute oral	LD_{50} 220 mg/kg bw (disodium salt)	harmful

Rabbit, acute oral	LD$_{50}$ 125 mg/kg bw (disodium salt)	toxic
Guinea pig, acute oral	LD$_{50}$ 500 mg/kg bw (dipotassium salt)	low toxicity
Rat, acute inhalation	LC$_{50}$ 1.11 mg/L/1 hour (hydrogen fluoride)	toxic
Rat, acute inhalation	LC$_{50}$ 3.3 mg/L/1 hour (silicon tetrafluoride)	harmful
Mouse, acute inhalation	LC$_{50}$ 0.436 mg/L/1 hour (hydrogen fluoride)	low toxicity
Monkey, acute inhalation	LC$_{50}$ 1.543 mg/L/1 hour (hydrogen fluoride)	low toxicity
Rabbit, skin irritation (fluorosilicates)		slightly irritating
Rabbit, eye irritation (fluorosilicates)		severely irritating
Genotoxicity – bacterial (*S. typhimurium*) reverse mutation		non-mutagenic
Genotoxicity – bacterial (*E. coli*) gene mutation		non-mutagenic

The toxic properties of various fluorinated compounds were found on the Hazardous Substance Data Bank (HSDB, 2003). Hexafluorosilicic acid corrodes glass and stoneware, like HF. It is toxic by inhalation, ingestion, or skin contact, and may cause severe injury or death. It is corrosive by skin contact and inhalation. Hexafluorosilicic acid, at concentrations not causing damage to intact skin, caused necrosis in injured skin that spread 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 of these workers had increased bone density, but displayed 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 include disablement and crippling in chronic poisoning (Goodman and Gilman, 1996, cited in HSDB, 2004).

HF and fluoride compounds

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 cross the placenta during pregnancy. About half of the absorbed fluoride is sequestered in bone and teeth (NICNAS, 2001). Fluoride exchanges with the 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, 1985).

The ACGIH (1992) states in their supporting documentation for setting exposure standard 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. 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 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 that is relevant to accidental exposure. Fatalities from accidental exposure to HF have occurred through inhalation and skin contact (Muriale *et al*, 1996; Tepperman, 1980, cited in NICNAS, 2001). Acute exposure results in burns, respiratory damage, and potentially fatal systemic effects. Systemic effects of HF include disturbance of calcium and other electrolyte homeostasis. 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 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, genotoxic or carcinogenic. Human data on reproductive toxicity of fluoride are inconclusive (NICNAS, 2001).

Symptoms following ingestion of soluble fluoride salts include: 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 characterized 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. Occasionally localised or generalised urticaria. The above symptoms are related to the 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 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, and 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 because 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 following oral exposure, whereas inhalation studies demonstrated that an excess of tumours is formed on rats exposed to a high dose. This observation is rat specific (not observed in mice) and it is believed to be associated with lung overload effects with insoluble, low toxicity dust (Egerton TA, 1997). This conclusion is 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).

Conclusions:

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

The major hazard of the notified chemical is its corrosive properties. By analogy with HF and silicon tetrafluoride, the notified chemical is very toxic by inhalation, ingestion or skin contact. There are no studies available to investigate sensitisation potential both in animals and 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 ion, 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; HSIS, 2006).

Based on these data, the notified chemical would be classified as a hazardous substance in accordance with the NOHSC Approved Criteria for Classifying Hazardous Substance (NOHSC, 2004), as:

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

9.2.4. Occupational health and safety – risk characterisation

The notified chemical will be introduced as a component of products for use in the treatment of metal substrates. The major OHS risks when handling the notified chemical are its corrosive properties and toxic effects by all routes of exposure. In addition, an OHS risk may also be posed from inhalation exposure to HF during metal treatment (NICNAS, 2001). Exposure to low concentrations of the notified chemical and HF during preparation of solutions for immersion or spraying may occur; however, the metal treatment itself will be mostly automated.

The notified chemical is comprised 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 the notified chemical will form unstable titanium species. In addition, hexafluorotitanic acid, although a source of low levels of HF, contains very little free fluoride in solution due to the capacity of titanium (IV) to complex fluoride. However, in the case of chronic effect of fluoride intake, the risk to fluoride exposure is determined by the amount of total fluoride ingested. Overall, the occupational exposure to fluorides when used as described in this notification is expected to be low.

The formulation of products from the concentrated form of the notified chemical (50% solution) will pose the greatest risk to workers. If the proposed PPE is used where exposure to the notified chemical is possible and that it is correctly cleaned and maintained and enclosed, automated engineering practices are used, the risk to workers is not expected to be significant. However, the consequences of dermal exposure to the (very toxic) notified chemical are serious and special care needs to be taken to avoid spillage. Likewise, the risk posed by the notified chemical in the formulated products is low, due to the lower concentrations of the notified chemical and HF, and the expected low exposures during use

9.2.5. Public health – risk characterisation

As the public will not be exposed to the notified chemical, the risk to public health posed by 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
R35	Causes severe burns.
S7/9	Keep container tightly closed and in a well-ventilated place.
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

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 notified 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

The notified chemical poses an acceptable risk to occupational health and safety under the conditions of the occupational settings described.

10.3.2. Public health

The notified chemical poses a negligible risk to public health when used as an ingredient of industrial metal coating formulations.

11. MATERIAL SAFETY DATA SHEET

11.1. Material Safety Data Sheet

The MSDS of the notified chemical and products containing the notified chemical provided by the notifier were in accordance with the NOHSC *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC 2003). They are 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 and products containing the notified chemical provided by the notifier were 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*
    - *R35* *Causes severe burns.*
    - *S7/9* *Keep container tightly closed and in a well-ventilated place.*
    - *S26* *In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.*
    - *S36/37/39* *Wear suitable protective clothing, gloves and eye/face protection.*
    - *S45* *In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).*

- 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 to 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 (Subsidiary: Class 6.1)
  - 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:
  - *Local and general exhaust ventilation should be applied wherever vapours of HF or the notified chemical may be expected to occur.*
  - *Wherever possible, direct handling of the notified chemical should be avoided; rather, some remote handling apparatus should be used.*

- Employers should implement the following safe work practices to minimise occupational exposure during handling of the notified chemical as introduced:
  - *Avoid contact with skin, eyes and clothing.*
  - *Avoid breathing vapours or mists.*
  - *A shower and eyewash station should be available.*
  - *Avoid spills and splashing during use.*
  - *After exposure, any contaminated PPE should be thoroughly cleaned before re-use.*

- Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified chemical as introduced:
  - *HF-resistant gloves*
  - *Face-shield*
  - *Acid resistant clothing which protects the body, arms, legs and feet*
  - *Respiratory protection suitable for inorganic acid vapours*
  - *Full-body encapsulation, including face and respiration, is recommended in areas where high-level exposure is probable.*

  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

- Do not allow material or contaminated containers to enter drains, sewers or watercourses.

Disposal

- The notified chemical in its oxide form should be disposed of to landfill.

Emergency procedures

- For small spillages, absorb or contain liquid with sand, earth or spill control material. Shovel up and place in a labelled, sealable container for subsequent disposal. Put leaking containers in a labelled drum or overdrum. Scrub contaminated surfaces with detergent solution. Retain washings as contaminated waste.

- For large spillages, transfer to a labelled, sealable container for product recovery or safe disposal.

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
  - the importation volume exceeds one tonne per annum notified chemical.

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.

13. BIBLIOGRAPHY

American Conference of Governmental Industrial Hygienists (ACGIH) (1992) Threshold limit values (TLVs) and biological exposure indices for Fluorides (various compounds). American Conference of Governmental Industrial Hygienists, Cincinnati, OH. pp 657-659.

Advanced Chemistry Development, Inc. (ACD/pKa DB 8.02) – Hydrogen Fluorophosphate.

ECB (2003) European Chemicals Bureau (ECB), International Uniform Chemical Information Database (IUCLID) Data Sheet. Hexafluorosilicic acid. In: International Uniform Chemical Information Database (IUCLID), Existing Chemicals, CD-ROM. Ispra, Italy, European Commission-JRC, Environment Institute.

Egerton TA (1997) Titanium and Titanium Alloys. In: Kroschwitz JI and Howe-Grant M ed. Kirk-Othmer Encyclopaedia of Chemical Technology, 4th Edition. New York, John Wiley & Sons, Inc, Vol 24.

Gosselin RE Smith RP and Hodge H (1984) Clinical Toxicology of Commercial Products. 5th Edition. Baltimore, Williams and Wilkins, pp111-190).

Goyer RA (1996) Toxic Effects of Metal. In: Klaassen CD ed. Casarett & Doull's Toxicology - The Basic Science of Poisons, 5th ed, New York, McGraw-Hill, p729.

HSDB: Hazardous Substance Data Bank (2003) Hexafluorosilicic acid. National Library of Medicine, Bethesda, Maryland, MICROMEDEX, Englewood, Colorado (Accessed July 2004). http://csi.micromedex.com/

HSIS: Hazardous Substances Information System (2006). Office of the Australian Safety and Compensation Council Australia, Commonwealth of Australia. http://www.nohsc.gov.au/applications/hsis/

Meshri DT (1994). Titanium. In: Kroschwitz JI & Howe-Grant M., Eds. Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed, New York, John Wiley & Sons, Inc., vol.11, pp 454-457.

NICNAS (2001) Hydrofluoric Acid (HF) – Priority Existing Chemical Assessment Report No.19. Commonwealth of Australia, Canberra, Australian Government Publishing Service.

NOHSC (1994) National Code of Practice for the Labelling of Workplace Substances [NOHSC:2012(1994)]. National Occupational Health and Safety Commission, Canberra, Australian Government Publishing Service.

NOHSC (1995) Exposure Standards for Atmospheric Contaminants in the Occupational Environment [NOHSC:3008(1995)]. National Occupational Health and Safety Commission, Canberra, AusInfo.

NOHSC (2004) Approved Criteria for Classifying Hazardous Substances [NOHSC:1008(2004)]. National Occupational Health and Safety Commission, Canberra, AusInfo.

NOHSC (2003) National Code of Practice for the Preparation of Material Safety Data Sheets, 2nd edn [NOHSC:2011(2003)]. National Occupational Health and Safety Commission, Canberra, Australian Government Publishing Service.

RTECS (2004) RTECS: Registry of Toxic Effects of Chemical Substances. National Institute of Occupational Safety and Health, Cincinnati, Ohio. (http://www.tomescps.com), MICROMEDEX, Englewood, Colorado.

Sengupta AK and Dasgupta HS (1978) Fluorotitanates & Fluorotitanic Acid. Indian Journal of Chemistry, 16(A):608-610.

United Nations (2003) Globally Harmonised System of Classification and Labelling of Chemicals (GHS). United Nations Economic Commission for Europe (UN/ECE), New York and Geneva.

US EPA (1985) Criteria Document: Fluoride (Draft). US EPA Office of Drinking Water, pp 11-19.