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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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# FULL PUBLIC REPORT

## Hexafluorotitanic acid

## 1. APPLICANT AND NOTIFICATION DETAILS

APPLICANT(S)
GE Betz Pty Ltd (ABN 84 001 221 941)
69-77 Williamson Road
Ingleburn NSW 2565

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

EXEMPT INFORMATION (SECTION 75 OF THE ACT)
No details are claimed exempt from publication.

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

- Physical and Chemical Data (use of analogue data);
- Toxicological Investigations (use of analogue data);
- Ecotoxicity Studies (use of analogue data); and
- Biodegradation.

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT(S)
None

NOTIFICATION IN OTHER COUNTRIES
None known

## 2. IDENTITY OF CHEMICAL

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

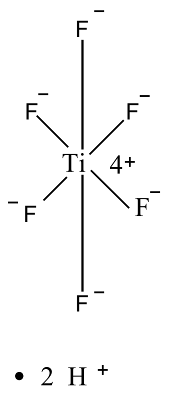
OTHER NAME(S)
Hexafluorotitanic acid
Fluorotitanic acid

MARKETING NAME(S)
Permatreat 1021B

CAS NUMBER
17439-11-1

MOLECULAR FORMULA
$H_2TiF_6$

### Structural Formula



### Molecular Weight

163.9

### Spectral Data

| | |
|---|---|
| Analytical Method | Infrared (IR) spectroscopy |
| Remarks | An infrared spectrum for an analogous compound, ammonium hexafluorotitanate, was provided with major absorbance peaks at approximately 3255, 3044, 2920, 2860, 2731, 1668, 1417, 1160, 1024 and 720 $cm^{-1}$. |

## 3. COMPOSITION

### Degree of Purity

60%

### Hazardous Impurities/Residual Monomers

| | | | |
|---|---|---|---|
| *Chemical Name* | Hydrofluoric acid | | |
| *CAS No.* | 7664-39-3 | *Weight %* | 0.5 |
| *Hazardous Properties* | Very toxic by inhalation, in contact with skin and if swallowed. Causes severe burns. | | |

### Non Hazardous Impurities/Residual Monomers (>1% by weight)

None

### Additives/Adjuvants

| | | | |
|---|---|---|---|
| *Chemical Name* | Water | | |
| *CAS No.* | 7732-18-5 | *Weight %* | 40 |

## 4. INTRODUCTION AND USE INFORMATION

### Mode of Introduction of Notified Chemical (100%) Over Next 5 Years

The notified chemical will not be manufactured in Australia. It will be imported either as a component of a product, Permatreat 1021B, containing <5% fluorotitanic acid in the form of a salt formed *in situ* or a component of a product, BetzDearborn DC20021, containing 10% hexafluorotitanic acid. The products may be used as supplied (<5% or 10% notified chemical). Alternatively, Permatreat 1021B may be diluted (<0.50% notified chemical) at the notifier's site prior to supply to customers.

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

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

USE
The notified chemical will be used as a replacement for chromic acid in the preparation of metal surfaces (metal treatment) prior to painting in the metal roofing, aluminium extrusion, aluminium can production and architectural and structural aluminium producers. The more concentrated form (10%) of the notified chemical will be used as an acid mist suppressant in copper refinery.

## 5. PROCESS AND RELEASE INFORMATION

### 5.1. Distribution, transport and storage

PORT OF ENTRY
Sydney, NSW

IDENTITY OF MANUFACTURER/RECIPIENTS
GE Betz Pty Ltd (ABN 84 001 221 941)
69-77 Williamson Road
Ingleburn NSW 2565

TRANSPORTATION AND PACKAGING
The products (Permatreat 1021B and BetzDearborn DC20021) containing the notified chemical will be imported in 200 L drums or 1500 L semi-bulk containers (SBCs). Both products will be transported by road to the notifier's warehouse where they may be repackaged into 15L pails, 200L drums, 1500L SBC and 1530L SBC.

### 5.2. Operation description

*Metal treatment*
The product, Permatreat 1021B, containing <5% notified chemical, will be transported by road to the notifier's warehouse where it may be repackaged and relabelled prior to delivery to customers. Alternatively, the product may be diluted (<0.5% notified chemical) at the notifier's site prior to supply to customers. At the notifier's site drums may be decanted to SBCs via metered pumps.

The product containing the notified chemical may be used as supplied or diluted. The dilution procedure involves a tank (200 L) mounted on a weigh cell connected to a deionised water source. A known weight of the product is either manually transferred or pumped from a base tank into the day tank and made up to 200 L with deionised water. In larger usage systems this process may be automated.

At customer sites, Permatreat 1021B is either sprayed onto the metal surface or the metal is dipped into a bath containing it along with other compounds. This anodising converts the metal surface to an oxide layer for corrosion resistance and paint adhesion. Some hydrofluoric acid (HF) may be formed during this process due to the fluorine content and low pH of the notified chemical.

For spraying, Permatreat 1021B is applied to metal through a chemcoater, which consists of a sprayer and two rollers to remove excess coating. The applied coating reacts at the surface and dries in seconds. The metal then passes through a drying oven and is immediately painted. After painting, the metal is moulded as required. The metal treatment and coating system is automated.

Alternatively, the metal to be coated is attached to a conveyer system, cleaned and rinsed in a confined chamber, and airblown dry. It is then immersed into a bath containing the notified chemical for a period of time. The size of the bath is from hundreds of litres to 10000 L depending on the size of the metal article. Several baths may occur in series. Once removed from the bath, the treated article is air dried with compressed air and proceeds to the painting process. Excess solution is returned to the bath and the coating system is both automated and enclosed.

Spraying produces less waste but the shape of the metal object may determine which application method is used.

*Acid mist suppressant*
The notified chemical will also be imported as a component of the product, BetzDearborn DC20021, at 10% concentration for use as an acid mist suppressant. Repackaging of the imported product is not expected and will be avoided. Copper is refined by dissolving ‘raw’ copper in acid and recovering the copper via an electrowinning process. When dissolving copper in acid, hydrogen is evolved and causes an acid mist or spray to form. The imported product containing the notified chemical will be added (approximately 100 ppm of BetzDearborn DC20021) to the acid circuit during copper refinery via an automatic dosing system to minimise the amount of mist formed. Some HF may be formed during this process due to the high fluorine content and low pH of the notified chemical. The acid used in the electro winning tank house will either be recycled back into other parts of the process, or sent to the tailings dam.

## 5.3. Occupational exposure

*Number and Category of Workers*

| *Category of Worker* | *Number* | *Exposure Duration* | *Exposure Frequency* |
|---|---|---|---|
| Waterside and transport | 3 - 6 | 2 – 3 hours/day | 20 – 30 days/year |
| Warehouse | 2 - 3 | 2 – 3 hours/day | 20 – 30 days/year |
| Plant Operators (relabelling, repackaging and dilution) | 6 - 10 | 8 hours/day | 20 – 30 days/year |
| Metal treatment and copper refinery workers | ~ 5000 | 8 hours/day | 20 – 30 days/year |

*Exposure Details*
*Metal treatment*
Dermal, and to a lesser extent ocular, exposure can occur when weighing and manually transferring the requisite amount of the product containing the notified chemical during repackaging or when diluting it prior to despatch to customers for use in metal treatment. Dermal, eye and inhalation exposure to the notified chemical is possible during metal treatment by spraying or dipping in a bath. Dermal exposure from spills, splashes and excess chemical during treatment can also occur. After treatment, the surface of the treated metal objects dry in seconds. Exposure to HF during metal treatment is possible due to the low pH and fluoride content in the product. It is recommended that similar safety procedures that apply to chromic acid treatment will be used for the notified chemical. Hence, workers are required to wear impervious gloves, coveralls and chemical splash proof goggles to prevent skin and eye exposure. Good local and general ventilation is used at all sites to capture fugitive emissions. Respirators will also be worn to minimise exposure to vapours.

*Acid mist suppressant in copper refinery*
Workers involved in the application of hexafluorotitanic acid as a mist suppressant will have higher exposure to HF than in metal treatment because of the lower pH and higher fluoride content in the product. However, the processes involved during refining of copper were described to be enclosed and automated. Dermal exposure to spills can occur when the dosing equipment malfunctions. Inhalation exposure to acid mist or spray can also occur during the refining process. Workers are required to wear chemical goggles, face shield, gauntlet type neoprene or PVC gloves, acid resistant jacket and pants and boots, and respirators when handling the notified chemical and during the refining process.

## 5.4. Release

RELEASE OF CHEMICAL AT SITE
The areas where the notified chemical will be handled, pumped and stored will be bunded. If there are any spillages, the contaminated area will be washed down with water, collected and disposed of to the Lidcombe Aqueous Waste Treatment Plant operated by WRAPS. During the dilution process, wastes may be generated when transferring the product from the import containers to the blending tanks, and from the blending tanks to the transport and storage tanks as a result of leaks or accidental spills. This is expected to account for 0.5% of the import volume (maximum 50 kg/year). Release may also result from residues in empty containers (100 kg/year in 200 L drums and 45 kg/year in 1500 L SBC). The notified chemical is not released to sewer at the formulation site. Any residual product or empty

containers will be returned to GE Betz for disposal.

RELEASE OF CHEMICAL FROM USE

At customer sites the product is either sprayed onto the metal surface or the metal is dipped into a bath containing the product along with other compounds. For spraying the product is applied to metal through a chemcoater, which consists of the sprayer and two rollers to remove excess. Any drip is collected in a drip pan and gravity fed back into the reservoir. There is minimal build up of contaminants and hence minimal cleaning of the chemcoater apparatus. The spent solution and the water used for cleaning of the system are sent to the on-site waste treatment plant. The same level of treatment is applied to the fluorotitanic acid containing waste as for chromic acid contaminated waste.

Alternatively, the metal to be coated is immersed into a bath containing the product for a period of time. Excess solution is returned to the bath and the system is both automated and enclosed. In bath immersion, losses occur as the product is consumed. With time there is a build up of contaminants in the bath – oxides, dirt etc. The bath life is approximately 6 months. The bath is emptied and cleaned with deionised water. The bath waste and the deionised water used for cleaning is sent to the on-site waste treatment plant and treated to the same standards as chromic acid contaminated solutions.

The notifier indicates that the waste treatment plant is designed to remove chromium from the waste stream and will also be effective at removing the notified chemical. Typically this involves the formation of hydroxides of the metals at pH 8.5-9.5 which precipitate from solution and are removed in the sludge. Under these conditions the notified chemical is also expected to end up in the sludge. The ultimate fate of the sludge is likely by immobilisation and disposal to secure landfill.

The application of hexafluorotitanic acid as a mist suppressant will result in higher conversion to hydrofluoric acid than in metal treatment because of the lower pH and higher fluoride content in the product. However, the processes involved during refining of copper were described to be enclosed and automated. At the warehouse and at the end use site, the chemical will be stored in a way that prevents discharge to the environment. At the end use site, sulphuric acid discharged to the tailings dam will have a fluoride concentration of 7 ppm or less. Any release of fluoride to the environment from the tailings dam is expected to be at a very low concentration.

### 5.5. Disposal

Washings from the empty containers, any residual product or discharge water at the notifier’s site will be disposed of to the Lidcombe Aqueous Waste Treatment Plant and ultimately be disposed to landfill.

### 5.6. Public exposure

The products containing the notified chemical will be sold for use in industrial applications only. Public exposure is not expected except in the event of transport accident. Exposure, if it occurs, will be dermal contact with treated metals. However, at this stage, there is no notified chemical in free form remaining on the metal. Dermal contact and inhalation exposure to spilled product containing the notified chemical by the public is considered to be a remote likelihood.

## 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%.

Conductometric and thermometric titrations of $H_2TiF_6$ against KOH show two peaks at $H_2TiF_6$: KOH = 1:1 and 1:2 corresponding to the first and second neutralisation points of the acid. Only the $pK_2$ value of the acid could be obtained and was calculated as 4.2 (Sengupta and Dasgupta, 1978).

There is no information on the thermal properties of the notified chemical except that thermal decomposition is likely to release HF.

The physico-chemical properties for an isostructural analogue chemical, hexafluorosilicic acid, was provided as read across data for the notified chemical. The most common oxidation state of both silicon and titanium is IV. Both silicon and titanium form stable and non-toxic dioxides, which occur naturally in the earths's crust. These dioxides react with aqueous HF to give the corresponding hexafluoroacids in solution (Besida, 2004).

Unless otherwise stated, the following physico-chemical properties have been cited in the International Uniform Chemical Information Database (IUCLID) and are for 35% aqueous solution of hexaflurosilicic acid.

| | |
|---|---|
| **Appearance at 20°C and 101.3 kPa** | Colourless fuming liquid with pungent odour |
| **Melting Point** | <-30°C |
| Remarks | Test report not provided. |
| **Boiling Point** | 110°C at 101.3 hPa |
| Remarks | The test material decomposes at boiling temperature. Test report not provided. |
| **Density** | 1380 kg/m$^3$ at 25°C |
| Remarks | Test report not provided. |
| **Vapour Pressure** | 3 kPa at 20°C |
| Remarks | Test report not provided. The result reflects the water content of the material. |
| **Water Solubility** | Not determined |
| Remarks | Hexafluorotitanic acid is soluble to 63% (w/v) in water. |
| **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 |
| **Dissociation Constant** | $pK_1$, <0; $pK_2$, approximately 4.2 (hexafluorotitanic acid) |
| Remarks | Hexafluorosilicic acid dissociates in water to protons and $SiF_6$-anions. In buffered systems the corresponding salt is formed. |
| **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 the structure..

**Reactivity**

Remarks In 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. An expert opinion outlining the suitability of hexafluorosilicic acid as an analogue has been provided. According to the expert statement, 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 (Besida, 2004).

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 strong acid. In order to determine the possible chronic effects of hexaflluorotitanic 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 (ECB, 2003). The report contained toxicity information on hexafluorosilicic 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 increase 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 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$^3$. 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 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 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 calcium 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/m3) caused upper airway and eye/skin irritation in volunteers. The no observed effect level (NOAEL) in animals is 0.72 mg/m3 (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 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 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 localized or generalized urticaria. 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 oral route whereas inhalation studies demonstrated that an excess of tumours is formed on 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 it will not undergo microbial degradation, though it is unstable under neutral to alkaline conditions, in dilute solutions, and the end products are expected to be fluoride ions and titanium dioxide.

### 8.2. Ecotoxicological investigations

No ecotoxicity data for the notified chemical were submitted.

Considering the insolubility of the notified chemical under neutral to alkaline conditions, it is unclear what would be the relevant species for testing of the aquatic toxicity.

Besida (2004) indicates that the most common oxidation state of both silicon and titanium is IV. Both compounds form stable and non-toxic dioxides, which occur naturally in the earth's crust. Both of these dioxides react with aqueous HF to give the corresponding hexafluoroacids in solution. Hexafluoroacids in general can be regarded as being sources of HF and in this respect, hexafluorosilicic and hexafluorotitanic acids would be expected to have similar toxicological properties which are also similar 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. As such the spent coating bath 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:

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

However, the notifier indicates that ecotoxicity of the spent solution is expected to be driven by the fluoride ion concentration despite the amount of free fluoride being small. Given a large excess of water, however, as would be expected in an effluent treatment facility, the equilibrium is driven to the right and some titanium would be precipitated as the hydrate leaving free fluoride in solution. The release of any pH neutral effluent is expected to contain stable forms of titanium oxides or hydroxide species and low concentration of free fluoride.

The European Chemicals Bureau has published a IUCLID data set for the analogue hexafluorosilicic acid (ECB, 2003) from which relevant data are summarised below.

*Table 1: Ecotoxicity data for the analogue hexafluorosilicic acid in the ammonium and sodium salts, and in 30% aqueous solution*

| **Species** | **Test substance** | **24 h $EC_0$ (mg/L)** | **96 h $LC_0$ (mg/L)** | **96 h $LC_{50}$ (mg/L)** | **96 h $LC_{100}$ (mg/L)** |
|---|---|---|---|---|---|
| Zebra fish (*Brachydanio rerio*) | 30 % aqueous hexafluorosilicic acid | | 10 | | 50 |
| Bluegill sunfish (*Lepomis macrochirus*) | $Na_2SiF_6$ | | | 65 | |
| Fresh water fish - ide (*Leuciscus idus*) | $Na_2SiF_6$ | | | 190 | |
| Marine fish (*Menidia beryline*) | $Na_2SiF_6$ | | | 160 | |
| Fathead minnow (*Pimephales promelas*) | $(NH_4)_2SiF_6$ | | | 28.7 | |
| Algae (*Scenedesmus quadricauda*) | Not specified | | 10 | | |
| Bacteria (*Escherichia coli*) | Not specified | 100 | | | |
| Bacteria (*Pseudomonas fluorescens*) | Not specified | 100 | | | |

Source: Bayer AG Leverkusen

The following results are based on a literature report (http://www.scientificjournals.com/sj/espr_special/Pdf/aId/3643) on the toxicity of “titanium fluoride” (related to use of titanium containing passivation baths) to fresh water fish, the guppy (*Poecilia reticulata*), *Daphnia magna* and algae (*Chlorella vulgaris*). Conventional acute bioassay 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* |
| Remarks – Method | The *in vitro* toxicity tests are based on the activity of the enzymes LDH and AchE. Only a brief summary was available. |
| 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 Similar to the OECD acute immobilisation bioassay
Species *Daphnia magna*
Remarks - Method The test was based on the OECD acute immobilisation bioassay. Only a brief summary was available.

RESULTS

Remarks - Results Mortality of *Daphnia magna* was observed at concentration equal 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 Similar to the OECD growth inhibition tests.
Species *Chlorella vulgaris*
Remarks - Method This is based on the OECD growth inhibition tests. Only a brief summary was available.

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, which are presently being used in the metal finishing industry.

## 9. RISK ASSESSMENT

### 9.1. Environment

### 9.1.1. Environment – exposure assessment

The notified chemical is not released to sewer at the formulation site. Any residual product or empty containers will be returned to GE Betz for disposal. At customer sites, the spent solution and the water used for cleaning of the chemcoater system and baths are sent to the on-site waste treatment plant. Fluorotitanic acid containing waste will undergo similar treatment as for chromic acid contaminated waste. Under these conditions the notified chemical is expected to end up in the sludge. The ultimate fate of the sludge is expected to be disposal to landfill.

The notified chemical contains very little free, or uncomplexed fluoride in solution due to the capacity of titanium (IV) to complex fluoride. As such the spent coating bath will contain various fluoro or oxofluoro species of titanium (IV), having a fluoride to titanium ratio of less than six. As the solutions having pH > 4 tend to hydrolyse forming the metal dioxides, it is expected that the release of any pH neutral effluent will contain stable forms of titanium oxides or hydroxide species and low concentration of free fluoride.

A calculated worst-case scenario daily PEC in the sewer effluent is 10,000 kg/365 × 200L × 5 × $10^6$ = 28 μg/L based on the usage volume of 10 tonnes maximum. In calculating the PEC, the following were assumed: (1) usage of the maximum import volume is evenly distributed over a 365 day period; (2) usage is limited to Sydney, with a population of 5 million contributing 200 L of water per person per day to the sewer, (3) there is no adsorption or degradation in the sewer prior to release (4) the wastes from the spent solution and cleaning of equipments have not undergone an on-site waste water treatment.

Based on the respective dilution factors of 1 and 10 for rural areas and coastal discharges of effluents, the PECs of the notified chemical in rural areas and coastal water may approximate 28 and 2.8 μg/L, respectively.

For application of the notified chemical as mist suppressant, the processes involved during refining of copper were described to be enclosed and automated. Sulphuric acid discharged to the tailings dam will have a fluoride concentration of 7 ppm or less. Tailings dams are enclosed systems and any release of fluoride to the environment is expected to be at a very low concentration, taking dilution also into account.

### 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. This is comparable to the lowest 96 h LC50 of 28.7 mg/L for the analogue hexafluorosilicic acid on fish. Therefore, the Predicted No Effect Concentration (PNEC) is 28.7 μg/L, using a safety factor of 1000 (because of the lack of test details).

### 9.1.3. Environment – risk characterisation

The worst-case PECs and Risk Quotients (PEC/PNEC) for the aquatic environment are summarised below:

| | PEC | Q |
|---|---|---|
| Sewage effluent/coastal city: | 2.8 μg/L | 0.098 |
| Sewage effluent/rural areas: | 28 μg/L | 0.98 |

The risk quotients indicate an acceptable hazard (Q<1) for marine and fresh water organisms. While the Q for rural areas is close to 1, an on-site treatment will greatly reduce concentration remaining in the aqueous phase.

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 preparatory process for metal treatment may involve manual operations; however, the actual metal treatment process is described as automated and enclosed processes. 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.

Higher exposure to HF is expected when the notified chemical is used as an acid suppressant in copper refinery due to the lower pH and higher fluoride content in the product containing it. However, the fully enclosed and automated processes during copper refinery should prevent direct exposure to HF and acid mists.

Chronic exposure through dermal and inhalation routes is likely to occur from exposure to low concentrations of HF during metal treatment and copper refining. 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 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 metal treatment and copper refinery, the use of personal protective equipment is mandatory to prevent exposure to the notified chemical and 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 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 hexaflurosilicic 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 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 both in animals and in humans The notified chemical is not expected to be genotoxic and 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 standards 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 data supplied, the notified chemical would be classified as hazardous substance in accordance with the NOHSC Approved Criteria for Classifying Hazardous Substance (NOHSC, 2002). The notified chemical has a low pH and the fact that HF is present and active at a low pH, 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 a component of products for use in metal treatment or as acid mist suppressant in copper refinery. 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 low concentrations of the notified chemical and HF during preparation of acid baths may occur; however, the metal treatment itself will be mostly automated. Fully automated processes are also involved when used as acid mist suppressant in copper refinery.

The notified chemical consists of titanium in oxidation 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 effect of fluoride intake, the risk to 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.

At a maximum concentration of 63% notified chemical, 0.5% excess HF is expected to be present. The notified chemical will be imported at a maximum concentration of 10%; therefore excess HF will be present at a much lower concentration (<0.1%HF).

Based on the low concentration of notified chemical and HF in the product, 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 polymer 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 hence not expected to 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 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 is 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

On the basis of the PEC/PNEC ratio:

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 in metal treatment and as an acid mist suppressant in copper refinery.

## 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; 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 III

- 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 and when used as an acid mist suppressant in copper refinery.

- 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

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

Disposal

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

Emergency procedures

- For small spillage, 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 spillage, 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
  - 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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