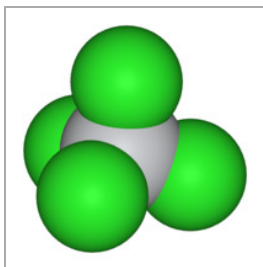


Introduction

Titanium tetrachloride (TiCl₄) contains four chlorine atoms which are bonded evenly around one titanium atom in the shape of a tetrahedron. It is a colourless to light yellow liquid, with irritating acidic vapours, which fume in air to give off a dense white smoke.



It is often loosely called 'tickle.'

It is formed, as part of the process, to purify titanium dioxide, which has been extracted from mineral sands. So what is so important about titanium dioxide, that requires the manufacture of tickle?

Titanium dioxide

Titanium dioxide is an extremely stable, unreactive powder, that interacts with light in a way that makes it one of the 'whitest' white materials available. It is ideal to use as a white pigment in both oil and water-based paints, as well as in paper, plastics, inks, and cosmetics. It is even allowed to be used this way in food and medicine. It is also used as a UV blocker in sunscreens, and in a range of high tech applications.

Titanium dioxide has replaced the white pigments based on lead carbonate, that were once widely used.

Properties of titanium dioxide

Chemical name	Titanium dioxide
Formula	TiO ₂
CAS	13463-67-7
Form	White powder
Specific gravity	4.23
Melting point	1870 deg C
Solubility	Insoluble

Mineral sands

Titanium dioxide as it is found in mineral sands, is anything but white. These sands are widespread throughout Western Australia,¹ and they contain a range of minerals which are of value. They are:²

Rutile (TiO₂) Impure titanium dioxide as brown red crystals. Specific gravity 4.3.

Ilmenite (FeTiO₃) Iron titanium oxide as black/grey crystals. Slightly magnetic with a specific gravity 4.5 to 5.0.

Zircon (ZrSiO₄) Zirconium silicate, usually off-white to cream in colour. Specific gravity 4.6 to 4.7.

Monazite [(Ce,La,Nd,Th)PO₄] Rare earth minerals and thorium as a phosphate, as brownish red crystals. Mildly radioactive due to thorium content (30%), and specific gravity of 4.6 to 5.4.

The mineral content of these sands make them relatively heavy, and this enables these minerals to be separated from the lighter quartz fraction of sand, by a series of centrifuges and the use of magnets.

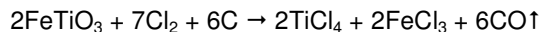
Zircon and monazite are exported overseas for processing, while the rutile and ilmenite are processed to form ultra pure titanium dioxide.

Manufacture of titanium tetrachloride

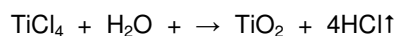
To prepare titanium tetrachloride, rutile or ilmenite are heated with carbon, under a flowing stream of chlorine, that is heated to 900 deg C.



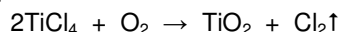
or



Titanium dioxide is formed again, either by reaction with water, or with pure oxygen.



or



The second option is preferred, since it allows chlorine to be regenerated and this reduces costs.

This process is also used worldwide to produce not only titanium dioxide, but also titanium metal and titanium sponge.

Dangerous Goods

Titanium tetrachloride is classified for the purposes of transport as Dangerous Goods:

UN 1838

Class 8 Corrosive

Packing Group II

Hazchem Code 4WE



Titanium tetrachloride however, is not transported in Western Australia, rather it is manufactured and consumed on-site in Kwinana, and in the Kemerton Industrial Park near Bunbury.

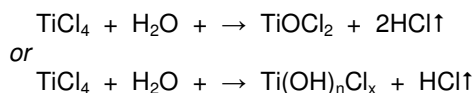
Properties

Chemical name:	Titanium tetrachloride
Formula	TiCl ₄
Molecular weight	189.7
CAS number	7550-45-0
Solubility	Reacts (extremely exothermic)
Melting Point	-24 deg C
Boiling Point	136.4 deg C
Specific gravity	1.73 (water = 1.00)
Vapour pressure	1.3 kPa (21.3 deg C)
Vapour density	6.5 (air = 1.00)
Flammability	Does not burn
Conversion	1 mg/m ³ = 7.76 ppm 1 ppm = 0.129 mg/m ³

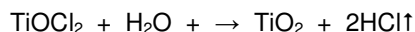
Effect of spillages

Whenever there is a spillage of titanium tetrachloride, the single most outstanding feature, is the production of dense, thick white clouds. Titanium tetrachloride vapour immediately reacts with moisture in the air, and once again it is the 'whiteness' of the titanium dioxide that gives it this appearance.

In reacting with moisture in air, it goes through a two stage process. First, it forms a range of compounds known as the titanium oxychlorides and hydrogen chloride.³ It can be described as follows:



These oxychlorides are also particles, and they will continue to react with water to form hydrogen chloride.



Exposure hazards - inhalation

The hazards of inhalation of titanium tetrachloride and its reaction products, is related to the formation of hydrogen chloride. However it has been found on experimental animals, that the toxic effect is much greater than for an equivalent amount of hydrogen chloride.⁴

Hydrogen chloride is extremely soluble in water, and if inhaled at concentrations within the capability of the body's defence system, it will be captured by the moisture in the upper respiratory tract and penetration into the lungs will be minimised.

Hydrogen chloride resulting from the titanium tetrachloride reaction however, can be transported deep into the lungs. It can do this by being absorbed on titanium dioxide particles, or as semi-reacted titanium oxychlorides, or even as titanium tetrachloride vapour. And then once deep in the lungs, it is in a position to do far greater damage.

There has been at least one recorded fatality from the effects of inhalation, after titanium tetrachloride splashed onto the face of a worker.⁵

Exposure hazards – skin contact

In another accident, three workers were splashed with titanium tetrachloride. However the situation was made worse when they were washed down with water. Titanium tetrachloride reacts so vigorously with water and in this case sufficient heat was generated to cause thermal burns. This enabled the corrosive effects of hydrochloric acid to penetrate more deeply, particularly in the areas covered by belts and boots. The consequences of both an acid and thermal burn, were far worse than if it had only been one or the other.

Any approach to titanium tetrachloride vapours, that may require entry into white clouds requires breathing protection. And if for any reason, contact with the liquid occurs, it must first be wiped off, and then washed down under a decontamination shower.

Incident in Guangzhou

On 17 Aug 2006, a leak of titanium tetrachloride occurred in a factory in Guangzhou in China as workers were dismantling a container of tickle.⁶ Look up the web-site while it is available for some interesting pictures.

¹ Fact Sheet 10, http://www.dmp.wa.gov.au/documents/G_SWA_MineralSandsPamphlet.pdf (15th April 2009)

² http://www.australianminesatlas.gov.au/education/down_under/minerals_sands/Australia.html (15th April 2009)

³ Hydrogen chloride once it is dissolved in water becomes hydrochloric acid. This will be its form once in the atmosphere, however for consistency, the term hydrogen chloride will continue to be used..

⁴ Toxicological Profile for Titanium Tetrachloride, US Department of Health and Human Services, Sept 1997, <http://www.atsdr.cdc.gov/toxprofiles/tp101.pdf> (15th April 2009)

⁵ Ibid

⁶

http://www.lifeofguangzhou.com/node_10/node_37/node_85/2006/08/18/11558733167091.shtml (10th May 2009)

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