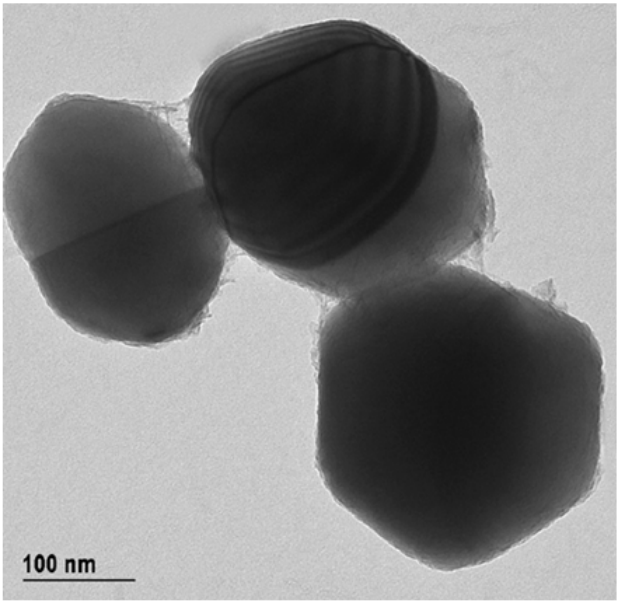
Ultrafine TiO_2 Handling Guide

Powders: Titanium dioxide (TiO_2) is a white inorganic substance that is thermally stable, non-flammable, and insoluble. In its Ultrafine (UF) or Nanoparticulate (NP) form, primary particles of UF TiO_2 typically range in size from 10 to 60 nm meeting most definitions of a nanomaterial. It typically develops a high surface area in the range from 20m^2/g to 300 m^2/g. It should be stressed that "nanomaterial" is a categorization based on the size of its constituent parts. It neither implies a specific risk nor does it necessarily mean that this material actually has new hazard properties compared to its constituent parts. UF TiO_2 does not exist as discreet primary particles but as aggregates or agglomerates, with secondary particle sizes typically >100 nm. These aggregates and agglomerates do not readily break down into the individual nanoparticulate primary particles - either during processing, industrial use or in biological systems. Consequently, the generation of isolated airborne primary particles during the handling of the material would be possible but very limited.

Aqueous dispersions: UF TiO_2 can also be found as an aqueous dispersion, also called TiO_2 hydrosol. In this form and by the aid of dispersants and/or wet milling, the aggregates and agglomerates may be separated into primary particles in the dispersion media and would remain within it. Additionally, the risk of release of isolated airborne primary particle is eliminated as the latter would readily re-aggregate/re-agglomerate during the elimination of the dispersion media. This form provides a convenient way to process UF TiO_2 and avoids the occupational hygiene constraints of handling powdery materials.

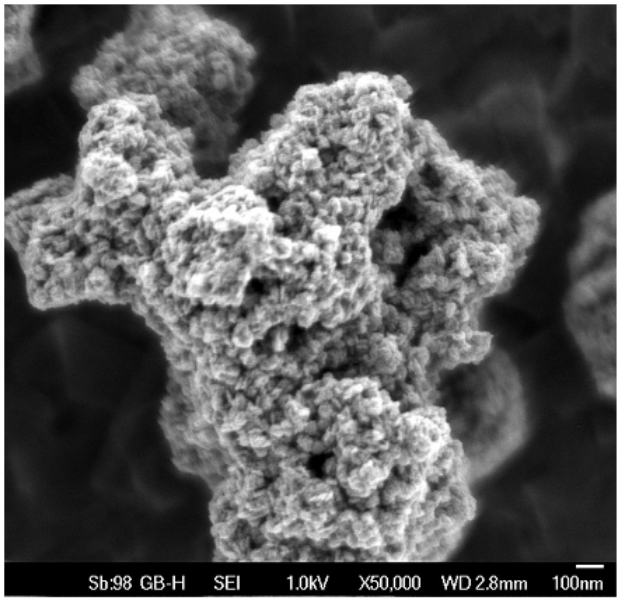
The following pictures exemplify the aggregated and agglomerated nature of UF TiO_2 in comparison to pigmentary TiO_2.

Pigmentary TiO_2



Single dense particles
150~300 nm range

Ultrafine TiO_2



Aggregate/Agglomerate
~1 μm range

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Human health and environmental impact considerations

Human Health

TiO_2 can be present in the workplace as a dust or poorly soluble particle. However, since its introduction in 1923, there have been no significant health concerns associated with TiO_2 exposures [1], [2].
Ultrafine forms of TiO2 are not classified in the European Union as dangerous under the Dangerous Substances Directive (EU Directive 67/548/EEC) or in the joint submission REACH registration dossier. TiO_2 has not been classified as hazardous according to Classification, Labelling and Packaging (CLP) Regulation (Regulation (EC) 1272/2008) or the UN Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Environmental Impact

Available information for UF TiO_2 indicates a low concern for environmental effects. Well-conducted studies following recognized international protocols indicate a low level of acute aquatic toxicity for UF TiO_2.

Exposure to particles during powder handling and preventive measures to be taken

The Titanium Dioxide Manufacturers Association (TDMA) has sponsored an occupational exposure assessment for the production of UF TiO_2 as a contribution to the EU technical guidance for how the REACH regulation (Regulation (EC) No. 1907/2006) should be implemented for nanomaterials. The conclusion was that any significant exposure to UF TiO_2 would only be possible in situations in which a closed system is breached or/and in which ventilation measures are inadequate.

In January 2011, the National Institute for Occupational Safety and Health (NIOSH) published Current Intelligence Bulletin 63, "Occupational Exposure to Titanium Dioxide". In this Bulletin an exposure limit (REL) of 2.4 mg/m^3 for pigmentary TiO2 and 0.3 mg/m^3 for UF TiO_2 was recommended. NIOSH also concluded that UF TiO_2 is a potential occupational carcinogen based on a single inhalation study at a single concentration in rats (a uniquely sensitive species to lung overload effects).

It is worth noting that nanoparticles are present in even our most clean atmospheric environments with concentrations ranging from 20,000 to 100,000 nanoparticles/cm^3. Comparatively, a REL of 0.3 mg/m^3 would represent concentrations ranging from 150,000 to 1,000,000 nanoparticles/cm^3 (respectively for 100 and 50nm TiO_2 particles). The aggregated and agglomerated nature of UF TiO_2 brings real life presence of TiO_2 nanoparticles well below amounts found in the cleanest environments.

As a matter of fact, multiple real-world epidemiological studies in the highest-exposed workers have found no association between TiO_2 exposures and lung cancer or non-cancer related lung effects in humans [2].

[1] In 2006, the International Agency for Research on Cancer (IARC) reviewed the carcinogenic risk of TiO_2 concluding that it is "possibly carcinogenic to humans" (Group 2B). The classification results from the fact that there is sufficient evidence in experimental animals for the carcinogenicity of TiO_2 but **inadequate evidence for the carcinogenicity in humans**.
[2] Besides, the results from four large human epidemiology studies involving more than 20,000 workers in the titanium dioxide industry at manufacturing locations in North America and Europe **indicate neither association with an increased risk of lung cancer nor with any other adverse lung effects**.

Therefore, TDMA and the Titanium Dioxide Stewardship Council's (TDSC) position on this issue were that:

- NIOSH RELs relied upon selective interpretation of experimental animal data and were inconsistent with the more relevant human results.
- TiO_2 is safe for the people who manufacture it.
- TiO_2 is safe for the people who work with it in its intended uses.
- TiO_2 is safe for the people who use finished products containing it.
- There is no human evidence to suggest that TiO_2, in any form, is an occupational carcinogen.

The overall conclusion is that evidence available at this time supports the safe manufacture and use of UF TiO_2. UF TiO_2 manufactured by Cristal and sold into Cristal approved current end uses is safe providing the following guidelines are followed.

Guidelines when handling UF TiO_2

As with all industrial particulate materials good handling and housekeeping practices are advisable.

For information,

- table 1 provides country specific occupational exposure limits for TiO_2, and,
- references [3], [4], [5], [6], [7], [8] provide a selection of publications reporting exposure assessment methodologies and/or good handling practices.

STORAGE

- Store UF TiO_2 powders in usual commercial packaging as bags or FIBCs to prevent accidental dust generation and to prevent possible contamination.
- Protect storage containers containing UF TiO_2 powders from physical damage as discussed in the appropriate bulk container storage and handling guide.
- Keep in a dry place.
- Store aqueous dispersions of UF TiO_2 in appropriate drums or bulk containers.
- Protect storage containers containing aqueous dispersions from physical damage as discussed in the appropriate bulk container storage and handling guide.

HOUSEKEEPING

- Continuous housekeeping and cleaning must be maintained to minimize accumulation of the powder on surfaces such as floors.
- Equipment must be maintained to minimize the escape of dust.

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[3] Approaches to Safe Nanotechnology, Managing the Health and Safety Concerns Associated with Engineered Nanomaterials, NIOSH, March 2009
[4] Current Intelligence Bulletin 63, Occupational Exposure to Titanium Dioxide, NIOSH, April 2011
[5] EU-OSHA, Workplace exposure to nanoparticles, European Risk Observatory, Report 2, 2009. http://osha.europa.eu/en/publications/literature_reviews/workplace_exposure_to_nanoparticles
[6] nd2355 INRS 1Q12 226 Recommendations for characterizing potential emissions and exposure to aerosols released from nanomaterials in workplace operations (in French)
[7] UIC-FFC March 2009 Nanomaterials and HSE guidance of good practices (in French)
[8] 10 Years of Research: Risk Assessment, Human and Environmental Toxicology of Nanomaterials, Status paper issued by the DECHEMA/VCI working group "Responsible Production and Use of Nanomaterials", October 2011

- Surfaces should be cleaned in a manner that minimizes the generation of dust. Vigorous sweeping or the use of compressed air should be avoided.

EMERGENCY PRECAUTIONS

- Collect spillage in a suitable container for disposal.
- Avoid dust formation.
- Do not allow entrance into sewage or drainage systems, groundwater or other bodies of water.
- In case of fire, all extinguishing media are applicable.
- No toxic substance release arising from UF TiO_2 involved in a fire
- Fire residues and contaminated extinguishing water must be disposed of in accordance with local regulations.

HANDLING/USE

- Wear personal protective equipment.
- In dusty conditions, wear respiratory protection as discussed below.
- Wear protective gloves.
- Wear safety glasses with side shields. In dusty conditions, wear safety goggles to protect eyes.
- Apply good hygiene practices as with all other powder substances.
- Dispose of according to local authority regulations.

Good practice is to provide workers with appropriate respiratory protection to enable keeping chronic exposure within the following limits:

- 2.4 mg/m^3 of fine TiO_2,
- 0.3 mg/m^3 of ultrafine TiO_2,

Cristal personnel manufacturing or handling UF TiO_2 use dust masks of class P2 or N95, or of higher class.

Table 1: Country specific occupational exposure limits for TiO_2

Substance CAS Number	**Occupational Exposure Limits**			
	Country	**Name of Standard**	**Total Inhalable (mg/m^3)**	**Respirable (mg/m^3)**
Titanium dioxide	Austria	MAK	NL	6 (annual)
CAS 13463-67-7	Belgium	TLV-TWA	10	5
	Czech Republic	TLV-TWA	10	NL
	Denmark	GV	6	NL
	Finland	HTP-arvot	10	NL
	France	VME	10	NL
	Germany	MAK	10	3
	Greece	TLV-TWA	10	5
	Ireland	LTEL	10	4
	Italy	TLV-TWA	10	NL
	Norway	TLV-TWA	10 / STEL 5 / 8 hr	5 5
	Portugal	TLV-TWA	10 (STEL)	5
	Spain	VLA-ED	10	NL
	Sweden	NGV	5	5
	Switzerland	MAK	10	3
	The Netherlands	MAC-waarden TGG	10	5
	United Kingdom	WEL-TWA	10	4
	United States	PEL	15	NL
	United States	TLV	10	NL
	NIOSH	**Recommendation**	**Ultrafine TiO_2 (mg/m^3)**	**Fine TiO_2 (mg/m^3)**
			0.3	2.4

DISCLAIMER:

The information provided herein is advisory only and have been promulgated solely as an illustrative example of certain health and safety practices that may be utilized to minimize exposure to ultrafine TiO_2 during its handling and use. Thus, this information should be regarded as a guide that the user may or may not choose to adopt, modify or reject. This information does not constitute a comprehensive or complete analysis and should not be relied upon as such. The user is responsible to determine and implement appropriate exposure control to assure safe handling and use. Cristal specifically disclaims all warranties, express or limited, including, but not limited to, the implied warranties of merchantability and fitness for a particular purpose, or any warranty otherwise arising out of any proposal, specification, or sample. **Cristal makes no warranties regarding the completeness, accuracy, reliability, applicability or availability of the information contained herein. In no event shall Cristal be liable for any damages, including without limitation, direct, indirect, special, exemplary or consequential damages, including lost profits, arising under the use of or reliance on information contained herein based in contract, negligence, strict liability, or otherwise, whether or not Cristal had any knowledge, actual or constructive, that such damages might be incurred. Additionally, Cristal shall not be liable in tort, contract, or otherwise, whether based in warranty, negligence, strict liability, or any other theory of liability for any action or failure to act in connection with the information contained herein, it being the user's intent and understanding to absolve and to protect Cristal, its successors, assigns, principals and employees from any and all liability in tort, contract or otherwise**.