TDMA
TITANIUM DIOXIDE MANUFACTURERS ASSOCIATION
for a brighter future

Titanium Dioxide Stewardship Council

2200 Pennsylvania Avenue, N.W. ◆ Suite 100W ◆
Washington, D.C. 20037 ◆ (202) 557-3800 tel. ◆
(202) 557-3836 fax

About Titanium Dioxide

What is titanium dioxide?

- Titanium dioxide (TiO_2) is a white solid inorganic substance that is thermally stable, non-flammable, poorly soluble, and not classified as hazardous according to the United Nations' (UN) Globally Harmonized System of Classification and Labeling of Chemicals (GHS).

- TiO_2, the oxide of the metal titanium, occurs naturally in several kinds of rock and mineral sands. Titanium is the ninth most common element in the earth's crust. TiO_2 is typically thought of as being chemically inert.

What products contain TiO_2?

- Titanium dioxide has been used for many years (ca. 90 years) in a vast range of industrial and consumer goods including paints, coatings, adhesives, paper and paperboard, plastics and rubber, printing inks, coated fabrics and textiles, catalyst systems, ceramics, floor coverings, roofing materials, cosmetics and pharmaceuticals, water treatment agents, food colorants and in automotive products, etc …

What are the differences between TiO_2 as a pigment and as a nanomaterial (ultrafine)?

- Pigment grade TiO_2 is manufactured to optimise the scattering of visible light and consequently white opacity. This requires a primary particle size of approximately half the wavelength of the light to be scattered, that is half of 400 - 700nm for visible light.

cefic sector group

Chemistry making a world of difference

European Chemical Industry Council
Avenue E. van Nieuwenhuyse 4 B - 1160 Brussels (Belgium)
Tel: +32 2 676 73 27 Fax: +32 2 676 73 59 pan@efic.be www.cefic.org

- Pigment grade TiO_2 is manufactured in order to maximise the number of primary particles in this size range (approx. 200 – 350 nm). However as in all production processes of particulate materials, there will be a distribution of primary particle sizes around the average value and it is likely that a small fraction of the primary particles are < 100 nm, and therefore covered by the nanoparticle ISO definition (ISO/TC 229 Nomenclature system for nanoparticles). In practice, all these particles tend to agglomerate into the micron (µm) size range.

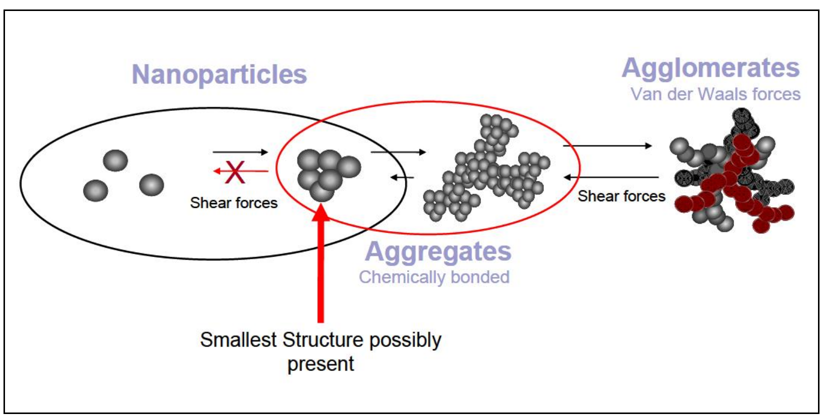
- TiO_2 nanomaterials (ultrafine) are transparent and more effective as UV absorbers or photocatalysts. The transparency and UV absorbance allow for effective use as a protective ingredient for sunscreens.

- Due to the smaller size of primary particles and higher surface area, TiO_2 as a nanomaterial allows the manufacture of various catalysts of enhanced activity.

- TiO_2 as a nanomaterial is engineered to have primary particles less than 100 nm in order to optimize such properties.

- TiO_2 as a nanomaterial is not used as a colorant as it is functionally different from pigment size particles and will not impart color or opacity to a product.

- Primary particles are strongly bound or fused together by chemical bonds to form aggregates. These aggregates further agglomerate via van der Waals attractive forces to form particles in the micron (µm) size range.



What are the benefits derived from TiO_2?

- As a pigment, TiO_2 has excellent **light-scattering** properties and is used in a variety of applications that require **white opacity and brightness**.

- It absorbs **UV light**. When TiO_2 pigment is incorporated in a polymer, it minimizes degradation of the system (embrittlement, fading and cracking). Surface treating of the TiO_2 can further improve this property.

- When used in paint or coating system, this effect ensures the longevity of the paint and the continued protection of the substrate.

- The use of light colored paints for interior applications provides an impression of openness and “space”. In addition, the high "luminosity" that comes from light colored paints reduces the energy needed to light the interior of buildings when compared to darker colors.

- In exterior applications the coolness conferred by TiO_2 colored surfaces leads to considerable energy savings in warm and tropical area by light reflectance thus reducing the need for air-conditioning.

- TiO_2 as a **nanomaterial** (ultrafine) appears **transparent** whilst still providing **UV light absorption**.

- Surface treatments allow dispersion in different media and efficient absorption of UV energy (e.g. in applications like sunscreens and light stabilization for wood coatings).

- When untreated, it can be used to decompose environmental pollutants by photocatalysis.

- TiO_2 as a nanomaterial (ultrafine) is used for example as a DeNOx catalyst support in exhaust gas systems in cars, trucks and power plants, thus minimizing their environmental impact.

Are there any human health concerns with TiO_2?

- TiO_2 use is ubiquitous in our society. Most of the surfaces and items that are white in color contain TiO_2. Thus, we are surrounded by TiO_2 containing materials in our homes, workplaces and public areas. Since the introduction of TiO_2 as a commercial product in 1923, there have been no identified health concerns associated with its exposure among consumers or the general population.

- These facts are supported by the results from four large epidemiology studies involving more than 40,000 workers in the titanium dioxide manufacturing industry in North America and Europe which indicate no association with an increased risk of cancer or with any other adverse lung effects ([1,2,3,4,6,10]) These studies did not specifically differentiate between the ultrafine and pigmentary TiO_2.

- In 2006, the International Agency for Research on Cancer (IARC) evaluated TiO_2 as "possibly carcinogenic to humans" (Group 2B) based primarily on studies in rats. Inhalation exposures to TiO_2 in rats can result in lung effects and lung tumors.

- However, it is generally recognized that the rat is uniquely sensitive to the effects of "lung overload" which is not observed in other species including humans. ([8 + TDMA IARC statement July 2011])

Potential Exposure

- by inhalation

- Workers at titanium dioxide manufacturing plants can be exposed to TiO_2 dust. Protection measures including engineering controls and personal protective equipment are applied for exposure control and worker risk mitigation in accordance with existing regulations.

- Downstream users can also be exposed to TiO_2 dust. Appropriate safe handling and use information are included in product documentation such as Safety Data Sheets (SDS).

- Consumer exposure to TiO_2 dust is presumed to be very low because TiO_2 is typically incorporated into a product matrix where it is tightly bound such as in paints or plastics. Thus, inhalation exposure is not considered as relevant for the general public.

- by oral intake

- Pigmentary TiO_2 which meets appropriate purity standards is approved as a colorant for use in foods (E171 - e.g. candies, cookies, sweets, coffee whitener, toothpaste, etc …) and pharmaceuticals (several Pharmacopoeias).

- by skin contact

- TiO_2 in pigmentary and ultrafine forms is used in cosmetics applications (e.g. lipsticks, make-up products and sunscreens). It has been conclusively demonstrated that TiO_2 is safe for use in sunscreen products to protect skin from harmful effects of solar UV radiation. Comprehensive in vivo and in vitro dermal penetration studies have been performed.

- Studies show TiO_2 particles (pigmentary or ultrafine) do not penetrate either intact or damaged skin ([5, 9]). Even if the skin is sunburned the penetration of TiO_2 nanoparticles from representative sunscreen formulations is not enhanced ([7]).

- The former European Scientific Committee on Cosmetic Products and Non-Food Products (SCCNFP) reviewed in 2000 data on TiO_2. Based on the results, SCCNFP concluded that TiO2 is "*safe for use in cosmetic products at a maximum concentration of 25% in order to protect the skin from certain harmful effects of UV radiation. This opinion concerns crystalline (anatase and/or rutile) titanium dioxide, whether or not subjected to various treatments (coating, doping, etc.) irrespective of particle size, provided only that such treatments do not compromise the safety of the product*" ([11]).

Are there specific health concerns associated with ultrafine TiO_2 exposure?

- Based on existing safety information, it can be concluded that the use of titanium dioxide nanomaterial (ultrafine) as an ingredient in cosmetic sunscreen products at a concentration up to 25 % poses no risks to human health ([12, 13]).

- New information obtained from research models should be put into a proper perspective by taking into account the relevance of the model used and the dose-levels or concentration tested that might not be representative of typical consumer exposure situation.

Life Cycle Thinking

- The value TiO_2 provides in product applications can often be equated with tangible environmental benefits. For example, TiO_2 is a potent opacifier, enabling thinner films and thus improved resource efficiency and avoided waste. In cradle-to-grave footprint analyses of products that contain TiO_2, both the upstream footprint of TiO_2 manufacture and the downstream environmental performance benefits facilitated by TiO_2 should be considered.

- To support the development of accurate and consistent product carbon footprints, TDMA is developing a standard methodology to calculate the cradle-to-gate carbon footprint of TiO_2 and plans to publish industry average TiO_2 carbon footprint data and the underlying method later this year.

Regulatory framework

- Depending on the use of the titanium dioxide products, different legislative definitions for the purity of the raw material must be fulfilled.

- A list of some key applications with relevant laws and provisions (depending on the country of use) can be found below:

  Use as a colorant

  - **Automotive:** Council directive 2000/53/EC (end-of life vehicles)
  - **Contact lenses:** FDA 21 CFR § 73.3126
  - **Cosmetics:** Council Directive 76/768/EEC ● FDA 21 CFR § 73.2575

- **Electronic equipment:** Council directives 2002/95/EC and 2002/96/EC (Restriction of the use of Certain Hazardous substances in electrical and electronic equipment (RoHS))
- **Food:** E171 in the European directive 2008/128/EC, replacing 95/45/EC ● FDA 21 CFR § 73.575 ● Food Chemical Codex (FCC) ● CODEX Alimentarius ● FAO JECFA Monographs
- **Food contact applications:** EU Regulation (EU) 10/2011 ● Council Directive 2004/19/EEC ● FDA 21 CFR § 178.3297 (Colorants for polymers) ● FDA 21 CFR § 175.300 (Resinous and polymeric coatings) ● FDA 21 CFR § 176.170 & 176.180 (Paper & Paperboard) ● Bundesinstitut für Risikobewertung (BfR) Section IX, LII, XXXVI, XXXVI-1, XXXVI-2
- **Packaging:** Council Directive 94/62/EC ● CONEG legislation (USA)
- **Paints:** Volatile Organic Compounds (VOC) according to the definition of the EU directive 2004/42/EC "decopaint directive"
- **Pharmaceuticals:** United States Pharmacopoeia (USP) ● European Pharmacopoeia (EP) ● Japanese Pharmacopoeia (JP) ● Food and Drugs Administration (FDA) 21 CFR § 73.1575
- **Toys:** DIN EN 71-3 (Security of toys) ● ASTM F963 – 11 Standard Consumer Safety specification for Toy Safety

Use without coloring effect

- **Cosmetics:** Council Directive 76/768/EEC ● FDA 21 CFR § 352.10 (Sunscreen active ingredients)

- Additional conformity with Good Manufacturing Practice (GMP), different ISO or other standards can be provided. Even the manufacture of Kosher or Halal titanium dioxide products can be achieved.

Conclusion

Titanium dioxide is a global product with many important applications that has been proven as safe in its intended uses over many decades.

References

1. Boffetta P, Gaborieau V, Nadon L, Parent M-E, Weiderpass E, Siemiatycki J. (2001). Exposure to titanium dioxide and risk of lung cancer in a population-based study from Montreal. *Scand. J. Work Environ. Health* 27:227-232.

2. Boffetta P., Soutar A., Cherrie J., Granath F., Andersen A., Anttila A., Blettner M., Gaborieau V., Klug S., Langard S., Luce D., Merletti F., Miller B., Mirabelli D., Pukkala E., Adami H-O., and Weiderpass E. (2004). Mortality among workers employed in the titanium dioxide industry in Europe. *Cancer Causes and Control* 15(7):697-706.

3. Chen J, and Fayerweather W. (1988). Epidemiologic study of workers exposed to titanium dioxide. *J. Occup. Med.* 30(12):937-42.

4. Fryzek J, Chadda B, Marano D, White K, Schweitzer S, McLaughlin J, and Blot W. (2003). A cohort mortality study among titanium dioxide manufacturing workers in the United States. *J. Occup. Environ. Med.* 45(4):400-09.

5. Gamer, A. O.; et al. (2006). The in vitro absorption of microfine zinc oxide and titanium dioxide through porcine skin. *Toxicology in Vitro* 20, 301-307.

6. Garabrant D.H., Fine L.J., Oliver C., Bernstein L., and Peters J.M. (1987). Abnormalities of pulmonary function and pleural disease among titanium metal production workers. *Scand. J. Work Environ. Health* 13(1):47-51.

7. Monteiro-Riviere NA.; et al (2011). Safety evaluation of sunscreen formulations containing Titanium Dioxide and Zinc Oxide nanoparticles in UV-B sunburned skin: An in vitro and in vivo study. *Toxicological Sciences, 123, 264-280.*

8. Levy L. S. (1994). Squamous Lung Lesions Associated with Chronic Exposure by Inhalation of Rats to p-Aramid Fibrils (Fine Fiber Dust) and to Titanium Dioxide: Findings of a Pathology Workshop. In: Mohr, U (Ed), Toxic and carcinogenic effects of solid particles in the respiratory tract, ILSI Press, 473-478.

9. Mavon, A.; et al. (2007). In vitro percutaneous absorption and in vivo stratum corneum distribution of an organic and a mineral sunscreen. *Skin Pharmacol. Physiol*. 20, 10-20.

10. Ramanakumar AV, Parent ME, Latreille B, Siemiatycki J. (2008). Risk of lung cancer following exposure to carbon black, titanium dioxide and talc: results from two case-control studies in Montreal. *Int J Cancer* 122:183-9.

11. SCCNFP (2000). Opinion of the scientific committee on cosmetic products and non-food products intended for consumer concerning titanium dioxide, Colipa No. S75, adapted by the SCCNFP during the 14th plenary meeting of 24 October 2000.

12. Personal communication COLIPA unpublished dossier on the Safety of TiO_2 nanomaterial, submitted in January 2012 to SCCS (Scientific Committee on Consumer Safety).

13. Schilling, K.; et al. (2010). Human safety review of “nano” titanium dioxide and zinc oxide. *Photochem. Photobiol. Sci*. 9:495-509.

March 2012