TDMA
Titanium Dioxide Manufacturers Association

„Sharing nano-knowledge in the value chain of coatings“
TDMA response to IVAM questions

A. About Titanium Dioxide

Titanium dioxide (TiO_2) - a white solid inorganic substance - is thermally stable, non-flammable, poorly soluble and not classified as hazardous.

This 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.

TiO_2 has been used as a white pigment 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, ceramics, floor coverings, roofing materials, cosmetics and pharmaceuticals and food colorants etc …

Pigment grade TiO_2 is manufactured to optimize 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.

In contrast TiO_2 as a nanomaterial (ultrafine TiO_2) is engineered to have primary particles less than 100 nm in order to optimize properties for non-pigmentary applications e.g. catalyst supports (DeNOX stationary and automotive), UV-absorbers (Cosmetics) and photo-catalysts. Due to their smaller size nanoparticles are transparent. The production volume of ultrafine TiO_2 is estimated to be approx. 1 percent of the total TiO_2 production.

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TiO2 use is ubiquitous in our society. Most of the surfaces and items that are white in color contain TiO2. Thus, we are surrounded by TiO2 containing materials in our homes, workplaces and public areas. Since the introduction of TiO2 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 in creased risk of cancer or with any other adverse lung effects (1,2,3,4,5,6) These studies did not specifically differentiate between the ultrafine and pigmentary TiO2.

B. <u>IVAM questions</u>

1. What is the approximate production volume of ultrafine TiO2 in Europe?

In 2011 European production of pigmentary TiO2 was approx. 1.500.000 tons. There are no statistics available however TDMA estimates that ultrafine TiO2 production equates to about 1% of the pigmentary production level (that is ca. 10.000 – 15.000 tons).
The major applications of ultrafine TiO2 are as catalyst supports and in cosmetic applications (sunscreens).

Consequently the amount of ultrafine TiO2 used in coating applications e.g. as an UV absorber in wood coatings will only be a small proportion of this 1% , the TDMA estimate is only 100 to 200 t/y for these applications.

2. What are the estimated emissions to the environment during production?

There is a need to differentiate between natural, incidental (e.g. unwanted production of nanoparticles in combustion processes and other industrial activities) and engineered particles. The detection sensitivity for engineered nanoparticles is limited by the high background noise due to natural and incidental nanoparticles. In future detection methods are expected to be developed which are more sensitive and based on a specific property of the engineered nanoparticle.

Measuring nanoparticles

The BAT reference document “Large volume inorganic chemicals – solids and others” formally adopted by the European Commission under the IPPC directive describes in Chapter 3 the Best Available Technology (BAT) for the production of TiO2 (sulfate and chloride technology) giving details to raw materials consumption, energy and water consumption as well as emissions into water and air. In this document no differentiation is made between pigmentary TiO2 and ultrafine TiO2.

Also in most cases ultrafine TiO2 production is integrated in the production sites of pigmentary TiO2.

3. Which production processes are mainly used to produce ultrafine TiO2 in the EU and what do they look like?

Common precursors for the production of ultrafine TiO2 are intermediates of the pigmentary production process e.g. titanium tetrachloride – mainly converted to titanium oxychloride (chloride technology) - and titanium oxysulfate and titanium oxyhydrate (sulfate technology). These intermediates are further processed by precipitation, thermal hydrolysis or flame hydrolysis. Secondary steps are milling, coating and then milling again. It is unknown to what extent organometallic precursors like Titanium alcoholates are used in an industrial scale. Nearly all of these processes are proprietary knowlege and patent protected and not commercially available.

4. Where in the production process may workers get exposed?

Workers at ultrafine TiO2 manufacturing plants can be exposed to TiO2 dust. Protection measures including engineering controls and personal protective equipment are applied for exposure control and worker risk mitigation in accordance with existing regulations.
TDMA members place paramount importance on the health and safety of their employees and the community at large, and strongly believe that is always prudent to take all possible precautions against all potential work place exposures (noise, dust, chemicals etc.)

C. Release of nanomaterials from coatings

Due to uncertainties concerning possible hazards to health, safety and the environment by the use of nanomaterials there is the need to develop appropriate and standardized methods for the characterization of nanoparticle releases from surfaces related to certain treatment processes. The attached publications describe the results for the potential of abrasion induced possible nanoparticle release; the clear result of the CEA-study, where paints with pigmentary and ultrafine TiO2 were tested, - presented at the NanoSafe2010 - comes to the conclusion that no free nanoparticles are emitted.

Prof.Stintz, 2010   NanoSafe 2010

At the beginning of 2011 the German VCI/VdMi (Association of chemical Industry/Verband der Mineralfarbenindustrie.e.V.) launched a project “FRINANO” to investigate the release of nanoparticles from coatings under various conditions, which means nanoparticle formation/detection with the following processes:

- Aspiration: simulation to the exposure of air
- Wipe off: simulation of contact with the skin
- Rubbing: simulation of processing.

In this project various particles will be tested. Three TDMA members will also participate in this project. First results are expected for the first quarter of 2012.

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References

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