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(Nano-)Titanium dioxide (Part I): Basics, Production, Applications

Summary

The basic component of titanium dioxide (TiO_2) is the element titanium, which is among the ten most abundant metals in the Earth's crust. In nature, TiO_2 is present in three different crystal structures, whereby all three exhibit different physical properties that find different applications. This makes TiO_2 a widely used product component that improves the texture of paints and lacquers, cosmetics, textiles, paper, plastics as well as foods. In sunscreens, nano-TiO_2 has been incorporated as a so-called physical UV-filter since about 1990. The photocatalytic effect of nano-TiO_2 is also exploited in a wide range of products. The high oxidation potential of nano-TiO_2 coatings is used to produce self-cleaning surfaces because this property helps decompose organic pollutants and therefore also kills bacteria. In the future, the photochromic and electrochromic properties (reversible color changes due to light or electric current) will find greater use. Finally, current research is focusing on the use of nano-TiO_2 in alternative energy production.

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Introduction

Titanium dioxide (TiO_2) is a widely used component in many consumer goods such as paints and lacquers, cosmetics, textiles, paper, plastics and foods. In 2011, more than 5 million t of TiO_2 were produced worldwide. TiO_2 can be produced in a regular size (micro-scale) or in a nano-scale dimension. Based on their size, TiO_2 nanoparticles (NPs) have specific physical and chemical properties that are finding increasing use in a wide range of sectors (computer science, chemistry, cosmetics, medicine). In order to incorporate them into the final product, the surfaces of NPs are often modified. TiO_2 NPs are often used as physical UV-filters in sunscreens or outdoor paints; they also find use in glass and cement due to their photocatalytic activity. This dossier provides an insight into the properties, production and applications of regular and nano-TiO_2.

Fundamental properties of titanium dioxide

The basic ingredient of TiO_2, the element titanium (Ti), is among the ten most common metals in the Earth's crust. In nature, TiO_2 exists in three different crystal structures: rutile, anatase and brookite (Figure 1). Industrially, TiO_2 can be produced from the titanium ore ilmenite ($FeTiO_3$). Titanium dioxide is a white powder that is insoluble in water and in organic solvents and that is inflammable, odorless and crystalline. Due to its high stability, low price (< 5 US $/kg)[1] and many applications, along with its advantageous optical properties, TiO_2 has been produced commercially since 1916. It is the most commonly used white pigment (high refractive index: 2.7-2.55 depending on the crystal form), with a very high covering power and excellent tinting strength. The three crystal structures of TiO_2 differ, beyond by their external appearance, also through their electronic and photoactive properties (reactions under the influence of light), as well in density and refractive index.

Figure 1:
The three crystal forms of TiO_2 in nature (from 16)

The **rutile** crystal is the thermodynamically more stable form of titanium dioxide; **anatas** has the strongest photoactive property. Both forms absorb UV radiation and parts of the visible spectrum. At temperatures above 915 °C, anatas transforms monotropically (only in one direction) into rutile. The third crystal form, **brookite**, currently has no particular commercial significance.

From an electronic perspective, titanium dioxide is a semi-conductor. This means that the conductivity of this metal lies between that of a conducting metal and that of an isolator. This is attributable to the energetic gap between the energy level assumed by the electrons in the material (the valence band) and the level of the next higher unoccupied band (conduction band). The conduction band is therefore free of electrons that could conduct the electric current. As this band gap is relatively small – in the region of a few electron volts (eV) – the electrons of the filled valence band can be shifted into the conduction band by the energy of the thermal vibrations or by light absorption. This requires the excitation energy of 3.2 eV for anatase TiO_2 and 3.0 eV for rutile. In order to apply this energy, UV light (wavelength below 380 nm) is sufficient, which is very effectively absorbed (resonance absorption). Visible light with longer wavelengths is reflected by TiO_2 particles or emitted as light with long wavelengths.

The excited state of the semi-conductor is generally unstable because the excited electrons soon revert again to the valence band. The duration of this excitation state is longer for TiO_2 than for other semi-conductors. For commercially available TiO_2 particles this is in the range of nanoseconds, although decay reactions into the range of seconds have been measured (e.g. P25, Degussa)[2]. In this excited state, oxidative processes (for example the formation of free radicals) can be triggered by TiO_2 particles, a property that can find practical use. This excellent photocatalytic activity has opened the door for a series of applications, whereby such processes can cause wanted but also unwanted effects.

Production of titanium dioxide

For more than 50 years, two major production processes have been applied to produce and process titanium dioxide[1]. The first is the sulfate process in which the crushed and enriched titanium ore is pretreated with concentrated sulfuric acid and subsequently oxidized to $TiO_2 \times H_2O$, filtered and then annealed in a rotary kiln at 800-1,000 °C. In this process, the crystal structure (anatas or rutile) and the grain size of the pigments can be temperature regulated. The process gives rise to diluted (25 %) sulfuric acid as a waste product (dilute acid), which can also contain heavy metals from the ore. Up until the late 1980s, most of these chemical loads (about 5 million tons per year in Europe) were dumped by freighters in open waters of the North Sea. As of 1989, an environmentally friendlier recycling-process was introduced for this sulfuric acid in Germany and later also in Great Britain. This, however, was more costly.

The predominant production process – encompassing nearly half of the global TiO_2 production – is the chloride process (licensed and further developed in 1940 by DuPont). Here, titanium ore is transformed at high temperatures into titanium tetrachloride vapor using chlorine and coke. Purification and distillation steps yield rutile TiO_2. The applied chlorine can be recovered. This chloride process is preferred when building new facilities based on its lower operating costs and minimal environmentally harmful wastes[1].

Additional processes must be used to produce TiO_2-NPs, namely processes that enable better control of the shape and size of the resulting TiO_2 particles and therefore a higher yield of NPs. These include the Sol-Gel process, hydrolysis as well as processes in which the created particles are produced via the separation from the gas phase (chemical vapor deposition, CVD, see also[3]). A subsequent grinding process in the aqueous phase ensures TiO_2-NPs with a diameter between 20 and 100 nm.

The above-described properties of TiO_2 as well as the production processes are principally equally valid for the regular TiO_2 white pigments that have been produced commercially for over 90 years as they are for those TiO_2-NPs that have been selectively generated over the last decade. One of the key differences between conventional or micro-scale and nano-scale TiO_2 is the much larger surface area of the nanoparticles at the same overall weight (see[4]). This larger surface area is associated with special properties such as catalytic activities and high light absorption capacity. These features explain the wide range of applications of TiO_2-NPs. At the same time, the gap in the range of dimensions of regular and nanoparticles has narrowed, complicating definitive differentiation. A case in point is the TiO_2 particles used in white pigment: they are typically produced with an average diameter of 250-350 nm, i.e. close to the nanoparticle dimension (< 100 nm)[5]. Due to the wide size ranges of the pigment particles, these can also contain significant amounts of nanoparticles. One study reports that more than one third of the TiO_2 particles contained in food, as the food additive E 171, have a diameter under 100 nm[6].

Production volume of titanium dioxide

Almost the entire volume (95 %) of mined titanium ore is used to produce TiO_2. The remaining 5 % is metallic titanium, which is mainly used in the airplane and automobile industry as well as in plant construction. TiO_2 also plays a role in the medical technology sector, for example in the production of implants.

The estimated global production volume in 2011 was more than 5 million tons of titanium pigment; this includes 1.4 million tons in the USA alone and an annual production of about 2 million tons in China. Further major producers are Germany with about 400,000 tons and Japan with ca. 300,000 tons[7].

The information on the production volumes of nano-sized TiO_2 is incomplete and in many cases contradictory. The total global production in 2005 was listed as being about 5,000 tons, with similar values for the period 2006-2010. For the 2011-2014 period, the estimate was more than 10,000 tons[8]. According to estimates by the US Environmental Protection Agency (EPA), 3630 tons of nano-TiO_2 were produced in 2007 in the USA, with overall global production being 12,500 tons[5]. In a study published in 2009[1], considerably higher production volumes were listed for the year 2002, whereby about 3,000 tons of nano-TiO_2 were produced in the USA alone. Those authors also predicted a strong increase up to an annual production of about 44,000 tons by 2009 – an amount that was apparently not reached according to the EPA report. In a further prognosis, the authors estimated the rate of increase up to 2015 to be about 10 %, i.e. 260,000 tons TiO_2. They justified this assumption with the increasing replacement of regular TiO_2 with nano-TiO_2 as well as with the opening of additional and more modern production facilities as production costs sink. This assumption is highly questionable because the pigment TiO_2, which makes up the main production volume, clearly cannot be replaced by nano-TiO_2. The values provided in another publication[9] largely support the estimates forwarded by the EPA and UNEP. The latter authors estimate the global production volume of nano-TiO_2 at ca. 5,000 tons per year from 2006 to 2010 and expect an increase to about 10,000 tons per year for the period 2011-2014. Clearly, however, nano-TiO_2 is currently one of the most widespread nanomaterials, and a doubling of production in the upcoming decade is a distinct possibility[8-10].

Fields of application

Beside inexpensive production processes, titanium dioxide exhibits numerous advantageous properties such as corrosion resistance, brilliant white and covering power, and a high efficacy in reducing ultraviolet light. TiO_2 is the most commonly used pigment worldwide (ca. 70 % of all pigments). Its primary application is in surface coatings, both in the form of liquid preparations as well as powder coatings (USA: ca. 57 % of the total volume in 2007)[5]. Paper production is also an important application, in which rutile TiO_2 is admixed as an optical brightener (USA: ca. 13 % of the total volume). Due to its UV-blocking properties, TiO_2 is also added to plastics components in low concentrations (< 3 % of the total volume of the final products) (USA: ca. 26 % of the total volume), from which a variety of products are manufactured.

TiO_2 is also used as a component in ceramics, catalytic converters and as a coating for textiles (USA: ca. 4 % of the total volume)[5]. An additional and important application of TiO_2 is in the cosmetics and food industry. Under the designation E 171, TiO_2 is used as a food additive to improve texture and in cosmetics to add color and provide UV protection.

Many of the advantageous properties of regular TiO_2 are also valid for nano-TiO_2. Due to the transparency of nano-TiO_2 for the visible light spectrum, it cannot be used as a white pigment. Nonetheless, nano-TiO_2 is increasingly being admixed in paints because these nanoparticles improve the surface properties such as hardness, reflectance and smear resistance.

Photocatalytic and biocidal properties

As described above, TiO_2 (anatase) is an effective photocatalyst. The especially large surface area of the NPs helps boost the photocatalytic effect. During this process, the UV-radiation (e.g. sunlight) completely oxidizes organic contamination in the presence of oxygen, yielding carbon dioxide and water. Note, however, that TiO_2 can also oxidize water, giving rise to hydroxyl radicals ($-OH^{\cdot}$) (see also[11]). These effects can be used to decompose pollutants, for example in drinking water and the air. The high oxidation potential of nano-TiO_2 coatings is expected to yield self-cleaning surfaces because they decompose organic pollutants and can therefore also kill bacteria. The photocatalytic properties are enhanced by the small particle size and targeted admixtures of other elements (among others Al^{3+}, Fe^{3+}, La^{3+}, Be^{2+}). Today, self-cleaning products such as tiles, mirrors and glass panes are already being sold commercially. They owe their properties to a ca. 40-nm-thin film of TiO_2 that is applied using a CVD process (see also[3]).

UV-blocking property (UV absorber)

Nano-TiO_2 has been used in sunscreens as a so-called physical UV-filter since about 1990. In contrast to chemical UV-protective substances, physical UV-filters do not absorb the UV-radiation but rather reflect or disperse them so that they cannot penetrate down to the skin surface (Figure 2). One property of nanoparticles is their transparency for visible light. They do not leave a milky-white film on the skin as the regular TiO_2-containing sunscreens. UV-radiation is divided into two main wavelength bands, namely UV-A (320-400 nm) and UV-B (290-320 nm). The UV-B band is primarily responsible for the skin's tanning reaction. Both UV-A and UV-B are considered to be responsible for skin aging, wrinkling and skin cancer. To date, the rating systems in many countries (SPF, sun protection factor) have only considered the protective effect against the UV-B band. In sunscreens, TiO_2 NPs are used by approximately 50 nm diameter, which provide for both UV bands good protection, using a weight percentage of about 10-15 % NPs. In the EU, Canada and Australia, an upper limit of 25 % has been specified for the admixture of TiO_2-NPs. Moreover, both the regular and the nano-sized TiO_2 in sunscreens are coated with organic compounds and metal oxides such as silica or aluminum in order to reduce the photocatalytic reactivity (see above) and hinder the formation of reactive radicals[1]. As sunscreens for allergy sufferers should not contain chemical UV-filters, TiO_2-NP-containing sunscreens are a good alternative.

TiO_2-NPs are also applied in UV-resistant coatings and as components of plastic to protect colors and objects from strong sunlight. Fabric fibers in light protection clothing also contain TiO_2.

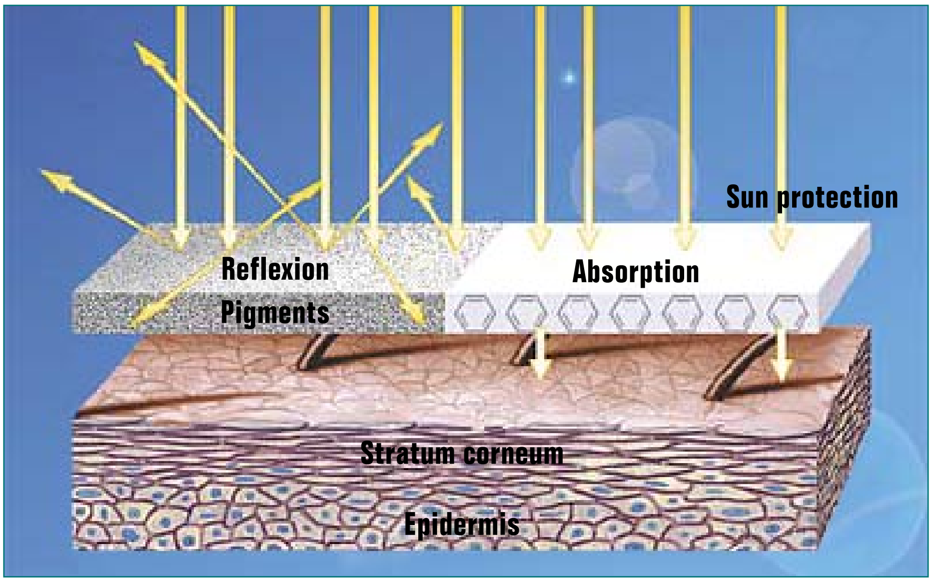

Figure 2: Effect of physical (left) and chemical (right) UV filters[17]

Future applications

Already at present, thin layers of TiO_2 particles are produced on glass plates – on a small scale for special applications. They are a key component of photochromic and electrochromic glass, which changes its color under the influence of sunlight or upon application of an electrical current. The transition from a colorless state to impermeability for visible light and heat radiation also enables their use in high-tech thermally insulating windows[12].

The use of TiO_2-NPs is also being examined for several novel developments in the sectors of alternative energy production and energy storage. Possibilities include the photocatalytic decomposition of water into H_2 and O_2 under the influence of sunlight, as well as the conversion of TiO_2 to fuel at a nano-TiO_2 electrode[13]. Equally, the effectiveness of dye sensitized solar cells can be improved by using TiO_2-NPs.

Nanotubes made of titanium dioxide also appear to be suitable as a storage medium for hydrogen (H_2). In such systems, nano-TiO_2 is a promising component in fuels for motor vehicles and also to increase the storage capacity of electric batteries[14].

Finally, materials made of nano-TiO_2 appear to be suitable for novel optical and electronic storage media, whereby the goal is to increase the storage capacity of CDs to 25 terabytes. Thus, using nano-Ti_3O_5, the reversible transition between a metallic and a semi-conductor form could be triggered through laser light pulses[15]. This compound is produced from commercial photocatalytic nano-TiO_2 in a hydrogen atmosphere under heat treatment. The Ti_3O_5-compound is in the form of ca. 20-nm-small crystals and is stable at room temperature. The exposure to low-intensity ultraviolet laser impulses triggers the transition from the metallic to the semi-conductor state of the Ti_3O_5. The prerequisites for high storage densities are given through the low wavelengths and the already very high degree of nano-structuring of the materials[15].

Summary *see Dossier 035en*

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