TECHNICAL INFORMATION 1243

AEROXIDE®, AERODISP® and AEROPERL® Titanium Dioxide as Photocatalyst

POWER TO CREATE

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1. Introduction

Titanium dioxide is widely used as a pigment for paints, printing inks, plastics, cosmetics and food. Typical titanium dioxide pigments are characterized by a primary particle size of between 0.2 and 0.5 µm. In contrast to pigmentary titanium dioxide, the nanostructured titanium dioxide products of Evonik Industries have an average primary particle size of between 14 and 21 nanometers and consequently almost no pigmentary properties. However, the primary particle size is only mentioned to indicate the application properties of a given product. The supplied product does not come in this form, but rather as tightly bonded aggregates of the primary particle, varying in size and shape to impart specific application properties. These aggregates form agglomerates during production usually into the powder or granulate form that is supplied to customers.

The nanostructured titanium dioxide products of Evonik are sold under the trade names AEROXIDE® and AEROPERL® and include the well-known AEROXIDE® TiO_2 P25. AEROXIDE® TiO_2 P25 is widely used as a catalyst, catalyst support, and heat stabilizer for silicone rubber. In terms of photocatalysis AEROXIDE® TiO_2 P25 has been subject of many studies over the years, including its use in wastewater treatment, the reduction of NOx in exhaust gases, and the manufacture of antibacterial, self-cleaning or antifogging surfaces. Because of its high photoactivity, AEROXIDE® TiO_2 P25 is often recognized as the "gold standard" in photocatalysis [1].

In order to provide you with the best solution for each application, the portfolio of AEROXIDE® TiO_2 also includes a highly dispersed fumed titania, AEROXIDE® TiO_2 P 90, VP AEROPERL® P 25/20 granulated fumed titania and AERODISP® dispersions thereof.

This Technical Information describes the properties and applications of our various nanostructured titanium dioxide products as photocatalysts. If you have any further questions, please contact our technical personnel at any time.

2. Fumed Titanium Dioxide

Titanium dioxide occurs in nature in the modifications rutile, anatase, and brookite. Rutile and anatase are produced industrially, either by the sulfate or chloride process, in large quantities and are used as pigments and catalysts, and in the production of ceramic materials. Titanium dioxide is of outstanding importance as a white pigment because of its scattering properties, its chemical stability, and lack of toxicity.

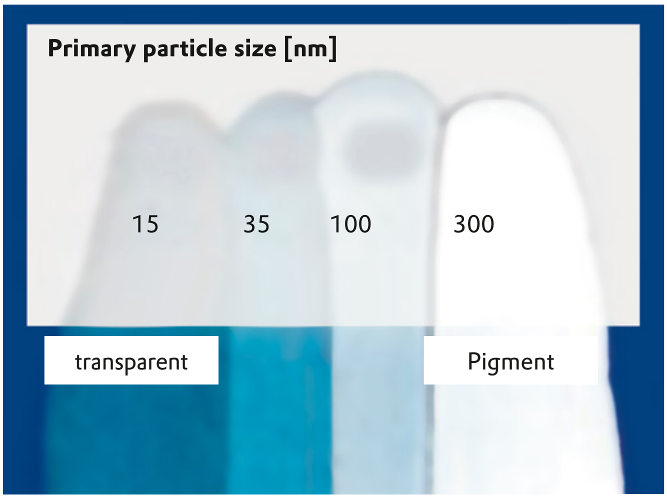
2.1 PRODUCTION

Evonik's titanium dioxides are produced in a similar manner to the AEROSIL® process by utilizing titanium chlorides as raw material: $TiCl_4$, a high-purity liquid, is vaporized, mixed with air and hydrogen. Immediately thereafter the gases are reacted at temperatures between 1000 and 2400 °C in a burner leading to the formation of pure and nanostructured titanium dioxide according to the following reaction:

$$TiCl_4 + 2\,H_2 + O_2 \rightarrow TiO_2 + 4\,HCl$$

The properties of fumed titania products can be varied widely by adjusting the process parameters.

FIGURE 1



Influence of the primary particle size (in nm) on the transparency of titanium dioxide

2.2 FUNDAMENTAL PROPERTIES

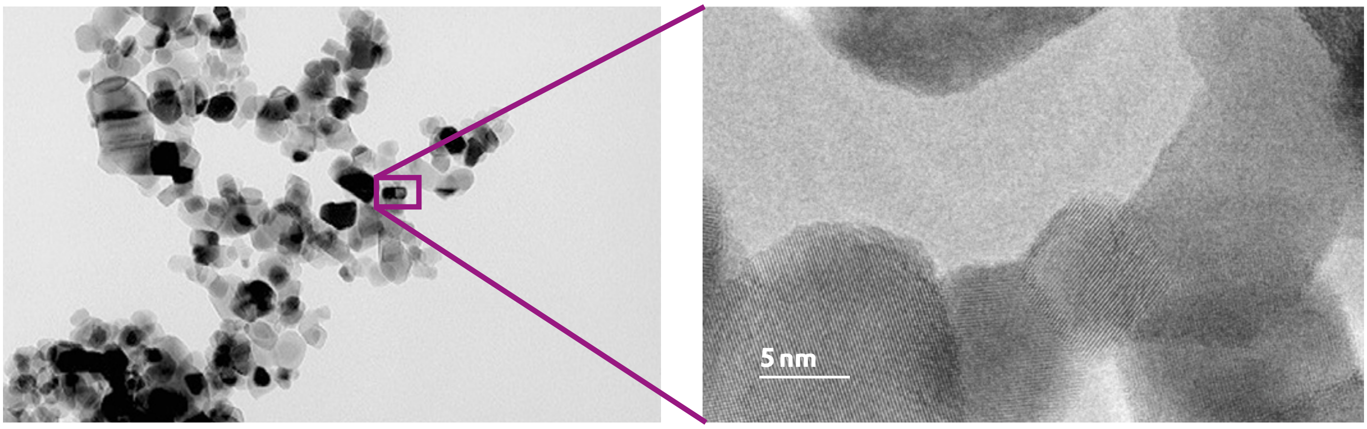
Evonik's titanium dioxide products are white powders with high specific surface areas. The products are pure titanium dioxide with an anatase content of 80–90 % by weight with a small portion of rutile. They are not surface treated. As mentioned above, Evonik's titanium dioxides are excellent photocatalysts. This is due to the very high surface area and the mixed anatase and rutile crystal structure. According to Hurum et al "the rutile acts as an antenna to extend the photoactivity into visible wave-lengths and the structural arrangement of the similarily sized TiO_2 crystallites creates catalytic "hot spots" at the rutile-anatase interface" [3].

As can be seen from **Figure 1** the pigmentary properties (white pigments have primary particle sizes around 200–500 nm) are no longer relevant for nanostructured particles.

2.3 PROPERTIES OF AEROXIDE® TiO_2 P 25

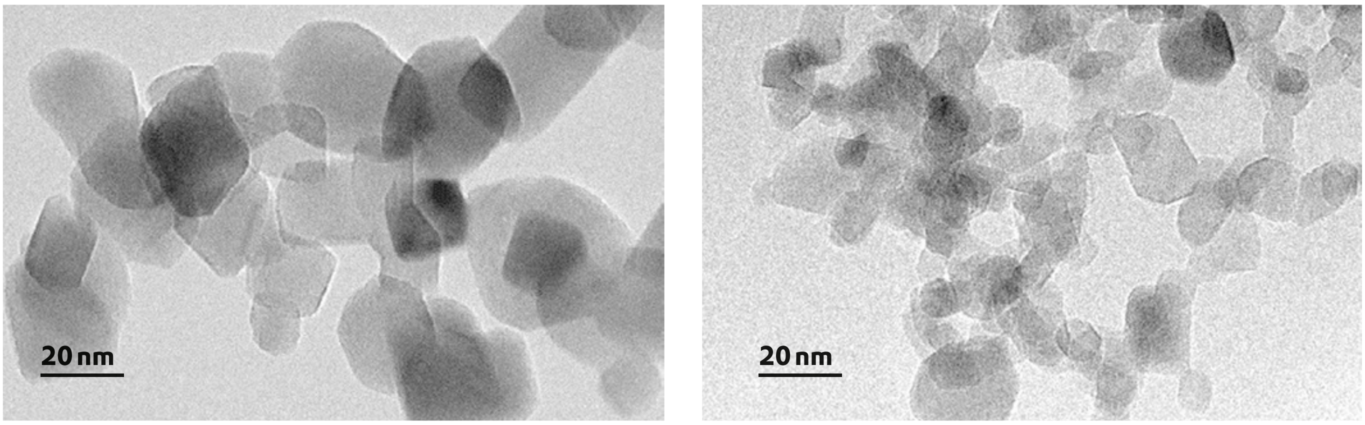
AEROXIDE® TiO_2 P25 is a fine white powder with hydrophilic character caused by hydroxyl groups on the surface [4]. It consists of aggregated primary particles. The aggregates are several hundred nm in size and the primary particles have a mean diameter of approx. 21 nm. Particle size and density of ca. 4 g/cm^3 lead to a specific surface of approx. 50 m^2/g. Due to the formation of aggregates and agglomerates, the tamped density of AEROXIDE® TiO_2 P25 is only about 130 g/l (determined acc. to DIN ISO 787/XI).
The weight ratio of anatase and rutile is approximately 80/20. Both crystal forms are tetragonal but with different dimensions of the elementary cell. At 300 °C, a slow conversion of anatase to the more stable rutile structure begins. At temperatures higher than 600 °C, the conversion runs faster combined with a reduction of the specific surface. AEROXIDE® TiO_2 P25 is suitable for many applications that require a high photoactivity.

FIGURE 2



TEM images of AEROXIDE® TiO_2 P25 depicting the primary crystals (right graph) and their aggregates and agglomerates (left graph)

FIGURE 3



TEM-images of AEROXIDE® TiO_2 P25 (left) and AEROXIDE® TiO_2 P 90 (right)

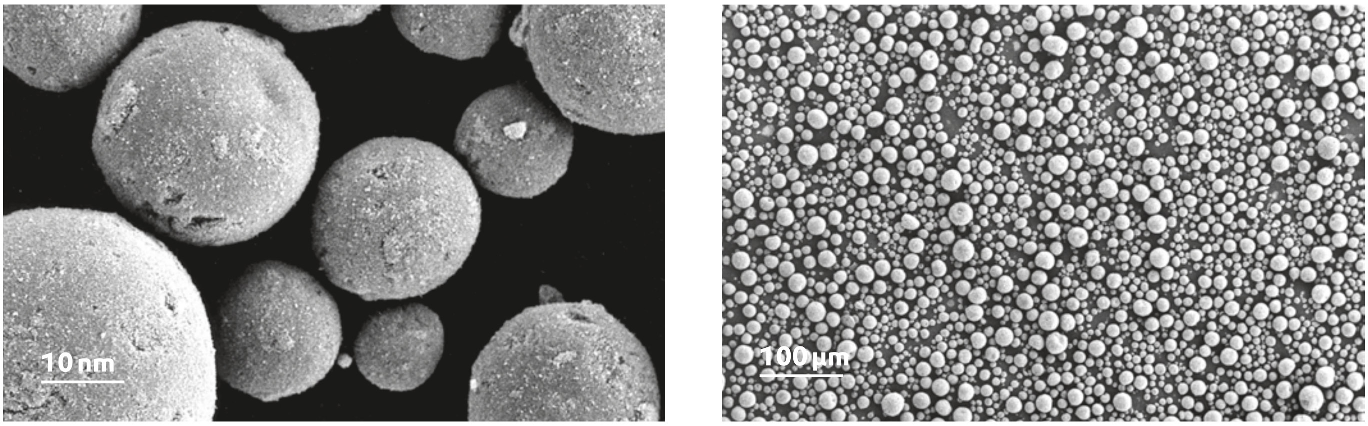
2.4 PROPERTIES OF AEROXIDE® TiO_2 P 90

Whereas the average primary particle size from AEROXIDE® TiO_2 P25 is 21 nm, Evonik developed by variation of the production parameters another grade in order to increase the photocatalytic properties: The result is AEROXIDE® TiO_2 P 90, a product with an average primary particle size of 14 nm. **Figure 3** shows the primary particle sizes of AEROXIDE® TiO_2 P 90 in contrast to AEROXIDE® TiO_2 P25.

2.5 PROPERTIES OF VP AEROPERL® P25/20

As a dust free alternative to AEROXIDE® TiO_2 P25 we offer a product grade named VP AEROPERL® P25/20. This special granulated titanium dioxide with an average particle size of 20 µm (**Figure 4**) enables easy separation due to good sedimentation. Moreover VP AEROPERL® P25/20 allows improved handling properties due to excellent flowability and a high tamped density.

FIGURE 4



Images of VP AEROPERL® P25/20

TABLE 1: Physico-chemical data of AEROXIDE® TiO_2 P25, AEROXIDE® TiO_2 P 90 and VP AEROPERL® P25/20

PARAMETER (TEST METHOD)	UNIT	AEROXIDE® TIO_2 P25	AEROXIDE® TIO_2 P 90	VP AEROPERL® P25/20
Specific surface area (BET)	m^2/g	50 ± 15	90 ± 20	50 ± 15
pH (in 4 % dispersion)		3.5 – 4.5	3.2 – 4.2	3.0 – 4.5
Tamped density (acc. to DIN EN ISO 787)	g/l	approx. 130	approx. 120	approx. 700
Moisture (2 hours at 105 °C)	wt.-%	≤1.5	≤ 2.0	≤ 2.5
Ignition loss (2 hours at 1000 °C based on material dried for 2 hours at 105 °C)	wt.-%	≤ 2.0	≤ 2.0	≤ 2.0
TiO_2 content (based on ignited material)	wt.-%	> 99.5	> 99.5	> 99.5
Average particle size (SEM)	µm	–	–	20

The data represent typical values and not production parameters.
Developmental products are labeled with the VP designation. Their commercialization depends on market response

2.6 PROPERTIES OF AERODISP® FUMED TITANIUM DIOXIDE DISPERSIONS

FIGURE 5

Quality of dispersions can vary significantly

In order to meet the customer requirements Evonik applies several posttreatment and handling technologies. Evonik's dispersion technology allows producing stable water based dispersions with aggregate sizes well below 0.1 µm.

To achieve these small diameters a high energy milling step is applied. These tailor-made dispersions are preferred in applications in which a very high transparency and a very high photoactivity are required.

TABLE 2: Physico-chemical data of AERODISP® W 740 X and VP Disp. W 2730 X

PARAMETER (TEST METHOD)	UNIT	AERODISP® W 740 X	VP DISP. W 2730 X
TiO_2 content (based on material ignited at 1000 °C)	wt. %	40 ± 1	30 ± 1
pH (DIN EN ISO 787/9)		5 – 7	3 – 7
Viscosity (Brookfield 50 rpm, 20 °C)	mPa s	< 3000	< 3000
Aggregate size (d–50 value)	µm	< 0.1	< 0.1
Density (20 °C)	g/cm^3	1.5	1.3

The data represent typical values and not production parameters.
Developmental products are labeled with the VP designation. Their commercialization depends on market response.

3. Photocatalytic Applications

3.1 FUNDAMENTALS

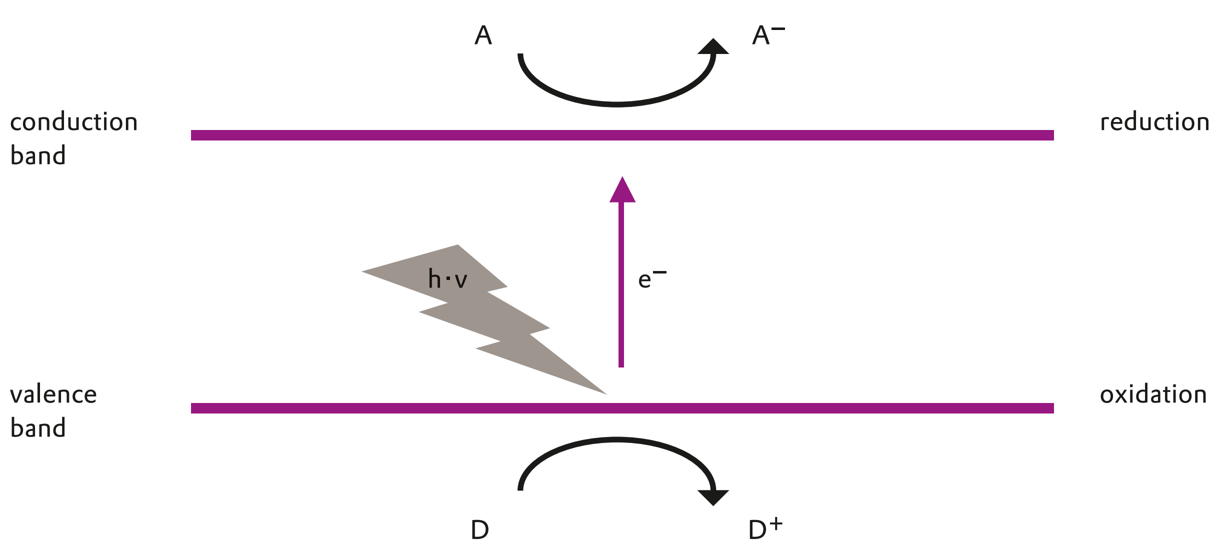
In order to understand semiconductor photochemistry, three modes of action need to be discussed: Photomineralization, photosterilization and photoinduced super hydrophilicity [5, 6, 7].

Titanium dioxide is a light-sensitive semiconductor, and absorbs electromagnetic radiation in the near UV region. The energy difference between the valence and the conductivity bands in the solid state is 3.05 eV for rutile and 3.29 eV for anatase, corresponding to an absorption band at < 415 nm for rutile and < 385 nm for anatase [8, 9].

Absorption of light energy causes an electron to be promoted from the valence band to the conduction band **(Figure 6)**. This electron and the simultaneously created positive "electron hole" can move on the surface of the solid where it can take part in redox reactions [10]. For example, water molecules can be oxidized, which are commonly adsorbed onto the titanium dioxide surface, generating $OH^{\bullet}$ radicals. These radicals are a far stronger oxidizing agent than either ozone or chlorine, both known as strong oxidants. On the other hand, reduction of oxygen forming superoxide anions ($O_2^{-\bullet}$) and in a second reduction step peroxide anions (O_2^{2-}) can occur. These anions bear intermediate oxidizing power. All these oxidizing species can cause complete oxidation of organic compounds to carbon dioxide and water [11].

The anatase form requires higher light energy than the rutile form, but shows a stronger photoactivity. This can be explained with the longer lifetime of the excited state in anatase and the better adsorption of oxygen in anionic form at the anatase surface [12].

FIGURE 6: Basic principle of the photoactivity of titanium dioxide



3.2 PHOTOMINERALIZATION

Depending on the reactions conditions, organic compounds can be fully mineralized to the following end products:

organic molecules → $CO_2 + H_2O$

organic **N**-compounds → $HNO_3 + CO_2 + H_2O$

organic **S**-compounds → $H_2SO_4 + CO_2 + H_2O$

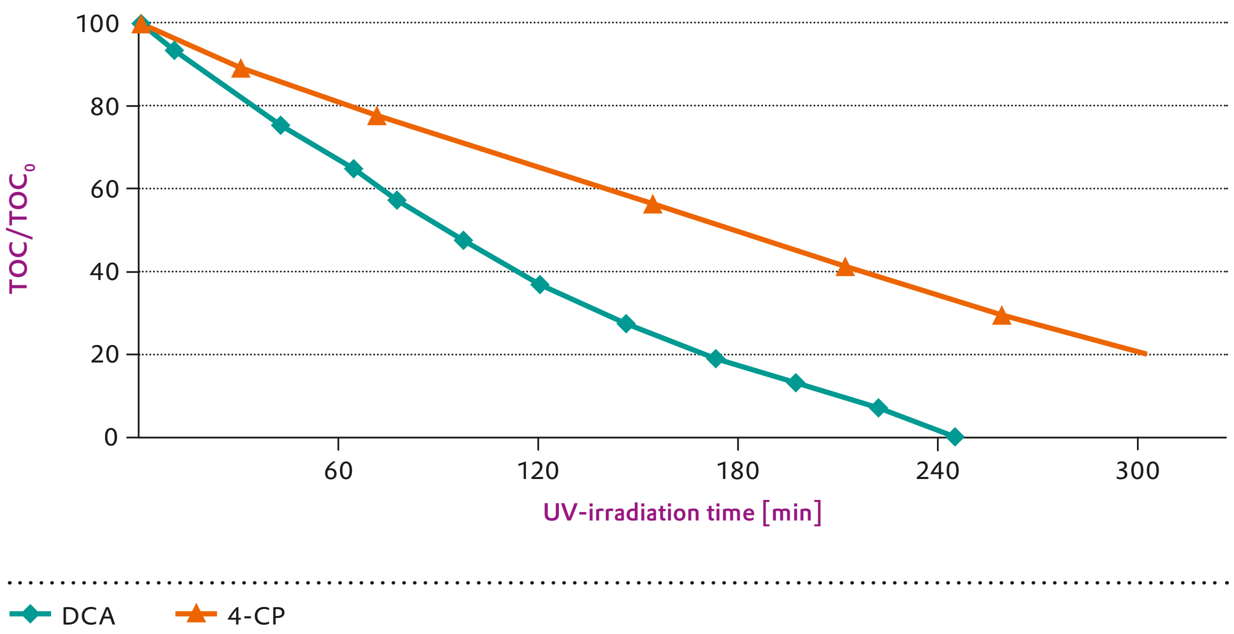
organic **Cl**-compounds → $HCl + CO_2 + H_2O$

Because the reactions take place at the surface of a solid, diffusion to the catalyst surface is the rate-determining step. In liquid phase reactions, the generation of various intermediate decomposition products occurs. In some cases, these intermediate products inactivate the catalyst surface [13].

Reactions found in the literature using AEROXIDE® TiO_2 P25 and UV-light include the complete decomposition of phenol [14, 15], chlorophenols [16], nitroaromates [17], aromatic amines [18], agricultural effluents [19], and crude oil in water [20].

Figure 7 shows typical decomposition rates of 4-chlorophenol and dichloroacetic acid using AEROXIDE® TiO_2 P25 irradiated with a 500 W high-pressure mercury vapor lamp (concentrations: 1 g/l titanium dioxide catalyst; 120 mg/l chlorohydrocarbon; TOC = total organic carbon).

FIGURE 7: Decomposition of 4-chlorophenol (4-CP) and dichloroacetic acid (DCA) using AEROXIDE® TiO_2 P25



3.3 PHOTOSTERILIZATION

As mentioned above, radicals are formed on the titanium dioxide surface when it is irradiated with UV light. These radicals can also attack the cells of microorganisms, so that nanostructured titanium dioxide can effectively be used to inhibit the growth of bacteria, viruses, algae, yeast, mold, and other microorganisms on surfaces or in liquids. AEROXIDE® TiO_2 can also be used in coatings for surfaces helping to prevent discoloration due to extensive algae (e.g. gloeocapsa magma) growth.

3.4 PHOTOINDUCED SUPER-HYDROPHILICITY

Another mechanism is discussed for the so-called photoinduced super hydrophilicity observed on surfaces coated with thin TiO_2 films: UV excitation produces electron-hole pairs; these holes can oxidize bridging O_2-species to oxygen; thus creating "oxygen vacancies". Following adsorption of water a hydroxylation takes place and the surface properties are changing to a considerably more hydrophilic behaviour. Water contact angles of less than 5° can be measured and such surfaces are considered as being super hydrophilic. The process is reversed in the dark.

The self cleaning and defogging action of such surfaces arises from the fact that dirt and grime that collects on the surfaces is readily washed away by water.

3.5 EXAMPLE APPLICATIONS

There are several opportunities for making use of the photocatalytic properties. An excellent summary, especially taking into account the Japanese market is described in a booklet entitled "TiO_2 Photocatalysis – Fundamentals and Applications", Bkc, Inc. Tokyo (1999) by A. Fujishima, K. Hashimoto and T. Watanabe. In addition a more recently published overview can be found at [1].

TABLE 3: Photocatalytic effects and example applications

EFFECT	EXAMPLE
Photomineralization	Depolluting cement
	Self cleaning paint
	Air & water purification
	Deodorisation
Photosterilization	Antimicrobial surfaces (e.g. roofings and tiles)
Photoinduced super hydrophilicity	Self cleaning tiles and glasses
	Antifogging mirrors

4. Literature

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