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Characterization of Nano-Sized Titanium Dioxide

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Titanium dioxide pigments are finely divided white powders which are chemically inert or unreactive, in contrast to all commonly used materials for paper filling or coating systems, and are used to increase opacity. Titanium dioxide is classified based on its crystalline arrangement as either anatase or rutile. The high light reflectivity, low light absorption and small particle size make this pigment ideal for obtaining high opacity. In their finely divided form, these pigments are very intensely white. With this characteristic, even at low concentration levels, titanium dioxide pigments are a major contributor to the optical performance of brightness and opacity of paper. If only brightness is needed, calcium carbonate is a more cost-effective pigment.

Titanium dioxide finds universal application as a whitening and brightening agent, and is extensively used in the paint, textile, rubber, plastic, paper, cosmetic, leather, ceramic, and food industry. In less purified grades, it is the basic natural pigment used in white house paint. There are two crystalline modifications of titanium dioxide: rutile and anatase. Only the anatase variety finds its use as a color additive for foodstuffs. The principal uses of this natural white pigment are in sub-coating of confectionery panned goods and in drinks. As with the other food grade pigments it must be dispersed to give full coloring power. It disperses quite easily in liquids. It remains suspended only in viscous liquids and semi-solid materials. Titanium dioxide is also used along with sugar syrup for usage in the sub-coating of tabletted products. This color additive has a permanent place in the list of food additives.

Titanium dioxide is a catalyst for the sunlight energized oxidation of organic polymers, and the semiconductor mechanisms involved are reasonably well understood. At its surface, titanium dioxide transforms the energy of ultraviolet light into chemical energy. This chemical energy reacts with oxygen and water to generate two free radicals, hydroxyl and peroxyl:

$$\eta v[TiO_2] + O_2 + H_2O \nearrow OH^{\bullet} + HO_2^{\bullet}$$

The free radicals can, in turn, react with and destroy almost any organic molecule:

$$OH^{\bullet} + HO_2^{\bullet} + \text{—}CH_2\text{—} \nearrow CO_2 + H_2O$$

As a result, paint films pigmented with unprotected titanium dioxide are said to chalk, that is, turn into dust by prolonged outdoor exposure. For anatase pigment, the effect is severe enough to all but preclude its outdoor use. Paint films pigmented with conventional rutile are less prone to degradation, but the chalking problems of titanium dioxide pigments were all but resolved by chemistry developed by Iler and subsequent extensions. This chemistry made it possible to encapsulate certain inorganic particulates in shells of silica glass. Today, silica encapsulated rutile pigments perform exceedingly well in even the most demanding outdoor applications.

Two other advantages of TiO_2 are its chemical stability and the fact that it can be manufactured in an optimum crystal size of ca. 0.2 μm. As a consequence of their high degree of light scattering and low absorption of visible light, titanium dioxide pigments are the whitest and brightest of all the commercial white pigments. There are three naturally occurring crystallographic forms of titanium dioxide: anatase, brookite and rutile. Rutile is the most common and stable form. Its structure, shown in Figure 1, is based on a slightly distorted hexagonal close-packing of oxygen atoms with the titanium atoms occupying half of the octahedral interstices. Anatase and brookite are both based on cubic packing of the oxygen atoms, but the coordination of the titanium is again octahedral.

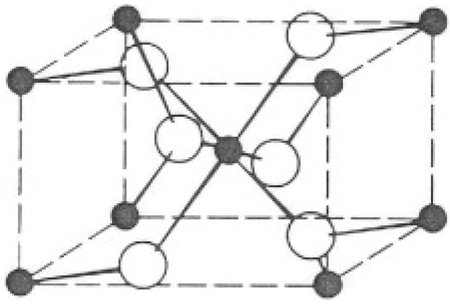

Figure 1. Unit cell of rutile. Black circles: titanium atoms; open circles: oxygen atoms.

Figure 2. Photograph of a crystal of anatase.

Only anatase and rutile are manufactured on a large scale. Anatase was the first to become commercially available, but rutile is now the more important. The small pigmentary crystals of both forms are strong absorbers of UV light: this leads to photo-catalysed degradation of organic molecules unless the TiO_2 surface is protected. The particularly high photoactivity of anatase renders it unsuitable for exterior finishes because of the rapid degradation of the protective film. The pigmentary rutile crystals are generally coated with alumina and/or silica and treated with organic compounds.

Titanium dioxide (TiO_2) is a multifunctional material of interest for a broad range of applications ranging from (photo)catalysis to energy storage. The low toxicity and the abundance of titanium have favored the emergence of Ti-based compounds. Over the years, several approaches have been developed to modify/improve the properties of TiO_2. These included reducing the particle size to the nanoscale, controlling their morphology, and doping with heteroatoms to tune the electronic structure and structural features.

Anatase, a natural mineral, is one of the polymorph of TiO_2. The name “anatase” is derived from the Greek word “ana,” which means “elongated” and refers to the mineral crystal's shape (Figure 2). Using Wulff construction and calculated surface energies, the equilibrium shape of a TiO_2 anatase crystal has been predicted to consist of a truncated octahedron, which agrees with experimental observations. The crystal exposes only two types of surfaces with 96% of (101) and 4% of (001) surface. Calculations of surface energies indicate 0.44 J/m^2 and 0.90 J/m^2 for (101) and (001) surface, respectively, highlighting the highest stability for the (101)-type surface. The difference of stability of the two types of surfaces has been explained in terms of the density and nature of undercoordinated Ti species. The stable (101) surface exhibits 50% titanium in a sixfold coordination mode and 50% titanium in a fivefold coordination mode, whereas the metastable (001) surface contains only fivefold coordinated Ti featuring enhanced interfacial properties. Such a difference in surface reactivity has led to extensive researches on the preparation of TiO_2 crystals with specific facets.

The role of anions during solution-based synthesis of inorganic compounds is multiple. Depending on their complexing ability toward cations, anions can drive the nucleation/crystallization toward a specific crystal structure. They can also adsorb onto surfaces thus orienting, in a particular direction, the growth of particles.