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Research Article

A Review on Nanoparticles of Titanium Dioxide: Characteristics, Methods of Synthesis and Their Application in Organic Coatings

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ABSTRACT:
Nowadays, the use of inorganic pigments to improve the polymeric coatings properties and nanocomposite coating with optimized properties is very common. Titanium dioxide is a white pigment used in the coatings industry is the most important because of the abundance of visible light may be used efficiently disperses.
Titanium dioxide is available in two main crystal structures of anatase and rutile. Titanium dioxide rutile pigments due to better disperse of the light, reliability, and durability are preferred to anatase. Titanium dioxide due to chemical resistance, photocatalytic properties, self- cleaning properties and non-toxicity is a good choice as a pigment. In this article, we will become familiar with different types of titanium dioxide nanoparticles, their photocatalytic performance, the environment factors, different methods of production and synthesis of nanocomposite and nanocomposite coatings corrosion resistance properties.

Key words: titanium dioxide, photocatalytic properties, corrosion resistance.

INTRODUCTION:

Organic coatings are common due to cheapness, versatility and relative ease of use and are as one of the cheapest means of corrosion control. However,they arevulnerable against a variety of factors such as high corrosive environment, ultraviolet radiation or mechanical shocks. One of the ways to improve physical, mechanical, optical, and anti-corrosion coating properties is the use of inorganic pigments(Jafari, 2015). Titanium dioxide for many years(approximately 90 years) due to the luminosity and refractive index (property that indicates the opacity that the material gives to background matrix) is the most common white pigment used in products such as paints, coatings, adhesives, paper, cardboard, plastics, rubber, printing ink, textile and knitting, catalysis systems, ceramics, laminate flooring, ceilings, cosmetics, pharmaceutical industry, water purifier agents, food colorings, the automobile industry etc.,. (Macwan, 2011). When the pigment is combined with other colors,a soft dough is achieved. Adding a small amount of titanium dioxide to some material improves refractive index(Kuznesof, 2006).

Titanium dioxide is insoluble in water, hydrochloric acid, dilute sulfuric acid and organic solvents. Slowly is solved in hydrofluoric acid and hot concentrated sulfuric acid. In alkaline solutions is almost insoluble(Kirk-Othmer, 1997).It is recommended for use in alkyd and latex paints for interior semi-gloss finish. This pigment is easily dispersed, makes good gloss and has the most coverage in the presence of a range of transparent material (Matskevich, 1977).Ultraviolet photons have high-energy and simply destroy materials. This phenomenon usually happens by broke through chemical linkages that is called photochemical decomposition (Fujishima, 2000). Titanium dioxide is able to absorb ultraviolet radiation and due to its photocatalytic properties,it reduce harmful effects.

Application and efficiency of titanium dioxide is strongly influenced by the crystal structure, shape and size of its particles. Threecommon crystalline structure of titanium dioxide are rutile, anatase andBrookite. Crystalline basic units in all three phases are TiO_6 octahedrons. These three phases difference is in the arrangement of the octahedron (Figure 1). Thermodynamically rutile is the most stable phase of titanium dioxide in normal pressure and the other two phases are semi-stable. Anatase is stable at ordinary temperatures but at temperatures up to 550 degrees Celsius, slowly converts to rutile. When the particle size is reduced to the nanometer range, startingtemperature of the transformation compared to mass mode reduces and temperature range of transformation extends(Chen X. a., 2007).

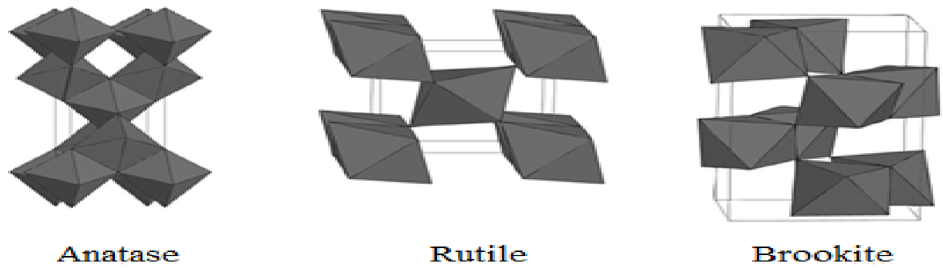

Figure 1: Schematic of titanium dioxide crystal structures.

Rutile is stable phase at high temperature and is obtained in more activities to obtain titanium dioxide. Rutile is a phase of titanium dioxide which is more studied and as a semiconductorwith much energy gap, is very useful in fundamental research such as optical and electrical devices. However, anatase phase at temperatures below 550 ° C can be stable in powdered form, ceramics, natural or synthetic crystals, thin films (Bickley, 1991)(Ohno, 2003).

Rutile and anatase structural differences

Rutile and anatase differences in the internal structure are shown on their properties. For example, rutile is more densethananataseandits gap is narrower, thus the catalytic activity of rutile excited electrons is more than anatase. Therefore, rutile is better against ultraviolet radiation (UV), while anatase is good forlight catalyze. Most of titanium dioxide in the anatase phase is produced as a white powder; whereas different types of rutile are cream to white in color dependent on the physical form affected by the reflection of light can even have a lighter color.

In order to improve the technological properties, titanium dioxide may be covered by small amounts of alumina and silica, like the coatingsthat prevent possible reactions between the highly reactive surfaces of tiny crystals of titanium dioxide and the matrix in which pigment are scattered , and improve titanium dioxide dispersion in the matrix (Kuznesof, 2006). The electrical and optical properties of anatase and rutile show that the biggest difference between the two phases is larger optical band gap and lower effective mass of anataseelectron to rutile. Rutile has one of the highest refractive indexes and has high dispersion.Anatase phase can be created at below 600 degrees Celsius during the crystallization process, but at higher temperatures, it transforms to more stable form of rutile. Low temperature anatase phase in the first place is considered due to production of effective electron holes on UV irradiation and photocatalytic effect. Rutile is stable at high temperatures, shows less photo activity, and is used for coatings such as optics, photonics, and microelectronics. Thin films of titanium dioxide due to special properties such as chemical stability, high refractive index, high dielectric constant and high transparency has applications in the visible region (Matskevich, 1977)

Photo catalyticperformance of titanium dioxide

Titanium dioxide has high flexibility against UV, and due to advantages such as being non-toxic, chemical stability at high temperatures and permanent stability in the presence of UV is very popular for practical applications. For example, Nano industry development and technology to improved performance of films resistant to UV, with the addition of titanium dioxide, has created new ways.The exact mechanism of titanium dioxide UV reflection clearly is not identified and researchers have different views on this issue(SCCNFP, Opinion of the scientific committee on cosmetic products and non-food products intended for consumer concerning titanium dioxide, 2000).Some believe that reflection or spread of UVis due to significant refractive index, and some other believe that it is due to semiconductor properties of the material. Others claim that in a mass of titanium dioxide, only nanometer-sized particles absorb UV radiation and particles with larger sizes are less able to do so. Due to the different and often conflicting views about this issue, it seems that more extensive studies must be done on this issue.

Environmental issues

Since the beginning of use of titanium dioxide as a commercial product,there was no concern about the health risk to consumers or other people. These facts are based on four large epidemiological studies of more than 20,000 workers in the titanium dioxide production industry in North America and Europe and it was included, there is no concern about the damaging effects on lung or cancer (Wu, 2002)(Boffetta P. G., 2001)(Boffetta P. S., 2004)(Chen J. a., 1988)(Fryzek, 2003). Titanium dioxide has high capacity to absorb UV light. In addition, itis resistant to the color change in the presence of UV radiation (Macwan, 2011). The possibility of being exposed to titanium dioxideis very low, because it is usually entered to matrix very limitedly (asthe amount used in the production of paints and plastics). Therefore, the risk of exposure and inhalation of the substance is not intended for all people (Macwan, 2011). Studies show that particles of titanium dioxide (pigment or very small sizes) can notpenetrate and damage skin (Gamer, 2006). In recent years, titanium dioxide considered important as a photo catalyst. Titanium dioxide photocatalytic activity is related to its crystalline structure, so many studies have been done on these dependencies. Recently it was discovered that combining titanium dioxide anataseand rutile anataseis more photocatalytic than pure forms(Products, 2000).

Synthesis methods

Several methods such as sol-gel [5], hydrothermal (Bavykin, 2006)(Yin, 2001), solvothermal(Yang, 2009)(Roy, 2011) and emulsion sedimentation (Chhabra, 1995), mechanochemical(Billik, 2007), radio-frequency thermal plasma (Li, 2007)(Seo, 2012), chemical vapor deposition method (Rausch, 1993) andMicro-Mixing Technique (Chen G. L., 2004) are obtained for the synthesis of nanoparticles of titanium dioxide.

While titanium dioxide nanoparticles were prepared successfully by these methods,however,titanium dioxide nanoparticles synthesized by traditional methods areinadequate incrystalline structureand are spread too far apart (Kuznesof, 2006).

Manufacturing processes

Titanium dioxide pigments are produced in two commercial processes: sulfate and chloride. Both anatase and rutile are produced by both methods. Chloride process gradually became the dominant process because it produces better pigment and has less waste. Sulfate method for the first time in 1931 was used for anatase and then in 1941 it was used for rutile. In this process, the ore of titanium is dissolved in sulfuric acid and a solution of titanium, iron and other metals sulfate is obtained. Then steps including chemical reduction, purification, sedimentation, washing and calcification are performed, toproducedtitanium dioxide pigment. Anatase or rutile crystal structure is determined by nuclearization and calcification (Kuznesof, 2006).

Due to the cost and environmental problems posed by the sulphate method, most of production capacity is dedicated tochloride method. Older production units that work with the sulphatemethod should follow stricter environmental requirements with recycling of waste acid and burning metal sulfates to recover sulfur trioxide to improve the process.

Corrosion resistance applications.

Nano-titanium dioxide pigments can enhance corrosion resistance. Mahulikar et al worked on anti-corrosion properties of nanocomposite coatings based on epoxy- polyaniline and titanium dioxide. The results of immersion corrosion tests showed that in the presence of titanium dioxide nanoparticles corrosion resistance rises to an acceptable level (Mahulikar, 2011). Shen et al worked on the corrosion resistance properties of Nano-particles of titanium dioxide coatings on 316 stainless steel substrate by sol-gel method. Electrochemical impedance spectroscopy showed improvement of corrosion resistance properties in the presence of titanium dioxide nanoparticles (Shen, 2005). In another study on anti-corrosion properties of nanocomposite coatings based on Nano-titanium dioxide and polyaniline, results showed improvement in corrosion resistance properties in the presence of titanium dioxide nanoparticles. (Radhakrishnan S, 2009). Lenz et al examined the anti-corrosion properties of polypyrrole- -titanium dioxidenono-composite. The results of weight loss and salt spray tests showed improved resistance to corrosion in the presence of titanium oxide. (Lenz, 2003). improved anti-corrosion properties in the presence of titanium dioxide nanoparticles is due to the barrier properties of the pigments in the coating and thereby reduction of ions transfer and electrolytes in the presence of nano-particles.

It should be noted dissipation of titanium nanoparticles in the polymeric matrix is very important. Nanoparticles accumulation in one spot decreased corrosion resistance properties of these coatings markedly.

CONCLUSION:

Mineral pigments have a special role in reducing the corrosion. One of the most useful white mineral pigment is titanium dioxide. This pigment hassignificant photocatalytic properties. Titanium dioxide pigment has three network structures of rutile, anatase and is Brookite. In the meantime, rutile crystal structure is more stable than the other two modes. The pigments are used in organic coatings for various reasons such as high photocatalytic properties, self- cleaning properties, optimalanti-corrosion properties. The photocatalytic properties of the pigments are related to their highenergy gap and high reflection coefficient of this pigment. Corrosion resistance properties are due to the barrier properties of the pigments in their matrix in the presence of corrosive materials and electrolyte. Due to the special properties of the pigments,it is expected in the future much more of titanium dioxide powders will be used in various industries, including the food, health and the coating.

REFERENCES:

1. Bavykin, D. F. (2006). Protonated titanates and TiO2 nanostructured materials: synthesis, properties, and applications. *Advanced Materials, 18*(21), 2807-2824.

2. Bickley, R. G.-C. (1991). A structural investigation of titanium dioxide photocatalysts. *Journal of Solid State Chemistry, 92*(1), 178-190.
3. Billik, P. a. (2007). Mechanochemical synthesis of nanocrystalline TiO 2 from liquid TiCl 4. *Scripta materialia, 56*(11), 979-982.
4. Boffetta, P. G. (2001). Exposure to titanium dioxide and risk of lung cancer in a population-based study from Montreal. *Scandinavian journal of work, environment & health*, 227-232.
5. Boffetta, P. S. (2004). Mortality among workers employed in the titanium dioxide production industry in Europe. Cancer Causes.
6. Chen, G. L. (2004). Anatase-TiO 2 nano-particle preparation with a micro-mixing technique and its photocatalytic performance. *Materials Science and Engineering: A, 380*(1), 320-325.
7. Chen, J. a. (1988). Epidemiologic study of workers exposed to titanium dioxide. *Journal of Occupational and Environmental Medicine, 30*(12), 937-942.
8. Chen, X. a. (2007). Titanium dioxide nanomaterials. *synthesis, properties, modifications, and applications. Chemical reviews, 107*(7), 2891-2959.
9. Chhabra, V. P. (1995). Synthesis, characterization, and properties of microemulsion-mediated nanophase TiO2 particles. *Langmuir, 11*(9), 3307-3311.
10. Fryzek, J. C. (2003). A cohort mortality study among titanium dioxide manufacturing workers in the United States. *Journal of occupational and environmental medicine, 45*(4).
11. Fujishima, A. R. (2000). Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 1*(1), 1-21.
12. Gamer, A. L. (2006). The in vitro absorption of microfine zinc oxide and titanium dioxide through porcine skin. *Toxicology in vitro, 20*(1), 301-307.
13. Jafari, D. S. (2015). Evaluation of nanoclays effect on the physical and mechanical properties of polymer-based nanocomposite coating. *Journal of Studies in Color World, 5*(2), 19-33.
14. Kirk-Othmer. (1997). *Encyclopedia of Chemical Technology* (4th ed., Vol. 24). New York: John Wiley and Sons.
15. Kuznesof, P. a. (2006). Titanium Dioxide—Chemical and Technical Assessment. *JECFA*, 1-8.
16. Lenz, D. D. (2003). Application of polypyrrole/TiO 2 composite films as corrosion protection of mild steel. *Journal of Electroanalytical Chemistry, 540*, 35-44.
17. Li, J. I. (2007). Control of particle size and phase formation of TiO2 nanoparticles synthesized in RF induction plasma. *Journal of Physics D: Applied Physics, 40*(8), 2348.
18. Macwan, D. D. (2011). A review on nano-TiO2 sol–gel type syntheses and its applications. *Journal of Materials Science, 46*(11), 3669-3686.
19. Mahulikar, P. J. (2011). Performance of polyaniline/TiO2 nanocomposites in epoxy for corrosion resistant coatings. *Iran Polym J, 20*(5), 367-376.
20. Matskevich, L. a. (1977). Titanium dioxide optical coatings. *Optiko Mekhanicheskaia Promyshlennost, 44*, 41-43.
21. Ohno, T. T. (2003). Synergism between rutile and anatase TiO 2 particles in photocatalytic oxidation of naphthalene. *Applied Catalysis A: General, 244*(2), 383-391.
22. Products, E. K.-F. (2000). Opinion of the Scientific Committee on Cosmetic Products and Non-Food Products Intended for. *Adopted by the SCCNFP During the 12th Plenary*.
23. Radhakrishnan S, S. C. (2009, January 30). Conducting polyaniline–nano-TiO 2 composites for smart corrosion resistant coatings. *Electrochimica Acta, 54*(4), 1249-1254.
24. Rausch, N. a. (1993). Thin TiO2 films prepared by low pressure chemical vapor deposition. *Journal of the Electrochemical Society, 140*(1), 145-149.
25. Roy, P. B. (2011). TiO2 nanotubes: synthesis and applications. *Angewandte Chemie International Edition, 50*(13), 2904-2939.
26. SCCNFP. (2000). *Opinion of the scientific committee on cosmetic products and non-food products intended for consumer concerning titanium dioxide*. Colipa.
27. Seo, J. a. (2012). Thermal plasma synthesis of nano-sized powders. *Nuclear Engineering and Technology, 44*(1), 9-20.
28. Shen, G. C. (2005). Corrosion protection of 316 L stainless steel by a TiO 2 nanoparticle coating prepared by sol–gel method. *Thin Solid Films, 489*(1), 130-136.
29. Wu, M. L. (2002). Sol-hydrothermal synthesis and hydrothermally structural evolution of nanocrystal titanium dioxide. *Chemistry of Materials, 14*(5), 1974-1980.
30. Yang, H. L. (2009). Solvothermal synthesis and photoreactivity of anatase TiO2 nanosheets with dominant {001} facets. *Journal of the American Chemical Society, 131*(11).
31. Yin, H. W. (2001). Hydrothermal synthesis of nanosized anatase and rutile TiO2 using amorphous phase TiO2. *Journal of Materials Chemistry, 11*(6), 1694-1703.