

# THE APPLICATION OF RUTILE NANO - CRYSTALLINE TITANIUM DIOXIDE AS UV ABSORBER

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**Key words:** titanium dioxide, rutile, co-precipitation method, UV absorber, surfactant

**Abstract:** Nano – crystalline titanium dioxide (TiO<sub>2</sub>) in rutile crystal form, generally used to indicate particles less than 100 nm in diameter, is mainly applied as pigment, adsorbent and UV absorber. The incorporation of a nano-sized titanium dioxide powder into a liquid media is made by dispersion process, that the final product consists of fine particles distribution throughout the medium. So it is regarded as necessary for us to investigate in detail the factors which may have important effect upon the homogenous distribution of TiO<sub>2</sub> nanoparticles in clearcoat as liquid media.

In this work, titanium dioxide nano-powders were prepared by the co-precipitation method. Using various techniques, including transmission electron microscopy (TEM) and X-ray diffraction (XRD), obtained powders were studied in order to find the possible elements of affecting the microstructures and grain size. The aim of this study is to determine the photostabilisation efficiency of TiO<sub>2</sub> in a clear coat as UV absorber considering the preparation of stable dispersions by using different surfactants and percentage of TiO<sub>2</sub>.

## Uporaba titanovega dioksida v rutilni kristalinični obliki kot UV absorber

**Ključne besede:** titanov dioksid, rutil, koprecipitacijska metoda, UV absorber, surfaktant

**Izvleček:** Nanodelci titanovega dioksida (TiO<sub>2</sub>) v rutilni kristalinični obliki so delci premera velikosti pod 100 nm, ki se večinoma uporabljajo kot pigment, adsorbent in UV absorber. Ko nanodelce TiO<sub>2</sub> vgradimo v tekoč medij z dispergiranjem, mora imeti disperzija ozko porazdelitev velikosti delcev. Analizirali smo dejavnike, ki vplivajo na homogenost porazdelitve velikosti nanodelcev TiO<sub>2</sub> v transparentnem premazu.

Nanodelce TiO<sub>2</sub> smo pripravili z koprecipitacijsko metodo. Da bi ugotovili, kaj vpliva na mikrostrukturo in velikost nanodelcev TiO<sub>2</sub>, smo uporabili različne analizne metode, med drugimi tudi presevno elektronsko mikroskopijo (TEM) in rentgensko praškovo difrakcijo (XRD). Cilj študija je bil določiti učinkovitost transparentnega premaza z nanodelci TiO<sub>2</sub> kot UV absorber v odvisnosti od priprave stabilne disperzije z uporabo različnih surfaktantov in deleža nanodelcev TiO<sub>2</sub>.

### 1. Introduction

The ultraviolet (UV) protection of organic and biological materials against photodestruction is of high practical interest. The protection can be realized by use of UV absorbers. UV absorbers are organic or inorganic compounds which absorb in the best case all UV light and are transparent for all visible light. UV absorbers are most frequently used in cosmetics to prevent sunburns and skin cancer /1-3/. Beside the protection of human skin, UV absorbers are often to protect materials properties of polymers or textiles /4, 5/.

Lignin in wood for instance highly absorbs ultraviolet light, which leads to radical induced depolymerisation of both lignin and cellulose or in other words to photodegradation of the wood substrate. Wood colour change is the first sign of its chemical modification when exposed to UV light /6 - 8/. One possibility of wood protection is the usage of pigmented coatings, where the pigments reflect the UV - radiation. However, in this case, the natural colour of the wood is changed. Consequently, for the last decade inorganic UV absorbers have received a great deal of attention in transparent wood coatings because of their function as UV blockers. One of the reasons for the limited commercial

use of certain nanoadditives is that they greatly affect the transparency of clearcoats because of its high tendency to agglomeration in dispersions. This is clearly undesirable in a treatment design to improve the longevity of clear varnishes, since the appeal of such finishes lies in their ability to maintain the natural appearance of wood /6/.

UV absorbers, based on fine nanoparticled titanium dioxide and zinc oxide (ZnO) have proved to be efficient /9/. Both TiO<sub>2</sub> and ZnO are commonly used as white pigments. TiO<sub>2</sub> in the rutile form is the most common white pigment due to its extremely high refractive index ( $n = 2,8$ ). Ultrafine TiO<sub>2</sub> and ZnO nanoparticles lose their capability to scatter visible light, but retain the ability to absorb UV light. The bandgap of ZnO (3,2 eV) is similar to that of TiO<sub>2</sub> in the anatase modification and a little larger than the rutile type. When using TiO<sub>2</sub> for UV protection the rutile type is more suitable due to its lower photocatalytic activity, which could destroy the organic surrounding matrix. The small particle of nano – crystalline titanium dioxide UV absorber can be synthesized using several methods. e.g. the sol – gel organic method /10, 11/, co-precipitation and micro-emulsion methods /12/ and hydrothermal method /13/. In this paper, titanium dioxide nano-powders were prepared by the liquid phase co-precipitation routes, typically involved

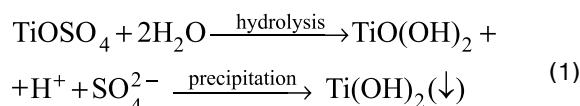
titanium dioxide particle growth steps, followed by aggregation, from high temperature treatment and control finished product particle size at the optimum required for performance. As already mentioned the biggest challenge of stable nanoparticle dispersion development is to prevent nanoparticles tendency to form agglomerates resulting in poor dispersion within the carrier matrix with low UV absorption efficiency. One of the ways to overcome this drawback is the addition of compatible surfactants.

The aim of our study was to determine the influence of the concentration of TiO<sub>2</sub> nanoparticles and different surfactants on dispersion homogeneity resulting as UV absorption efficiency of clearcoating.

## 2. Methods

### *Synthesis of titanium dioxide Nano Crystalline Particles in rutile crystal structure*

Synthesis of titanium (IV) oxide nanoparticles with rutile crystal structure takes place as described below [15, 16]. Regarding the stoichiometry of reaction (eq. 1) an appropriate amount of 12.5 % titanyl sulfate (TiOSO<sub>4</sub>) acid solution with density 1.4 g/cm<sup>3</sup> was hydrolyzed in a stirred tank and precipitated with an excess amount of 2.4-M aqueous solution of dialkylamide, which served as a precipitating reagent.



Precipitation was conducted for 6 hours at a constant temperature of 100 ± 2 °C. Pigmented nanoparticles of hydrolyzed titanium (IV) oxide (TiO<sub>2</sub>·xH<sub>2</sub>O·ySO<sub>3</sub>) obtained after the precipitation were sedimented with the addition of 0.33 % aqueous solution of anionic polyacrylic flocculent, separated from mother liquor in the next step and finally dried at temperature 120±2 °C. Dried nanoparticles of hydrolyzed titanium (IV) oxide were annealed for 2 hours at 900 °C in air in order to obtain pure rutile crystal structure. After annealing, rutile nanoparticles were deagglomerated in a high-energy horizontal zirconium attrition mill for 8 hours. Obtained nanoparticles were analyzed with X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and specific surface area (BET) measurements.

Deagglomerated rutile nanoparticles were surface treated with organic surface active agents (Byk 333, ethilen glycol) in high-energy horizontal attrition mill. The pH value was sustained between 8 and 9 using 25 % of ammonia aqueous solution in order to prepare stable and transparent pigmented aqueous dispersion of titanium (IV) oxide with rutile crystal form. The pH of a coating, in which we mixed in water dispersion of nanoparticles, was approximately 8.

### *Preparation of clearcoat with integrated rutile crystalline particles of TiO<sub>2</sub>*

We prepared clearcoat in the laboratory by mixing pure acrylic resin with styrene acrylic copolymer resin for 20 minutes. Commercial polysiloxane defoamer from Byk Additives&Instruments and previously prepared premix of chemical additives were added for optimal coating application properties like leveling and wetting. Then we add different glycols as coalescents, water, wax emulsion and flattening aqueous wax dispersion, both from Byk Additives&Instruments, during the mixing process. At the end nonionic rheology modifier from Rohm and Haas was mixed in for 20 minutes to achieve appropriate viscosity (100-200 mPas).

The dispersions of TiO<sub>2</sub> nanoparticles in liquid media were prepared by milling 30 wt.% of TiO<sub>2</sub> nanoparticles in rutile crystal form, water and different surfactants (Table 1). Water based dispersions of TiO<sub>2</sub> nanoparticles were then added to clearcoat and prepared for the testing.

Table 1: Samples and their composition.

Sample	Composition
1	clearcoating
2	clearcoating with TiO <sub>2</sub> nanoparticles ethilen glycol octanol 2
3	clearcoating with TiO <sub>2</sub> nanoparticles Byk 333 Byk 024

### *Transparency and photostabilization performance assessments*

Wood blocks measuring 15x7 cm<sup>2</sup> (longitudinal x tangential) x 0,5 cm width were cut from air dried boards from the specie pine. Two layers of clear coat of thickness of 200 µm were applied on pine blocks. Coated wood plates were used to assess weathering exposure degradation (QUV accelerated weathering tester, Q – PANEL LAB PRODUCTS, standard SIST EN ISO 11507:2002). Simulation of exterior use was done by six weeks weathering by an optimised cycle defined: 4h at (60±3) °C and 4h water shower at (50±3) °C. Only light of the solar type was activated on the QUV with sources type UVA-340 nm.

Color evaluation was done in the CIE L\*, a\*, b\* system. The initial value of the sample colour before exposure and after coating application was compared. Color difference (ΔE\*) was calculated with the following formula (eq. 1):

$$\Delta E^* = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2} \quad (1)$$

where L\* is the lightness from the black (0) to the blank (100), a\* (from green colour to red) and b\* (from blue to yellow) are the chromatic coordinates. The colour measurement of coated wood specimens was conducted using spectrophotometer (Datacolor SF600).

### 3. Results and discussion

Nano  $\text{TiO}_2$  powders were calcined at different temperatures and taken XRD (Fig. 1). It can be obviously seen that partial crystallization appears just after drying and the phase structure of the powder calcined at temperature below  $600^\circ\text{C}$  is mainly of anatase type. The phase transformation from anatase to rutile occurred at about  $600^\circ\text{C}$  and completed at about  $900^\circ\text{C}$ .

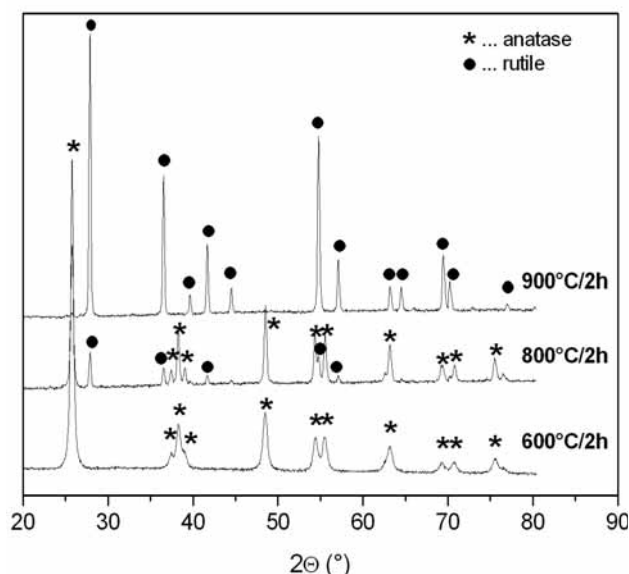


Fig. 1: The XRD pattern of nano-crystalline  $\text{TiO}_2$  at different calcination temperatures.

From the TEM images of the milled  $\text{TiO}_2$  powders presented in Fig. 2, finally dispersed particles with a relatively wide distribution of sizes, ranging from 20–70 nm for rutile and from 10–30 nm for anatase, together with almost the rounded shapes thereof, typical for milling treatments in general, can be observed.

Changes in colour of painted pine wood samples (wood discolouration) during UV exposure have been widely used to assess wood degradation [11, 17–20]. By measuring the colour change of the coated wood with different UV absorbers during artificial weathering it is possible to obtain information on their efficiency. We prepared three different samples of clearcoating with and without addition of  $\text{TiO}_2$  nanoparticles as defined in Table 1. The concentration of  $\text{TiO}_2$  nanoparticles in clearcoat was also varied. For weathering simulation colour changes  $\Delta E^*$  during the UV irradiation of samples of UV protection clear coat on wood substrate are displayed in Fig 3. The data revealed a number of interesting features. Sample 3 with polyether modified dimethylpolysiloxane copolymer surfactant proved to be the most efficient in inhibiting colour change. We also noticed that different concentration of  $\text{TiO}_2$  nanoparticles does not have a significant influence on photostability of the clear coat.

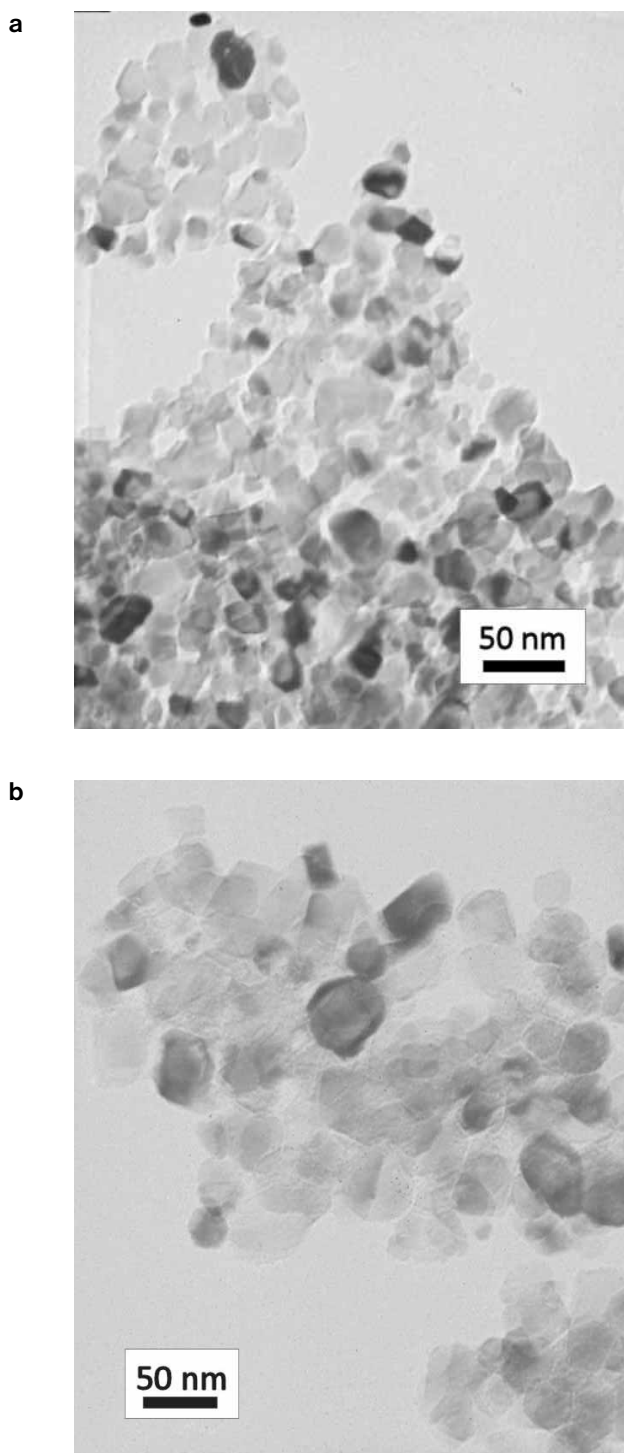
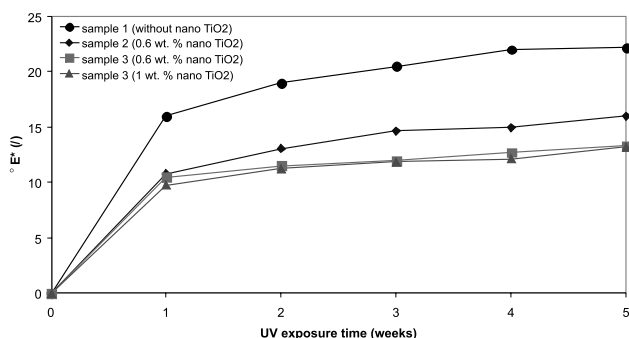


Fig. 2: The typical TEM micrographs of the nano -  $\text{TiO}_2$  powders calcined at a.)  $600^\circ\text{C}$  (anatase crystal form) and b.)  $900^\circ\text{C}$  (rutile crystal form).

### 4. Conclusion

A successful pathway for the preparation of titanium (IV) oxide in rutile crystal form and some of the basic properties of a material, such as UV-absorbance and photostabilization, have been presented. Hydrolysis of titanyl sulfate ( $\text{TiOSO}_4$ ) followed by a precipitation with dialkylamide, and the subsequent calcinations in air at  $900^\circ\text{C}$  for 2h, com-



**Fig. 3:** Colour change vs. UV irradiation (weeks) in QUV apparatus for different samples of UV protection clearcoating.

prised the basic synthesis steps toward the final material. The pure rutile particles produced at 900 °C were in the range of 40-100 nm, whereas the final anatase nanoparticles were almost uniformly ~ 20 nm in size.

By measuring the colour change of the clear coated wood with different UV absorbers during artificial weathering we revealed that the clearcoating with 0,6 and 1 wt. % of rutile TiO<sub>2</sub> nanoparticles stabilized by polyether modified dimethylpolysiloxane copolymer surfactant surface additive (Byk 333) has the best photostabilization performance of UV protection clear coat. We also noticed that UV efficiency did not improve when the concentration of TiO<sub>2</sub> nanoparticles was higher. We assume that higher concentration of TiO<sub>2</sub> nanoparticles leads to agglomeration. Nevertheless we improve the photostability of the clear coat by the addition of stable dispersion of TiO<sub>2</sub> nanoparticles in rutile crystal form for more than 40 % according to colour change of protected wood panels.

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