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Nano-Scaled Titanium Dioxide – Properties and Use in Coatings with Special Functionality

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Summary: Nano-scaled titanium dioxides are used as UV-absorbers and to obtain certain color effects in pigmented coatings. For this they are generally required to have good phototresistivity. This is accomplished by doping of the crystal lattice with other elements than titania and by surface treatment with layers of inorganic substances. Currently the use of photoreactive nano-scaled titanias is being studied to formulate self cleaning and antimicrobial coatings.

Keywords: Nano-scaled titanium dioxide; inorganic UV-absorbers; frost effect; blue color shift; titanium dioxide photocatalyst

Introduction

Titanium dioxide white pigments are manufactured so that they scatter all wavelengths of the visible spectrum between 380 and 700 nm optimally. Contrarily, nano-scaled titanias that were originally developed with the aim to achieve transparent UV protection ideally scatter no visible light at all. In practice, there is , however, some selective scattering of blue light so that apart from the use as UV absorbers these materials are also found in metallic coatings and in other pigmented coatings where they lead to interesting color effects.

Titanium dioxide is itself also a photocatalyst. New research is focussing on the development of materials that will enable the formulation of self cleaning and/or anti microbial coatings.

The frost effect

When nano-titanias are put into metallic base coats these formulations obtain a viewing angle dependent appearance (1). When observed at a facial angle the coatings look yellowish whereas a slanting viewing angle brings forth a blue color tone.

Figure 1 helps to explain this phenomenon The incident light with all the wavelengths of the visible spectrum penetrates the coating. The red and green parts of the spectrum are hardly scattered so that they are reflected by the metallic pigments in an angle close to the incident angle. The blue part of the spectrum is preferentially scattered so that the reflected blue light leaves the paint film in a low angle.

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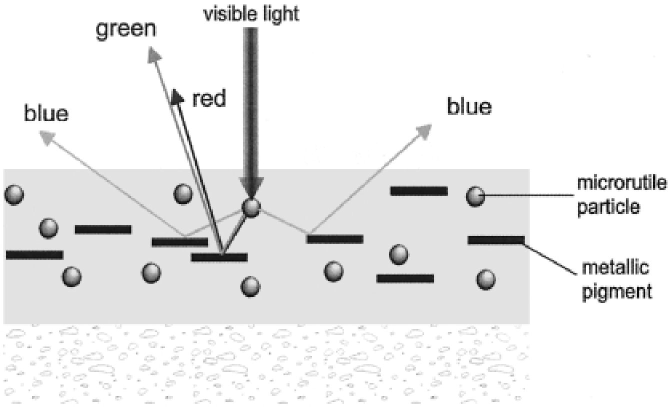


Figure 1. Schematic representation of scattering phenomena leading to the frost effect

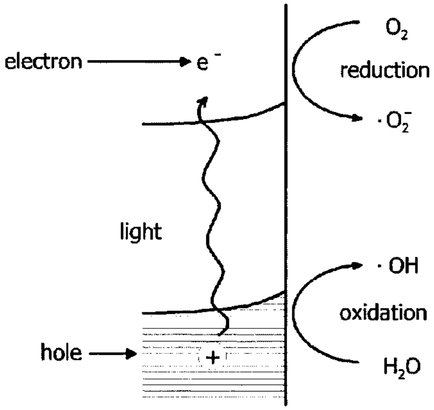
Blue color shift

When combined with colored pigments nano-titanias will change the appearance of the colored pigments by selectively scattering blue light (2). Unlike the frost effect, this effect is independent from the viewing angle. Nano-titanias may be used to turn a red color into magenta or to formulate very clean blue colors in combination with copper phthalocyanines, for example. Although the effect resembles the well known “carbon black undertone” (CBU) effect of conventional titanium dioxide pigments (3) it is still quite different since nano-titanias have a low CBU when tested under standard conditions and, more important even, they lack the scattering power in the visible region of the spectrum so that there is no lightening effect on the coating.

Photoactivity of TiO_2

When UV light is absorbed by titania electrons from the valence band are hoisted into the conduction band of the semi conductor TiO_2 and so called excitons (separated charges) are formed. The electrons may migrate to the surface of the crystal where they can reduce species at the interface of the particle. Likewise, the positive holes remaining in the valence band may by successive electron transfers from their neighbors rearrange to the TiO_2 surface where they can oxidize adjacent molecules. Figure 2 depicts the generation of excitons and the type of reactions possible from then on.

This so called “chalking cycle” consisting of an oxidation reaction and a reduction reaction is well known (4) and in the presence of water and oxygen leads to a deterioration of the resin matrix surrounding the titania particles. Interestingly, this happens more pronounced on the illuminated sides of the pigment particles and less on the sides away from the light. At the end, the particles may even rest only on a pillar of resin (5). Since they are then no longer firmly attached they are easily wiped off the surface of a coating, thus causing the expression "chalking".



Reaction mechanism of TiO_2 photocatalysis

Figure 2.

In paint industry chalking is normally disliked although there are some exceptions such as road marking paints and also in some exterior wall paints. The reason is because chalking goes along with a self cleaning effect.

It is well known that titania in the crystal modification of anatase chalks more than rutile. This is surprising at first because the absorption edge of anatase (385nm or 3.29eV) is shifted more to the ultraviolet range than is the case for rutile (415nm or 3.05eV). Hence, under natural daylight conditions where far less photons are available below 385 nm than in the range between 385 and 415 nm less excitons will be formed in the case of anatase in comparison to rutile. Gesenhues (6) attributed the higher photocatalytic activity of anatase to the energy level of a positive hole in the valency band which, according to him, is 210mV lower than that of rutile. Therefore, the oxidation potential of a positive hole in an anatase crystal is higher than a comparable hole in a rutile crystal.

In order to suppress the photoactivity of rutile pigments the crystal lattices are doped with aluminum ions . The aluminum is introduced as $AlCl_3$ along with $TiCl_4$ into the burner in the chloride process. In the sulfate process, different aluminum chemicals are added prior to the calcination stage. The aluminum ions mostly take the place of titanium ions in the crystal lattice (7) and act as sites where exciton recombination preferentially takes place.

A further trick of the trade is to coat the particles with layers of inorganic matter. Although it is quite evident that this posttreatment is beneficial in decreasing the photoactivity the mechanism is unclear and the impact of a certain posttreatment is certainly not foreseeable. It is understood that the coverage should be 100% and that there is a certain threshold value where a further increase in thickness fails to further improve lightfastness or weatherability. The improvement with a certain kind of inorganic posttreatment depends to some extent on the core particle that is coated. For that reason, different pigment manufactureres have their own preferences when it comes to inorganic posttreatments. In the last fifty years more than two thousand patents dealing with inorganic surface treatments of titanium dioxide pigments have been filed (8)!

Nano-scaled titanias as UV absorbers

Since nano-titanias have a much higher surface area in comparison to pigment grades it is more difficult to suppress photoactivity. When durability is aspired the same steps like in TiO_2 pigment must be employed. As far as inorganic posttreatments are concerned their levels have to be raised, of course. Figure 3 shows an example for the effect of an aluminum oxide posttreatment on the photoactivity of a nano-titania with a particle diameter of approximately 20nm. The ordinate depicts a measure for photoactivity in a standard test. It is seen that in this particular case 12 weight% of inorganic posttreatment are necessary to inhibit photoactivity.

When manufactured accordingly, nano-scaled titanias in the rutile modification may be used as transparent UV-absorbers for substrate- as well as matrix-protection. In substrate protection the object that is to be protected from harmful UV radiation is covered with a clear coat containing about 0.5 to 1.5% pigment volume concentration (PVC) of nano-titania. An example for this is wood protection (9). As the Lambert Beer law is in effect, the PVC may be reduced if the film thickness is raised and vica versa. For matrix protection, that is when the nano-titania plays the role of protecting the resin itself, higher PVC levels are necessary.

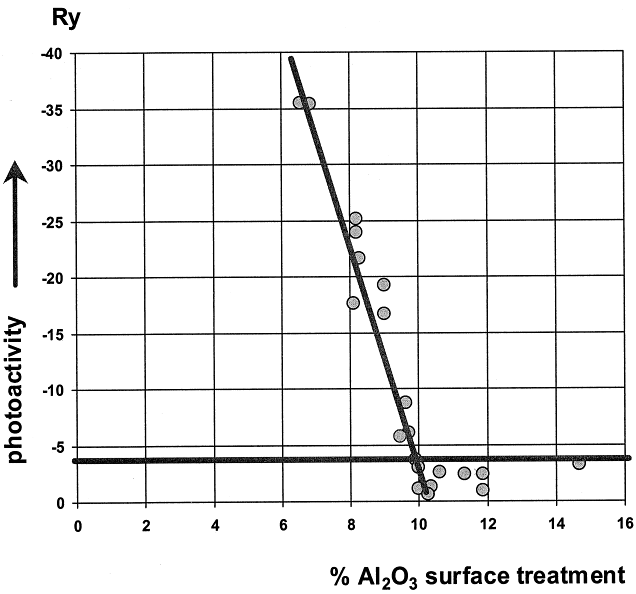


Figure 3. Effect of aluminium oxide posttreatment on the activity of a nano-titania with a particle diameter of ca. 20 nm.

Nano scaled titanias as photocatalysts

For photocatalytic applications the titania should either be in the anatase modification or otherwise x-ray amorphous. Naturally, when a highly active titania is aspired any measures that enhance its lightfastness or weather resistance should be avoided. A high specific surface area is beneficial and when the photocatalyst is to be evenly distributed in a certain matrix, dispersibility is an issue to keep in mind. Furthermore, the titania should have the tendency or at least the ability to adsorb whatever substance is to be degraded. In many cases, such as in water purification, this is a limiting factor. If at a given pH value the zeta potential of the photocatalyst has the same sign as the charge of the substance that is supposed to be mineralized no adsorption will occur and hence no catalytic oxidation will take place. The same problem can arise if during the course of photocatalytic oxidation charged intermediates are generated.

The quantum yield of photocatalytic processes is generally higher with low illumination intensities because mass transfer is inevitably the rate determinating factor in these reactions.

Photocatalytically active coatings

In order to be photocatalytically active the titania catalyst surface must be accessible for the adsorbates. In a suspension reactor or in the case of titania ceramics this presupposition is fulfilled.

When trying to formulate photocatalytic coatings a way has to be found to incorporate the titania into the resin matrix without covering all of its surface with binder. This means that PVCs exceeding the critical PVC must be chosen, so glossy coatings cannot be formulated. Of course one has to compromise between film integrity and photocatalytic activity.

The next thing to consider is that the resin itself will inevitably be oxidized provided that it is vulnerable for this type of attack. By experience, any conventional organic resins will soon be destroyed and the coatings will loose their mechanical stability. The only exemptions are to some extent fluorinated polymers such as tetrafluoroethylene or polyvinylidenefluoride. It seems that the C-F bond is strong enough to withstand oxidation by titania photocatalysts. The drawback is that these polymers have extremely poor adhesion to substrates. Therefore, photoactive free films but unfortunately no coatings can be accomplished in this manner.

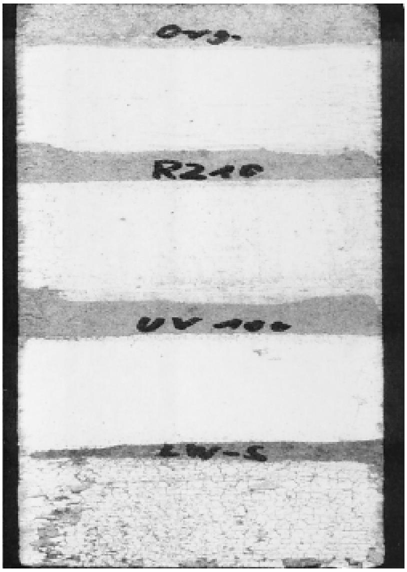


Figure 4. Lime sand stone with four differently pigmented silicate coatings. See text.

Not surprisingly, the best way to formulate photoactive, yet durable coatings is with silicate resins as binders. Figure 4 demonstrates the self cleaning properties of a formulation containing a nano-titania (“UV 100”; PVC 48%) in comparison to a formulation containing only clacium carbonate ("Org.", PVC 62%), one with a rutile ("R210", PVC 48%) and one with a standard pigment grade anatase ("LW-S",PVC 48%). A lime sanstone brick with the four formulations is shown after 6 months of outdoor weathering. There is an onset of growth of algea on all formulations except for the one containing the photocatalyst. The standard anatase grade formulation exhibits cracking and loss of adhesion as well. Since some titania photocatalysts are proven to have antimicrobial properties, these type of formulations may become important in the near future.

Last but not least, there is tremendous amount of development work focussing on the generation of transparent photoactive titania layers either by chemical vapor depositon or by sol gel methods. These layers show "superhydrophilicty" when illuminated with daylight, meaning that condensing moisture will not form droplets. Apart from that, these layers are self cleaning.

Conclusions

Standard applications of nano-titanias today are as UV-absorbers, and as effect pigments. In future, maybe a further use in photocatalytically active paint formulations or pure titania layers will become important. The possibility for this to occur seems promising.

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