Alumina Surface Treated Pigmentary Titanium Dioxide with Suppressed Photoactivity

N. Veronovski*, M. Lešnik and D. Verhovšek

Cinkarna-Metallurgical and Chemical Industry Celje, Inc., Kidričeva 26, 3001 Celje, Slovenia

Abstract: The aim of the optimization of the technological process was to coat the surface of the pigment in a controlled manner and to suppress photoactivity in the titanium dioxide (TiO₂) pigment. As part of this research, a systematic approach to TiO₂ pigment surface treatment with alumina was conducted. Surface treatment with alumina plays a significant role in the improvement of TiO₂ properties (e.g. weather resistance and photostability). This research encompasses a raw material analysis and process conditions study. Sodium aluminate and aluminium sulphate were used as a source of alumina hydroxide. The effectiveness of surface treatment was determined using scanning-transmission (STEM) and transmission (TEM) electron microscopy. The photoactivity of pigmentary TiO₂ was determined before and after surface treatment. A controlled surface treatment process resulted in pigmentary TiO₂ particles with uniform amorphous layers, which suppressed the photoactivity of the pigment.

1. INTRODUCTION

Titanium dioxide (TiO₂) pigment properties are determined by the base pigment and finishing process. The base pigment is affected by the manufacturing process, the crystal structure, the particle size distribution and the additives used during manufacture. Finishing includes an inorganic surface treatment [1]. TiO₂ is a semiconductor. Under the influence of weathering and sunlight the photoactivity of TiO₂ pigments can cause the degradation of organic matrices in which they are imbedded. Like most organic materials, when coatings pigmented with TiO₂ are used in exterior applications they undergo ageing; this leads to changes in appearance and in their physical and chemical properties and can also impair the effectiveness of the coating [2]. Typical damage includes reduction in gloss, fading, embrittlement and chalking. The photoactivity of TiO₂ is generally disliked. Therefore, the TiO₂ pigment industry goes through significant effort to diminish the photoactivity [2]. Most frequently, the stabilisation is generated by layers of aluminium oxide (Al₂O₃) and/or silicon dioxide (SiO₂). Inorganic surface treatments play a role in improving weather resistance and photostability, as well as the colloid chemical and optical properties of pigmentary TiO₂ [2]. Several published papers deal with the surface treatment of TiO₂ pigments with inorganic layers [3-7].

Hydrous alumina is probably the most common treatment agent of TiO₂ pigments. It can be deposited from sodium aluminate when it reacts with an acid; or aluminium sulphate when it reacts with a base. Alumina can also be deposited from a combination of sodium aluminate and aluminium sulphate, which neutralize one another. The morphology of the alumina layer depends on the deposition conditions. Aluminium oxide and hydrous alumina have many different structures, which can give many different properties to coated particles. It was reported that the structure of the alumina layer on TiO₂ pigment varied with the pH, i.e., the alumina tends to deposit as a pseudoboehmite in basic solutions. Alumina deposits are in an amorphous form in acid solutions. The transition pH is temperature-sensitive and tends to shift to a lower pH at higher temperature [1].

The particles coated with alumina behave in some ways that are characteristic of alumina. A layer of alumina layer can increase the amount of -OH groups on the particle surface, which can improve the dispersibility of the particles in an aqueous solution and provide more active sites for further organic modification [8]. A thin and uniform film layer can improve both the pigment's weather durability and optical properties. The alumina also acts as a spacer for the particles and improves the gloss and opacity of the pigment. The amorphous alumina can provide a moderate amount of durability, and does not seem to provide as effective spacing as the pseudoboehmite alumina. When multiple treatment
layers are deposited on a pigment, alumina is most often the final layer [1, 9-11].

This research was oriented towards taking full advantage of the suppressing of the phoactivity of pigmentary TiO$_2$, which can only be taken if TiO$_2$ is completely coated by an oxide layer. For that reason, significant efforts were directed towards this goal.

2. EXPERIMENTAL

2.1. Materials

Pigmentary TiO$_2$ particles in rutile crystalline form, produced by the sulphate process in Cinkarna Celje (Slovenia) were used in this research. The starting TiO$_2$ suspension contained approximately 350 g/L of solid material.

Alumina-coated pigmentary TiO$_2$ particles were prepared starting from Na-aluminate (c = 270 g/L Al$_2$O$_3$) or Al-sulphate (c = 90 g/L Al$_2$O$_3$) by the chemical liquid deposition method.

Surface treatment began after a precursor addition to TiO$_2$ suspension. The precipitation of oxide particles from a precursor started with a gradual adjustment of the pH. The initial aluminium hydroxide gel precipitate resulted from the reaction of Al-sulphate with a base or from the reaction of Na-aluminate with an acid. During the precipitation process, alumina hydroxides bind on the surface of TiO$_2$. After a successful layer process, the surface of the particle was entirely surrounded by a metal hydroxide.

2.2. Methods

2.2.1. Potentiometric Titration

Potentiometric titration is a basic method for exploring the conversion of Al species in hydrolysis-polymerization. According to existing literature [12] the Al species can be quantitatively divided into four regions by three characteristic points on the titration curves: $\text{Al}^{3+}$/$\text{Al}_5^0$ region, consist chiefly of $\text{Al}^{3+}$ and mononuclear Al; the small/middle polynuclear Al region, including $\text{Al}_2^+$-$\text{Al}_{12}^-$; the large-size polynuclear aluminium region, consistent with predominantly $\text{Al}_{13}^2$-$\text{Al}_{54}^-$ and a little sol/gel Al(OH)$_3$; the dissolving region of sol/gel Al$_6$, only Al(OH)$_3$ (aq or am.) and Al(OH)$_4$ species, which set up a base to study on the hydrolysis-polymerization of Al$^{3+}$. By analysing the simplest titration curve (pH vs. V) our study focused on the conversion trends of the species in the hydrolysis-polymerization of Al$^{3+}$.

Diluted Na-aluminate and Al-sulphate solutions and a 0.1 M acid or base solution were prepared with corresponding reagents dissolving in distilled water. The titrator 905 Titrando (Metrohm Swiss made, Switzerland) was used to inject titrant (acid/base) drop by drop, and allows one to easily determine whether a supplier is properly controlling a particular product [13].

2.2.2. Surface Morphology Determination by (S)TEM

The morphology of surface treated pigmentary TiO$_2$ was observed at different magnifications.

2.2.3. Electrochemical Properties Determination

Pure oxides have well-defined isoelectric points (IEP) which can be used to verify the cleanliness of their surfaces. Although the IEP value for TiO$_2$ is usually quoted as pH 5.8, this value is rarely observed because commercial TiO$_2$ is normally covered with one or more layers of either silica (SiO$_2$), alumina (Al$_2$O$_3$) or zirconia (ZrO$_2$) or a combination of those oxides, in order to improve its performance in various situations. The IEP remains an important characteristic of the surface in this case because it helps in identifying the layer and allows one to easily determine whether a supplier is properly controlling a particular product [13].

The Mütek™ PCD-04 Particle Charge Detector (BTG Instruments GmbH, Germany) was used to determine the isoelectric point (IEP) of the aqueous samples. The IEP is the pH-dependent point of zero charge (PZC) of a particle. By adding a titrant (acid/ base) drop by drop, the sample’s pH is shifted until the IEP (streaming potential $= 0$ mV) is reached. Cationic samples are titrated with a base and anionic samples with an acid up to the point of 0 mV.

2.2.4. Microstructure Determination Using Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of untreated and surface treated pigmentary TiO$_2$ were obtained on a Bruker spectrometer IFS 66/S with the integration sphere Optosol. The spectra of studied samples were recorded over the range 1300-400 cm$^{-1}$ in absorbance mode.

2.2.5. Photoactivity Determination

The photocatalytic activity of untreated and surface-treated pigmentary TiO$_2$ particles was determined by examining photoactivity in the system gas/solid using FTIR spectroscopy. Measurements were performed at the Slovenian National Building and Civil Engineering Institute (ZAG, Ljubljana). Photoactivity was measured in a gaseous medium by monitoring the decay of model organic substance in the gas phase by FTIR spectroscopy.

Veronovski et al.
2.2.6. Application of Alumina Surface Treated Pigmentary TiO₂ Particles in Coatings

Inorganic surface treatment plays a role in improving weather resistance and photostability, as well as colloid chemical and optical properties of TiO₂ grades [2]. The full advantages of the optical and application-oriented properties of TiO₂ pigments can only be taken if the pigment is properly distributed in the binder, i.e. if it is dispersed as thoroughly as possible [14]. Surface treated pigmentary TiO₂ particles were incorporated in coatings, which were applied on a dark surface to determine particle distribution. A microscope camera (Veho VMS-004 Discovery Deluxe) with a x400 magnification was applied for coatings observation.

3. RESULTS AND DISCUSSION

3.1. Potentiometric Titration and Formation of Al-Hydrogel

To understand how the alumina shell is formed, we have to know the reactions involved. Figure 1A and 1B represent sodium aluminate and aluminium sulphate solution titration curves and Endpoint Recognition Criterion (ERC) curves for endpoints, where EP signifies the equivalent point.

Referring to the potentiometric titration experimental method, there are 3 characteristic points on the base titration curve when titrating Al solutions with a base under the medium rate of injecting base/acid. The OH/Al vs. pH curve can be divided into four regions quantitatively by these three critical points. These three critical points express different meanings, respectively: At the first critical point, a lot of mononuclear Al begins to convert into small/middle polynuclear Al (oligomer). At the second critical point, it is very likely that the small/middle polynuclear Al begin to form large polynuclear Al. At the third critical point, the amorphous gel or sediment appears (Figure 2). Detailed contents thereof can be found in the literature [12].

In the standard S-titration curve (black curve) titrator determines the inflection point on the curve. It is displayed as a dot on the ERC curve (grey curve).

At the first point of inflection the precipitate formed during precipitation from Na-aluminate in the form of needles (Figure 3). TiO₂ pigment grades with such morphology of the precipitate don’t provide required durability which is achieved by applying dense alumina coating.

Figure 1: Na-aluminate (A) and Al-sulphate (B) solution titration curve and endpoint recognition criterion (ERC) curve for endpoints.

Figure 2: STEM image of Al-hydrogel, yielded in a neutral medium from precursor Al-sulphate.

Figure 3: A STEM image shows the precipitate formed during precipitation from Na-aluminate at the first point of inflection.
3.2. Surface Morphology of Untreated and Surface Treated Pigmentary TiO$_2$

The TEM image in Figure 4 demonstrates the morphology of pigmentary TiO$_2$ particles in rutile crystalline structure before surface modification. Particles are non-spherical in shape, and approximately 200 nm in size. Crystal planes and the sharp edges of pigmentary TiO$_2$ particles can be seen.

![TEM image of pigmentary TiO$_2$ particles.](image)

**Figure 4:** TEM image of pigmentary TiO$_2$ particles.

Uniform amorphous layers were formed in the heterogeneous nucleation of alumina molecules on the surface of TiO$_2$ under controlled conditions. Controlled precipitation resulted in the formation of a uniform oxide layer, which is graphically represented in Figure 5. Therefore, the surface of TiO$_2$ particles became rougher due to amorphous alumina precipitation.

Hydrous alumina layer on the surface of pigmentary TiO$_2$ particles is produced through the collision and condensation of -OH groups on the core particle surface.

The zeta potential ($\zeta$) of the TiO$_2$ particles varies with the pH, which indirectly reflects the amount of -OH groups on the particle surface that could provide protons. When the -OH groups can easily provide protons, the particles carry a negative charge. The pH affects the “hydrolysis-polymerization-precipitation” process of the coating reagent, as well as the coating morphology. Hydrolysis products depend on the solution pH. At pH>IEP TiO$_2$, positively charged OH-Al species form [15]. Positively charged hydrolysis products are the main counter ions in the absorption layer. When OH-Al species collide with TiO$_2$ particles through random collisions and break through the

![Schematic representation of the uniform oxide layer formation.](image)

**Figure 5:** Schematic representation of the uniform oxide layer formation.

![Condensation](image)

**Figure 6:** At a pH higher than the IEP, the number of -OH groups on the particle surface that can provide protons is large and condensation with the OH-Al species easily occurs.
At weak acid to neutral pH, the OH-Al species are small in size, and random sedimentation dominates the precipitation process. Under these conditions, uniform and continuous film layers that tightly bind to the core particle surface are produced (Figure 7A and B).

When the pH is lower than the IEP, the number of -OH groups on the particle surface that can provide protons is small and condensation with the OH-Al species hardly occurs, homogeneous nucleation or the dotted layer is preferred (Figure 8A). At a high pH, the OH-Al species are large, having a certain shape, and their sedimentation leads to a loose floccule or flake-like layer (Figure 8B). When the pH is higher than the IEP, the number of -OH groups on the particle surface that could provide protons is large and the condensation with the OH-Al species easily occurs, and heterogeneous precipitation is preferred. The layer morphology mainly depends on the sedimentation speed and the directed growth speed of the OH-Al species. When the temperature is in the middle range, the sedimentation speed and the directed growth speed of the OH-Al species are about the same. At increased temperatures, the directed growth speed of the OH-Al species dominates the
precipitation process regardless of the pH and size of the OH-Al species, which results in directed growth [5, 11, 13, 17]. Layer morphology changes from uniform and continuous film, to loose floccule, as shown in Figure 8D.

It is evident from the semi-quantitive elemental analysis (EDS) results that the element aluminium (Al) was present in the surface treated with TiO₂ particles (Figure 9). Approximately 3 wt. % Al was detected, which proves the existence of alumina.

3.3. Electrochemical Properties of Untreated and Surface Treated Pigmentary TiO₂

The electrochemical properties of untreated and surface treated TiO₂ were also determined. The results of streaming potential (U) as a function of pH value are graphically presented in Figure 10. The isoelectric point (IEP) of untreated TiO₂ lies around pH 4, while the presence of alumina on the surface of TiO₂ shifted the IEP of surface-treated TiO₂ to higher pH values. The IEP of alumina in its hydroxide form is accepted as pH 7.4. This corresponds to the point of minimum solubility of aluminium hydroxide. Surface treated particles altered their electrokinetic behaviour in a way similar to alumina hydroxide. The U values, obtained for surface-treated TiO₂, differ depending on surface layer efficiency. Complete layers contributed to the shift of IEP to a pH value of 6.4, which demonstrates a successful surface treatment, since IEP values of surface treated samples lie close to the IEP values, characteristic for aluminium hydroxide. The results are in agreement with the existing literature [16]. IEPs of alumina layers yielded from sodium aluminate (NaAl) and aluminium sulphate (AlS) lie at about the same pH value. This indicates that the selection of a precursor was not fundamental in the surface layer production.

3.4. Surface Microstructure

In order to determine the surface microstructure, the FTIR analysis of untreated and surface treated pigmentary TiO₂ was performed. The spectra of studied samples were recorded over the range of 1300 - 400 cm⁻¹ in absorbance mode. The FTIR spectra of untreated and surface treated pigmentary TiO₂ are shown in Figure 11. The bands at 800–400 cm⁻¹ were observed over all of the samples. The peak at ~ 670 cm⁻¹ is attributed to the Ti-O bond and refers to the symmetric O–Ti–O stretch while 505 cm⁻¹ is due to the vibration of the Ti-O bond. These findings are in accordance with Nur [18]. The FTIR spectrum of the sample obtained via hydrolysis of the alumina precursor shows a band at 1130 cm⁻¹, which is attributed to the Al–O stretching vibration [3, 4, 19]. In addition, evidence for a successful surface treatment by aluminium hydroxide can be seen in the emergence of an absorption band with a peak located at 1100 cm⁻¹, which is attributed to OH bonds vibrations in the aluminium hydroxide gel and the proof of the presence of an Al-O bond in the Al-OH system.
3.5. Application of Alumina Surface Treated Pigmentary TiO₂ in Coatings

The results in Figure 12 demonstrate pigmentary TiO₂ particle distribution in a coating. Microscope camera was applied for coatings observation. Particles with uniform surface layers yielded coatings with homogeneous particle distribution, as shown in Figure 12A. In the meantime, particles with incomplete surface layers formed agglomerates when incorporated in a coating (Figure 12B). Agglomerates are clearly visible as white dots. The results demonstrate the influence of surface treatment efficiency on coating formulation.

3.6. Activity in UV Region

TiO₂ has an undesirable property: TiO₂ is a photo-semiconductor. The surface area that is available for reactions plays a part in photocatalysis, which is evident from the results collected in Table 1. The activity of pigmentary TiO₂ particles is much lower in comparison to the activity of TiO₂ nanoparticles. Activity in the UV region for rutile nanoparticles CCR 500, produced in Cinkarna Celje, is 500.0 ppm/h. The activity of pigmentary TiO₂ is significantly lower, at 12.0 ppm/h. In addition, supressed photocatalytic activity was demonstrated after surface modification of pigmentary TiO₂ particles by an oxide layer (1.5 ppm/h).

Table 1: Activity of Untreated and Surface-Treated Pigmentary TiO₂ Particles in the UV Region

| Sample            | UV activity [ppm/h] |
|-------------------|--------------------|
| TiO₂              | 12.0               |
| TiO₂-Al-hydroxide | 1.5                |
| TiO₂ CCR 100      | 500.0              |

4. CONCLUSIONS

Alumina surface-treated pigmentary TiO₂ particles were prepared, starting with sodium aluminate or aluminium sulphate by the chemical liquid deposition method. Uniform alumina layers formed on the surfaces of the TiO₂ particles under a mild hydrolysis rate of sodium aluminate or aluminium sulphate in gel precipitation and aging. The morphology of the layers was affected by the pH value of the reaction solution. Rapid hydrolysis of the precursor resulted in aggregated hydrated alumina. On the other hand, slow hydrolysis of the precursor was beneficial to the formation of thin alumina flocules. We can conclude that inappropriate pH conditions can lead to undesirable phases of alumina or an incomplete layer. By applying a layer of colourless alumina hydroxide, the photoactivity of TiO₂ pigments was successfully suppressed.

REFERENCES

[1] Tyler F. Tailoring TiO₂ Treatment Chemistry To Achieve Desired Performance Properties. Paint & Layers Ind 2000; 32:16-32.
[2] Winkler J. Titanium Dioxide. Hanover: Vincentz 2003.
[3] Liu Y, Ge C, Ren M, Yin H, Wang A, Zhang D, Liu C, Chen J, Feng H, Yao H, Jiang T. Effects of layer parameters on the morphology of SiO₂-coated TiO₂ and the pigmentary properties. App Surf Sci 2008; 254:2809-2819. http://dx.doi.org/10.1016/j.apsusc.2007.10.021
[4] Liu Y, Zhang Y, Ge C, Yin H, Wang A, Ren M, Feng H, Chen J, Jiang T, Yu L. Evolution mechanism of alumina layer layer on rutile TiO₂ powders and the pigmentary properties. Appl Surf Sci 2009; 255:7427-7433. http://dx.doi.org/10.1016/j.apsusc.2009.04.013
[5] Zhang Y, Liu Y, Ge C, Yin H, Ren M, Wang A, Jiang T, Yu L. Evolution mechanism of alumina nanofilms on rutile TiO₂ starting from sodium metaaluminate and the pigmentary properties. Powder Technol 2009; 192:171-177. http://dx.doi.org/10.1016/j.powtec.2008.12.009
[6] Zhang Y, Yin H, Wang A, Ren M, Gu Z, Liu Y, Shen Y, Yu L, Jiang T. Deposition and characterization of binary Al₂O₃/SiO₂ coating layers on the surfaces of rutile TiO₂ and the pigmentary properties. App Surf Sci 2010; 257:1351-1360. http://dx.doi.org/10.1016/j.apsusc.2010.08.071
[7] Zhang Y, Yin H, Wang A, Li C, Yu L, Jiang T, Hang Y. Evolution of zirconia coating layer on rutile TiO₂ surface and the pigmentary property. J Phys Chem Solids 2010; 71:1458-1466. http://dx.doi.org/10.1016/j.jpcs.2010.07.013
[8] Lin YL, Wang TJ, Jin Y. Surface characteristics of hydrous silica coated TiO₂ particles. Powder Technol 2002; 123: 194-198. http://dx.doi.org/10.1016/S0032-5910(01)00470-3
[9] Edward CM. Titanium dioxide pigment and process making same. US patent 4,022, 1977.
[10] Thomas FS, Woburn M. Nongelling Titania pigments. US patent 3,523,810, 1966.
[11] Wu HX, Wang TJ, Jin Y. Morphology Phase Diagram of the Hydrous Alumina Layer on TiO₂ Particles during Aqueous Precipitation. Ind Eng Chem Res 2006; 45:5274-5278. http://dx.doi.org/10.1021/ie0601910

[12] Wang C, Han Z, Wang P, Cui N, Lao T, Hong P. Potentiometric titration curves of aluminium salt solutions and its species conversion in the hydrolysis-polymerization course. Bull Chem Soc Ethiop 2008; 22:155-164. http://dx.doi.org/10.4314/bcse.v22i2.61276

[13] Liu Y, Zhang Y, Ge C, Yin H, Wang A, Ren M, Feng H, Chen J, Jiang T, Yu L. Evolution mechanism of alumina layer on rutile TiO₂ powders and the pigmentary properties. App Surf Sci 2009; 255:7427-7433. http://dx.doi.org/10.1016/j.apsusc.2009.04.013

[14] Brock T, Groekeley M, Mischke P. European Layers Handbook, 2nd revised ed. Hannover: Vincentz Network; 2010, p 127.

[15] Franks GV, Gan Y. Charging Behavior at the Alumina–Water Interface and Implications for Ceramic Processing. J Am Ceram Soc 2007; 90:3373–3388. http://dx.doi.org/10.1111/j.1551-2916.2007.02013.x

[16] Wu HX, Wang TJ, Jin Y. Film-Layer Process of Hydrated Alumina on TiO₂ Particles. Ind Eng Chem Res 2006; 45:1337-1342. http://dx.doi.org/10.1021/ie0510167

[17] Shen Z, Zhao ZG, Wang GT. Colloid and Surface Chemistry. Chemistry Industry Press, Beijing, China; 2004.

[18] Nur H. Modification of titanium surface species of titania by attachment of silica nanoparticles. Mater Sci Eng B 2006; 133:49–54. http://dx.doi.org/10.1016/j.mseb.2006.05.003

[19] Morterra C, Bolis V, Magnacca G. IR Spectroscopic and Microcalorimetric Characterization of Lewis Acid Sites on (Transition Phase) Al₂O₃ Using Adsorbed CO. Langmuir 1994; 10:1812-1824. http://dx.doi.org/10.1021/la00018a033