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Alumina Surface Treated Pigmentary Titanium Dioxide with Suppressed Photoactivity

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Abstract: The aim of the optimization of the technological process was to coat the surface of the pigment in a controlled manner and to supress photoactivity in the titanium dioxide (TiO_2) pigment. As part of this research, a systematic approach to TiO_2 pigment surface treatment with alumina was conducted. Surface treatment with alumina plays a significant role in the improvement of TiO_2 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 TiO_2 was determined before and after surface treatment. A controlled surface treatment process resulted in pigmentary TiO_2 particles with uniform amorphous layers, which supressed the photoactivity of the pigment.

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1. INTRODUCTION

Titanium dioxide (TiO_2) 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].

TiO_2 is a semiconductor. Under the influence of weathering and sunlight the photoactivity of TiO_2 pigments can cause the degradation of organic matrices in which they are imbedded. Like most organic materials, when coatings pigmented with TiO_2 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 TiO_2 is generally disliked. Therefore, the TiO_2 pigment industry goes through significant effort to diminish the photoactivity [2]. Most frequently, the stabilisation is generated by layers of aluminium oxide (Al_2O_3) and/or silicon dioxide (SiO_2). Inorganic surface treatments play a role in improving weather resistance and photostability, as well as the colloid chemical and optical properties of pigmentary TiO_2 [2]. Several published papers deal with the surface treatment of TiO_2 pigments with inorganic layers [3-7].

Hydrous aluminium oxide is probably the most common treatment agent of TiO_2 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 TiO_2 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

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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_2O_3) or Al-sulphate (c = 90 g/L Al_2O_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 entirety 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: Al^{3+}/Al_a region, consist chiefly of Al^{3+} and mononuclear Al; the small/middle polynuclear Al region, including Al_2-Al_{12}; the large-size polynuclear aluminium region, consistent with predominantly Al_{13}-Al_{54} and a little sol/gel $Al(OH)_3$; the dissolving region of sol/gel Al_c, 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) and record the pH value automatically.

2.2.2. Surface Morphology Determination by (S)TEM

The morphology of surface-treated pigmentary TiO_2 particles can only be identified directly with the use of electron microscopy, i.e. a scanning-transmission (STEM) and a transmission microscope (TEM). In the case of STEM utilization, bright field+dark field mode has been used.

A drop of TiO_2 suspension was dropped on the Cu-grid for observation on a Zeiss SIGMA VP Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany), with a maximum resolution up to 1.5 nm at 20 kV. STEM images were collected and elaborated according to standard procedures.

In addition, a morphology analysis of the surface-treated pigmentary TiO_2 was performed using a transmission electron microscope (TEM, JEOL 2100F, Japan). For the analysis, a drop of suspension was dropped on the Cu-grid.

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_2O_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.

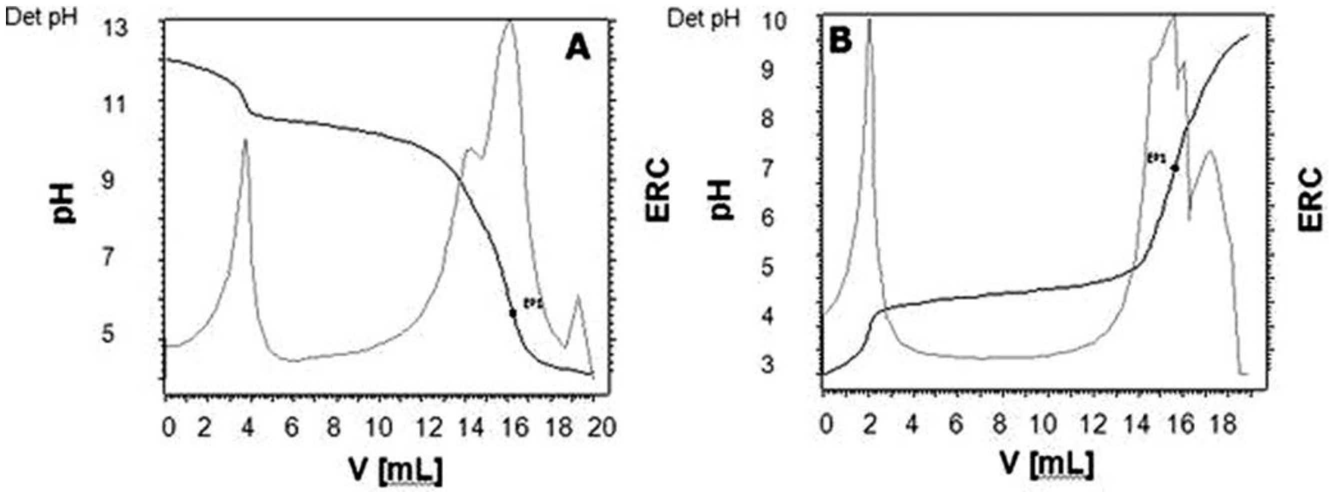

Figure 1: Na-aluminate (**A**) and Al-sulphate (**B**) solution titration curve and endpoint recognition criterion (ERC) curve for endpoints.

2.2.6. Application of Alumina Surface Treated Pigmentary TiO_2 Particles in Coatings

Inorganic surface treatment plays a role in improving weather resistance and photostability, as well as colloid chemical and optical properties of TiO_2 grades [2]. The full advantages of the optical and application-oriented properties of TiO_2 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 TiO_2 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).

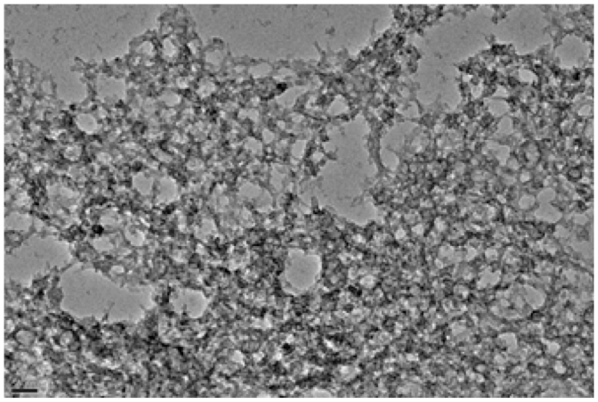

Figure 2: STEM image of Al-hydrogel, yielded in a neutral medium from precursor Al-sulphate.

At the first point of inflection the precipitate formed during precipitation from Na-aluminate in the form of needles (Figure **3**). TiO_2 pigment grades with such morphology of the precipitate don't provide required durability which is achieved by applying dense alumina coating.

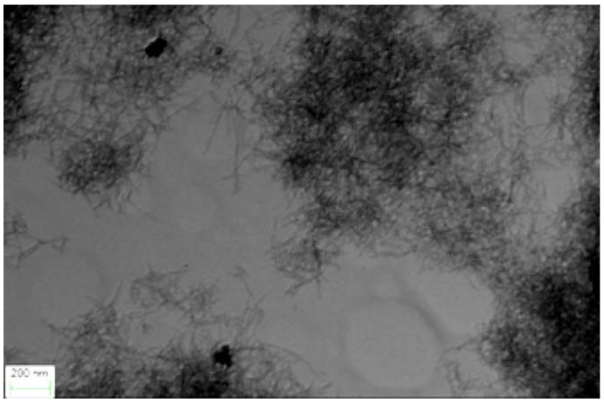

Figure 3: A STEM image shows the precipitate formed during precipitation from Na-aluminate at the first point of inflection.

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.

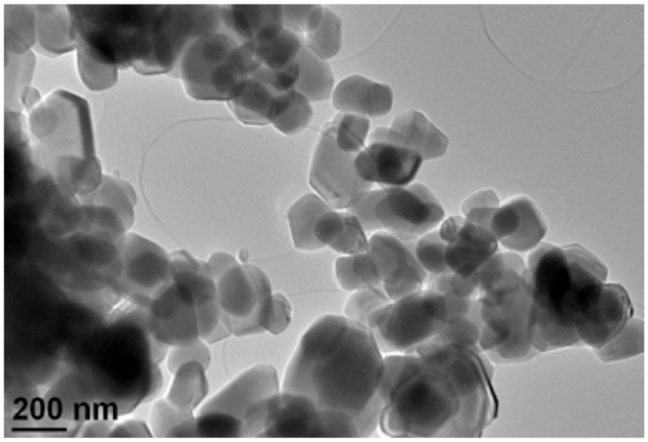

Figure 4: TEM image of pigmentary TiO_2 particles.

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 (ζ) 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>IEPTiO_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

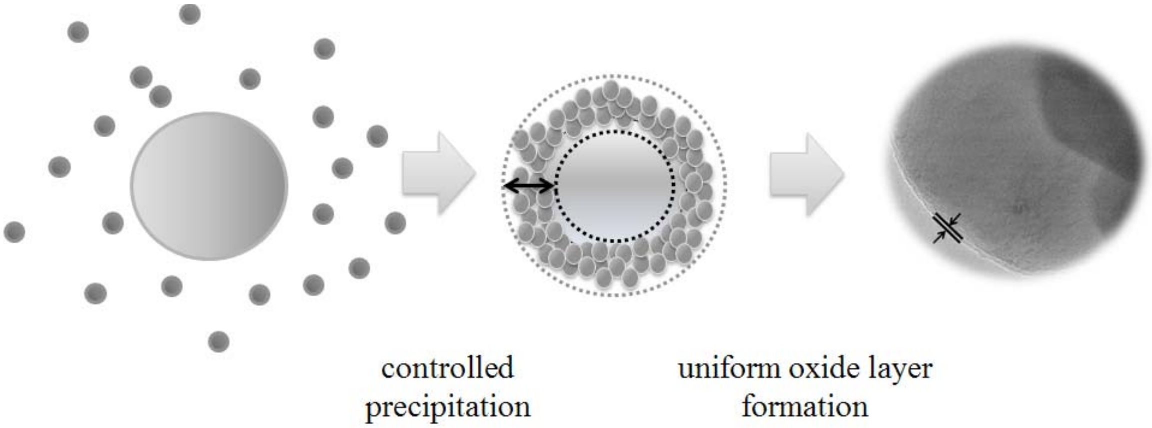

Figure 5: Schematic representation of the uniform oxide layer formation.

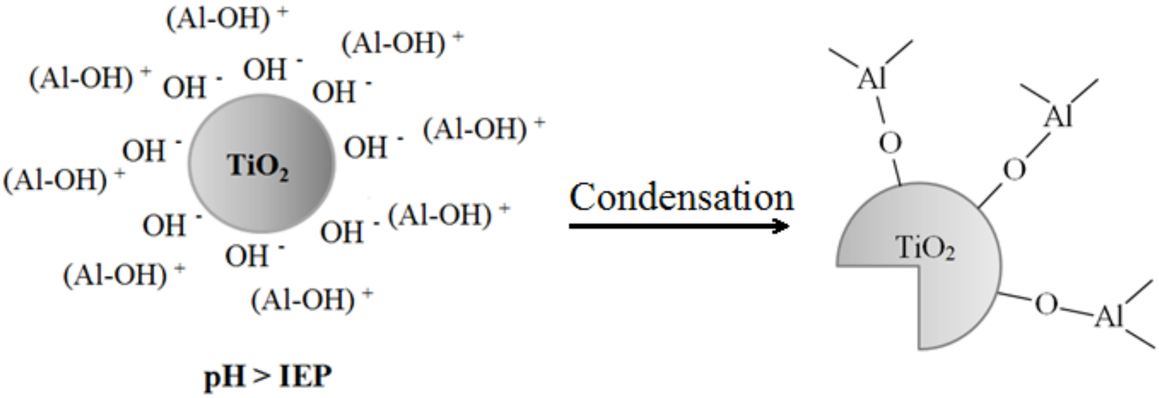

Figure 6: At a pH higher than the IEP, the number of -OH groups on the particle surface that can provide protons is large and condensation with the OH-Al species easily occurs.

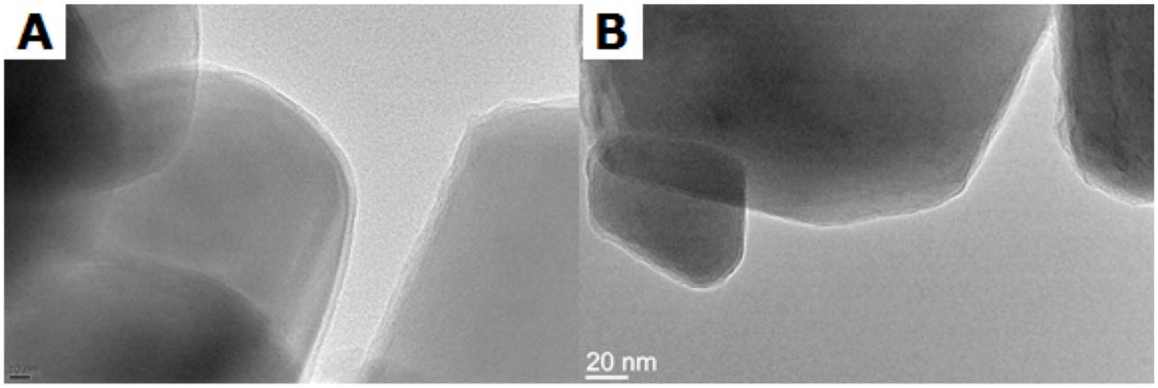

Figure 7: TEM images of 3 wt. % alumina coated pigmentary TiO_2 particles yielded *via* precipitation from Na-aluminate (**A**) and Al-sulphate (**B**) under neutral pH conditions.

threshold of repulsion between them, condensation occurs between OH-Al species and -OH groups on the TiO_2 particle surface [16]. Ti-O-Al bond formed *via* condensation of – OH groups from TiO_2 surface and OH-Al species (Figure **6**). The existence of the Ti-O-Al bond was confirmed *via* FTIR analysis.

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

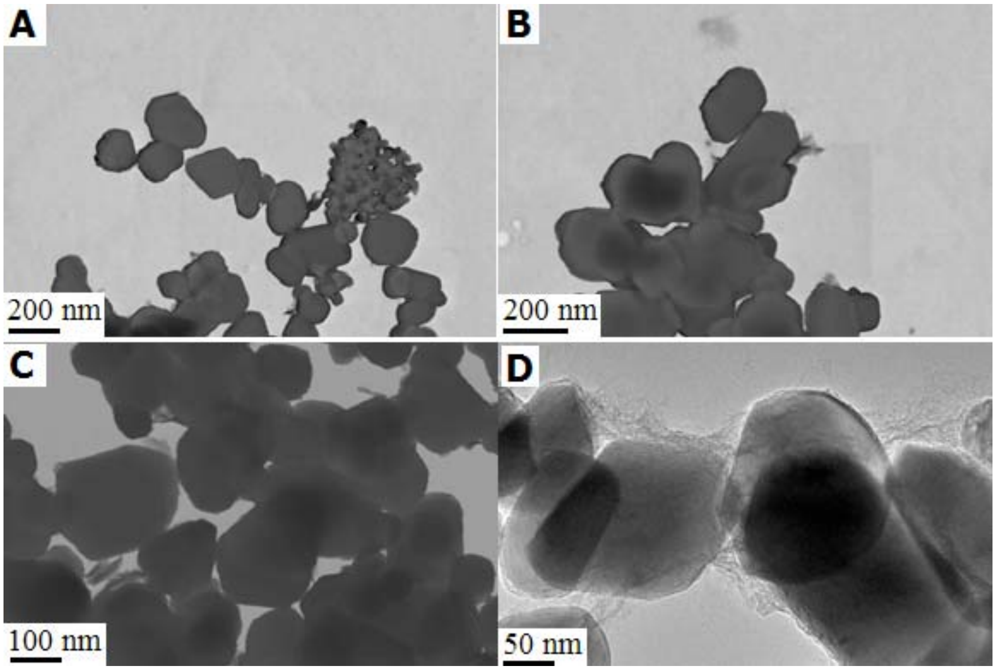

Figure 8: STEM images of alumina-coated pigmentary TiO_2 particles prepared under various process conditions:

A. at low pH dotted layer formed.

B, C. at high pH loose floccule or flake-like layer formed.

D. at increased temperature loose floccule formed.

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 TiO_2 particles (Figure **9**). Approximately 3 wt. % Al was detected, which proves the existence of alumina.

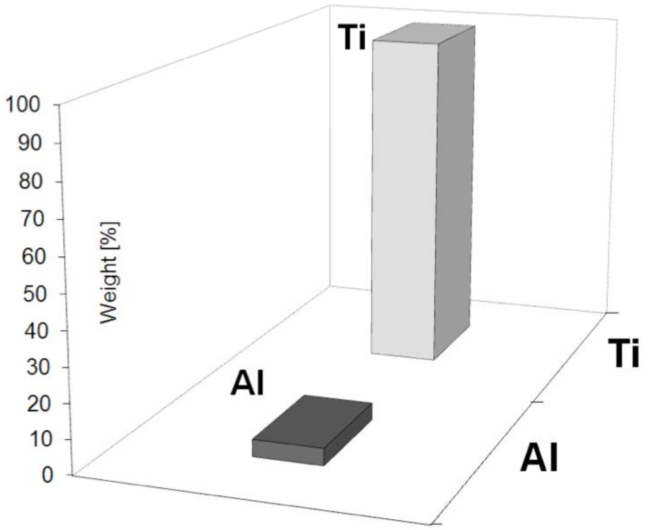

Figure 9: EDS analysis of pigmentary TiO_2 surface treated with approximately 3 wt. % alumina.

3.3. Electrochemical Properties of Untreated and Surface Treated Pigmentary TiO_2

The electrochemical properties of untreated and surface treated TiO_2 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 TiO_2 lies around pH 4, while the presence of alumina on the surface of TiO_2 shifted the IEP of surface-treated TiO_2 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 TiO_2, 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.

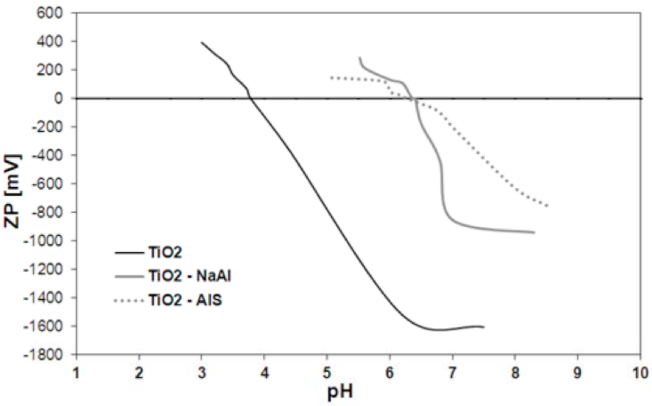

Figure 10: Function of U vs. pH for untreated and alumina surface treated pigmentary TiO_2.

3.4. Surface Microstructure

In order to determine the surface microstructure, the FTIR analysis of untreated and surface treated pigmentary TiO_2 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 TiO_2 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.

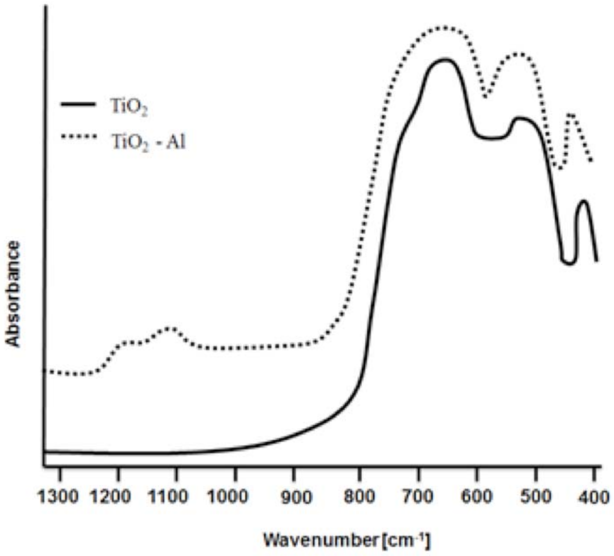

Figure 11: FTIR spectra of untreated and alumina surface treated pigmentary TiO_2 over the range of 1300 - 400 cm^{-1}.

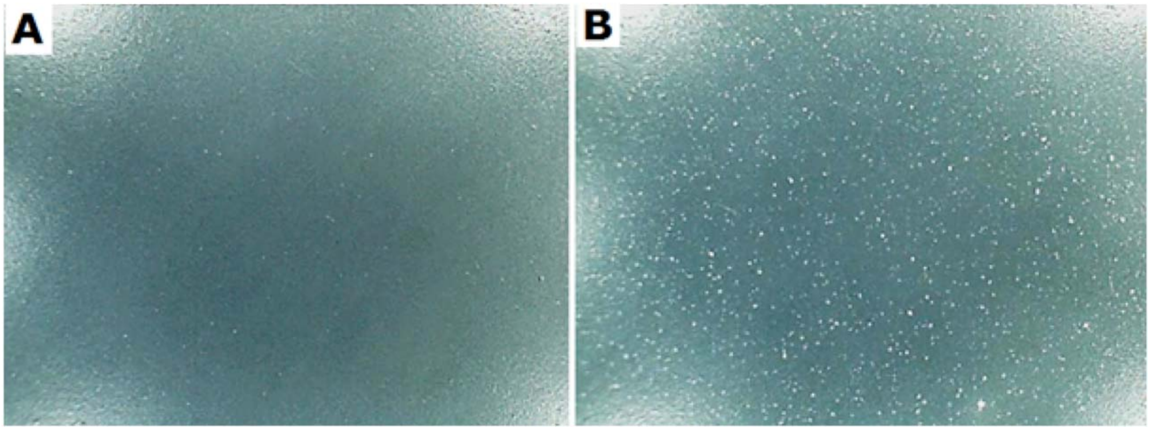

Figure 12: Particles distribution in coatings.

3.5. Application of Alumina Surface Treated Pigmentary TiO_2 in Coatings

The results in Figure **12** demonstrate pigmentary TiO_2 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

TiO_2 has an undesirable property: TiO_2 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 TiO_2 particles is much lower in comparison to the activity of TiO_2 nanoparticles. Activity in the UV region for rutile nanoparticles CCR 500, produced in Cinkarna Celje, is 500.0 ppm/h. The activity of pigmentary TiO_2 is significantly lower, at 12.0 ppm/h. In addition, supressed photocatalytic activity was demonstrated after surface modification of pigmentary TiO_2 particles by an oxide layer (1.5 ppm/h).

Table 1: Activity of Untreated and Surface-Treated Pigmentary TiO_2 Particles in the UV Region

Sample	UV activity [ppm/h]
TiO_2	12.0
TiO_2-Al-hydroxide	1.5
TiO_2 CCR 100	500.0

4. CONCLUSIONS

Alumina surface-treated pigmentary TiO_2 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 TiO_2 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 floccules. 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 TiO_2 pigments was successfully suppressed.

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