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Chapter 21

TiO$_2$ Applications as a Function of Controlled Surface Treatment

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Abstract

For the end use, the structure and morphology of the coated film are very important since they determine the final properties of the resultant material. The effect of coatings largely depends on their composition and method of application, which may give porous or dense coatings. To achieve uniform coatings on dispersed TiO$_2$ particles, various compounds were deposited one after another under specific conditions by the wet chemical deposition method starting from rutile TiO$_2$ produced by the sulfate method in Cinkarna Celje. With the synthesis of composite particles consisting of a core TiO$_2$ particle coated with a functional shell with dimensions in the nano scale, we prepared advanced materials, where the shell protects the particles from undesirable interactions with the environment and improves surface reactive properties of the dispersed particles to meet special requirements. The morphology of surface-treated TiO$_2$ particles has been identified directly using electron microscopy, while the degree of functionalization by various hydroxides was determined using X-ray fluorescence spectrometer (XRF). In addition, zeta potential (ZP) measurements have been utilized to determine the electrochemical properties of resultant particles. The precipitation of hydroxides on the TiO$_2$ surface resulted in the shift of the isoelectric point (IEP). UV-Vis spectroscopy has been used for determining light scattering efficiency. In addition to internal characterization, light fastness of durable grade intended for the application in laminates has been tested by the end user.

Keywords: TiO$_2$, pigment, surface treatment

1. Introduction

Titanium dioxide (TiO$_2$) is used in a variety of applications, all of which have different sets of performance requirements. As a result, the pigments designed for the various applications
are different. Variations in crystal structure (anatase/rutile), inorganic coating and organic treatments provide a wide range of titanium dioxide grades, each with different properties.

Generally, the properties of a pigment are determined by the particle size distribution of the base pigment, the chemical composition and the morphology of the surface treatment. The morphology of the treatment layers can, in turn, have an effect on the final properties of the pigment.

\( \text{TiO}_2 \) pigments are generally coated to improve their performance in many end-use applications. Thus, the pH, temperature, reagents, order of addition and other factors can affect product characteristics. Optimum treatment conditions need to be determined after the surface treatment chemicals have been selected [1].

There are differences between grades, partially based on the fact that \( \text{TiO}_2 \) particle surfaces may be modified differently with inorganic and organic post treatments. With regard to colloidal chemistry, a \( \text{TiO}_2 \) with an \( \text{Al}_2\text{O}_3 \) surface treatment behaves completely different from one having a \( \text{SiO}_2 \) surface treatment [2]. Both of these, again, are different from a pure, untreated \( \text{TiO}_2 \) which has its IEP at pH values between 4.5 and 6.5.

Surface treatment of \( \text{TiO}_2 \) particles by colorless inorganic compounds of low solubility affects dispersibility of the pigments in the matrix and weather resistance and lightfastness of the pigmented organic matrix [3].

These treatments are most commonly precipitated in layers. However, some of the components can be co-precipitated to alter the pigment characteristics [1]. There are many works regarding this subject in literature [4–14].

Inorganic surface treatment influences optical performance of the pigment approximately in proportion to the decrease in the \( \text{TiO}_2 \) content. Surface coatings prevent direct contact between the binder matrix and the reactive surface of the \( \text{TiO}_2 \). The treatment process also affects dispersibility of the pigment, and therefore a compromise often has to be made. High weather resistance and good dispersibility of the pigment in the binder or matrix are usually desired. These effects are controlled by using different coating densities and porosities. In addition, organic substances can be added during the final milling of the dried pigment [3].

Several types of treatment are known:

- Deposition from the gas phase by hydrolysis or decomposition of volatile substances.
- Addition of oxides, hydroxides or substances that can be absorbed onto the surface during pigment grinding, which results in partial coating of the pigment surface.
- Precipitation of the coating from aqueous solution onto the suspended \( \text{TiO}_2 \) particles by batch processes in stirred tanks starting from various compounds, which are deposited one after another under specific conditions. The most common are oxides, oxide hydrates, silicates and/or phosphates of titanium, zirconium, silicon and aluminum.

Typical groups of inorganic coatings are as follows:

1. Pigments with dense surface coatings for paints or plastic made by
   - Homogeneous precipitation of \( \text{SiO}_2 \) with precise control of temperature, pH and precipitation rate.
After-treatment with Zr, Ti, Al and Si compounds.

After-treatment with merely 1–3% of alumina [15–18].

2. Pigments with porous coating for use in emulsion paints obtained by simple treatment with Ti, Al and Si compounds, giving a silica content of 10% and a TiO$_2$ content of 80–85%.

3. Lightfast pigments with dense surface coatings for the paper laminate industry that have a highly stabilized lattice and a surface coating based on silicates or phosphates of titanium, zirconium and aluminum: cca. 90% TiO$_2$.

For coloring of plastics, usually smaller TiO$_2$ particles are used with typically less than 3% of inorganic coating (TiO$_2$ typically >95%).

Before micronizing the pigment in a jet-mill and sometimes also before drying, the pigment surface is further modified by adding organic substances to improve dispersibility and facilitate further processing. The nature of the compounds used depends on the intended use of the pigment [3].

1.1. About TiO$_2$

1.1.1. Pigment properties

Scattering power, hiding power (tinting strength), brightness, mass tone (or color), gloss formation, gloss haze, dispersibility, lightfastness and weather resistance are the most important pigment properties of TiO$_2$ pigments; these properties are a function of chemical purity, lattice stabilization, primary particle size, particle size distribution and the coating.

TiO$_2$'s theoretical optimum particle size is between 0.2 and 0.3 μm, but the pigment obtained is considerably larger mainly because of the formation of agglomerates while handling during the manufacturing process. The presence of agglomerates affects hiding power, tinting strength and other end-use properties of the coating. The graph in Figure 1 illustrates the effect of TiO$_2$'s dispersion states vs. particle size distribution on pigment properties. A well-dispersed system helps to develop coatings with improved optical properties, hiding power, tinting strength and gloss.

1.1.2. Uses of TiO$_2$

Titanium dioxide pigment (TiO$_2$) is an important material used in many applications due to its opacity, high chemical stability, excellent whiteness and brightness. It is required in applications such as the following:

- paints and coatings
- printing inks
- plastics
- paper
1.1.3. Stability towards light and weather

When subjected to intense radiation or weathering, systems with incorporated TiO$_2$ show color or structural changes. Yellowing, chalking and loss of gloss occur due to photocatalytic activity of TiO$_2$. Formation of extremely reactive radicals (\(\cdot\)OH, HO$_2$\(\cdot\)), that cause deterioration of the coating matrix can be suppressed by doping or coating the surface of the pigment [3, 19–21].

1.2. About surface treatment

1.2.1. Silica

Rutile TiO$_2$ particles must be coated with protective layers of SiO$_2$ and Al$_2$O$_3$ through wet chemistry processes in order to decrease their photoactivity, increase weather durability and increase dispersibility in certain media [4, 22–24]. The morphology of the SiO$_2$ coating layers on the surface of TiO$_2$ powders can be controlled by adjusting the reaction temperature, pH value of the reaction solution and the SiO$_2$ loading [4].

Depending on the silica precipitation conditions, very disparate pigment characteristics could be produced. “Fluffy” coating, which provides better spacing and optical efficiency, increases oil absorption and decreases gloss forms at acidic or neutral pH [1]. An example of a “fluffy” coating composed of submicroscopic particles joined together in a gel-like structure is presented in Figure 2.

During slow deposition at basic pH, silica can also be formed as a dense, glassy shell that encapsulates the particle and provides the highest durability available. Durability of the silica layer and the amount of energy needed to develop gloss are proportional to the amount of silica in the layer [1]. A dense, glass-like coating is shown in Figure 3. Coating is a few nm thick, encapsulating the entire surface of the pigment.

Island-like SiO$_2$ coating layers can be formed on a TiO$_2$ surface when the reaction temperature, the pH value and the mole ratio of Na$_2$SiO$_3$ to TiO$_2$ are low. Continuous and uniform SiO$_2$ coating layers form in an alkaline pH ranging from 9 to 10. The thickness of the coating
layer increases with the increase of the mole ratio of Na$_2$SiO$_3$ to TiO$_2$. The SiO$_2$ coating layers are anchored onto the TiO$_2$ surface by the Ti─O─Si bonding. Dispersibility of the SiO$_2$-coated TiO$_2$ powders is affected by the morphology of the SiO$_2$ coating [4].

1.2.2. Coating process of the SiO$_2$ layer

Isoelectric point (IEP) of rutile TiO$_2$ is usually located around pH 3.5 [24, 25]. The rutile TiO$_2$ surface is negatively charged under conditions where the pH value of the reaction solution is greater or equal to 7. Under conditions where pH values of the reaction solutions are in the range 7–8, Na$_2$SiO$_3$ rapidly hydrolyzes to form a large number of siliceous micelles. The resultant siliceous micelles anchor on the surface of TiO$_2$ powders via Ti─O─Si bonding to obtain island-like coating layers.

The hydrolysis rate of Na$_2$SiO$_3$ should be lowered by increasing the pH value to 9–10. This results in the formation of small-sized or less aggregated siliceous micelles. Small-sized micelles anchor on the surface of TiO$_2$ powders initially via Ti─O─Si bonding. Later, the micelles present in the solution and the anchored micelles condense via Si─O─Si bonding resulting in the formation of continuous and uniform coating layers. Over pH 10.5, silicon

Figure 2. Silica surface treatment as a fluffy layer.

Figure 3. Silica surface treatment as a dense, glass-like layer.
species exist as single silicate anions, or less aggregated siliceous micelles with very small particle size, which should be more negatively charged. The single silicate anions and the highly negatively charged siliceous micelles do not react with the negatively charged TiO$_2$ surface due to the strong electrostatic repulsion. Therefore, no SiO$_2$ coating layers forms on the TiO$_2$ surface at this high pH value.

Raising the temperature of the reaction affects the covering extent and causes the formation of a dense SiO$_2$ coating layer on the surface of the rutile TiO$_2$ powder.

1.2.3. Alumina

Hydrous aluminum oxide is probably the most common treatment agent of TiO$_2$ pigments. Various reagents can be used for deposition, e.g., sodium aluminate, which reacts with acid (see Figure 4), or aluminum sulfate, which reacts with base (see Figure 5).

Alumina can also be deposited from a combination of sodium aluminate and aluminum sulfate, which neutralize each other (Figure 6).

Irrespective of the reagent used, under controlled conditions of surface treatment, a thin, even layer, which entirely encapsulate the surface of TiO$_2$ is formed.

1.2.4. Coating process of the Al$_2$O$_3$ layer

By coating the surface of TiO$_2$ uniformly with alumina, coated particles behave in some ways similar to pure alumina. Alumina coating increase the amount of $\sim$OH groups on particle surface and consequently improve dispersibility of particles in aqueous solution and provide more active sites for further organic modification [24].

The level of alumina depends on the gloss, tint strength and opacity needed in the pigment. Low alumina levels yield better gloss but lower tint strength compared with higher levels [10].

The morphology of the alumina layer depends on the deposition conditions. Aluminum oxide and hydrous alumina have many different structures, which can give many different properties to coated particles. Formation of aluminum layers as a function of the suspension’s pH is

Figure 4. Sodium aluminate as a source of aluminum hydroxide.
presented in Figure 7. From literature, we know that the structure of the alumina layer on TiO$_2$ pigment varies with the pH, i.e., the alumina tends to deposit as a pseudoboehmite in basic solutions. Alumina deposits in an amorphous form in the acid solutions. The transition pH is temperature-sensitive and tends to shift to lower pH at higher temperature [1].

Parameters such as temperature, pH, coating reagent concentration, core particle concentration and particle surface characteristics significantly affect precipitation coating process [26]. Hydrolysis polymerization, a precipitation process of the coating reagent as well as the coating morphology is influenced by pH and temperature. At high pH values, hydrolysis of Al$^{3+}$ is accelerated and more multinuclear OH─Al species are formed compared to the situation at low pH [27]. The number of Al$^{3+}$ ions depends on pH and Al$^{3+}$ concentration, while the structure of the OH─Al species depends on the process conditions, e.g., concentration of Al$^{3+}$, temperature and stirring strength [28]. pH also affects the protonation and deprotonation reactions on the core particle surface [29].

Condensation between OH─Al species and –OH groups on the TiO$_2$ particle surface occurs when the OH─Al species collide with TiO$_2$ particles through random collisions. Formation of

Figure 5. Aluminum sulfate as a source of aluminum hydroxide.

Figure 6. Sodium aluminate and aluminum sulfate as a source of aluminum hydroxide.
Ti–OvAl bond formed via condensation of –OH groups from TiO$_2$ surface and OH–Al species is presented in Figure 8.

When the pH is higher than the isoelectric point, the TiO$_2$ particles carry negative charge [11]. The number of –OH groups on the particle surface that could provide protons is large; the surface is easy to provide protons, which facilitated the condensation between the OH–Al species and the –OH groups on the particle surface. In such a case, heterogeneous precipitation is

Figure 8. At pH 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 [13].
preferred. Since a large amount of $-\text{OH}$ groups on the particle surface could provide protons at higher pH, there were many OH–Al species that condense with the $-\text{OH}$ groups on the particle surface; neighboring condensed OH–Al species easy condense each other, forming a continuous film coating, as shown in Figure 9.

When the pH is lower than the IEP, the number of $-\text{OH}$ groups on the particle surface that could provide protons is small and condensation with the OH-Al species hardly occurs; here, homogeneous nucleation or the dotted layer is preferred (Figure 10).

At high pH, the OH–Al species are large, having a certain shape, and their sedimentation leads to a loose flocule or flake-like layer (Figure 11).

The layer morphology mainly depends on the sedimentation speed and the directed growth speed of the OH–Al species [30]. 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 temperature, the directed growth speed of the OH–Al species dominates the precipitation.

![Figure 9. TEM image of a continuous film aluminum hydroxide coating.](image)

![Figure 10. Image of TiO$_2$ particles with dotted alumina layer.](image)
process regardless of the pH and size of the OH–Al species, which results in a directed growth [10]. Layer morphology changes from uniform and continuous film to loose flocs.

Temperature has a significant effect on the direction and growth speed of the OH–Al species in gel precipitation or coating, while also affecting the self-assembly of the OH–Al species in the aging process. Under high pH conditions, the OH–Al species form a large particle size, which facilitates the formation of boehmite Al(OH)$_3$ gels or a flocule/flake coating. Amorphous Al(OH)$_3$ gel forms only under conditions when the precipitation and aging proceed at a low temperature and pH; it can be converted to boehmite under high pH or temperature conditions. However, boehmite gel cannot be converted to the amorphous form when the pH and temperature are low in the aging process [10].

2. TiO$_2$ grades

2.1. Highly coated TiO$_2$ grades

There is a special route for improving TiO$_2$ light scattering efficiency that is closely related to targeted spacing—the encapsulation of the TiO$_2$ particles by a thick, porous material. This coating material, which in practice is aluminosilicates, needs to be thick enough to effectively prevent close contact of the TiO$_2$ portion of these pigments and highly porous because a solid coating would unnecessarily dilute the TiO$_2$ content of the pigment. Even with high porosity, these coatings dilute the weight percent of TiO$_2$ in the pigment to roughly 80%.

It is important to manage the process under controlled conditions. Figures 12 and 13 indicate differences between two highly coated TiO$_2$ produced under controlled and uncontrolled conditions. Surface of TiO$_2$ coated under appropriate conditions is uniform with coatings covering the entire surface of the particles (Figure 13). Increased SiO$_2$ loading up to 10 wt.% resulted in thicker layers. Coating TiO$_2$ particles under neutral conditions yields fluffy coatings with coating thickness up to 50 nm. Pigment particles are separated from each other, showing no agglomeration.

On the contrary, uncontrolled coating process yielded incomplete coatings (Figure 12). Homogeneous coating was not attained and some particles were not coated with the silica layer.

Figure 11. TEM image provides an excellent view of the shell covering of a crystalline core of TiO$_2$ with a loose flocule or flake-like layer.
2.1.1. Particle size distribution

The particle size relevant for inorganic pigments stretch between several tens of nanometers for transparent pigment types to approximately 2 μm. For practical applications, it is desirable to determine not only the mean particle size but also the whole distribution [3].

The distribution of highly surface-treated TiO₂ in a controlled process indicates narrow particle size distribution, while an uncontrolled process yields material with broad particle size
distribution. Different populations are evident, meaning that the sample consists of many small and many over-sized particles (Figure 14).

Surface modification treatment in the suspension brings a significant shift in the pattern toward the higher particle diameter region due to high hydroxide loadings of silica and alumina imparted on the TiO$_2$ surface. The higher degree of surface modification and greater tendency for particle agglomeration can be attributed for the higher average particle diameter.

If we take into account only the mean particle sizes, we can conclude that we have two very similar samples. But, if we look at the whole distribution, it is obvious that the samples consist of very different populations. With this, we confirmed the fact that it is significant to determine not only the mean particle size but also the whole distribution.

After the grinding operation, particle size distribution again shifted to the lower particle diameter region. The sample produced by an uncontrolled process again contain over-sized particles (Figure 15).

2.1.2. Optical density

The problem with particle size distribution measurements is that the data cannot be directly related to the scattering power without using a theoretical model. An optical density test has been developed to provide a direct measure of the actual pigment scattering potential, which can then be used to evaluate performance in end-use applications [31–33].

A lab-dispersed sample in water is accurately diluted and analyzed for its total light transmission $T$. We have used the ‘DuPont optical density’, which is defined as $-\log(\text{total } T)/\text{concentration}$ and defines the scattering potential of the pigment. Compared to standard end-use tests of scattering power such as tint strength, optical density (OD) measurement offers the advantage of faster turn-around and improved precision with standard deviations less than 0.5% of the mean value.

The optical density was determined by UV-Vis spectrophotometer. To determine the optical density, 1 L of the diluted suspension of pigment particles TiO$_2$ in ethanol ($c \text{ TiO}_2 = 30 \text{ mg/L}$) was prepared. During the analysis, the suspension was subjected to ultrasound stirring. The

![Figure 14. Particle size distribution of highly coated TiO$_2$ in slurry after controlled (narrow curve) and uncontrolled (wider curve) surface treatment.](image-url)
optical density method determines the optical properties of the particles. This method determines the dispersibility or degree of particles agglomeration.

The results of the optical density determination indicated the differences between particles coated under different process conditions, controlled and uncontrolled (Figure 16). The light scattering highly depends on the particle size and the distribution of the size and degree of agglomeration of the material. Agglomeration always reduces the effectiveness of pigment light scattering. With the results obtained, we gained information about the light scattering efficiency, which is most likely a consequence of the particle size distribution and the degree of dispersion. Differences in dispersion between differently coated particles are the result of a different particle size distribution, the degree of milling step and the controlled coating mode, where the particle surface was completely coated with a layer of hydroxide. Surface treatment is important in determination of the physical properties of the particle surface and thus, affects the dispersion in a particular medium. The quality of surface treatment defines how the pigment will perform when incorporated into a particular medium. Light scattering efficiency (LSE) will depend on how well the pigment will be dispersed. Differently agglomerated particles should exhibit different OD value.

Results of the OD method indicate that coating the surface in a controlled manner resulted in particles with higher LSE (gray curve) in comparison with the particles coated under
uncontrolled conditions (black curve). Consequently, differences in undertone for both samples were evident.

Smaller particles (≤0.2 μm) scatter the light of the short wavelength more strongly; therefore, they have a slightly blue undertone, while the larger particles scatter the light of a longer wavelength, i.e., they have a yellow undertone.

2.2. Weather resistant grades

Due to the light absorption in the near UV, electrons are hoisted from the energy level of the valence band of TiO$_2$ into that of the conductive band, thus leaving a positively charged hole in the valence band. The separated electron-hole pair is called an ‘exciton’. The generation of excitons is the cause for the light induced semiconductor properties of TiO$_2$. The photoactivity of TiO$_2$ is generally not preferred, since the excitons can have an oxidizing influence on its surroundings and, for example, destroy a polymer matrix in which it is embedded. Therefore, the TiO$_2$ pigment industry takes some efforts to diminish the photoactivity of TiO$_2$. On the other hand, this property is utilized purposefully in TiO$_2$ photocatalysts [2].

From experience, anatase pigments are generally much less photo- and weather-resistant than rutile pigments [2]. Since a durable pigment is in demand, a heavy dense silica treatment is used. In addition, alumina has been chosen as the final layer over the silica treatment. Examples of surface treatment for weather resistant grades are presented in Figures 17 and 18. Figure 17 presents the dense silica-alumina coating while Figure 18 presents the dense silica-zirconia-alumina coating, covering the entire surface of TiO$_2$ particles.

Due to the fact that anatase is more photocatalytically active in the crystalline form than rutile, we selected material with the highest level of rutile crystalline structure as a base material. The level of rutile crystalline structure was determined before surface treatment using XRD (see Table 1).

Weather resistant grades can be produced by various surface treatments. We decided on two different versions, depending on the final applications. The structure of the coatings is presented in Table 2.

Figure 17. Dense silica-alumina coating.
2.3. TiO$_2$ for applications in printing inks

2.3.1. Gloss effect

Gloss is a visual impression gained when light is reflected at a surface in a preferential direction. The gloss of a coating system is determined by a number of factors. Pigments can influence the gloss of a coating through their concentration, particle size distribution and degree of dispersion in the binder system \[34\].

A conventional, high quality TiO$_2$ pigment has a mean particle diameter (weight average) of approximately 0.3 μm. The particle size distribution should not exceed the 1 μm limit in order to be useful for high gloss coatings \[2\].

Only those pigment particles lying directly below the surface of the coating are involved in this process. The higher the concentration of pigment, the greater the number of gloss-reducing particles and lower the gloss \[34\].
2.3.2. Rheology

An ink with required rheological properties can be successfully applied to the image on a plate, transferred correctly to the stock and finally, retain its form as a print. Each printing technique has specific requirements. For opacity, it is important to select pigment and pigment volume concentrations that play a role on opacity, gloss and whiteness, but also on the rheology of the ink. Different pigment grades have different medium absorption. As a consequence, the rheology of the ink at the time of application will be affected. Many ingredients, apart from TiO₂ pigments, will affect the final rheology of the ink. It is important to note that formulation of inks calls for much practical experience and skill.

It is vital to incorporate TiO₂ pigment into the printing ink medium in a way that maximum dispersion is achieved. In the case of a poor dispersion stability even viscosity could be affected.

2.3.3. Solubility parameters and dispersion

From the economical point of view, the best dispersion state of TiO₂ should be obtained in the shortest time and with minimum expenditure of energy.

Inorganic and organic surface treatments of TiO₂ could be optimized in order to maximize pigment affinity with both binder and solvents. This results in pigments with better dispersion and stabilization in a wide range of printing ink formulations, i.e., improved opacity, gloss and color [35].

The end-user of printing inks has the skill to select a range product (TiO₂ grade); the best suited grade for a particular purpose.

Optical properties of the pigment are defined by the particle size distribution, while the applicative properties are determined by the surface treatment. By implementation of more intensive milling, we prepared a slurry of more dispersed TiO₂ particles. The prepared TiO₂ slurry has been used for further surface treatment. Our goal was to keep the particles separated from each other through the whole process.

The influence of milling and coating process on optical properties are presented in Table 3. In order to improve the applicable properties, it is important to coat TiO₂ particles under

![Figure 19. Alumina surface-treated TiO₂ intended for printing inks applications.](image-url)
controlled conditions (T, pH, precursor dosing rate). Under such conditions, the alumina surface-treated particles are separated from each other; coating is uniform and dense, covering the entire surface of the particle (Figure 19). Such particles exhibit excellent optical properties, as demonstrated in Table 3. In the case where the process of surface treatment started from suspension with more dispersed or deagglomerated particles (intense milling), higher gloss was obtained for the system with incorporated TiO$_2$.

2.3.4. Optical density

A layer of alumina oxide layer can increase the amount of –OH groups on the particle surface, which can improve the dispersibility of the particles and provide more active sites for further organic modification; this was evidenced from the results obtained by OD method. TiO$_2$ particles surface-treated under controlled conditions exhibit significantly higher light scattering efficiency due to complete aluminum layer coating the entire TiO$_2$ surface. Lower LSE was determined for TiO$_2$ particles with incomplete coatings, produced under uncontrolled conditions (Figure 20).

Printing ink with incorporated TiO$_2$ particles with incomplete coatings was highly viscous. For printing inks production approximately 10% more solvent was needed. Since the viscosity

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gloss</th>
<th>Scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poorly milled material</td>
<td>24.4</td>
<td>97.4</td>
</tr>
<tr>
<td>More intense milling</td>
<td>40.5</td>
<td>104.1</td>
</tr>
</tbody>
</table>

Table 3. Influence of milling and coating process on optical properties.
of the dispersion and the type of optical properties (especially the undertone and gloss) are strongly dependent on the degree of particulate dispersion, we can conclude that in controlled surface treatment, we obtained more dispersed particles.

2.4. TiO\(_2\) applications in paper laminates

As already mentioned before, TiO\(_2\) is a semi-conducting material and show some intrinsic photocatalytic activity. During weathering, interaction of UV light with TiO\(_2\) occurs resulting in the formation of free electrons and electron-holes in the crystal lattice. These radicals react easily with neighboring organic molecules and, result in degradation of the medium [36–38]. The interaction of UV light with TiO\(_2\) particles results in the formation of Ti\(^{3+}\) centers that are violet-colored species. For that reason, discoloration (greying) of the exposed area might be observed. This is usually described in terms of the lightfastness [37].

Generally, commercial TiO\(_2\) grades are surface-treated with hydrated compounds of alumnum, silicon and zirconium [39–42]. Silica contributes to durability, while zirconia improves gloss and durability. Alumina is usually used as a final layer to increase dispersion stability. Sometimes, special surface treatment, for example, with aluminum phosphate is required to provide high lightfastness in applications such as decorative papers [43]. Scanning transmission electron microscopy (STEM) image of TiO\(_2\) surface treated with aluminum phosphate is presented in Figure 21.

2.4.1. Lightfastness

The lightfast properties of printing inks can be defined as the amount of resistance to fade or color change of a printed surface when exposed to daylight (or an artificial light source) over a set period of time.

For determination of lightfastness of prints, Blue Wool Scale is utilized. According to this method, samples are exposed to a standard xenon light in appropriate equipment.

Figure 21. STEM image of TiO\(_2\) with aluminum phosphate coating.
The lightfastness is indicated by the grades on the Blue Wool Scale: BWS 1 = poor, BWS 2 = low, BWS 3 = average, BWS 4 = rather good, BWS 5 = good, BWS 6 = very good, BWS 7 = extremely good, BWS 8 = excellent.

TiO₂ with aluminum phosphate coating successfully underwent testing by the end-user with grades 4/5 on the Gray Scale (grades 1–5) and with grade > 6 on the Blue Wool Scale; we met the requirements of the user.

2.4.2. Electrochemical properties determination

IEP of pure TiO₂ particles is about pH 4. Modifying the pigment surface with inorganic layers of, for example, Al₂O₃, SiO₂, ZrO₂, phosphates changes the IEPs [2]. Whereas, for example, Al₂O₃ (IEP = 9) and Al(OH)₃ species (IEP is about 6.8) shifts the IEP to higher pH values, other substances normally tend to reduce the IEP to lower pH values (IEP of SiO₂ = 2, IEP of ZrO₂ = 4). Phosphates, used for surface treatment form acidic groups on the surface of particles, which are acidic and becomes a potential determinant [2, 14].

In Figure 22, the zeta potential as a function of pH for untreated and surface-treated TiO₂ pigments are presented. IEP of pure TiO₂ particles is about 4 and according to literature [2], IEP of aluminum surface-treated TiO₂ is 8.65, which is close to the values determined for Al₂O₃. IEP of Si surface-treated TiO₂ shifted to pH 2.5, close to IEP characteristic for SiO₂. Complete alumina layers contributed to shift IEP to higher pH values (pH 8.6), which proves a successful surface treatment, since the IEP value of surface-treated samples lies close to the IEP value characteristic for alumina. The results are in agreement with literature. Multi-layered surface treatments, alumina in combination with silica and phosphate, shifted IEP to lower pH. IEP values for all samples are presented in Table 4. The uniformity and the properties of hydroxide coatings influenced the surface properties of the pigment particles because the coated particles show similar surface characteristic, such as surface charge and surface active sites or groups, as the coating material.

Figure 22. Zeta potential as a function of pH.
3. Conclusions

Surface treatment of TiO$_2$ particles is one of the most important steps in the production of TiO$_2$ pigment. It is a delicate and complex process. Process parameters such as pH and temperature have to be carefully controlled, as this is essential to ensure the formation of uniform oxide coatings and achieving the desired useful features. Surface-treated TiO$_2$ particles were prepared starting from various precursors by the chemical liquid deposition method. Uniform hydroxide layers formed on the surfaces of the TiO$_2$ particles under mild hydrolysis rate of, for example, sodium aluminate, aluminum sulfate or sodium silicate in gel precipitation and aging. The morphology of the layers was significantly affected by the temperature and pH value of the reaction solution. Formation of thin and uniform hydroxide layers influenced optical and electrochemical properties. Surface-treated particles altered their electrokinetic behavior in a way similar to the coating material, suggesting formation of a complete hydroxide layer on the TiO$_2$ surface. We can conclude that inappropriate pH conditions can lead to undesirable phases of hydroxides or to an incomplete layer. By applying a dense silica layer of colorless alumina phosphate, photoactivity of TiO$_2$ pigments was successfully suppressed.

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