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Alumina Surface Treated TiO_2 – From Process to Application

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Abstract: Titanium dioxide (TiO_2) has found widespread use. Typically it is used in another matrix to impart certain properties. For example, it is widely used as a white pigment for paints and polymers. The aim of this research work was to achieve improvements in the sense of processability as well as the dispersion performance of alumina surface treated pigmentary TiO_2in polymer matrix. Wet chemical method was used to modify the surface of the TiO_2 pigment. Surface treatment included precipitation of hydrous oxides of aluminium on the surface of TiO_2 particles. During controlled surface treatment, agglomeration has been avoided, which has been proved to improve applicative properties of TiO_2 particles. In addition to that, organic additives were applied to enhance performance attributes of the pigmentary TiO_2. The effectiveness of surface treatment was determined using scanning-transmission (STEM) and transmission (TEM) electron microscopy. Quantitative evaluation of quality and dispersion of the pigments has been performed using Filter pressure test. Lower pressure generated during filter pressure test when particles were well dispersed in a polymer matrix. Surface treatment also affected pigment processibility; i.e. filterability and settling, which is of high importance for process planning.

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1. INTRODUCTION

Titanium dioxide (TiO_2) pigments are 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. 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. After treatment or coating of the pigment particles improves the applicable properties of pigments in matrix [1]. The treatment consists of coating the individual pigment particles with colorless inorganic compounds of low solubility by precipitating them onto surface. There are many of literature on this subject [2-11]. However, this reduces the optical performance of the pigment approximately in proportion to the decrease in the TiO_2 pigment. The effect of these coatings largely depends on their composition and method of application, which may give porous or dense coatings. The treatment process also affects the dispersibility of the pigment, and therefore a compromise often has to be made. Good dispersibility of the pigment in the binder or matrix is usually desired. These effects are controlled using different coating densities and porosities [12, 13]. Hydrous aluminum oxide is probably the most common treatment on TiO_2 pigments. The hydrous alumina particles on the pigment surface reduce the particle-particle attractive forces and improve dispersibility [1].

Following the inorganic surface treatments, the pigments are filtered, rinsed, dried and then further modified with an organic surface treatment, before being ground in a steam jet mill [12, 13]. Many pigments are treated with an organic coating during the final milling stage, but some pigments contain no organic treatment. Organic treatments are used to improve compatibility with the coating or plastic and to improve dispersion [1].

The aim of research was to coat the surface of the pigment in a controlled manner to prepare material with high level of dispersibility in polymer matrix. With the intention of improving applicable properties, uniform layers of aluminium hydroxide on the surface of pigmentary TiO_2 were formed during wet chemical deposition method. In addition to improved applicable properties, the optimization of the coating process affected positively the procesibility of surface treated TiO_2.

2. EXPERIMENTAL SECTION

2.1. Materials

Optimization of the process for production of alumina surface treated pigmentary TiO_2 for applications in masterbatches

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(MB) on the laboratory scale was carried out. Pigmentary TiO_2 particles in rutile crystalline form, produced by the sulphate process in Cinkarna Celje (Slovenia) were used in this research. The TiO_2 particles used had a mean diameter of 250 nm, with a surface area of 6.9 m^2/g. Sodium aluminate (Na-aluminate) with c = 270 g/L Al_2O_3 was used as a source of alumina hydroxide. Micronization of dried pigment was carried out on a pilot jet mill.

Coating Process

Hydroxides must precipitate on the surface of the TiO_2 particles under controlled conditions (pH, T, the time of dosing). The chemistry that provides precipitation of hydroxides onto the surface of pigment only is very complex.

Solubility and Solution Species

The morphology of alumina layers depends on the deposition conditions. Aluminium oxide and hydrous alumina have many different structures, which can give many different properties to coated particles. The solubility limit and the type of solution species depend upon the solution pH, T, other ionic species, and the solid phase. The total Al(III)aq concentration in equilibrium with various aluminas and aluminum hydroxides has a minimum pH about 6–7 [14-17]. Only at low pH (below about pH 4 or 5) the species Al^{3+} exist as the majority solution species. As pH increases the metal cation reacts with hydroxide anions in solution progressively to produce soluble hydrolysis products according to the solution equilibria [16-18]:

$$Al^{3+} \rightarrow Al(OH)^{2+} \rightarrow Al(OH)_2^+ \rightarrow Al(OH)_3 \rightarrow Al(OH)_4^-$$

The hydrolysis reactions of aluminium with hydroxide occur between about pH 5 and pH 8 at room temperature and low Al(III) concentration so that the dominant solution species is the negatively charged $Al(OH)_4^-$ above about pH 8.

Designations of uncoated and differently coated pigmentary TiO_2 are collected in Table **1**.

Table 1: Samples Designations

Sample	Designation
SAMPLE 1	Uncoated TiO_2
SAMPLE 2	Poorly alumina coated TiO_2
SAMPLE 3	Completely alumina coated TiO_2 (alumina deposition under neutral pH conditions)
SAMPLE 4	Completely alumina coated TiO_2 (alumina deposition under slightly acidic pH conditions)

2.2. Methods

Characterization part has been performed using the following analytical methods:

- Particle charge detector and Zetameter for electrochemical properties determination
- Electron microscopy for coatings morphology determination
- Gas adsorption analyzer for specific surface area (S_{BET}) determination
- Contact angle (CA) measurements for hydrophobicity determination
- Settling and filtration tests for processibility determination
- Filter pressure test for determination of dispersibility in polymer matrix

a. Particles Characterization

2.2.1. Electrochemical Properties Determination

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 [3].

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.

In addition, ZetaPALS (Brookheaven Instruments Coorporation) was used for the measurment of zeta potencial of dispersed particles in solution.

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.

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. Specific Surface Area (S_{BET}) Determination

S_{BET} method was used in this research for the calculation of surface areas of pigmentary TiO_2 by physical adsorption of gas molecules. The specific surface area S_{BET} was determined using an automated gas adsorption analyzer Tristar 3000 (Micromeritics Instrument Co.).

2.2.4. Contact Angle Measurements

Hydrophobicity is mostly achieved by the employment of silicone coatings or of silicone modified systems [19]. Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. Generally, if the water contact angle is smaller than 90°, the solid surface is considered hydrophilicand if the water contact angle is larger than 90°, the solid surface is considered hydrophobic [20, 21].

Goniometer (Krüss) was used for contact angles determination.

<u>b. Processinng Properties Determination</u>

2.2.5. Settling Characteristics of Suspended Particles

In the batch settling test a suspension of particles of known concentration is prepared in a measuring cylinder. The cylinder is shaken to thoroughly mix the suspension and placed upright to allow the suspension to settle. The positions of the interfaces formed are monitored in time. Three zones of constant concentratiion are formed; zone A – clear liquid, zone B – of concentration equal to the initial suspension concentration; and zone S – the sediment concentration [22].

2.2.6. Filtration

Cake filtration is widely used in industry to separate solid particles from suspension in liquid. Cake filtration occurs when a liquid containing solid particles is forced through a porous filter medium which is open enough to allow the passage of the liquid, but tight enough to retain the solid particles.It involves the build up of a bed or cake of particles on a porous surface known as the filter medium, which commonly takes the form of a woven fabric. As more liquid is forced through the medium, the solids form thicker filter cake. This filtration process can be analysed in terms of the flow of fluid through a packed bed of particles, the depth of which is increasing with time. In practice many materials give rise to compressible filter cakes. The main characteristic of cake filtration is that the cake which is formed must be porous enough to permit continued fluid flow through it as filtration progresses [22, 23].

<u>c. Applicable Properties Determination</u>

2.2.7. Filter Pressure Test

A thin and uniform hydroxide layer can improve applicable properties of TiO_2. The alumina also acts as a spacer for the particles. Aluminium hydroxide coating enhanced the amount of –OH groups on the particles, which improves the dispersibility of the powder in polymer matric. Full advantage 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. dispersed as thoroughly as possible [9].

Filter pressure test makes quantitive evaluation possible. The filter pressure value (FPV) describes the quality and dispersion of the pigments. The pressure index (PI) is a measure of the fineness of dispersion of pigments in a masterbatch. Low pressure index values (PI) stand for high dispersion quality [24].

3. RESULTS AND DISCUSSION

3.1. Electrochemical Properties

The ζ-potential 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. The pH and T affect the hydrolysis-polymerization precipitation process of the coating reagent, as well as the coating morphology. A high pH environment speeds up the hydrolysis of Al^{3+}, and more multinuclear OH-Al species are formed compared with the situation at low pH [8, 25].

In the Figures **1** and **2** we can see how changing the pHconditions influences the formation of Al species on the surface of TiO_2 particles and, consequently, the change of electrochemical properties of pigment, as evidenced by the shift of IEP.

IEP is defined as the pH, where in the value of ζ-potential is equal to 0, while the PZC is determined using titration. IEP and PZ Care the same, when the electrolyte is neutral, that is, when the ions are not adsorbed specifically. In this study both methods were used; i.e. determination of the IEP and PZC. Similar results can be observed with both methods.

From the results presented in Figure **1** and formation of soluble hydrolysis products according to the solution equilibria, we could assume that the surface of SAMPLE 3 is formed mostly of $Al(OH)^{2+}$ species, while due to the pH changes during alumina precipitation from precursor Na-aluminate, the surface of SAMPLE 4 consists mostly of $Al(OH)_3$ species.

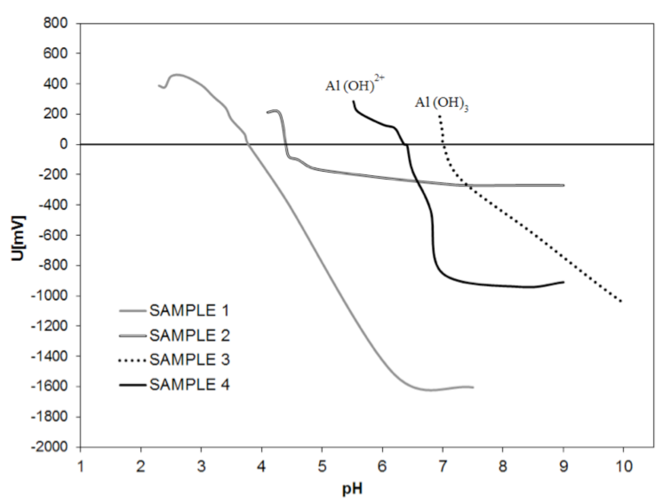

Figure 1: PZC for TiO_2 particles without and with alumina layers formed under various pH conditions.

The difference between poorly and entirely coated TiO_2 can be seen in Figures **1** and **2**. The uniformity and the properties of hydroxide coating 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. IEP of pure TiO_2 particles is about 4 and according to the literature [9] IEP of $Al(OH)_3$ species is about 6.8. IEP values of SAMPLE 3 and SAMPLE 4, which are considered as samples with complete coatings lie close to the IEP values, characteristic for aluminium hydroxide, while the IEP of poorly coated TiO_2 lies closer to IEP of untreated TiO_2.

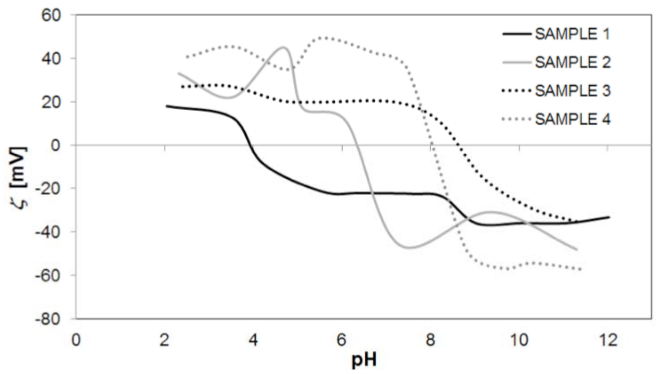

Figure 2: IEP for untreated TiO_2 and TiO_2 particles with alumina layers formed under various pH conditions.

3.2. Surface Morphology

In order to improve the applicable properties, it is important to coat pigmentary particles under controlled conditions (T, pH, precursor dosing rate). Under such conditions, surface treated particles are separated from each other; coating is uniform, covering the entire surface of the particle (Figure **3**).

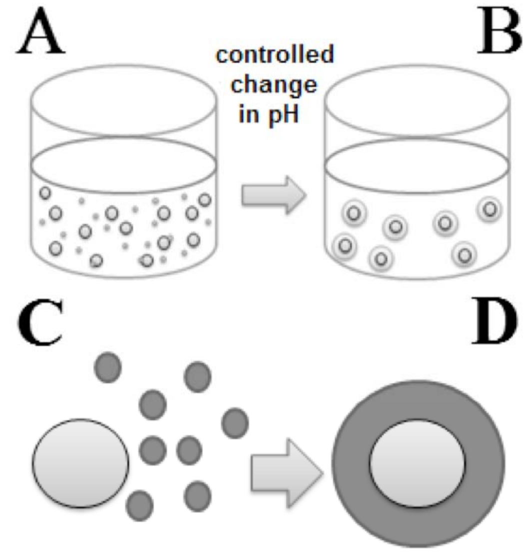

Figure 3: Graphical illustration of controlled precipitation.

A. Dissolved inorganic precursor in a suspension of TiO_2 particles.

B. By gradual adjustment of the pH value towards neutral, the inorganic substances are finely precipitated on the surface of TiO_2 particles.

C. At the beginning of the surface treatment process, precursor moleculesare homogeneously distributed in a suspension of TiO_2 particles.

D. TiO_2 particles are subsequently covered with a layer of Al-hydroxide.

Alumina surface-treated pigmentary TiO_2 particles were prepared, starting from precursor Na-aluminate by the chemical liquid deposition method.The effectiveness of surface treatment was determined using scanning-transmission (STEM) and transmission electron microscopy (TEM). Figure **4** shows a TEM image of a pigmentary TiO_2, surface treatedwith alumina hydroxide. TiO_2 has crystalline structure, while the coating is amorphous and more structured than the core TiO_2. Uniform amorphous layers which entitely encapsulateTiO_2 particles were formed in the heterogeneous nucleation of alumina molecules on the surface of TiO_2 under controlled conditions.

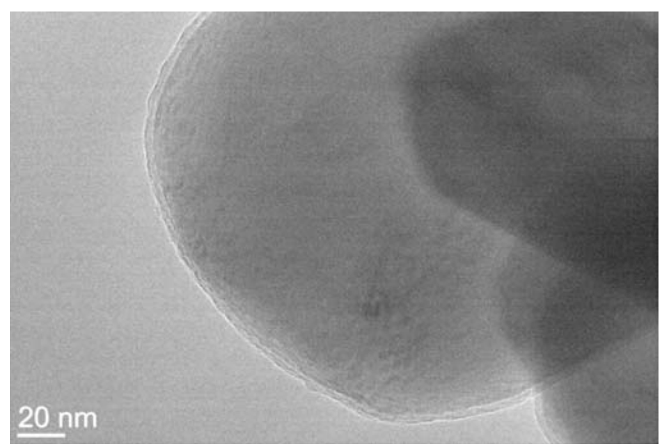

Figure 4: TEM image of alumina coated pigmentary TiO_2 particles yielded *via* precipitation from Na-aluminate under controlled conditions. Uniform alumina layer formed on the surface of the TiO_2 particles under mild hydrolysis rate of Na-aluminatein gel precipitation and aging.

On the contrary, when surface treatment doesn't proceed under controlled conditions, the coating formed wasn't uniform due to the fact that the structure of the alumina layer on TiO_2 pigment varied with the process conditions. STEM image of SAMPLE 2 is presented in Figure **5**.

Consequently, surface treatment resulted in increased S_{BET} ofa pigment. S_{BET} was affected by the synthesis conditions (e.g. pH and T), which have been already noticed when analysing the morphology of coating susing electron microscopy. Depending on the synthesis conditions, S_{BET} varies between17.8 and 22.8m^2/g (Table **2**). It can be concluded that S_{BET} was influenced by the morphology of coatings.

3.3. Influence of the Coating on TiO_2 Dispersibility

STEM images in Figure **6** show how the dispersibility of TiO_2 particles was affected by a layer of alumina hydroxide. A level

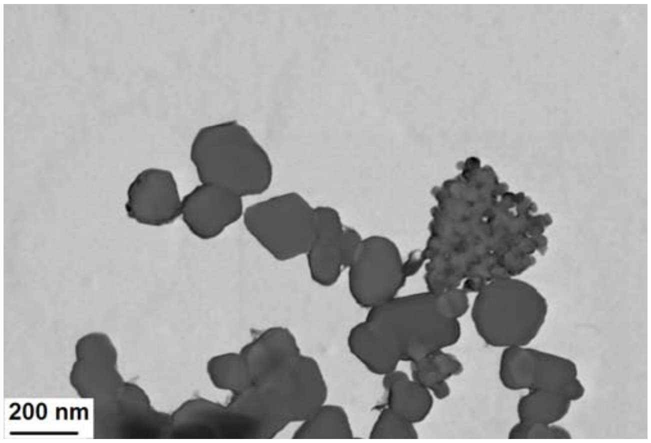

Figure 5: STEM image of alumina coated pigmentary TiO_2 particles yielded *via* precipitation from Na-aluminate under uncontrolled conditions.

Table 2: **S_{BET} of Uncoated and Completely Alumina Coated TiO_2 Particles**

	SAMPLE 1	SAMPLE 3	SAMPLE 4
S_{BET} [m^2/g]	6.9	22.8	17.8

of agglomeration in suspension of poorly coated particles - SAMPLE 2 is higher (Figure **6A**) in comparison to suspension of particles with coating, which entirely surround the surface of particles – SAMPLE 1 (Figure **6B**).

3.4. Hydrophobization of Pigmentary TiO_2

Hydrophobic character of organically surface treated pigment depends on the silicon emulsion used. Untreated TiO_2 and alumina surface treated TiO_2 without organic surface treatment were hydrophilic. In that case contact angle (CA) measurements were not feasible. In the Table **3** CA determined for completely coated TiO_2 pigment with and without organic surface treatment are listed. For organic surface treatment 2 siloxanes were used. The results of CA measurements show that siloxane 2 was significantly more effective in comparison to siloxane 1. Alumina surface treated TiO_2, organically modified using siloxane 2 was much more hydrophobic (see Figure **7B**). All TiO_2 remain on the surface of water. In the meantime, alumina surface treated TiO_2 organically modified with siloxane 1 began to settle emediately after contact with water (see Figure **7A**). With this test we proved that selecting the appropriate agent for organic surface treatment is of great importance for TiO_2 performance. In addition to that, several aspects of positive or negative influences of the additives for the organic post-treatment have to be considered; e.g. influence of handling in production, influence on end application (migration, sealing, printing), recommended loadindg, etc.

Processing Properties

3.5. Settling Characteristics of Suspended Particles

Rinsing after surface treatment is of significant importance due to the fact that large amount of salt generated during the surface treatment process.

Sedimentation processes affected by such factors as particle size and density, liquid density and viscosity, and the conditions which influence these factors [26].

Settling tests showed that pigment, which is entirely surrounded by Al-hydroxide species posseses appropriate processing properties. Figure **7** shows that a suspension of

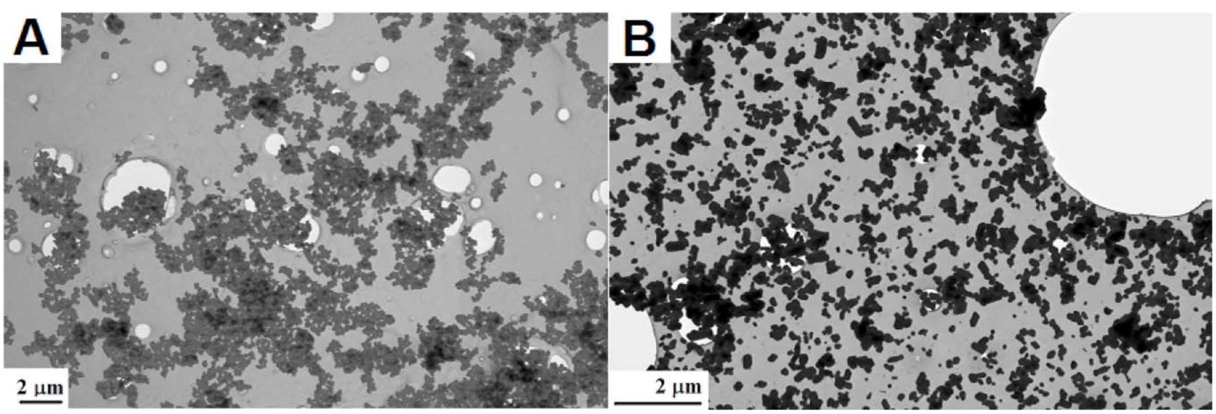

Figure 6: STEM images of more (**A**) and less agglomerated (**B**) alumina coated pigmentary TiO_2 particles.
A. Suspension of poorly coated TiO_2 particles.
B. Suspension of completely coated TiO_2 particles.

Table 3: **CA Determined for Completely Coated TiO_2 Pigment with and without Organic Surface Treatment**

	SAMPLE 3 (Without Siloxane)	SAMPLE 3 + Siloxane 1	SAMPLE 3 + Siloxane 2
CA [°]	/	92	102

Figure 7: Hydrophobization of alumina surface treated pigmentary TiO_2 using 2 different siloxanes.

A. Organic surface treatment with Siloxane 1.

B. Organic surface treatment with Siloxane 2.

entirelycoated particles settles better (the compression phase of increased density) in comparison with a suspension containing poorly coated particles. The results confirmed that the characteristics of particle settling changed. The suspension of entirely coated particles (SAMPLE 3) is comprised of more uniform particles. In that case entire hydroxide precipitated on the surface of the pigment particles only, which was confirmed by the results obtained with the use of electron microscopy. In the case of poorly coated TiO_2, the hydroxide beside on the TiO_2 surface precipitated in the suspension as well, thus negatively influenced the settling ofthe particles. This negative influence is attributed to lighter Al-hydroxide species, formed as a separated particles, comparing to heavier composite of alumina hydroxide and TiO_2 particles.

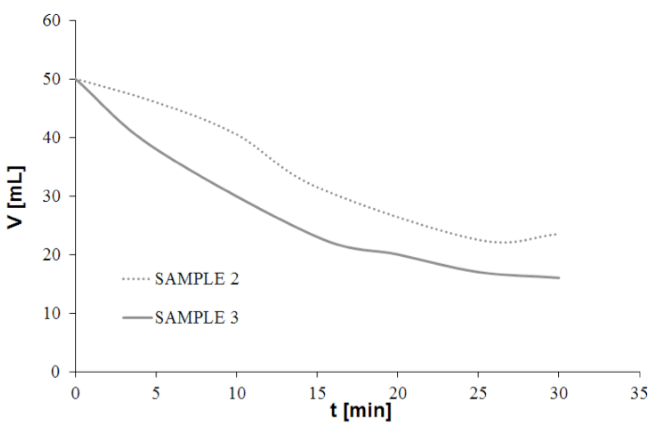

Figure 8: Settling of poorly and entirely alumina coated pigmentary TiO_2.

3.6. Filtration

After treatment in aqueous media, the pigments are washed on vacuum filter until they are free of salt, and then dried. The same process conditions were used during the test (filter cloth, pressure).

Filter test showed similar trend as settling test. Suspension of entirely coated TiO_2 particles (SAMPLE 3) was filtered approximately 2-times faster than suspension, which contained poorly coated particles (SAMPLE 2). According to the tests, filterability of suspension with uniform particles was better. The results of filter test are presented in Table **4**.

Table 4: Filterability of TiO_2 Suspensions

SAMPLE	SAMPLE 2	SAMPLE 3
Time of filtration [h]	0.745	0.35
Filterability [kg /m^{2}h]	39.525	95.257
The depth of filter cake [mm]	37	47

Applicable Properties

3.7. Filter Pressure Test

Masterbatch (MB), based on low-density polyethylene (PE) was prepared on the laboratory exstrudor. MB was used for foil formation.

A layer of alumina hydroxide increased the amount of -OH groups on the particle surface and provided more active sites for further organic modification, which in turn improved the dispersibility of the TiO_2 in polymer. In Figure **9** intersection of PE foil with incorporated alumina surface treated TiO_2 particles is presented, showing evenly distributed pigmentary particles in the binder. With surface treatment we influenced TiO_2 surface characteristics, and consequently the quality and degree of pigment dispersion in the polymer matrix.

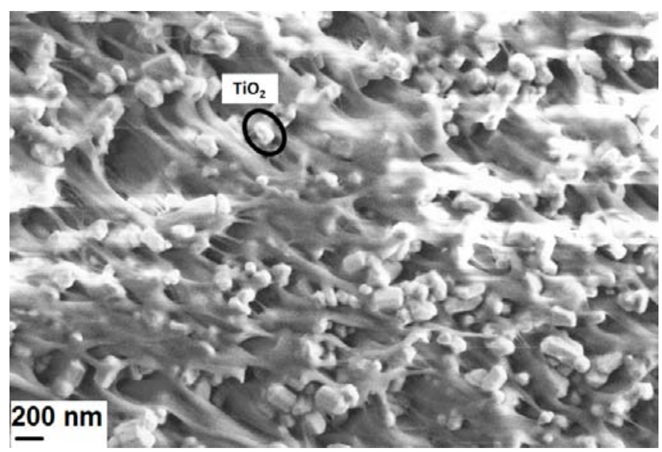

Figure 9: SEM image of intersection of PE foil with incorporated completely alumina surface treated TiO_2 particles.

Table 5: Filter Pressure Value for Dispersion of TiO_2 in MB

SAMPLE 2	
FPV	0.84 bar/g
SAMPLE 3	
FPV	0.35 bar/g

Application of filter pressure test indicated good quality and dispersion of alumina surface treated TiO_2 in PE. In Table **5**

FPV of poorly coated (SAMPLE 2) and evenly coated pigmentary TiO_2 particles (SAMPLE 3) are presented. FPV determined for dispersion of completely coated pigments in MB was significantly lower (0.35 bar/g), indicating high dispersion quality.

CONCLUSIONS

New pigmentary TiO_2 type has been designed for improved dispersion performance. Pigmentary TiO_2, entirely coated with alumina layer performed best with regard to its technical producibility; it was the easiest to filtrate and settle. Generally, better settling and filtration contribute to shortening of the batch duration.

Controlled surface treatment influenced surface characteristics of TiO_2 and consequently the dispersion of pigment in polymer matrix. In addition, the use of proper organic surface treatment imparted an improvements of hydrophobic properties. This resulted in outstanding dispersibility and significantly improved masterbatch processing conditions.

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