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MODIFICATION OF HYDROPHILIC/HYDROPHOBIC CHARACTER OF TiO₂ SURFACE USING SELECTED SILANE COUPLING AGENTS

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In the studies R-213 titanium white was used, produced by Chemical Works Police S.A. Modification of titanium dioxide surface was conducted in order to alter its physicochemical properties. In this aim for modification organic coupling agents were employed, containing vinyl, amine and metacryloxy functional groups. Effects of concentration of the silane coupling agent (0.5, 1 or 3 weight parts) on dispersive properties and on morphology of TiO₂ particles were examined. In the studies advantage was taken of SEM and NIBS techniques. For the obtained in this way products elemental composition, particle size distribution, BET specific surface area and rate of sedimentation in water were examined. Surface modification changes hydrophilic/hydrophobic character of the obtained preparations, promoting also agglomeration of TiO₂ particles.

Key words: titanium dioxide, surface modification, silane coupling agents, adsorption isotherms, surface morphology, dispersion, particle size

INTRODUCTION

Inorganic pigments, as compared to organic pigments, remain insoluble, chemically neutral, resistant to elevated temperatures and environmental factors such as extreme pH of the environment or chemical agents. They used to manifest augmented resistance to light, higher ability to become dispersed and higher coating potential. Their disadvantages include lower brightness, colour intensity and staining power. Such properties of the pigments are significantly affected by particle shape and size distribution, chemical composition and surface properties of pigment particles (Binkowski 2000, Kohler 1997, Chantrapornchai 2000, Sobolewski 2004).

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Therefore, the role of inorganic pigments progressively increases, as compared to the role of organic pigments (Krysztafkiewicz 1995, 1999, Endri 1998, Carter 1998).

Apart from carbon black, titanium white belongs to one of the most frequently applied pigments. It used to be applied in paints and varnishes and it finds wide application in staining plastics, first of all due to its excellent coating properties, and in paper industry (Bieniek 2004, Sobolewski 2004). In contrast to colourful pigments (inorganic and organic ones) titanium white absorbs no visible light of any wavelength (Macionga 2005). In the paper studies are described on modification of TiO₂ using selected alkoxysilanes. Moreover, effects of the modification were examined on physicochemical characteristics of titanium dioxide.

EXPERIMENTAL

MATERIALS

TYTANPOL[®]R-213 represents a pigment of a rutile variety, deeply surface processed using compounds of aluminium and silicon (amounting to 4.7% of Al₂O₃ and 8.3% of SiO₂, respectively) and modified with organic compounds of a hydrophilic nature. Principal properties of the pigment, produced by Chemical Works Police S.A. using the sulphate technique are listed in Table 1.

Table 1. Principal properties of the titanium dioxide R-213

Physicochemical parameter	Value
Density (g/cm ³)	3.7
Content of titanium dioxide (wt. %)	82
Content of volatile substances at 105°C (wt. %)	1.5
Content of water soluble materials (wt. %)	0.7
Residue on a sieve of 45 µm mesh (wt. %)	0.02
Brightness	95.5
Shade in a white paste	7.1
Relative scattering ability	86
Ability to tone down the shade	1730
Shade in a gray paste	2.0
pH in water suspension	8.0
Oil absorption number (g/100g pigment)	40

Silane proadhesive compounds produced by PIW Unisil (Tarnów, Poland) were used as the agents capable of modifying titanium white surface. The following organic coupling agents were used: 3-metacryloxypropyltrimethoxysilane (U-511), CH₂=C(CH₃)COO-(CH₂)₃Si(OCH₃)₃, vinyltrimethoxysilane (U-611), CH₂=CHSi(OCH₃)₃ and *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D), H₂N(CH₂)₂NH(CH₂)₃Si-(OCH₃)₃.

METHODS OF STUDIES

The process of modification of titanium white surface was conducted by „the dry technique”: a reactor of 500 cm³ capacity was charged with 40 g titanium dioxide sample to which a solution of the organic modifying agent was dosed. The solution contained silane coupling agent at the amount of 0.5; 1 or 3 wt./wt. of TiO₂ and 10 cm³ of the solvent (mixture of methanol and water at 4:1). The system was mixed for 1 h to assure complete wetting of the titanium white with the solution of modifying agent. Subsequently, titanium white was dried in a stationary drier for 2 h at the temperature of 105°C.

The modified titanium white samples were subjected to morphological and microstructural analysis using scanning electron microscopy (Philips SEM 515). Size of titanium white particles as well as particle size distribution were documented using Zeatasizer Nano ZS instrument (Malvern Instruments Ltd.) employing the technique of non-invasive back scattering (NIBS). Particle size distribution curves permitted also to calculate polydispersity (as a measure of uniform character of the pigment). In order to characterize adsorptive properties of the product nitrogen adsorption/desorption isotherms were determined and parameters such as specific surface area, pore volume, mean pore size were estimated using ASAP 2010 apparatus (Micromeritics Instruments Co.). Moreover, sedimentation profiles for selected TiO₂ using Tensiometer K100 (Krüss) were evaluated.

RESULTS AND DISCUSSION

Particle size distribution, with appropriate attention given to band intensity and volume share, and the respective SEM electron microphotograph of the unmodified titanium dioxide R-213 are presented in Fig.1.

Particle size distribution analyzed in relation to intensity (Fig.1a) demonstrated a single band. The band was linked to the presence of particles of smaller and larger sizes in the range of 220 – 5560 nm (with maximum intensity of 11.2 for the particles of 615 nm in diameter). Polydispersity, representing the scatter of particle diameters, amounted to 0.233. Also in the particle size distribution analyzed by volume share (Fig.1b) a single diffuse band was present. It reflected the presence of particles, primary and secondary agglomerates of 190 – 6440 nm in diameter (with the maximum volume share of 10.2 for the agglomerates of 5560 nm in diameter). The SEM microphotograph (Fig.1c) documented the presence of spherical particles of low diameters, which formed larger aggregates and agglomerates.

Particle size distribution analyzed by band intensity or volume share for titanium dioxide R-213 modified with 3 wt./wt. 3-metacryloxypropyltrimethoxysilane are presented in Fig.2.

The particle size distribution analyzed by intensity (Fig.2a) manifested a single band. The band was linked to the presence of particles, primary and secondary

agglomerates of 190 – 5560 nm in diameter (with maximum intensity of 18.1 for the particles of 396 nm in diameter). The polydispersity amounted to 0.397. The particle size distribution analyzed by volume share showed bimodal character (Fig.2b). It was linked to the presence of particles of lower and higher diameters, ranging from 190 to 6440 nm (with maximum volume share of 13.2 for the particles of 396 nm in diameter).

Particle size distribution for titanium dioxide R-213 modified with 3 wt./wt. of vinyltrimethoxysilane is presented in Fig. 3.

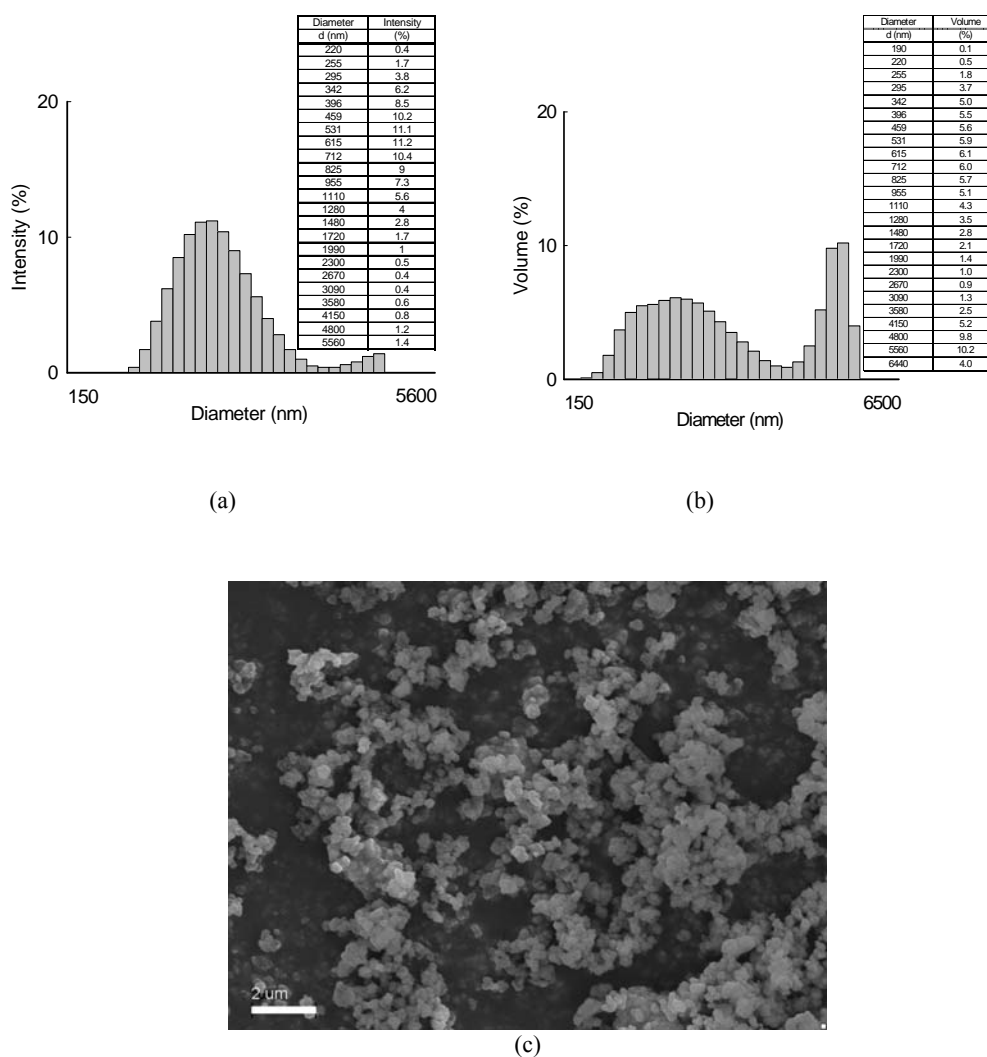


Fig. 1. Particle size distribution: (a) by intensity (b) by volume and (c) SEM image of titanium dioxide R-213

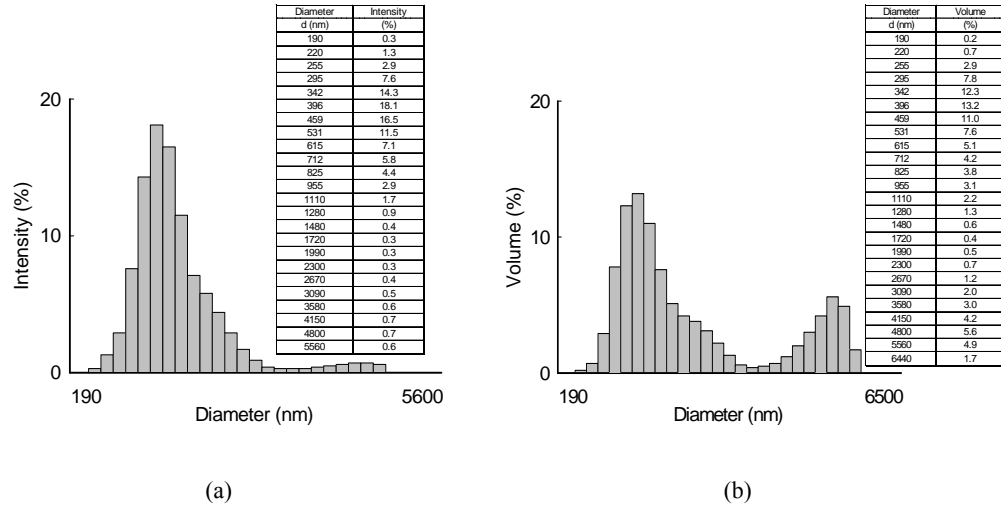


Fig. 2. Particle size distribution: (a) by intensity (b) by volume of titanium dioxide R-213 modified with 3 wt./wt. of 3-metacryloxypropyltrimethoxysilane

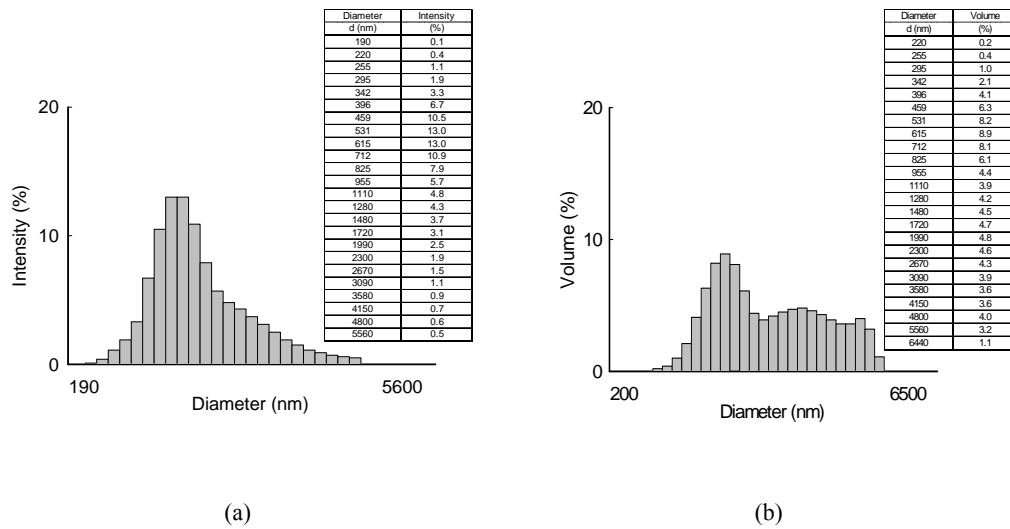


Fig. 3. Particle size distribution: (a) by intensity (b) by volume of titanium dioxide R-213 modified with 3 wt./wt. of vinyltrimethoxysilane

The particle size distribution analyzed by intensity demonstrated a single band (Fig.3a). The band was linked to the presence of primary and secondary agglomerates in the diameter range of 190 – 5560 nm (with maximum intensity of 13.0 for the particles of 531 and 615 nm in diameter). In the particle size distribution analyzed by

the volume share (Fig.3b) also a single band was noted. The band was linked to the presence of particles of smaller and higher diameters, ranging from 220 to 6440 nm (with maximum volume share of 8.9 shown by particles of 615 nm in diameter). Polydispersity of the sample amounted to 0.273.

Particle size distribution analyzed by intensity and by volume share as well as SEM microphotograph of R-213 titanium white modified with 1 wt./wt. of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane is shown in Fig.4.

The particle size distribution analyzed in relation to intensity (Fig.4a) demonstrated a single band. The band was linked to the presence of larger and smaller particles within the diameter range of 164 – 5560 nm (with the maximum intensity of 11.7 for the particles of 459 nm in diameter). The polydispersity, reflecting the scatter of particle diameters, amounted to 0.326. Also the particle size distribution analyzed by volume share showed a single band (Fig.4b) which was linked to the presence of primary and secondary agglomerates with diameters ranging from 190 to 6440 nm (with maximum volume share of 19.2 shown by agglomerates of 5560 nm in diameter). The respective SEM microphotograph (Fig.4c) documented presence of spherical particles of a low diameter, which clumped into larger agglomerates.

Titanium white R-213 demonstrated adsorptive capacity with the range of hysteresis loop encompassing relative pressures of 0.6 – 1.0. The BET specific surface area for the R-213 white was 34.7 m²/g, while size and total volume of pores amounted to 9.8 nm and 0.08 cm³/g, respectively. The course of adsorption/desorption isotherms, which did not rise until the relative pressure of 0.6 was exceeded, and pore diameter of 9.8 nm were typical of mesoporous adsorbents. For the titanate white R-213, surface processed using aluminium and silicon compounds (in the amount of 4.7% and 8.3%, respectively), the BET specific surface area proved to be satisfactory due to the presence of higher numbers of surface active centres (silanol and aluminol groups).

Elemental analysis of the titanium white R-213 modified with the applied coupling agents is presented in Fig.5.

Following the conducted modification an increased amount of coupling agent used for the modification was found to be linked to rising elemental contents of carbon, nitrogen and hydrogen. Titanium white samples which were not modified with organic compounds manifested very low contents of carbon and hydrogen (0.1615%C and 0.4395%H). Application of any modifying agents increased contents of carbon and hydrogen, as compared to those in the unmodified titanium white R-213. The amount and the type of the applied coupling agent significantly affected the contents of carbon and hydrogen.

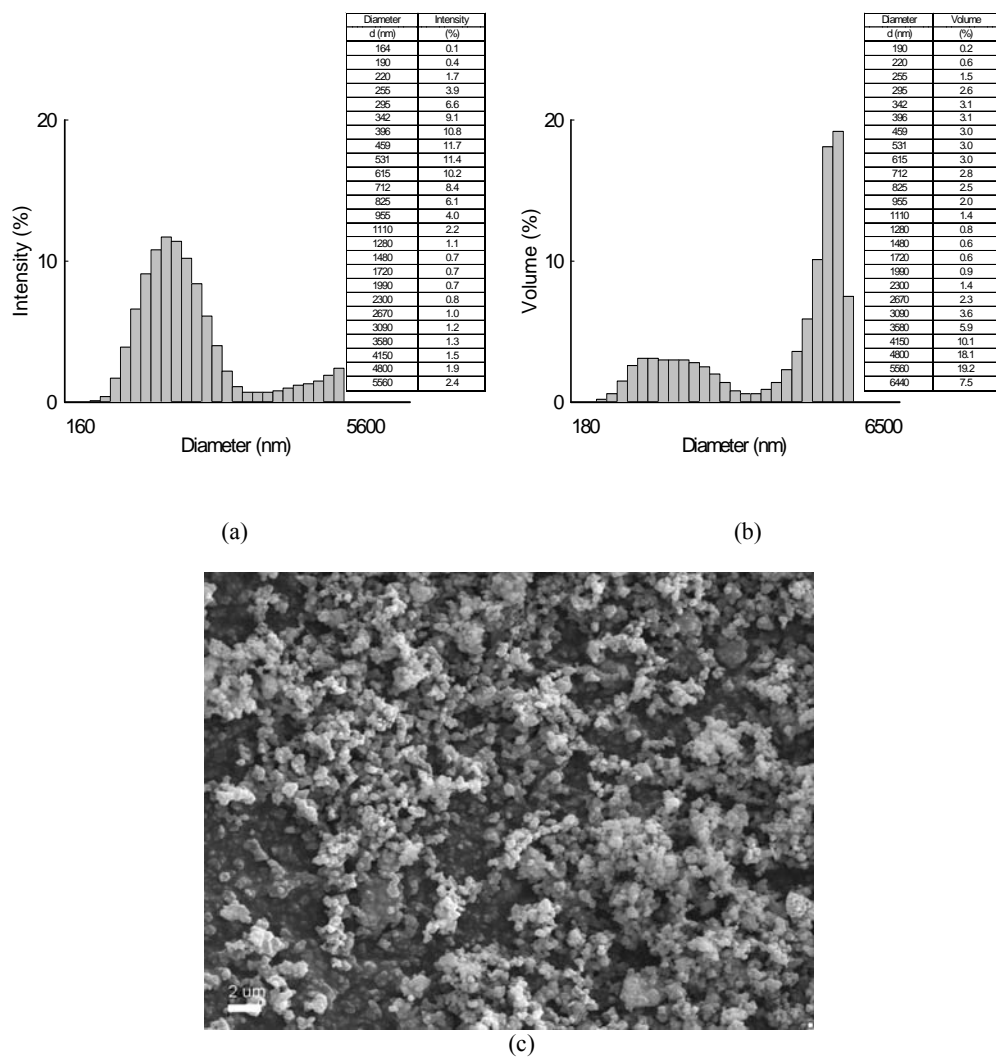


Fig. 4. Particle size distribution: (a) by intensity (b) by volume and (c) SEM image of titanium dioxide R-213 modified with 3 wt./wt. of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane

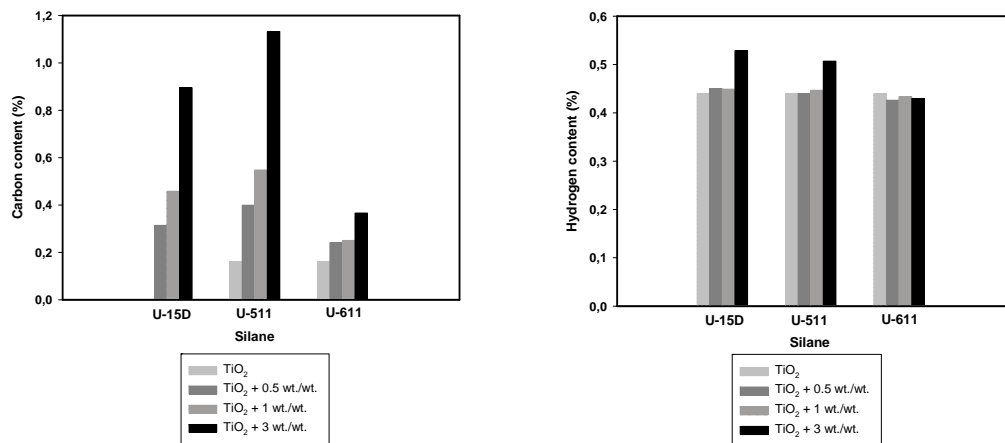


Fig. 5. Elemental content of (a) carbon and (b) hydrogen for titanium dioxide R-213

Water sedimentation profiles for titanium dioxide modified with 1 wt./wt. of the applied proadhesive compounds are presented in Fig. 6.

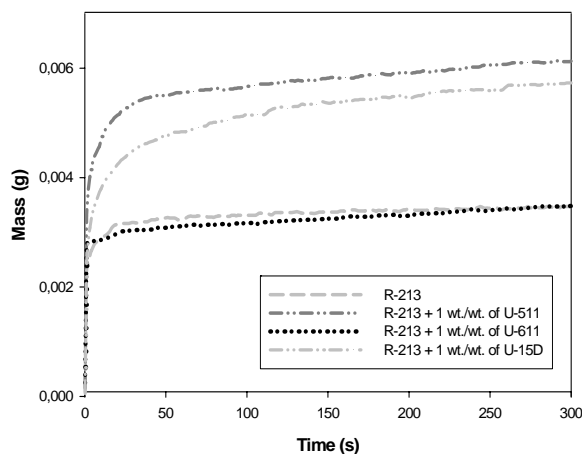


Fig. 6. Profiles of sedimentation in water of titanium dioxide R-213 modified with 1 wt./wt. of appropriate proadhesive compound

The course of curves of sedimentation in water allowed to conclude that the highest time-related increase in sediment weight was demonstrated by titanium dioxide modified with metacryloxysilane, which might be related to C and H contents in the coupling agent, which amounted to 0.548% and 0.4465%, respectively. The lowest

increase in sediment weight in time was manifested by titanium white modified with vinyltrimethoxysilane, the elemental contents of which amount to 0.2505%C and 0.433%H.

CONCLUSIONS

All the titanium white samples subjected to modification with silane coupling agents manifested particles of spherical shape. Thus, we have found that surface modification has not deteriorated morphological and microstructural character of titanium dioxide. Modification of titanium white surface using the applied silanes has promoted changes in polydispersity and in the range of particle diameters. Titanium dioxide modified with 3-metacryloxypropyltrimethoxysilane has manifested particles within a lower range of diameters as compared to the unmodified R-213, and R-213 modified with the two remaining silanes. Nevertheless, independently of the type of employed alkoxysilane modification promotes particle agglomeration which, in a sense, represents an undesirable phenomenon.

The applied for modification titanium white R-213 has demonstrated BET specific surface area of 35 m²/g. It can be included to the group of mesoporous adsorbents. Elemental analysis confirmed efficacy of the conducted modification and may be used for evaluation of the extent to which surface of titanium white is coated with an appropriate modifying agent.

3-Metacryloxypropyltrimethoxysilane has been found to be the best modifier. Titanium dioxide modified with the silane has demonstrated the most pronounced time-related increase in weight of the sediment (as compared to the two other proadhesive compounds used for the modification).

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W badaniach wykorzystano biel tytanową R-213 produkowaną przez Zakłady Chemiczne Police S.A. Modyfikację powierzchni ditlenku tytanu prowadzono w celu zmiany jej charakteru fizykochemicznego. W tym celu do modyfikacji zastosowano organiczne związki wiążące z następującymi grupami funkcyjnymi: winylową, aminową i metakryloksy. Badano wpływ stężenia silanowego związku wiążącego (0,5; 1 i 3 cz.wag.) na właściwości dyspersyjne i morfologię cząstek TiO_2 . W badaniach wykorzystano techniki SEM i NIBS. Dla otrzymanych w ten sposób produktów określono skład elementarny, rozkład wielkości cząstek, powierzchnię właściwą BET oraz tendencję do sedymentacji w wodzie. Modyfikacja powierzchni zmienia charakter hydrofilowo-hydrofobowy otrzymanych preparatów, jednocześnie przyczyniając się do aglomeracji cząstek TiO_2 .