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Characterization of TiO_2 surface following the modification with silane coupling agents

[1]Teofil Jesionowski, [1]Katarzyna Siwińska-Stefańska, [1]Andrzej Krysztafkiewicz, [2]Jadwiga Sójka-Ledakowicz, [2]Joanna Koprowska, [2]Beata Pęczkowska

[1]Poznan University of Technology, Institute of Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland, e-mail: Teofil.Jesionowski@put.poznan.pl
[2]Textile Research Institute, ul. Brzezinska 5/15, 92-103 Łódź, Poland

Studies were conducted on the modification of titanium white surface using selected silane coupling agents. The effect of the concentration of the organic coupling agents was examined (0.5; 1 or 3 weight parts per 100 weight parts of TYTANPOL R-003, TYTANPOL R-211 or TYTANPOL R-213 preparation of titanium white). The dispersive properties were determined by an estimation of the particle size distribution curves and of the polydispersity index. Moreover, microscopic observations were conducted permitting to evaluate the surface morphology of the modified TiO_2 particles. The profiles of sedimentation in water were also determined for the titanium whites and the BET specific surface areas were determined. Selected samples of the modified and unmodified titanium whites were subjected to elemental analysis.

Keywords: titanium dioxide, surface modification, silane coupling agents, PSD, surface morphology, adsorption/desorption isotherms, dispersion.

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INTRODUCTION

White inorganic pigments are fully dominated by titanium dioxide. Titanium dioxide (titanium white) represents the most important pigment in paint and varnish industry due to its excellent optical properties manifested by the high staining and coating abilities as well as its whiteness[1-3]. Titanium dioxide can acquire three crystalline forms, including brookite, which is not applied as a pigment, anatase, which is used for the purpose only occasionally and which manifests a higher extent of whiteness than the widely used rutile[4]. Independently of the technology of titanium white production, pigments of high purity are obtained, with a specific size and size distribution of the crystalline particles. In order to improve the utilitarian properties of the coating pigment, the surface of titanium white is modified with various chemical compounds. The advantages of using titanium white as a pigment are determined by its high index of light refraction, physical and chemical stability, the potential for control of crystalline particle size and for the modification of surface morphology. The pigment particle size and the particle size distribution represent the prime parameters, which affect the properties of the paint. The optimum size of the TiO_2 particles, which assures the maximum light scatter and, thus, high coating power of paint coats, averages at around 0.23 μm. The physical and chemical resistance of pigment affects the durability of the formed coat. Under the effect of the UV light, coat-forming polymers used to undergo decomposition and, therefore, supplementation with the UV light-absorbing substances makes the coats more durable[5-10].

EXPERIMENTAL

The modification of titanium white surface was conducted using the following silane coupling agents: 3-methacryloxypropyltrimethoxysilane (U-511); vinyltrimethoxysilane (U-611) and *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D). The effect of the concentration of the modifiers was examined (0.5; 1 or 3 weight parts per 100 weight parts of TYTANPOL R-003, TYTANPOL R-211 or TYTANPOL R-213 preparation of titanium white).

The process of titanium white surface modification was conducted by „the dry technique". In a reactor of the 500 cm^3 capacity, charged with 40 g of respective titanium white sample, and dosing the solution of the organic modifying agent. The solution contained 0.5; 1 or 3 weight parts of the silane coupling agent per 100 weight parts of TiO_2 and 10 cm^3 of the solvent, comprising the 4:1 v/v mixture of methanol and water. The content was mixed for 1 h to ensure perfect homogenization of titanium dioxide with the solution of the modifying compound. Subsequently, titanium white was dried at the temperature of 105°C in a stationary drier for 2 h. Then, the obtained product was passed through a sieve (mesh size: 80 μm).

The size of titanium white particles and the respective particle size distribution were determined with the help of Zetasizer Nano ZS (Malvern Instruments Ltd.) using the non-invasive back light scattering method (NIBS).

The cumulants analysis give a width parameter known as the polydispersity, or the polydispersity index (PdI). The cumulants analysis is actually the fit of a polynomial to the log of the G1 correlation function:

$$Ln[G1] = a + bt + ct^2 + dt^3 + et^4 + ...$$

The value of b is known as the second order cumulant, or the z-average diffusion coefficient.

The coefficient of the squared term, c, when scaled as $2c/b^2$ is known as the polydispersity.

The sedimentation rate was established in the K100 type tensiometer (Krüss). The modified titanium whites were also subjected to the morphological and microstructural analysis using the Philips SEM 515 electron microscope. The particle size distribution permitted to establish the polydispersity index (as a measure of the uniform character of the pigment). In order to characterize the adsorptive prop-

erties isotherms of nitrogen adsorption/desorption were determined and the parameters such as the specific surface area, pore volume and an average pore size were determined using the ASAP 2010 instrument (Micromeritics Instruments Co.). The elemental analysis of the selected modified and unmodified titanium white samples was performed in the Elementar Vario EL III apparatus.

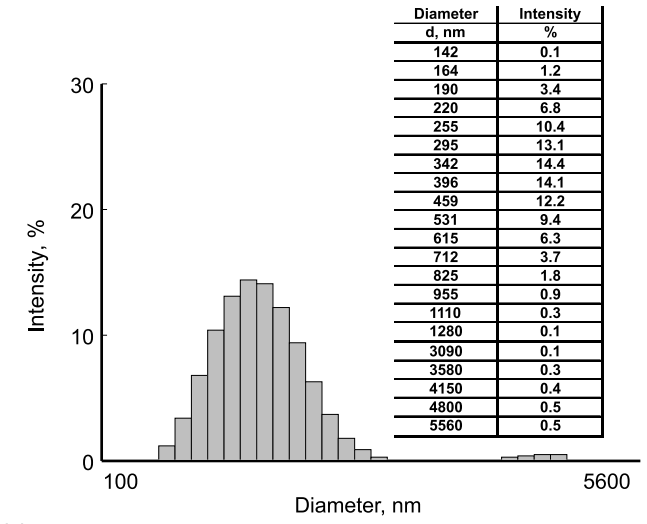
RESULTS AND DISCUSSION

The performed studies on the modification of the titanium white surface character employing the silane coupling agents showed that the application of 1 weight part of the silane altered the surface character of TiO_2. Favourable results were obtained for the modified R-211 white.

The particle size distribution, taking into account the intensity and the volume share of the particles and the SEM microphotograph for the commercial titanium white, TYTANPOL R-211 are shown in Fig.1. The particle size distribution, taking into account the band intensity (Fig.1a), demonstrated two bands, of which the first very intense band reflected the presence of primary particles and primary agglomerates in the range of 142 – 1280 nm (with the maximum intensity of 14.4 for the particles of 342 nm in diameter). The polydispersity, which reflected the scatter of particle diameters amounted to 0.170. The low intensity band in the range of 3090 – 5560 nm corresponded to the secondary agglomerates (the maximum intensity of 0.5 corresponded to the agglomerates of 4800 – 5560 nm in diameter). Also the particle size distribution with an appropriate attention given to the volume share of the particles (Fig.1b) demonstrated two bands of a similar intensity. The first band was linked to the presence of the particles of a lower diameter and it fitted the range of 142 – 1280 nm (with the maximum volume of 11.7 for particles of 295 – 342 nm in diameter). The second band in the range of 2300 – 6440 nm corresponded to the secondary agglomerates of higher diameters (the maximum volume of 8.4 corresponded to the agglomerates of 4480 nm in diameter). The SEM microphotograph (Fig.1c) confirmed the presence of spherical particles.

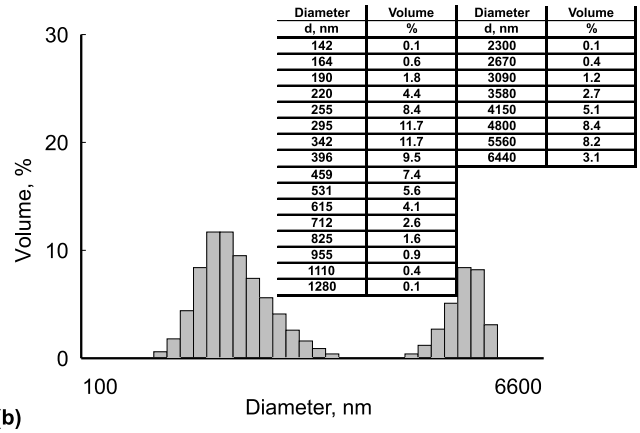
The particle size distribution, paying appropriate attention to the band intensity (Fig.2a) for R-211 titanium dioxide modified with 1 wt./wt. of 3-methacryloxypropyltrimethoxysilane, manifested two bands. The first band of a very high intensity was linked to the presence of primary particles and primary agglomerates in the range of 142 – 2670 nm (with the maximum intensity of 13.8 for the particles of 615 nm in diameters). The band in the range of 4800 – 5560 nm corresponded to the secondary agglomerates (the maximum intensity of 0.4 corresponded to the agglomerates in the range of 5560 nm in diameter). The polydispersity amounted to 0.194. On the other hand, in the particle size distribution considering the volume share (Fig.2b), a single band was noted. It was linked to the presence of the primary and secondary agglomerates in the range of 164 – 6440 nm (with the maximum volume of 9.9 for the particles of 712 nm in diameter). The SEM microphotograph (Fig.2c) documented also the presence of spherical particles.

Particle size distributions, while taking into account the band intensity and the volume share and the SEM microphotograph of R-211 titanium white modified with 1 wt./wt. of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane are presented in Fig.3. The particle size distribution, considering the band intensity (Fig.3a), demonstrated two bands. The intense band was linked to the presence of the primary particles and primary agglomerates in the range of 164 – 955 nm (with the maximum intensity of 18.7 for the particles of 342 nm in diameter). Polydispersity which characterized the scatter of particle diameters amounted to 0.161 only. The other band of a lower intensity in the range of 3580 – 5560 nm corresponded to the secondary agglomerates (the maximum intensity of 0.9 core responded to the agglomerates of around 5560 nm in diameter). Also in the particle size



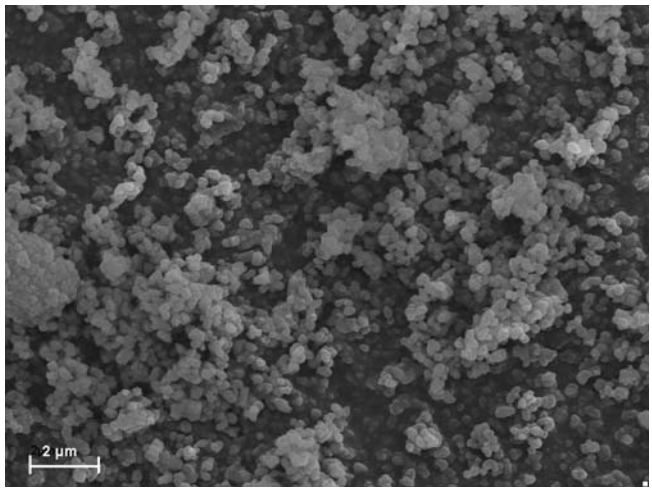
Diameter d, nm	Intensity %
142	0.1
164	1.2
190	3.4
220	6.8
255	10.4
295	13.1
342	14.4
396	14.1
459	12.2
531	9.4
615	6.3
712	3.7
825	1.8
955	0.9
1110	0.3
1280	0.1
3090	0.1
3580	0.3
4150	0.4
4800	0.5
5560	0.5

(a)



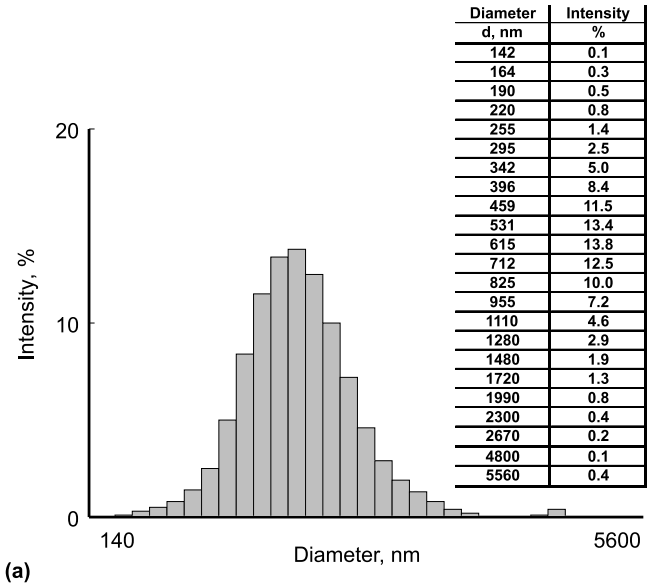
Diameter d, nm	Volume %	Diameter d, nm	Volume %
142	0.1	2300	0.1
164	0.6	2670	0.4
190	1.8	3090	1.2
220	4.4	3580	2.7
255	8.4	4150	5.1
295	11.7	4800	8.4
342	11.7	5560	8.2
396	9.5	6440	3.1
459	7.4		
531	5.6		
615	4.1		
712	2.6		
825	1.6		
955	0.9		
1110	0.4		
1280	0.1		

(b)



(c)

Figure 1. Particle size distribution: (a) by intensity, (b) by volume and the SEM image (c) of TYTANPOL R-211



Diameter d, nm	Intensity %
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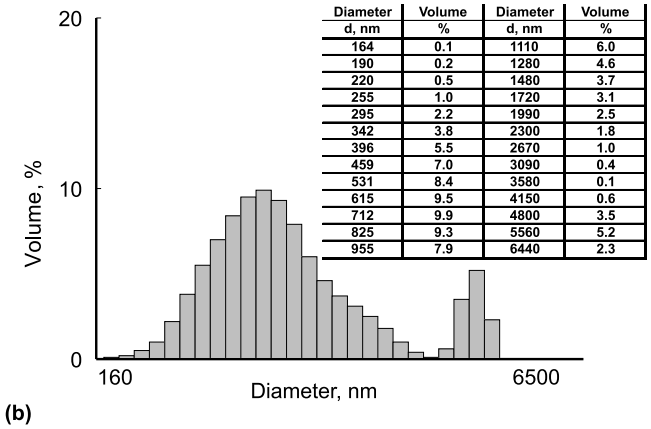
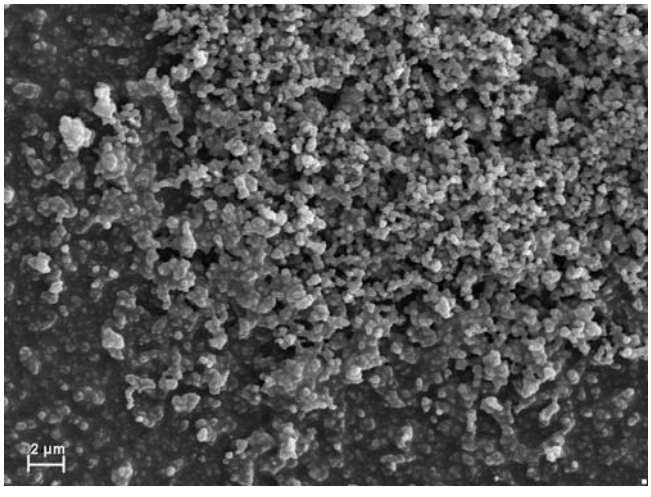
164	0.3
190	0.5
220	0.8
255	1.4
295	2.5
342	5.0
396	8.4
459	11.5
531	13.4
615	13.8
712	12.5
825	10.0
955	7.2
1110	4.6
1280	2.9
1480	1.9
1720	1.3
1990	0.8
2300	0.4
2670	0.2
4800	0.1
5560	0.4

(a)



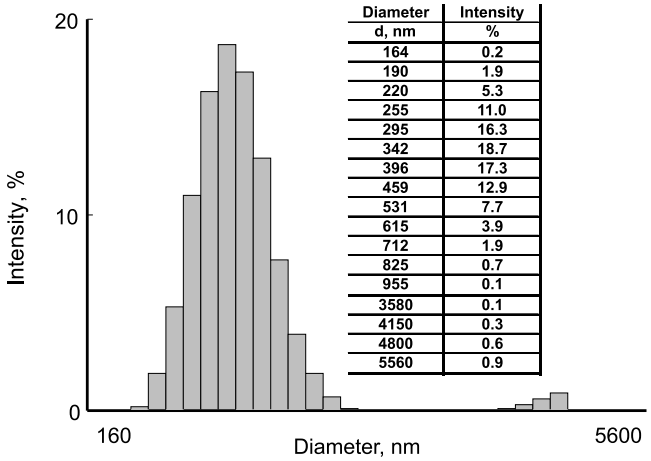
Diameter d, nm	Volume %	Diameter d, nm	Volume %
164	0.1	1110	6.0
190	0.2	1280	4.6
220	0.5	1480	3.7
255	1.0	1720	3.1
295	2.2	1990	2.5
342	3.8	2300	1.8
396	5.5	2670	1.0
459	7.0	3090	0.4
531	8.4	3580	0.1
615	9.5	4150	0.6
712	9.9	4800	3.5
825	9.3	5560	5.2
955	7.9	6440	2.3

(b)



(c)

Figure 2. Particle size distribution: (a) by intensity, (b) by volume and the SEM image (c) of TYTANPOL R-211 modified with 1 wt./wt. of 3-methacryloxy-propyltrimethoxysilane



Diameter d, nm	Intensity %
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295	16.3
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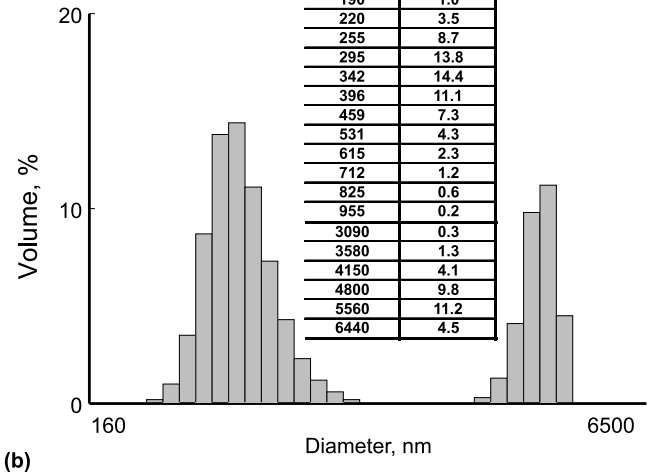
396	17.3
459	12.9
531	7.7
615	3.9
712	1.9
825	0.7
955	0.1
3580	0.1
4150	0.3
4800	0.6
5560	0.9

(a)



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164	0.2
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295	13.8
342	14.4
396	11.1
459	7.3
531	4.3
615	2.3
712	1.2
825	0.6
955	0.2
3090	0.3
3580	1.3
4150	4.1
4800	9.8
5560	11.2
6440	4.5

(b)

(c)

Figure 3. Particle size distribution: (a) by intensity, (b) by volume and the SEM image (c) of TYTANPOL R-211 modified with 1 wt./wt. of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane

distribution with appropriate attention paid to the volume share, two bands were noted (Fig.3b) but they exhibited a similar intensity. The first band was linked to the presence of the particles of lower diameters in the range of 164 – 955 nm (with the maximum volume of 14.4 for the particles of around 342 nm in diameter). The other band, in the range of 3090 – 6440 nm corresponded to the agglomerates of higher diameters (the maximum volume of 11.2 corresponded to the agglomerates of 5560 nm in diameter). The SEM microphotograph (Fig.3c) confirmed the presence of spherical particles.

The sedimentation profiles in water for titanium white samples, modified using various quantities of 3-methacryloxypropyltrimethoxysilane, are presented in Fig.4. The results demonstrated that the sedimentation of titanium white samples accelerated with the increased amounts of the organic coupling agent. The highest weight gain in time was

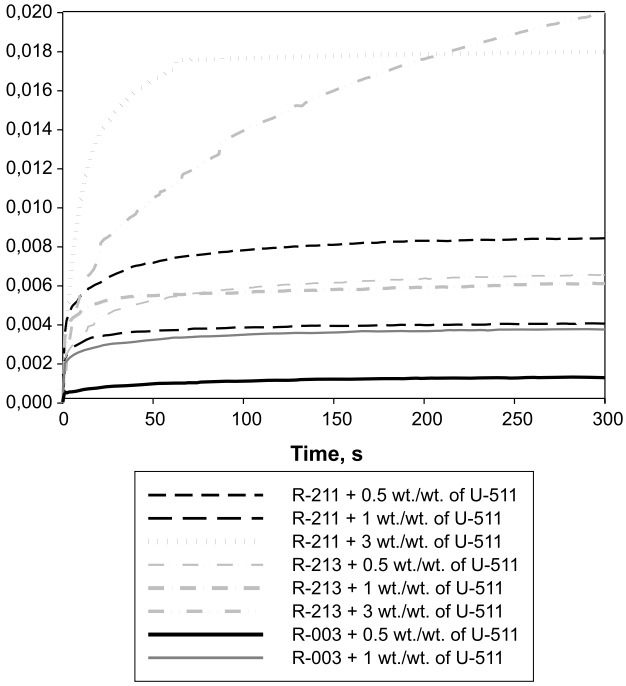

Figure 4. Sedimentation profiles examined in water for selected titanium dioxide samples modified with 3-methacryloxypropyltrimethoxysilane

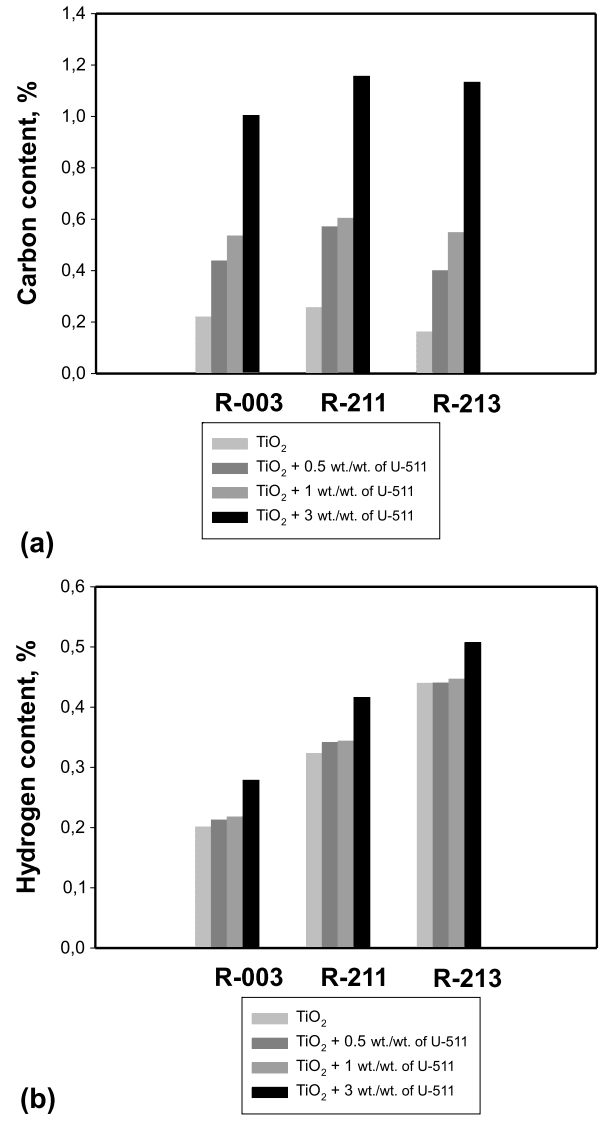

Figure 5. Comparison of carbon (a) and hydrogen (b) contents in samples of titanium white modified using 3-methacryloxypropyltrimethoxysilane

demonstrated by the R-11 sample modified with 3 wt./wt. of U-511 silane.

As a result of the conducted modification, the content of carbon, nitrogen and hydrogen increased in the system with the growing amounts of the supplemented coupling agent. 3-Methacryloxypropyltrimethoxysilane proved to be the best among the three examined silanes. The percentage of carbon and hydrogen content in titanium whites modified with various amounts of 3-methacryloxypropyltrimethoxysilane is shown in Fig.5.

The content of carbon and hydrogen permitted to determine the extent of the modification of titanium white with 3-methacryloxypropyltrimethoxysilane. Titanium whites, which were not modified with the organic compounds demonstrated a low content of carbon and hydrogen (R-003: 0.22%C and 0.20%H; R-211: 0.26%C and 0.32%H; R-213: 0.16%C and 0.44%H). The effect of the amount of organic coupling agent on the content of carbon and of hydrogen in titanium dioxide samples could be observed in the results of elemental analysis. The modification of titanium white samples yielded best results in the case of R-211 titanium white. The contents of carbon and hydrogen increased, respectively, in R-211 modified with 0.5 wt./wt. of U-511 silane to 0.57%C and 0.34%H, in R-211 modified with 1 wt./wt. of 3-methacryloxysilane to 0.60%C and 0.34%H and in R-211 modified with 3 wt./wt. of 3-methacryloxysilane to 1.16%C and 0.42%H.

Adsorption studies were also performed, which permitted to estimate the BET specific surface area as well as the size and the total volume of pores in titanium white samples.

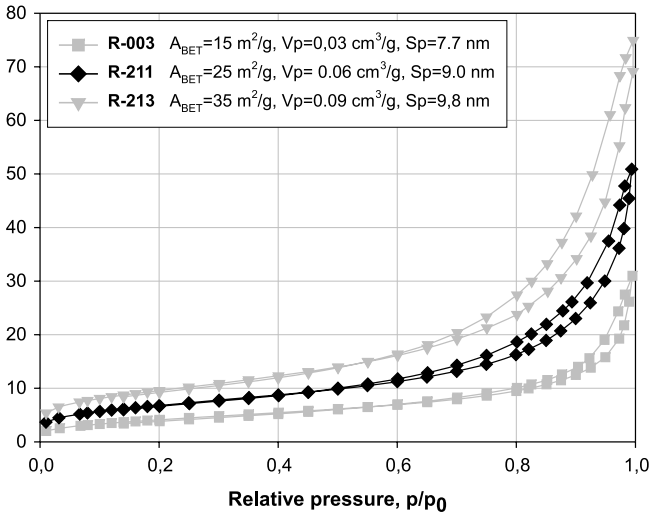

Figure 6. N_2 adsorption/desorption isotherms of the unmodified titanium dioxides

They determined the suitability of titanium dioxide as a filler and a pigment.

The highest adsorptive abilities were manifested by R-213 titanium white, for which the range of hysteresis loop spanned the relative pressures of 0.6 – 1.0 (Fig.6). The BET specific surface area for R-213 white amounted to 35 m^2/g, while the pore diameter and the total pore volume were 9.8 nm and 0.08 cm^3/g, respectively. In the case of titanium white R-003, on the other hand, the hysteresis loop spanned a small compartment of 0.8 – 1.0 in relative pressures, and the respective low activity was confirmed by the low specific surface area of 15 m^2/g. The courses of nitrogen adsorption/desorption isotherms (the arms of the isotherms did not rise until the relative pressures of over 0.6 were reached) and the diam-

eters of pres (R-003: 7.7 nm, R-211: 9.0 nm and R-213: 9.8 nm) were typical for the mesoporous adsorbents.

CONCLUSIONS

All titanium white samples subjected to the modification with silane coupling agents manifested a spherical shape of particles. Thus, the surface modification did not alter the morphological and microstructural character of titanium dioxide.

The studies on the modification of titanium white surface using silane coupling agents proved a favourable effect of using one weight part of silane on the TiO_2 surface character. The best results were obtained for the modified white R-211. Surface modification significantly affected the particle size distribution and the uniform character of the sample. The best results were obtained for the R-211 white modified with 1 wt./wt. of 3-methacryloxypropyltrimethoxysilane and *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane.

The sediment weight upon the sedimentation of titanium white particles in water, following the modification of the particles using 3-methacryloxypropyltrimethoxysilane increased with the growing amount of the applied organic coupling agent.

The increasing amounts of the applied coupling agent were accompanied by the growing content of carbon and hydrogen in the system. 3-methacryloxypropyltrimethoxysilane proved to be the most effective and the best results were obtained for the R-211 white, for which elemental content of carbon and hydrogen markedly increased, as compared to the remaining samples of titanium white (R-003 or R-213).

The applied commercial samples of titanium white belong to mesoporous adsorbents.

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