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EFFECT OF INORGANIC OXIDES TREATMENT ON THE TITANIUM DIOXIDE SURFACE PROPERTIES

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Studies were conducted involving evaluation of titanium white, surface-coated with inorganic oxides. The studies aimed at determining dispersion properties, i.a. particle size distribution and polydispersity index. Moreover, microscopic observation allowed to evaluate surface morphology of the modified TiO_2 particles. Colourimetric data of titanium white was measured and the specific surface area was estimated using BET method. Effect of the surface modification with oxides on electrokinetic properties and zeta potential were appraised. Increased amounts of aluminium oxide and silicon dioxide used for modification of titanium dioxide surface deteriorate uniform character of the sample and results in an increase in diameter of pigment particles. The titanium white pigments belong to mesoporous adsorbents. Value of the isoelectric point (IEP) depends on the amounts of aluminium oxide and silica used for surface processing of titanium white.

key words: titanium dioxide, surface modification, PSD, surface morpholgy, zeta potential, adsorption/desorption isotherm

INTRODUCTION

Titanium dioxide particles crystallize mosty in two polymorphic forms: rutile and anatase. Anatase, as a metastable phase, is chemically and optically active, thus is suitable for catalysts and supports (Ding 1997) while rutile, the thermodynamically stable polymorph, has the highest refractive index and ultrafiolet absorptive and is widely used as white pigments (Zhao 1998). It has been extensively demonstrated that the physicochemical properties of TiO_2 are strongly dependent on its crystal structure and morphology as well as grain size (Cozzali 2003).

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Many methods such as sol-gel process (Zhang 2003), hydrothermal methods (We 2002), solvothermal methods (Kim 2003) and emulsion precipitation (Ramakrishna 2003) have been developed for the synthesis of titanium dioxide nanoparticles.

The properties of TiO_2, including a hight refractive index (Schmidt 2005), light absorption/scattering (Brand 2003) and photocatalytic activity (Legrini 1993, Paz 1997, Linsebigler 1995, Chen 2004, Hashimoto 2005, Hoffmann 1995, Blade 1999, Hirakawa 2004) have led to the exploitation of titanium dioxide in a variety of fields.

The studies aimed at determining effect of titanium white surface modification, using inorganic oxides, on its dispersion and physicochemical properties.

EXPERIMENTAL

MATERIALS

In the studies pigments of rutile titanium dioxide, TYTANPOL R-210, R-211 and R-213 were used, produced by Chemical Works „Police" S.A. using the sulphate technique. The pigments are surface processed with aluminium and silica compounds and modified using organic compounds of a hydrophilic-hydrophobic character (R-210 and R-211) and a hydrophilic character (R-213).

METHODS OF STUDIES

Size of titanium white particles and the respective particle size distribution were determined using Zetasizer Nano ZS (Malvern Instruments Ltd.) using the non-invasive back light scattering method (NIBS). Particle size distribution permitted to establish polydispersity index (as a measure of uniform character of the pigment). The cumulants analysis give a width parametr 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.

A Zetasizer Nano analyzer allowed also to estimate zeta potential on the basis of electrophoretic mobility, using laser Doppler velocimetry (LDV).

The modified titanium whites were also subjected to morphological and microstructural analysis using scanning electron microscopy (Zeiss VO 40) and transmission electron microscopy (Jeol 1200 EX 2). In order to characterize adsorptive properties isotherms of nitrogen adsorption/desorption were determined and parameters such as specific surface area, pore volume and average pore size were determined using ASAP 2010 instrument (Micromeritics Instruments Co.).

Using SPECBOS 4000 colourimeter, colour of the titanium whites was measured. The results were given in L a b colour spaces. Examination in the CIE L a b colourimetric system yields data on colour of a pigment. L* denotes lightness, a* and b* coordinates denote a colour, +a* defining the share of red colour, –a* denoting the share of green colour, +b* representing the share of yellow colour and –b* denoting the share of blue colour. C* indicates colour intensity, h* - shade of the colour while dE is a colour difference representing the resultant of differences for individual components (dE*, da*, db*).

RESULTS AND DISCUSSION

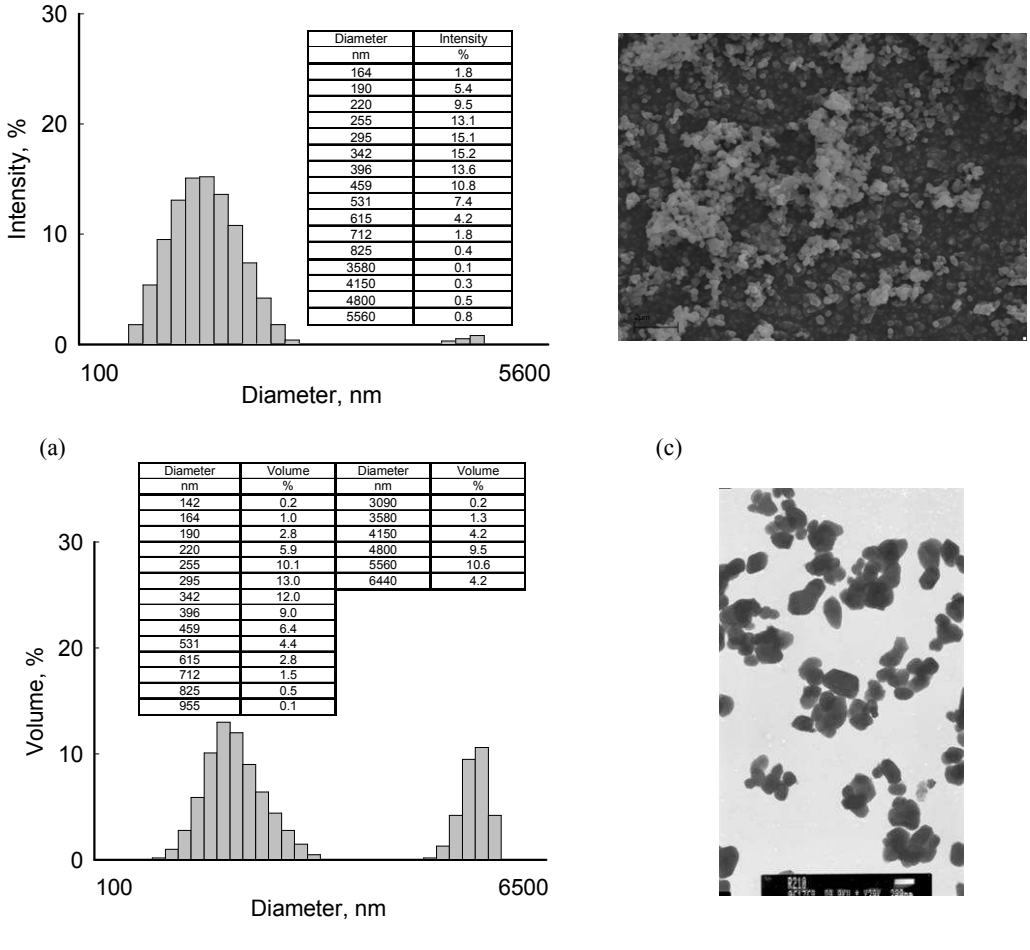
The titanium whites represent pigments of rutile variety, surface processed with aluminium and silica compounds. They differ from each other in the amount of inorganic oxide used for surface modification of TiO_2. Principal properties of the titanium dioxide pigments, are presented in Table 1.

Tabela 1. Principal parameters of commercial titanium dioxide samples TYTANPOL

Sample	Inorganic suface treatment	Organic surface modification, character of organic compound	Content, %		Polydispersity	Content of titanium dioxide, %
			Al_2O_3	SiO_2		
R-210	Al_2O_3, SiO_2	+, hydrophilo-hydrophobic	3.0	1.0	0.174	94
R-211	Al_2O_3, SiO_2	+, hydrophilo-hydrophobic	4.7	2.0	0.170	92
R-213	Al_2O_3, SiO_2	+, hydrophilic	4.7	8.3	0.233	82

In the particle size distribution for R-210 titanium dioxide which took into account band intensity (Fig. 1a) the presence of two bands was noted. The first, more intense band was linked to the presence of particles and primary agglomerates and it fitted the range of 164 – 825 nm (with maximum intensity of 15.2% for particles of 342 nm in diameter). Polydispersity, which is a function of particle diameter scatter, showed the value of 0.174. The band within the range of 3580 – 5560 nm corresponded to secondary agglomerates (maximum intensity of 0.8% corresponded to agglomerates of 5560 nm in diameter). Also in the curve of particle size distribution, which took into account their volume (Fig. 1b) two bands of a similar intensity were present. The first band was linked to the presence of particles of lower diameter and of primary agglomerates. The band demonstrated the range of 142 – 955 nm (with maximum volume of 13.0% for particles with 295 nm in diameter). In the range of diameters the particles comprised almost 70% of the sample. The other band, in the range of 3090 – 6440 nm, reflected the presence of agglomerates with higher diameters (maximum

volume of 10.6% corresponded to agglomerates of 5560 nm in diameter), which comprised 30% of the sample. SEM image (Fig. 1c) confirmed the presence of spherical in shape primary agglomerates, which tended to form clumps. On the other hand, TEM image (Fig. 1d) demonstrated scanty coverage of titanium white surface with the inorganic oxides.



Diameter nm	Intensity %
164	1.8
190	5.4
220	9.5
255	13.1
295	15.1
342	15.2
396	13.6
459	10.8
531	7.4
615	4.2
712	1.8
825	0.4
3580	0.1
4150	0.3
4800	0.5
5560	0.8

Diameter nm	Volume %	Diameter nm	Volume %
142	0.2	3090	0.2
164	1.0	3580	1.3
190	2.8	4150	4.2
220	5.9	4800	9.5
255	10.1	5560	10.6
295	13.0	6440	4.2
342	12.0		
396	9.0		
459	6.4		
531	4.4		
615	2.8		
712	1.5		
825	0.5		
955	0.1		

Fig.1. PSD by (a) intensity, (b) volume and images (c) SEM, (d) TEM of TYTANPOL R-210

In the particle size distribution for R-211 titanium white, which took into account band intensity (Fig. 2a), two bands were noted. The more intense band within the range of 142 – 1280 nm, with maximum intensity of 14.4% for particles of 342 nm in diameter, was linked to the presence of particles and primary agglomerates. On the other hand, the second band reflected the presence of secondary agglomerates in the range of 3090 – 5560 nm in diameter (maximum intensity of 0.5% corresponded to

agglomerates of 4800 and 5560 nm in diameter). The polydispersity amounted to 0.17. The particle size distribution curve which took into account particle volume (Fig. 2b) demonstrated two bands of a similar intensity. The first band was linked to the presence of particles and agglomerates with lower diameters, in the range of 142 – 1280 nm, with maximum volume share of 11.7% for particles of 295 and 342 nm in diameter (particles of the range (142 – 1280 nm) comprised over 70% of the studied sample). On the other hand, the second band reflected the presence of secondary agglomerates in the range of 2300 – 6440 nm (the maximum volume share of 8.4% was comprised by particles of 4800 nm in diameter). The respective SEM image (Fig. 2c) demonstrated the presence of spherical particles with low diameter and few clumps. The TEM image (Fig. 2d) documented coating of titanium dioxide with aluminium and silica oxides, used for surface modification.

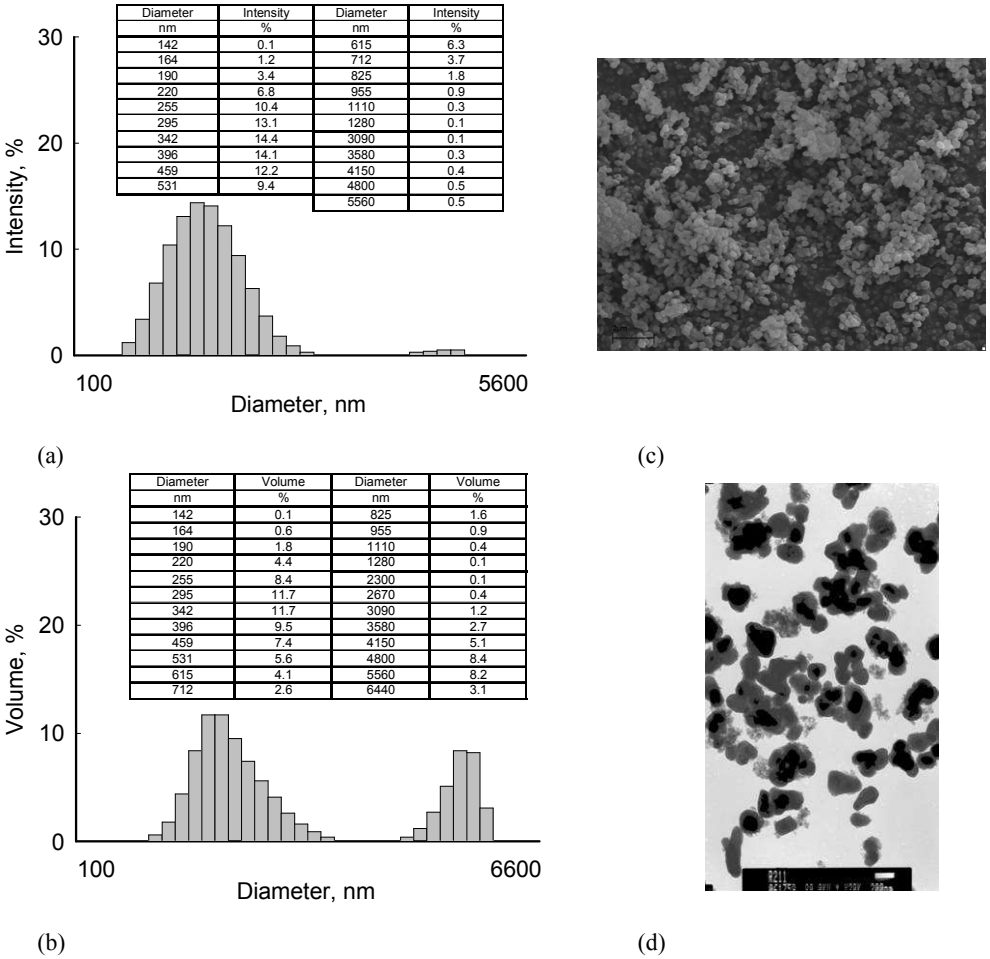
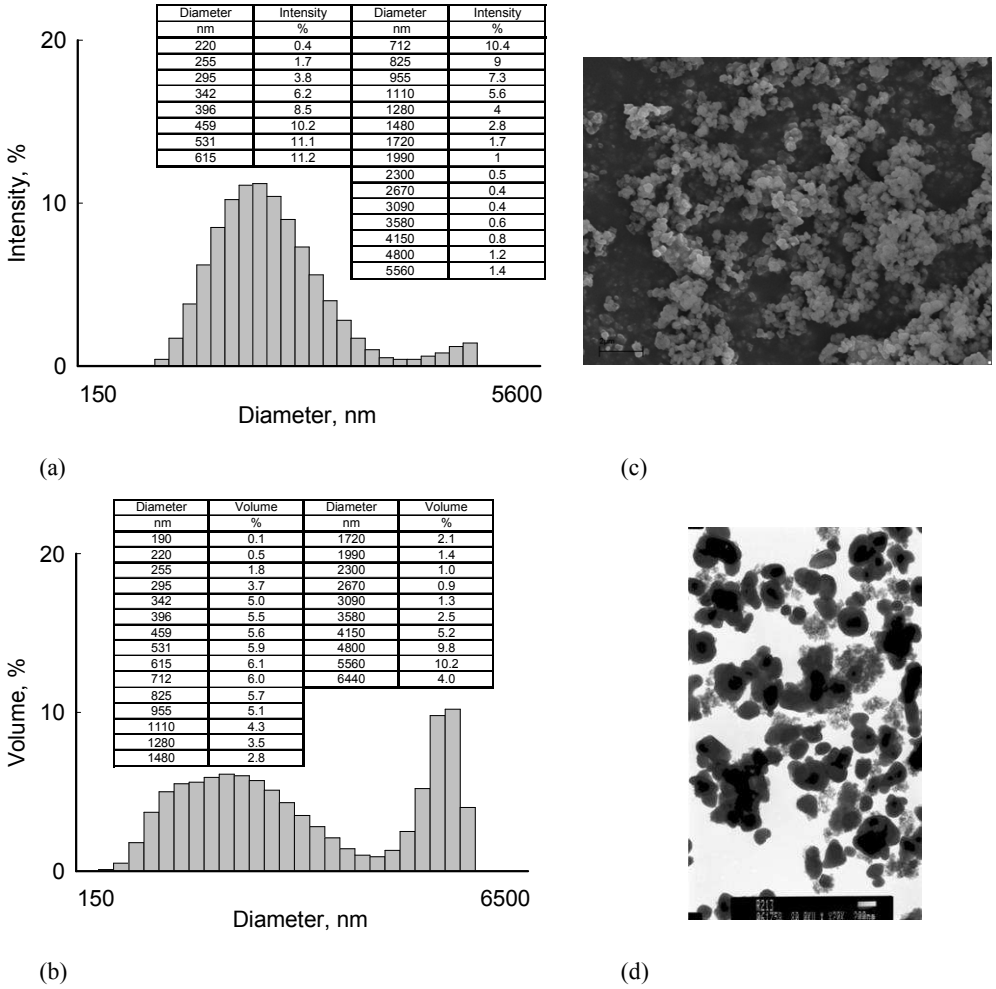


Fig.2. PSD by (a) intensity, (b) volume and images (c) SEM, (d) TEM of TYTANPOL R-211

For R-213 titanium white, the particle size distribution, which took into account intensity (Fig. 3a), a single band was present. The band was linked to the presence of clumps of low and high diameter and it fitted the range of 220 – 5560 nm (with maximum intensity of 11.2% for particles of 615 nm in diameter). On the other hand, on the particle size distribution curve taking volume into account (Fig. 3b) a single band was present. It was linked to the presence of primary and secondary agglomerates and fitted the range of 190 – 6440 nm (with maximum volume of 10.2% for agglomerates of 5560 nm in diameter). The polydispersity manifested value of 0.233. The SEM image (Fig. 3c) manifested the presence of particles spherical in shape which showed a much higher tendency to conglomerate. The TEM image (Fig. 3d) provided an excellent account on the surface processing of titanium white with inorganic oxides.



Diameter nm	Intensity %	Diameter nm	Intensity %
220	0.4	712	10.4
255	1.7	825	9
295	3.8	955	7.3
342	6.2	1110	5.6
396	8.5	1280	4
459	10.2	1480	2.8
531	11.1	1720	1.7
615	11.2	1990	1
		2300	0.5
		2670	0.4
		3090	0.4
		3580	0.6
		4150	0.8
		4800	1.2
		5560	1.4

Diameter nm	Volume %	Diameter nm	Volume %
190	0.1	1720	2.1
220	0.5	1990	1.4
255	1.8	2300	1.0
295	3.7	2670	0.9
342	5.0	3090	1.3
396	5.5	3580	2.5
459	5.6	4150	5.2
531	5.9	4800	9.8
615	6.1	5560	10.2
712	6.0	6440	4.0
825	5.7		
955	5.1		
1110	4.3		
1280	3.5		
1480	2.8		

Fig.3. PSD by (a) intensity, (b) volume and images (c) SEM, (d) TEM of TYTANPOL R-213

TYTANPOL R-213 manifested the highest BET surface area (Fig. 4), which amounted to 35 m^2/g, probably reflecting the fact that the pigment was surface coated with the highest amounts of aluminium and silicon oxides, i.e. with 4.7% of Al_2O_3 and 8.3% of SiO_2. For T-213 titanium white, the loop of hysteresis included relative pressures within the scope of $p/p_0 = 0.6 – 1.0$. Pore diameter amounted to 9.8 nm, and the total volume of pores was 0.09 cm^3/g. A lower BET specific surface area was demonstrated by R-211 titanium white, which amounted to 25 m^2/g. A decrease in diameter and volume of pores could also be noted, which amounted to 9.0 nm and 0.06 cm^3/g, respectively. The lowest value of BET specific surface area, of 19 m^2/g, was noted for TYTANPOL R-210. Moreover, the dioxide showed also decreased diameter and volume of pores (8.6 nm and 0.04 cm^3/g, respectively). Processing with inorganic aluminium oxide and silica significantly increased the specific surface area. This was probably associated with the fact that aluminium oxide and, first of all, silica manifested high specific surface areas. In the case of silica, its effect on specific surface area of titanium white clearly depended also on its physicochemical character.

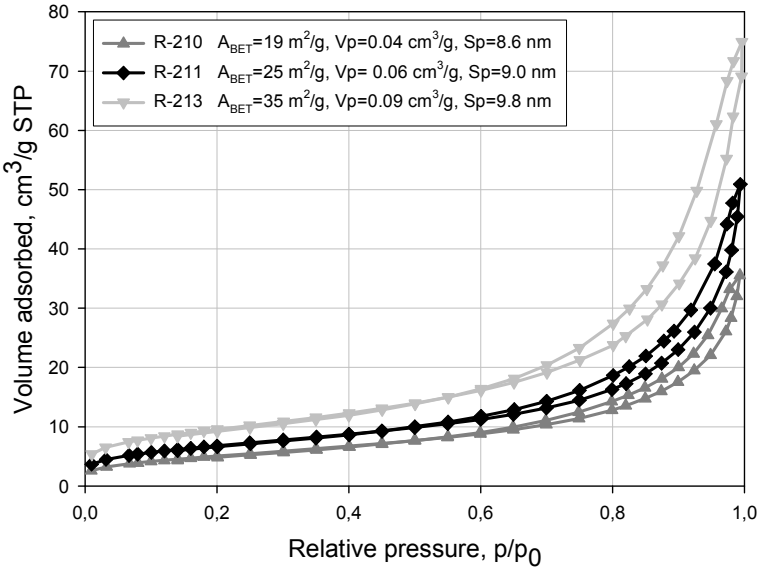
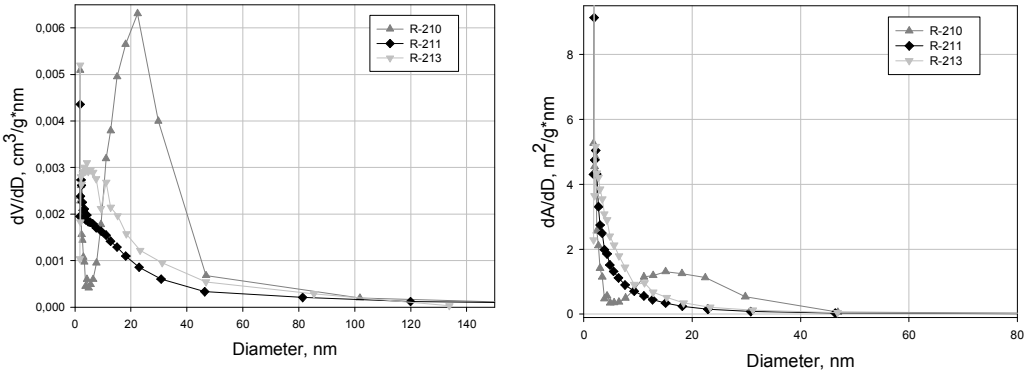


Fig. 4. N_2 adsorption/desorption isotherms of titanium dioxides

Volume distributions and distribution of pore surface as related to pore diameter, presented in Fig.5, demonstrated decrease in both volume and in surface of pores in line with increasing diameter in the studied samples. Effect of such alterations might reflect increasing amounts of inorganic oxides used for surface modification of titanium white samples.



a) b)

Fig. 5. Distribution of pore volumes (a) and of surface area (b) of titanium white samples as related to their particle diameter

In the case of titanium dioxide pigments their lightness could be noted to increase in line with the increasing shares of Al_2O_3 and SiO_2 on TiO_2 surface (respective values of L* amounted to 89.17 for R-210, 92.28 for R-211 and 93.31 for R-213) (Fig. 6).

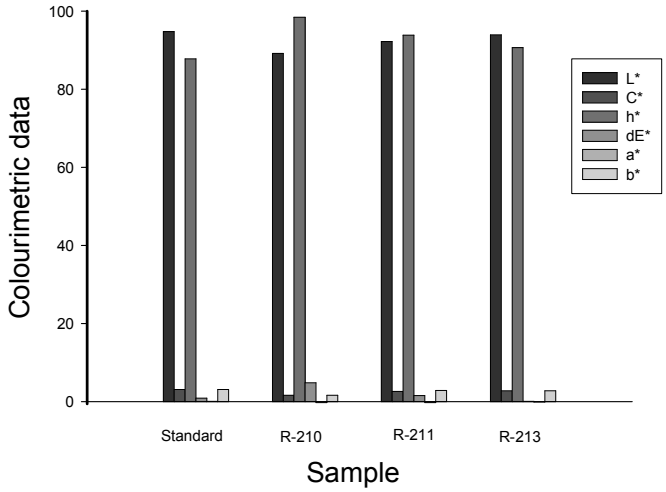


Fig. 6. Colourimetric data of commercial titanium dioxide samples TYTANPOL

In parallel to the increasing content of aluminium oxide and of silica, rising values of C* parameter were also observed, characterizing colour intensity (Table 2).

Table 2. Colourimetric data of commercial titanium dioxide samples TYTANPOL

Sample	Colourimetric data							
	L*	a*	b*	C*	h*	dL*	dH	dE*
Standard	94.79	0.12	3.14	3.14	87.85	0.89	-0.21	0.95
R-210	89.17	-0.25	1.67	1.69	98.45	-4.69	0.32	4.85
R-211	92.28	-0.2	2.93	2.94	93.89	-1.59	0.19	1.6
R-213	93.91	-0.03	2.8	2.8	90.65	0.04	0.02	0.09

All the pigments of titanium dioxide were characterized by low shares of green and yellow colours, which was linked to the method of TiO_2 production. This reflected the presence of contaminations which could not be eliminated during production due to the specificity of the sulphate procedure. As compared to the standard, an increase in the colour shade could also be noted. However, the relationship was inversely related to contents of silica and aluminium oxide (increasing percentage of the oxides content was paralleled by a decrease in the value of colour shade).

Estimation of zeta potential allowed to determine adsorptive properties. The potential was also decisive for stability of dispersion. Indirectly, it allowed to characterize stability of the studied dispersion systems.

Changes in electrokinetic potential, taking place with pH changes, and value of TiO_2 isoelectric point were strongly related to the type and quantity of inorganic substances used for modification. For pure substances the isoelectric point corresponded to pH 4 for titanium dioxide, to pH 2 for silicon dioxide and to pH 9 for aluminium oxide.

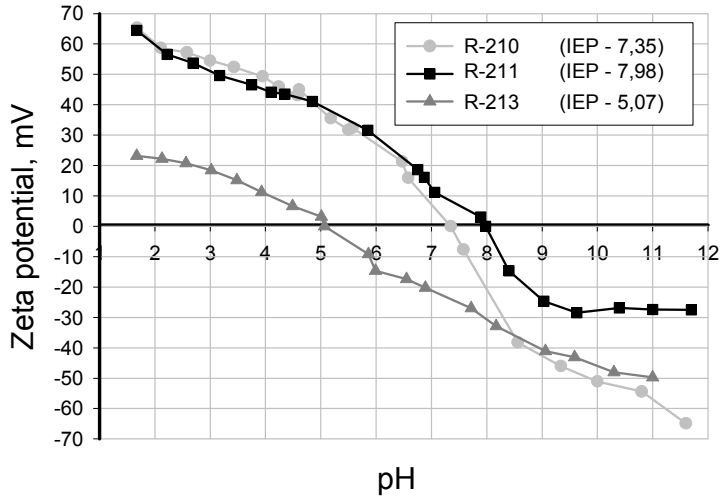


Fig.7. Electrokinetic curves of the examined TiO_2 powders

For TiO_2 pigments of a high SiO_2 content isoelectric point was shifted toward low pH values. On the other hand, involvement of aluminium oxide resulted in a shift of the isoelectric point toward high pH values. Values of isoelectric point amounted to 7.35 for R-210 white, 7.98 for R-211 whit and 5.07 for R-213, respectively (Fig.7).

CONCLUSIONS

The studied TiO_2 samples have demonstrated presence of spherical particles.

The particle size distribution curves have permitted to conclude that surface modification of titanium white using inorganic oxides exerts a significant effect on character and size of pigment particles. We conclude that increased amounts of aluminium oxide and silica used for modification of titanium dioxide surface deteriorate uniform character of the sample and results in an increase in diameter of pigment particles.

The highest adsorptive capacity is manifested by R-213 titanium white. Probably, the size of BET surface area of the white is most pronounced due to the presence of higher number of active centres on the surface.

The titanium white pigments belong to mesoporous adsorbents. Luminosity of titanium dioxide pigments surface modified with inorganic oxides, such as aluminium oxide and silica, increases in parallel to rising share of the oxides. All samples of titanium white are characterized by involvement of yellow and green colours, which results from contaminations introduced during synthesis of the pigments.

Value of the isoelectric point (IEP) depends on the amounts of aluminium oxide and silica used for surface processing of titanium white.

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Siwińska-Stefańska K., Krysztafkiewicz A., Jesionowski T., *Wpływ powierzchniowej obróbki tlenkami nieorganicznymi na właściwości dwutlenku tytanu,* Physicochemical Problems of Mineral Processing, 42 (2008), 141-152 (w jęz. ang)

Przeprowadzono badania nad oceną powierzchniowo modyfikowanej bieli tytanowej tlenkami nieorganicznymi. Badania miały na celu określenie właściwości dyspersyjnych, m. in. rozkładu wielkości cząstek oraz indeksu polidyspersyjności. Dokonano ponadto obserwacji mikroskopowych pozwalających na ocenę morfologii powierzchni modyfikowanych cząstek TiO_2. Wykonano pomiar barwy bieli tytanowych oraz określono wielkość powierzchni właściwej metodą BET. Oceniono wpływ powierzchniowej modyfikacji tlenkami na zmianę potencjału zeta. Stwierdzono, że zwiększenie udziału tlenku glinu i krzemionki do modyfikacji powierzchni ditlenku tytanu powoduje pogorszenie jednorodności próbki oraz wpływa na zwiększenie średnic cząstek pigmentu. Pigmenty bieli tytanowej zaliczamy do adsorbentów mezoporowatych. Wartość punktu izoelektrycznego (IEP) zależy od ilości tlenku glinu i krzemionki użytych do powierzchniowej obróbki bieli tytanowej.

słowa kluczowe: dwutlenek tytanu, modyfikacja powierzchni, PSD, morfologia powierzchni, potencjał dżeta, izotermy adsorpcji i desorpcji