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The morphological and dispersive characterization of commercial titanium dioxides

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The physicochemical and dispersive characterizations were conducted on the selected commercial titanium dioxides produced by Z.Ch. POLICE S.A. The dispersive properties were defined in detail by an analysis of particle size distribution and polydispersity index. Moreover, the microscope studies were executed to evaluate the surface morphology of the studied TiO_2 forms. The profiles of titanium dioxides sedimentation in water were determined and the specific surface areas were defined by the BET method.

Keywords: TiO_2, surface morphology, particle size, polydispersity, sedimentation, specific surface area.

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INTRODUCTION

Titanium dioxide pigments (commonly termed the titanium white) represent the most important and most widely applied inorganic pigments. They owe their popularity, first of all, to their unique ability to make the pigmented products nontransparent, lucid and bright, which is accompanied by a high safety of use. Apart from its exceptional pigment value, titanium dioxide represents an excellent absorber of destructive ultraviolet light, is chemically neutral, insoluble (and, therefore, it is not prone to migration), thermically stable and non-toxic[1].

Titanium dioxide manifests higher refractive index (2.7) than any other white pigment and the difference between the refractive indices of pigment and binding material determines the coating capacity of the paint (the more pronounced the difference is, the higher the coating capacity is). As a result, titanium dioxide has substituted other white pigments used in painting coats. Out of the three polymorphous varieties of TiO_2, rutile manifests the best pigment potential. As compared to the remaining varieties, it demonstrates higher hardness, higher density and the higher refractive index. Rutile is subjected to modification with metal oxides in order to improve its properties. Due to its high relative electric permeability, titanium dioxide is used for the production of electrotechnical ceramics[2 – 8].

An important application of titanium dioxide involves its use for staining materials in plastic and paper industries. Together, the branches of industry use 33% of TiO_2 production. In plastic industry, the pigment is used for the production of polyethylene, polypropylene, vinyl polychloride. It is also used for whitening the PCV, linoleum, epoxide plastics and of many other materials. In paper products it serves as a pigment and not as a filler, as is the case with other pigments, strengthening the product and increasing its quality. The nanocrystalline titanium dioxide with the particle size of 10 – 50 nm, which manifests the photocatalytic properties, deserves particular attention[4, 5, 9 – 17].

EXPERIMENTAL

In the studies commercially available samples of titanium dioxide were used, produced and supplied by Z.Ch. POLICE S.A. The principal properties of selected samples of titanium dioxide are presented in Table 1.

Titanium dioxides were subjected to the morphological and microstructural analysis using the scanning electron microscopy (Philips SEM 515) and transmission electron microscopy (Jeol 1200 EX 2). Particle size distribution

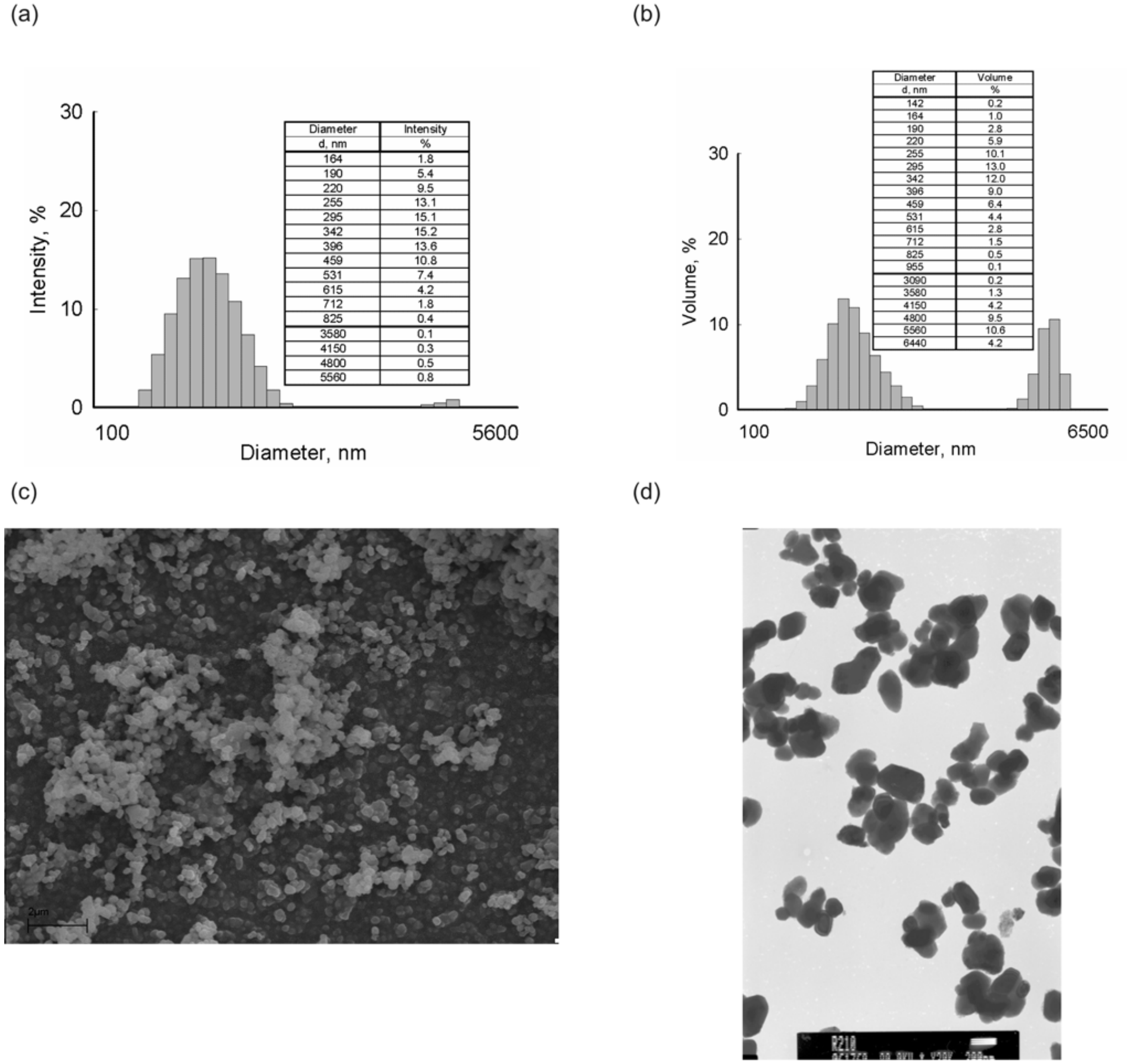
Table 1. The principal parameters of the commercial titanium dioxide samples TYTANPOL

Sample	Inorganic surface treatment	Organic surface modification	Content, %			Polydispersity	Mean size of pores, nm	Volume of pores, cm^3/g	Specific surface area, m^2/g	Particle diameter range, nm	
			Al_2O_3	SiO_2	ZrO_2					by intensity	by volume
R-001	Al_2O_3	+	3.0	–	–	0.242	7.7	0.03	14	255 – 5560	255 – 6440
R-003	Al_2O_3, ZrO_2	+	3.0	–	0.35	0.239	7.7	0.03	15	164 – 3090, 4150 – 5560	190 – 6440
R-210	Al_2O_3, SiO_2	+	3.0	1.0	–	0.174	8.6	0.04	19	164 – 825, 3580 – 5560	142 – 955, 3090 – 6440
R-211	Al_2O_3, SiO_2	+	4.7	2.0	–	0.170	8.9	0.06	25	142 – 1280, 3090 – 5560	142 – 1280, 2300 – 6440
R-213	Al_2O_3, SiO_2	+	4.7	8.3	–	0.233	9.8	0.09	35	220 – 5560	190 – 6440
R-310	Al_2O_3	+	4.8	–	–	0.124	7.8	0.02	9	220 – 1480	220 – 1720
RS	Al_2O_3	+	1.0	–	–	0.130	7.8	0.02	9	190 – 1480, 2670 – 5560	164 – 1480, 2300 – 6440
A-11	–	–	-	–	–	0.218	7.6	0.02	10	295 – 5560	342 – 6440

permitted to estimate the polydispersity (as a measure of the uniform character of the studied substance). The size of titanium dioxide particles and their particle size distribution were measured using the Zetasizer Nano ZS (Malvern Instruments Ltd.) and the technique of the non-invasive light scattering (NIBS). The TiO_2 sedimentation rate in water was also estimated using the K100 tensiometer (Krüss). In order to characterize the adsorptive properties, isotherms of nitrogen adsorption/desorption were determined and the parameters such as the specific surface area and a mean pore size were determined using the ASAP 2010 apparatus (Micromeritics Instruments Co.).

RESULTS AND DISCUSSION

The TYTANPOL R-210 and the R-211 samples belong to the rutile variety pigments, processed on the surface with aluminium and silicon compounds and modified with organic hydrophilic/hydrophobic compounds. The particle size distribution, taking into account the intensity and the volume of the particles, as well as the SEM and TEM images of the commercial titanium dioxide, TYTANPOL R-210 is presented in Fig.1. The particle size distribution (Fig.1a) estimated taking into account the band intensity, documented the presence of two bands. The first and more intense of them reflected the presence of primary particles and primary agglomerates and it fitted the range of 164 – 825 nm (with the maximum intensity of 15.2 for the particles of 342 nm in diameter). The polydispersity, which represented a function of particle diameter scatter, amounted to 0.174. The band ranging from 3580 to 5560 nm corresponded to secondary agglomerates (the maximum intensity of 0.8 corresponded to the agglomerates of 5560 nm in diameter). Also the particle size distribution, which took into account the particle volume (Fig.1b) documented the presence of two bands of a similar intensity. The first band reflected the presence of the particles of lower diameters, in the range of 142 to 955 nm (with the maximum volume of 13.0 for the particles of 295 nm in diameter). The other band in the range of 3090 to 6440 nm corresponded to the particles of higher diameters (the maximum intensity of 10.6 corresponded to the agglomerates of 5560 nm in diameter). The SEM and TEM



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

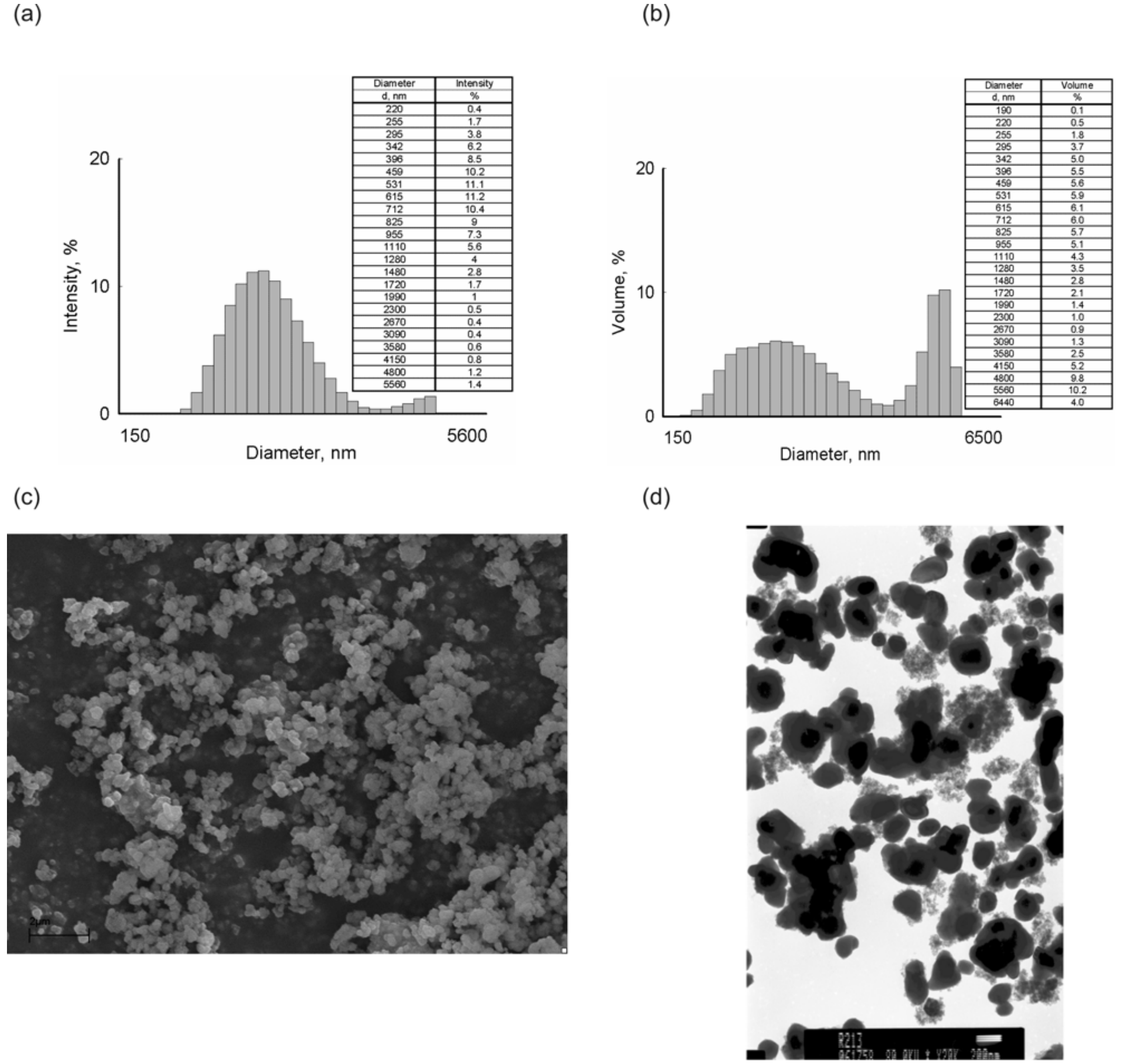
Figure 1. PSD (a) by intensity, (b) by volume and (c) SEM, (d) TEM images of TYTANPOL R-210

photos (Figs.1c and d) documented the presence of spherical particles.

TYTANPOL R-213 belongs to the pigments of the rutile variety surface processed with aluminium and silicon compounds and modified with the organic compounds of a hydrophilic character. The particle size distribution, taking into account the band intensity (Fig.2a) demonstrated a single band. The band represented the particles of lower and higher diameters spanning the range of 220 to 5560 nm (with the maximum intensity of 11.2 for the particles of 615 nm in diameter). Also, the particle size distribution, taking into account the volume share (Fig.2b) demonstrated a single band. The band reflected the presence of primary and secondary agglomerates and fitted the range of 190 to 6440 nm (with the maximum volume of 10.2 for the particles of 5560 nm in diameter). The polydispersity amounted to 0.233. The SEM and TEM images (Figs.2c and d) documented the presence of spherical particles.

On the other hand, TYTANPOL R-003 is also a rutile variety pigment, the surface processed with aluminium and zirconium compounds and modified with organic the compounds of a hydrophilic character. The particle size distribution, considering the intensity (Fig.3a) demonstrated the presence of two bands. The first, more intense band in the range of 164 – 3090 nm (the maximum intensity of 12.8 represented the particles of 712 nm in diameter) represented the primary particles and the primary agglomerates. The other band represented the secondary agglomerates in the range of 4150 – 5560 nm (with the maximum intensity of 0.4 corresponding to the agglomerates of 5560 nm in diameter). The polydispersity amounted to 0.239. On the other hand, the particle size distribution, considering the volume share (Fig.3b) documented the presence of a single band. The band represented the particles of lower and higher diameters, spanning the range of 190 – 6440 nm (the maximum volume of 9.9 corresponded to the particles of 955 nm in diameter). The pigment particles manifested a spherical shape, as noted in the SEM and TEM images (Figs.3c and d).

The pigments of the rutile variety surface, processed using aluminium compounds and modified, using the organic compounds of a hydrophilic character included the R-001 and R-310 samples. The particle size distribution, considering the intensity and the volume share as well as the SEM and TEM photos of titanium dioxide



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

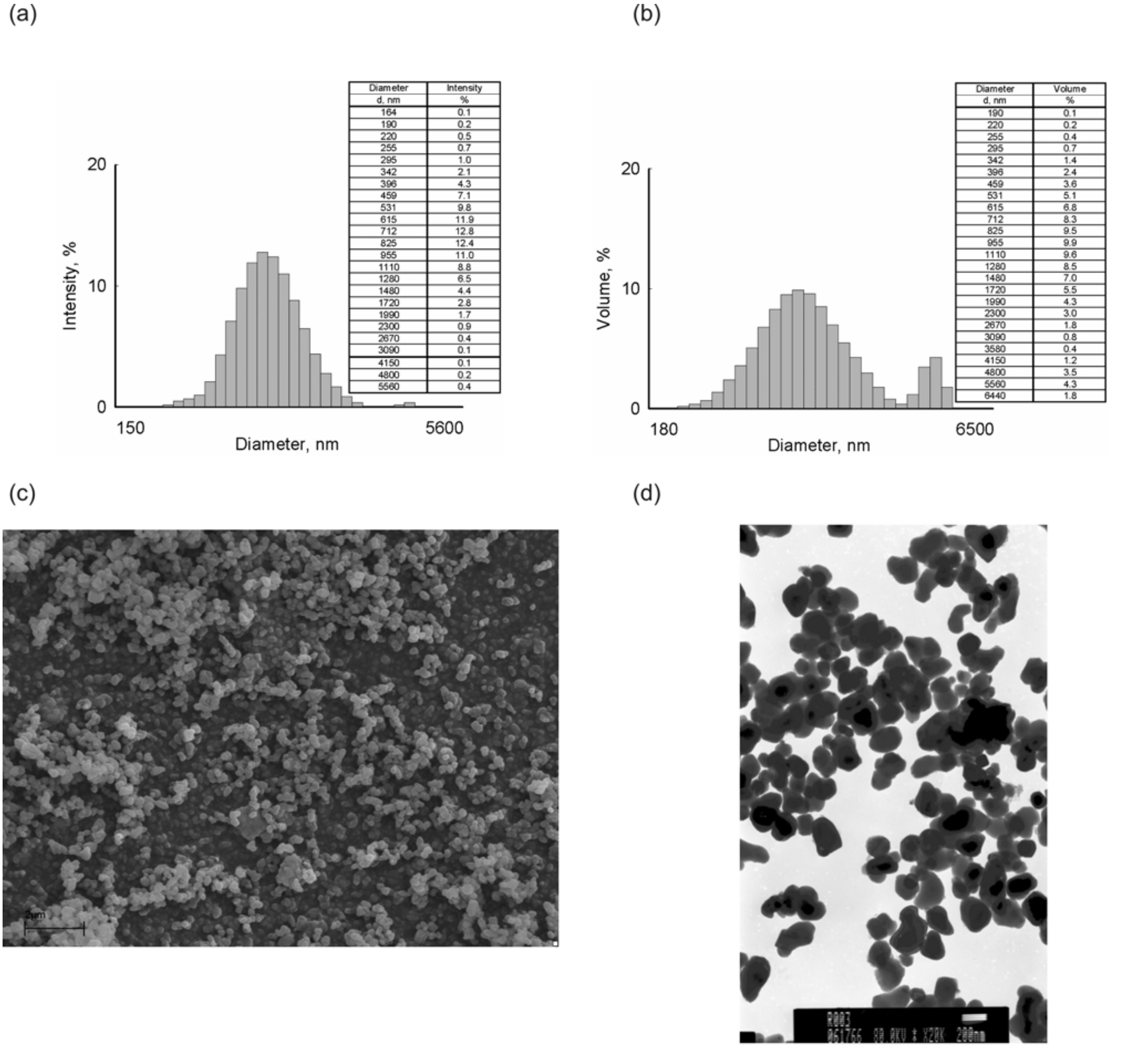
Diameter d, nm	Volume %
190	0.1
220	0.5
255	1.8
295	3.7
342	5.0
396	5.5
459	5.6
531	5.9
615	6.1
712	6.0
825	5.7
955	5.1
1110	4.3
1280	3.5
1480	2.8
1720	2.1
1990	1.4
2300	1.0
2670	0.9
3090	1.3
3580	2.5
4150	5.2
4800	9.8
5560	10.2
6440	4.0

Figure 2. PSD (a) by intensity, (b) by volume and (c) SEM, (d) TEM images of TYTANPOL R-213

TYTANPOL R-310 are presented in Fig.4. The particle size distribution, considering the intensity (Fig.4a) documented the presence of a single band. The band represented the primary particles and primary agglomerates and it fitted the range of 220 – 1480 nm (with the maximum intensity of 16.5 corresponding to the particles of 531 nm in diameter). The polydispersity, representing a function of the particle diameter scatter, amounted to 0.124. A single band was documented also in the sample testing the particle size distribution, taking into account the volume share (Fig.4b). It was linked to the presence of the particles of lower diameters, spanning the range of 220 – 1720 nm (with the maximum volume of 13.1 for the particles of 531 nm in diameter). The SEM and TEM images (Figs.4c and d) ilustrated the presence of spherical particles.

TYTANPOL RS represents a pigment of the rutile variety, insignificantly surface processed, using aluminium compounds and modified with organic compounds of a hydrophobic character. The particle size distribution, considering the intensity (Fig.5a) demonstrated two bands. The first, much more intense band in the range of 190 – 1480 nm (the maximum intensity of 14.1 represented the particles of 459 nm in diameter) was linked to the presence of primary particles and primary agglomerates. The other band corresponded to the presence of secondary agglomerates in the range of 2670 – 5560 nm (with maximum intensity of 0.3 for the particles of 4800 and 5560 nm in diameter). The polydispersity amounted to 0.130. On the other hand, the particle size distribution, taking into account the volume share (Fig.5b) demonstrated two bands. The first band was linked to the presence of the particles of lower diameters in the range of 164 – 1480 nm (the maximum intensity of 10.5 corresponded to the particles of 342 nm in diameter). The other band in the range of 2300 – 6440 nm corresponded to the particles of higher diameters (the maximum volume of 4.5 corresponded to the agglomerates of 4800 nm in diameter). The SEM and TEM photos (Figs.5c and d) documented the presence of spherical particles.

On the other hand, the TYTANPOL A-11 represents a pigment of the anatase variety that is subjected to no surface processing. The particle size distribution, taking into account the intensity (Fig.6a) documented the presence of a single band in the range of 295 – 5560 nm (the maximum intensity of 14.4 corresponded to the particles



Diameter d, nm	Intensity %
164	0.1
190	0.2
220	0.5
255	0.7
295	1.0
342	2.1
396	4.3
459	7.1
531	9.8
615	11.9
712	12.8
825	12.4
955	11.0
1110	8.8
1280	6.5
1480	4.4
1720	2.8
1990	1.7
2300	0.9
2670	0.4
3090	0.1
4150	0.1
4800	0.2
5560	0.4

Diameter d, nm	Volume %
190	0.1
220	0.2
255	0.4
295	0.7
342	1.4
396	2.4
459	3.6
531	5.1
615	6.8
712	8.3
825	9.5
955	9.9
1110	9.6
1280	8.5
1480	7.0
1720	5.5
1990	4.3
2300	3.0
2670	1.8
3090	0.8
3580	0.4
4150	1.2
4800	3.5
5560	4.3
6440	1.8

Figure 3. PSD (a) by intensity, (b) by volume and (c) SEM, (d) TEM images of TYTANPOL R-003

of 712 nm in diameter) linked to the presence of the primary and secondary agglomerates. The polydispersity amounted to 0.218. The particle size distribution, taking into account the volume (Fig.6b) demonstrated one band. The band was linked to the presence of the particles of lower diameters and agglomerates of higher diameters and spanned the range of 342 – 6440 nm (the maximum volume of 10.6 corresponded to the particles of 825 nm in diameter). The SEM and TEM images (Figs.6c and d) documented the presence of spherical particles.

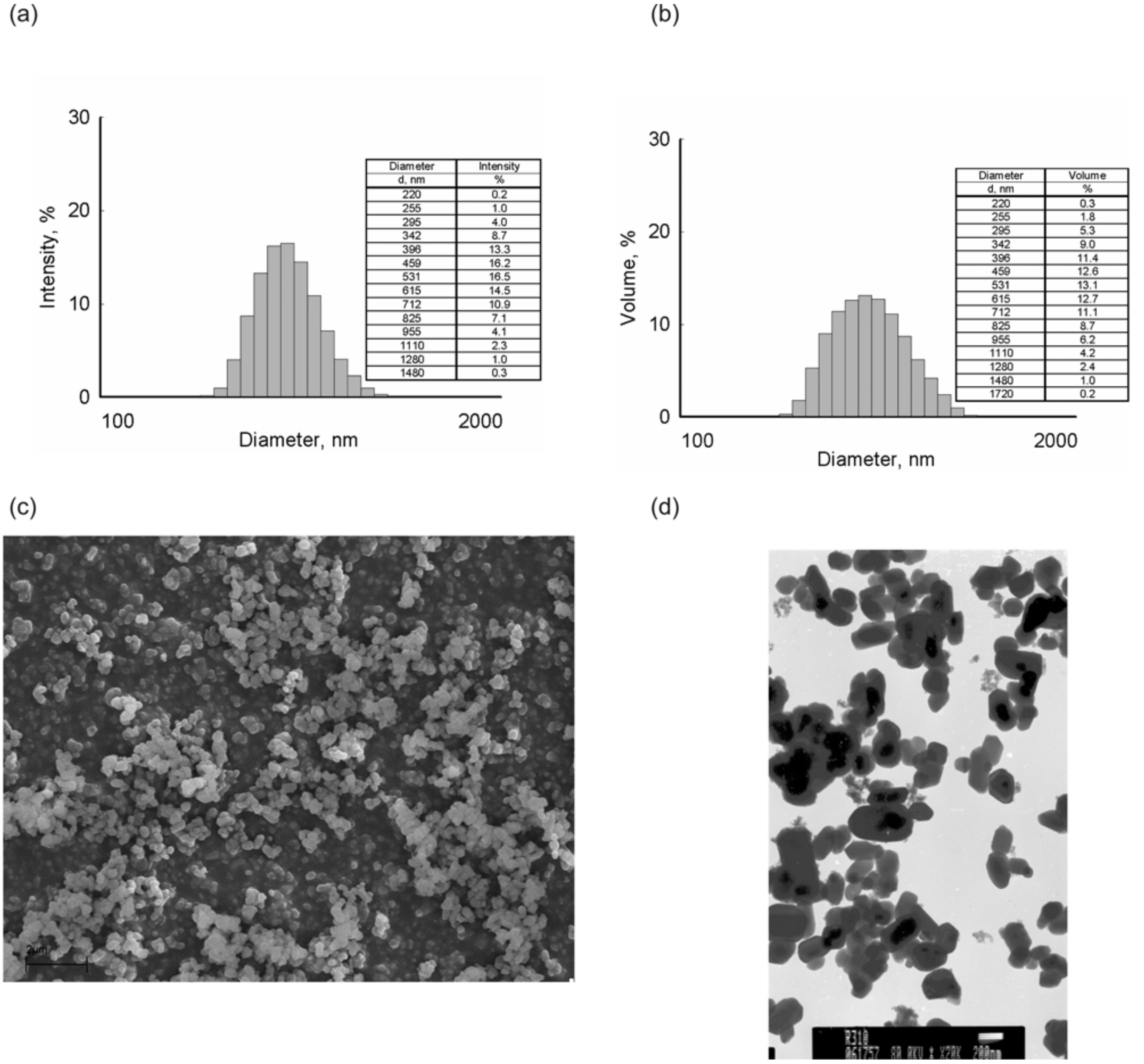
The profile of sedimentation in water for the selected samples of titanium dioxide is presented in Fig.7. The performed tests showed that the increase in a uniform character of titanium dioxide was linked to the increasing rates of sedimentation. The situation looked as follows: the polydispersity for the titanium dioxide pigment R-210 amounted to 0.174, for A-11 – 0.218, for R-213 – 0.233, for R-003 – 0.239, and for R-001 it amounted to 0.242. Thus, the increasingly uniform system (the decreasing values of polydispersity) was accompanied by increasing weight gains in time, which determined the sample sedimentation rate in water.

TYTANPOL R-213 was characterized by the most extensive BET surface area, which was 35 m^2/g, possibly reflecting the fact that the pigment was surface processed with the highest amounts of aluminium and silicon compounds, i.e. with 4.7% of Al_2O_3 and 8.3% SiO_2. On the other hand, the least extensive value of the BET surface area (~ 10 m^2/g) was shown by TYTANPOL A-11, which might reflect the absence of surface processing of the pigment.

CONCLUSIONS

All the varieties of commercial titanium dioxides are characterized by the spherical shape of particles, which may be linked to their surface processing and to the technique of drying (which results in the spherical shape of the particles).

In the case of titanium dioxides, the surface of which is coated with aluminium and silicon oxides, the polydispersity value reflects the effects of the organic compound. When a hydrophilic/hydrophobic compound is applied, the scatter of particle diameters or polydispersity is lower, as compared to the use of a hydrophilic organic compound. The other variable that controls the polydispersity value, involves the amount of silicon dioxides that have been used for surface processing of



Diameter d, nm	Intensity %
220	0.2
255	1.0
295	4.0
342	8.7
396	13.3
459	16.2
531	16.5
615	14.5
712	10.9
825	7.1
955	4.1
1110	2.3
1280	1.0
1480	0.3

Diameter d, nm	Volume %
220	0.3
255	1.8
295	5.3
342	9.0
396	11.4
459	12.6
531	13.1
615	12.7
712	11.1
825	8.7
955	6.2
1110	4.2
1280	2.4
1480	1.0
1720	0.2

Figure 4. PSD (a) by intensity, (b) by volume and (c) SEM, (d) TEM images of TYTANPOL R-310

the surface. The higher is their amount, the more uniform the sample is.

The surface of TiO_2 which has been coated with aluminium oxide only and modified with an organic compound of the hydrophilic character the polydispersity value can be expected to deteriorate when lower amounts of Al_2O_3 are used for the modification.

Modification with an organic compound of a hydrophobic character improves the uniformity of the sample.

The increased uniformity of the system is linked to the augmented weight gain in the sediment of titanium dioxide samples, sedimented in water. The amount of oxides used for surface processing affects the extent of the BET surface area and the value of the mean particle diameter. The higher is the amount of oxides used for surface processing is, the more extensive the adsorbing surface is, which may reflect an introduction by the surface processing of new, e.g. silanol or aluminol groups to the titanium dioxide surface, which form active adsorption sites.

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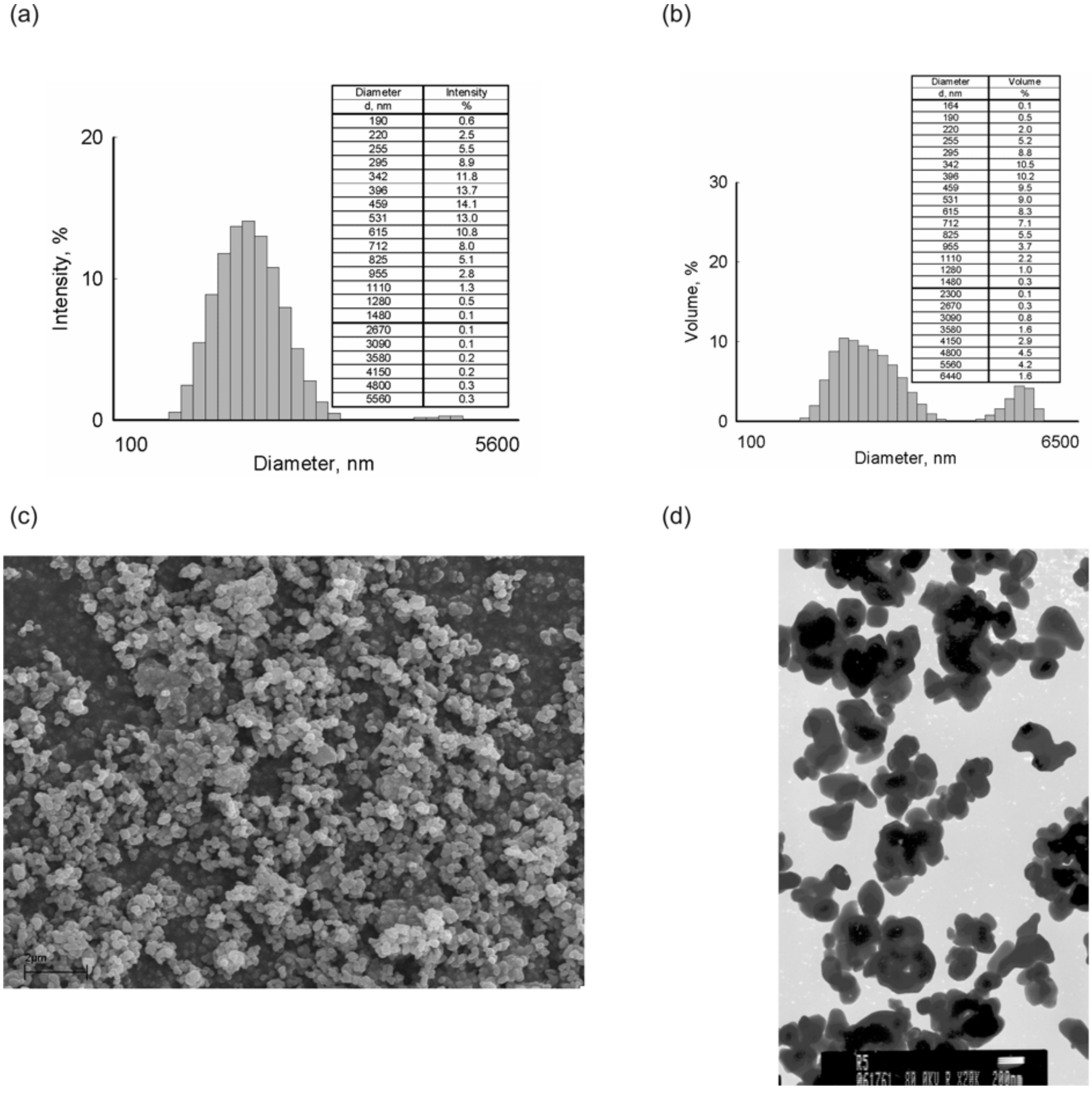
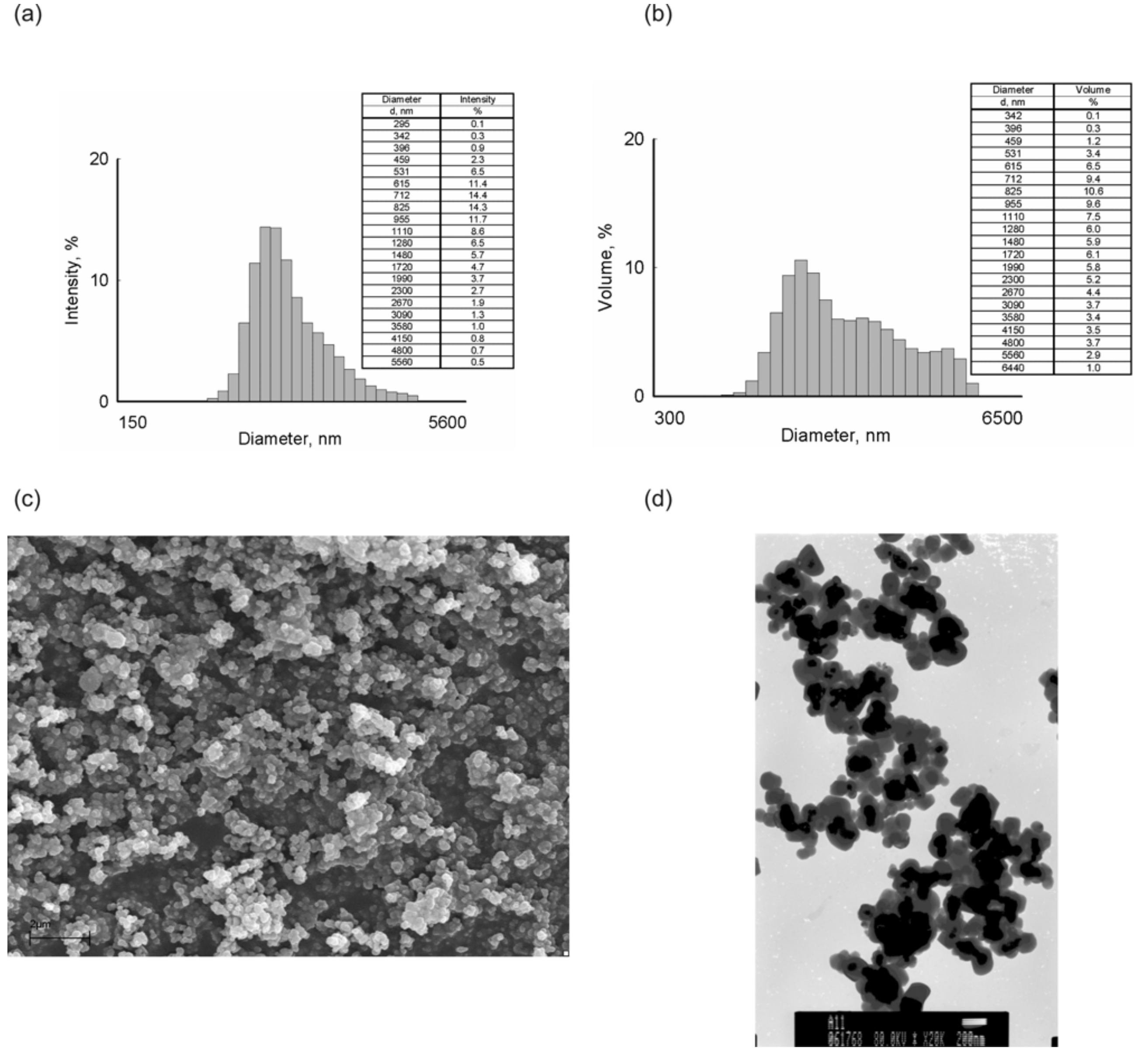


Diameter d, nm	Intensity %
190	0.6
220	2.5
255	5.5
295	8.9
342	11.8
396	13.7
459	14.1
531	13.0
615	10.8
712	8.0
825	5.1
955	2.8
1110	1.3
1280	0.5
1480	0.1
2670	0.1
3090	0.1
3580	0.2
4150	0.2
4800	0.3
5560	0.3

Diameter d, nm	Volume %
164	0.1
190	0.5
220	2.0
255	5.2
295	8.8
342	10.5
396	10.2
459	9.5
531	9.0
615	8.3
712	7.1
825	5.5
955	3.7
1110	2.2
1280	1.0
1480	0.3
2300	0.1
2670	0.3
3090	0.8
3580	1.6
4150	2.9
4800	4.5
5560	4.2
6440	1.6

Figure 5. PSD (a) by intensity, (b) by volume and (c) SEM, (d) TEM images of TYTANPOL RS



Diameter d, nm	Intensity %
295	0.1
342	0.3
396	0.9
459	2.3
531	6.5
615	11.4
712	14.4
825	14.3
955	11.7
1110	8.6
1280	6.5
1480	5.7
1720	4.7
1990	3.7
2300	2.7
2670	1.9
3090	1.3
3580	1.0
4150	0.8
4800	0.7
5560	0.5

Diameter d, nm	Volume %
342	0.1
396	0.3
459	1.2
531	3.4
615	6.5
712	9.4
825	10.6
955	9.6
1110	7.5
1280	6.0
1480	5.9
1720	6.1
1990	5.8
2300	5.2
2670	4.4
3090	3.7
3580	3.4
4150	3.5
4800	3.7
5560	2.9
6440	1.0

Figure 6. PSD (a) by intensity, (b) by volume and (c) SEM, (d) TEM images of TYTANPOL A-11

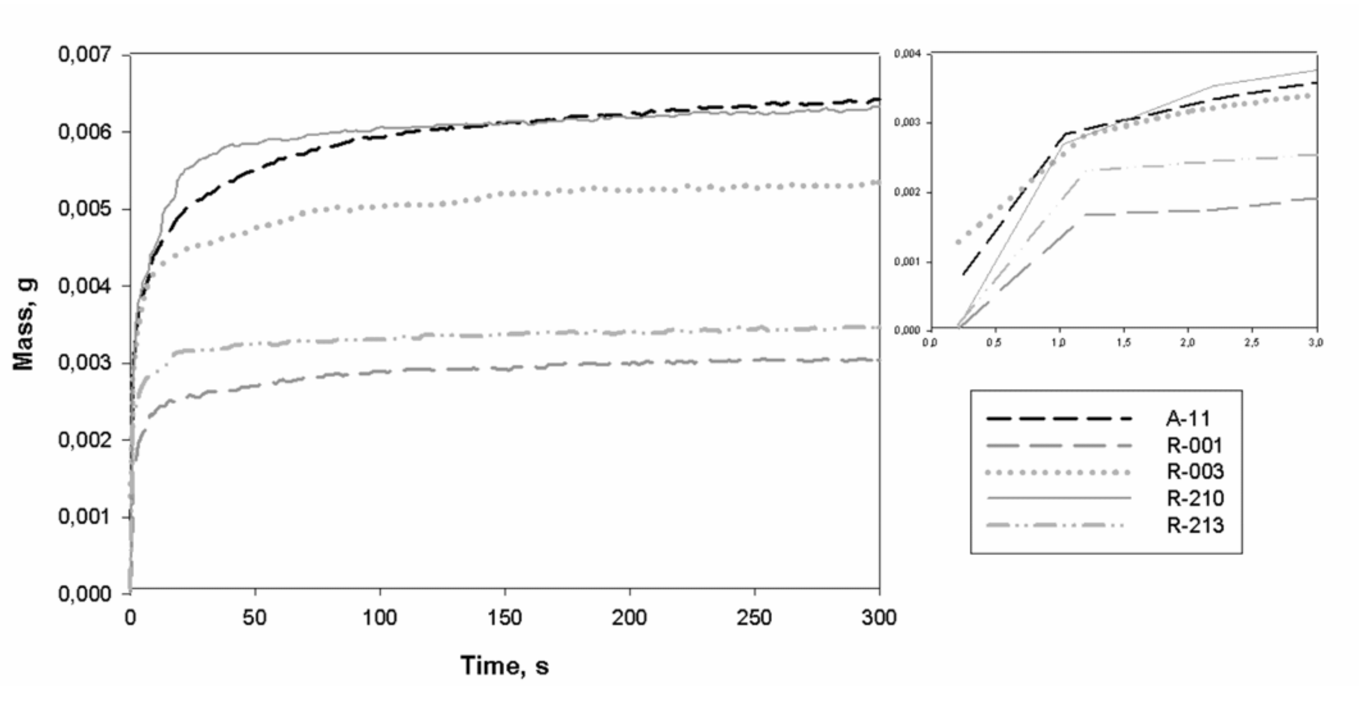


Figure 7. Sedimentation profiles examined in water for selected titanium dioxide samples

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