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MODIFIED, Al_2O_3 - TREATED TITANIUM WHITES AS PIGMENTS OF ACRYLIC PAINTS

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In the studies, aluminium-oxide treated titanium white (R-001 type) was used, produced by the Chemical Works Police S.A. Surface of titanium white was modified with silane coupling agents. For the purpose 3-methacryloxypropyltrimethoxysilane (A-174), vinyltrimethoxysilane (U-611) and N-2-aminoethyl-3-aminopropyltrimethoxysilane (U-15D) were used.

The unmodified and the modified titanium whites were subjected to physicochemical analysis. Moreover, tests were conducted in order to define morphology, surface structure and particle dispersion, as affected by the type of applied modifier. The analysis involved modern investigative techniques, SEM and DLS.

The modified and the unmodified titanium whites were applied as pigments in acrylic paints. The modified TiO_2 were particularly effective in improvement of strength and utility parameters of acrylic paints.

Key words*: titanium dioxide (R-001), surface modification, silane, particle size distribution, SEM, acrylic paint*

INTRODUCTION

Titanium dioxide pigments include spherical particles of various size. The particle size range used to be 0.005 to 1.0 μm but the fraction showing sizes of 0.2 to 0.4 μm prevails (Braun, 1997). The particle size strictly determines the extent of whiteness of titanium dioxide pigments. Even if pure TiO_2 is colourless, at high dispersion it represents the most effective white pigment. Within the visible light spectrum, titanium white practically does not absorb the incident light. The light is transmitted or deflected by the crystals or reflected from the surfaces of crystal contacts (Braun et al., 1992).

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On the surface of titanium dioxide particles the associated hydroxyl ions cause that surface of titanium white exhibits an ionic character (Buxbaun, 1993). Depending on the type of the bonds, particle surface exhibits an acidic or an alkaline character. Coating of the surface with hydroxyl groups affects several properties of the pigments, e.g., their dispersive potential, absorptive capacity, electrokinetic potential or resistance to external influences. The size and nature of the surface of TiO_2 pigment particles affect adsorption of dispersive or wetting agents, solvents and ahesives. The presence of hydroxyl groups opens potential for accomodating in the site photochemically-inducible reactions (Woodbridge, 1991).

Surface processing exerts immense effects on the character and size of pigment surface area. The most frequently applied inorganic processing with hydrated aluminium oxide and silica may even double specific surface area of titanium white (Wicks et al., 1992). Effect of silica clearly depends on the character of silica. The compact form of silica, which coats TiO_2 particles augments specific surface area of the pigment only slightly. On the other hand, the so called fluffy form (e.g., pyrogenic silica) may markedly elevate the specific surface area.

EXPERIMENTAL DETAILS

MATERIALS

Titanium dioxide (R-001) was obtained by the sulfate technology in the Chemical Works "Police" S.A. (Poland). Principal physicochemical data of the pigment are shown in Table 1. The data of Table 1 allowed us to conclude that a standard titanium white was used, of typical pH and oil absorption number.

Table 1. Principal properties of the applied titanium white

Physicochemical variable	Titanium white R-001
Density (g/cm^3)	4.1
Content of titanium dioxide (% w/w)	at least 95
-including rutile	at least 98
Content of volatile substances at 105°C (% w/w)	max. 0.5
Content of water soluble materials (% w/w)	max. 0.5
Residue on a sieve of 45 μm. mesh (% w/w)	max. 0.02
Brightness	95.5
Shade in a white paste	7.0
Relative scattering ability	100
Ability to tone down the shade	1850
Shade in a gray paste	3.5
pH in water suspension	7.5
Oil absorption number (g/100g pigment)	21
Specific resistance of water extract (Ohm x cm)	12000
Inorganic surface treatment	Al_2O_3

3-Methacryloxypropyltrimethoxysilane (A-174), vinyltrimethoxysilane (U-611) and N-2-aminoethyl-3-aminopropyltrimethoxysilane (U-15D) produced by Witco Co. (USA) and UniSil Co. (Poland) were used as modifiers.

METHODS

Modification process

Modification of the surface of TiO_2 was carried out in a mixer. For modification, solutions of appropriate silane were prepared, while solutions of the silane coupling agents were prepared in a mixture of water and methanol (4:1 v/v). Solutions containing 0.5 weight parts of these compounds in appropriate solvents per 100 weight parts of the modified titanium dioxide were used. The amount of solutions of modifying compounds was always selected in such a way as to ensure optimum wettability of the surface of TiO_2. After mixing, the solvent was removed by evaporation and the modified powders were dried at 110^{o}C.

Examination of physicochemical properties

Following the modification, the titanium dioxide was subjected to physicochemical tests, the bulk density as well as water, dibutyl phthalate and paraffin oil absorption capacity was estimated. The end point of water absorption capacity was observed when an excess of a single drop induced an evident liquefaction of the paste being formed. The end point of dibutyl phtahalate or paraffin oil absorption capacities was registered when an excess of a single phthalate or oil drop altered abruptly the consistency of the paste which adhered to a glass plate.

Table 2. Systems of acrylic dispersion paints for studies on the application of samples of titanium dioxide

1. AKRYL LAKMA Acrylic dispersion paint, white, water soluble, for facade use	Amount (wt%)
Acrylic-styrene dispersion (acrylic-styrene polymer, 50 wt% in water)	20-25
Carbonate fillers	30-35
Titanium white R-001 unmodified or modified	15-17
Dispersing agents, wetting agents, densifiers	23-35
2. AKRYBET Acrylic dispersion paint, white, organic solvent soluble, for exterior use	Amount (wt%)
Acryl resin in a solvent (whitespirit)	20-25
Carbonate fillers	30-35
Titanium white R-001 unmodified or modified	15-17
Dispersing agents, wetting agents, densifiers	23-35

Studies on morphology and microstructure were performed in order to obtain data on dispersion, particle shape and morphology of the granules, structure of individual particles and on TiO_2 aggregation and agglomeration type. The researches were conducted using scanning electron microscopy (SEM). The observations were performed using a Phillips SEM 515 microscope.

Size distributions of TiO_2 particles were estimated using a ZetaPlus instrument (Brookhaven Instruments Inc., USA), by the dynamic light scattering method.

Application of modified titanium white

Titanium white was applied as a pigment in acrylic dispersion paints (Jesionowski et al., 2001) Two types on acrylic paints were selected, listed in Table 2. Titanium whites were introduced to paints for interior or exterior use.

RESULTS AND DISCUSSION

The conducted studies on TiO_2 surface modification using silane coupling agents aimed at altering the hydrophilic/hydrophobic character of the surface.
Basic physicochemical parameters of unmodified and the modified titanium white are presented in Table 3. Only insignificant alterations in the surface character were noted in the surface modified pigments.

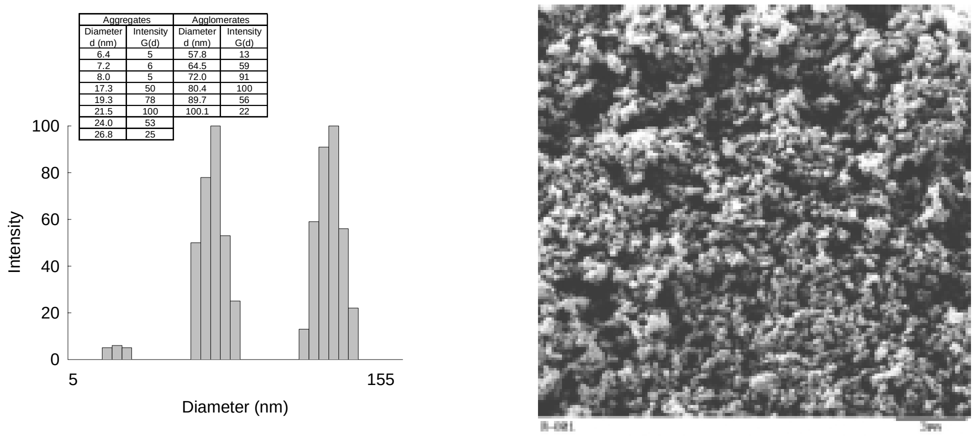
Table 3. Physicochemical parameters of unmodified and modified titanium dioxide (R-001)

Bulk density (g/dm^3)	Water absorbing capacity (cm^3/100g)	Dibutyl phthalate absorbing capacity (cm^3/100g)	Paraffin oil absorbing capacity (cm^3/100g)
TiO_2 - unmodified			
716	150	150	200
TiO_2 + U-611			
909	100	150	250
TiO_2 + A-174			
908	100	150	250
TiO_2 + U-15D			
900	150	100	250

An increased capacity to absorb water by TiO_2 surface could be observed only after modification of the surface with U-15D aminosilane. Since surface of the so modified titanium white carries amine groups which can interact by hydrogen bonds with water molecules, the surface exhibits a slightly hydrophilic character.

The use of silane coupling agents for the modification was followed by a distinct increase in bulk densities of the titanium white samples.

Particle size distribution of the unmodified sample of titanium white, R-001, is presented in Fig.1a, while the appropriate electron micrograph of the titanium pigment sample is shown in Fig.1b.

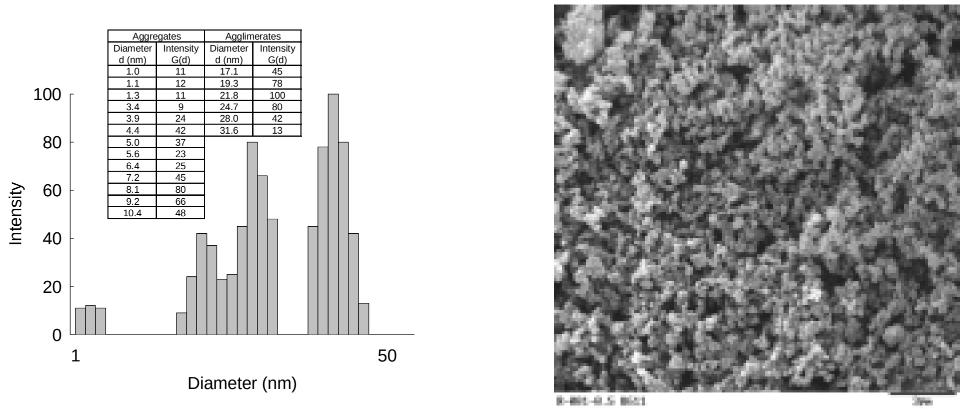


a) b)

Fig. 1. a) Multimodal particle size distribution and b) SEM of unmodified TiO_2

The particle size distribution (Fig.1a) manifested the presence of two bands, responsible for the presence of primary particles and of aggregates. One of the bands fitted the range of 6.4 to 8.0 nm and the other corresponded to the range of 17.3 to 26.8 nm (maximum intensity of 100 corresponded to the particle diameter of 21.5 nm). The third band proved that somewhat larger particles (agglomerates) were present. Size range of the latter included particles of 57.7 to 100.1 nm in diameter. Maximum intensity of 100 corresponded to agglomerates of 80.4 nm in diameter. Mean diameter of particles of this unmodified titanium white amounted to 49.7 nm and the polydispersity was 0.262. Also the respective electron microphotographs (Fig. 1b) provided an evidence for the presence of particles of a variable diameter and for the tendency to form aggregates and agglomerates. The observed dispersive and morphological properties of titanium white, R-001 resulted from coating of the pigment surface with aluminium oxide in the course of the technological process.

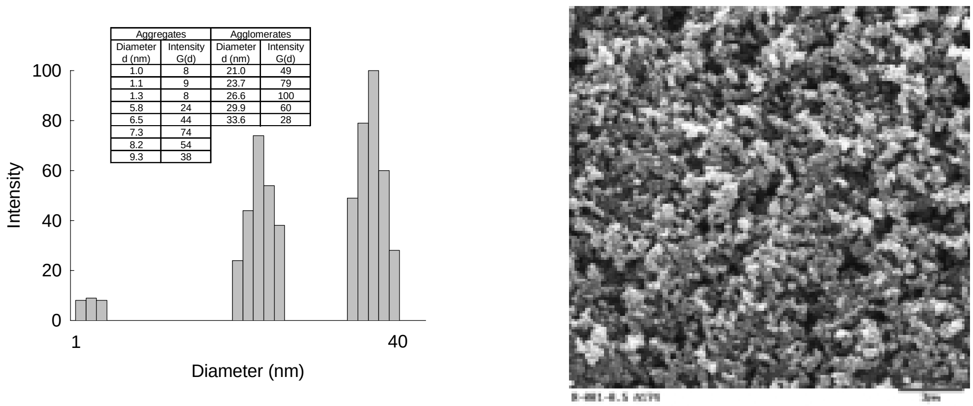
Titanium white modified with U-611 silane manifested quite a variable disperse character. In the particle size distribution (Fig. 2a) four bands were observed. The first band of low intensity documented the presence of very small particles (1.0-1.3 nm), the second and the third band included a broad range of diameters (3.4 to 10.4 nm). Maximum intensities for the bands were as follows: for the band of 3.4 to 5.0 nm intensity of 42 has corresponded to particles of 4.4 nm in diameter, for the band of 5.6 to 10.4 nm the intensity of 80 corresponded to the particle diameter of 8.1 nm. The most intense particle band fitted the range of 17.1-31.6 nm (maximum intensity of 100 corresponded to particles of 21.8 nm in diameter). The very clear electron microscopical pattern (Fig. 2b) pointed to the presence of isolated primary TiO_2 particles and provided an evidence for low tendency to form particle agglomerates.



a) b)

Fig. 2. a) Multimodal particle size distribution and b) SEM of TiO_2 modified with U-611 silane

Mean diameter of particles in U-611 silane-modified titanium white reached 13.6 nm and the polydispersity amounted to 0.228.

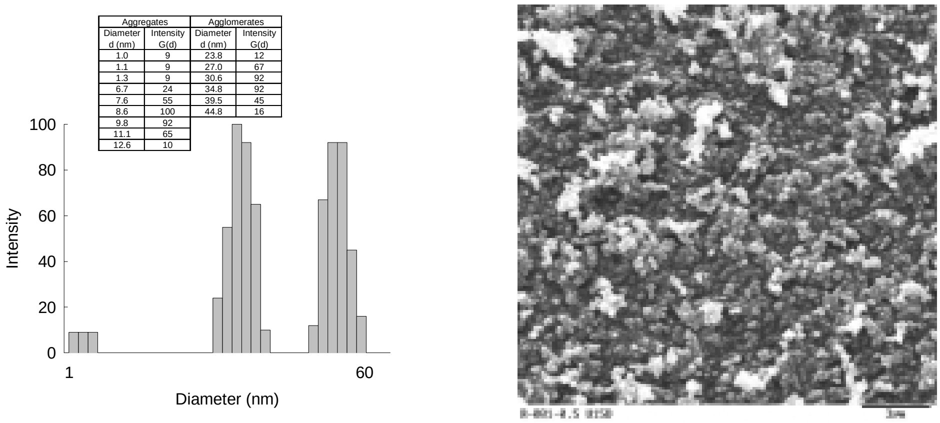


a) b)

Fig. 3. a) Multimodal particle size distribution and b) SEM of TiO_2 modified with A-174 silane

Very similar results were obtained following modification of the surface of R-001 titanium white using metacryloxypropyltrimethoxysilane, A-174. Mean particle diameter reached 17.5 nm and the polydispersity was 0.273. The particle size distribution and electron micrograph of so modified titanium white are shown in Fig. 3. Two bands were particularly intense (Fig. 3a): one within the range of 6.5-9.3 nm (maximum intensity of 74 has corresponded to particle diameter of 7.3 nm) and the other, more intense band within the range of 21.0-33.6 nm (maximum intensity of 100 corresponded to the particles of 26.6 nm in diameter).

Modification of titanium white with silane U-15D agent induced no significant changes in disperse and morphological characteristics of titanium white (Fig.4).



Aggregates		Agglomerates	
Diameter d (nm)	Intensity G(d)	Diameter d (nm)	Intensity G(d)
1.0	9	23.8	12
1.1	9	27.0	67
1.3	9	30.6	92
6.7	24	34.8	92
7.6	55	39.5	45
8.6	100	44.8	16
9.8	92		
11.1	65		
12.6	10		

a) b)

Fig. 4. a) Multimodal particle size distribution and b) SEM of TiO_2 modified with U-15D silane

Mean particle diameter was 19.9 nm and polydispersity amounted to 0.241. The particle size distribution (Fig. 4a) included three bands.

One of the bands fitted the range of 1.0-1.3 nm and showed very low intensity (maximum intensity of 9 corresponded to particles of 1.1 nm diameter). The remaining two bands were very intense. The more intense band fitted the range of 6.7-12.6 nm (maximum intensity of 100 corresponded to particle diameter of 8.6 nm). On the other hand, the less intense band corresponded to particles diameter in the range of 23.8-44.8 nm (maximum intensity of 92 corresponded to partocle diameter of 30.6-34.8 nm). SEM photograph (Fig.4b) proved that particles of aminosilane-modified titanium white exerted the most pronounced effect on interactions between the particles.

Results of studies on the application of modified or unmodified R-001 titanium white in *ACRYL LAKMA* and *AKRYBET* facade and external paints are shown in Tables 4-5.

As shown by the presented data, all the studied paint systems fitted the required range of density and viscosity. Problems were encountered with grinding of aminosilane-modified pigments in a grindometer. Such parameters as adhesion to the sublayer, spreading capacity and quality coating were consistent with the norms and all standards.

CONCLUSIONS

- Surface modification of R-001 titanium white surface with silane coupling agents induced evident increase in their bulk densities.
- Vinyltrimethoxysilane (U-611) and 3-methacryloxypropyltrimethoxysilane (A-174) were most effective in increasing hydrophobicity of titanium white and of homogeneity of its particles.
- N-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D) modified TiO_2 surface exhibited hydrophilic character.
- The modified titanium white (R-001), employed in studied paint types, improved quality of the paints and, in particular, their resistance and utility parameters.

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Jesionowsk T., Krysztafkiewicz A., Dec D., *Modyfikowane biele tytanowe obrabiane Al_2O_3 jako pigmenty farb akrylowych,* Fizykochemiczne Problemy Mineralurgii, 36, (2002) 307-316 (w jęz. ang.).

W badaniach zastosowano biel tytanową obrabianą tlenkiem glinu produkowaną przez Zakłady Chemiczne Police S.A. typu R-001. Powierzchnię bieli tytanowej modyfikowano silanowymi związkami wiażącymi. W tym celu użyto metakryloksypropylotrimetoksysilan (A-174), winylotrimetoksysilan (U-611) oraz N-2-(aminoetylo)-3-aminopropylotrimetoksysilan (U-15D).

Biel tytanową niemodyfikowaną i modyfikowaną poddano analizie fizykochemicznej. Ponadto przeprowadzono badania mające na celu określenie morfologii, budowy powierzchni i dyspersji cząstek przede wszystkim w zależności od rodzaju modyfikatora. Przy ocenie wykorzystano nowoczesne techniki badawcze – SEM i DLS.

Modyfikowane i niemodyfikowane biele tytanowe zastosowano jako pigmenty w farbach akrylowych. W szczególności modyfikowane biele tytanowe poprawiają właściwości wytrzymałościowe i użytkowe farb akrylowych.