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# MODIFIED TITANIUM WHITE - CHARACTERISTICS AND APPLICATION

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In the studies, type R-211 was used, produced by Chemical Works, Police S.A. (Poland). Surface modification of titanium white was performed in order to alter its physicochemical character. In this aim, silane coupling agents were used, carrying methacryloxy, vinyl and amine groups.
Basic characteristics of the titanium white included estimation of bulk density, water, dibuthyl phthalate and paraffin oil absorbing capacities. Moreover, studies were conducted to define morphology, surface structure and dispersion of $TiO_2$, as affected by the type of applied modifier. The parameters were examined using scanning electron microscopy (SEM). Using dynamic light scattering (DLS) effects of the applied modifiers were tested on tendency to form particle agglomerates. Significant changes were observed in the tendency to form primary and secondary agglomerate structures, particularly upon modification with U-15D aminosilane. The fillers permitted to improve physicochemical and utility properties of the façade acrylic paints.

*Key words: titanium dioxide, surface modification, acrylic paint*

## INTRODUCTION

Titanium dioxide (titanium white) is a natural product, which enters into the composition of ilmenite, $FeTiO_3$. In the nature, it exists in three polymorphic varieties: anatase, rutile, and brookite, which differ in arrangement of elementary particles.

Titanium dioxide is obtained from natural raw materials, such as rock ilmenites, ilmenite sands, leucoxen, or from enriched ores, like enriched ilmenites, titanium slags, or synthetic rutiles. Titanium pigments are produced by two distinct technologies: the sulphate technology and the chloride technology (Wypych, 1999).

Titanium whites are the most frequently applied white pigments, commonly used in the paint, plastic, rubber, paper, ceramic, cosmetic and textile industries.

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Moreover, titanium white is used as a polymer filler in, i.a., PVC, polyolefines, polystyrene and many other (Spychaj et al.,1993). Dispersion of pigments and fillers in the vehicle significantly affects the quality and properties of the obtained paints and coats. Dispersion of a pigment (e.g., of titanium white) in the vehicle involves decomposition_of the agglomerate structures and their dispersion in the form of primary particles. In the process the size of agglomerates gradually decreases while the total surface of the pigment gradually increases. When pigment dispersion is completed, the wetted particles may show a tendency for re-agglomeration (flocculation). For this reason, it is important to maintain a stable balance between deflocculation and flocculation (Kobayashi, 1997).

Pigment dispersion affects coat properties, such as its lustre, coating power, rheological properties and its stability during storage (Gesenhues, 1999). Fine dispersion of its particles is indispensable for an even distribution of the pigment in a coat and, thus, for the most economic use of the pigment. The smaller is the size of dispersed particles, the more homogeneous is distribution of the pigment (Brown et al.,1997). The raw materials are selected and the formulations are determined depending upon the purpose of the dispersion paints (for interior or exterior use).

Titanium white is subjected to surface processing in order to improve its insufficient refractoriness to weather conditions, its whiteness and dispersion. The processing includes mainly a stabilisation (Sales et al., 1998; Pownceby et al., 1999), involving introduction of other elements to its crystallic lattice, and surface modification (Esumi et al., 1998, 1999; Innocenzi et al., 2000; Shirai et al., 1999), aimed at altering its physicochemical properties. The most frequently applied modifiers include silane, titanate, and zirconate coupling agents, as well as fatty acids and their derivatives and surfactants.

## EXPERIMENTAL DETAILS

### MATERIALS

Titanium dioxide (R-211) 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 to conclude that a standard titanium white was used, of typical pH and oil absorption number. 3-Methacryloxypropyltrimethoxysilane (U-511), vinyltrimethoxysilane (U-611) and N-2-aminoethyl-3-aminopropyltrimethoxysilane (U-15D) produced by UniSil Co. Tarnów (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°C.

Table 1. Principal properties of the applied titanium white

| Physicochemical variable | Titanium white R-211 |
|---|---|
| Density [g/cm$^3$] | 3.9 |
| Content of titanium dioxide [% w/w] | at least 92 |
| -including rutile | at least 98.5 |
| 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 | 95.0 |
| Shade in a white paste | 7.0 |
| Relative scattering ability | 94 |
| Ability to tone down the shade | 1800 |
| Shade in a gray paste | 2.5 |
| pH in water suspension | 7.8 |
| Oil absorption number [g/100g pigment] | 28 |
| Specific resistance of water extract [Ohm x cm] | at least 8,000 |

## PHYSICOCHEMICAL PROPERTIES EXAMINATION

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 noted 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.

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 the Phillips SEM 515 microscope.

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

## APPLICATION OF MODIFIED TITANIUM WHITE

Titanium white was applied as a pigment in acrylic dispersion paints. Two types on acrylic paints were selected, listed in Table 2.

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

| 1. AKRYL LAKMA<br>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-211 unmodified or modified | 15-17 |
| Dispersing agents, wetting agents, densifiers | 23-35 |
| 2. AKRYBET<br>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-211 unmodified or modified | 15-17 |
| Dispersing agents, wetting agents, densifiers | 23-35 |

Titanium whites were introduced to paints for interior or exterior use.

## RESULTS AND DISCUSSION

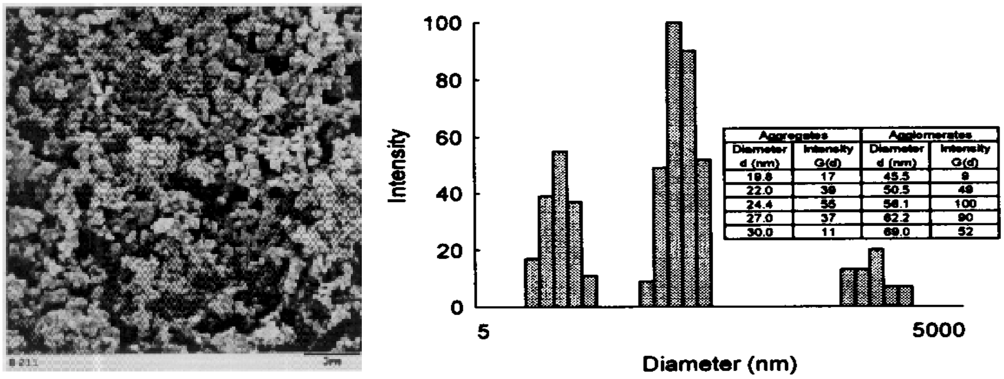
The conducted studies on $TiO_2$ surface modification using silane coupling agents aimed at altering the hydrophilic/hydrophobic character of the surface. Basic physicochemical parameters of unmodified and the modified titanium white are presented in Table 3. Only insignificant alterations in the surface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

Table 3. Physicochemical parameters of unmodified and modified titanium dioxide.

| 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 | | | |
| 651 | 150 | 100 | 200 |
| $TiO_2$ + U-611 | | | |
| 778 | 100 | 150 | 250 |
| $TiO_2$ + U-511 | | | |
| 756 | 100 | 200 | 250 |
| $TiO_2$ + U-15D | | | |
| 732 | 150 | 100 | 200 |

An increased capacity to absorb water by $TiO_2$ surface could be noted 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 for modification of silane coupling agents was followed by a slight increase in bulk densities of the titanium white samples. The electron micrograph of the unmodified sample of titanium white, R-211, is presented in Fig.1a while the appropriate particle size distribution of the titanium pigment sample is shown in Fig.1b.




a) b)

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

In the electron micrograph (Fig.1a), a slight tendency of the unmodified white particles was noted for agglomerate formation. The sample was not uniform, which was confirmed by the particle size distribution, containing three bands (Fig.1b). The first two bands corresponded to particles of less than 100 nm in diameter and showed distinct intensity. The particles of 19.8 to 30.0 nm in diameter formed a low intensity band (maximum intensity of 55 corresponded to particles of 24.4 nm in diameter). On the other hand, particles of diameters in the 45.5 to 69.0 nm range formed an intense band (maximum intensity of 100 corresponded to particles of 56.1 nm in diameter). The particle size distribution contained also a very narrow, intense band corresponding to particles of 195.5 to 296.5 nm in diameter (maximum intensity of 20 corresponded to particles of 240.8 nm in diameter). The distribution of unmodified titanium white particles into the three bands of various intensities proved the relatively high heterogeneity of the pigment. The effective particle diameter was 45.5 nm.

Particle size distribution for the titanium white modified with 0.5 weight parts of U-611 vinylsilane is shown in Fig.2. The distribution contained only two bands of particles of similar intensities, which indicated a greater homogeneity of the modified, as compared to the unmodified, titanium white particles. The band of higher intensity was formed by particles of 34.6 to 44.5 nm in diameter (maximum intensity of 100 corresponded to particles of 39.3 nm in diameter). On the other hand, the particles of 121.8 to 166.8 nm in diameter formed the less intense band (maximum intensity of 94 corresponded to particles of 147.1 nm in diameter). The effective particle diameter was 63.5 nm.

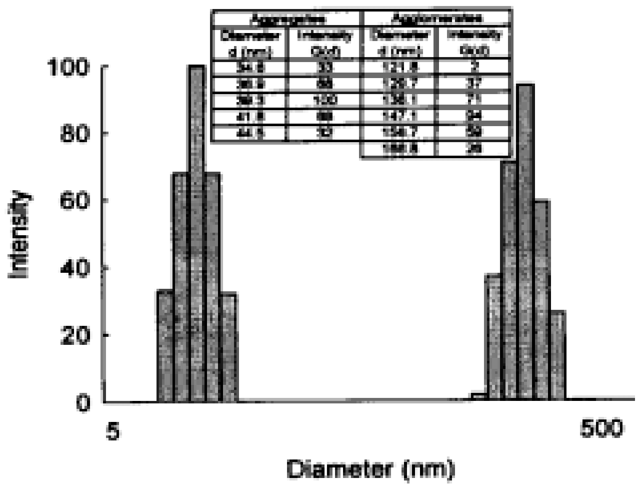
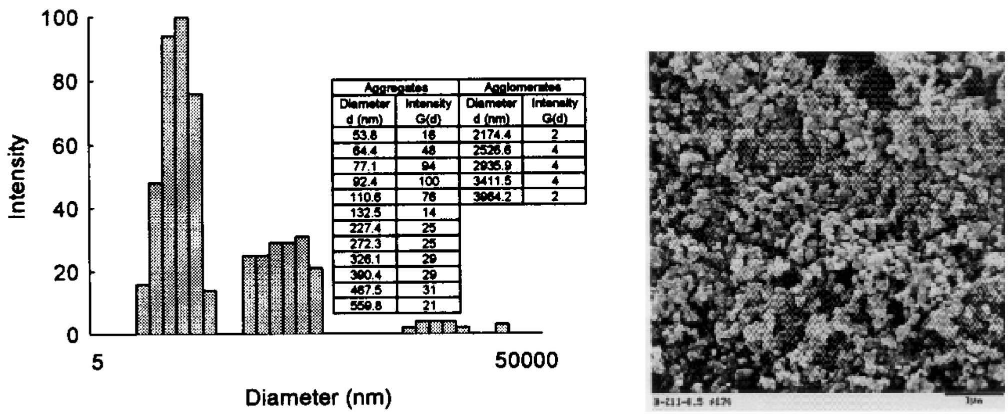



Fig. 2. Particle size distribution of $TiO_2$ modified with U-611 silane

Following modification of titanium white with methacryloxysilane A-174, the particle size distribution (Fig.3a) presented presence of even four bands of distinct intensities. This proved a deteriorated homogeneity of titanium white, linked to strong adhesive interactions of methacryloxy groups, which induced formation of larger particle clumps (Fig.3b).




a) b)

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

The band of the highest intensity was shifted toward particles of a greater diameter and was formed by particles of 53.8 to 132.5 nm in diameter (maximum intensity of 100 corresponded to particles of 92.4 nm in diameter). Particle accumulations of higher diameters and of a low intensity fitted the diameter range of 224.4 to 559.8 nm (maximum intensity of 31 corresponded to particles of 467.5 nm in diameter). The particle agglomerate range contained two bands of a very low intensity: one fitting the range of 2,174.4 to 3,964.2 nm (maximum intensity of 4 corresponded to the particle diameter of 2,935.9 nm) and the other of intensity of 3 corresponding to particles of the high diameter of 6,974.4 nm. The effective particle diameter increased to 125.3 nm.

In the size distribution curve (Fig.4) after modification of titanium white using U-15D aminosilane formed two intense bands in the range of 6.0 to 38.0 nm (intensity of 100 corresponded to the particle diameter of 29.9 nm). The effective particle diameter was as low as 15.7 nm.

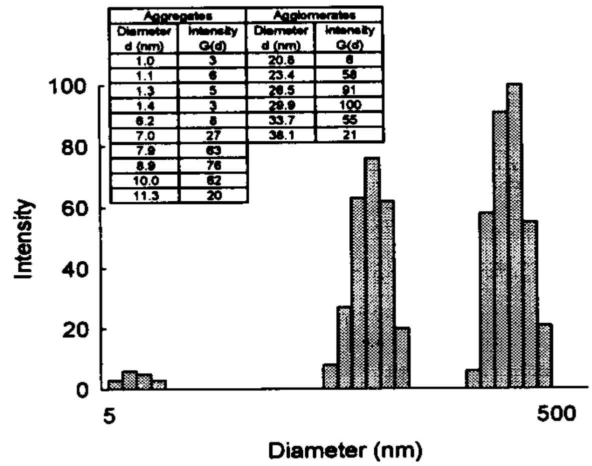



Fig. 4. Particle size distribution of $TiO_2$ modified with U-15D silane

Results of studies on application of the unmodified titanium white, R-211, and the respective modified titanium white in acrylic paints: ACRYL LAKMA facade paint and AKRYBET paint for exterior use are presented in Table 4 and Table 5.

As evident from the Tables data, densities of the facade paints fitted the required density range of 1.43 to 1.55 g/cm$^3$. Similarly the densities of the paints for exterior use were consistent with the required range of 1.35 to 1.50 g/cm$^3$. Moreover, also the other parameters, like viscosity, drying time, and resistance to scrubbing corresponded to those of the best standard types of paints based on titanium white. A test was also made of grinding the paints in a grindometer. The paints which contained aminosilane modified titanium white yielded results inconsistent with the requirements (particles of around 100 μm in size). In the remaining cases grinding yielded a very good result (particles of around 50 μm in size).

Table 4. Parameters of AKRYL LAKMA acrylic dispersion white, water soluble paint for facade use

Table 5. Parameters of AKRYBET acrylic white, organic solvent soluble paint for exterior use

## CONCLUSIONS

- Following modification of titanium white with $TiO_2$ methacryloxysilane, a deteriorated homogeneity of was observed. This proved a homogeneity of $TiO_2$ linked to strong adhesive interactions of methacryloxy groups, which induced formation of larger particle clumps.
- Modified titanium whites used in paints for exterior use and facade paints augment quality of the paints and, in particular, their resistance and utility parameters.

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**Jesionowski T., Krysztafkiewicz A., Dec A.,** Modyfikowane biele tytanowe charakterystyka i zastosowanie, Fizykochemiczne Problemy Mineralurgii, 35, 195-205 (w jęz. ang.)

W badaniach wykorzystano biel tytanową marki R-211 produkowaną przez Zakłady Chemiczne Police S.A.. Modyfikację powierzchni bieli tytanowej prowadzono w celu zmiany jej charakteru fizykochemicznego. W tym celu do modyfikacji zastosowano silanowe związki wiążące z następującymi grupami funkcyjnymi: metakryloksy, winylową oraz aminową.

W celu otrzymania podstawowej charakterystyki bieli tytanowej oznaczano jej: gęstość nasypową, chłonności – wody, ftalanu dibutylu oraz oleju parafinowego. Ponadto przeprowadzono badania mające na celu określenie morfologii, budowy powierzchni i dyspersji cząstek ditlenku tytanu w zależności od rodzaju modyfikatora. Oceny dokonano przy zastosowaniu skaningowej mikroskopii elektronowej (SEM). Techniką dynamicznego rozpraszania światła (DLS) badano wpływ użytych modyfikatorów na tendencję do tworzenia aglomeratów cząstek.

Modyfikowane i niemodyfikowane biele tytanowe zastosowano jako pigmenty w farbach akrylowych.

Stwierdzono, że winylosilan w największym stopniu hydrofobizuje powierzchnię bieli tytanowej, natomiast aminosilan podwyższa hydrofilowość tej powierzchni. Modyfikowane biele tytanowe przyczyniają się ponadto do poprawy parametrów fizykochemicznych i użytkowych fasadowych farb akrylowych.