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# Adsorption of organic dyes on the aminosilane modified $TiO_2$ surface

Agnieszka Andrzejewska, Andrzej Krysztafkiewicz, Teofil Jesionowski*

*Poznan University of Technology, Institute of Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznan, Poland*

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## Abstract

Studies were performed on modification of the rutile titanium dioxide surface using 3-aminopropyltriethoxysilane and *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane in various solvents (methanol, toluene, acetone and methanol-water mixture). The modified titanium white was subjected to physicochemical evaluation, aimed at estimating its bulk density, capacity to absorb water, dibutyl phthalate and paraffin oil. Organic dyes were deposited on the surface of the modified titanium white. For the obtained pigments their dispersion, grain morphology, structure of individual particles, particle size distribution, and specific surface area were estimated. In the studies DLS and SEM techniques, and BET method were employed.

*Keywords:* Titanium dioxide; Modification process; Dyes adsorption; Particle size distribution

## 1. Introduction

As compared to organic ones, inorganic pigments are chemically neutral, insoluble, insensitive to elevated temperatures and to environmental factors, including extreme values of environmental pH and chemicals. They also exhibit higher coating power. On the negative side, they are less bright, they exhibit lower colour intensity and lower staining power. Such properties of the pigments operate to a significant extent the chemical composition, particle shape and size distribution as well as surface properties of pigment particles [1–3]. For these reasons, the role of inorganic pigments systematically increases as compared to that of organic pigments [4–9].

In protective coats, titanium dioxide of rutile variety plays an important role. In particular, titanium dioxides that have been processed with inorganic oxides (e.g., $Al_2O_3$, $SiO_2$, $ZrO_2$) represent pigments of improved specific properties (i.e., a potential exists for chemical modification of $TiO_2$ surface) [10–16]. In recent years, papers have been published that report the production of novel pigments by adsorption or incorporation of organic dyes on the surfaces of various inorganic solids [17]. By selecting a core of starting material of, e.g., known particle size, and by linking it with specific dyes, pigments of a desired colour, purity

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* Corresponding author. Tel.: +48-61-6653-720/626; fax: +48-61-6653-649.

*E-mail address:* teofil.jesionowski@put.poznan.pl (T. Jesionowski).

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or transparency can be obtained. Systems of the type were prepared in order to produce water-dispersed pigments to be applied in printing inks [18]. Moreover, in a gradual synthesis of a chromophore on a silica surface [19] azo pigments can be obtained, and applied in toners, in copying machines.

In this paper we present the results of studies that were performed in order to obtain pigments by adsorption of organic dyes on a modified surface of a titanium dioxide pigment system.

## 2. Experimental

### 2.1. Materials

The raw material for obtaining pigments was titanium dioxide, R-213, produced by Chemical Works "Police" S.A. (Poland). Its general physicochemical characteristics are given in Table 1.

Silane coupling agents, produced by the UniSil Company (Poland), Tarnów, were used as agents for modifying the surface of the titanium dioxide. Two types of silane coupling agents were employed, with the following amine groups:

- 3-aminopropyltriethoxysilane (U-13): $H_2N(CH_2)_3Si(OC_2H_5)_3$
- *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D): $H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$.

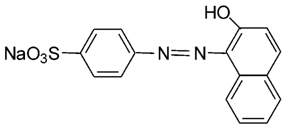
Table 1
Physicochemical properties of titanium dioxide R-213

| Parameter | Value |
|---|---|
| Inorganic surface treatment | $Al_2O_3$ and $SiO_2$ |
| Brightness | 95.5 |
| Shade in a white paste | 7.1 |
| pH in water suspension | 8.0 |
| Oil absorption number (g 100 $g^{-1}$ pigment) | 40 |
| Degree of rubbing (Hegman's scale) | 6.0 |
| Average size particle (μm) | 0.35 |
| Density (g $dm^{-3}$) | 3700 |
| Top density (g $dm^{-3}$) | 650 |
| Content of titanium dioxide (% w/w) | 82.0 |
| Content of volatile substances at 105 °C, (% w/w) | max. 1.5 |
| Residue on a sieve of 45 μm mesh (% w/w) | max. 0.02 |

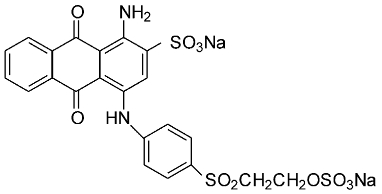
The principal physicochemical properties of the two silanes are listed in Table 2.

For the preparation of the pigments, C.I. Acid Orange 7 and C.I. Reactive Blue 19 were used as obtained from Boruta-Kolor (Poland), of the following structure:

- C.I. Acid Orange 7



- C.I. Reactive Blue 19



### 2.2. Procedures and methods

#### 2.2.1. Modification process

The modification was conducted in a reactor of 0.5 $dm^3$ capacity, charged with 100 g titanium dioxide and a solution of the modifying compound. The solution contained silane coupling agents (2 parts by mass of $TiO_2$) dissolved in an appropriate solvent [methanol, toluene, acetone or methanol–water (4:1) mixture]. The modifying solution was very slowly introduced to the $TiO_2$-containing reactor. The system was mixed for 1 h to ensure complete mixing of the $TiO_2$ with the solution of the modifying compound.

Table 2
Physicochemical properties of aminosilanes

| Parameter | Silane U-13 | Silane U-15D |
|---|---|---|
| Molecular weight (u) | 221.2 | 222.1 |
| Boiling point (°C) | 123 | 140–150 |
| Specific gravity (g $cm^{-3}$) | 0.94 | 1.05 |
| Refractive index $n_{D25}$ | 1.42 | 1.45 |
| Flash-point (°C) | 104 | 130 |

### 2.2.2. Adsorption of organic dye

Dye selection reflected the potential for formation of stable chemical bonds of the surface functional groups of $SiO_2$-coated $TiO_2$ and $Al_2O_3$-coated $TiO_2$ (silanol groups, aluminol groups) with selected organic dyes of acidic or alkaline character. C.I. Reactive Blue 19 belongs to the group of antraquinone dyes and contains an active amine group while C.I. Acid Orange 7 belongs to azo dyes and contains in its structure an active hydroxyl group.

The reactor was charged each time with a defined amount of unmodified or modified titanium white (10 g) and with solution of an appropriate dye at 1.5 mg $cm^{-3}$. The amount of the dye in the solution was optimized earlier [20]. The adsorption process was conducted at room temperature. Adsorption of C.I. Reactive Blue was conducted at pH just above 8 while adsorption of C.I. Acid Orange at pH 6–7. The content was mixed for an hour and then filtered under vacuum. The obtained sediment was dried at 105 °C. In the filtrate, content of unadsorbed dye was established.

### 2.2.3. Elution of unadsorbed dye from the pigment surface

Pigment (0.1 g) was added to a water-containing reactor. The so obtained suspension was mixed for an hour. Subsequently, the pigment was separated by filtration and, in the filtrate, the concentration of the pigment surface-desorbed dye was established.

### 2.2.4. Testing of physicochemical properties

The principal tested parameters which permit to evaluate the course of alterations on $TiO_2$ surface under effect of its modification included bulk density ($D_n$), its capacity to absorb water ($H_w$), and the capacities to absorb dibutyl phthalate and paraffin oil ($H_f$, $H_o$ respectively).

The morphology and microstructure were examined in order to obtain data on dispersion, grain morphology, structure of individual particles and on agglomeration type in the obtained titanium dioxide and $TiO_2$ hybrids. In the studies, a scanning electron microscope, Philips SEM 515 was used. Since $TiO_2$ does not conduct electric currents, irradiation with the electron beam in the scanning electron microscope results in charge accumulation at their surfaces with the resulting deformation of surface topography image. In order to avoid such a charge accumulation, titanium dioxide specimens were prepared in tertiary butyl alcohol.

Particle size distributions were obtained using a ZetaPlus apparatus (Brookhaven Instruments Co., USA). The particle size was measured using a dynamic light scattering (DLS) technique.

Specific surface areas of titanium dioxide and pigments were determined by $N_2$ adsorption (BET method) using ASAP 2010 instrument (Micrometrics Instrument Corporation). Moreover, the volume and size of pores of powders were examined. Samples were heated at 120 °C for 2 h prior to measurements.

## 3. Results and discussion

The principal parameters characterising the unmodified $TiO_2$ and the aminosilane-modified $TiO_2$ are listed in Table 3.

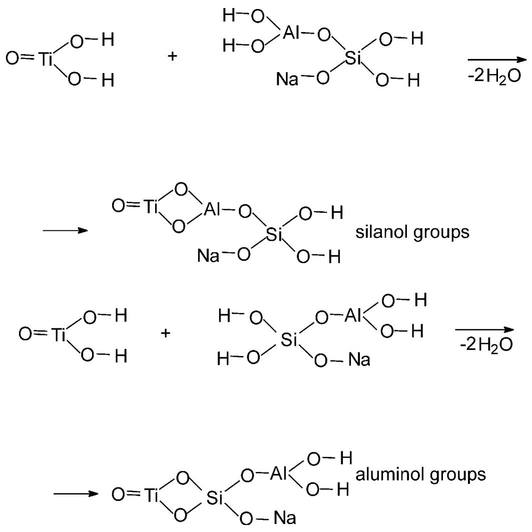
The conducted studies on $TiO_2$ surface modification using silane coupling agents were aimed at altering its surface character in the hydrophilic–hydrophobic system.

Introduction of the silane coupling agent to the surface of $TiO_2$, R-213, induced an increase in its bulk density. This resulted from introduction of appropriate amounts of the applied modifier to the surface of $TiO_2$, which augmented the weight of the $TiO_2$. Application of silane U-13 and toluene as a solvent and of methanol-dissolved silane U-15D for modification of $TiO_2$ resulted in a slight, hardly noticable increase in the bulk densities of the samples (Table 3). On the other hand, $TiO_2$ R-213 modification using U-13 silane in acetone, U-15D silane in toluene or U-13 silane in methanol (following additional acidification with one weight part of 5% HCl solution) caused the bulk densities of the samples to provide the greatest increase.

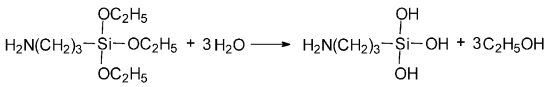
The modifier silane coupling agent became adsorbed on the surface of the $TiO_2$ first of all due to the presence of an aluminium oxide and a silica monolayer deposited on the surface. Titanium white R-213, precipitated in the presence of sodium-aluminium silicate, carries on its surface active silanol groups and aluminol groups. There are formed as follows:

Table 3
Physicochemical properties of $TiO_2$ after modification with silane

| Sample | Bulk density (g dm$^{-3}$) | Water absorbing capacity (cm$^3$ 100 g$^{-1}$) | Dibutyl phthalate absorbing capacity (cm$^3$ 100 g$^{-1}$) | Paraffin oil absorbing capacity (cm$^3$ 100 g$^{-1}$) |
|---|---|---|---|---|
| Unmodified $TiO_2$ | 444 | 150 | 300 | 500 |
| $TiO_2$ + U-13 + methanol | 487 | 100 | 250 | 450 |
| $TiO_2$ + U-13 + toluene | 445 | 100 | 330 | 450 |
| $TiO_2$ + U-13 + acetone | 521 | 100 | 250 | 350 |
| $TiO_2$ + 1 cm$^3$ HCl 5% + U-13 + methanol | 514 | 150 | 350 | 450 |
| $TiO_2$ + U-15D + methanol | 459 | 150 | 300 | 400 |
| $TiO_2$ + U-15D + toluene | 515 | 150 | 300 | 400 |

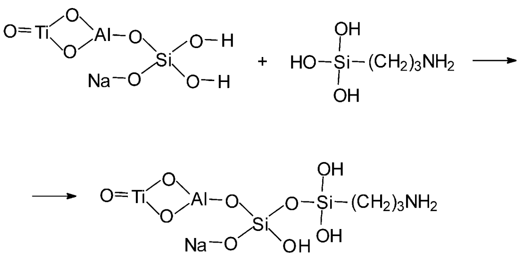


The silanol and aluminol groups are responsible for surface modification of $TiO_2$. They are able to condense with silanol groups of the hydrolysed silane coupling agent. The mechanism of the reaction with 3-aminopropyltriethoxysilane can be presented as follows. At first, aminosilane undergoes hydrolysis with formation of silanol groups:



$$H_2N(CH_2)_3Si(OC_2H_5)_3 + 3H_2O \longrightarrow H_2N(CH_2)_3Si(OH)_3 + 3C_2H_5OH$$

As a result of the hydrolysis, the silanol groups of the silane molecule may undergo condensation with the surface silanol groups and aluminol groups of $TiO_2$. The condensation with participation of silanol groups on the $TiO_2$ surface occurs as follows:



Studies on water adsorption on the surface of $TiO_2$ R-213 demonstrated that modification with U-13 silane decreased the capacity of the $TiO_2$ to absorb water or induced an increase in its hydrophobicity. On the other hand, $TiO_2$ R-213, modified with the silane coupling agent, U-15D absorbed the same amount of water as the unmodified sample. In the latter situation the modified surface of titanium white carried increased numbers of amine groups which resulted in the tendency for hydrogen bonding interaction with the water molecules and, therefore, the surface exhibited slightly hydrophilic character.

The type of solvent used for modification exerted no significant effect on the potential to absorb water, dibutyl phthalate or paraffin oil. A positive effect was also observed of $TiO_2$ R-213 modification with silane U-13 in the presence of 5% HCl solution. Addition of the acid did not increase water-absorbing capacity but led to a clear increase in the dibutyl phthalate absorbing capacity and is an increase in the hydrophobicity of $TiO_2$ surface.

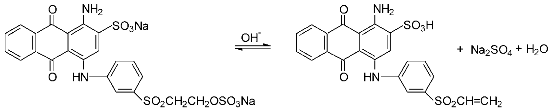
The data relating to the efficiency of adsorption and elution of dyes from the surface of modified pigments are presented in Table 4.

Table 4
Adsorption extent and amount of eluted dye of the investigated titanium whites

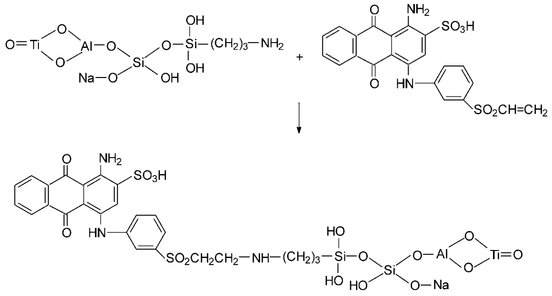
| Sample | Adsorption extent (%) | Amount of dye eluted from $TiO_2$ surface (%) |
|---|---|---|
| C.I. Acid Orange 7 | | |
| Unmodified $TiO_2$ | 42.0 | 10.6 |
| $TiO_2$ + U-13 + methanol | 65.1 | 16.4 |
| $TiO_2$ + U-13 + toluene | 66.0 | 11.4 |
| $TiO_2$ + U-13 + acetone | 66.3 | 15.4 |
| C.I. Reactive Blue 19 | | |
| Unmodified $TiO_2$ | 63.0 | 9.7 |
| $TiO_2$ + U-15D + methanol | 61.0 | 5.9 |
| $TiO_2$ + U-15D + toluene | 59.8 | 6.1 |
| $TiO_2$ + U-13 + methanol | 64.6 | 8.8 |
| $TiO_2$ + U-13 + toluene | 66.0 | 9.1 |
| $TiO_2$ + U-13 + acetone | 64.6 | 5.4 |
| $TiO_2$ + U-13 + toluene (adsorption 5 h) | 65.3 | 6.2 |
| $TiO_2$ + U-13 + toluene (adsorption temperature 70 °C) | 51.6 | 4.5 |

As is evident from the data of Table 4, modification of $TiO_2$ was a sensible manoeuvre. Following modification of $TiO_2$ surface with aminosilane U-13, the efficiency of adsorption of C.I. Acid Orange 7 dye increased by over 20% compared as it the use of unmodified $TiO_2$ as the adsorbent. However, the extent of elution of the adsorbed dye from the surface of unmodified titanium white was slightly lower than that from the aminosilane-modified surface. No evident solvent effect was noted in the course of the $TiO_2$ surface modification with aminosilane on efficiency of Acid Orange 7 adsorption or on the extent of its elution from the surface using water. Following modification of $TiO_2$ surface with U-15D silane, the efficiency of C.I. Reactive Blue 19 slightly decreased by 2–3% as compared to the unmodified titanium white. The extent of elution of the adsorbed dye was around 6% when the modified $TiO_2$ was used. Avalue 9.7% was recorded when unmodified titanium white was applied. Using silane U-13-modified $TiO_2$ as an adsorbent, a slight increase in efficiency of C.I. Reactive Blue 19 adsorption was noted, as compared to the unmodified titanium white, R-213. On the other hand, the extent of elution of the adsorbed dye was slightly lower as compared to the unmodified titanium white.

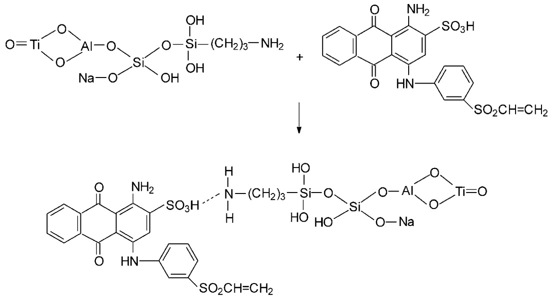
The mechanism of C.I. Reactive Blue 19 adsorption on the surface of modified titanium white at the first stage involves transformation of β-sulphateethylsulphonic group, $SO_2CH_2CH_2$-$OSO_3Na$, of the dye to vinylsulphonic group, $SO_2CH=CH_2$. Under effect of alkali the group splits off the residue of sulphuric acid as follows:



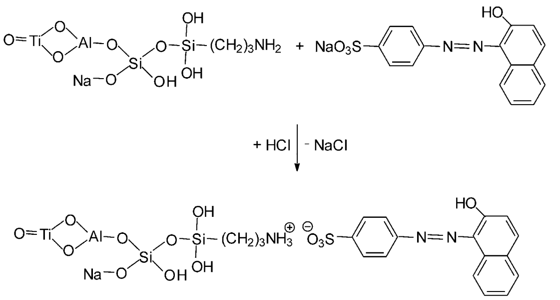
Subsequently, the so formed vinylsulphonic group may react with the silanol group-coated surface of aminosilane-modified titanium white, forming covalent bonds [21].



Another mechanism assumes that a hydrogen bond may form between nitrogen atom of a modified pigment amine group and hydrogen atom of sulphonic group in the organic dye.

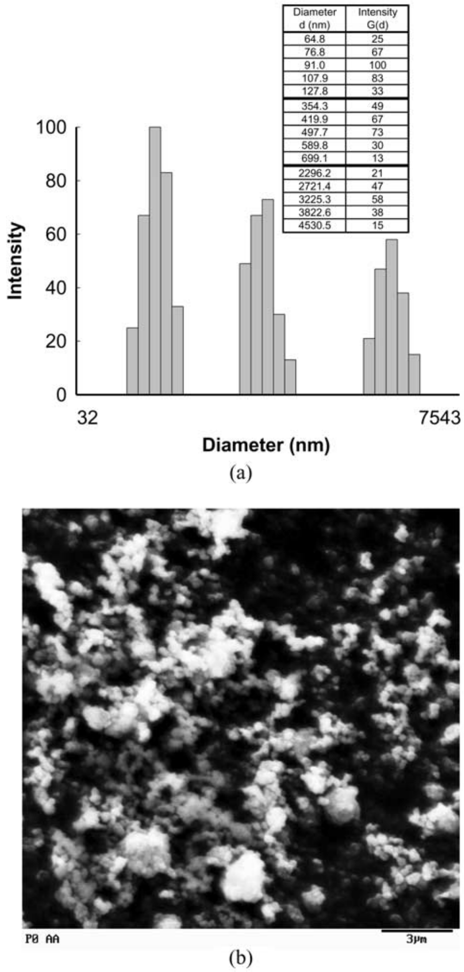


On the other hand, a probable mechanism of binding C.I. Acid Orange 7 dye at the modified $TiO_2$ surface could be suggested:



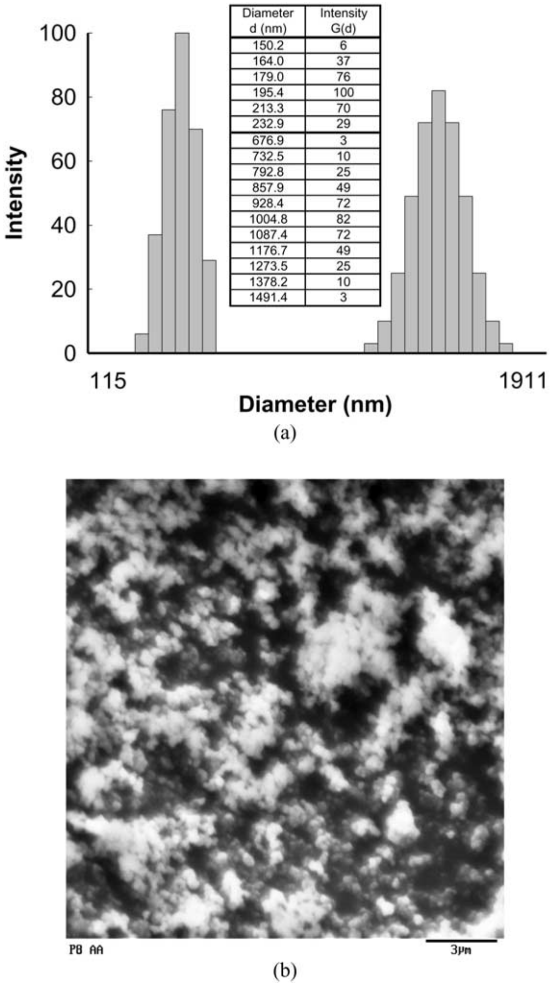
The lowest elution of the adsorbed dye was observed when the adsorption was carried out at the temperature of 70 °C, but in such conditions efficiency of adsorption was as low as 51.6%. However, the efficiency proved much lower as compared to the efficiency for the same modified sample of titanium white on which the dye was adsorbed at room temperature (66%). The adsorption at elevated temperatures was associated with a significant expense of energy making this way of dye application on titanium white economically unprofitable.

Particle size distribution for the unmodified titanium white R-213 is presented in Fig. 1a. Such a titanium white underwent an additional surface processing and for this reason its particles were



| Diameter d (nm) | Intensity G(d) |
|---|---|
| 64.8 | 25 |
| 76.8 | 67 |
| 91.0 | 100 |
| 107.9 | 83 |
| 127.8 | 33 |
| 354.3 | 49 |
| 419.9 | 67 |
| 497.7 | 73 |
| 589.8 | 30 |
| 699.1 | 13 |
| 2296.2 | 21 |
| 2721.4 | 47 |
| 3225.3 | 58 |
| 3822.6 | 38 |
| 4530.5 | 15 |

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



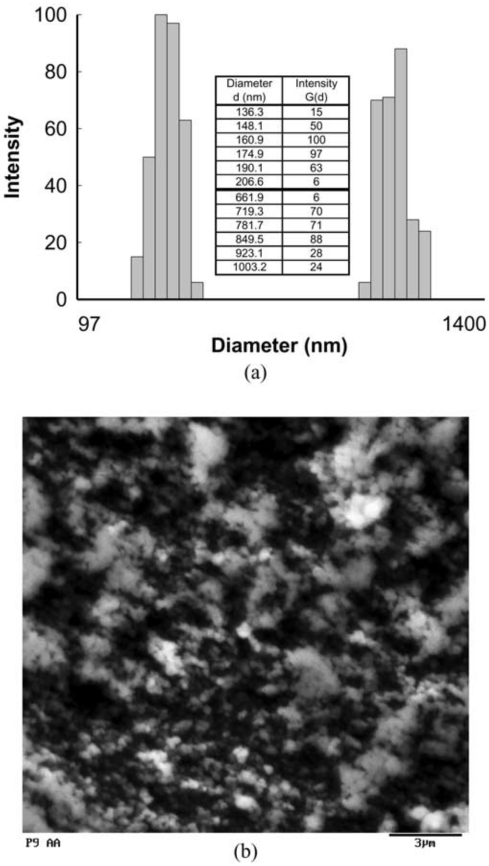
| Diameter d (nm) | Intensity G(d) |
|---|---|
| 150.2 | 6 |
| 164.0 | 37 |
| 179.0 | 76 |
| 195.4 | 100 |
| 213.3 | 70 |
| 232.9 | 29 |
| 676.9 | 3 |
| 732.5 | 10 |
| 792.8 | 25 |
| 857.9 | 49 |
| 928.4 | 72 |
| 1004.8 | 82 |
| 1087.4 | 72 |
| 1176.7 | 49 |
| 1273.5 | 25 |
| 1378.2 | 10 |
| 1491.4 | 3 |

Fig. 2. Multimodal particle size distribution (a) and SEM micrograph (b) of unmodified $TiO_2$ with adsorbed C.I. Reactive Blue 19.

relatively large and manifested a tendency to form agglomerates. The band in the range of 65–128 nm (maximum intensity of 100 corresponded to the particle of diameter 91nm) pointed to the presence of primary particles. The primary agglomerate band could be noted in the range of 354–699 nm (maximum intensity of 73 corresponded to agglomerates of 498 nm in diameter). The secondary agglomerate band was observed in the range of 2296–4530 nm (maximum intensity of 58 corresponded to agglomerates of 3225 nm in diameter). The tendency of titanium white to form agglomerates was corroborated by the SEM micrograph (Fig. 1b).

Particle size distribution of the unmodified titanium white following deposition of C.I. Reactive Blue 19 dye, is presented in Fig. 2a. The band of primary particles occupied the range of 150–233 nm (maximum intensity of 100 corresponded to particles of 195 nm in diameter), while the band of primary agglomerates was observed in the range of 677–1491 nm (maximum intensity of 82 corresponded to agglomerate diameter of 1005 nm). The sample proved to be more uniform, as confirmed by SEM micrograph (Fig. 2b).

A good quality pigment was obtained in the case of titanium white modified with aminosilane U-13 in methanol following deposition of C.I. Reactive Blue 19. The particle size distribution presented two bands (Fig. 3a). The band of primary particles occupied the range of 136–207 nm (maximum intensity of 100 corresponded to particles of 161

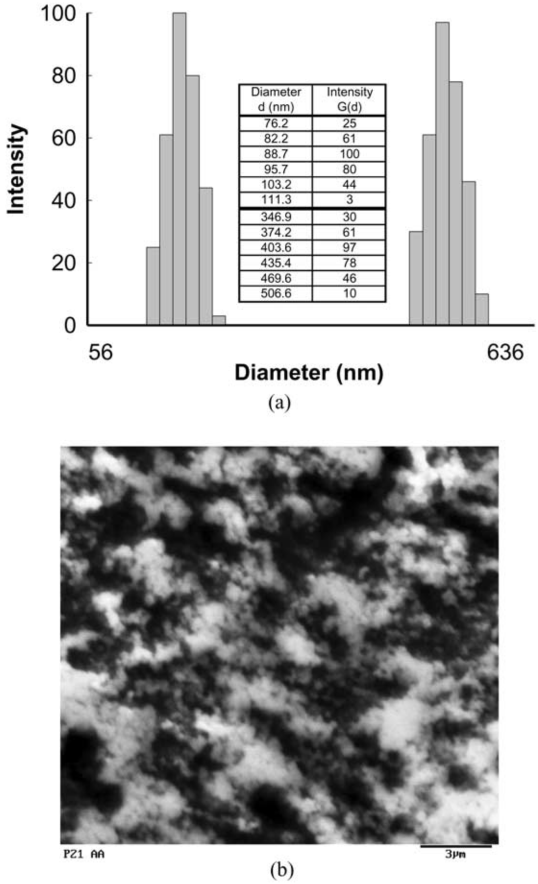


| Diameter d (nm) | Intensity G(d) |
|---|---|
| 136.3 | 15 |
| 148.1 | 50 |
| 160.9 | 100 |
| 174.9 | 97 |
| 190.1 | 63 |
| 206.6 | 6 |
| 661.9 | 6 |
| 719.3 | 70 |
| 781.7 | 71 |
| 849.5 | 88 |
| 923.1 | 28 |
| 1003.2 | 24 |

(a)

(b)

Fig. 3. Multimodal particle size distribution (a) and SEM micrograph (b) of $TiO_2$ modified with U-13 silane (in methanol solution) and with adsorbed C.I. Reactive Blue 19.



| Diameter d (nm) | Intensity G(d) |
|---|---|
| 76.2 | 25 |
| 82.2 | 61 |
| 88.7 | 100 |
| 95.7 | 80 |
| 103.2 | 44 |
| 111.3 | 3 |
| 346.9 | 30 |
| 374.2 | 61 |
| 403.6 | 97 |
| 435.4 | 78 |
| 469.6 | 46 |
| 506.6 | 10 |

(a)

(b)

Fig. 4. Multimodal particle size distribution (a) and SEM micrograph (b) of $TiO_2$ modified with U-15D silane (in toluene solution) and with adsorbed C.I. Reactive Blue 19.

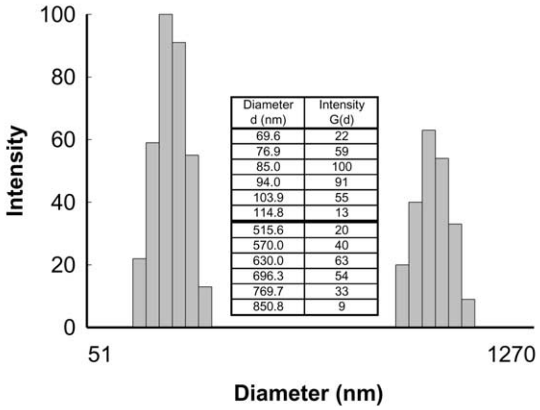


Fig. 5. Multimodal particle size distribution of $TiO_2$ modified with U-13 silane (in methanol solution) and with adsorbed. C.I. Acid Orange 7.

nm in diameter) while the band of primary agglomerates fitted the range of 662–1003 nm (maximum intensity of 88 corresponded to particles of 850 nm in diameter). Particles of the sample demonstrated a decreased tendency to agglomerate, which was confirmed by SEM micrograph (Fig. 3b).

A subsequent sample was obtained by modification of titanium white with the silane U-15D (in toluene, in the presence of HCl), and by adsorption of C.I. Reactive Blue 19 dye. As demonstrated (Fig. 4a), the particle size distribution contained two bands, of which the band of primary particles was very intense and occupied the range of 76–111 nm (maximum intensity of 100 corresponded to particles of 89 nm in diameter). The primary agglomerate band was observed in the range of 347–507 nm (maximum intensity of 97 corresponded to particles of 404 nm in diameter). The respective SEM micrograph (Fig. 4b) confirmed the low tendency to agglomerate and reasonably uniform character of the pigment.

A good pigment was obtained by modification of titanium white with silane U-13 in methanol followed by deposition of the acidic dye, C.I. Acid Orange 7 (Fig. 5). A highly intense band of primary particles was noted in the range of 70–115 nm (maximum intensity of 100 corresponded to particles of 85 nm in diameter). Primary agglomerates were present in the range of 516–851 nm (maximum intensity of 63 corresponded to particles of 630 nm in diameter).

Thus, the modification process, including the type of the solvent applied to prepare modifier solution, was found to affect quality of the final product (properties of the pigment).

Porosities of the examined pigment hybrid systems and their specific surface areas are listed in Table 5 and in Fig. 6.

Unmodified $TiO_2$ exhibits a much greater specific surface area (up to 40 $m^2\ g^{-1}$). Direct adsorption of organic dyes on unmodified titanium white favours evident decrease in pigment specific surface area and results in a decreased amount of adsorbed nitrogen (isotherms of adsorption–desorption), as illustrated in Fig. 6a.

The developing surface alterations correlate with efficiency of dye adsorption and with their elution from $TiO_2$ surface, which is particularly evident in pigments obtained in presents of C.I. Reactive Blue 19 (specific surface area decreases to 12 $m^2\ g^{-1}$).

Modification of titanium white surface with aminosilane U-13 exerts only a very low effect on

Table 5
Surface and adsorptive characteristics of obtained pigment's hybrids

| Sample | Specific surface area BET ($m^2\ g^{-1}$) | Total volume of pores ($cm^3\ g^{-1}$) | Average size of pores (Å) |
|---|---|---|---|
| $TiO_2$ | 39.9 | 0.0981 | 98.4 |
| $TiO_2$ + U-13 | 36.9 | 0.0877 | 95.2 |
| $TiO_2$ + C.I. Reactive Blue 19 | 12.0 | 0.0248 | 83.0 |
| $TiO_2$ + U-13 + Reactive Blue 19 | 21.3 | 0.0439 | 82.6 |
| $TiO_2$ + C.I. Acid Orange 7 | 21.5 | 0.0435 | 80.9 |
| $TiO_2$ + U-13 + C.I. Acid Orange 7 | 26.4 | 0.0557 | 84.3 |

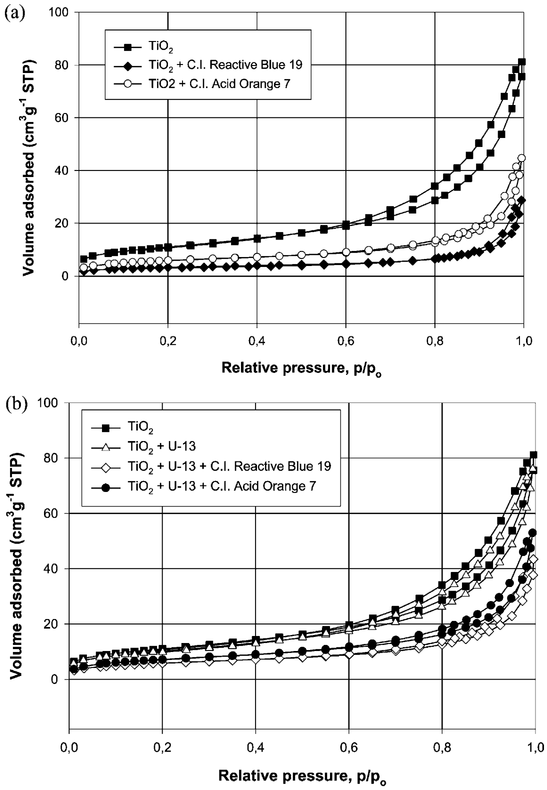


Fig. 6. Nitrogen adsorption–desorption isotherms of unmodified $TiO_2$ and unmodified $TiO_2$ with adsorbed dyes (a) and $TiO_2$ modified with U-13 silane and with adsorbed dyes (b).

its specific surface area and on the course of nitrogen adsorption–desorption isotherms (Fig. 6b). On the other hand, specific surface area of pigments on silane U-13-modified titanium white carrier and following adsorption of both studied organic dyes becomes clearly restricted. The course of adsorption–desorption isotherms is very similar. The so evident decrease in pigment specific surface area is linked to the highly efficient adsorption of the dyes and to small amount of eluted dye. The effect is particularly pronounced following adsorption of C.I. Reactive Blue 19 dye, the adsorption showing a chemical character.

## 4. Conclusions

1. Modification of titanium white surface with silane proadhesive compounds resulted in a slight increase in bulk density of titanium white. This reflected introduction to the surface of titanium white of appropriate amounts of the applied modifier. In addition, specific surface area slightly decreased and, practically, the adsorption–desorption isotherm manifested the course similar to that for titanium white.
2. Application of silane U-13 to modify titanium white surface proved to be more advantageous than use of silane U-15D since the formed decreased the capacity to absorb water and, thus, augmented hydrophobicity of the surface. Modification of titanium white with silanes U-13 and U-15D augmented efficiency of adsorption of C.I. Acid Orange 7 dye on its surface. The adsorption–desorption isotherms documented a clear decrease in specific surface areas of the obtained pigments.
3. A higher efficiency of adsorption of C.I. Reactive Blue 19 dye on titanium white was obtained following modification with the silane U-13. When titanium white was modified with the silane U-15D, efficiency of C.I. Reactive Blue 19 dye adsorption slightly decreased.
4. Adsorption studies provided evidence for chemical nature of titanium white surface modification. For both applied organic dyes mechanisms were suggested for formation of hybrid structures consisting of titanium white coated with layers of $SiO_2$ and $Al_2O_3$—aminosilane—organic dye.

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## References

[1] Binkowski S, Jesionowski T, Krysztafkiewicz A. Dyes Pigments 2000;47:247.
[2] Kohler K. Paint Ink Intern 1997;6:23.

[3] Fryer JR. Surf Coat Intern 1997;9:421.

[4] Krysztafkiewicz A, Rager B, Maik M, Wieczorek W. Polish J Appl Chem 1995;39:73.

[5] Krysztafkiewicz A, Michalska I, Jesionowski T, Bogacki M. Fizykochem Problemy Mineralurgii 1999;33:83.

[6] Endriβ BH, Inorganic Coloured Pigments Today, Curt R. Vincentz Verlag, Hannover, 1998.

[7] Carter S, Bristow D. Paint Ink Intern 1998;7:15.

[8] Pigment Update. Coat World 1998;3:36.

[9] Bowtell M. Polym Paint Colour J 1997;187:61.

[10] Gesenhues U. Farbe Lack 1999;3:151.

[11] Reck E, Wilford J. Eur Coat J 1998;1-2:28.

[12] Köhler K. Paint Ink Intern 1997;6:9.

[13] Morris GE, Skinner WA, Self PG, Smart RC. Colloids Surf A 1999;155:27.

[14] Reck E, Richards M. Surf Coat Intern 1997;12:568.

[15] Zarko VI. Colloid J 1999;61:620.

[16] Chilcott P. Polym Paint Colour J 1995;185:81.

[17] Wu G, Koliadima A, Her Y-S, Matijević E. J Colloid Interf Sci 1997;195:222.

[18] Winnik FM, Keoshkerian B, Fuller JR, Hofstra PG. Dyes Pigments 1990;14:101.

[19] US. Patent 4 566908, 1986.

[20] Krysztafkiewicz A, Binkowski S, Kaczmarek A, Jesionowski T. Pigment Resin Technol 2003;32:149.

[21] Jesionowski T. Dyes and Pigments 2002;55:133.