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Effect of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane surface modification and C.I. Acid Red 18 dye adsorption on the physicochemical properties of silica precipitated in an emulsion route, used as a pigment and a filler in acrylic paints

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Abstract

Studies were performed on the synthesis of spherical silica particles in an emulsion route, and its surface modification using *N*-2-(aminoethyl)-3-aminopopyltrimethoxysilane. Onto the aminosilane-treated silica surface, C.I. Acid Red 18 dye was adsorbed. The ensuing silica and its derivatives were subjected to comprehensive physicochemical and dispersion analysis. Both the size and shape of the particles were estimated and the surface specific area (BET) and porosity were characterised using adsorption/desorption curves. Moreover, chemical and surface compositions were determined using elemental analysis and XPS. A mechanism was suggested for the interaction betweeen the aminosilane-modified silica and an organic dye. The obtained pigment was tested in an acrylic paint system; the precipitated monodisperse silica was found to exhibit optimum properties as a carrier of organic dye, particularly after modification of the former with aminosilane, thus acting as a valuable filler and pigment in modern paint systems.

Keywords: Precipitated silica; Aminosilane surface modification; Adsorption of organic dye; Particle size; Surface morphology; Acrylic paints

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1. Introduction

Studies on the change the physicochemical and dispersion properties of colloidal silicas, induced by adsorptive interactions of various organic compounds, deal with very important scientific and technological problems.

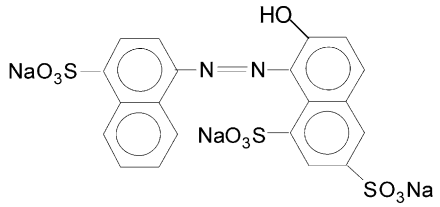
So called pigment cores have critical influence on the chemical and morphological properties of such inorganic-organic hybrids [1,2]. In most cases, the core is a synthetic silica derivative (colloidal precipitated silica, fumed silica, or Stöber's silica) [3–6] or a natural form of silicate (kaolinite) [7]. Numerous investigators have shown that mechanism of the reactions that take place on the surface of inorganic substances are extremely difficult to clarify and describe [8,9]. For example, the reaction taking place on the surface of silica, modified with 3-aminopropyltriethoxysilane, with the fluorescein results in the formation of covalent bonds between the reagents [10]; the interactions may involve formation of hydrogen bonds, van der Waals or electrostatic interactions [11].

The present study concerns the synthesis of a chemically and morphologically defined silica carrier via an emulsion route. The hydrophobic–hydrophilic carrier obtained was subjected to surface modification with aminosilane. So as to amplify its potential for interaction with a selected dye. Attempts were also made to study the chemical and dispersion characteristics of the silica carriers and pigments obtained. Moreover, the pigment was tested in acrylic interior and exterior paints.

2. Experimental

2.1. Materials

Newly synthetised silica was used, precipitated in an emulsion medium from sodium metasilicate and hydrochloric acid solution. For silica surface modification, *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (UniSil) was used. Colouration of silica was conducted using C.I. Acid Red 18 (Boruta-Kolor) (I).



(I)

2.2. Procedures and methods

The silica synthesis was preceded by the preparation of two emulsions. Emulsion (*A*) comprised an aqueous solution of sodium metasilicate and cyclohexane while emulsion (*B*) comprised of hydrochloric acid and cyclohexane. In both emulsions, a non-ionic surfactant [general formula $RO(CH_2CH_2O)_nH$, $R = C_{1622}$, $n \cong 7$)] obtained form ROKITA S.A. was used as emulsifier. The emulsions were prepared employing a homogeniser operating at 19,000 rpm.

Silica precipitation was conducted in a reactor of 5 dm^3 capacity, charged with emulsion *B*. Emulsion *A* was dosed at a constant rate, and the reaction mixture stirred using an *ULTRA TURRAX T50* basic homogeniser (IKA Labortechnik) at 10,000 rpm. Reaction was conducted at room temperature and the ensuing silica yielded the third emulsion which was destabilised at 80 °C and the hot mixture distilled to remove the organic phase. The remaining silica was filtered and the filter cake placed in a stationary dryer at 105 °C for 48 h.

Surface modification of the silica precipitated in the emulsion system was performed using *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (3 parts by mass of SiO_2), pre-hydrolysed in methanol/water, 4:1, v/v prepared directly before modification to avoid ageing effects. The modification was performed in a specially designed reactor [14] over 1h and the solvent was distilled off.

C.I. Acid Red 18 dye was adsorbed on to the silica surface modified with 3 parts by mass of aminosilane or on the unmodified silica. An aqueous solution of the dye (2 mg cm^{-3}) was introduced to the silica-containing reactor (at acidic pH) and formation of the inorganic–organic hybrids was performed over 30 min under mixing

at 10,000 rpm. The ensuing product was filtered and absorbance was measured in S750 spectrophotometer (*SECOMAM*).

Leakage of the dye from the pigment surface was also determined by suspending the pigment for 1 h at 100 °C.

The morphology and surface structure of both the unmodified and the modified silica carrier and the pigment were examined using a Philips 515 scanning electron microscope. The size of the silica particles was measured in a ZetaPlus apparatus (Brookhaven) using dynamic light scattering (DLS). Particle and size distribution curves permitted the polydispersity to be measured. The extent of modification and the character of the reaction between the silane coupling agents, dye and the silica surface were studied using an FT-IR EQUINOX (Bruker) equipment, with KBr tablets. The specific surface areas of the silica powders were determined by N_2 adsorption (BET method) using a Micrometrics ASAP 2010 instrument. The volume and size of the pores of the precipitated materials were examined; samples were outgassed at 120 °C for 2 h prior to measurement.

The raw silica material and functionalised silica samples were characterised by quantitative elemental analysis (C, H, N and S analysis) using an EA 1108 instrument (Carlo-Erba).

The chemical composition of the obtained silicas was determined using X-ray photoelectron spectroscopy (XPS) on a SPECS ESCA system equipped with a Phoibos 100 energy analyser. The spectra were recorded using a non-monochromated MgK_α X-ray source. Survey scans were recorded using pass energy of 30 eV and X-ray energy of 100 W; the high resolution spectra were recorded using 5 eV pass energy and 200 W. Charging of the sample surface was neutralised with a flood gun after calibration at 284.6 eV for C 1s peak.

In order to investigate the application potential of the red pigment obtained on the silica core it was used as a TiO_2 substitute in three dispersive acrylic paints, the compositions of which are listed in Table 1. The studies were performed as specified by Polish norms [12,13].

3. Results and discussion

The hydrophobic–hydrophilic silica powder (Sample A) precipitated using an emulsion route

Table 1
Systems of acrylic dispersion paints for exterior and interior use selected for studies on application of obtained silica pigment

	Amount (mass%)
1. *TOP AKRYL LAKMA W*	
Acrylic dispersion single layer paint, white, water soluble, for interior use	
Acrylic–styrene dispersion (acrylic–styrene polymer, 50 mass% in water)	20–25
Carbonate fillers	30–35
Titanium white	20–22
Dispersing agents, wetting agents, densifiers	18–30
2. *AKRYL LAKMA*	
Acrylic dispersion paint, white, water soluble, for exterior use	
Acrylic–styrene dispersion (acrylic–styrene polymer, 50 mass% in water)	20–25
Carbonate fillers	30–35
Titanium white	15–17
Dispersing agents, wetting agents, densifiers	23–35
3. *AKRYBET*	
Acrylic dispersion paint, white, organic solvent soluble, for exterior use	
Acryl resin in a solvent (whitespirit)	20–25
Carbonate fillers	30–35
Titanium white	15–17
Dispersing agents, wetting agents, densifiers	23–35

manifested high bulk density (283 g dm^{-3}), and a capacity to absorb water of 250 cm^3 100 g^{-1}. The capacities to absorb paraffin oil and dibutyl phthalate were relatively low (300 cm^3 100 g^{-1} and 200 cm^3 100 g^{-1}, respectively). The silica treated by *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (Sample B) exhibited a slightly lower bulk density (261 g dm^{-3}) and a slightly lower capacity to absorb water (200 cm^3 100 g^{-1}). In contrast, the capacities to absorb paraffin oil and dibutyl phthalate showed insignificant increases (to 350 cm^3 100 g^{-1} and 250 cm^3 100 g^{-1}, respectively). Adsorption of the C.I. Acid Red 18 on the surface of the modified silica (Sample C) caused a significant change in bulk density. The principal physicochemical parameters for the pigment were as follows: bulk density—234 g dm^{-3}; water-absorbing capacity—200 cm^3 100 g^{-1}; capacity to absorb paraffin oil—350 cm^3 100 g^{-1}, and capacity to absorb dibutyl phthalate—200 cm^3 100 g^{-1}.

In a subsequent stage of our study, the effects of a modifier and the dye were examined in terms of the particle size and homogeneity of dispersion; particle shape and morphology were also studied. Results are shown in Figs. 1–3.

The particle size distribution and electron-micrographs of the unmodified silica are presented in Fig. 1a and b, respectively. The mean particle diameter was 792 nm and polydispersity was 0.059. The latter value proved that the silica particles were highly uniform. In the particle size distribution (Fig. 1a) two bands could be noted. The more intense band reflected the presence of silica particles of lower diameter and fitted the range of 392–685 nm (maximum intensity of 100 corresponded to a particle diameter of 490 nm). The band in the range of 3659–5906 nm showed the presence of particles of much higher diameter and of aggregates. The scanning electron-micrograph (Fig. 1b) confirmed the presence of almost ideally spherical particles of low diameter. Some of the particles formed larger accumulations (so-called agglomerates).

The particle size distribution and SEM micrograph of a silica modified with 3 parts by mass of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane are shown in Fig. 2. The mean particle diameter of the silica was 507 nm while its polydispersity value was as low as 0.005. This indicated a most advantageous effect of the aminosilane on silica dispersion. In the particle size distribution (Fig. 2a) two bands were seen, related to the presence of particles of low and of much higher diameter, respectively. The more intense band was linked to the presence of particles of low diameter, in the range of 316–472 nm (maximum intensity of 100 corresponded to particles of 371 nm in diameter). Silica modified with 3 parts by mass of aminosilane manifested the presence of particles of low diameter compared to the unmodified silica. The band in the range of 2105–2571 nm was indicative of the presence of larger particles and of agglomerates; this was lower intensity (maximum intensity of 7 corresponded to the particle diameter of 2250 nm). The spherical shape of the particles is evidenced by Fig. 2b which shows that the modified silica was highly uniform. The silica particles were present in the form of much smaller, spherical grains, the system was more uniform and showed a lower tendency towards agglomeration.

Adsorption of C.I. Acid Red 18 on the silane-functionalised silica surface markedly reduced particle diameter to 358 nm. In this case, polydispersity was much reduced to 0.005. The particle size distribution (Fig. 3a) showed two bands. The first band of highest intensity represented particles of much lower particle diameter (262–331 nm) than those found for the unmodified silica (maximum intensity of 100 corresponded to particles of 301 nm in diameter). In contrast, the other band represented particles of diameter considerably lower than those of the unmodified silica and the aminosilane-treated silica. This particular band occupied a range of 669–808 nm (maximum intensity of 24 corresponded to particles of 735 nm in diameter). The extensive homogeneity of the particles in the formed pigment are clearly evident in the respective microphotographs (Fig. 3b). Such a pigment, of a narrow scatter of diameters and, thus, a high homogeneity, may represent a very valuable application material, particularly for colouring plastics. Moreover, pigments of the type exhibit strong thixotropic properties which markedly broadens their application potential (mainly as paint and varnish fillers).

The FT-IR spectrum shown in Fig. 4 defines the character of the chemical modification and of dye adsorption on the aminosilane-treated silica surface. The results show that their surfaces did not carry typical isolated silanol groups (3748 cm^{-1}). This probably reflects the methods of silica preparation (in an organic solvent). On the other hand, the band which is characteristic of C–H stretching vibrations (2965–2850 cm^{-1}) was present.

The specific surface area and pore volume for all three types of sample: the unmodified silica, aminosilane-modified silica and the pigment on the silica carrier) are listed in Table 2. Nitrogen adsorption/desorption isotherms for the studied powder substances are compared in Fig. 5.

It is evident that the unmodified silica exhibited the highest specific surface area (182 $m^2\ g^{-1}$) and, accordingly, the highest total volume of pores

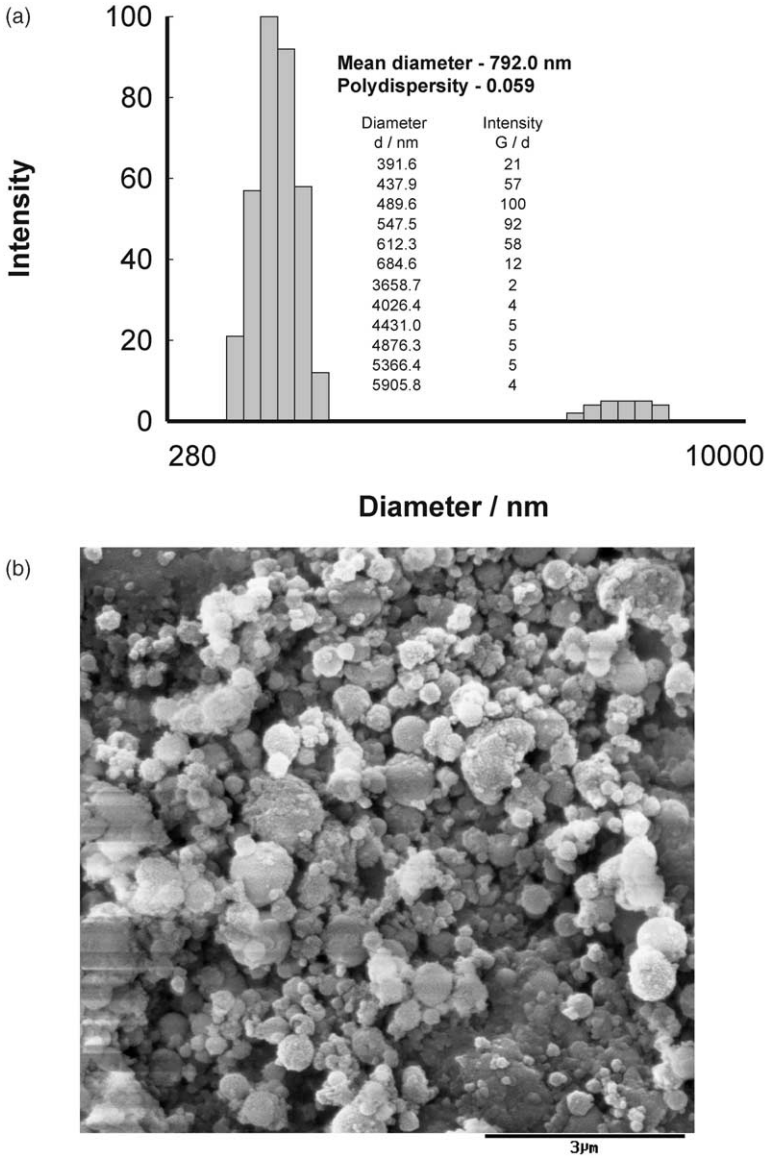


Fig. 1. (a) Multimodal particle size distribution and (b) scanning electron micrograph (SEM) of raw silica material.

(0.45 $cm^3\ g^{-1}$); the mean pore diameter was 99.24 Å. The isotherm (Fig. 5a) clearly demonstrated an increase in the relative pressure range of 0.3–1.0; at $p/p_o = 1$, the volume of nitrogen adsorbed exceeded 300 $cm^3\ g^{-1}$. Such silica exhibited high adsorptive capacity. Modification of the silica with aminosilane markedly lowered its adsorptive capacity as proven by the nitrogen adsorption/desorption isotherm which indicated an increase in the volume of the nitrogen adsorbed on the surface of the modified silica (the rising adsorption curve) could not be noted before the relative pressure range of 0.5–1.0 was reached (Fig. 5b). The volume of N_2 adsorbed at $p/p_o = 1$ in this case did not exceed 250 $cm^3\ g^{-1}$ (Table 2). The mean diameter of the pores in the silica modified with *N*-2-

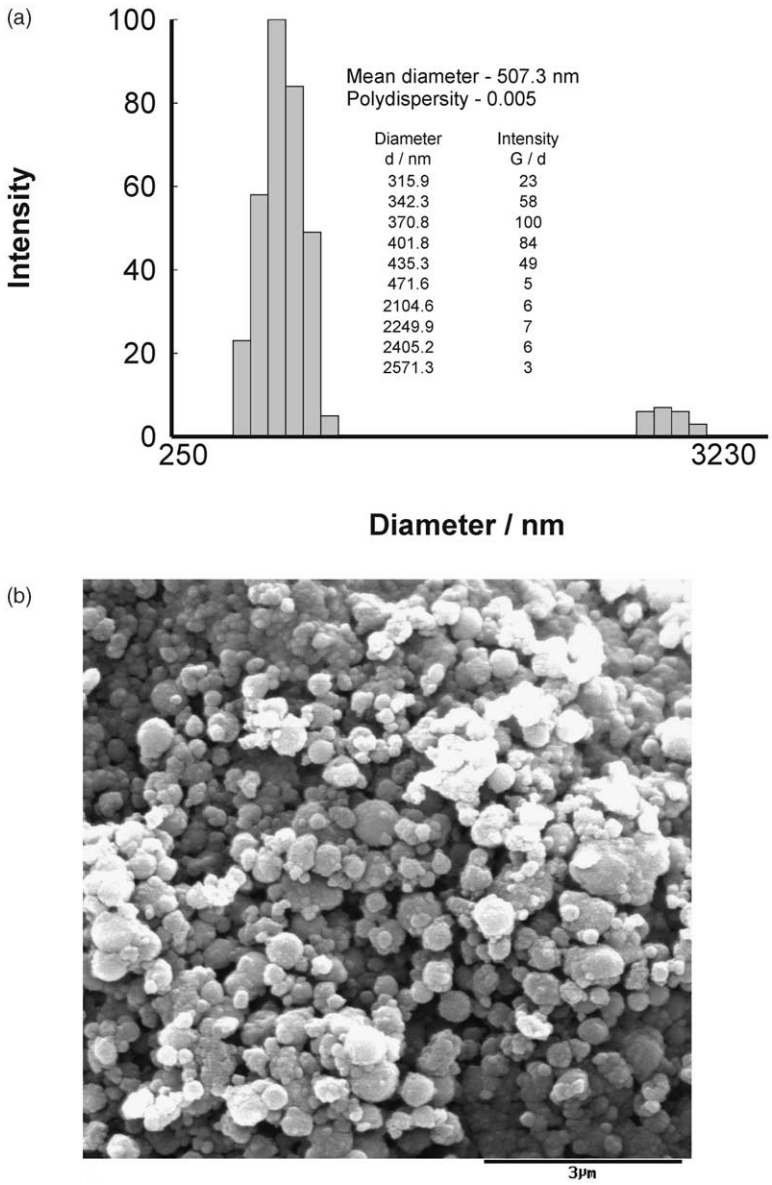


Fig. 2. (a) Multimodal particle size distribution and (b) scanning electron micrograph (SEM) of aminosilane-modified silica.

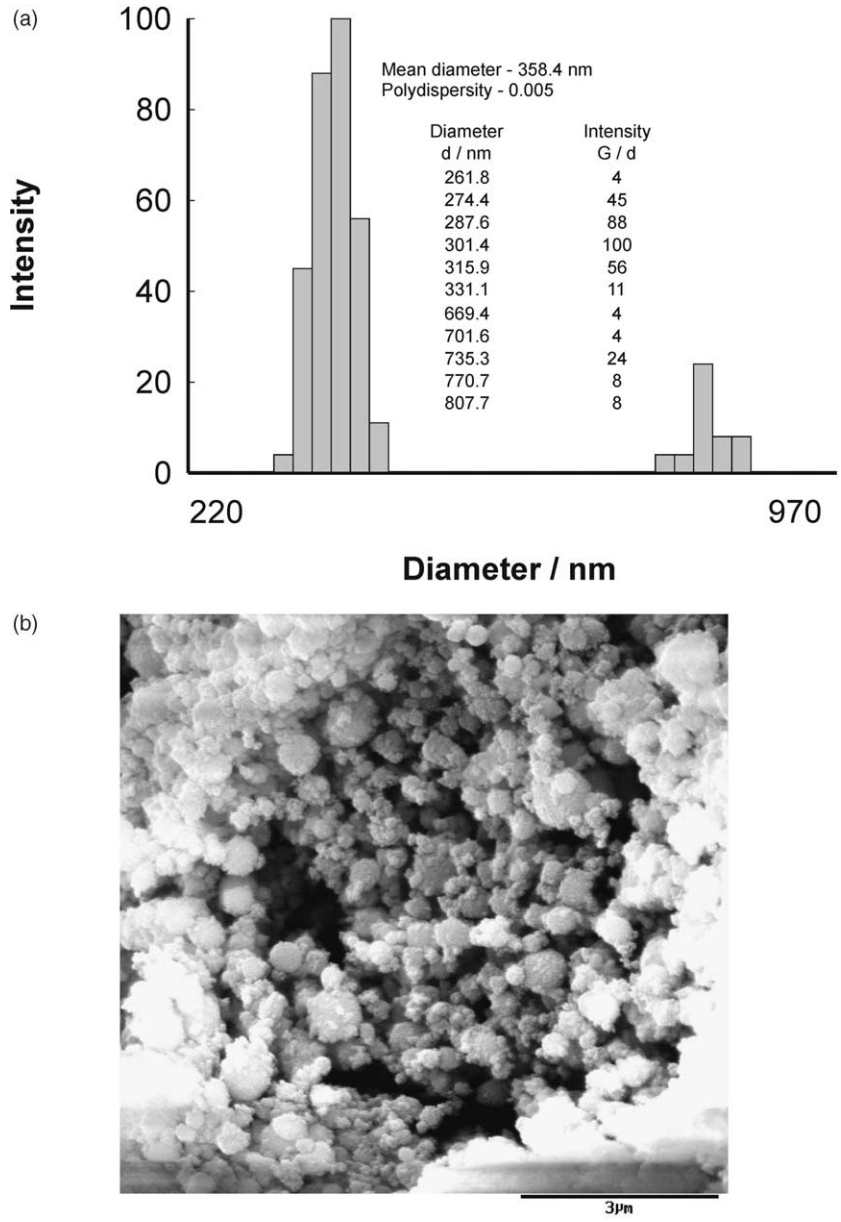


Fig. 3. (a) Multimodal particle size distribution and (b) scanning electron micrograph (SEM) of a dye adsorbed on the aminosilane-functionalised silica surface.

(aminoethyl)-3-aminopropyltrimethoxysilane was 114.16 Å. Coating of the modified silica with the red dye did not significantly affect the adsorption/desorption isotherm; at $p/p_o = 1$, the volume of nitrogen adsorbed was around 250 $cm^3\ g^{-1}$. Values of specific surface area (113 $m^2\ g^{-1}$) and of total pore volume (0.32 $cm^3\ g^{-1}$) resembled those obtained for the silane-modified silica (Fig. 5c).

The analysed silicas and pigments exhibited a structure that was typical mesoporous adsorbents of average activity.

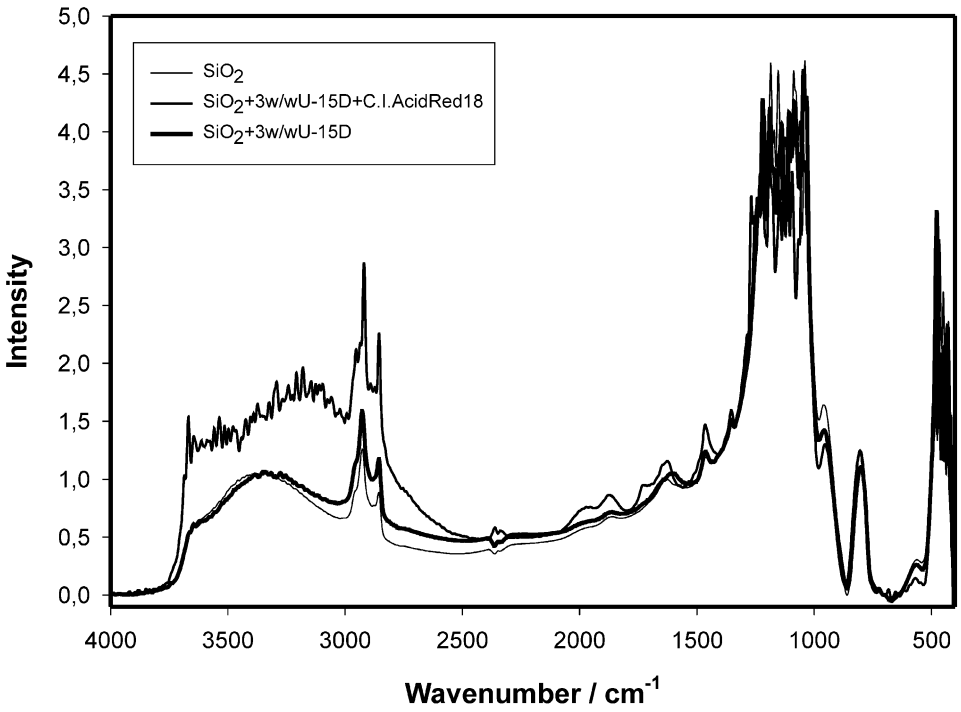


Fig. 4. The FT-IR spectrum for the examined powders.

As shown by elemental analysis (Table 3), modification of silica with the aminosilane was followed by an increase in the nitrogen content at the silica surface (up to 0.35%). In contrast, adsorption of C.I. Acid Red 18 (which contains nitrogen and sulphur) on the silica surface resulted in a further increase in nitrogen content (to 0.49%) and the appearance of sulphur (0.28%). It should be noted that the surface of the unmodified silica contained significant amounts of carbon (10.21%), originating silica precipitation method used. Modification with aminosilane and adsorption of the dye were each followed by a further increase in carbon content.

X-ray Photoelectron Spectroscopy (XPS) documented changes in surface composition, dependent upon the type of the silica sample. A marked increase in nitrogen content was observed following

Table 2
Specific surface area, volume and average size of pores of obtained silicas

Sample no.	Specific surface area BET ($m^2\ g^{-1}$)	Total pores volume ($cm^3\ g^{-1}$)	Average size of pores[a] (Å)
A	182	0.45	99.24
B	119	0.34	114.16
C	113	0.32	113.81

[a] Calculated from BET equation (4V/A).

Table 3
Elemental analysis and surface composition of the examined silicas products

Sample no.	Elemental analysis			XPS analysis				
	Content (%)			Content (%)				
	C	N	S	Si	O	C	N	S
A	10.21	0.00	0.00	22.6	55.0	22.3	0.0	0.0
B	14.75	0.35	0.00	18.9	46.7	33.4	1.0	0.0
C	15.09	0.49	0.28	17.4	45.9	33.5	1.0	0.2

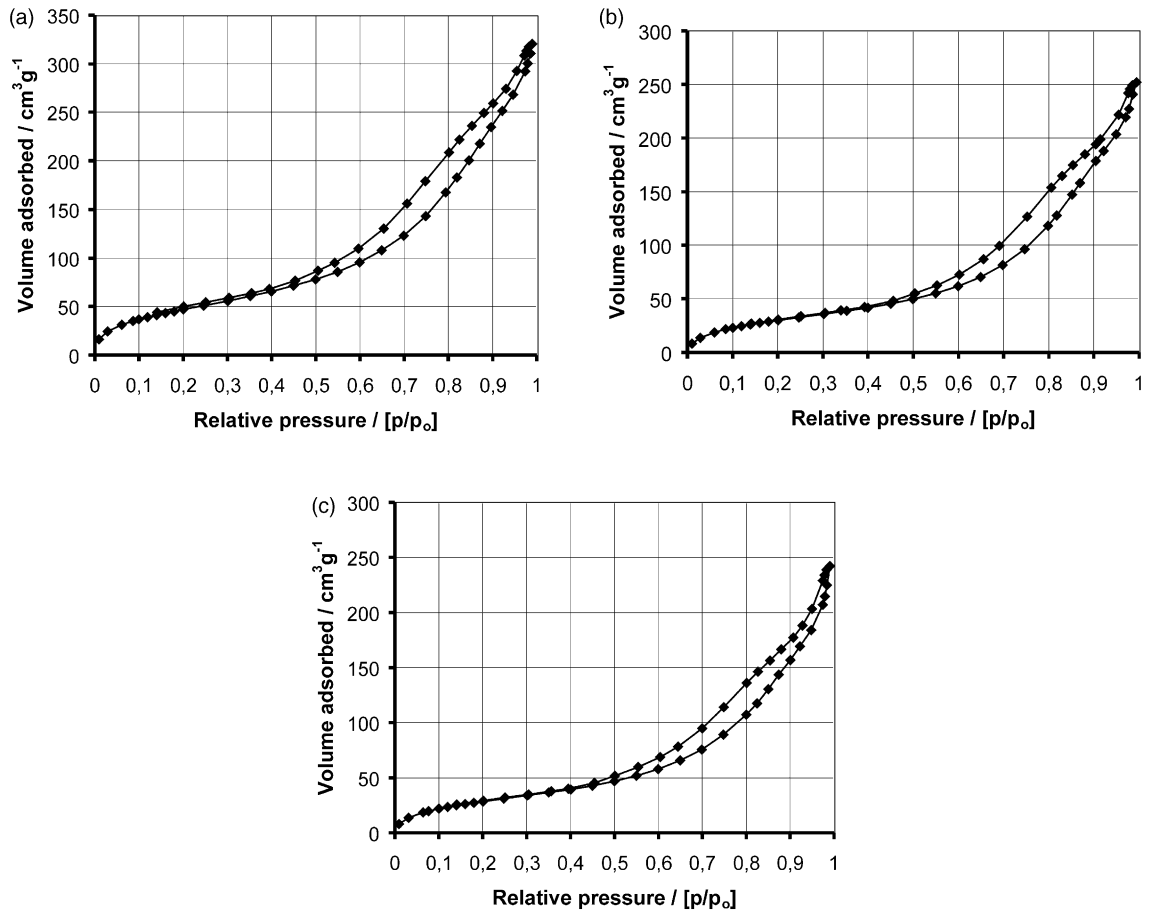


Fig. 5. Adsorption/desorption isotherms of (a) unmodified silica powder, (b) aminosilane-treated silica and (c) the dye adsorbed on the aminosilane-functionalised silica surface.

Table 4
Adsorption extent and amount of eluted dye of the investigated silicas

Sample no.	Dye concentration before adsorption (mg cm^{-3})	Dye concentration after adsorption (mg cm^{-3})	Disposal extent (%)	Dye concentration after elution (mg cm^{-3})	Amount of dye eluted from silica surface (%)
C	2.000	0.178	91.1	0.005	1.0

silane modification and sulphur appeared as a result of dye adsorption on the core of the modified silica.

The extent of adsorption of C.I. Acid Red 18 on the aminosilane-functionalised silica surface is given in Table 4. A high adsorption extent, 91.1%, was achieved and the ensuing pigment exhibited high stability: water was capable of eluting less than 1% dye from the silica surface.

Upon analysis of the above results, and considering the high adsorption and low leakage of dye, the following is proposed

Obtained for the application of the pigment are presented in Tables 5–7 and in Fig. 6.

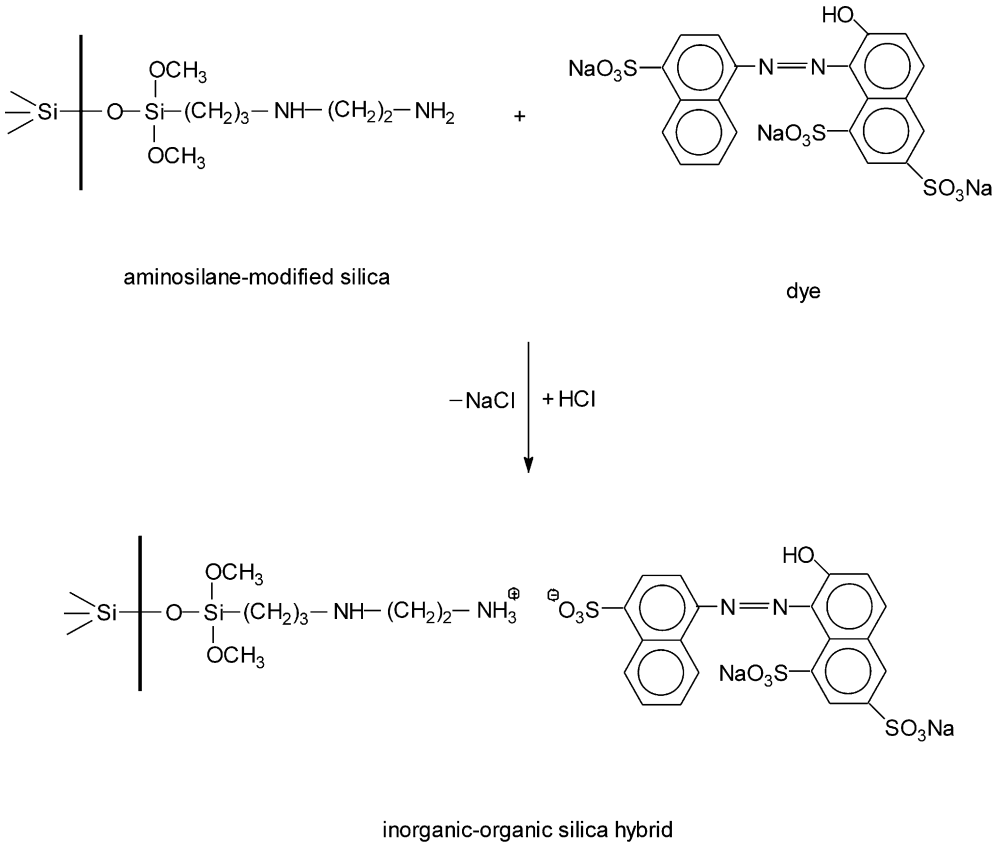


Table 5
Parameters of *TOP AKRYL LAKMA W* acrylic dispersion single layer, water soluble paint for interior use

Parameter	Norm requirement (PN-C-81914: 1998)	*TOP AKRYL LAKMA W*	*TOP AKRYL LAKMA W* containing silica pigment
			Sample C
Density (g cm^{-3})	1.45–1.55	1.48	1.49
Viscosity KW10 estimated by time of dripping	Drips after 10–30 s	Drips after 23 s	Drips after 10 s
Viscosity acc. to Brookfield (cP) (S03, 2RPM)	–	16,520	44500
Drying time		(20 °C, 58% air humidity)	(20 °C, 62% air humidity)
1°	–	23 min	14 min
5°	⩽5 h	28 min	21 min
Resistance to wet scrubbing	⩾750 advances	Base exposure after 800 advances	Base exposure after 500 advances
Quality coating of paint	⩽III	II	II

Table 6
Parameters of *AKRYL LAKMA* acrylic dispersion white, water soluble paint for exterior use

Parameter	Norm requirements (PN-91/B-10102)	AKRYL LAKMA	AKRYL LAKMA containing silica pigment
			Sample C
Density (g cm^{-3})	1.45–1.55	1.48	1.24
Viscosity KW10 estimated by time of dripping	Drips after 17–24 s	Drips after 17 s	Drips after 12 s
Viscosity acc. to Brookfield (cP) (S03, 2RPM)	–	18,480	3710
Drying time		(20 °C, 58% air humidity)	(19 °C, 55% air humidity)
1°	–	13 min	25 min
5°	⩽3 h	20 min	28 min
Resistance to wet scrubbing	⩾1500 advances	No base exposure after 10,000 advances	No base exposure after 10,000 advances
Quality coating of paint	⩽III	III	I

Table 7
Parameters of AKRYBET acrylic white, organic solvent soluble paint for exterior use

Parameter	Norm requirements (PN-91/B-10102)	*AKRYBET*	*AKRYBET* containing silica pigment
			Sample C
Density (g cm^{-3})	1.35–1.50	1.39	1.31
Viscosity KW4 estimated by time of dripping	Drips after 50–150 s	Drips after 136 s	Drips immediately
Drying time		(20 °C, 58% air humidity)	(19 °C, 55% air humidity)
1°	–	30 min	59 min
5°	⩽3 h	35 min	75 min
Resistance to wet scrubbing	⩾1500 advances	No base exposure after 10,000 advances	No base exposure after 10,000 advances
Quality coating of paint	⩽III	III	I

Tables 5–7 show that the physicochemical and resistance parameters of the paints were no worse than those of standard paints which contained titanium as exclusive pigment. The coating power of the former paints was slightly lower. Good coating power was shown by *TOP AKRYL LAKMA W* paint (Fig. 6a) while a lower coating power was obtained for *AKRYL LAKMA* paint, in which 11% of the TiO_2 was substituted by the pigment (Fig. 6b). The particular abrasion resistance of *AKRYL LAKMA AKRYBET* paint deserved attention.

4. Conclusions

Adsorption of C.I. Acid Red 18 on to an amino-silane-modified silica surface improved the homogeneity of the pigment and minimised the tendency to form agglomerates. Adsorption–desorption studies proved that both silane modification and adsorption of the dye on silica surfaces decreased the adsorptive capacity of the latter. Indirectly, this provides evidence that both modification and adsorption took place at the surface of SiO_2. Very high adsorption of C.I. Acid Red 18 was achieved on

Fig. 6. Coating power indices for the studied pigment in: (a) *TOP AKRYL LAKMA W* paint and (b) *AKRYL LAKMA* paint.

the surface of modified silica (over 90%). The resulting pigment exhibited high stability and leakage of the dye did not exceed 1%. An electrostatic mechanism is suggested for interaction of C.I. Acid Red 18 with the surface of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane-modified silica. The formation of inorganic–organic hybrids was assumed. The substitution of titanium in acrylic paints by optimum amounts of the dye adsorbed on the silica core imported no negative effects on the pysicochemical and resistance parameters of the paint and imported to the paint a red colour.

Acknowledgements

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