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Dyes and Pigments 65 (2005) 267–279
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Adsorption of the selected organic dyes on the functionalized surface of precipitated silica via emulsion route

Teofil Jesionowski*, Sławomir Binkowski, Andrzej Krysztafkiewicz

Poznań University of Technology, Institute of Chemical Technology and Engineering, sq. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland

Received 5 July 2004; received in revised form 3 August 2004; accepted 12 August 2004
Available online 4 October 2004

Abstract

Physicochemical analysis was performed on silicas precipitated according to a novel method, in an emulsion system. Substrates for the process involved solutions of sodium metasilicate and sulphuric acid while the organic phase consisted of cyclohexane and non-ionic emulsifiers. The silicas were used to obtain hybrid structures of the formed inorganic pigments. For this purpose, the adsorption of organic dyes on the silica surface was preceded by modification of the surface with silane coupling agent containing amine groups. Specific surface area (BET) and porous structure of the raw silicas were estimated. The silicas and pigments were subjected to studies on surface morphology, zeta potential, particle size and distribution of particle diameters were also established. Effects of modification with the aminosilane were appraised using FTIR and ^{29}Si CP MAS NMR techniques.

Stable pigments were obtained on silica core, the surface of which was modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane. Particles of the obtained pigment manifested a spherical shape and particle size distribution proved that no agglomerate structures were present. High stability of the obtained pigments proved that the organic dye was chemically bound to the modified silica surface. Mechanisms of inorganic–organic hybrid formation were also suggested.

Keywords: Precipitated silica; Emulsion; Aminosilane; Organic dyes adsorption; Inorganic–organic hybrid

1. Introduction

In this paper, we describe the general synthetic mechanism to incorporate selected dyes by covalent interactions or hydrogen bonds into monodisperse, colloidal silica, obtained via precipitation route in emulsion system. In order to effectively introduce organic dyes, silicas are prepared of specific defined hydrophilic–hydrophobic properties and their adsorptive properties are augmented by the surface modification with aminosilane.

Numerous reports have appeared, related to evaluation of interaction of organic dyes, procedures of their introduction and mechanisms of adsorption on inorganic synthetic oxides, minerals, carbon or its derivatives.

For example, Chun et al. prepared the inorganic hybrid of TiO_2/SiO_2 with augmented adsorptive and photocatalytic capacity for azo dyes [1]. In turn, numerous groups of aromatic and polyaromatic dyes were "introduced" to the surface of kaolin and aluminium oxide [2]. In the study, general adsorption selectivity was examined as a function of pH for individual adsorbates. Due to the stratified structure of silicates, the high adsorptive capacity reflects charged outer surface as well as the internal (inter-packette) charge. Studies continue on organic dye incorporation to montmorillonites [3–6]. Since the summative montmorillonite charge is negative, it seems more advantageous to modify the mineral with positively charged dyes, e.g., applying Methylene Blue.

* 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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doi:10.1016/j.dyepig.2004.08.002

Mechanism of adsorption on activated carbons and carbon derivatives has been described [7,8]. Adsorptive capacity of activated carbon has been examined, establishing adsorption isotherms and changes in zeta potential resulting from interaction between the dye and the carbon adsorbent.

Pigments formed by adsorption of organic dyes on a silica core are of a particular cognitive and technological importance. Pigments of the type can be obtained within a broad range of colours, depending upon the original organic dye used [9,10]. The pigments show many advantages as compared to the conventional pigments [11–13]. Hydrophilic silicas are colourless and carry surface silanol groups ($\equiv$ Si–OH), which react with multiple functional groups forming covalent bonds. The process of colouring the silicas involves first a reaction of silica surface silanol groups with a silane coupling agent (most frequently containing amine groups) to condense molecules of the silane with the surface of silicon dioxide. Subsequently, the organic dye reacts with the bound silane, forming silica particles carrying the dye trapped by a covalent bond [14–19]. Pigments formed by synthesis of silica are also of importance. Pigments of this type are obtained using as a carrier the silica obtained by hydrolysis and condensation of alkoxysilanes (mainly TEOS) in ethanol/water/ammonia mixture and in the presence of appropriate dyes [20–22].

Dispersion and morphological properties of the obtained pigments on the silicon dioxide core strictly depend on the matrix, i.e. on the size and shape of the silica particles, their homogeneity and surface development [9,18,19,23].

In the present study, a novel method has been presented of precipitating silicas of specified properties (spherical shape of particles, low polydispersity, high chemical activity), which may find application as selective carriers of organic dyes. The process of precipitating such silicas is based on a solution of sodium metasilicate.

2. Experimental section

2.1. Materials

In the studies newly synthesized silica was used, precipitated in an emulsion medium from sodium metasilicate and sulphuric acid. Organic phase involved cyclohexane (POCh, Poland). As the emulsifiers, nonylphenylpolyoxyethyleneglycol ethers with mean oxyethylenation extent 5 (Rokafenol N-5) or 6 (Rokafenol N-6) were tested, both produced by Chemical Works "Rokita" S.A. (Poland). For the silica surface modification *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (UniSil) was applied. Colouration of silica was conducted using selected organic dyes produced by Boruta-Kolor (Table 1).

2.2. Preparation and modification of silicas

2.2.1. Emulsion preparation

Two emulsions were prepared. The 'alkaline' one (E_1) contained 100 cm^3 5 wt% Na_2SiO_3 solution and 110 cm^3 cyclohexane, supplemented with an emulsifier. Mass ratio of Rokafenol N-5 to Rokafenol N-6 was 1.0:1.5. The 'acidic' emulsion (E_2) consisted of 33 cm^3 5 wt% of H_2SO_4 and 35 cm^3 of cyclohexane, supplemented with an emulsifier of the same composition as in E_1 but in appropriately lower amount. The predissolved emulsifiers were diluted in cyclohexane. The aqueous phase (for E_1 5 wt% solution of Na_2SiO_3, for E_2 5 wt% solution of H_2SO_4) was dosed in few portions and the mixture was homogenized at 19 000 rpm for 5 min. The so prepared emulsions were used in precipitation reactions.

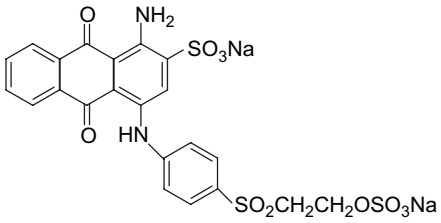
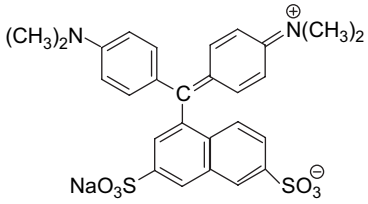
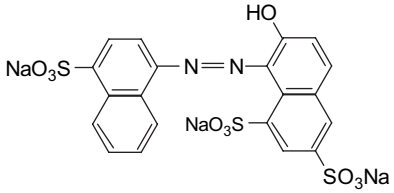
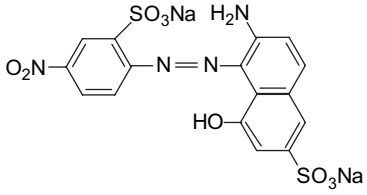
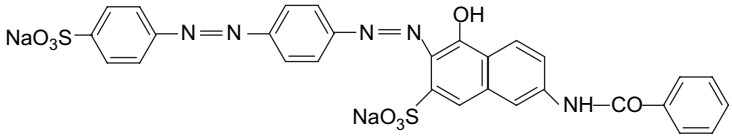
2.2.2. Process of formation of colloidal silica

2.2.2.1. Dispersing (precipitation) using a top stirrer – (E11-Silica). Precipitation was conducted in a 0.5 dm^3 capacity reaction accompanied with the propeller stirrer EUROSTAR digital type (Ika Labortechnik, Germany). Using the appliance, the system was subjected to intense mixing (2000 rpm). The E_2 emulsion was placed in the reaction vessel and subjected to intense mixing. Emulsion E_1 was dosed to emulsion E_2 at a constant rate using peristaltic pump. As a result of the reaction taking place in the reaction vessel, a silica-containing emulsion was obtained. The emulsion was heated to 80 °C in order to destabilize it. Subsequently, cyclohexane was separated from it by distillation. The subsequent stage involved filtration of the remaining mixture under a lowered pressure. In this way, the obtained sample was washed with hot water and, then, with acetone in order to wash out the remaining surfactants. Acetone was separated by distillation. Subsequently, the sample was subjected to drying for 48 h in a stationary dryer at 105 °C.

2.2.2.2. Precipitation in an ultrasonic bath – (E19-Silica). A reactor of 0.5 dm^3 capacity was placed in an ultrasonic bath of INTERSONIG - 102 (30 kHz), 100 W type, in which formation of the silica was conducted using ultrasound. The remaining functions were analogous to those applied in the above method.

2.2.2.3. Formation (precipitation) using a homogenizer – (E27-Silica). The precipitation was conducted in the reactive vessel of 0.5 dm^3 capacity. Mixing took place in a homogenizer of ULTRA TURRAX T25 basic type (Ika Labortechnik, Germany) at 19 000 rpm. The remaining

Table 1
Dyes applied during studies

Type of dye	Short	Formula
C.I. Reactive Blue 19	RB 19	
C.I. Acid Green 16	AG 16	
C.I. Acid Red 18	AR 18	
C.I. Acid Violet 1	AV 1	
C.I. Direct Red 81	DR 81	

functions were analogous to those used upon application of ultrasound and batch mixing using a top stirrer.

2.2.3. Functionalization of the silica surface

The surface modification of the silica precipitated in the emulsion system was performed using *N*-2-(amino-ethyl)-3-aminopropyltrimethoxysilane, named U-15 (3 weight parts by mass of SiO_2), pre-hydrolyzed in a solution (methanol/water, 4:1, v/v) prepared directly before the modification in order to avoid aging effects. The modification was performed in a specially designed reactor [24] in the course of 1 h and the solvent was distilled off.

Adsorption of the appropriate organic dyes was conducted on the silica surface modified with 3 weight parts of aminosilane or on the unmodified silica. Solution of the dyes (0.4 mg/cm^3 or 0.8 mg/cm^3) was introduced to the silica-containing reactor. Formation of inorganic–organic hybrid was performed in 4 h at an intense mixing. In case of acidic dyes, the HCl was introduced to the reaction mixture. The obtained product was subjected to filtration. In the remaining filtrate, absorbance was tested in the S750 spectrophotometer (SECOMAM) following dye adsorption both on the unmodified and on the modified silica.

2.3. Physicochemical and morphological characterization

The unmodified silicas and the obtained silica–dye hybrids were subjected to a broad physicochemical and morphological evaluation.

Specific surface areas of the selected silica powders were determined by N_2 adsorption (BET method) using ASAP 2010 instrument (Micrometrics Instrument Co.). Moreover, the volume and size of pores of precipitated materials were examined. Samples were outgassed at 120 °C for 2 h prior to measurements.

Zeta potentials were estimated by a direct measurement of electrophoretic mobility, employing the technique of electrophoretic light scattering (ELS) in the ZetaPlus apparatus (Brookhaven Instruments Co.).

The multimodal particle (aggregate and agglomerate) size distribution was evaluated also in the ZetaPlus apparatus, employing the technique of a dynamic light scattering (DLS). On the other hand, polydispersity was calculated as a function of particle size distribution.

The extent of modification and the type of reaction between a silane coupling agent and silica were evaluated in FTIR EQUINOX (Bruker) apparatus. For this purpose, silica suspensions of appropriate concentration were prepared in CCl_4. Before the analysis, silica samples were heated at 600 °C.

NMR analysis of unmodified and modified silicas was conducted in DSX spectrometer (Bruker). The sample of around 100 mg was placed in a rotator, made of ZrO_2, of 4 mm in diameter, which permitted spinning of the sample. Centrifugation at a magic angle was performed at spinning frequency of 8.4 kHz. ^{29}Si CP MAS NMR spectra were recorded at the pulse duration of 4.5 μs, contact time of 1.5 ms and pulse spacing of 6 s.

3. Results and discussion

3.1. Adsorptive characteristics

The obtained substances were subjected to a detailed evaluation of their adsorptive properties. Specific surface area and pore characteristics were established for two distinct temperatures of outgassing the materials (120 and 300 °C; Table 2). Temperature of the preliminary sample processing significantly affected its specific surface area. At higher outgassing temperatures desorption of emulsion (emulsifier) components used for precipitation was more pronounced. The desorption resulted in unblocking of active centres at the silica surface and in a more pronounced N_2 adsorption. Thus, silicas outgassed at higher temperatures demonstrated decisively higher specific surface areas. The highest BET surface area was manifested by the silica precipitated using a top stirrer or a homogenizer (at any temperature of sample outgassing). Similar relations could be noted following estimation of total pore volume in silicas precipitated from the emulsion. On the other hand, the highest pore volume was shown by silicas precipitated in an ultrasonic bath. The two relations: volumes of N_2 adsorbed on surface of examined silicas (outgassed at 120 °C or 300 °C) are related to relative pressure and volumes of pores in silica and related to pore radius.

Table 2
Adsorptive characteristics of obtained silica cores

Silica core	Specific surface area BET (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
120 °C			
E11-Silica	278	0.73	53
E19-Silica	122	0.49	81
E27-Silica	266	0.67	51
300 °C			
E11-Silica	364	0.80	44
E19-Silica	149	0.55	74
E27-Silica	325	0.73	45

The shape of adsorption–desorption curves was very similar for all three precipitation techniques. The isotherm shape pointed to mesoporous character of the examined silica adsorbents (Fig. 1).

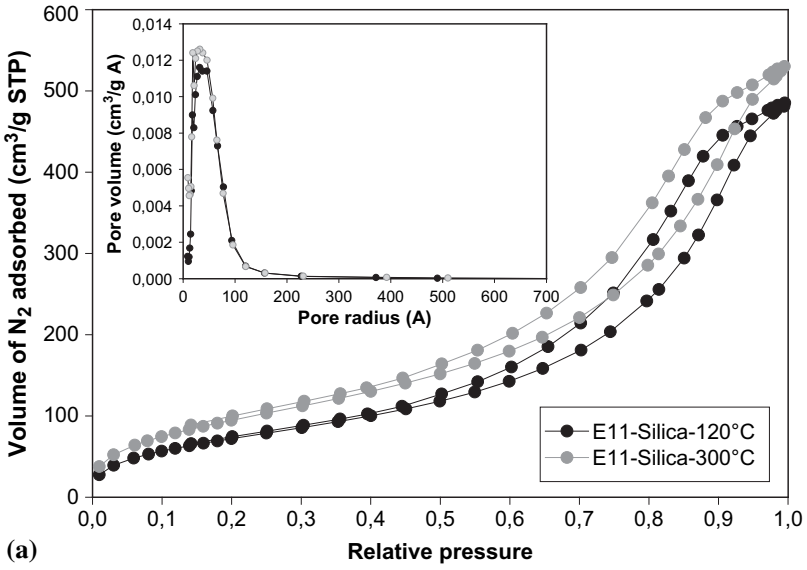
3.2. Morphological and particle size determinations

Mean particle diameters, values of polydispersity and zeta potentials for unmodified silicas, silicas modified with aminosilane and pigments obtained by adsorption of organic dyes on the surface of modified silica are presented in Table 3.

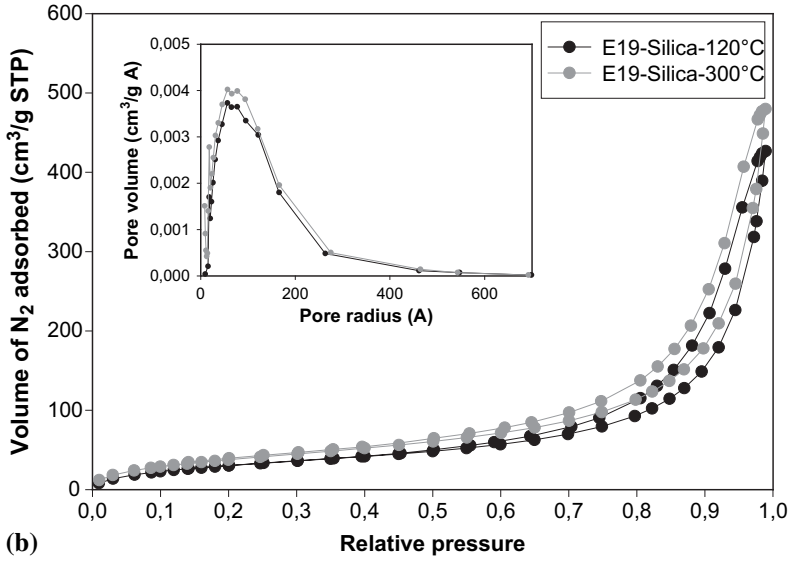
The lowest polydispersity or the most pronounced uniform character was demonstrated by silicas precipitated using a top stirrer (polydispersity values: 0.005) and it remained unchanged following modification and dye adsorption on the surface. The uniform character only insignificantly deteriorated in the modified silica and the pigment obtained on the core of silica precipitated using a homogenizer (polydispersity in the range of 0.005–0.031). Definitely, the highest polydispersity (the lowest homogeneity) was shown by silica and its derivatives prepared using ultrasounds. They also manifested the highest size of particles. Polydispersity of the powders ranged from 0.209 to 0.230 and the mean diameter of particles of the blue pigment exceeded 1800 nm. The lowest mean diameters of particles were shown by silicas and pigments obtained by precipitation in a homogenizer. This reflected maximum effectiveness of dispersing the reactive mixture in the course of SiO_2 particle formation. At pH 7.0, zeta potentials of all examined samples acquired negative value (Table 3). No evident change in the electrokinetic potential took place due to surface modification with aminosilane or upon formation of inorganic–organic hybrids. The highest stability of dispersion was seen in silicas precipitated using a top stirrer. The phenomenon reflected the very highly uniform character of particles, which significantly influenced the type of geminal electric layer.

Electron micrographs (SEM) and particle size distributions for unmodified silicas and pigments obtained of them are presented in Figs. 2–10.

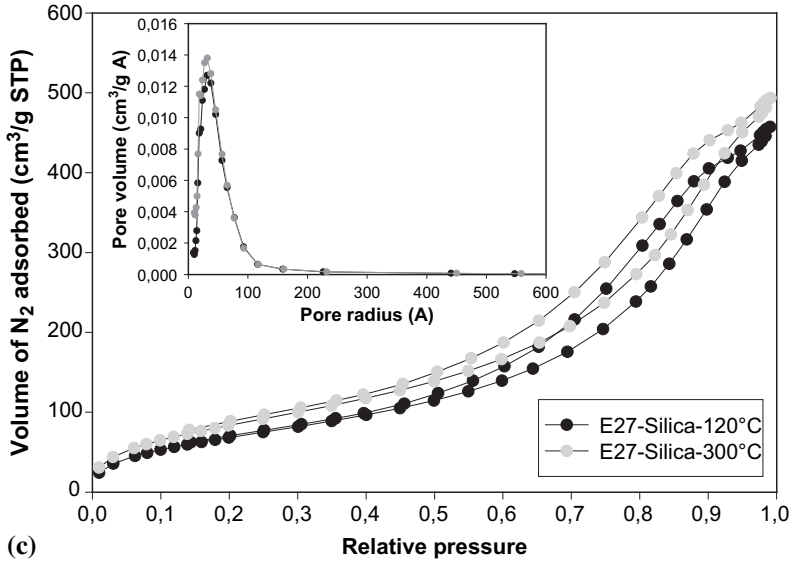
Particle size distribution of silica particles precipitated from the emulsion system (H_2SO_4–cyclohexane, Na_2SiO_3–cyclohexane, mixture of Rokafenol N-5 and



(a)



(b)



(c)

Fig. 1. Relation between volume of N_2 adsorbed on surface of SiO_2 (outgassed at 100 °C or 300 °C) and relative pressure, and relation between pore volume and pore diameter for: (a) silica precipitated using top stirrer (E11-Silica), (b) silica precipitated using ultrasounds (E27-Silica) and (c) silica precipitated using homogenizer (E19-Silica).

Table 3
Particle diameter, polydispersity and zeta potential of unmodified and functionalised silicas

Sample	Mean particle diameter (nm)	Polydispersity	Zeta potential (mV)
E11-Silica	1248.8	0.005	−28.88
E11-Silica + 3(m/w)U-15	1024.5	0.005	−18.27
E11-Silica + 3(m/w)U-15 + RB19	660.1	0.005	−23.82
E19-Silica	811.8	0.209	−13.30
E19-Silica + 3(m/w)U-15	1145.3	0.215	−18.53
E19-Silica + 3(m/w)U-15 + RB19	1812.2	0.230	−16.54
E27-Silica	951.5	0.005	−11.41
E27-Silica + 3(m/w)U-15	809.1	0.031	−14.18
E27-Silica + 3(m/w)U-15 + RB19	674.5	0.016	−16.62

Rokafenol N-6) using a top stirrer is presented in Fig. 2. The obtained silica contained spherical particles of only slightly variable size. Mean particle diameter of the silica was 1249 nm (Table 3). The particle size distribution demonstrated a narrow band (typical for most uniform products) in the range of 1231–1263 nm. Maximum intensity of 100 corresponded to the particle diameter of 1251.2 nm.

Morphology and particle size distribution for a silica obtained from emulsion using a top stirrer, following modification with 3 weight parts of aminosilane U-15 are illustrated in Fig. 3. The modification clearly induced more homogenous character of particles, which could also be noted in the respective particle size distribution (Fig. 3a) and SEM micrograph (Fig. 3b). The band of particle manifestation became narrowed and shifted toward lower diameters as compared to the unmodified silica. The particles were present within the range of 1011–1037 nm. Mean particle diameter of the modified silica was around 1025 nm. The particles remained spherical and formed a very uniform dispersion system.

The same silica precipitated and subjected to the surface modification with the silane, and then coloured using C.I. Reactive Blue 19 is presented in Fig. 4. Introduction of the organic dye to the surface of modified silica markedly improved uniform character of the particles. The presence of the spherical silica particles, creating a very disperse system of the formed pigment, was evident (Fig. 4b). Production of the very

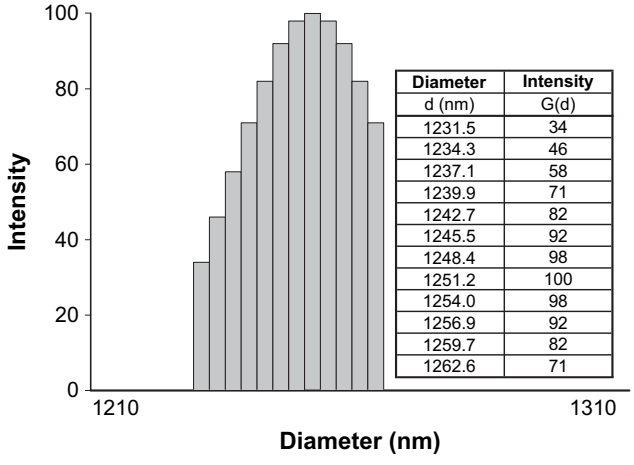


Fig. 2. Multimodal particle size distributions of silica precipitated (E11-Silica) using a top stirrer.

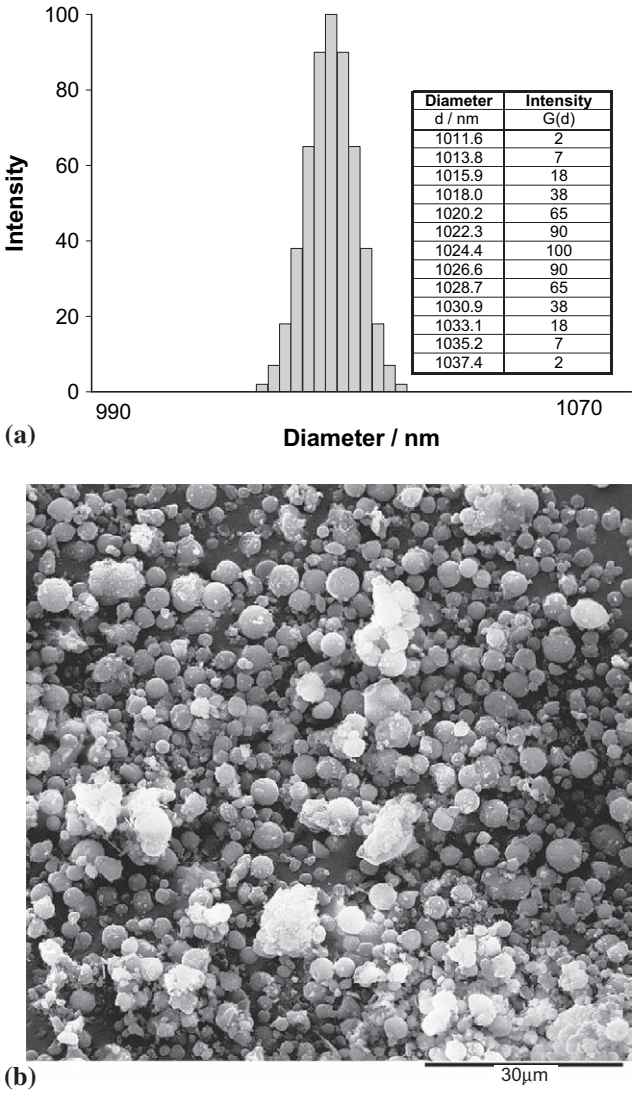
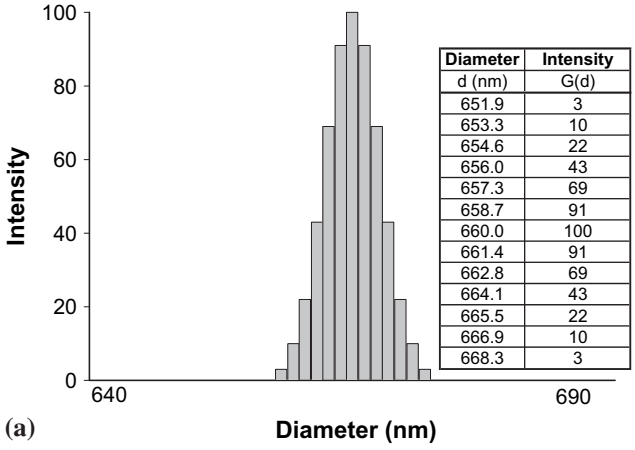


Fig. 3. Multimodal particle size distributions (a) and SEM micrograph (b) of aminosilane-modified E11-Silica.



Diameter d (nm)	Intensity G(d)
651.9	3
653.3	10
654.6	22
656.0	43
657.3	69
658.7	91
660.0	100
661.4	91
662.8	69
664.1	43
665.5	22
666.9	10
668.3	3

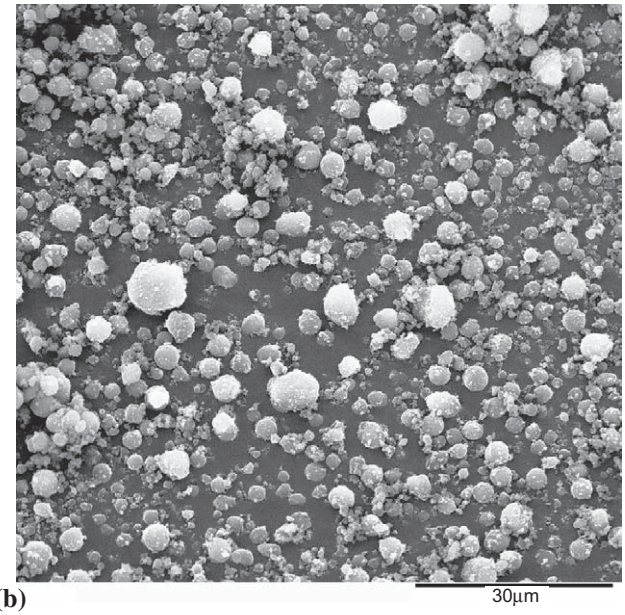
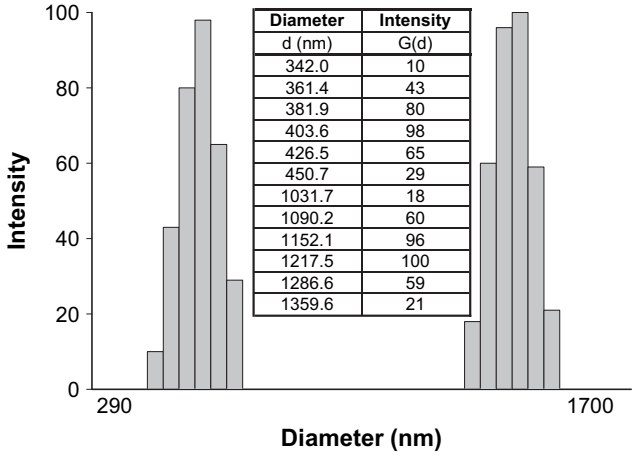


Fig. 4. Multimodal particle size distributions (a) and SEM micrograph (b) of aminosilane-modified E11-Silica after adsorption of C.I. Reactive Blue 19 dye.

uniform system was most advantageous for employing the silicas as carriers of dyes or, in effect, as fillers of paints and varnishes. The particle size distribution (Fig. 4a) demonstrated an even more evident narrowing and decisive shifting of the band of the obtained pigment particles toward their lower diameters (particles fitted the diameter range of 652–668 nm). Mean diameter of particles of the so obtained pigment was 660 nm (Table 3). Moreover, the obtained polydispersity value of 0.005 documented that the obtained pigment contained particles of almost the same size (highly uniform).

On the other hand, particle size distribution of a silica formed in the ultrasonic field is presented in Fig. 5. Application of the ultrasonic waves in the course of silica precipitation from the emulsion system resulted in formation of agglomerates in two ranges of diameter.



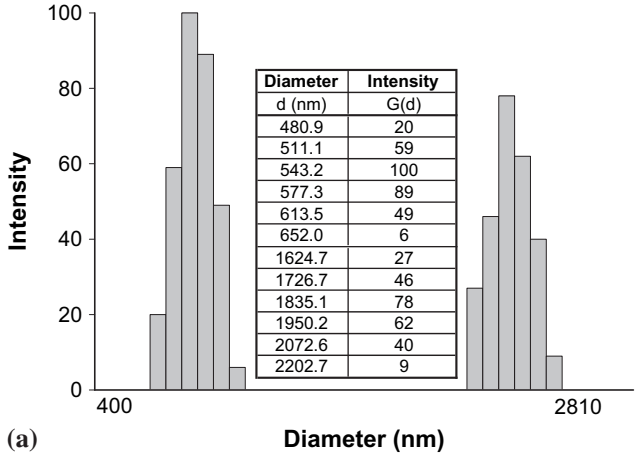
Diameter d (nm)	Intensity G(d)
342.0	10
361.4	43
381.9	80
403.6	98
426.5	65
450.7	29
1031.7	18
1090.2	60
1152.1	96
1217.5	100
1286.6	59
1359.6	21

Fig. 5. Multimodal particle size distributions of silica precipitated (E19-Silica) using an ultrasonic bath.

Primary structures manifested in low diameters of 342–451 nm range (maximum intensity of 98 corresponded to the particle diameter of 403.6 nm). On the other hand, secondary structures could be noted in the range of 1032–1360 nm (maximum intensity of 100 corresponded to the agglomerate diameter of 1217.5 nm). In the silica, mean particle diameter was 812 nm. Particles of silica so precipitated formed non-uniform systems, which contained aggregates and agglomerates. Silicon dioxide precipitated in this way exhibited a non-uniform shape.

Following modification of the silica with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane morphology and size of the particles were evaluated (Fig. 6). The studies showed that, following modification, the silica manifested certain tendency to form particle agglomerates. The particle size distribution demonstrated two bands (Fig. 6a). The more intense band, in the diameter range of 481–652 nm, corresponded to primary particles of the so modified silica. On the other hand, the other band was less intense and fitted the diameter range of 1625–2203 nm, corresponding to primary agglomerates (aggregates). In the silica, mean particle diameter was 1145 nm. Particles of the silica demonstrated an irregular shape, as shown by the respective micrograph (Fig. 6b). Spherical particles formed a minority.

Particle size distribution and SEM electron micrograph of a pigment obtained on a silica precipitated from emulsion system using ultrasonic bath, aminosilane-modified and coloured also with C.I. Reactive Blue 19 is presented in Fig. 7. In the system, the applied blue dye deteriorated uniformity of silica, which contained evident aggregates and agglomerates. In the particle size distribution (Fig. 7a) the obtained pigment showed an intense band, corresponding to agglomerates in the range of 1966–2711 nm. Aggregates were also present, forming a band of low intensity in the range of 580–800 nm. Mean particle diameter in the pigment



Diameter d (nm)	Intensity G(d)
480.9	20
511.1	59
543.2	100
577.3	89
613.5	49
652.0	6
1624.7	27
1726.7	46
1835.1	78
1950.2	62
2072.6	40
2202.7	9

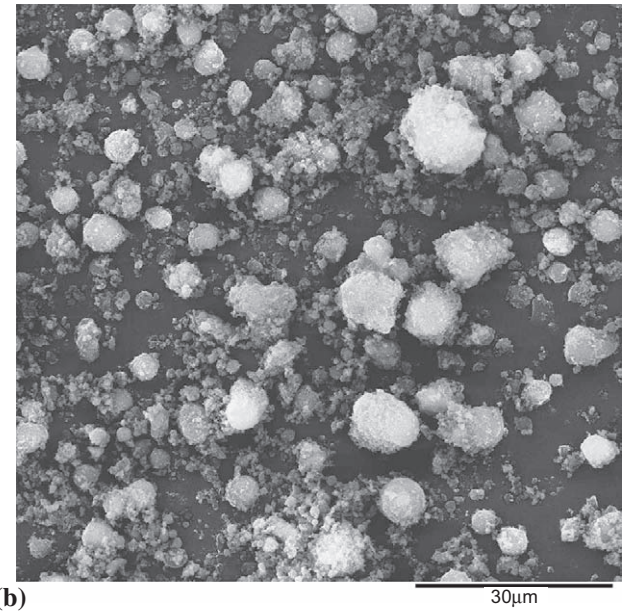
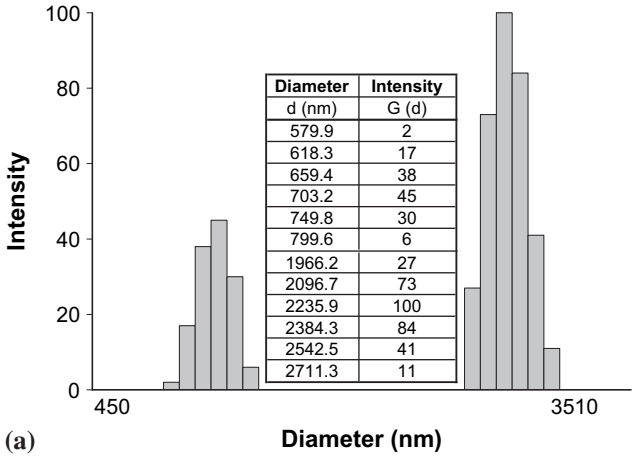


Fig. 6. Multimodal particle size distributions (a) and SEM micrograph (b) of aminosilane-modified E19-Silica.



Diameter d (nm)	Intensity G (d)
579.9	2
618.3	17
659.4	38
703.2	45
749.8	30
799.6	6
1966.2	27
2096.7	73
2235.9	100
2384.3	84
2542.5	41
2711.3	11

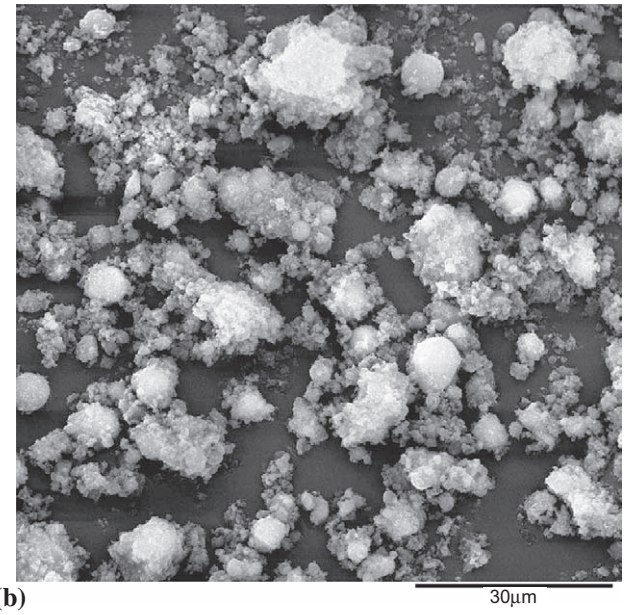


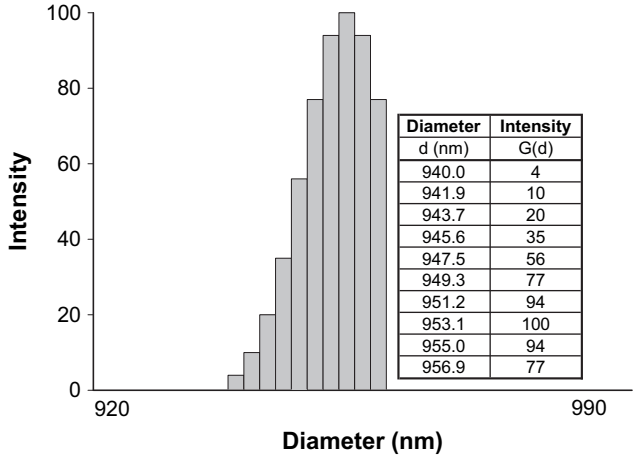
Fig. 7. Multimodal particle size distributions (a) and SEM micrograph (b) of aminosilane-modified E19-Silica after adsorption of C.I. Reactive Blue 19 dye.

amounted to 1812 nm, or was significantly higher than either in the raw precipitated or in the modified silica. The non-uniform nature of pigment obtained on the carrier was expressed by its polydispersity value of 0.230, much higher than that for the pigment obtained on silica precipitated using a top stirrer.

Silica precipitation from the emulsion system was also conducted using a homogenizer. Silica obtained in such conditions is presented in Fig. 8. The silica core so obtained exhibited highly uniform particles. Mean particle diameter was 951 nm. Moreover, the silica manifested the presence of a band in the narrow range of particle diameters (940–960 nm). The highly uniform character of the obtained carrier was expressed also by the polydispersity values of 0.005.

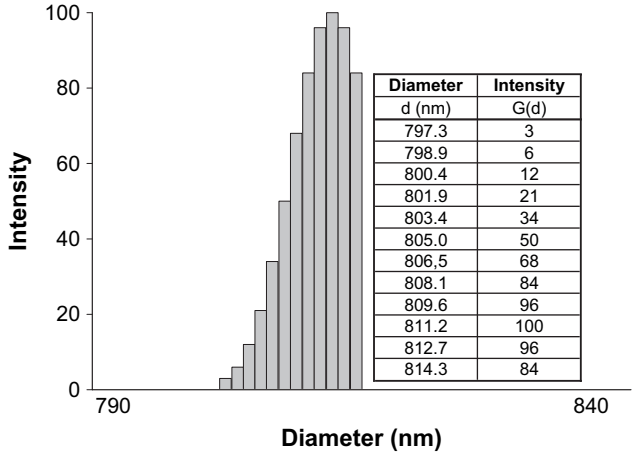
Surface modification of the silica precipitated using a homogenizer and 3 weight parts of aminosilane permitted to obtain highly monodisperse silica of almost perfectly spherical particles (Fig. 9). Mean particle diameter was 809 nm and it was lower than in the original silica (Table 3). The particle size distribution demonstrated a single band, pointing to highly uniform particles of diameter range of 797–814 nm with polydispersity value as low as 0.031. The mean particle diameter was markedly lower than in the unmodified sample.

Pigment obtained by adsorption of C.I. Reactive Blue 19 on the so modified silica exhibited low tendency to form agglomerates and manifested relatively high homogeneity (Fig. 10). Its polydispersity value (0.016) approached that for a monodisperse pigment. The particle size distribution (Fig. 10a) demonstrated two bands of a different intensity. The band of low intensity reflected the presence of secondary agglomerates in the range of 1265–1571 nm. On the other hand, the band of



Diameter d (nm)	Intensity G(d)
940.0	4
941.9	10
943.7	20
945.6	35
947.5	56
949.3	77
951.2	94
953.1	100
955.0	94
956.9	77

Fig. 8. Multimodal particle size distributions of silica precipitated (E27-Silica) using a homogenizer.



Diameter d (nm)	Intensity G(d)
797.3	3
798.9	6
800.4	12
801.9	21
803.4	34
805.0	50
806,5	68
808.1	84
809.6	96
811.2	100
812.7	96
814.3	84

Fig. 9. Multimodal particle size distributions of aminosilane-modified E27-Silica.

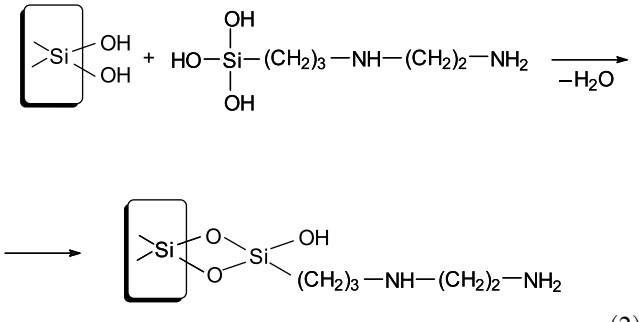
high intensity was related to aggregates of 450–580 nm in diameter. Mean diameter of pigment particles decreased to 675 nm and was the lowest in the pigments.

3.3. FTIR and NMR investigations

Spectra of silica (3000–3800 cm^{-1}), the unmodified one and that modified with 3 weight parts of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane, precipitated using a top stirrer, are presented in Fig. 11a.

The tests performed using FTIR spectroscopy showed that geminal and vicinal silanol groups dominated on the surface of SiO_2. The probable mechanism of hydrolysis (1) of aminosilane and of condensation (2) with silica surface could proceed as follows:

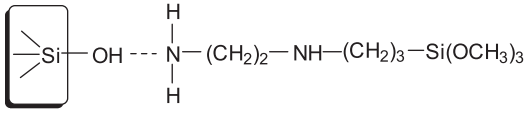
$$H_2N{-}(CH_2)_2{-}NH{-}(CH_2)_3{-}Si(OCH_3)_3 \xrightarrow[-3CH_3OH]{+3H_2O} H_2N{-}(CH_2)_2{-}NH{-}(CH_2)_3{-}Si(OH)_3 \quad (1)$$



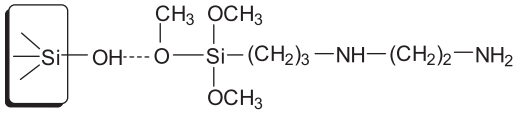
(2)

The above mechanism involved reactions consistent with covalent interactions. The phenomenon was confirmed by the band of almost twofold lower intensity, reflecting the presence of vicinal (or geminal) silanol groups (3660 cm^{-1}).

Apart from the above reactions, interaction mechanisms (3) and (4) analogous to those suggested by Piers and Rochester could also take place [25–28].



(3)

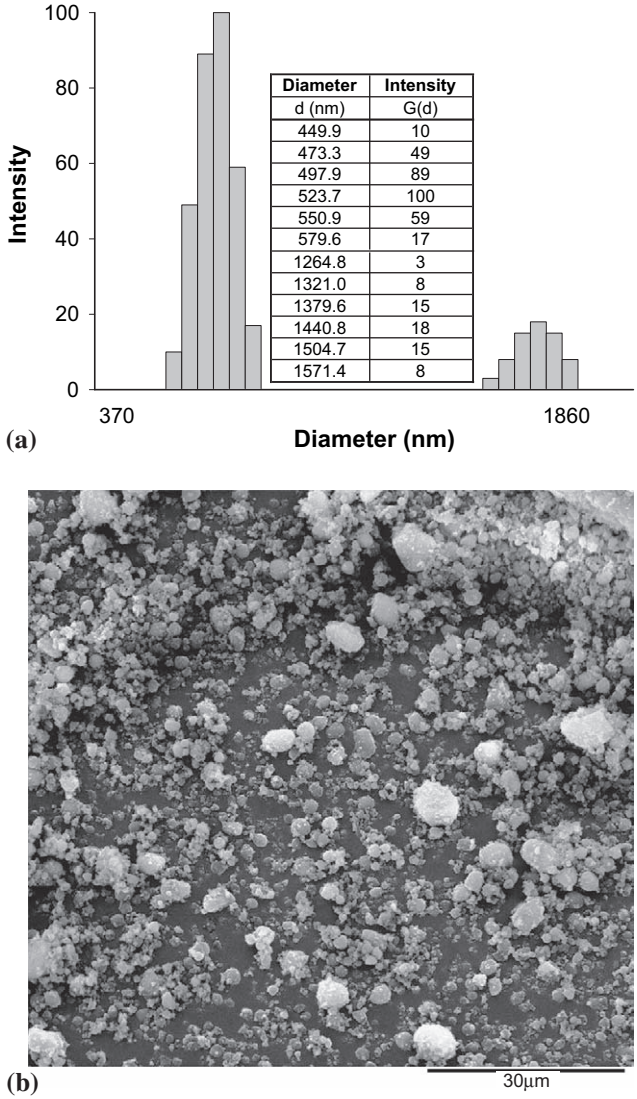


(4)

An almost complete substitution of functional silanol groups on SiO_2 surface due to modification with U-15 silane was noted in the silica precipitated using a homogenizer (Fig. 11b).

^{29}Si CP MAS NMR spectrum of the unmodified silica (E11-Silica) precipitated using top stirrer exhibited three resonance signals at −110, −100, and −91 ppm, as shown in Fig. 12a. The main intense signal at −100 ppm could be assigned to Q^3 units, corresponding to silicon with three siloxane bridges and one silanol. The next shoulder peak at −110 ppm was assigned to Q^4 units, corresponding to four siloxane bridges (≡Si–O–Si≡). On the other hand, the Q^2 silicon sites described the presence of geminal silanol groups (corresponding to two siloxane bridges and two silanol).

In the case of the *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane modification, as shown in Fig. 12b, several signals attributable to the silicon atom attaching aminoethylaminopropyl group were observed at −49 ppm (unidentate anchored, $-Si(C_3H_6NHC_2H_4NH_2)(OR)_2$, R:H or CH_3); −59 ppm (bidentate, $=Si(C_3H_6NHC_2H_4NH_2)(OR)-$), and −67 ppm (tridentate, $\equiv Si-C_3H_6NHC_2H_4NH_2$), respectively, besides the Q^2, Q^3, and Q^4 signals at −91, −100, −110 ppm, respectively.



Diameter	Intensity
d (nm)	G(d)
449.9	10
473.3	49
497.9	89
523.7	100
550.9	59
579.6	17
1264.8	3
1321.0	8
1379.6	15
1440.8	18
1504.7	15
1571.4	8

Fig. 10. Multimodal particle size distributions (a) and SEM micrograph (b) of aminosilane- modified E27-Silica after adsorption of C.I. Reactive Blue 19 dye.

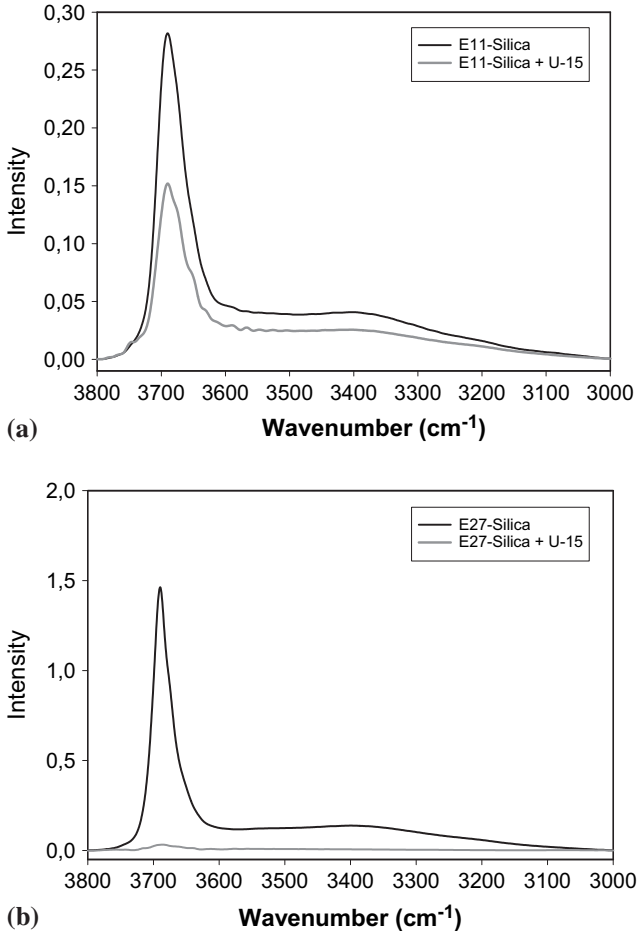


Fig. 11. FTIR spectrum for the examined unmodified and modified silica (a) E11-Silica and (b) E19-Silica.

The presence of dominating T^2 and T^3 structures suggest that the SiO_2 surface was successfully modified by the *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane treatment [29–31].

NMR studies with ^{29}Si CP MAS proved that not all silanol groups underwent condensation with alkoxysilanes to the same extent. Isolated silanol groups reacted with aminosilane to only a scanty extent.

3.4. Dyes adsorption and stability of obtained inorganic–organic hybrids

As evident in the data of Table 4, modification of silica surface with aminosilane significantly affected efficiency of organic dye adsorption on the surface. The lowest adsorption efficiency was obtained on unmodified silicas, obtained in the emulsion system (11–17%). Surface modification of the silicas evidently augmented the efficiency of adsorption of C.I. Reactive Blue 19 dye. A particularly high efficiency was obtained for the silica produced in the emulsion system using a homogenizer (98.9%). Very high efficiencies for the same silicas were obtained adsorbing dyes such as: C.I. Direct Red 81, C.I. Acid Green 16 or C.I. Acid Violet 1. When pigments were obtained using dyes such as C.I. Acid Green 16 and C.I. Acid Violet 1, slightly higher adsorption efficiencies were obtained for silicas produced using top stirrer or a homogenizer (96% and 96% for the first dye or 88.5% and 93.2% for the second dye, respectively). On the other hand, for C.I. Reactive Blue 19 and C.I. Direct Red 81 higher adsorption efficiencies were noted for silicas obtained in an ultrasonic bath (98.9% and 90.2%).

As documented by the data of Table 5, the highest amount of C.I. Reactive Blue 19 dye was eluted with water from the surface of pigments obtained on unmodified silicas (maximum of 55.8% from the surface

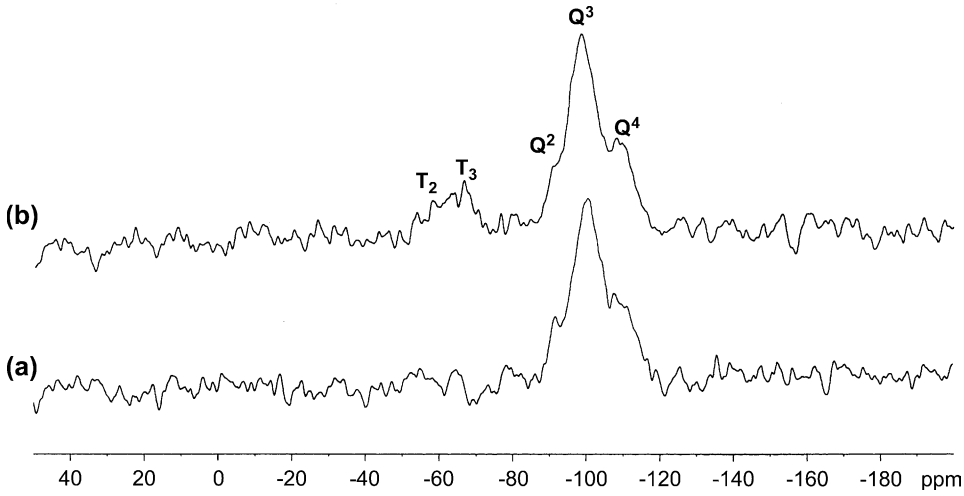
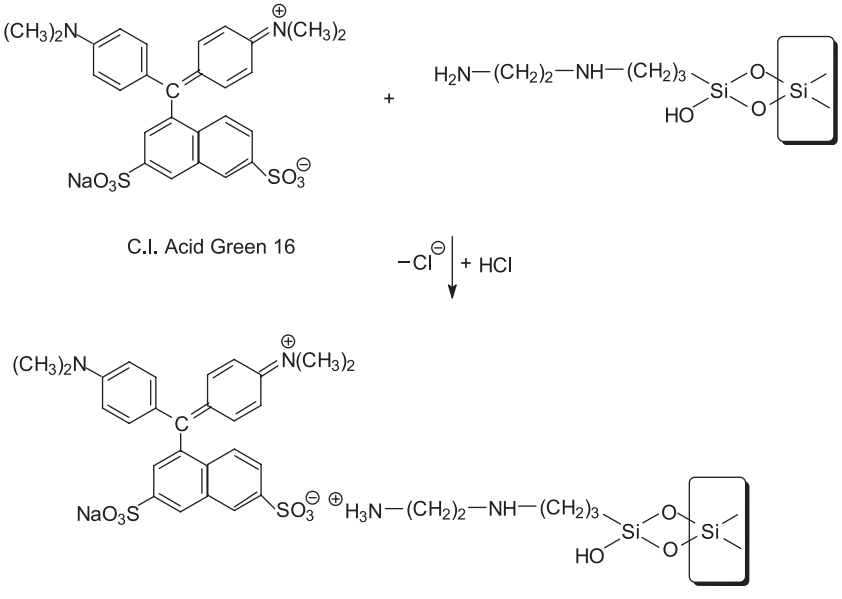
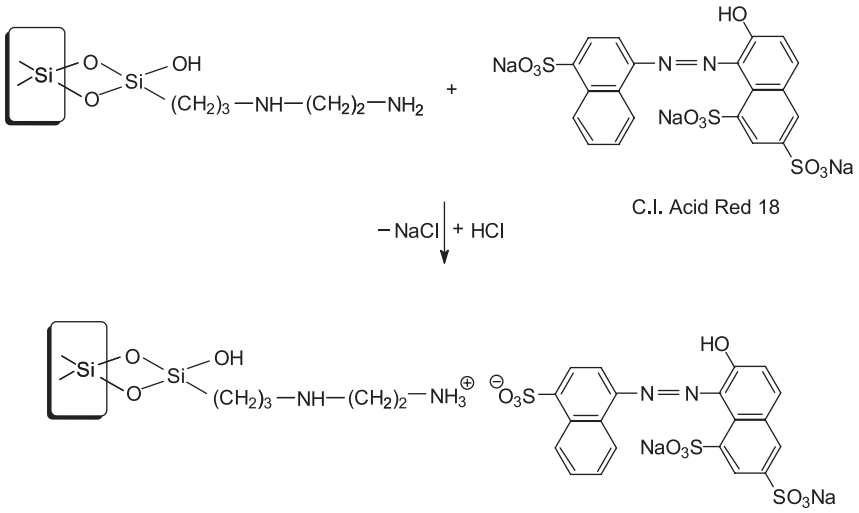


Fig. 12. ^{29}Si CP MAS NMR spectrum of (a) unmodified E11-Silica and (b) aminosilane-modified E11-Silica.

of silica obtained in a homogenizer and minimum of 47.1% from the surface of silica obtained in an ultrasonic bath). Surface modification of the silicas clearly promoted formation of a stable chemical bond of the covalent type with C.I. Reactive Blue 19. Mechanism of the interactions involved, at the first stage, transformation of β-sulphateethylsulphonyl group ($SO_2CH_2CH_2OSO_3Na$) into vinylsulphonyl group ($SO_2CH{=}CH_2$) [32,33]. In an alkaline medium the group lost the residue of sulphuric acid. Subsequently, the formed vinylsulphonyl group of the dye could react with the modified surface of silica carrier. Detailed course of the reaction was demonstrated earlier [18], describing adsorption of C.I. Reactive Blue 19 dye on the surface of silica formed in emulsion system using emulsifier in the form of oxyethylenated non-saturated fatty alcohol. The obtained pigment did not dissolve in water, as shown by the results of Table 5. In the case of using acidic dyes (C.I. Acid Green 16 and C.I. Acid Red 18) for formation of pigments on the silica core, it was noted that a slight amount of the pigments dissolved in water. Therefore, the following probable mechanism of binding the dyes at the modified silica surface could be suggested (5 and 6):



(5)



(6)

A significant amount of the dye becomes stably bound to SiO_2 surface, which may reflect the presence of chemical bonds formed, of ionic character.

In the case of aminosilane-modified carriers, the least favourable result was obtained for pigments produced by adsorption of C.I. Direct Red 81. This most probably reflected a relatively weak interaction of $-SO_3Na$ group with silanol groups of SiO_2 and the developed structure of the dye, which hampered a direct access of reactive centres to positively charged groups of $-NH_3^+$. In this case interactions of a purely physical type prevailed.

4. Conclusions

Silicas precipitated using a top stirrer or a homogenizer manifest the highest specific surface area while the silica precipitated in an ultrasonic bath features the

Table 4
Adsorption extent of the examined hybrids

Silica type	Amount of silane (wt%/wt%)	Dye concentration before adsorption (mg/cm^3)	Dye concentration after adsorption (mg/cm^3)	Disposal extent (%)
C.I. Reactive Blue 19				
E11-Silica	0	0.4	0.33770	15.6
E19-Silica	0	0.4	0.32950	17.6
E27-Silica	0	0.4	0.35310	11.7
E11-Silica + U-15	3	0.4	0.06495	83.7
E19-Silica + U-15	3	0.4	0.00448	98.9
E27-Silica + U-15	3	0.4	0.01645	97.1
C.I. Acid Red 18[a]				
E11-Silica + U-15	3	0.4	0.01592	95.9
E19-Silica + U-15	3	0.4	0.01695	96.0
E27-Silica + U-15	3	0.4	0.01597	96.1
C.I. Direct Red 81				
E11-Silica + U-15	3	0.4	0.13630	65.9
E19-Silica + U-15	3	0.4	0.03940	90.2
E27-Silica + U-15	3	0.4	0.04347	89.1
C.I. Acid Green 16[a]				
E11-Silica + U-15	3	0.4	0.01594	96.0
E19-Silica + U-15	3	0.4	0.01614	96.0
E27-Silica + U-15	3	0.4	0.01586	96.0
C.I. Acid Violet 1[a]				
E11-Silica + U-15	3	0.8	0.09200	88.5
E19-Silica + U-15	3	0.8	0.13410	83.2
E27-Silica + U-15	3	0.8	0.05422	93.2

[a] With addition of HCl.

Table 5
Stability of the obtained pigment systems

Pigment type	Modification environment	Dye concentration after elution (mg/cm^3)	Amount of dye eluted from silica surface (%)
E11-Silica + RB19	–	0.03368	54.1
E19-Silica + RB19	–	0.03322	47.1
E27-Silica + RB19	–	0.02615	55.8
E27-Silica + 3U-15 + RB19	methanol–water	0.00000	0.0
E27-Silica + 3U-15 + AR18	methanol–water	0.00000	0.0
E27-Silica + 3U-15 + DR81	methanol–water	0.00711	2.0
E27-Silica + 3U-15 + AG16	methanol–water	0.00000	0.0
E27-Silica + 3U-15 + AV1	methanol–water	0.00104	0.2

highest pore diameter. The course of N_2 adsorption isotherms points to mesoporous character of the silicas.

The most pronounced monodisperse character is shown by unmodified silica, precipitated using a top stirrer, and its derivatives, obtained by the surface modification and adsorption of organic dyes. Moreover, the pigment on the carrier of E11-Silica following adsorption of C.I. Reactive Blue 19 dye shows highly uniform character and an almost complete absence of tendencies to form agglomerate structures. Particles of the pigment are perfectly spherical.

FTIR and ^{29}Si CP MAS NMR studies demonstrated substitution of silica surface groups by alkoxy (or silanol) groups of silane coupling agent. Chemical bonds in the form of siloxane groups develop at SiO_2 surface.

The lowest efficiency of dye adsorption has been noted on surfaces of unmodified silicas. Application of the aminosilane-modified silicas to obtain hybrid pigment systems has promoted an evident increase in efficiency of organic dye adsorption on silica surface (the efficiency has frequently approached 100%).

Stability of pigments formed on silica core depends on silica surface modification. Dye elution from the aminosilane-modified silica surface is low (it does not exceed 2%, regardless of the organic dye used). The performed studies and the suggested mechanisms provide evidence for chemical reaction of the dye with the aminosilane-modified silica surface.

Acknowledgements

This work was supported by the Polish Scientific Committee research grant No. 4 T09B 042 24. The authors thank the Chemical Works "Rokita" S.A. Brzeg Dolny for the gift of the non-ionic surfactants, and Boruta-Kolor for the gift of organic dyes used in these studies.

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