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Dyes and Pigments 47 (2000) 247–257

DYES and PIGMENTS

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Preparation of pigments on modified precipitated silicas

Sławomir Binkowski *, Teofil Jesionowski, Andrzej Krysztafkiewicz

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

Received 2 May 2000; received in revised form 14 June 2000; accepted 17 July 2000

Abstract

Pigments were obtained by attaching C.I. Direct Red 81 dye to a modified silica surface. Two types of precipitated silicas were applied, namely the commercial Syloid 244 and the precipitated EG-SILICA which was prepared according to a novel procedure. The silica surface was modified with silane coupling agents, such as 3-aminopropyltriethoxysilane and *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane. The staining process was conducted in an aqueous suspension of silica in the presence of the dye. Various amounts of modifiers were applied in order to determine their effect on the dye adsorption process. The physicochemical, structural and microscopic properties of the modified silicas and of the obtained pigments were examined. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nanosize pigments; Silica; Silane coupling agents; Adsorption of dyes

1. Introduction

Compared to inorganic pigments, organic pigments exhibit greater vividness and higher colour intensity as well as higher staining potential. Their drawbacks include greater sensitivity to the action of chemical compounds, temperature and solvents [1].

In view of the above, the present study was directed at obtaining organic pigments permanently attached to the silica core so as to improve the resistance of the pigments to chemical and thermal treatments.

The preparation of silica-based pigments has been described in many papers [2,3]. The method developed by the Mita Company [4,5] involves a gradual synthesis of chromophores on the silica surface (the aromatic group of the dye is coupled by a covalent bond to the modified silica surface). Subsequently, the immobilized aromatic group undergoes nitration, reduction, diazo transformation and coupling. In the present paper we suggest a less time-consuming procedure for obtaining coloured silicas that involves attaching the dye to a modified silica surface [6]. The procedure has been made possible due to access to a wide range of commercial dyes. The ensuing pigment exhibits a structure in which silanol groups on the surface of the silica are chemically coupled to an organic dye, e.g. azo dye, through a coupling agent, aminosilane [7–9]. The pigment structure may be presented schematically using the following formula:

$$\mathrm{S{-}(O{-}\boxed{Si{-}R^1{-}Z{-}}D)}_n$$

in which S denotes the silica, R^1 the alkyl group, Z the fragment of the amine bridge, D the dye, n a number not lower than 1 and $\boxed{\mathrm{Si{-}R^1{-}Z{-}}}$ represents a group originating from the silane coupling agent.

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* Corresponding author. Tel.: +48-61-665-3626; fax: +48-61-665-3649.
E-mail address: biniu@fct.put.poznan.pl (S. Binkowski).

0143-7208/00/$ - see front matter
PII: S0143-7208(00)00054-1

Previous studies [10,11] showed that adsorbing dyes on solid surfaces, or incorporating them into inorganic particles, can yield reproducible pigments with superior optical and stability properties.

In this paper, the procedure of preparing the pigments is presented and the charactersitics of pigments, prepared from various types of silicas, are compared.

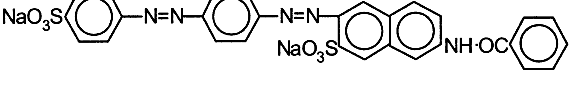
2. Experimental

2.1. Materials

The precipitated silicas Syloid 244 (Grace Davison) and EG-SILICA, precipitated according to our novel procedure [12,13], were employed. Precipitation of a highly dispersed silica was conducted in such a way that ethylene glycol solution was introduced to a reactor and heated to 85°C. Sodium metasilicate solution was then added during which the mixture was carbonized with gaseous CO_2. The entire contents were intensely mixed. Addition of the sodium metasilicate solution was halted when the pH of the system reached 8.0. Subsequently, the pH of the reactive mixture was adjusted to around 5, using a 2.5% aqueous solution of hydrochloric acid; a white sediment of silica resulted. The sediment was isolated by filtration, washed and subjected to stationary drying using a warm air fan. The precipitation of the silica was paralleled by its modification; the following silane coupling agents were used for the silica surface modification:

- U-13 — $H_2N(CH_2)_3Si(OC_2H_5)_3$, 3-aminopropyltriethoxysilane,
- U-15 — $H_2NC(O)NH(CH_2)_3Si(OCH_3)_3$, *N*-2-(aminoethyl)-3-aminopropyltriethoxysilane, both produced by UniSil.

For the preparation of the pigments, C.I. Direct Red 81 was used obtained from Boruta-Kolor, of the following structure:



2.2. Silica surface modification

This was conducted using U-13 and U-15 silanes. Solutions were prepared, containing 1, 2, 3, 5 and 10 parts by mass of the modifier in methanol/water (4:1) per 100 parts by mass of the silica. A sufficient amount of the modifier solution was used to ensure uniform wetting of the silica surface took place.

Appropriate modifier solutions were prepared directly before the process (to prevent their deterioration) and were added dropwise to a round bottomed flask, containing 35 g of Syloid 244. Mixing was continued for 1 hour, after which time, the silica was dried at 105°C and passed through a sieve of 0.2 mm mesh.

EG-SILICA was modified in the course of its precipitation. The aim of the silica surface modification, conducted in parallel to its precipitation, was to eliminate the need to carry out the modification following precipitation of the highly dispersed product.

2.3. Colouration of the modified silicas

An aqueous solution (0.4 g/dm^3) of the dye was introduced to a flask containing the same amount of the modified silica. The suspension was mixed for 2 h using a magnetic stirrer and the solution was then filtered under vacuum. The ensuing sediment was dried at 105°C and ground in an electric mortar. The same procedure was applied to the unmodified silica. The filtrate was centrifuged and the content of the unadsorbed azo dye was estimated by absorbance measurement using a Secomams.750 spectrophotometer; an identical estimation was made for the unmodified silica.

2.4. Evaluation of the physicochemical properties of silicas and of the obtained pigments

Study in the near infra-red range was conducted in order to obtain data on the extent of condensation of the surface silanol groups. Silica suspensions in CCl_4 were used, in which the highly dispersed silicas formed transparent gels. The procedure for sample preparation, for studies in the infra-red range, was conducted as fast as possible to prevent contact with humidified air. Before measurement, the sample-containing cuvette was shaken so as to obtain an homogenous suspension. NIR spectra were recorded for the studied silica samples before and after modification, using a Beckmann UV–Visible–NIR spectrophotometer. The wavenumber 7326 cm^{-1} was used, which, in parallel to the 3748 cm^{-1} band, is typical for the surface bound silanol groups. The first wavenumber was selected as the closely positioned band of 3440 cm^{-1}, typical for water, could introduce bias to measurements at 3748 cm^{-1} . As shown by Fink and Müller [14], results obtained in either of the bands are almost identical. The extent of condensation was calculated using the formula:

$$K = \frac{H-h}{H} \cdot 100\%$$

where H represents the height (or area) of the unmodified silica sample peak (cm or cm^2) and h is the height (or area) of the modified silica peak (cm or cm^2).

Studies of the morphology and microstructure of the pigments were performed to obtain data on the dispersion, particle size, grain morphology and structure of individual particles and on the type of silica agglomeration. Studies were performed using scanning electron microscopy (Phillips SEM 515) to provide reliable surface images of the obtained silicas. As silicas are non-conductive materials, following exposure to the electron beam of the scanning electron microscope, their surface accumulates electric charges, which disfigure the surface topography pattern.

Particle size distribution was determined using a ZetaPlus (Brookhaven Instruments) instrument employing the dynamic light scattering (DLS) technique. The technique involved weighing out an appropriate sample, placing it in a small amount of water (0.1 g in 50 cm^3 H_2O) and stabilizing the dispersion using an ultrasonic bath (50 KHz). The prepared sample was placed in a cuvette and the particle size distribution of the silica particles was then measured.

3. Results and discussion

Table 1 shows the principal physicochemical properties of both the unmodified silicas as well as silicas which had been modified with the two types of silanes (3-aminopropyltriethoxysilane and *N*-2-(aminoethyl)-3-aminopropyltriethoxysilane). The unmodified silicas Syloid 244 and EG-SILICA differed in their physicochemical parameters. Syloid 244 was of very low bulk density (slightly above 50 g/dm^3) and displayed a very high capacity to absorb water, dibutyl phthalate, paraffin oil (the capacity to absorb water was very high: 850 g/100 g and the capacity to absorb paraffin oil as high as 1600 g/100 g). EG-SILICA demonstrated a somewhat higher bulk density (75 g/dm^3) and lower absorptive capacities (e.g., the capacity to absorb paraffin oil was 1450 g/100 g). EG-SILICA also displayed the particularly advantageous character of relatively low capacity to absorb water (around 550 g/100 g). Modification of both silicas altered their physicochemical parameters; modification with the U-15 aminosilane increased the bulk densities of the silicas, particularly in the case of EG-SILICA. Importantly, modification imparted reduced water absorbing capacity to both silicas which clearly resulted in increased hydrophobicity of the silica surface and, therefore, an augmented chemical affinity towards functional groups. The increased hydrophobicity of the modified silica surface is clearly dependent upon the amount of the aminosilane that was used in modification. Increasing amounts of the silanes, especially in the case of U-15 aminosilane, resulted in reduced water absorbtion. The extent of surface modification was determined mainly by the extent of condensation of silanol groups at the silica surface with hydrolyzed alkoxy groups of the aminosilane coupling agents.

The extent of condensation of the surface silanol groups following modification of both silicas with silane coupling agents, in relation to the amount of the compounds used in the modification, is shown in Table 2. The extent of condensation was calculated on the basis of the spectrophotometrically determined peaks at 7326 cm^{-1}. As indicated by the data in Table 2, the amount of silane used in the modification markedly affected the extent of the surface silanol group condensation. This was particularly evident following modification of Syloid 244 silica with either the U-13 or U-15 silane. When the amount of silane increased from 1 to 5

Table 1
Basic physicochemical properties of silicas

Amount of modifying agent (weight parts)	Bulk density (g/dm^3)	Water absorbing capacity (g/100 g)	Dibutyl phthalate absorbing capacity (g/100 g)	Paraffin oil absorbing capacity (g/100 g)
Syloid 244				
0	53	850	1400	1600
U-13				
1	57	850	1400	1500
3	60	900	1250	1200
5	63	900	1250	1200
U-15				
1	64	650	1150	1600
3	68	600	1200	1650
5	67	550	1250	1650
EG-SILICA				
0	75	550	900	1450
U-15				
3	130	300	800	1200
5	144	350	650	1100

Table 2
Peak's surfaces for 7326 cm^{-1} band and the condensation extent of silanols on the surface unmodified and modified silicas Syloid 244 and EG-SILICA

	Planimetric method		Geometric method	
Amount of modifying agent (weight parts)	Peak surface (cm^2)	Condensation extent (%)	Peak surface (cm^2)	Condensation extent (%)
Syloid 244				
0	3.46	–	3.09	–
U-13				
1	2.90	18.18	2.74	11.30
3	2.75	20.52	2.56	17.15
5	2.23	35.55	2.01	34.89
U-15				
1	3.25	6.07	3.01	2.59
3	3.00	13.29	2.86	7.44
5	2.50	27.74	2.39	22.65
EG-SILICA				
0	5.10	–	14.35	–
U-13				
3	2.03	60.20	4.83	66.34
U-15				
1	1.45	71.57	4.35	69.68
3	1.43	71.91	4.06	71.70
5	1.50	70.59	4.36	69.61
10	1.56	69.41	4.60	67.94

parts by mass, the extent of condensation (calculated by the two techniques) increased. After modification with the U-13 silane, the extent of condensation increased from 11.3%, following modification with 1 part by mass of silane, to 34.9% following modification with 5 parts by mass of silane. A somewhat less pronounced increase in the extent of condensation was observed for Syloid 244 which had been modified with the U-15 silane; following modification with 5 parts by mass of U-15 silane the extent of condensation increased to only 22.7%.

In the case of EG-SILICA, the increase in the extent of condensation imparted by modification was higher than that achieved with Syloid 244. The data shown in Table 2 clearly indicates that in the case of EG-SILICA modification, a maximum of 3 parts by mass of aminosilane should be used; an increase in the amount used failed to impart further condensation of the surface silanol groups.

The extent of adsorption of the C.I. Direct Red 81 dye on the silicas is presented in Table 3.

Clearly, adsorption of the dye on the silica surface was significantly affected by modification of the surface with the aminosilanes. The lowest extent of dye adsorption was observed for unmodified silicas or for silicas which had been modified with 1 part by mass of U-13 aminosilane (the efficiency

Table 3
Adsorption extent of C.I. Direct Red 81

Amount of modifying agent (weight parts)	Dyes concentration before adsorption (mg/cm^3)	Adsorption time (h)	Dyes concentration after adsorption (mg/cm^3)	Disposal extent (%)
EG-SILICA				
0	0.4	2	0.03717	90.71
U-13				
1	0.6	2	0.06828	88.62
1	0.4	2	0.00802	97.99
2	0.6	2	0.21000	65.00
2	0.4	2	0.13860	65.35
3	0.4	2	0.00243	99.39
5	0.4	2	0.00322	99.19
10	0.4	2	0.00288	99.28
10	0.4	1	0.00203	99.49
10	0.4	4	0.00305	99.24
U-15				
1	0.4	2	0.00028	99.93
1	0.6	2	0.17390	71.02
1	0.8	2	0.26220	67.23
2	0.6	2	0.02845	95.26
3	0.6	2	0.00136	99.78
5	0.6	2	0.00203	99.67
10	0.6	2	0.00226	99.63
Syloid 244				
0	0.4	2	0.03379	91.55
U-13				
1	0.4	2	0.04945	87.64
3	0.4	2	0.00034	99.92
5	0.4	2	0.03240	91.99
U-15				
1	0.4	2	0.00011	99.97
3	0.4	2	0.00000	100.00
5	0.4	2	0.00110	99.73

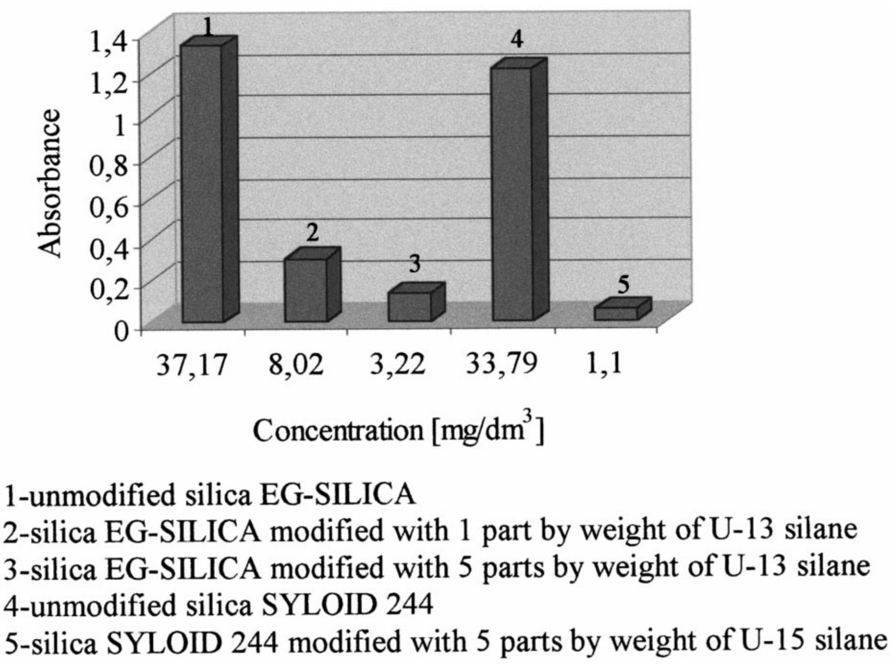


Fig. 1. Dyes concentration in the filtrate following unmodified and modified silica coloration.

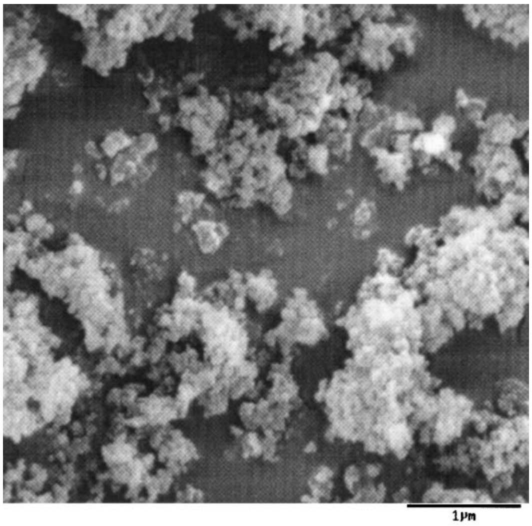


Fig. 2. Scanning electron micrograph (SEM) of silica EG-SILICA modified with one part by weight of U-15 silane.

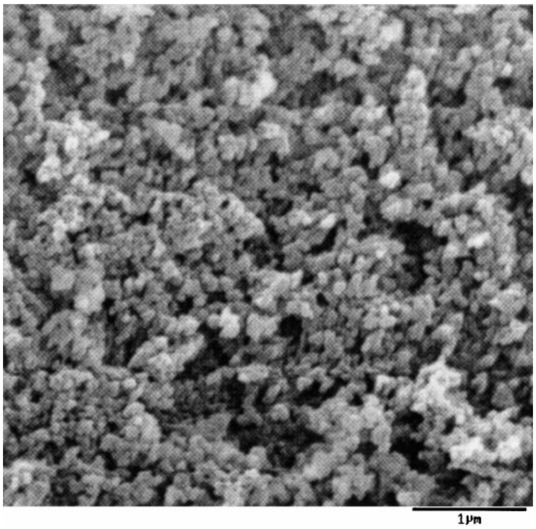


Fig. 3. Scanning electron micrograph (SEM) of silica EG-SILICA modified with one part by weight of U-15 silane after adsorption of C.I. Direct Red 81.

amounted to 88–90%). For both the Syloid 244 and EG-SILICA preparations, modification imparted increased dye adsorption to the silica surface; in this context, very high adsorption efficiency was obtained for those silicas which had been modified using 3 parts by mass of the U-13 and U-15 aminosilanes.

In the case of silicas modified with higher amounts of aminosilanes (5 and 10 parts by weight), dye adsorption remained at the level observed for those silicas which had been modified with 3 parts by mass of the silanes. This corroborated the earlier observation that 3 parts by mass of the silanes was sufficient to achieve optimum modification effect.

The effect of the modification of both silicas on the efficiency of azo dye adsorption is also documented in Fig. 1. Modification resulted in more efficient adsorption of C.I. Direct Red 81 on the modified silica.

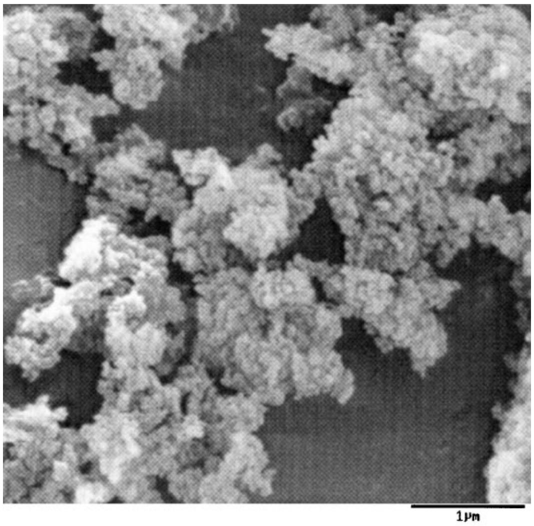


Fig. 4. Scanning electron micrograph (SEM) of silica EG-SILICA modified with three parts by weight of U-15 silane.

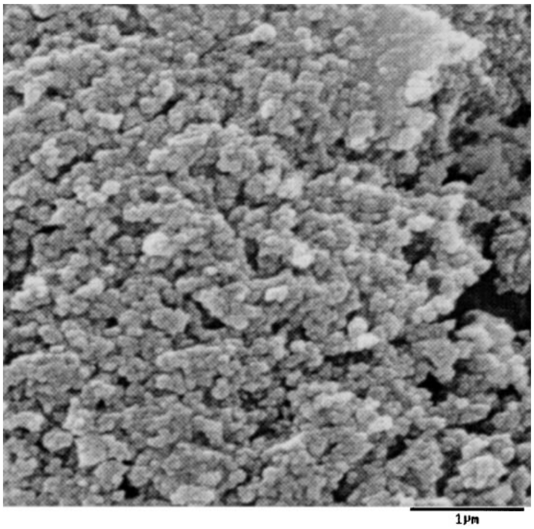


Fig. 5. Scanning electron micrograph (SEM) of silica EG-SILICA modified with three parts by weight of U-15 silane after adsorption of C.I. Direct Red 81.

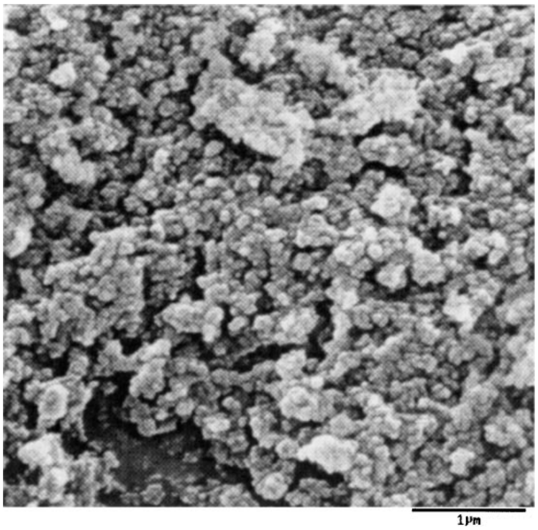


Fig. 6. Scanning electron micrograph (SEM) of silica EG-SILICA modified with ten parts by weight of U-15 silane.

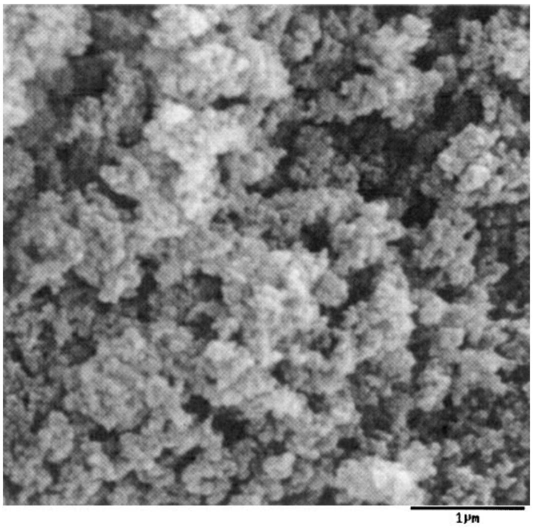


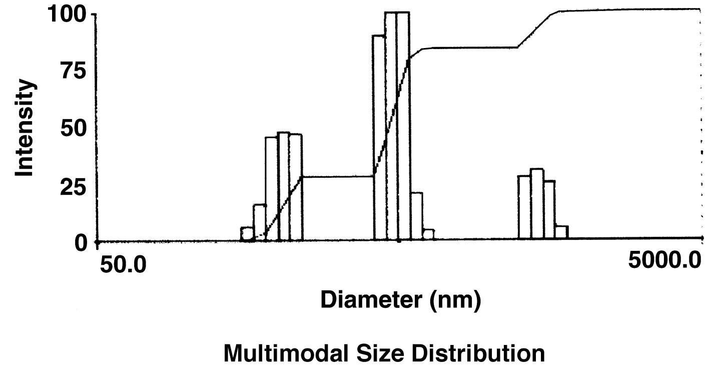
Fig. 7. Scanning electron micrograph (SEM) of silica EG-SILICA modified with ten parts by weight of U-15 silane after adsorption of C.I. Direct Red 81.

Figs. 2–7 are electron photomicrographs obtained for the EG-SILICA series.

The micrograph of the EG-SILICA preparation, following modification with 1 part by mass of U-15 silane is shown in Fig. 2; clearly, the silica exhibits a tendency to form spherical agglomerates. Following adsorption of the azo dye on to the surface of EG-SILICA, which had been modified with 1 part of U-15 aminosilane, breakdown of the agglomerate was seen (Fig. 3). The ensung red pigment exhibited a highly uniform particle size. Thus, adsorption of the dye onto the silica carrier resulted in a homogenous inorganic pigment. A similar situation was observed following adsorption of C.I. Direct Red 81 dye on EG-SILICA, which had been modified with 3 parts of U-15 aminosilane. In this case also, a clearly improved silica-based pigment was obtained, with respect to homogeneity, following adsorption of the azo compound, as compared to pure silica, modified with 3 parts of U-15 silane (Figs. 4 and 5).

Electron photomicrographs of EG-SILICA samples modified with 10 parts of U-15 silane and of the pigment obtained by adsorption of the dye on a silica surface modified with 10 parts by mass of aminosilane, are presented in Figs. 6 and 7. In this case, a homogenous pigment was not obtained after dye adsorption. It can be concluded, therefore, that excessive levels of U-15 aminosilane had an advense affect on the adsorption of C.I. Direct Red 81. Thus, electron microscopy indicates that pigments of a highly uniform character are obtained using silica carriers which have been modified with 1–3 parts by mass of U-15 aminosilane.

In order to examine the homogeneity of the samples (silica, modified silica and silica based pigment), studies on the particles size distribution of agglomerates were performed. The respective



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
119.6	0	0	327.3	0	29	898.1	0	84
131.0	0	0	358.7	0	29	982.0	0	84
143.6	0	0	393.1	0	29	1076.2	0	84
157.4	6	1	430.8	89	44	1179.4	0	84
172.5	16	4	472.1	100	62	1292.4	28	89
189.0	46	12	517.4	100	80	1416.3	31	94
207.1	48	20	567.0	21	83	1552.1	26	99
227.0	47	29	621.3	5	84	1700.9	6	100
248.7	0	29	680.9	0	84	1864.0	0	100
272.6	0	29	746.2	0	84	2042.7	0	100
298.7	0	29	817.7	0	84	2238.5	0	100

Fig. 8. Particle size distribution of unmodified silica EG-SILICA.

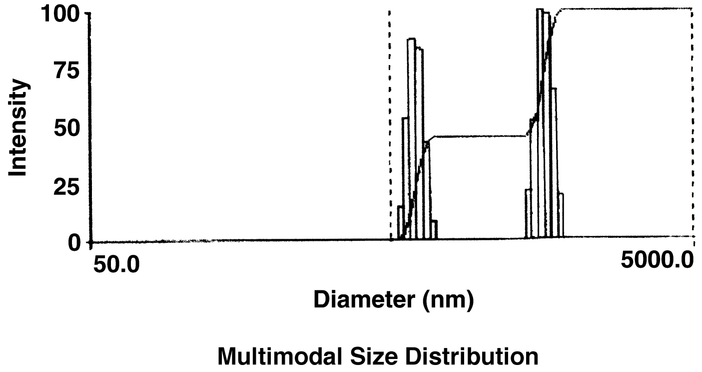
particles size distributions for unmodified EG-SILICA, EG-SILICA modified with 1 part U-13 aminosilane and EG-SILICA modified with 1 part U-13 silane following adsorption of the azo dye, are shown in Figs. 8–10.

As demonstrated in Fig. 8, the unmodified EG-SILICA exhibited heterogeneity and a tendency to form both primary and secondary agglomerates. Two well marked ranges of primary agglomerates were observed, namely one of a lower intensity (maximum intensity of 48) in the range of 170–300 nm and the other of a high intensity (maximum intensity of 100) in the range of 430–600 nm. Moreover, the structure of particles in the unmodified EG-SILICA contained a band in the range between 1180 and 1700 nm (with maximum intensity of 31) which might be ascribed to secondary agglomerates.

Upon modification of EG-SILICA with 1 part by mass of U-13 silane (Fig. 9) an increased tendency was noted for the formation of secondary agglomerates (this was also confirmed in the electron microscopy study — see Fig. 2). Two strong bands of agglomerate manifestation were seen, one for primary agglomerates in the range of 530–700 nm (maximum intensity of 88) and the other for secondary agglomerates in the range between 1400 and 1800 nm (maximum intensity of 100). Thus, following modification, while the silica displays reduced homogeneity, the agglomerate system has improved adsorptive properties.

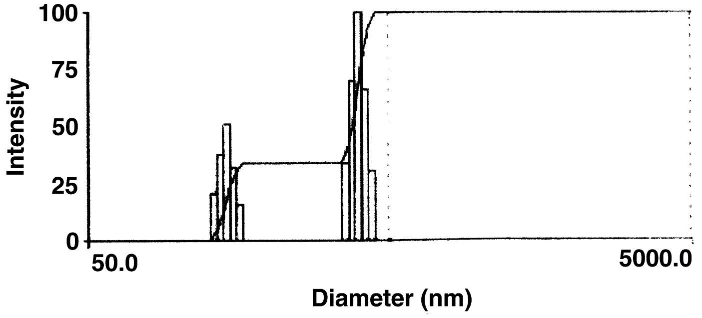
Adsorption of the dye at the surface of the modified silica markedly improved the homogeneity of the obtained silica-based pigment.

The ranges of agglomerate bands had clearly shifted toward smaller particles. Only two bands were noted which corresponded to primary agglomerates. One of these indicated a very low diameter of agglomerate particles (130–160 nm, maximum intensity of 51) while the other comprised



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
438.4	0	0	748.3	0	45	1277.5	0	45
460.2	0	0	785.6	0	45	1341.1	0	45
483.1	0	0	824.8	0	45	1407.9	21	48
507.2	0	0	865.9	0	45	1478.1	52	56
532.5	14	2	909.0	0	45	1551.7	100	72
559.0	53	10	954.3	0	45	1629.0	99	87
586.9	88	24	1001.8	0	45	1710.2	65	97
616.1	84	37	1051.7	0	45	1795.4	19	100
646.8	43	44	1104.1	0	45	1884.8	0	100
679.0	8	45	1159.1	0	45	1978.7	0	100
712.8	0	45	1216.9	0	45	2077.3	0	100

Fig. 9. Particle size distribution of silica EG-SILICA modified with one part by weight of U-13 silane.



Multimodal Size Distribution

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
106.7	0	0	185.4	0	34	322.0	0	34
112.2	0	0	194.9	0	34	338.6	0	34
118.0	0	0	204.9	0	34	356.0	34	42
124.0	0	0	215.5	0	34	374.3	70	57
130.4	21	5	226.6	0	34	393.6	100	79
137.1	38	13	238.2	0	34	413.9	66	93
144.2	51	24	250.5	0	34	435.2	31	100
151.6	32	31	263.4	0	34	457.6	0	100
159.4	15	34	277.0	0	34	481.1	0	100
167.6	0	34	291.2	0	34	505.9	0	100
176.3	0	34	306.2	0	34	531.9	0	100

Fig. 10. Particle size distribution of silica EG-SILICA modified with one part by weight of U-13 silane after adsorption of C.I. Direct Red 81.

a somewhat higher diameter of agglomerate particles (360–440 nm, maximum intensity of 100). This finding confirms those results obtained during the earlier electron microscopy study and proves that adsorption of the dye at the surface of aminosilane modified silica, markedly improves the homogeneity of the silica-based pigment. Hence, the technique of obtaining stable inorganic pigments from the adsorbed azo dye offers potential for obtaining pigments with improved resistance to both chemicals and light fading.

4. Conclusions

Following modification with U-13 and U-15 aminosilanes, EG-SILICA and Syloid 244 silica preparations exhibit significantly lowered physicochemical parameters (bulk density and surface absorbing capacity). Increasing amounts of the modifying silanes imparted a gradual decrease in water absorbing capacity by the silica surface. This advantageous effect indicates that the silica surfaces have undergone a hydrophobic transformation.

The augmented extent of condensation, resulting from modification of silica with aminosilanes, confirms the increased hydrophobicity of the silica surface. Moreover, it proves that silanol groups, present on the silica surface, are substituted by groups of silane compounds. The extent of condensation achieved for EG-SILICA, following modification with aminosilanes, was markedly higher than that secured for the Syloid 244 silica.

Scanning electron microscopy demonstrated that dye adsorption on an aminosilane-modified silica carrier yields a uniform pigment. The studies have also proven that pigments of a highly uniform character can be obtained using at most 1–3 parts by mass of U-15 aminosilane.

Adsorption of the dye at the surface of a modified silica markedly improves the homogeneity of the obtained silica-based pigment. The ranges of agglomerate bands are shifted towards smaller particles (two bands of primary agglomerates).

Aminosilane-modified silicas exhibit significantly augmented adsorption of C.I. Direct Red 81 at their surface; particularly high efficiencies of dye adsorption are noted for silicas modified with 3 parts of U-13 and U-15 aminosilanes.

Acknowledgements

The authors are indebted to Boruta-Kolor Sp. z o.o. for the gift of the dye used in the studies. This work was supported by the research grant No. BW 32/1/2000. Teofil Jesionowski was awarded a grant by the Foundation for Polish Science '99.

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