Available online at www.sciencedirect.com
SCIENCE DIRECT®
Dyes and Pigments 60 (2003) 233–242
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

# Application of silica-based pigments in water-borne acrylic paints and in solvent-borne acrylic paints

Andrzej Krysztafkiewicz[a,*], Sławomir Binkowski[a], Aleksandra Dec[b]

[a]*Poznañ University of Technology, Institute of Chemical Technology and Engineering, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznañ, Poland*
[b]*LAKMA S.A., ul. Frysztacka 173, 43-400 Cieszyn, Poland*

Received 24 February 2003; received in revised form 19 June 2003; accepted 14 July 2003

**Abstract**

The amorphic silica, Syloid 244 was modified using *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane. Pigments based on the silica carrier were obtained by coupling the organic dye, C.I. Reactive Blue 19 to the modified surface of the silica. The adsorption process was conducted in an aqueous suspension of the silica, supplemented with the dye. An extent of modification was evaluated using infrared spectroscopy and nuclear magnetic resonance spectroscopy. Structural and microscopic properties of the product were examined as were the zeta potential and the particle size distribution. The specific surface area was estimated using a BET approach. The efficiency of the adsorption process and the effects of the amount of dye and type of dye, on the final product, were determined. Moreover, the stability of the chemical bonds that were formed between the dye and the carrier was examined in elution tests. The pigments obtained were tested in water soluble binders and in organic solvent-solubilised acrylic paints.


*Keywords:* Silica; Silane coupling agents; Pigments; Organic dyes; Acrylic paints

## 1. Introduction

Hydrophilic silicas core created to be colourless and to carry surface silanol groups, that can react with several functional groups, forming covalent bonds. The process of staining the silica involves at first a reaction of the silica with a hydroxysilane or aminosilane coupling agent in order to bind the silyl chain to the silica surface [1–3]. Next, the organic dye should react with the adsorbed silane yielding silica particles that contain the dye, coupled by a covalent bond. The organic dye should be stably bound by a covalent bond to the silane functional group on the silica so that IT cannot be eluted with solvents. This is a method of lowering the toxicity of inks and simplifying printing ink formulations. The sequence of reactions taking place in such an approach has been schematically presented in [4].

Pigments of the above type can also be obtained in the course of silica synthesis. Such pigments are

* Corresponding author. Tel.: +48-61-831-3326; fax: +48-61-831-3349.
*E-mail address:* tolek.jesionowski@fct.put.poznan.pl (A. Krysztafkiewicz).

0143-7208/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0143-7208(03)00149-9

obtained using as a carrier the silica that was obtained in the reactions of hydrolysis and condensation of tetraethoxysilane (TEOS) in ethanol/water/ammonia solution in the presence of dyes of an acidic type [5]. In order to synthesize inorganic particles that contain a dye in their mass, appropriate solutions of salts and the dye are mixed to yield a stable final product. In many examples, the entire amount of the dye becomes incorporated into the structure of the obtained pigment. The completion of the process is ascertained by the remaining solution being colourless [6].

The structure of the Syloid 244 surface, before and following modification with silane coupling agents, can be examined using solid NMR tests ($^{29}$Si CP/MAS NMR), a technique that is widely applied by several investigators [7–9]. A typical silica spectrum is characterised by three signals. The geminal silanol groups ($Q_2$) yield a signal at −91 ppm, single silanol groups ($Q_3$) yield a signal at −100 ppm, while siloxane groups ($Q_4$) yield a signal at −109 ppm. Thus, the technique allows us to distinguish single groups and geminal silanol groups and to monitor the reactivity of silanol groups. As indicated by literature of the subject [10], the geminal silanol groups are more reactive. Values of chemical shifts (δ) of bands that were obtained for structures of the chemically coupled phases formed at the silica surface following silane modification were provided by Albert and Bayer [11].

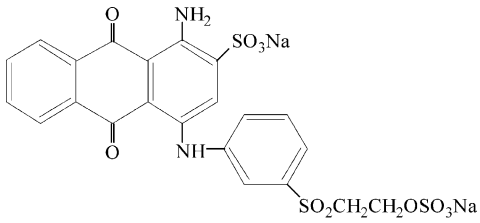
Present studies are aimed at obtaining coloured silica particles through adsorption from aqueous solution of appropriate organic dyes on the surface of modified silicas for use as potential paint pigments. Subsequently, the pigments obtained are tested in water- and solvent-soluble acrylic paints.

## 2. Experimental

### 2.1. Materials

For the preparation of pigments on a silica carrier, the following substrates were used:

- synthetic amorphic silica, Syloid 244 (Grace Davison, USA)
- silane coupling agent, *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane $H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$ (UniSil, Poland)
- organic dye, C.I. Reactive Blue 19 (Boruta-Kolor, 50 g/dm$^3$, Poland), of the following structure:




### 2.2. Procedures and methods

The silica, Syloid 244 was modified by a drying technique, according to the procedure previously described in detail [12]. In the same paper the technique was described of estimating the extent of surface silanol group condensation on the basis of near infra-red (NIR) measurements. Studies on microporous structure (specific surface area, diameter and volume of pores) of the silicas and pigments took advantage of measurements performed with the aid of ASAP 2010 instrument (SY-LAB Micrometrics Instruments Corporation, USA). For the tests, an approximately 0.2 g sample was weighed out and degassed for 2 h at 120 °C. Nitrogen adsorption/desorption measurements were performed at −196 °C, on a wide range of relative pressures (0.01–0.995). The specific surface area was estimated according to the BET model. The mean pore diameter and pore size distribution during adsorption/desorption were estimated by the BJH approach, using Halsey's equations or Harkins–Jury's equations.

The determination of carbon and nitrogen was performed on a single 10 mg sample, using an automatic type EA 1108 analyser (Carlo-Erba, Italy). The sample was burned in an oxygen atmosphere and the gases formed were passed in a stream of helium through appropriate catalysers,

separated in a chromatographic column, and recorded as $N_2$ and $CO_2$ using a catharometer.

Solid state NMR measurements were performed in a DSX 300 spectrometer (Brüker, Germany). A sample of around 100 mg was placed in a rotor, 4 mm in diameter, made of $ZrO_2$ and allowing rotary motion of the sample. Centrifugation at the magic angle was conducted at 8.4 kHz. CP/MAS NMR spectra of $^{29}Si$ were recorded at a 4.5 μs impulse duration, 1.5 ms time of contact and an impulse repetition time of 6 s.

Studies of dye elution from the surface of pigments were performed in such a way that 0.1 g pigment was added to a conical flask of 250 $cm^3$ capacity, containing 20 $cm^3$ water. The content was mixed with a magnetic stirrer (SLK 6, Schott, Germany) for 1 h at room temperature and at 100 °C. The contact time was established in earlier experiments. The suspension was subjected to filtration at a lowered pressure. The sediment of pigment obtained was subjected to drying in a stationary drier at 105 °C. The concentration of soluble pigment fractions in the filtrate was estimated by absorbance measurements (750 type spectrophotometer, SECOMAM, France).

The preparation of the pigments at a semi-technical level was conducted as follows. A 5000 $cm^3$ reactor containing 100 g of Syloid 244 silica, modified with 3 weight parts of silane U-15 in a 4:1 methanol/water mixture, was charged with a 2500 $cm^3$ aqueous solution of the organic dye, C.I. Reactive Blue 19, at the concentration of 2 $g/dm^3$. The obtained suspension was intensely mixed ($10^4$ rpm) for 30 min using an ULTRA-TURRAX T 50 basic type of homogeniser (IKA, Germany). The pigment obtained was subjected to filtration under a lowered pressure. Then, the pigment sample was dried in a stationary drier at 105 °C and subjected to grinding in an electric mortar (02 type mortar, Fritsch Pulverisette, Germany). The dried and ground product was passed through a sieve of 0.2 mm mesh in order to equalise it appropriately.

In order to determine the surface morphology of the pigments obtained, selected samples were examined by scanning electron microscopy. Thus three-dimensional replicas of solid rough surfaces, e.g. of fracture planes, surface structure and of particle agglomerates were obtained. The preparations were made in such a way that a sample was smeared on an object stage (on conducting carbon foils) of a microscope and a thin film of gold was deposited on the smear by sputtering, (Balzers SCD 050 apparatus). The studies were performed using a Philips SEM 515 scanning electron microscope.

Studies by electrophoretic light scattering (ELS) and by dynamic light scattering (DLS) were performed employing a ZetaPlus apparatus (Brookhaven Instruments Co., USA). The techniques have been described in detail earlier [13–15].

The pigment that was obtained was applied in the following paints:

- water-soluble façade acrylic paint, AKRYL LAKMA (Table 1)
- organic solvent-soluble outdoor acrylic paint, AKRYBET (Table 2)
- water-soluble, dispersive indoor acrylic paint, AKRYL W LAKMA (Table 3).

The obtained results were compared with those presented by commercially available paint, offered by LAKMA S.A. (Poland, see Tables 8, 9). The range of tests included determination of density, viscosity, coating ability, extent of drying, time of drying, resistance to wet scrubbing, base adherence, capacity to dilution with water, capacity to be applied with a brush and curtaining from vertical surfaces. The tested paints showed general compositions listed in Tables 1–3. In every paint studied, the titanium white, R001, was substituted by a new pigment on a silica base. In the case of the AKRYL LAKMA paint 9% of the titanium white was substituted by the obtained pigment. In the AKRYBET paint, in turn, the new pigment accounted for 11% and in the AKRYL W LAKMA paint for 5% of the mass.

## 3. Results and discussion

A decrease in the bound surface silanol groups permits us to evaluate the extent of surface modification using the silane coupling agent. On the other hand, the calculated extent of condensation allows us to evaluate efficiency of modification, in the form of a chemical reaction. As indicated by

Table 1
Composition of waterborne acrylic paint AKRYL LAKMA for outdoor use

| Component | Amount (wt.%) |
|---|---|
| Acrylic dispersion | 20–25 |
| Titanium white R001[a] | 14–16 |
| Carbonate and dolomite fillers | 40–45 |
| Dispersing agents, wetting agents, densifiers | 1–3 |
| Water | 25–30 |

[a] Zakłady Chemiczne Police.

Table 2
Composition of solventborne acrylic paint AKRYBET for outdoor use

| Component | Amount (wt.%) |
|---|---|
| Acrylic resin | 10–15 |
| Titanium white R001[a] | 14–16 |
| Carbonate and dolomite fillers | 40–45 |
| Dispersing agents, wetting agents | 1–2 |
| Organic solvent | 25–35 |

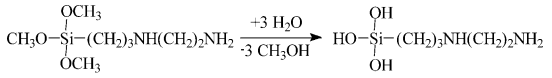
[a] Zakłady Chemiczne Police.

Table 3
Composition of waterborne acrylic paint AKRYL W LAKMA for indoor use

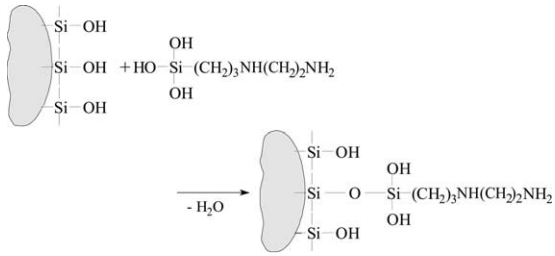
| Component | Amount (wt.%) |
|---|---|
| Acrylic dispersion | 5–10 |
| Titanium white R001[a] | 4–8 |
| Carbonate and dolomite fillers | 40–45 |
| Dispersing agents, wetting agents, densifiers | 1–3 |
| Water | 35–40 |

[a] Zakłady Chemiczne Police.

the data presented in Table 4, the extent of surface silanol group condensation has been increasing slowly due to modification with the silane U-15 as well as with an increasing amount of the applied silane. In the course of preparation of the modifying solution, the aminosilane U-15 has been undergoing a hydrolysis:




The hydrolysed silane has contained hydroxy groups and, therefore, has been capable of condensation with the silica surface silanol groups, as presented below:




Increasing amounts of silane in the modifying solution have resulted in increasing frequency of silanol group condensation with hydroxy groups of the silane. Therefore, an increased extent of condensation has been observed (Table 4).

CP/MAS NMR spectra of $^{29}Si$ for the unmodified Syloid 244 silica and for the silica modified with 3 weight parts of the silane U-15 in a methanol/water mixture are presented in Fig. 1. Analysis of the obtained spectra has confirmed the chemical

Table 4
Peaks surfaces for 7326 $cm^{-1}$ band and the condensation extent of silanols on the surface unmodified and aminosilane U-15 modified silica Syloid 244

| Modification medium | Amount of silane (parts by weight) | Planimetric method | | Geometric method | |
|---|---|---|---|---|---|
| | | Peak surface ($cm^2$) | Condensation extent (%) | Peak surface ($cm^2$) | Condensation extent (%) |
| – | 0 | 3.46 | – | 3.09 | – |
| Methanol/water | 1 | 3.25 | 6.1 | 3.01 | 2.6 |
| Methanol/water | 3 | 3.00 | 1.3 | 2.86 | 7.4 |
| Methanol/water | 5 | 2.50 | 2.7 | 2.39 | 22.7 |

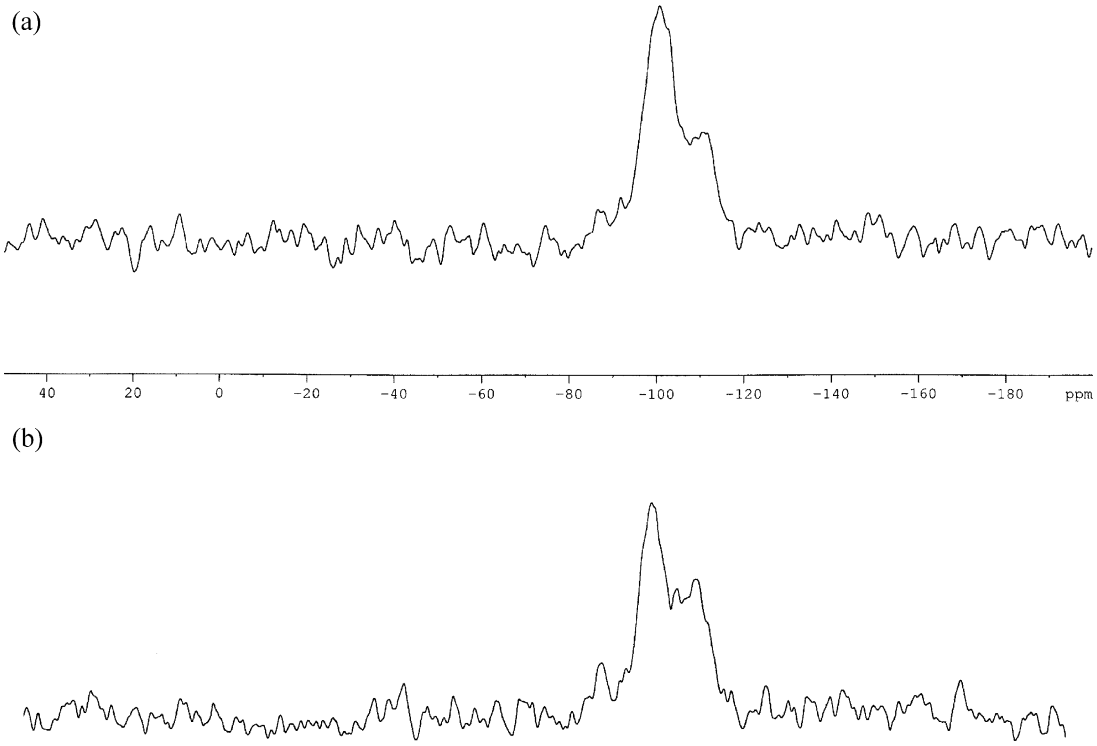



Fig. 1. $^{29}$Si CP/MAS NMR spectrum of silica Syloid 244 unmodified (a) and modified with three parts by weight of U-15 silane (b).

course of silica surface modification. The modification could have been noted to promote reduction of the clearly noticeable signal $Q_2$ ($\delta = -91$ ppm) in the spectrum of the original silica, which has become less intense in the case of the modified silica. Moreover, increased intensity of the $Q_4$ band ($\delta = -109$ ppm) has been observed in the spectra for the modified silica, pointing to formation of new siloxane bonds. In the spectrum, no clearly distinguishable bands have been noted, originating from the bound silanes, probably due to a low surface concentration of the reagents. Nevertheless, results of tests in near infrared range and elementary analysis have confirmed that the modification has in fact taken place and that it has been of a chemical nature.

The extent of coating silica surface with the reacting with it silane has been determined on the base of elementary analysis data and the calculated surface concentrations of the bound silane. The calculations have been performed basing on the relation suggested by Berendsen and Galan [16], Hemetsberg et al. [17]. As can be concluded from the data of Table 5, only a fraction of silica surface silanol groups has reacted with the aminosilane. Surface concentrations of the silane ranged between 0.1 and 0.5 μmol/m$^2$. Silanol group concentration on the surface of precipitated silica is estimated at around 8 μmol/m$^2$, but for spherical reasons only a fraction of the groups may undergo the reaction. The presented data allow to note that the extent of coating has increased with increasing amounts of aminosilane used for the modification.

Particle size distribution for the unmodified precipitated Syloid 244 silica is presented in Fig. 2a. The silica structure has comprised aggregates and agglomerates. The primary structures (aggregates) have yielded a definitely more intense band in the range 429.4–569.3 nm (maximum intensity of 100 has corresponded to the aggregate size of 508.6 nm). The much less intense band has corresponded

Table 5
Elemental analysis of unmodified silica Syloid 244 and modified with U-15 silane

| Sample | Amount of carbon (%) | Amount of nitrogen (%) | α (μmol/m$^2$) |
|---|---|---|---|
| Syloid 244 | 0.22 | 0 | – |
| Syloid 244 + 1(m/w)U-15 | 0.58 | 0.21 | 0.11 |
| Syloid 244 + 3(m/w)U-15 | 0.62 | 0.22 | 0.12 |
| Syloid 244 + 5(m/w)U-15 | 1.65 | 0.67 | 0.46 |

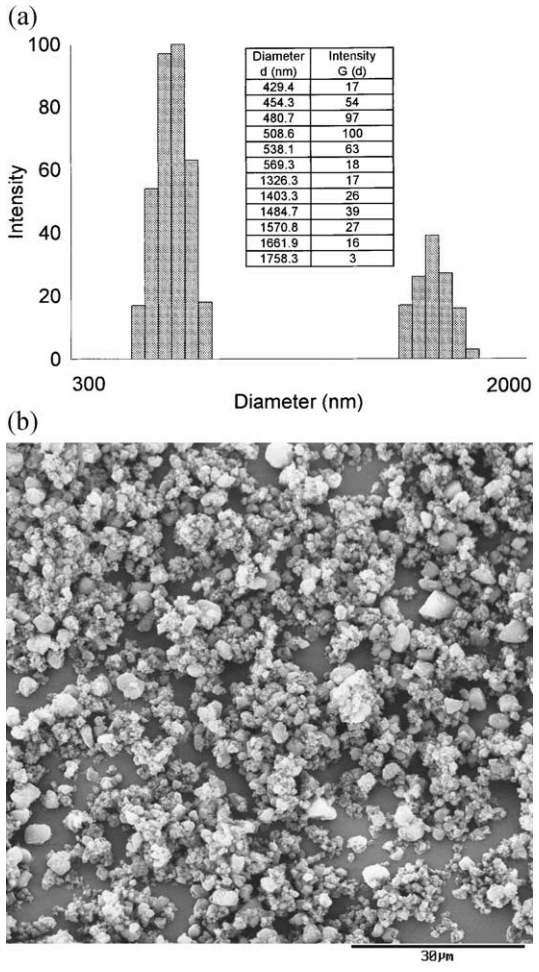



Fig. 2. Particle size distribution (a) and scanning electron micrograph (b) of unmodified silica Syloid 244.

to the formed secondary structures (agglomerates) in the diameter range 1326.3–1758.3 nm (maximum intensity of 39 has corresponded to the diameter of 1484.7 nm). The silica has exhibited polydispersity of 0.132 order and a high zeta potential (−39.40 mV). The mean particle diameter has amounted to 765.0 nm. Thus, the silica manifested certain heterogeneity. Additional data on the parameter have been provided by the electron microphotograph presented in Fig. 2b. The obtained pigment has manifested a highly uniform character (Fig. 3b). The observation has been corroborated by the particle size distribution. The pigment on a silica carrier manifested a single band only, which corresponded to the formed aggregates (Fig. 3a). The band has spanned the very narrow range 660.2–676.5 nm. The particle size and the polydispersity value of 0.005 ascertained the highly uniform character of the obtained pigment. The mean particle diameter has been 668.3 nm and zeta potential has amounted to −13.88 mV.

As indicated by the data of Table 6, efficiency of adsorption of the helactine blue R (C.I. Reactive Blue 19) on the silica surface has been significantly affected by modification of the surface with the silane. On the unmodified silica surface no dye could have been adsorbed (zero adsorption efficiency). Silica modification has resulted in an increased adsorption. A particularly high efficiency of the adsorption has been obtained for the silica modified with 5 weight parts of U-15 silane (97%). The higher amounts of the appropriate silane have been used for silica modification, the higher organic dye adsorption efficiency has been noted.

In studies on microporous structure, BET isotherm has been applied. Nitrogen adsorption/desorption isotherm for the pigment obtained on the Syloid 244 silica is presented in Fig. 4. The obtained isotherm is typical for compounds of wide pores. As documented in Table 7, the unmodified silica manifested the specific surface area of 333.5 m$^2$/g, total pore volume of 1.3693 cm$^3$/g and the mean pore diameter of 164.23 Å. Modification with the aminosilane in methanol/water (4:1) mixture decreased both the specific surface area and the pore volume while the mean pore diameter increased to 195.65 Å. The pig-

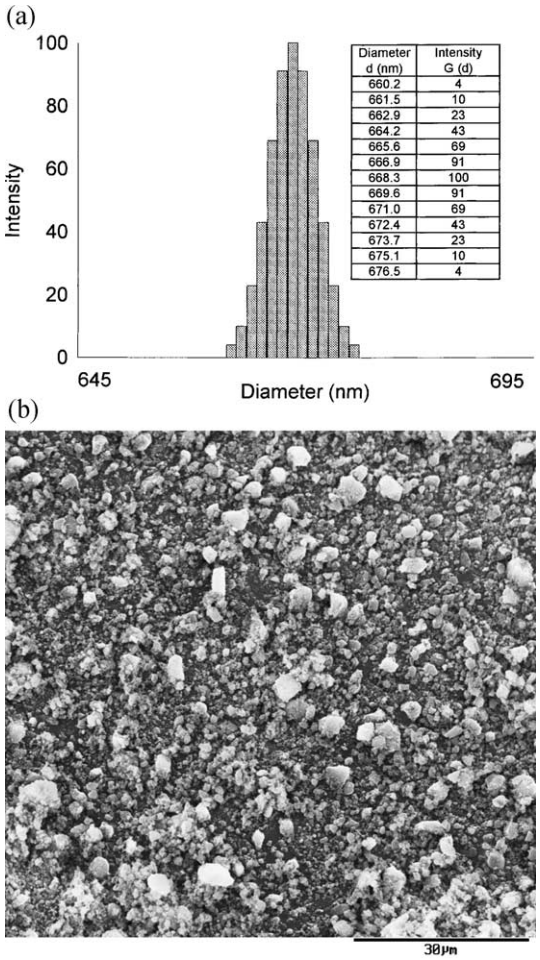



Fig. 3. Particle size distribution (a) and scanning electron micrograph (b) of silica Syloid 244 modified with three parts by weight of U-15 silane (in methanol/water mixture) after adsorption of C.I. Reactive Blue 19.

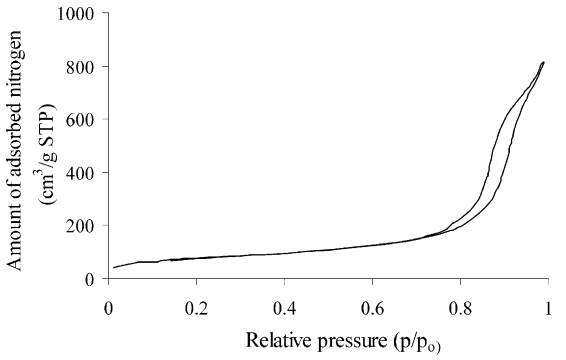



Fig. 4. Adsorption/desorption isotherm for pigments obtained by adsorption of C.I. Reactive Blue 19 on silica Syloid 244 modified with three parts by weight of U-15 silane in methanol/water mixture.

ment obtained by binding of the organic dye, C.I. Reactive Blue 19 to silica surface has manifested the lowest specific surface area, the lowest total pore volume while the mean pore diameter was intermediate between the values noted for the unmodified silica and the modified silica: it amounted to 167.54 Å. The decrease in specific surface area might have resulted from blockade of active sites both due to modification of silica surface with organofunctional silane and due to adsorption of the organic dye.

The test of preparing a water-soluble façade acrylic paint, AKRYL LAKMA using 9% supplementation with the tested pigment has proven unsuccessful. No positive result could have been obtained even is the paint recipe were modified by decreasing the contents of the pigment or of the fillers. The pigment has proven to be exceedingly hygroscopic.

Table 6
Adsorption extent of C.I. Reactive Blue 19 dye (adsorption time—4 h)

| Modification medium | Amount of silane (parts by weight) | Dyes concentration before adsorption ($mg/cm^3$) | Dyes concentration after adsorption ($mg/cm^3$) | Disposal extent (%) |
|---|---|---|---|---|
| – | 0 | 0.400 | 0.400 | 0 |
| | | U-15 | | |
| Methanol/water | 1 | 1.200 | 0.272 | 77 |
| Methanol/water | 3 | 1.200 | 0.309 | 74 |
| Methanol/water | 5 | 1.200 | 0.002 | 97 |

Table 7
Specific surface area, pore volume and pore diameter for unmodified, modified silica Syloid and obtained pigment after adsorption of C.I. Reactive Blue 19 dye

| Sample | Specific surface area BET ($m^2/g$) | Total pore volume ($cm^3/g$) | Mean pore diameter (nm) |
|---|---|---|---|
| Syloid 244 | 333.5 | 1.3693 | 16.4 |
| Syloid 244 + 3U-15(m/w) | 288.5 | 1.4109 | 19.5 |
| Syloid 244 + 3U-15(m/w) + RB19 | 273.4 | 1.1449 | 16.7 |

Good results have been obtained applying the studied pigment in the dispersion acrylic paint for indoor use, AKRYL W LAKMA. The paint was prepared with 5% content of the pigment (standard content ranges between around 6 and 10%). However, after some time the paint consistency became semi-gelatinous. It seems that excessive amounts of the pigment were added the amounts have been lower than required by the standard. As can be noted in Table 8, the paint obtained corresponded in quality to the commercial paint, i.e. the paint containing in its composition no tested pigment. The paint exhibited the same resistance to wet scrubbing (1500 advances) as required by both the product quality control of the LAKMA company and by the Polish Norm. The so high value of the parameter reflects the effects of the binder, the pigment and the silica. The remaining parameters, such as density, viscosity or quality of coating, were consistent with requirements of the norm. Each paint should exhibit a high coating capacity. When the paint coats the painted surface more effectively lower amounts of the paint have to be used and the painting is more economical. Moreover, an exceedingly thick paint coat may crack and chip off the base. In the case of coating power an excellent result was obtained (Fig. 5a) although the coating effect cannot be noticed until some time elapses (it cannot be evaluated during painting). At the wet stage the paint seems to fail in coating the surface. In cases of other water-soluble paints such a problem cannot be noticed. Thus, should the tested pigment be applied in paint production on an industrial scale, the problem remains of overcoming human painting habits. Also the tests of coat adherence to the base have yielded good results. Studies on the extent of drying and on coat drying time have shown that the first degree of drying is obtained after 15 min (the applied small spheres can be removed completely with a brush without damaging the coat). This indicates that the superficial layer of the coat is dry. The fifth degree of drying is obtained after 27 minutes, i.e. after that time another layer of the paint can be applied (a paper does not stick to the coated surface and the sites of pressing the surface manifest no perceptible changes in the painted surface). A coat consisting of the paint having

Table 8
Parameters of waterborne acrylic paint AKRYL W LAKMA for indoor use[a]

| Parameter | Norm requirement PN-98/C-81914 | AKRYL W LAKMA white | AKRYL W LAKMA containing S + 3U-15 + RB19 |
|---|---|---|---|
| Density ($g/cm^3$) | 1.60 | 1.50–1.60 | 1.29 |
| Viscosity KW10 (Pa s) | – | Drips after 10–30 | drips after 8 |
| Drying time | | | (20 °C, 62% air humidity) |
| 1° (min) | – | – | 15 |
| 5° (min) | $\leqslant$3h | – | 27 |
| Resistance to wet scrubbing | 750 | $\geqslant$1500 | 1500 advances |
| Quality coating | II | II | II |

[a] Example: S–3U-15–RB19 means silica Syloid 244 modified with three parts by weight of U-15 silane (in methanol/water mixture) after adsorption of C.I. Reactive Blue 19 dye.

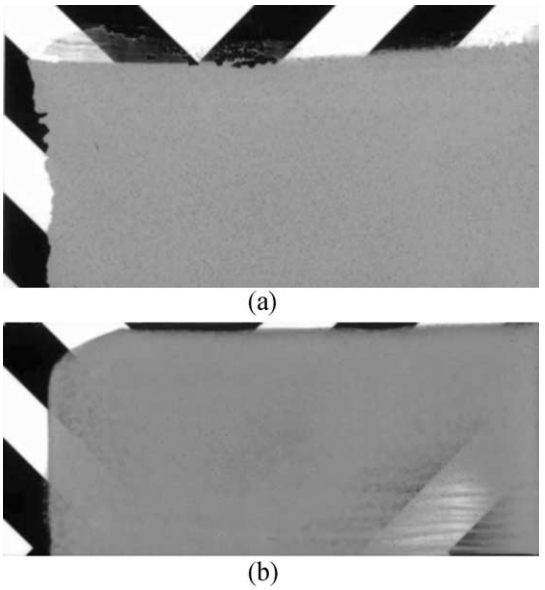



Fig. 5. Degree of coverage (a) AKRYL W LAKMA paint (b) AKRYBET paint.

been incised with a grid pattern, has demonstrated a satisfactory adherence and the margins of the cuts have made no splinters of the coat. Upon the tests of the paint capacity to be applied with a brush the composition obtained was found to be easily distributed and the coat obtained exhausted all the respective requirements. Moreover, the paint could have been diluted at will with water. It should be noted that the obtained coat has been rough to the touch. It is tempting to conclude that the obtained roughness effect provides us with a product which resembles a structural paint (with a visible fine structure). However, the obtained coat was more resistant to soiling as compared to coats obtained with a typical structural paint.

Applying the tested pigment in the organic solvent-soluble outdoor acrylic paint, AKRYBET a positive result was obtained after a significant decrease (by 50%) in the prescribed amount of added fillers (Table 5). In the successful composition the pigment content has amounted to 11% (standard: 12%). Similarly to the case of AKRYL W LAKMA paint, a coat rough to the touch was obtained. Thus, also in this case the paint of a visible fine structure was obtained. The coat obtained following after application of the tested AKRYBET paint has exhibited an excellent resistance to wet scrubbing but a moderate quality of coating (Fig. 5b). However, also in the case of this paint the coating effect cannot be appreciated until the coat has dried completely. Tests on the extent of drying and on drying time demonstrated that the first degree of drying was obtained after 40 min and the second degree after 48 min. Tests of adherence to the base have demonstrated no torn sites on edges of the testing cuts. Moreover, the obtained paint has created no problems upon its application with a brush.

## 4. Conclusion

The designed technique for modification of silica surface with aminosilanes has created a potential for obtaining products showing stable binding of silanes with the silica surfaces. Efficiency of the modification has been estimated on the basis of spectrophotometric studies (NIR) and tests of

Table 9
Parameters of solventborne acrylic paint AKRYBET for outdoor use

| Parameter | Norm requirement PN-91/B-10102 | AKRYBET white | AKRYBET containing of S + 3U15 + RB19 |
|---|---|---|---|
| Density (g/cm$^3$) | $\leqslant$1.60 | 1.35–1.50 | 1.15 |
| Viscosity KW10 (Pa s) | Stable—2 h | Drips after 50–150 | drips after 65 |
| Drying time | | | (20 °C, 62% air humidity) |
| 1° (min) | – | – | 40 |
| 5° (min) | – | – | 48 |
| Resistance to wet scrubbing | 1500 | 1500 | No base exposure after 12000 advances |
| Quality coating | II | II | II |

nuclear magnetic resonance ($^{29}$Si CP/MAS NMR). The studies have confirmed a marked change in the number of surface silanol groups on the modified silicas. The estimated extent of condensation of surface silanol groups has clearly increased following modification with increasing amounts of the applied modifying compounds. Elemental analysis has provided additional proof for the chemical reaction-based course of modification: it has permitted us prove that the extent of coating of the silica surface has increased with the increasing amounts of aminosilane used for the modification.

In the modern systems of paints and varnishes the stability of pigments represents an important variable, crucial for their application potential. Stability of the obtained pigments is tested by their sensitivity to elution with cold and hot water of the potentially unbound dye molecules. The tests performed have proved that no dye could have been eluted from the tested pigments. This has proved that the tested pigments have been obtained by chemical sorption of organic dyes on the modified silica surface. Adsorption of organic dyes on the surface of silica carriers has promoted a significant increase in homogeneity of the particles, destruction of agglomerate structures and an evident decrease in polydispersity. Such parameters are typical for high quality, highly dispersed, solid pigments.

A significant effect has been noted of silane modification and, then, of adsorption of organic dyes on the silica surface on their specific surface area and on their porous structure. The modification and the adsorption have clearly decreased the specific surface area as well as the pore diameter. The blue pigment obtained on a technological scale may find application both in water- and organic solvent-soluble paints for indoor and outdoor use. The potential has been confirmed by tests performed on semi-technological scale in LAKMA S.A. in Cieszyn.

## Acknowledgements

The authors are indebted to "Boruta-Kolor" Sp. z o.o. for a gift of the dye used in the studies. This work was supported by grant No. BW 32/117/2003.

## References

[1] Ledger R, Stellwagen E. Journal of Chromatography, A 1984;299:175.
[2] Giesche H. Matijević, E Dyes and Pigments 1991;17:323.
[3] Wu G, Koliadima A, Her Y-S, Matijević E. Journal of Colloid & Interface Science 1997;195:222.
[4] Winnik FM, Keoshkerian B, Fuller JR, Hofstra PG. Dyes and Pigments 1990;14:101.
[5] Hsu WP, Yu R. Matijević, E Dyes and Pigments 1992;19:222.
[6] Tentorino A, Matijević E, Kratohvil JP Journal of Colloid & Interface Science 1980;77:418.
[7] Albert K, Brindle R, Schmid J, Buszewski B, Bayer E. Chromatographia 1994;38:283.
[8] Legrand AP, Hommel H, d'Espinose de la Caillerie JB. Colloids & Surfaces A 1999;158:157.
[9] Brindle R, Albert K, Harris SJ, Tröltzsch C, Horne E, Glennon JD. Journal of Chromatography, A 1996;731:41.
[10] Nawrocki J. Journal of Chromatography, A 1997;779:29.
[11] Albert K, Bayer E. Journal of Chromatography, A 1991; 544:345.
[12] Krysztafkiewicz A, Binkowski S. Pigment and Resin Technology 1999;28(5):270.
[13] Binkowski S, Jesionowski T, Krysztafkiewicz A. Dyes and Pigments 2000;47:247.
[14] Krysztafkiewicz A, Jesionowski T, Binkowski S. Colloids & Surfaces A 2000;173:73.
[15] Binkowski S, Krysztafkiewicz A. Pigment and Resin Technology 2002;31:2 96.
[16] Berendsen GE, de Galan L. Journal of Liquid Chromatography 1978;1:561.
[17] Hemetsberger H, Kellerman M, Ricken H. Chromatographia 1977;10:726.