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New Water-Dispersible Silica-Based Pigments: Synthesis and Characterization

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ABSTRACT

Water-dispersible pigments were prepared by grafting reactive dyes to the surface of derivatized silicas. The silica core consisted of either fumed hydrophilic silica with surface areas of 200 or 380 $m^2\,g^{-1}$ *or monodisperse spherical silica ranging in diameter from 40 to 500 nm. The silica surface was derivatized with silane coupling agents, such as aminopropyltriethoxysilane (APS) and* N,N-*bis(2-hydroxyethyl)-3-aminopropyltriethoxysilane (BHAPS). The coloration proceeded on suspensions of the derivatized silica in water in the presence of a soluble reactive dye. The resulting brightly colored pigments were characterized by particle size analysis and visible absorption spectroscopy.*

INTRODUCTION

Surface modification of inorganic particles with organic compounds is an area of considerable activity. It has applications in organic synthesis,[1] catalysis,[2] enzyme analysis,[3] chromatography,[4,5] and ion-exchange.[6,7] It has also been used in the field of color chemistry. Two major applications have been sought out: (1) new supports for affinity chromatography prepared by attachment of dyes to silica-based chromatographic supports;[8,9] and (2) new colorants for electrophotographic toners.[10,11] These materials

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offer many advantages over conventional pigments. Their particle sizes are determined by the size of the starting silica which ranges from 20 nm to 2 μm. Also, from a single core material it is possible to prepare pigments identical in particle size, density and surface properties, but varying greatly in color and hue.

The preparation of silica-based pigments disclosed in a patent to Mita proceeds by a stepwise synthesis of the chromophore on the surface of the silica: an aromatic group is covalently bound to a surface-treated silica, the immobilized aromatic group is then subjected to nitration, reduction, diazotization, and coupling.[7] A shorter synthesis of colored silicas was developed in this laboratory. It consists of the grafting of reactive dyes onto surface-modified silicas. This single-step procedure takes advantage of the large inventory of commercial reactive dyes employed in the textile industry. We present here a detailed description of this coloration procedure. Optimal reaction conditions and purification procedures are reported. Properties of pigments prepared from different types of silicas are compared.

EXPERIMENTAL

Materials

Chemicals were purchased from Aldrich Chemicals Co. unless otherwise stated. The silicas Aerosil-200 and Aerosil-380 were obtained from Degussa. Monodisperse silicas were prepared by hydrolysis of tetraethoxysilane with ammonia in aqueous ethanol, following the procedure described by Stöber *et al.*[13] The reactive dyes Procion Turquoise HA, and Procion Yellow MX-8G were obtained from ICI. Levafix Brilliant Red EGBA, Levafix Brilliant Blue EFFA, and Levafix Black EB were obtained from Bayer.

Equipment

Visible absorption spectra were recorded with a Hewlett Packard 8450A diode array spectrometer. Particle sizes were determined using a Brookhaven BI-90 particle sizer. Ultrafiltration was performed with a Minitan Acrylic System (XX42 ASY MT) from Millipore, equipped with four 0·1 μm membranes. Titrations were performed with a System 7000 Acoustophoretic Titrator from PenKem. Centrifugations were at 12 000 rpm with a Beckman Centrifuge. Transmission electron microscopy was carried out on a Philips EM400 Transmission Electron Microscope operated at 120 kV.

Preparation of surface modified silica: general procedure (see Table 3)

A three-necked round-bottom flask equipped with a mechanical stirrer, a dropping funnel, a Dean–Stark condenser and a nitrogen inlet was charged with silica (dried at 160°C under vacuum for 24 h and cooled in a desiccator) and dry toluene. The coupling agent (APS, AMPS, or BHAPS) was added dropwise to the stirred suspension. At the end of the addition the suspension was heated at reflux for 5 h. The cooled suspension was filtered. The solid was washed once with toluene and twice with methanol. Filtrations or centrifugations were executed after each solvent treatment. An aliquot of the solid was separated. After being dried *in vacuo* it was fully characterized. The remaining solid was dispersed in water to prepare a 2% (by wt) dispersion which was used in the coloration step.

Coloration of the surface modified silicas: general procedure for amino-silicas

A solution of the reactive dye in water (*c.* 20 g litre^{-1}) was added to a stirred suspension of the amino-silica in water (2% by wt). The suspension was stirred at room temperature for 24 h. It was purified by ultrafiltration to remove excess unreacted dye. The ultrafiltration was continued until the amount of unreacted dye was less than 1% by weight of silica, as determined by the optical density of the filtrate at the wavelength of maximum absorbance of the dye. The suspension of colored silica in water was then concentrated to 5% by wt. The colored silica was isolated by freeze-drying.

Coloration of hydroxy-silicas

Levafix Blue EFFA (13·0 g) was added to a suspension of hydroxy-silica (Aerosil-380-BHAPS, 3·0 g) in 10% aqueous sodium bicarbonate (300 ml). The suspension was stirred at room temperature for 2 days. The colored silica was purified by filtration to remove the excess dye. It was isolated by freeze-drying (1·4 g).

Titration of the amino-functionalized silicas

Sulfuric acid (5·0 ml, 0·3M) was added to a suspension of the amino-silica (0·50 g) in water (250 ml). The silica was separated by filtration from the acidified suspension and the titration was effected by addition of KOH to the filtrate. The number of amino groups grafted to the silica surface was calculated from the end point of the titration (Table 3).

Determination of the amount of silica-bound dye by visible absorption spectroscopy

A known amount of silica was dispersed in DMSO ($n_D^{20} = 1{\cdot}4783$) to yield an optically clear suspension. The visible spectrum of the suspension was recorded and the optical density at the wavelength of maximum absorbance was determined. With Reactive Blue 2 it was possible to calculate the dye concentration, using a molar extinction coefficient of 13 600 at 610 nm.

Effect of reaction time on the coloration procedure

A solution of Reactive Blue 2 (6·5 g) in water (10 ml) was added to a stirred suspension of amino-functionalized silica (5·0 g, Aerosil-380, $2{\cdot}19 \times 10^{-3}$ mol NH_2 g^{-1}) in water (150 ml). Aliquots (10 ml) of the suspension were taken at regular time intervals. They were purified by ultrafiltration to remove the excess dye. The purified sample was analyzed by visible spectroscopy to determine the amount of dye attached to the silica surface.

RESULTS AND DISCUSSION

Preparation of the pigments

The core material

The pigments were prepared from two types of silicas: (1) commercial fumed hydrophilic silicas prepared at high temperature by reaction of tetrachlorosilane with hydrogen, oxygen and water;[12] and (2) monodisperse spherical silicas prepared in the laboratory by an ammonia-catalyzed hydrolysis of tetraethoxysilane in aqueous ethanol.[13] Physical characteristics of the samples are listed in Table 1. It can be seen that the silicas differ greatly in particle size and in surface area. The chemical reactivity of the silica surface is due to the presence of silanol groups. Their surface density has approximately the same value in both types of silicas (*c*. 5×10^{18} m^{-1}).[14] Both types of materials are extremely hydrophilic and under normal conditions their surface is covered with a layer of water hydrogen-bonded to silanol groups. In order to perform reactions with the silanol functionalities on the surface it is crucial to dry the silicas thoroughly by heat treatment under vacuum. The silanol groups then become extremely reactive, especially towards condensation with alkoxysilanes.[15]

TABLE 1
Physical Characteristics of the Silicas[13]

Silica	*Particle size* (m^9)	*Surface area* $(m^2\,g^{-1})$	*Silanol density* $(mmol\,g^{-1})$
Aerosil-200	12	200	0·93–1·4
Aerosil-380	7	380	1·2–2·0
Monodisperse spherical silica	40, 120, 500	<60	

The colorant

In reactive dyes a chromophore is linked to a functional group capable of undergoing a chemical reaction with hydroxyl, amino, or thiol groups.[16] Reactive dyes find their major industrial application in the dying of fibers, to which they impart generally wet-fast colorations due to the covalent linkage between dye and fiber. The dyes are classified according to the chemical structure of the reactive groups and the type of chromophore.[17] In this study we selected dyes which react with primary amines and alcohols by a nucleophilic aromatic substitution of chlorosubstituted heterocycles, except in the case of a black dye for which the linkage to the substrate occurs by a nucleophilic addition to an activated double bond (Table 2). While the precise structure of the dyes was not always known, in most cases we had sufficient information on the reactive groups and on the chromophores to carry out the coloration of the silicas and their characterization. For experiments requiring quantitative determination of dye concentrations, we used Reactive Blue 2, a dye of known structure and purity.

TABLE 2
Reactive Dyes Used in this Study

Dye	*Reactive group*	*Chromophore*
Levafix Brilliant Red E-6BA C.I. Reactive Red 159	Dichloroquinoxaline	Azo
Levafix Brilliant Blue EFFA C.I. Reactive Blue 181	Dichloroquinoxaline	Anthraquinone
Levafix Black EB C.I. Reactive Black 5 (20505)	Vinylsulfonyl	Disazo
Procion Turquoise HA C.I. Reactive Blue 71	Monochlorotriazine	Phthalocyanine
Procion Yellow MX-8G C.I. Reactive Yellow 86	Dichlorotriazine	Azo
C.I. Reactive Blue 2	Monochlorotriazine	Anthraquinone

The coloration process

Initial experiments with either fumed silicas or monodispersed silicas indicated that the direct grafting of reactive dyes to the silica surface is inefficient. For example treatment of Aerosil-200 dispersed in an aqueous potassium hydroxide solution with the reactive dye Levafix Brilliant Blue EFFA gave light blue particles. To prepare deeply colored pigments it was necessary to render the silica surface more reactive towards the dyes. This was achieved by grafting short hydroxy- or amino-terminated alkyl chains on the surface following well-established techniques (Fig. 1). Reaction of the silicas with *N*,*N*-bis(2'-hydroxyethyl)-3-aminopropyltriethoxysilane (BHAPS) gave hydroxy-substituted silicas. The amount of organic material on the treated silica was calculated from elemental analysis for nitrogen. Reactions of silica with 3-aminopropyltriethoxysilane (APS) or 3-aminopropyltrimethoxysilane (APMS) led to amino-substituted silicas. In this case

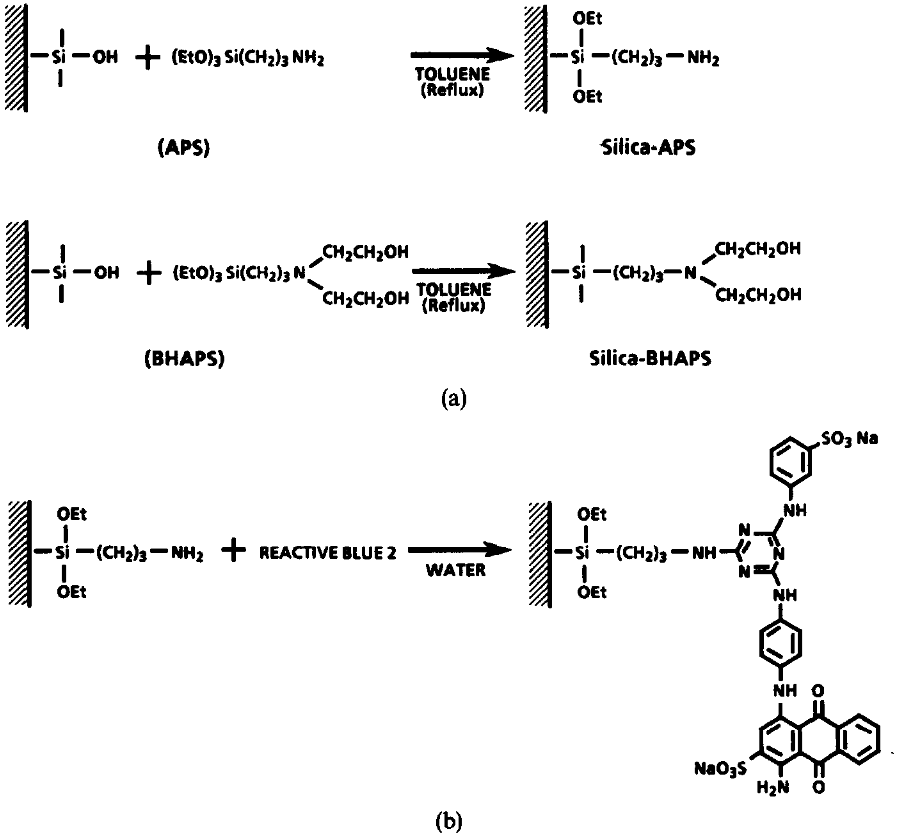

Fig. 1. Preparation of colored silicas: synthetic scheme. (a) Silica surface treatment; (b) silica coloration.

TABLE 3
Preparation of Surface Modified Silicas Reaction Conditions

Silica		*Coupling agent*			*Toluene (ml)*	*NH_2 content ($10^3\,mol\,g^{-1}$)*
Type	*Amount*	*Type*	*Amount*			
Aerosil-200	12·7 g	APMS	8·4 g	0·047 mol	200	0·8
Aerosil-380	45·0 g	APS	53·8 g	0·248 mol	500	2·2
Aerosil-380	20·0 g	BHAPS	52·5 ml[a]	0·105 mol	500	—
45-m^{-9}	5·0 g	APS	0·62 g	0·0028 mol	100	1·0
120-m^{-9}	5·0 g	APS	0·43 g	0·0019 mol	100	0·4
500-m^{-9}	3·0 g	APS	0·94 g	0·0042 mol	70	0·01

[a] Volume of a 62% ethanolic solution.

the number of amino groups on the treated silicas was determined by a reverse acid–base titration (Table 3).

The surface-treated silicas were then colored. In the case of the amino-substituted silicas, coupling occurred efficiently in aqueous dispersions with many reactive dyes, as indicated by the formation of deeply colored pigments. The reaction of the hydroxy-substituted silicas required the addition of a soluble base to the aqueous dispersions. It also led to highly colored materials.

The progress of the coloration reaction as a function of time was monitored in the case of an amino-functionalized Aerosil-380 treated with Reactive Blue 2. The composition of the initial reaction mixture was chosen to correspond to a situation where there is an excess dye relative to the amino groups on the silica ($[\text{dye}]:[NH_2] = 1:9$). Under these circumstances the reaction reached completion after *c.* 8 h (Fig. 2).

Characterization of the pigments

Particle size

Evidence from transmission electron microscopy and light scattering measurements confirms that the coloration does not affect the size of the silica, either in the case of the Aerosil-based materials, or in the case of spherical silicas (Fig. 3). Also the electron micrographs corroborate light scattering results on the monodispersity in size of the silicas prepared from tetraethoxysilane.

Color

The colors of the silicas closely match those of the starting reactive dyes, reflecting the fact that the chromophore is not affected by the coupling

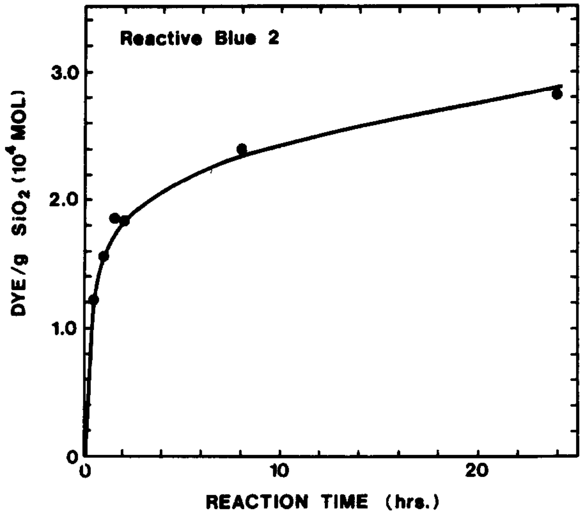

Fig. 2. Effect of reaction time on the amount of Reactive Blue 2 grafted to silica (APS-derivatized Aerosil-380).

reaction. Through proper selection of the starting dyes, yellow, magenta, and cyan pigments were prepared (Fig. 4). The quantitative determination of the amount of dye attached to the silica poses a difficult problem because in most cases neither the structure of the chromophores nor their extinction coefficients are known. In addition most dyes are not available in pure form, but rather as a mixture with water-soluble colorless materials.

To compare the dying efficiencies of various dyes and silicas, the absorbance at the wavelength of maximum absorption in the visible spectrum was determined for each colored silica sample. This value scaled to a given weight of silica (e.g. 1 g) permits a direct comparison of the color density of various samples without making any assumption on the extinction coefficient or the molecular weight of the chromophore. It is also an extremely valuable criterion for selecting the silica of highest optical density to be used in developers or inks. The values are represented in graphical form to highlight specific features of the coloration process.

- —For a given set of dye and silica (e.g. Levafix Blue EFFA and Aerosil-380) the highest level of coloration was achieved with the BHAPS-functionalized silica. This may be attributed to the fact that in BHAPS–silica, each silanol group is converted into two hydroxyl groups, thus doubling the number of sites available for reaction with the dye (Fig. 5).
- —The level of coloration of APS-Aerosil for a given dye exhibits only a mild dependence on the surface area of the starting silica. This confirms

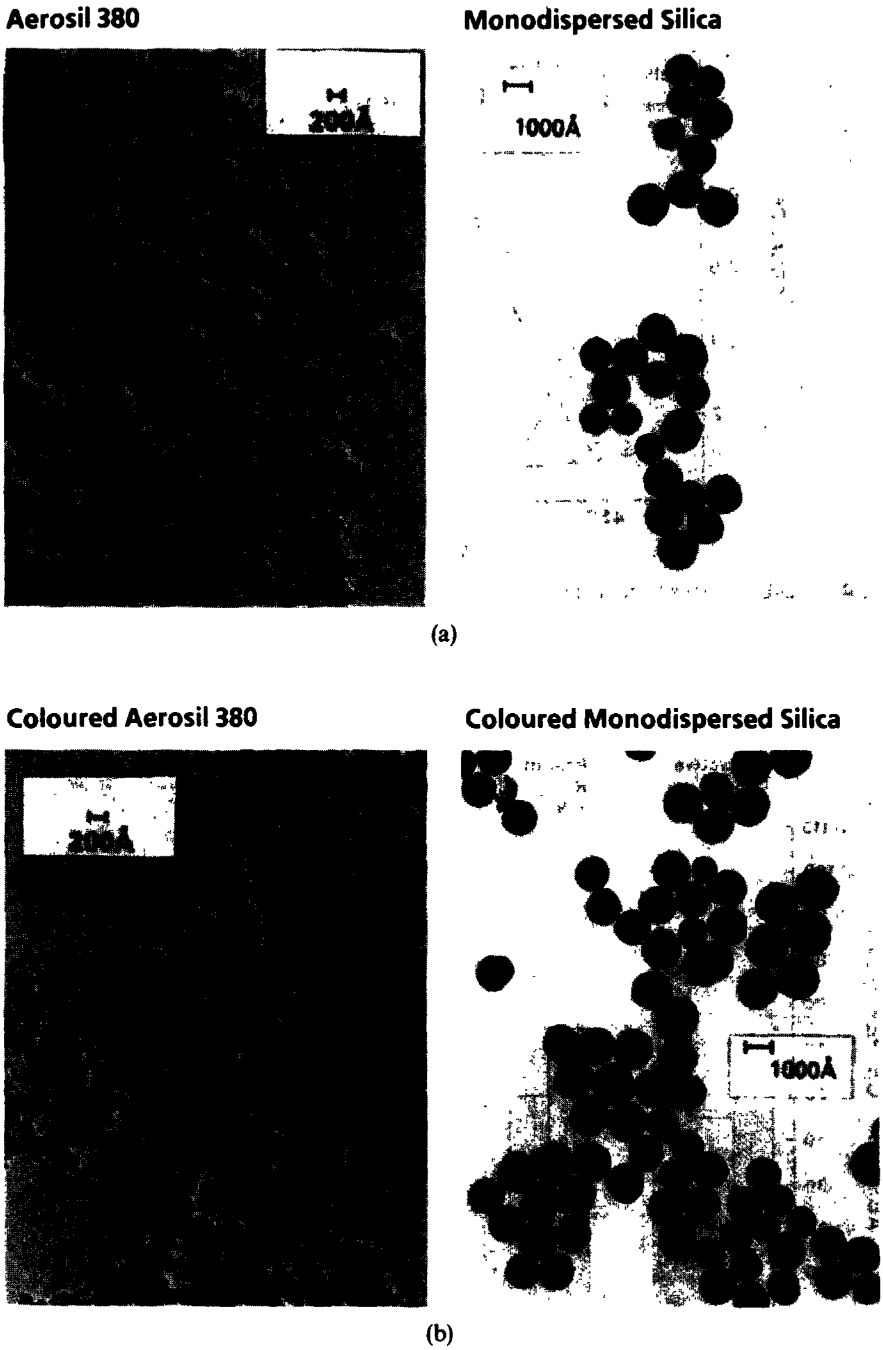

Fig. 3. Transmission electron micrographs of silicas (a) before coloration and (b) after coloration. Sample 1, Aerosil-380; sample 2, spherical silica ($d = 120\,\mathrm{nm}$).

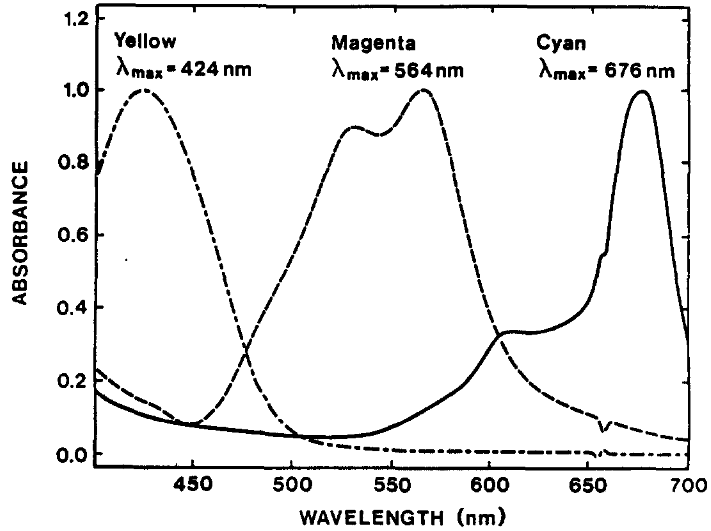

Fig. 4. Visible absorption spectra of suspensions in DMSO of colored silicas, prepared from APS-derivatized Aerosil-380 and Procion Yellow MX-8G (yellow), Levafix Brilliant Red E-6BA (magenta) or Procion Turquoise HA (cyan).

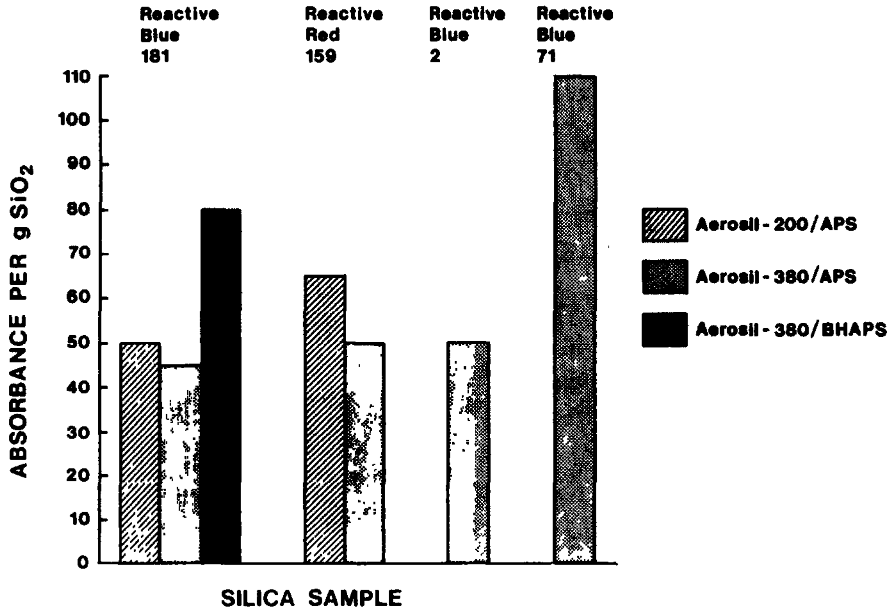

Fig. 5. Color density of pigments prepared from fumed silicas.

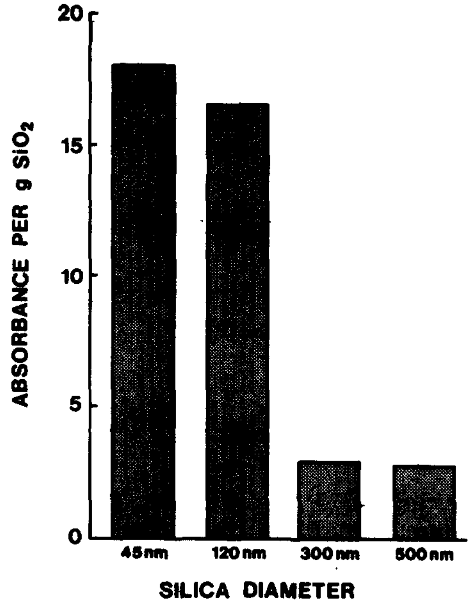

Fig. 6. Color density of pigments prepared from spherical silicas and Procion Turquoise HA (Reactive Blue 71).

the fact that the number of silanols per gram of silica is approximately the same for the two samples (Fig. 5).

- For a given derivatized silica, the color density depends on the extinction coefficient of the dye. This situation is illustrated by a comparison of the samples of APS-derivatized Aerosil-380 samples colored with four different dyes. The highest color density is achieved with Procion Turquoise HA (phthalocyanine chromophore, $\varepsilon(640\,nm) > 80\,000$). The color density obtained with the other dyes (anthraquinone or azo chromophores, $\varepsilon < 20\,000$) is lower (Fig. 5).
- For spherical silicas the color density increases with decreasing particle size, reflecting changes in surface areas. Only the samples of diameter 120 nm or less are suitable colorants (Fig. 6).

CONCLUSION

Silica-based colored pigments have been prepared by a straightforward two-step procedure that can be used with a wide range of silicas and reactive dyes. Fumed silicas and spherical silicas exhibit the same chemical reactivity in this coloration procedure. The physical properties of the resulting pigments depend on the nature of the silica core. Fumed silicas lead to pigments of tinctorial strength superior to that of spherical silica-based pigments. Other physical properties of importance concern the stability of aqueous dispersions of silica-based pigments. These will be described in a forthcoming paper.

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