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Well-Defined Pigments: I. Monodispersed Silica–Acid Dyes Systems*

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ABSTRACT

Well-defined pigment particles were produced by binding different acid dyes to monodispersed spherical silica particles. The surface of the cores was modified by coupling various aminosilanes and the dyes were converted into the acid chloride form in order to promote mutual interactions. Several methods were used to control the composition of the outermost layers of the pigments so produced. The optical properties could be altered widely, depending on the kind and amount of dye. The interfacial potential of these pigments varied with the dispersion pH and with the surface chemistry of the particles, which could be affected by the sequence of the preparation steps.

NOTATION

Si_{or}	Original silica dispersion
Si_{rt}	Silica dried at room temperature
$Si_{300-900}$	Silica calcined (at temperatures in °C)
Si_{rh}	Silica rehydroxylated
TASi	Triethoxy(aminopropyl)silane
DASi	Diethoxymethyl(aminopropyl)silane
MASi	Monoethoxydimethyl(aminopropyl)silane
TEOS	Tetraethoxysilane
FL	Flavazin L

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AR	C.I. Acid Red 183
VR	Violamin R
AB_{blue}	C.I. Acid Blue 45 (extraction residue used)
AB_{black}	C.I. Acid Blue 45 (extraction product used)

Subscripts

rt	Kept at room temperature
rf	Refluxed
ds	Ammonia and ethanol distilled off

Examples

$Si_{or}.TASi_{ds}.AB_{black}$	Original silica suspension, amino-modified with TASi and reaction completed by distilling off the NH_3 and EtOH, then Acid Blue 45 (extraction product, black) coupled to the amino group on the surface.
Si_{or}.AR–TASi/TEOS.TEOS	The Acid Red 183–TASi complex in a mixture with TEOS was grown onto the original silica particles, then a shell of silica was added.

1 INTRODUCTION

Until very recently, organic pigment research has been concerned with the production of new chromophores and insolubilizing groups, in an attempt to improve the basic fastness and coloristic properties. However, in many applications pigments have to fulfill certain other requirements, including a well-defined particle size, dispersion properties, and surface charge characteristics. It is doubtful that such specifications could be met by the synthesis of new compounds.

Smaller particles (0·02–1 μm) of narrow size distribution are of major concern to pigment users for optical and rheological reasons. Oversized dispersed solids result in adverse performance characteristics, such as brushing-up, poor gloss, 'tramlines' in printing, poor color values and storage properties.[1] Of particular interest are pigments consisting of uniform spherical particles, as their color (the purity and the dominant wavelength) can be quantitatively evaluated from the exact Mie functions.

To meet some of the above requirements, dyes have been either incorporated or covalently bound to latex,[2,3] aluminum hydroxide particles,[4] or to aminoaerosil powders.[5] However, no systematic evaluation of the optical and dispersion properties of such systems has been reported.

In this work, different dyes have been either incorporated in silica particles or adsorbed on the latter. The carrier powder consisted of exceedingly uniform spheres, the surface of which was modified in different ways in order to promote the binding of dye molecules. The resultant pigments were then analyzed in terms of their optical and charge characteristics.

2 EXPERIMENTAL

2.1 Materials

Tetraethoxysilane (TEOS, 98% Aldrich) was distilled before use (b.p. 167°C). Other reagents employed in the process, including (3-aminopropyl)triethoxysilane (Aldrich), (3-aminopropyl)methyldiethoxysilane, (3-aminopropyl)dimethylethoxysilane (Petrarch), C.I. Acid Blue 45 (Sigma), Flavazin L, C.I. Acid Red 183, and Violamin R (Aldrich), were not further purified.

2.2 Silica particles

Silica particles of diameter ~100 nm were prepared by the hydrolysis and polycondensation reaction of tetraethoxysilane (TEOS) in an ethanol/water/ammonia mixture.[6,7] For this purpose 1·66 kg dehydrated ethanol, 1·5 kg distilled water, and 0·14 kg ammonium hydroxide solution were placed in a flask and heated to 40°C; then 0·175 kg TEOS, premixed with an equal volume of dehydrated ethanol, was added under vigorous stirring. A milky white dispersion, which appeared after a few minutes, was kept overnight at 40°C without stirring to complete the reaction.

The silica particles were either (a) stored in the original reaction solution (Si_{or}), (b) filtered and vacuum-dried at room temperature (Si_{rt}), (c) calcined at different temperatures in air [at 300°C (Si_{300}), 500°C (Si_{500}), 700°C (Si_{700}), and 900°C (Si_{900})] or (d) 'rehydroxylated' after calcination at 500°C by boiling in 1 mol dm^{-3} HNO_3 for four days (Si_{500rh}). The different samples were then employed in the following surface-modification procedures.

2.3 Amino surface modification

Differently pretreated silica particles were dispersed in a mixture of 1:10:14 by vol. ammonia solution (28–30%)/water/ethanol to give a Si concentration ~0·2 mol dm^{-3}. In separate experiments three aminosilanes $\{NH_2(CH_2)_3Si(CH_3)_{3-x}(OC_2H_5)_x;\ x = 1, 2, \text{or } 3\}$ were added to these dispersions in amounts (*c.* 0·5 g aminosilane/g silica) much higher than actually needed to achieve a complete surface coverage. After a short (5 min) sonication, the samples were kept overnight at room temperature. In a second series of preparations, dispersions were kept at a higher temperature (80°C) for different periods of time. All samples were finally cleaned from an excess of aminosilane by at least five cycles consisting of centrifugation and redispersion in ethanol of the solids, which were finally vacuum-dried.

A growth process was employed to achieve an even higher aminosilane content.[7] A mixture of the aminosilane with TEOS (*c.* 1 : 1) was slowly added (over a period of 24 h) to the original silica suspension. By this process, the aminosilane was incorporated in a shell 20–25 nm thick around the original silica particles.

2.4 Dye acid chloride preparation

The acid dyes used in this study, commercially available as sodium salts, were not sufficiently reactive to be coupled to the amino group. Therefore, they were converted to their acid chloride forms.[8] For this reaction Flavazin L and Violamin R were pretreated with hydrochloric acid prior to the acid chloride preparation, whilst C.I. Acid Red 183 and C.I. Acid Blue 45 were used as received.

About 5 g dye, mixed with 10 g PCl_5 and 15 g $POCl_3$, were refluxed for 45 min in a bath at 140°C. After cooling, 40 g benzene was added, the mixture again heated to reflux, and finally quenched in an ice–water bath. The resulting mixture was then placed in a filtration thimble and the dye acid chloride (along with $POCl_3$) extracted with benzene. Finally, the solvents were distilled off and the dye dried in vacuum at temperatures not exceeding 120°C.

In the case of C.I. Acid Blue 45, the extraction did not work out as expected; only a black compound could be removed, whereas the thimble residue remained blue. Surprisingly, both parts (black and blue) could be bound to the amino-modified silica surface resulting in black- or blue-colored silica particles. The structural change of this dye molecule was not studied in this work.

2.5 Dye binding to the amino-modified silica surfaces

The amino-modified silica particles were dispersed in different solvents (ethanol, ethanol/water, or benzene). Pyridine was added to some of the mixtures to bind the hydrochloric acid, which otherwise may block some of the amino groups. Different amounts of the dye acid chloride were then admixed to the silica dispersion and the samples were either kept at room temperature or at 80°C in sealed test-tubes for 20–80 h. The solids were separated by centrifugation, redispersed in ethanol, and these steps repeated until the supernatant solution remained colorless. The same procedure was continued with an ethanol/water mixture as rinsing solution and, finally, with distilled water. The purified samples were vacuum-dried at room temperature.

2.6 Characterization

The particle size distribution histograms were obtained from transmission electron micrographs (JEOL TEM 1200 EX). The specific surface area of the dried powders was determined by the BET multipoint method with a Monosorb Surface Analyzer (Quantachrome Corp.).[9]

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out with Perkin–Elmer TGA 7 and DSC 4 systems.

The electrophoretic mobility was measured with a DELSA 440 (Coulter Electronics) instrument as a function of the pH. All samples were first dispersed in 0·010 mol dm^{-3} $HClO_4$ and sonicated for a few minutes. To achieve an essentially constant ionic strength, small amounts of a solution of NaOH were then added to adjust the pH stepwise. The problem of a partial dissolution of silica particles was avoided by exposing the samples to high pH values for a short period of time. The time effect of this treatment at different pH values on the surface characteristic was tested by electrophoresis, as discussed later.

To record the UV–visible spectra, the samples were either dissolved in 0·4 mol dm^{-3} NaOH or dispersed in polyethylene glycol (PEG, MW 200). The refractive indices of silica and of PEG 200 were well matched, thus eliminating any light-scattering effect of the core on the color determination of dyed particles.

For the reflectance measurements, the samples were first dispersed in water and then filtered using Millipore membranes. It is noteworthy that the reflectance data were recorded for a constant amount of sample (1 mg cm^{-2}) rather than an infinite particle-layer thickness. The chromaticity values x and y, as well as the purity and luminescence (Y) were calculated according to Nimeroff[10] and Judd[11] for a light source C.

3 RESULTS AND DISCUSSION

3.1 Silica particles

Silica particles of diameter *c.* 100 nm, prepared as described in the Experimental section, may have some ultramicropores, as indicated elsewhere.[7] Indeed, the original silica powder, Si_{rt}, had a specific surface area of 53 $m^2\ g^{-1}$, whereas the sample, calcined at 500°C (Si_{500}), had a corresponding area of only 34 $m^2\ g^{-1}$. The latter value is fairly close to the geometric surface area of equivalent spheres (30 $m^2\ g^{-1}$) for a particle diameter of 100 nm and a particle density of 2000 $kg\ m^{-3}$.

The samples could be redispersed when calcined at 300°C and 500°C, whereas calcination at 700°C and 900°C resulted in considerable agglomeration. Heating samples at 500°C was intended to remove the above-mentioned ultramicropores, to eliminate impurities, such as

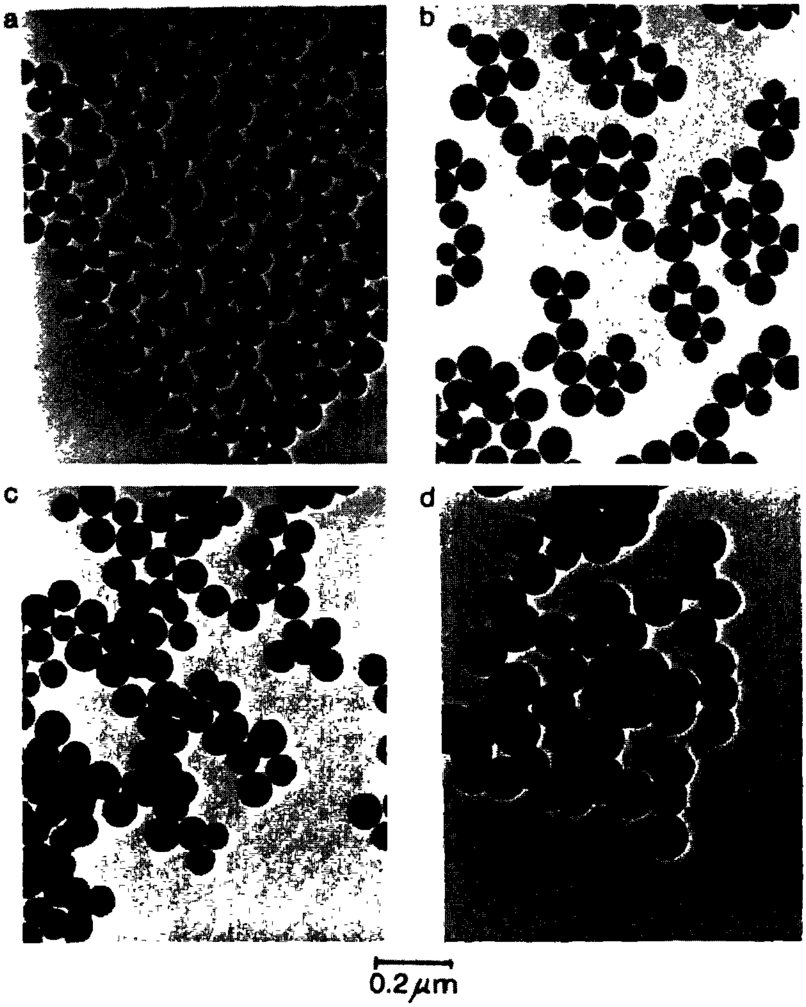

Fig. 1. Transmission electron micrographs (TEM) of silica particles: (a) original, Si_{or}; (b) calcined at 500°C, Si_{500}; (c) surface amino-modified, Si_{or}.$TASi_{rt}$; (d) TASi/TEOS (1:1) grown silica particles, Si_{or}.TASi/TEOS.

remaining ethoxy groups or incorporated ethanol and ammonia, and to alter surface characteristics, especially the number of hydroxyl groups (Müller, U., pers. comm.). However, no difference in reactivity between the original and calcined solids could be established, as described below. On calcination the number of hydroxyl groups should be reduced, as the weak groups are removed at temperatures ≤500°C, but the surface can be readily rehydroxylated.[12]

Electron micrographs in Fig. 1, (a) and (b), illustrate silica particles as prepared and calcined at 500°C for 16 h. Figure 2 shows that the size distribution of these particles remains essentially unchanged on calcination at 500°C and subsequent rehydroxylation by boiling the dispersion for four days in 1 mol cm^{-3} HNO_3.

Electrokinetic mobilities (Fig. 3) demonstrate that calcination of samples up to 500°C had no effect on surface charge characteristics of silica particles.

Thermogravimetric analysis indicated that the original silica lost water and some of the hydroxy and ethoxy groups by heating up to *c.* 350°C. Samples calcined at 500°C or 900°C showed no loss in weight when further treated up to 1200°C.

3.2 Amino-modified silica

Mono-, di-, and tri-ethoxy(aminopropyl)silanes (MASi, DASi, and TASi) were used for surface modification of the original and pretreated silica

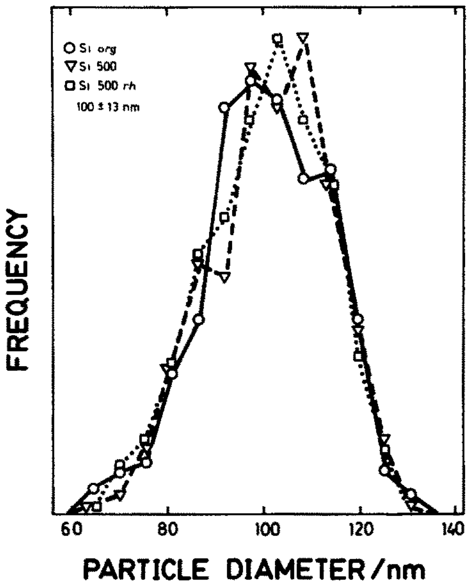

Fig. 2. Particle size distribution curves for silica particles: ○, Si_{or}, Fig. 1(a); △, Si_{500}, Fig. 1(b); □, Si_{500rh}. In all cases the mean particle diameter was 100 ± 13 nm.

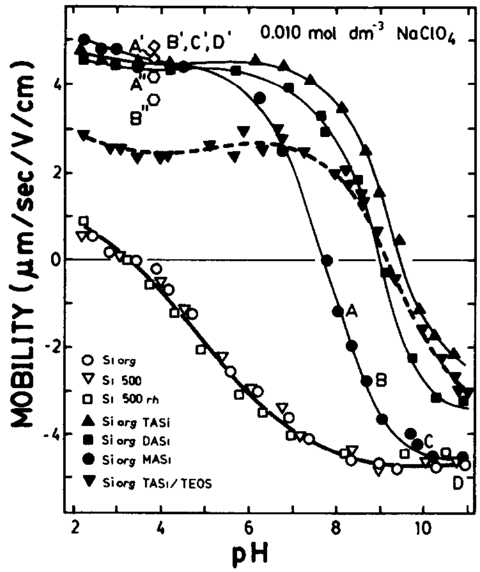

Fig. 3. Electrophoretic mobility as a function of pH of silica particles as prepared [○, Si_{or}, Fig. 1(a)]; of the same particles after calcination at 500°C [∇, Si_{500}, Fig. 1(b)]; the same sample rehydroxylated in HNO_3 after calcination at 500°C (□, Si_{500rh}). Full symbols represent amino-modified samples as follows: ●, Si_{or} + MASi; ■, Si_{or} + DASi; ▲, Fig. 1(c), Si_{or} + TASi; ▼, Fig. 1(d), Si_{or} + TEOS and TASi. Mobilities measured at pH 4 described by A′, B′, C′, and D′ (◇) are for samples A, B, C, and D aged for 1 h at the corresponding basic pH values, whilst those designated by A″ and B″ (○) are for samples A and B aged for 1 day before acidification to pH 4. Samples C and D, when aged for 1 day in basic solutions, dissolved.

particles to study their influence on reactivity. It was found that solids which interacted with MASi and DASi resulted in stable dispersions with no increase in particle size. The addition of TASi caused flocculation, but the system could be repeptized after washing several times with water and ethanol.

In principle, it would appear feasible to grow silica particles in the presence of TASi, but this was not the case unless TEOS was also admixed [Fig. 1(c) and (d)]. The ratio TASi/TEOS had an effect on the properties of the final product; when it was too high some bridging of particles was observed [see Fig. 1(d)].

The electrophoretic mobilities as a function of the pH of amino-modified silica with the three silanes (Fig. 3) show that the isoelectric point (i.e.p.) was shifted to much higher pH values, most notably when TASi was used. Very similar behavior was observed with calcined (at 500°C) and rehydroxylated silicas treated with the same aminosilanes. The particles grown in TASi/TEOS mixtures had the same mobility over the basic pH range, but showed lower absolute values over the acidic range (Fig. 3).

The electrokinetic measurements were also used to test the bond strength between the particles and the adsorbed aminosilanes. To do so, modified silica which was kept at pH 8–11 for up to one day, was separated by centrifugation, washed several times with water, and redispersed in sodium perchlorate solution of pH 4. The electrophoretic mobility of amino-modified silica aged at pH up to *c.* 9 was the same as that of samples originally prepared at the low pH (Fig. 3). Dispersions stored at pH 10–11 for 1 h reverted to the same mobility as was measured at pH 4. However, long aging at high pH caused particle dissolution.

Microcalorimetry for silica showed no change between 200°C and 500°C, but an exothermic peak was observed at *c.* 330°C for amino-modified samples (Fig. 4). Table 1 summarizes the heats of combustion as calculated from the calorimetric data for three samples of silica surface modified with different aminosilanes. Whilst the core material, differently treated, scarcely influenced the results, the aminosilanes showed distinct effects. Taking into consideration the heat of combustion for the aminopropyl group (*c.* 530 kcal mol^{-1}) and for each methyl group (*c.* 195 kcal mol^{-1}),[13] one can estimate the bound amounts of MASi, DASi, and TASi on silica to be approximately 4, 11, and 22 μmol g^{-1}, respectively, which values are lower than expected for a complete surface coverage. According to Lork *et al.*,[14] and Philipse & Vrij,[15] the uptake of aminosilanes can be increased by raising the reaction temperature. For this purpose, the original silica dispersion was refluxed in the presence of TASi, then the ammonia and ethanol were removed by distillation, and the sample analyzed by microcalorimetry. The measured heat of combustion was much higher than with analogous solids prepared at room temperature [Table 1(a) and (b)], yielding a maximum surface coverage of 87 μmol g^{-1}. This amount corresponds to an area per TASi molecule of 58 Å^2, which is in excellent agreement with a value of 55 Å^2 reported by

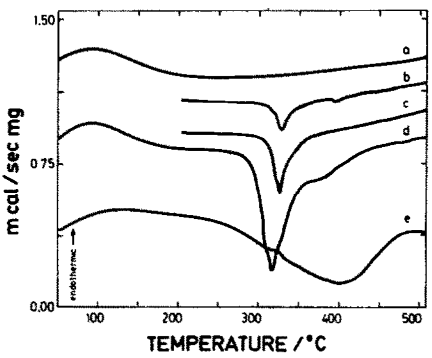

Fig. 4. DSC of (a) the original, Si_{rt}; (b)–(d) amino-modified, Si_{or}.$TASi_{rf}$, Si_{or}.$TASi_{ds}$ and Si_{or}.TASi/TEOS; and (e) dye-incorporated silica particles, Si_{or}.FL–TASi/TEOS1. The scanning rate was 10° min^{-1} for curves (a), (d), and (e), and 20° min^{-1} for curves (b) and (c).

TABLE 1

(a) Heat of Combustion ($\mathrm{cal\,g^{-1}}$) of Amino-Modified Silicas, Employing Differently Pretreated Silica Core Materials with Mono-, Di-, or Tri-ethoxyaminosilanes

Aminosilane	*Core material*		
	Si_{or}	Si_{500}	Si_{500rh}
MASi	5·0 ± 0·7	4·1 ± 0·2	2·7 ± 0·7
DASi	8·0 ± 1·7	7·9 ± 0·6	8·7 ± 1·2
TASi	12·1 ± 1·8	10·7 ± 0·8	12·9 ± 1·7

(b) Heat of Combustion ($\mathrm{cal\,g^{-1}}$) Determined by Differential Scanning Calorimetry for Different Surface-Modified Silica Samples

Sample	*Heat of combustion*
$\mathrm{Si_{or}.TASi_{rt}}$	12
$\mathrm{Si_{or}.TASi_{rf}}$	21
$\mathrm{Si_{or},TASi_{ds}}$	40
$\mathrm{Si_{or}.TASi/TEOS}$	370
$\mathrm{Si_{or}.TASi_{ds}.FL4 = C.FL4}$	88
$\mathrm{Si_{or}.FL{-}TASi/TEOS1}$	260

Horner & Roth[16] as the maximum surface coverage of an aerosol sample. Differences in the amino modification could also be detected through changes in color intensity after coupling the dye molecules.

3.3 Dye coupling

To establish the optimum conditions for attaching a dye to silica particles, several parameters were varied relating both to the surface of the carrier and to the solution in which the dye was dissolved. A complete such study was carried out with Flavazin L and the entire scheme of experiments conducted is given in Fig. 5. Vertical lines indicate separate process sequences employed. Different reaction efficiencies were observed by the color intensities of the samples, as shown in the same table. It appears that the heat treatment during the amino modification and the addition of pyridine, during the reaction with the dye acid chloride, had a beneficial effect on the color intensity. Furthermore, surface treatment of silica with TASi gave better results than when MASi was used.

The most favorable conditions (TASi, ethanol as solvent, pyridine as catalyst, and heat treatment during the amino modification, as well as during

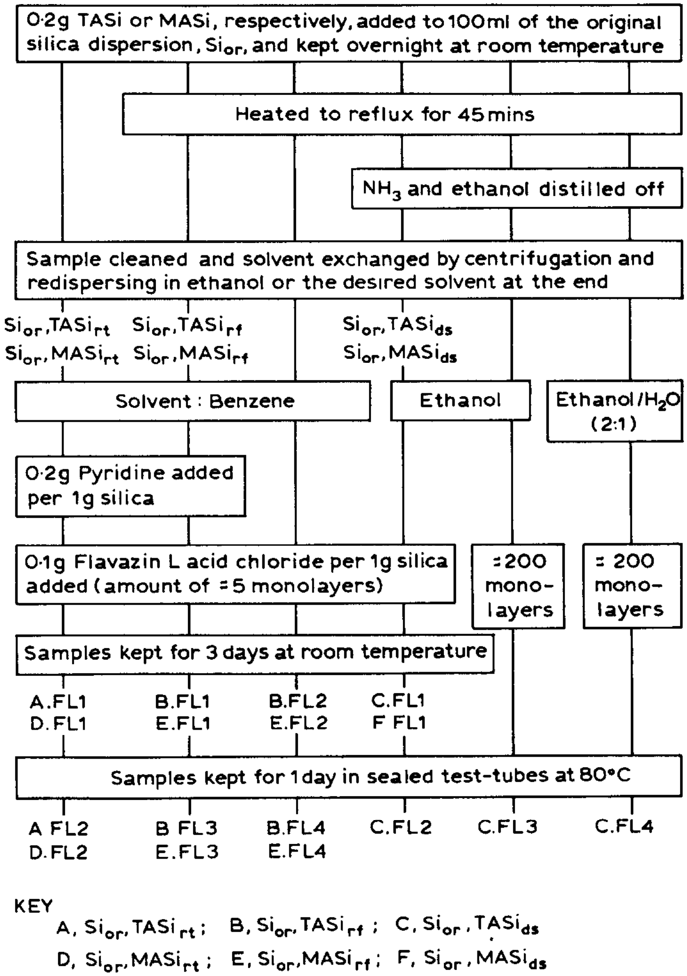

Fig. 5. The scheme showing experimental routes in the preparation of pigments.

the dye coupling) were then applied to the acid chloride forms of other dyes (C.I. Acid Blue 45, C.I. Acid Red 183, Violamin R).

Figure 6 gives the reflectance spectra of several pigments so prepared, while the corresponding chromaticity data are shown in Table 2. Obviously, by attaching different dyes to modified silica particles, it is possible to obtain pigments of varying optical properties. It is noteworthy that silica cores had no effect on the spectral characteristics of the final products. The chromaticity data of the samples listed in Table 2 refer to measurements carried out with a constant amount of the pigment, i.e. 1 mg cm^{-2}, and not for an 'infinite layer thickness'. The reflectance spectra as a function of increasing dye content for Violamin R on silica are shown in Fig. 7.

TABLE 2

Chromaticity Data Calculated from the Reflectance Spectra of Different Samples (all data refer to measurements using 1 mg cm^{-2})

Sample	*Chromaticity coordinates*		*Luminous reflectance, Y*	*Purity (%)*	*Dominant wavelength (nm)*
	x	*y*			
Amino-modified					
$\mathrm{Si_{or}.TASi_{rt}}$	0·31	0·32	1·00	—	—
$\mathrm{Si_{or}.TASi/TEOS}$	0·31	0·32	1·00	—	—
Flavazin L coupled					
$\mathrm{Si_{or}.TASi_{rf}.FL1}$	0·33	0·34	0·97	11	570
$\mathrm{Si_{or}.TASi_{rf}.FL2}$	0·34	0·36	0·96	20	570
$\mathrm{Si_{or}.TASi_{ds}.FL1}$	0·33	0·36	0·95	17	571
$\mathrm{Si_{or}.TASi_{ds}.FL2}$	0·33	0·35	0·97	15	571
$\mathrm{Si_{or}.TASi_{ds}.FL3}$	0·38	0·42	0·91	44	572
$\mathrm{Si_{or}.TASi_{ds}.FL4}$	0·37	0·41	0·90	43	572
$\mathrm{Si_{or}.MASi_{ds}.FL2}$	0·34	0·36	0·95	18	572
Flavazin L–aminosilane grown					
$\mathrm{Si_{or}.FL\text{–}TASi/TEOS1}$	0·43	0·44	0·71	64	576
$\mathrm{Si_{or}.FL\text{–}TASi/TEOS2}$	0·40	0·43	0·86	53	574
$\mathrm{Si_{or}.FL\text{–}TASi/TEOS3}$	0·38	0·42	0·90	46	572
C.I. Acid Blue 45 coupled					
$\mathrm{Si_{or}.TASi_{ds}.AB_{blue}}$	0·24	0·22	0·15	38	472
$\mathrm{Si_{or}.TASi_{ds}.AB_{black}}$	0·32	0·30	0·06	7	510
C.I. Acid Red 183 coupled					
$\mathrm{Si_{or}.TASi_{ds}.AR1}$	0·47	0·33	0·36	48	606
Violamin R coupled					
$\mathrm{Si_{or}.TASi_{ds}.VR1}$	0·32	0·20	0·07	49	548
$\mathrm{Si_{or}.TASi_{ds}.VR2}$	0·32	0·20	0·09	47	548
$\mathrm{Si_{or}.TASi_{ds}.VR3}$	0·31	0·19	0·06	52	553
$\mathrm{Si_{or}.TASi_{ds}.VR4}$	0·31	0·18	0·16	53	552
$\mathrm{Si_{or}.TASi_{ds}.VR5}$	0·31	0·22	0·33	38	550
$\mathrm{Si_{or}.TASi_{ds}.VR6}$	0·32	0·26	0·50	25	545
$\mathrm{Si_{or}.TASi_{ds}.VR7}$	0·33	0·31	0·78	7	497
$\mathrm{Si_{or}.TASi_{ds}.VR8}$	0·32	0·31	0·90	4	(505)
$\mathrm{Si_{or}.TASi_{ds}.VR9}$	0·31	0·32	0·96	0	—

The amount of dye coupled to each particle was determined spectrophotometrically after the silica–dye particles were dissolved in 0·4 mol dm^{-3} NaOH. The results are summarized in Table 3. As expected, the amount of the dye adsorbed depended on its concentration in solution. From adsorption isotherms (not shown here), it was established that saturation,

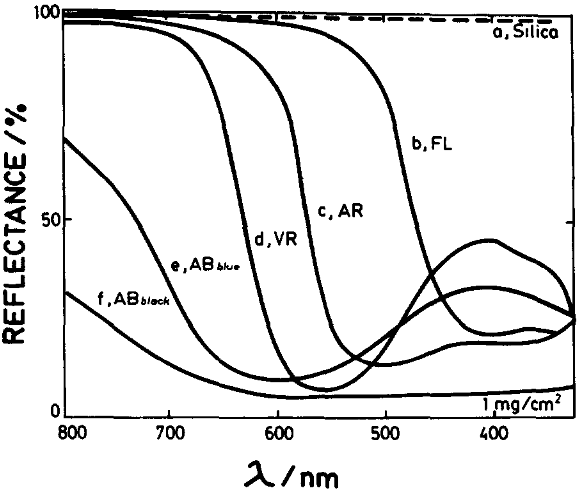

Fig. 6. Reflectance spectra of powder samples of different dyes coupled to (a) amino-modified silica particles, $Si_{or}.TASi_{ds}$; (b) Flavazin L, $Si_{or},TASi_{ds}.FL3$; (c) C.I. Acid Red 183, $Si_{or}.TASi_{ds}.AR1$; (d) Violamin R, $Si_{or}.TASi_{ds}.VR4$; (e) and (f) C.I. Acid Blue 45, $Si_{or}.TASi_{ds}.AB_{blue}$ and $Si_{or}.TASi_{ds}.AB_{black}$. The spectra refer to a constant amount of 1 mg sample per cm².

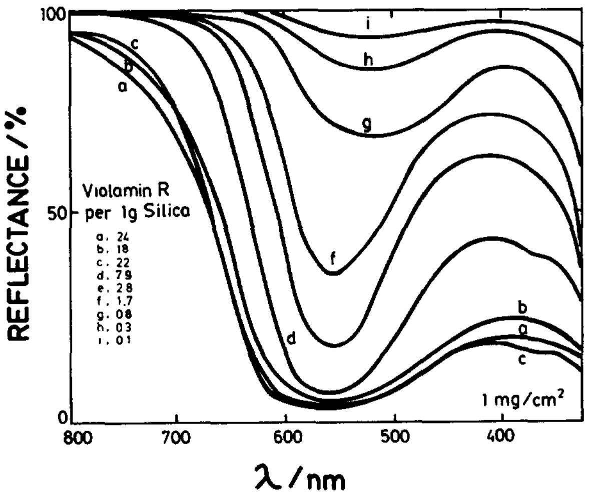

Fig. 7. Reflectance spectra of powder samples of different amounts of Violamin R coupled to amino-modified silica particles. The spectra refer to a constant amount of 1 mg sample per cm². (a)–(i) $Si_{or}.TASi_{ds}.VR1–9$.

TABLE 3
Amount of Dye Bound to Silica Particles
Amino-modified silica particles ($\mathrm{Si_{or}.TASi_{ds}}$) were dispersed in ethanol and different amounts of the acid chloride form of the dye were added

Sample	*Amount of dye employed (mg dye/g silica)*	*Amount of dye bound to silica (mg dye/g silica)*
Violamin R		
$\mathrm{Si_{or}.TASi_{ds}}$.VR1	10 × 10^3	24
$\mathrm{Si_{or}.TASi_{ds}}$.VR2	2 × 10^3	18
$\mathrm{Si_{or}.TASi_{ds}}$.VR3	580	22
$\mathrm{Si_{or}.TASi_{ds}}$.VR4	125	7·9
$\mathrm{Si_{or}.TASi_{ds}}$.VR5	42	2·8
$\mathrm{Si_{or}.TASi_{ds}}$.VR6	13	1·7
$\mathrm{Si_{or}.TASi_{ds}}$.VR7	4·2	0·8
$\mathrm{Si_{or}.TASi_{ds}}$.VR8	1·3	0·3
$\mathrm{Si_{or}.TASi_{ds}}$.VR9	0·4	$\approx$0·1
C.I. Acid Red 183		
$\mathrm{Si_{or}.TASi_{ds}}$.AR1	3600	29
$\mathrm{Si_{or}.TASi_{ds}}$.AR2	360	15
$\mathrm{Si_{or}.TASi_{ds}}$.AR3	36	2
$\mathrm{Si_{or}.TASi_{ds}}$.AR4	3·6	0·2
Flavazin L		
$\mathrm{Si_{or}.TASi_{ds}}$.FL3	420	20
$\mathrm{Si_{or}.TASi_{ds}}$.FL4	4000[a]	18

[a] Ethanol/water mixture was used instead of pure ethanol as solvent.

which amounts to 1–2 μmol of dye per m^2, was achieved at sufficiently high dye concentrations. This value corresponded to an area of 110–140 $Å^2$ per molecule, which compares well with 116 $Å^2$ for Methyl Red on silica,[12] frequently used for surface area determinations. Hiemenz,[17] Gregg & Sing,[18] and McClellan & Harnsberger[19] reported values of 42 $Å^2$ for benzene, 67 Å for naphthalene, and 83 $Å^2$ for anthracene. All these aromatic molecules are believed to lie flat on the solid surface. A comparison of the structures and sizes of dyes used in this work, with their estimated cross-sectional areas, would suggest the same flat conformation in the adsorbed state.

The uptake of dyes greatly affects the surface charge characteristics of pigment dispersions. Figure 8 shows that with an increasing amount of the dye (Violamin R) on the particles, the isoelectric point (i.e.p.) shifts to lower pH values; indeed, amino-modified silica covered by a monolayer of this dye is negatively charged over the entire pH range studied. Different dyes adsorbed in comparable amounts on the same substrate resulted in a considerable variation in mobilities at the same pH (Fig. 9).

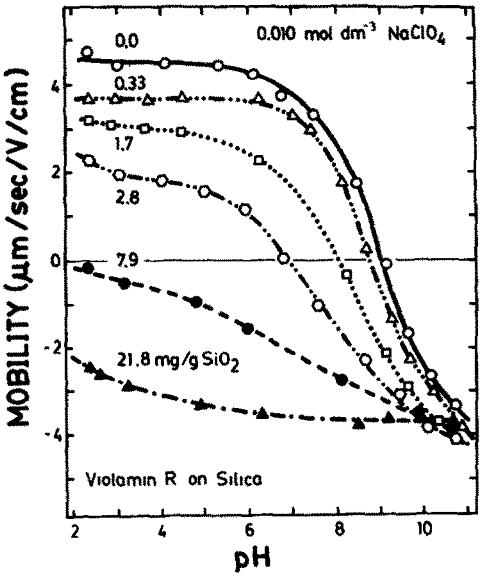

Fig. 8. Electrophoretic mobilities as a function of pH for samples of different amounts (see Table 3) of Violamin R bound to amino-modified silica particles (○, Si_{or}.$TASi_{ds}$). The symbols ▲, ●, ○, □, and △ refer to Si_{or}.$TASi_{ds}$.VR3, 4, 5, 6, and 8, respectively.

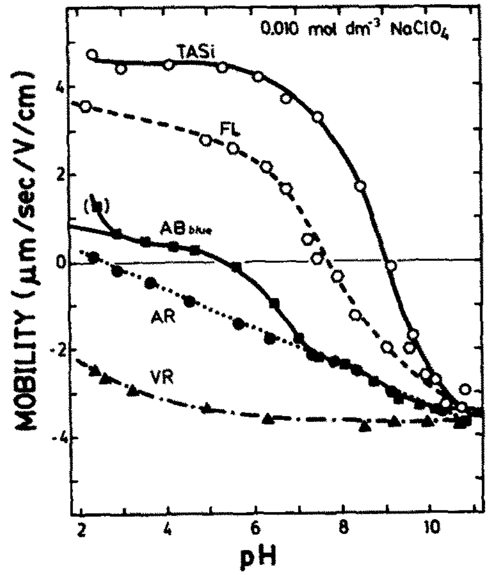

Fig. 9. Electrophoretic mobility as a function of pH for samples of different dyes bound to amino-modified silica particles (○, Si_{or}.$TASi_{ds}$). The symbols ▲, ●, ■, and ○ refer to Si_{or}.$TASi_{ds}$.VR3, AR1, AB_{blue}, and FL4, respectively.

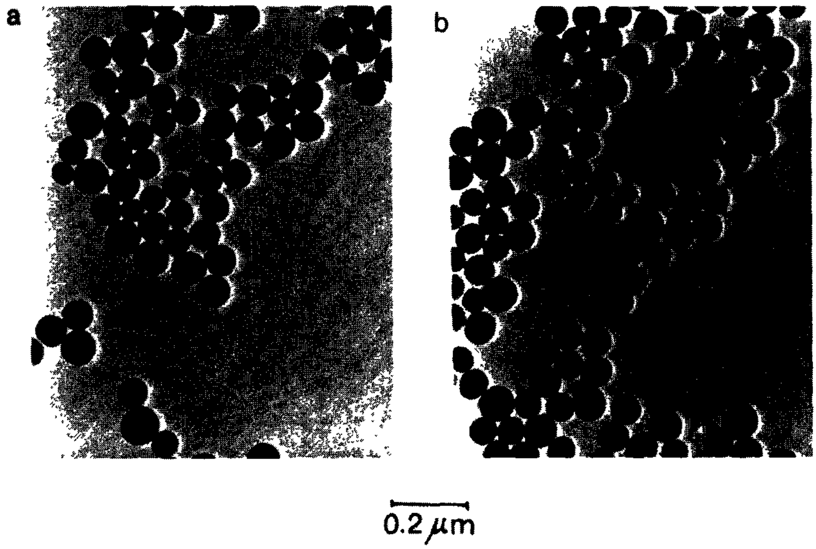

Fig. 10. Transmission electron micrographs of (a) Violamin R, Si_{or}.TASi_{ds}.VR3; (b) Acid Red 183, Si_{or}.TASi_{ds}.AR1, coupled to amino-modified silica.

As expected, the particle size did not change by coupling of dyes, since a monolayer at most is formed [Fig. 10(a) and (b)].

4 CONCLUSIONS

This study has shown that tailormade pigment particles of given characteristics can be produced by interaction of organic dyes with inorganic cores. Spherical silica particles are convenient for such applications since they can be readily produced as powders of exceedingly narrow size distributions with modal diameters ranging from a few nanometers to a few micrometers.

This process is, however, not limited to silica; other colloids consisting of spherical particles, such as titania, yttria, etc., are now available and could be used in the same manner. Different refractive indices of core particles will affect optical properties of the resulting pigments and offer another parameter for controlling the color.

Binding the dye via the sulfonic acid– or carbonic acid–aminosilane bond is a rather general pathway. Since the sulfonic acid group is used in many dyes to improve their water solubility and reactivity, there is a large variety of compounds which can be used, in principle, to produce pigment particles of nearly every color. Whether it is better to amino-modify the surface first and then couple the dye, or to bind the entire complex, depends very much on the eventual applications.

Depending on the nature of the reagents and the sequence of the preparation steps, the surface charge characteristics of pigments can be changed over a wide range. For example, pigment particles coated with an outermost layer of aminosilane bore the same potential as the pure silica amino-modified in the same manner. Furthermore, the surfaces can be made either hydrophobic or hydrophilic by adjusting the amount of polar groups (e.g. hydroxyl) or by blocking these groups by a final 'end-capping' step, such as with trimethylchlorosilane.

Finally, it was found that differential scanning calorimetry (DSC) may be a useful tool in the quantitative detection of low amounts of organic groups in an inorganic matrix, providing these groups (e.g. aminopropyl) undergo a well-defined exothermic or endothermic change.

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