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Well-Defined Colloidal Pigments. II: Monodispersed Inorganic Spherical Particles Containing Organic Dyes

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ABSTRACT

Colloidal pigments of well-defined characteristics were obtained by using inorganic particles as carriers in which organic dyes were either incorporated or adsorbed. The coprecipitation of inorganic salts with water-soluble anionic dyes was affected by the chelating ability of the latter, the valence of the metal, and the reaction parameters during the particle formation. The dye retention in the core was similar to that in the 'mordant' process of dyeing. Optical studies of the pigments made by using $Y(OH)CO_3$ *as a core showed good color properties (purity, lightness) in a variety of hues. The amount of cationic dyes adsorbed on silica particles depended on the molecular structure of the dyes and on the pH of the solutions, which influenced the surface charge of* SiO_2.

INTRODUCTION

Colorants (pigments or dyes) have been traditionally classified as 'organic' and 'inorganic'. Organic dyes generally exhibit very good tinctorial strength and brightness but show low-to-moderate fastness to light and chemicals. Inorganic pigments demonstrate excellent light- and chemical-resistance but are duller in color and weaker in color strength. Both organic and inorganic colorants appear in different chemical structures and shapes; hence their surface, dielectric, and optical characteristics may vary considerably. In order to control all these properties, it is necessary that pigments are of well-defined composition and morphology, especially as spheres of uniform size.

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When this goal cannot be directly accomplished, one can use 'monodispersed' inorganic particles as carriers, in which the organic dye molecules are either incorporated in the bulk or adsorbed on the surface. The advantages of these approaches are several, as follows.

(*a*) The spherical geometry of particles of a narrow size distribution and of controlled diameter can be programmed to achieve the desirable opacity.
(*b*) The refractive index (n_p, real part) of the carrier can be chosen and maintained constant, once the dye is introduced into the particles. When n_p is matched with that of the medium, n_s, one can obtain the optimum conditions for color and transparency.
(*c*) By proper surface modifications, the dispersibility of the pigment in aqueous or organic solvents can be improved.
(*d*) The light- and chemical-resistance of such particles may be enhanced.
(*e*) The color-mixing can be simplified and quantified.

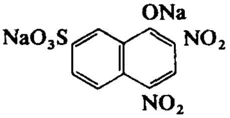
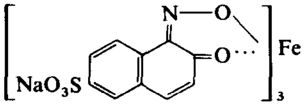
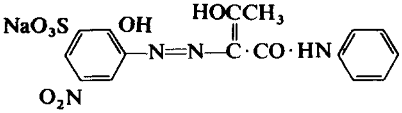
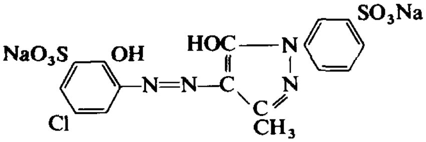
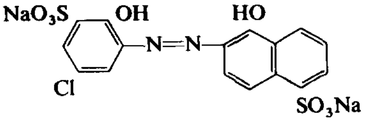
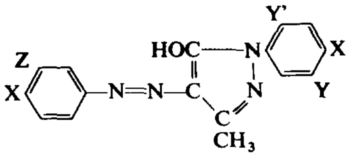
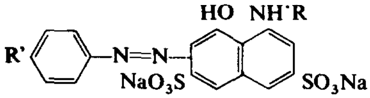
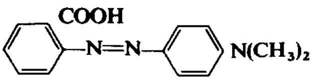
In recent years, a variety of 'monodispersed' inorganic colloids has been prepared[1-3] with well-defined particles of different compositions and morphologies. Some of the sols have been used as model systems to study the stability and other properties of colloids.[4-6] In addition, processes for the production of uniform pigments included organic dyes precipitated as spherical particles by addition of water,[7] as well as toner-like inks prepared by binding dyes to surface-modified silica particles[8-12] and polymeric latices. In this work, inorganic sols of $Y(OH)CO_3$, $Al(OH)_3$, $Zr(OH)_2CO_3$, $TiO_{1\cdot9}(SO_4)_{0\cdot1}$, $Cd_3(PO_4)_2$, and SiO_2, consisting of uniform spherical particles of known modal diameters, were used as core materials, which were then interacted with different dyes to produce pigments of controlled optical and charge characteristics. This purpose was achieved either by generating inorganic particles in the presence of soluble dyes, in which case the latter are incorporated in the bulk of the solid phase, or by the adsorption of a dye onto the carrier particles. The retention of dyes in the cores is explained in terms of their acid–base characteristics, as well as by specific interactions between the functional groups.

EXPERIMENTAL

Materials

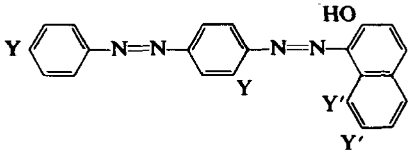
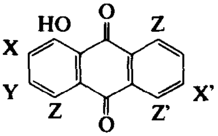
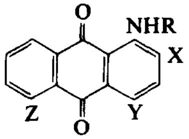
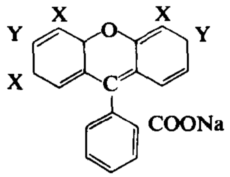
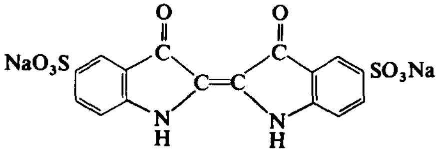
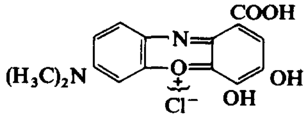
The commercial dyes (along with the name abbreviations) used in these studies are listed in Table 1. The anionic (acid) dyes are sodium salts of

TABLE 1
Organic Dyes Used in This Work

No.	*Name*	*Abbr.*	*Dye content*	
	Anionic dyes			
1	Naphthol Yellow S (Acid Yellow 1)	AY1	75%[a]	
2	Naphthol Green B (Acid Green 1)	AG1	60%[b]	
3	Acid Yellow 99	AY99	45%[a]	
4	Acid Red 183	AR183	60%[a]	
5	Chrome Azurol S (Mordant Blue 9)	MB9	50%[b]	
6	Flavazin L (Acid Green 1)	AY11	60%[b]	
7	Acid Yellow 17	AY17	75%[b]	
8	Acid Yellow 29	AY29	55%[b]	
9	Acid Red 106	AR106	50%[b]	
10	Acid Violet 7	AV7	50%[b]	
11	Methyl Red (Acid Red 2)	AR2	50%[b]	

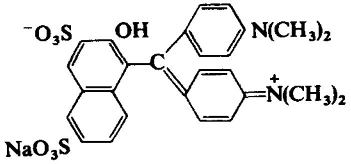
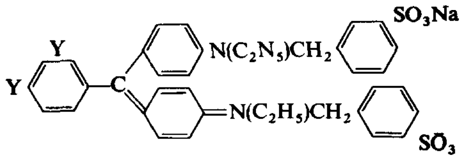
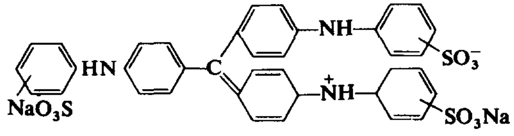
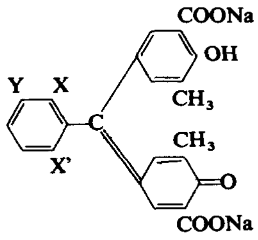
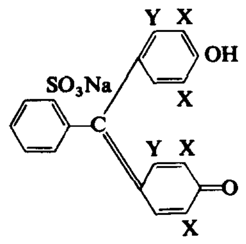
continued

TABLE 1—*Contd*

No.	*Name*	*Abbr.*	*Dye content*	
12	Brilliant Crocein Moo (Acid Red 73)	AR73	—[a]	
13	Biebrich Scarlet (Acid Red 66)	AR66	50%[a]	
14	Amido Black 10B (Acid Black 1)	ABk1	85%[b]	
15	Alizarin Red S (Mordant Red 3)	MR3	50%[b]	
16	Acid Blue 45	AB45	40%[b]	
17	Acid Blue 40	AB40	50%[a]	
18	Alizarin Violet R (Acid Violet 34)	AV34	50%[b]	
19	Copper PCSS (Acid Blue 249)	AB249	60%[b]	
20	Violamine R (Acid Violet 9)	AV9	65%[b]	
21	Eosine Y (Acid Red 87)	AR87	80%[c]	
22	Indigo Carmine (Acid Blue 74)	AB74	93%[b]	
23	Gallocyanine (Mordant Blue 10)	MB10	90%[b]	

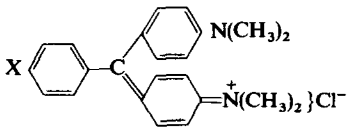
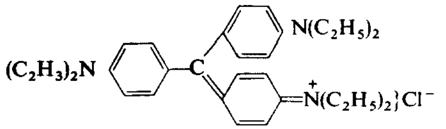
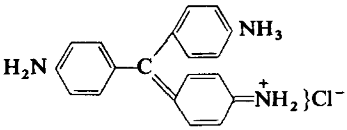
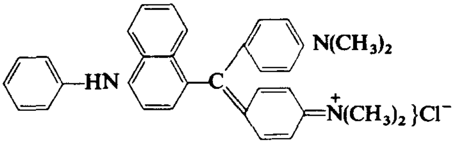
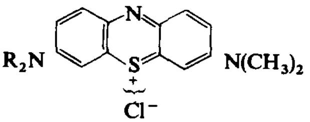
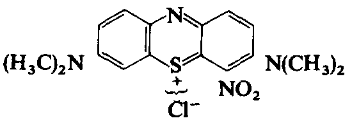
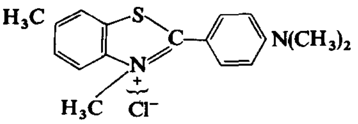
continued

TABLE 1—*Contd*

No.	*Name*	*Abbr.*	*Dye content*	
24	Nigrosin (Acid Black 2)	ABk2	55%[a]	
25	Lissamine Green B (Acid Green 50)	AG50	72%[b]	
26	Fast Green FCF (Food Green 3)	FG3	90%[c]	
27	Acid Violet 17	AV17	75%[b]	
28	Brilliant Blue G (Acid Blue 90)	AB90	60%[d]	
29	Aniline Blue (Acid Blue 93)	AB93	—[a]	
30	Chromoxane Cyanine R (Mordant Blue 3)	MB3	40%[a]	
31	Chrome Azurol S (Mordant Blue 29)	MB29	60%[b]	
32	Phenol Red (pH indicator)	IPR	95%[c]	
33	Bormophenol Blue (pH indicator)	IBB	95%[c]	
34	Bromophenol Green (pH indicator)	IBG	95%[c]	

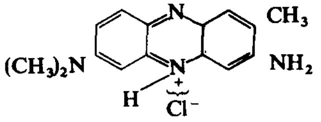
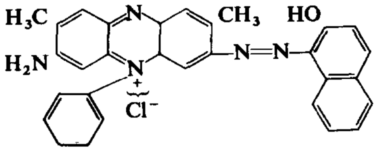
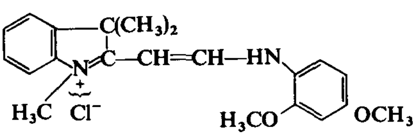
continued

TABLE 1—*contd.*

No.	*Name*	*Abbr.*	*Dye content*	
	Cationic dyes			
35	Malachite Green (Basic Green 4)	BG4	98%[a]	
36	Crystal Violet (Basic Violet 3)	BV3	92%[a]	
37	Ethyl Violet (Basic Violet 4)	BV4	80%[a]	
38	Basic Fuchsin (Basic Violet 14)	BV14	95%[a]	
39	Victoria Blue B (Basic Blue 26)	BB26	85%[a]	
40	Azure A	BAA	85%[d]	
41	Methylene Blue (Basic Blue 9)	BB9	89%[a]	
42	Methylene Green (Basic Green 5)	BG5	65%[a]	
43	Thioflavine T (Basic Yellow 1)	BY1	75%[a]	

continued

TABLE 1—*Contd.*

No.	*Name*	*Abbre.*	*Dye content*	
44	Neutral Red (Basic Red 5)	BR5	55%[a]	
45	Indoine Blue (Basic Blue 16)	BB16	70%[a]	
46	Basic Yellow 11	BY11	40%[b]	

[a] Aldrich; [b] Sigma; [c] Spectrum; [d] Fisher.

sulfonic or carboxylic acids of widely varying constitution: nitro (no. 1), nitroso (no. 2), monoazo (nos 3–11), diazo (nos 12–14), anthraquinone (nos 15–18), phthalocyanine (no. 19), xanthene (nos 20 and 21), indigoid (no. 22), oxazine (no. 23), azine (no. 24), and triphenylmethane (nos 25–34). The cationic (basic) dyes consist of amino or alkylamino groups in which the positive charge is delocalized throughout the chromophore: triphenylmethane (nos 35–39), thiazine (nos 40–42), thiazole (no. 43), azine (no. 44), indigoid (no. 45), and cyanine (no. 46). All dyes and other reagent-grade chemicals, including tetra-ethoxysilane (TEOS, 98%, Aldrich), were used without further purification.

Pigment preparations

The core materials, all consisting of uniform spherical particles, were prepared by aging appropriate salt solutions at elevated temperatures, by means of procedures described earlier.[13–18] Some modifications were introduced to meet the specifications needed in the present work. The actual conditions are summarized in Table 2. Most precipitation experiments were carried out in test tubes that were tightly sealed with screw-caps during aging.

The dye stock solutions, in concentrations ranging from $1{\cdot}0 \times 10^{-3}$ to $5{\cdot}0 \times 10^{-3}$ mol dm^{-3}, were prepared in aqueous media, except for AB90,

TABLE 2
Experimental Conditions for the Preparation of Inorganic Hydrosols

Sols[a]	*Reactant concentrations*	*Diameter* (*μm*)	*Figure 1* (*Ref.*)
$Y(OH)CO_3$	$Y(NO_3)_3$: 5×10^{-3} mol dm^{-2} urea: 0·5 mol dm^{-3}	0·33	A (8)
$Al(OH)_3$	$AlK(SO_4)_2$: $1{\cdot}8 \times 10^{-3}$ mol dm^{-3} $Al(NO_3)_3$: $3{\cdot}2 \times 10^{-3}$ mol dm^{-3} urea: 0·4 mol dm^{-3}	0·30	B (9)
$Zr(OH)_2CO_3$	$Zr(SO_4)_2$: $5{\cdot}0 \times 10^{-3}$ mol dm^{-3} HNO_3: $5{\cdot}0 \times 10^{-3}$ mol dm^{-3} urea: 0·5 mol dm^{-3} polyvinylpyrrolidone: 1%	0·41	C (10)
$TiO_{1{\cdot}9}(SO_4)_{0{\cdot}1}$	$TiOSO_4$: $5{\cdot}0 \times 10^{-3}$ mol dm^{-3} polyvinylpyrrolidone: 0·05% hydroxypropyl cellulose: 0·005%	0·25	D (11)
$Cd_3(PO_4)_2$	$CdSO_4$: $5{\cdot}0 \times 10^{-3}$ mol dm^{-3} NaH_2PO_4: $5{\cdot}0 \times 10^{-3}$ mol dm^{-3} urea: 1·0 mol dm^{-3} sodium dodecylsulfate: 0·01 mol dm^{-3}	0·47	E (12)
SiO_2	TEOS: 0·21 mol dm^{-3} NH_4OH: 0·55 mol dm^{-3} H_2O: 21 mol dm^{-3} in ethanol (40°C)	0·18	F (13)

[a] Except for SiO_2, all aqueous solutions of reactions were aged at 90°C for 1 h.

BB26, BB16, which were dissolved in a 10 vol% ethanol/water mixture. All stock solutions were filtered through Nuclepore membranes of 0·2-μm pore size.

In order to synthesize inorganic particles incorporating a dye in the solid bulk, the corresponding salt and dye solutions of appropriate concentrations were mixed to give a constant final volume and then aged at elevated temperatures for a desired period of time. The actual conditions were the same as those given in Table 2 except that the dye concentration varied as needed. In most cases, the entire amount of the dye was incorporated in the particles, as easily recognized by a colorless supernatant solution at the completion of the coprecipitation. The resulting colored particles were filtered and washed with distilled water until no dye could be detected in the filtrate. To test the dye retention by the carrier particles, the pigments were redispersed in ethanol or acetone, this being followed by ultrasonication and centrifugation. This procedure was carried out several times in order to follow the extent of dye-leaching, if any, from the particles.

Characterization

The pigment particle size was evaluated from transmission electron micrographs (JEOL-1200 EX TEM), and the electrophoretic mobility was measured with a DELSA 440 (Coulter Electronics) instrument.

A Perkin–Elmer Lambda 3 UV/VIS spectrophotometer, equipped with an integrating-sphere attachment, was used for the reflectance and transmittance measurements. The powdered pigment (0·01 g) was dispersed in an ultrasonic bath in 20 cm^3 of aqueous solutions containing 0·1 wt% sodium dodecylsulfate. The samples for reflectance measurements were prepared by filtering the dispersion through a Millipore membrane (0·2-μm pore size). It is noteworthy that the reflectance data were recorded for a constant amount of solid (0·9 mg/cm^2) rather than an infinite layer thickness. For transmittance measurements, the dried powders were dispersed in liquid 1-chloronaphthalene or polyethylene glycol (MW 200) to reduce the light-scattering effect of the core particles.

The chromaticity values, x and y, as well as the dominant wavelength, purity, and luminosity (Y%), were calculated according to the CIE Standard Colorimetric System for a light source C.[19]

Adsorption experiments were conducted by the addition of 0·1 g of SiO_2 powder (Fig. 1(F), Table 2) to aqueous cationic dye solutions (10 cm^3) of known concentrations. The dispersions were kept in an ultrasonic bath for 10 min, and the resulting colored particles were then separated by centrifugation at 700 r/min. The dye solutions were freshly prepared owing to their low-to-moderate light-fastness. The equilibrium concentration of dye molecules was determined by measuring the extinction coefficient of the free dye in the supernatant solution after the solids were removed. Before analysis, the solutions were sufficiently diluted to avoid the effects of dye association on the extinction coefficient.[20,21]

RESULTS

A. Metal-compound carriers

As listed in Table 2, the mean diameters of the carrier particles ranged from 0·2 to 0·5 μm with a standard deviation less than 0·2 (Fig. 1). It is also noted that $Zr(OH)_2CO_3$ and $Cd_3(PO_4)_2$ particles are partly aggregated, whereas $TiO_{1\cdot 9}(SO_4)_{0\cdot 1}$ shows a fair amount of doublets. For this reason, most of the studies were carried out with $Y(OH)CO_3$ and silica. Solids of $Al(OH)_3$ and

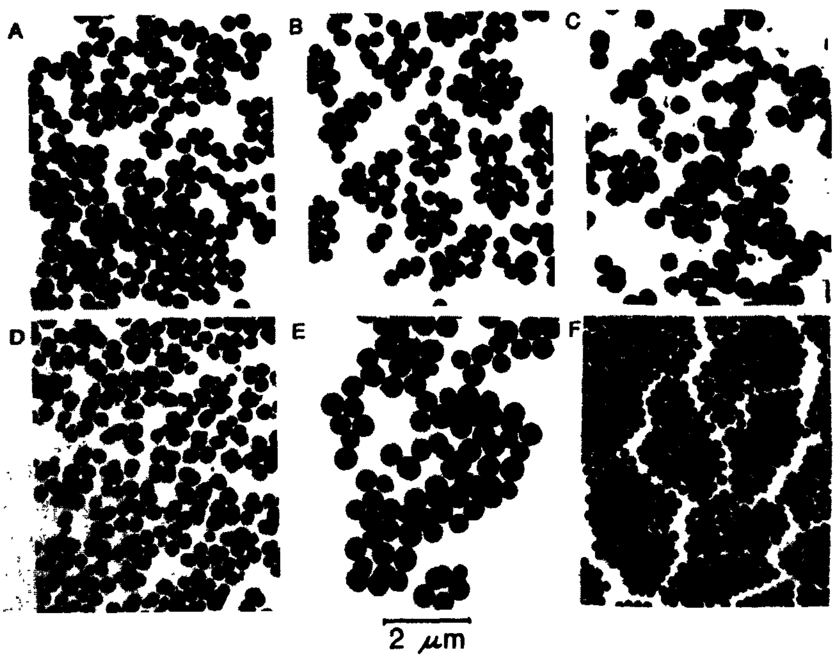


Fig. 1. Transmission electron micrographs (TEM) of (A) $Y(OH)CO_3$, (B) $Al(OH)_3$, (C) $Zr(OH)_2CO_3$, (D) $TiO_{1\cdot9}(SO_4)_{0\cdot1}$, (E) $Cd_3(PO_4)_2$, and (F) SiO_2 particles obtained by precipitation from homogeneous solutions under conditions given in Table 1.

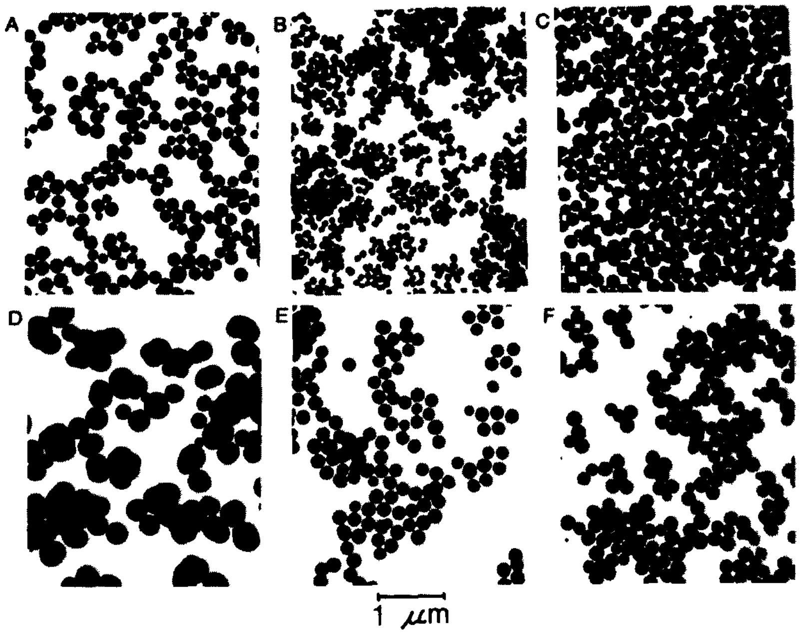


Fig. 2. TEM of pigment particles of (A) MB3–$Y(OH)CO_3$, (B) ABk3–$Y(OH)CO_3$, (C) AY99–$Y(OH)CO_3$, (D) AG1–$Y(OH)CO_3$, (E) AR183–$Y(OH)CO_3$, and (F) AR183–$Al(OH)_3$, obtained by aging of the reactant solutions of metal salts (Table 1) in the presence of $1\cdot0 \times 10^{-4}$ mol dm^{-3} of each dye.

TABLE 3

Pigments Obtained by Coprecipitating Inorganic Salts with Organic Dyes

Dye no.	*Abbr.*	*Carrier particles*					
		$Y(OH)CO_3$	$Al(OH)_3$	$Zr(OH)_2CO_3$	TiO_2	$Cd_3(PO_4)_2$	SiO_2
Acid dyes							
1	AY1	*x*	*x*	*x*	*x*	*x*	*x*
2	AG1	*b*	*b*	*x*	*x*	*x*	*x*
3	AY99	*b*	*b*	*x*	*x*	*b*	*x*
4	AR183	*b*	*b*	*x*	*x*	*b*	*x*
5	MB9	*b*	*b*	*x*	*x*	*x*	*x*
6–14		*x*	*x*	*x*	*x*	*x*	*x*
15	MR3	*b*	*b*	*b*	*b*	—	*x*
16	AB45	*b*	*b*	*b*	*b*	*x*	*x*
17–18		*x*	*x*	*x*	*x*	*x*	*x*
19	AB249	*l*	*l*	*l*	*l*	*l*	*x*
20	AV9	*l*	*l*	*l*	*l*	*l*	*x*
21–22		*x*	*x*	*x*	*x*	*x*	*x*
23	MB10	*b*	*b*	*x*	*x*	*b*	*x*
24	ABk2	*b*	*b*	*x*	*x*	*b*	*x*
25	AG50	*l*	*l*	*x*	*x*	*l*	*x*
26	FG3	*x*	*x*	*x*	*x*	*x*	*x*
27	AV17	*l*	*l*	*l*	*l*	*l*	*x*
28	AB90	*l*	*l*	*l*	*l*	*l*	*x*
29	AB93	*l*	*l*	*l*	*l*	*l*	*x*
30	MB3	*b*	*b*	*b*	*b*	*b*	*x*
31	MB29	*b*	*b*	*b*	*b*	*b*	*x*
32–34							
Basic dyes							
35–39		*x*	*x*	*x*	*x*	*x*	*x*
40	BAA	*x*	*x*	*x*	*x*	*x*	*b*
41	BB9	*x*	*x*	*x*	*x*	*x*	*b*
42–46		*x*	*x*	*x*	*x*	*x*	*x*

Symbols: dye incorporated (*b*), leachable in acetone (*l*), no reaction (*x*).

$Zr(OH)_2CO_3$ contain small amounts of sulfate ion as impurity, which can be removed by washing, whereas, in titanium dioxide, sulfate ion is coordinated, to give an approximate composition of $TiO_{1\cdot 9}(SO_4)_{0\cdot 1}$.

Table 3 summarizes the results obtained with a number of organic dyes interacted with different inorganic salts by coprecipitation only. In some systems, the dyes were permanently bound and could not be removed by washing the pigments either with water or with organic solvents (acetone or ethanol). These pigments are coded by letter '*b*' in Table 3, and the dispersions are illustrated in Fig. 2. In some other cases, the incorporated dye

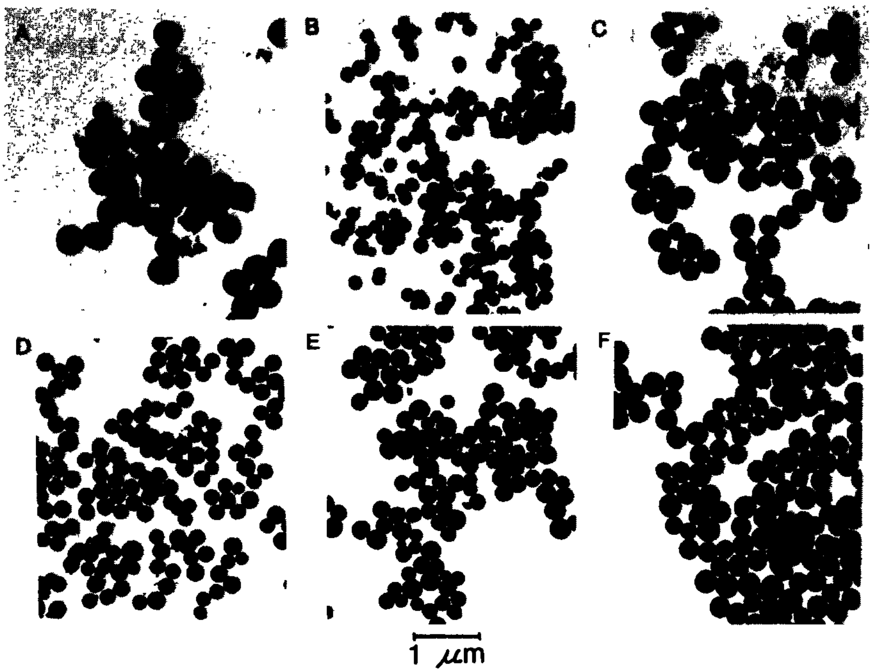


Fig. 3. TEM of pigment particles of (A) AB249–$Y(OH)CO_3$, (B) AB249–$Cd_3(PO_4)_2$, (C) AV9–$Y(OH)CO_3$, (D) AV9–$Al(OH)_3$, (E) AB93–$Y(OH)CO_3$, and (F) AR183–$Al(OH)_3$, obtained by aging of the reactant solutions of metal salts (Table 1) in the presence of $1{\cdot}0 \times 10^{-4}$ mol dm^{-3} of each dye.

TABLE 4

Mean Diameters (in μm) of Colored Yttrium Basic Carbonate Particles Obtained by Aging at 85°C for 2 h Solutions of $5{\cdot}0 \times 10^{-3}$ mol dm^{-3} $Y(NO_3)_3$ and 0·5 mol dm^{-3} Urea Containing either $0{\cdot}5 \times 10^{-4}$ (First Row) or $1{\cdot}0 \times 10^{-4}$ mol dm^{-3} (Second Row in Each Column) Organic Dyes

	AG1	*AY99*	*AR183*	*MB9*	*MR3*	*AB45*	*AB249*
Particle diameter[a] (μm)	0·40 0·55	0·18 0·20	0·18 0·15	0·12 0·07	0·18 0·15	0·15 0·12	0·32 —

	MB10	*ABK2*	*AB90*	*AB93*	*MB3*	*MB29*	*AG50*
Particle diameter[a] (μm)	0·17 0·09	0·30 0·25	0·25 0·29	0·27 0·45	0·20 0·18	0·25 0·19	— 0·18

[a] Particle diameter in the absence of dye: 0·32 μm.

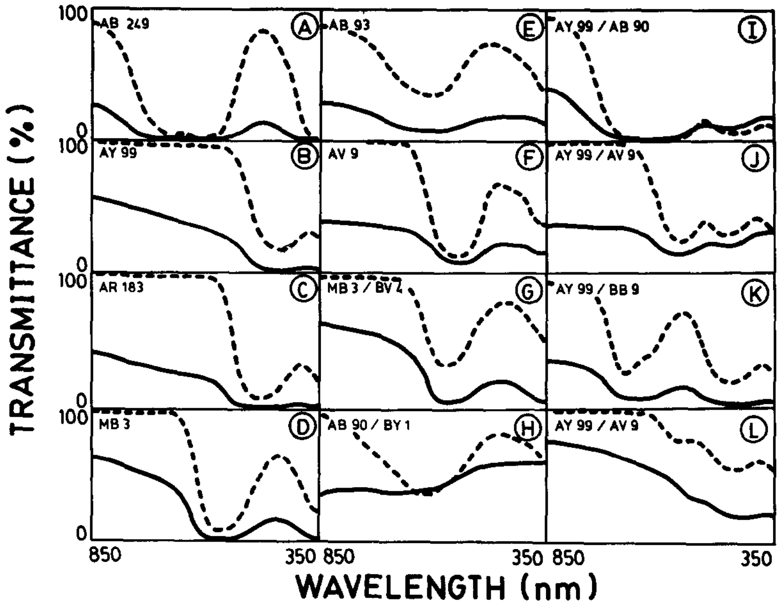


Fig. 4. Transmittance spectra of twelve different pigments in water (solid line) and in 1-chloronaphthalene (dashed line). The pigments consisted of $Y(OH)CO_3$ particles with incorporated dyes (1×10^{-4} mol dm^{-3}) as indicated in each case.

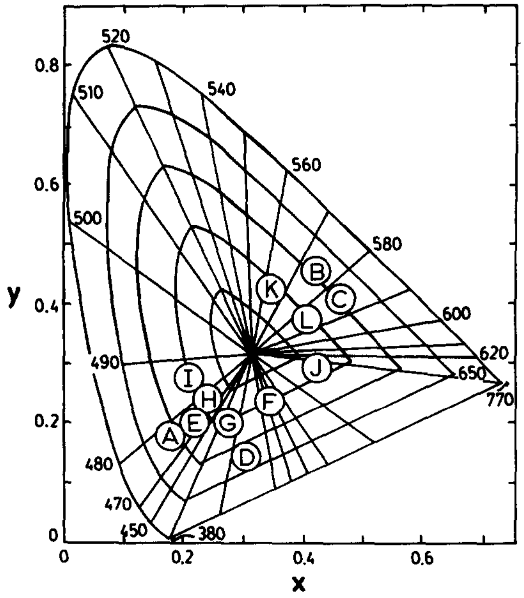


Fig. 5. Chromaticity diagram of the dye–$Y(OH)CO_3$ pigments in 1-chloronaphthalene (shown by the same letter code as in Fig. 4).

was leachable with acetone as coded by '*l*' in the same table. Figure 3 shows several electron micrographs of the latter kind of system, which indicate a certain amount of surface roughness of the particles in contrast to those displayed in Fig. 2.

The particle size of pigments, prepared by coprecipitation as described above, differed in most cases from the size of the carrier particles, obtained under the same conditions in the absence of dyes. Table 4 summarizes such effects with $Y(OH)CO_3$ used as the carrier material. In most cases, the diameter of the pigment was smaller than that of the corresponding pure inorganic particles.

The relative refractive index, n_p/n_s, has a significant effect on the color appearance of dye-incorporated pigments. A few transmittance spectra of $Y(OH)CO_3$–dye particles dispersed in water ($n_s = 1{\cdot}33$) and 1-chloronaphthalene ($n_s = 1{\cdot}63$) are given in Fig. 4, and a corresponding chromaticity diagram for the $Y(OH)CO_3$–dye powders in 1-chloronaphthalene is shown in Fig. 5. Since the relative refractive index of $Y(OH)CO_3$ ($n_p = 1{\cdot}64$) with

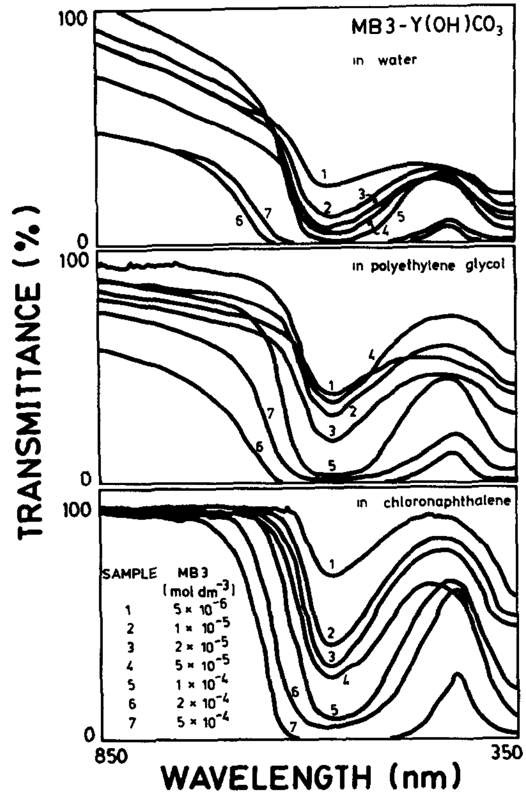


Fig. 6. Transmittance spectra of MB3-$Y(OH)CO_3$ pigments containing different amounts of the dye (5×10^{-6}–5×10^{-4} mol dm^{-3}) in (A) water, (B) polyethylene glycol, and (C) 1-chloronaphthalene.

respect to chloronaphthalene is close to 1, the carrier particles scatter little light and thus appear transparent, which results in enhanced pigment lightness (luminous reflectance) and in a shift of the dominant-color wavelength.

The purity (saturation) of the pigment increases to an optimum value with the amount of dye incorporated in the $Y(OH)CO_3$ particles and then decreases. Figure 6 demonstrates that the transmittance of seven samples of $Y(OH)CO_3$–MB3 pigments, containing different amounts of the dye, increases with n_s, from 1·33 (water), to 1·46 (polyethylene glycol), to 1·63 (1-chloronaphthalene).

Table 5 lists the corresponding chromaticity data for the $Y(OH)CO_3$–MB3 pigments. The optimum concentration of dye, which gives the highest color purity, is approximately 2×10^{-4} mol dm^{-3} (sample 6 in Fig. 6 and Table 5) for $Y(OH)CO_3$ particles. The corresponding values for other carrier particles were all in the range from 1×10^{-4} to 2×10^{-4} mol dm^{-3}, which

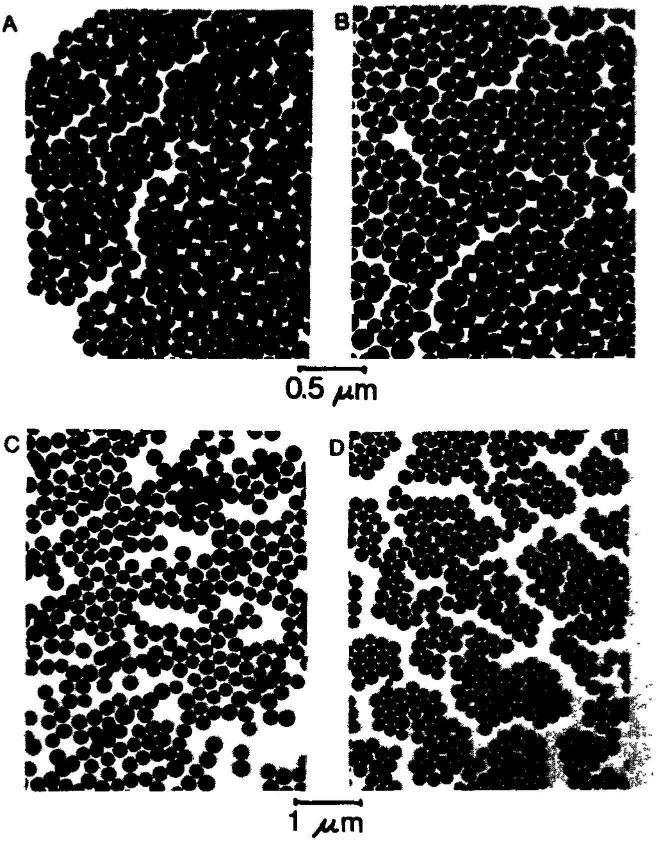


Fig. 7. TEM of the dye-incorporated particles of BB9 in SiO_2 (A) and BAA in SiO_2 (B), and of the dye-surface-adsorbed particles of BV4 on SiO_2 (C) and BY1 on SiO_2 (D). In all examples, the dye concentration was $1{\cdot}0 \times 10^{-4}$ mol dm^{-3}.

TABLE 5
Chromaticity of the $Y(OH)CO_3$–MB3 Pigments[a]

n_p/n_s	*Chromaticity co-ordinates*		*Dominant wavelength (mm)*	*Luminous reflectance, Y%*	*Hue*	*Purity (%)*
	x	*y*				
Sample 1 (5×10^{-6} mol dm^{-3} MB3)						
1·01	0·306	0·292	558c	80	rPurple	10
1·14	0·317	0·294	530c	46	pPink	10
1·25	0·330	0·296	505c	19	pPink	11
Sample 2 (1×10^{-5} mol dm^{-3} MB3)						
1·01	0·301	0·260	559c	58	rPurple	20
1·14	0·307	0·265	553c	41	pPink	20
1·25	0·325	0·249	536c	12	pPink	28
Sample 3 (2×10^{-5} mol dm^{-3} MB3)						
1·01	0·297	0·247	558c	49	rPurple	26
1·14	0·307	0·251	551c	30	pPink	26
1·25	0·314	0·294	530c	13	pPink	12
Sample 4 (5×10^{-5} mol dm^{-3} MB3)						
1·01	0·307	0·247	553c	41	rPurple	28
1·14	0·302	0·258	556c	46	rPurple	23
1·25	0·322	0·261	535c	12	pPink	25
Sample 5 (1×10^{-4} mol dm^{-3} MB3)						
1·01	0·289	0·176	557c	22	rPurple	52
1·14	0·261	0·140	563c	11	Purple	62
1·25	0·310	0·155	552c	6	rPurple	64
Sample 6 (2×10^{-4} mol dm^{-3} MB3)						
1·01	0·277	0·085	557c	20	rPurple	87
1·14	0·214	0·052	564c	5	Purple	90
1·25	0·224	0·055	563c	2	Purple	88
Sample 7 (4×10^{-4} mol dm^{-3} MB3)						
1·01	0·262	0·145	563c	13	Purple	60
1·14	0·271	0·130	561c	4	Purple	70
1·25	0·258	0·088	561c	1	Purple	80

[a] Aging solution of $2{\cdot}0 \times 10^{-2}$ mol dm^{-3} $Y(NO_3)_3$, 0·5 mol dm^{-3} urea, and dyes of different dye concentration (as specified in the above series of samples) at 85°C for 30 min. c = complementary color; r = reddish; p = purplish.

corresponds to one dye molecule or less per every 50 metal ions in the solid phase.

B. Silica carrier

The cationic dyes do not interact with metal-compound carriers (Table 3), but two of the investigated dyes could be incorporated into silica by coprecipitation from ethanolic solutions. Figures 7(A) and 7(B) illustrate such pigments obtained with BB9 and BAA, respectively. Preformed suspended silica particles could also be used for pigment preparation by the uptake of cationic dyes from aqueous solutions (Figs 7(C) and 7(D)).

The adsorption isotherms for some selected cationic dyes on negatively charged silica particles (at pH = 9·3) are of the normal Langmuir type (Fig. 8). Replotting data according to Langmuir,[22] we obtain

$$c_2/(n_s/w) = mc_2 + b \qquad (1)$$

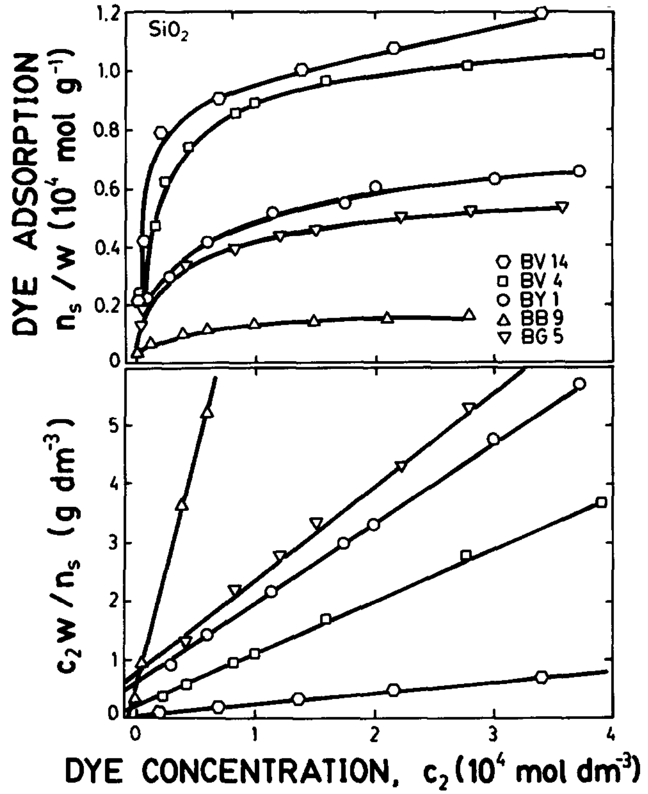


Fig. 8. The isotherms for the adsorption of cationic dyes (BV14, BV4, BY1, BB9, and BG5) on silica particles from aqueous solutions (upper). The lower plots are according to eqn (1).

TABLE 6
The Effect of the pH on the Adsorption of BB9 on SiO_2

pH[a]	*Equilibrium concentration of dye* c_2 *(mol dm*$^{-3}$*)*	*Area per molecule of dye,* θ *(Å*^{2}*)*	*Mobility* *(*10^{-4} *cm*^{2} *V*$^{-1}$ *s*$^{-1}$*)*
9·3		50	
	1×10^{-4}		−4·3
	$2{\cdot}5 \times 10^{-4}$		−2·5
9·0		110	
	$1{\cdot}0 \times 10^{-4}$		−4·1
	$2{\cdot}5 \times 10^{-4}$		−1·5
8·8		140	
	$1{\cdot}0 \times 10^{-4}$		−3·3
	$2{\cdot}5 \times 10^{-4}$		−0·4
8·1		150	
	$1{\cdot}0 \times 10^{-4}$		−1·2
	$2{\cdot}5 \times 10^{-4}$		−0·3
7·0		220	
	$1{\cdot}0 \times 10^{-4}$		−0·8
	$2{\cdot}5 \times 10^{-4}$		+0·3
4·3		350	
	$1{\cdot}0 \times 10^{-4}$		+0·5
	$2{\cdot}5 \times 10^{-4}$		+1·6
2·3		550	
	$1{\cdot}0 \times 10^{-4}$		+2·5
	$2{\cdot}5 \times 10^{-4}$		+3·0

[a] The isoelectric point of silica particles is at pH = 3·6.

which gives a straight line with slope m and intercept b (Fig. 8), where c_2 is the equilibrium concentration of the dye in solution, the ratio n_s/w is the number concentration of the dye adsorbed per unit weight of SiO_2 particles, and m and b are constants. The area occupied per dye molecule, θ, can be calculated from

$$\theta = 3m/\rho r N_A \qquad (2)$$

where ρ and r are the density (2·0 g cm^{-3}) and the radius (0·1 μm) of SiO_2 particles, respectively, and N_A is Avogadro's number. The values of θ are 6, 17, 25, 50, and 110 Å^2 per dye molecule of BV14, BV4, BY1, BB9, and BG5, respectively.

The affinity of cationic dyes for the silica substrate greatly affects the surface-charge characteristics of the pigments. Table 6 shows that, with the addition of the BB9 dye at two different equilibrium concentrations, the electrokinetic mobility of silica particles decreases significantly and the isoelectric point (i.e.p.) shifts to higher pH values (approximately 6·0 at $[\text{BB9}] = 1 \times 10^{-4}$ mol dm^{-3}; approximately 7·5 at $[\text{BB9}] = 2{\cdot}5 \times 10^{-4}$ mol dm^{3}) from i.e.p. = 3·6 of the original silica particles. Furthermore, the extent of the dye adsorption increases with the pH as indicated by the lower values of the area per adsorbed dye molecule.

Most of the adsorbed cationic dyes, except BB9 and BAA, leached from silica in an organic solvent (e.g. ethanol). As expected, these dyes could not be adsorbed on silica from ethanol solutions.

DISCUSSION

In the early history of dye-making, most natural dyes having no direct affinity for textiles were applied by means of mordants, i.e. metallic salts that functioned as fixing agents. Usually, reactive dyes containing a chelating species were able to form insoluble compounds of 'color lakes', giving a range of hues with different metallic mordants.[23] Salts of trivalent metals (aluminum, chromium, and iron) have been commonly employed for this purpose.[24]

This work shows that the coprecipitation of metal salts with anionic dyes was affected by the structure of the latter, the valence of the metal, and the nature of anions. The complexation during the particle formation is similar to that of the mordant treatments on dyeing.

The anionic dyes coprecipitated with metal salts (Table 3, code '*b*') consist of at least two suitable ligands for the interaction with the transition-metal ions.

The bidentate dye molecules used in this study (MR3, AB45, MB3, MB29, and MB10), with exception of AG1, were readily incorporated in all carriers containing metal ions. The pigments prepared in this way remained stable in aqueous, acetone, and ethanol solutions. In all cases, the salicylic acid acted as the chelating group.

The *o,o*′-dihydroxy (or *o*-amino-*o*′-hydroxy) azo dyes, such as AY99, AR183, and MB9, act as tridentate ligands occupying three co-ordination sites (one of the two azo nitrogen atoms and two hydroxy groups) in the octahedral configuration.[21] The central metal atom may bind either one or two dye molecules. The complexation, however, is not achievable in the solutions of Ti(IV) or Zr(IV) salts owing to the formation of bulky metal oxy-ions (MO^{2+}) or hydroxy-ions $\text{M(OH)}_n^{(4-n)-}$,[25] which cannot complex the dye.

It is noteworthy that the bidentate molecules (nos 6–14, Tables 1 and 3), which contain only one *o*-hydroxy or *o*-carboxy group, are not incorporated with any of the carriers, which suggests the importance of at least two of these ligands per dye to form a stable ring structure.

The phthalocyanine dye (AB249) is a tetradentate; four nitrogen atoms associated with four isoindole units are co-ordinated with the central metal atom. This dye forms complexes with all metal ions, and the carrier particles produced in the presence of this molecule show some surface roughness (Fig. 3). Similar behavior is observed with AV9 and AB93.

The finding that the dye-incorporated $Y(OH)CO_3$ pigments are smaller than the original carrier particles (Table 4) indicates that the dye molecules in solution affect the nucleation stage during the precipitation process; more nuclei are formed than in the absence of the dye. Such an effect has been observed when particles were formed in the presence of some surface-active agents.[15,17]

Only a few pigments using silica as a carrier were prepared by the hydrolysis of TEOS in ethanol in the presence of cationic dyes (Table 3). In the alcohol medium, interactions of BB9 (methylene blue) and BAA (Azur A) with silica may be due to the co-ordination of the sulfur atom of dyes with the silanolic group. An addition of an *o*-nitro group on the heterocyclic ring of BB9, to yield BG5, prevents such bonding. Apparently, the presence of an electronegative group in the vicinity of the positively charged sulfur atom in the BG5 molecule inhibits the $\equiv\mathrm{SiO}^- \cdots {}^+\overset{\|}{\underset{|}{\mathrm{S}}}$ bond formation.

As shown in Fig. 5, the extent of dyes adsorbed on silica in water at a pH of approximately 9 was in the order BV14 > BV4 > BY1 > BB9 > BG5. These molecules, except for BG5, appear to be adsorbed either in end-on or in edge-on orientation, since a monolayer of these dyes in a flat orientation would require an area in excess of $100\,\text{Å}^2$ per molecule.[26,27] Owing to differences in the position of the cationic ligand in the molecule (Table 1), the BY1 and BB9 dyes are adsorbed long edge (edge-on) on the silica surface, whereas BV14 and BV4 dyes are oriented in either a perpendicular position (end-on) or a sandwich-type association.

The amount of the adsorbed dye depends on the pH of the aqueous solutions. As summarized in Table 6, the uptake of BB9 on SiO_2 increases gradually as the pH becomes higher, owing to an increase in the number of the bonding sites ($\mathrm{Si{-}O^-}$) for cationic dyes. With enhanced adsorption of dyes, the negative charge of the pigment particles is reduced and eventually reversed to positive in acidic media, which is due to over-compensation of the weakly charged silica particles by the bound dye molecules.

With increasing uptake of a dye by the carrier particle, the shape of the transmittance or reflectance curve changes in a systematic but complex manner. The spectra in Fig. 6 represent a variety of the purple colors obtained from $YOHCO_3$–MB3 pigments dispersed in different media. Their relative purity is indicated by the sharpness of the peaks in the violet region (390–420 nm). Increased dye incorporation causes a narrowing of the transmittance peak and a corresponding enhancement in chroma purity of the pigments up to an optimum dye concentration (Sample 6, Table 5), while the color is darkened, which results in a smaller value of $Y\%$.

Different solvents as vehicles show little change in color purity but affect the lightness ($Y\%$) and the dominant wavelength of pigments. This influence on the optical contrast of the pigment particles is the result of light-scattering. The color condition may also be altered by the physical state of the dyes, such as their retention and association, owing to the dye–solvent interactions,[20,21] which explain some spectral bathochromic or hyperchromic shifts of the pigments dispersed in an aqueous or polyethylene glycol medium (Fig. 6).

The formulation of a colorant mixture is usually carried out with the aid of a color-matching computer. The computation is extremely complex[28,29] because of different coefficients of absorption (K) and scattering (S), characteristic of each pigment. The use of one kind of carrier particles for different dyes can facilitate the calculations, since a single value for S could be used. In addition, different pigments with the same carrier may have consistent retention properties, which is an important factor in color-matching.

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