Journal of the European Ceramic Society 18 (1998) 1357–1364

PII: S0955-2219(98)00065-X
0955-2219/98/$—see front matter

Preparation and Characterization of Well Defined Powders and their Applications in Technology*

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Abstract

Methods for the preparation of uniform dispersions of inorganic particles of simple and composite natures in varying shapes, ranging in size from several nanometers to several micrometers are described. The advantages of the use of such powders in different applications, including ceramics, catalysis, and pigments are illustrated. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

The preparation of monodispersed inorganic colloids can be traced back to Faraday, who produced the colorful gold sols,[1] followed by occasional reports describing uniform particles of elements (e.g. sulfur,[2] selenium[3]), or of various compounds (e.g. $BaSO_4$,[4] $Pb(IO_4)_2$,[5] WO_3[6]). Systematic studies of such systems were initiated some quarter of a century ago, which resulted in procedures for the synthesis of a large number of well defined dispersions. Presently, uniform particles of simple or composite (internally or externally) natures in modal sizes ranging from several nanometers to several micrometers, and in a variety of shapes can be obtained.[7–10]

For a long time this entire area of materials science was essentially considered to be of only academic interest. Most studies were concerned with the mechanisms of the formation of uniform dispersions, which are still not fully understood, and with the relationship between various properties of matter (optical, magnetic, electric, adsorptive, etc.) and the size and shape of particles, in addition to their chemical composition.

Recently, the importance of such colloids has been widely recognized in numerous applications in technology and medicine, especially when stringent specifications with respect to the size and shape of the materials and their reproducibility are required. Indeed, with the need for products of increased sophistication for uses in modern civilization, the availability of well defined dispersed matter has become an absolute necessity.

Here, a few examples are offered to demonstrate advantages of uniform particles in several diverse applications.

2 Preparation of Monodispersed Fine Particles

In the past, the finely dispersed matter, needed in many products or processes, was mostly obtained by grinding. This mechanical procedure does not yield, as a rule, powders of sufficiently narrow size distribution, and it certainly cannot produce particles of a given desired morphology. Instead, condensation processes are needed, in which atoms or molecules interact in a controlled manner, to yield uniform dispersed solids. Such reactions can be carried out in vapor or liquid phases. In the latter case the precipitation from homogeneous solutions offers the widest opportunities to generate monodispersed colloids and for this reason it will be discussed in this review.

The actual procedures for the preparation of such particles by precipitation have been described in several review articles and books.[11–15] To illustrate a variety of dispersions obtained by such processes, Fig. 1 shows different particles of simple composition,[14] while Fig. 2 displays examples of coated particles.[10]

In view of the fact that so many diverse systems have been obtained, one could assume that the mechanisms of their formation are fully understood. For a while the LaMer concept[22] was generally accepted, according to which identical

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*Based on the Plenary lecture at the Conferences on Powder Characterization for Advanced Materials Manufacturing, Gijón, Spain, 16–20 June 1997.

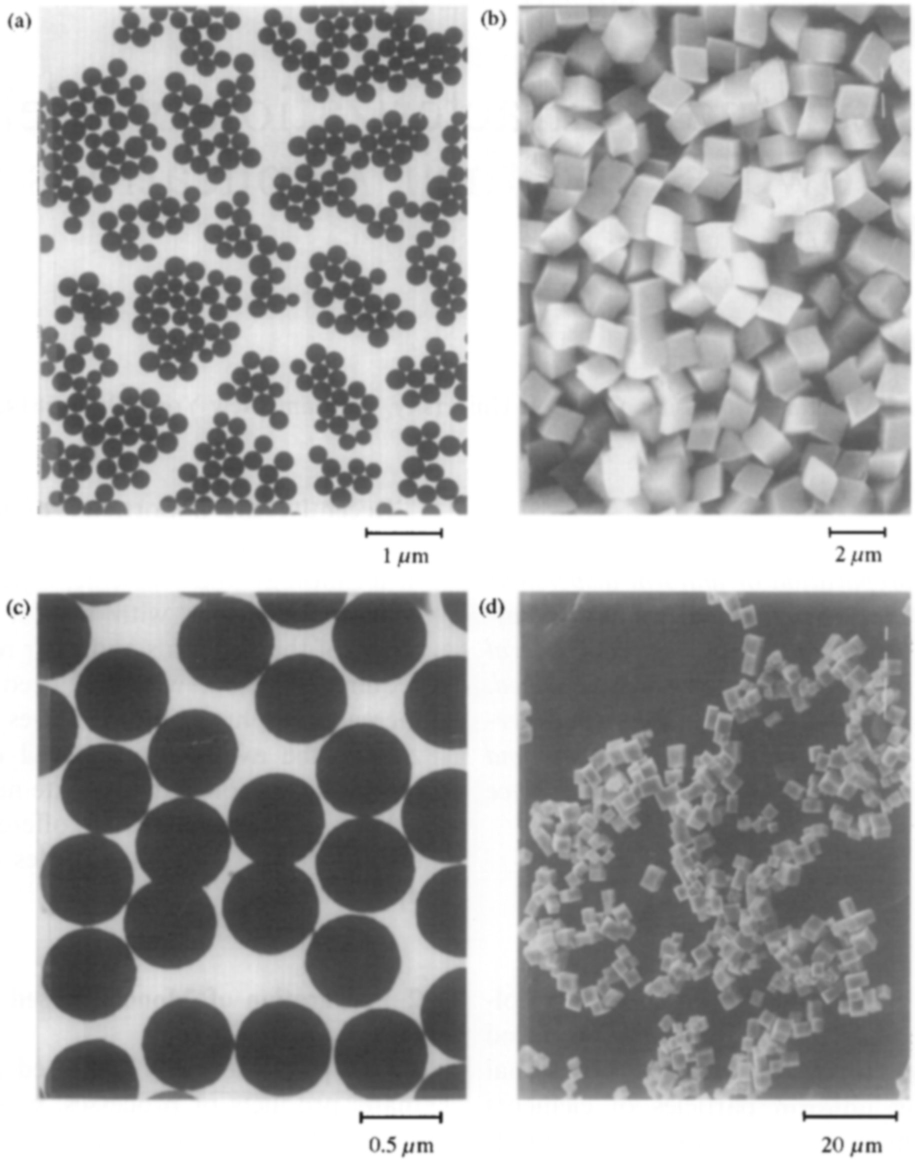

Fig. 1. (a) Transmission electron micrograph (TEM) of basic gadolinium carbonate particles obtained by aging at 90°C for 1 h a solution $5{\cdot}0\times10^{-3}$ mol dm^{-3} in $GdCl_3$ and 0·5 mol dm^{-3} in urea.[16] (b) Scanning electron micrograph (SEM) of $CdCO_3$ particles obtained by mixing 40 cm^3 of a 10^{-3} mol dm^{-3} urea solution (preheated before addition at 80°C for 24 h) and 40 cm^3 of a $2{\cdot}10^{-3}$ mol dm^{-3} solution of $CdCl_2$ at room temperature.[17] (c) TEM of ZnS particles obtained by ageing a 'seed' sol at 60°C for 1·5 h in the presence of $6{\cdot}2\times10^{-2}$ mol dm^{-3} HNO_3 and $1{\cdot}1\times10^{-1}$ mol dm^{-3} thioacetamide (TAA).[18] (d) SEM of PbS particles obtained by ageing at 26°C for 20 min a 'seed' sol in the presence of $1{\cdot}25\times10^{-3}$ mol dm^{-3} TAA.[19]

particles are formed when a short burst of nuclei is followed by uniform growth caused by diffusion of constituent solute species onto these initial solids.

Presently, it appears that the suggested LaMer mechanism is operational only in a limited number of cases, especially when amorphous spheres appear as the end product of a precipitation process, such as in the formation of colloidal silica,[23] aluminum hydroxide,[24] or chromium hydroxide[25] particles.

Instead, considerable evidence has become available showing that the primary particles, present after the nucleation stage, aggregate to the final uniform dispersed solids, which show crystalinity by the X-ray diffraction analysis.[26,27] It is now necessary to explain the effect by which a large number of small subunits interact to yield much larger identical particles. The understanding of the underlying principles should help to explain many properties of matter present in the form of fine powders.

For any practical applications of monodispersed colloids, it is of fundamental importance to develop techniques for their production in quantities. Two such procedures are described here.

Figure 3 is a schematic presentation of a plug-flow type of reactor,[28] in which different uniform particles of simple and composite natures, such as $Y(OH)CO_3$,[28,29] $Al(OH)_3$, SiO_2, $BaTiO_3$,[30] have been successfully prepared in a continuous manner.

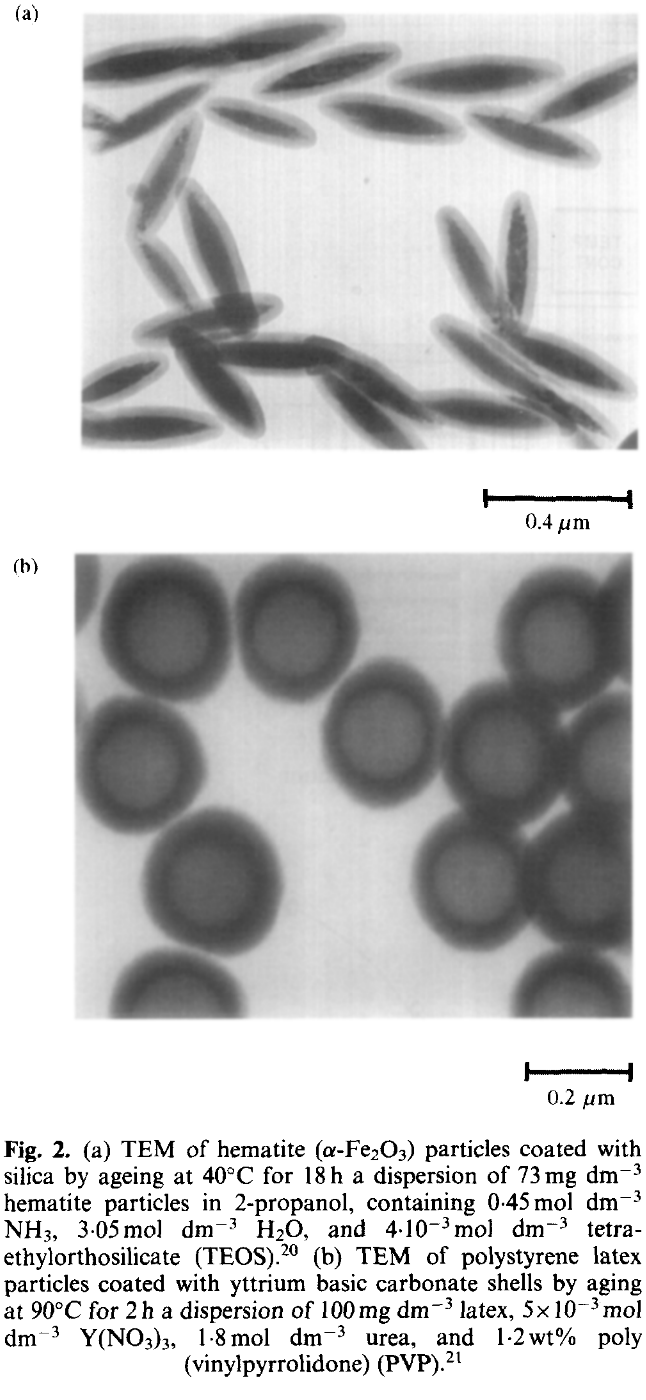

Fig. 2. (a) TEM of hematite (α-Fe_2O_3) particles coated with silica by ageing at 40°C for 18 h a dispersion of 73 mg dm^{-3} hematite particles in 2-propanol, containing 0·45 mol dm^{-3} NH_3, 3·05 mol dm^{-3} H_2O, and $4{\cdot}10^{-3}$ mol dm^{-3} tetraethylorthosilicate (TEOS).[20] (b) TEM of polystyrene latex particles coated with yttrium basic carbonate shells by aging at 90°C for 2 h a dispersion of 100 mg dm^{-3} latex, 5×10^{-3} mol dm^{-3} $Y(NO_3)_3$, 1·8 mol dm^{-3} urea, and 1·2 wt% poly (vinylpyrrolidone) (PVP).[21]

The laboratory scale model yields several kilograms of powders per day. The important aspect of this process is that the optimum conditions for producing a given monodispersed system, established by batch experiments, must be reproduced in the reactor. Any change in the concentrations of the reactants, temperature, reaction time, etc., would, as a rule, change the physical and often chemical characteristics of the products.

The other useful technique is the so called controlled double (or triple) jet precipitation (CDJP or CTJP), which is commercially being used in the photographic industry.[31] A laboratory set-up is schematically given in Fig. 4. This procedure allows for rapid introduction of reactants into a vessel, which may contain solutions of additional compounds, such as stabilizers (surfactants or polyelectrolytes), reducing agents, etc. While the method was originally designed to produce relatively large particles (several micrometers),[32] more recently it has been demonstrated that it can also yield much finer, even nanosized dispersions, such as of palladium and nickel sulfides,[33,34] zinc oxide,[35] and pure or doped $BaTiO_3$.[36,37]

3 Applications of Monodispersed Colloids

3.1 Ceramics

Having uniform powders in quantities made it possible to test some aspects of ceramics related to various particle characteristics. Uniform spherical colloidal yttria was pelletized and the density of the resulting solids was measured and compared with commercial products. Figure 5 clearly shows that the monodispersed powder on sintering yielded a product of theoretical density, in contrast to the powder consisting of irregular polydispersed matter, which never reached the same condition.[38]

In another example, composite particles of silica coated with yttria and vice versa were prepared with cores and shells of different size.[39] At temperatures > 1000°C these powders converted partly to yttrium silicate, the extent of which depended on the relative amounts of yttria and silica, while the compound present in excess in the particles remained unchanged. The schematic Fig. 6 indicates a variety of combinations in compositions of such particles before and after heat treatment. Of specific interest was the case where larger silica cores were coated with thinner yttria shells, which left part of the core unreacted. These powders were sintered, the pellets were cleaved and subsequently etched with HF. The latter only dissolved silica, making it possible to visualize the structure of a ceramic body obtained with coated particles, as displayed in Fig. 7.[39]

It is also important to note that other properties of solids produced from coated particles depend on the composition of cores and shells. Reversing the latter, but keeping the molar ratios the same, does not necessary result in the same physical characteristics, as illustrated on the example of densification of two samples, one having particles with silica cores and yttria shells and the other with yttria cores and silica shells (Fig. 8).

As mentioned before, controlled double jet precipitation (CDJP) was used in the preparation of uniform pure and doped barium titanates.[36,37] Crystalline powders of less than a micrometer in modal size were obtained in 5–8 min at a temperature of 90°C. By careful control of the concentrations of the reacting solutions, exact stoichiometries of

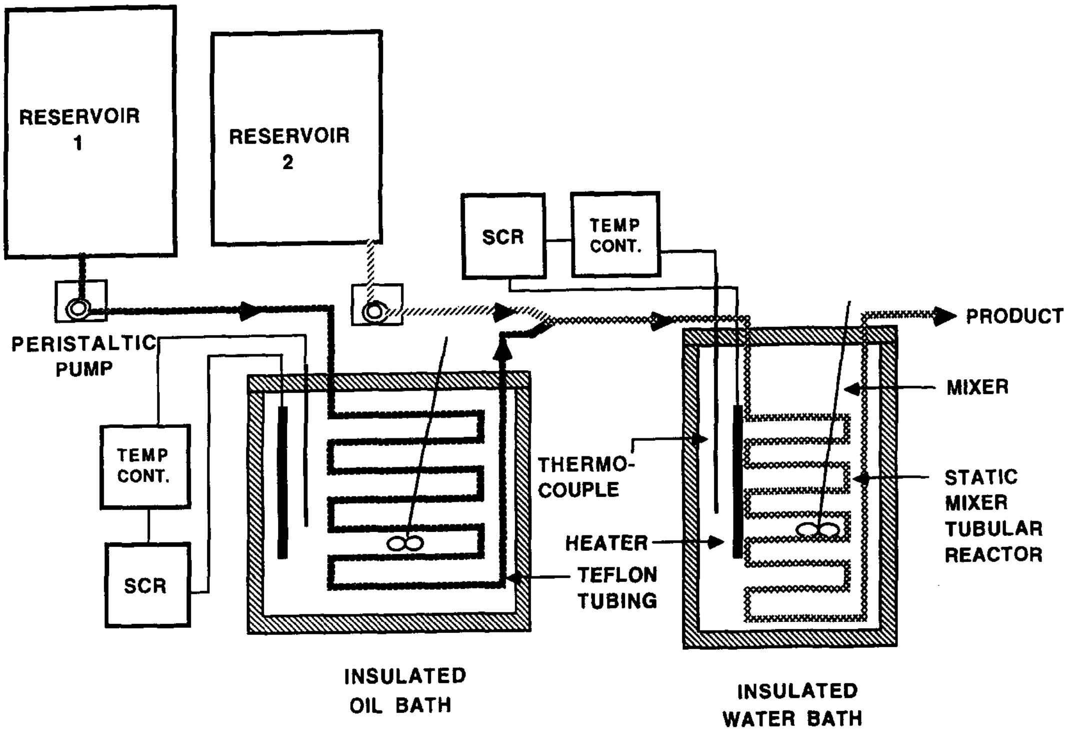

Fig. 3. Systematic presentation of the reactor for continuous flow precipitation.[28]

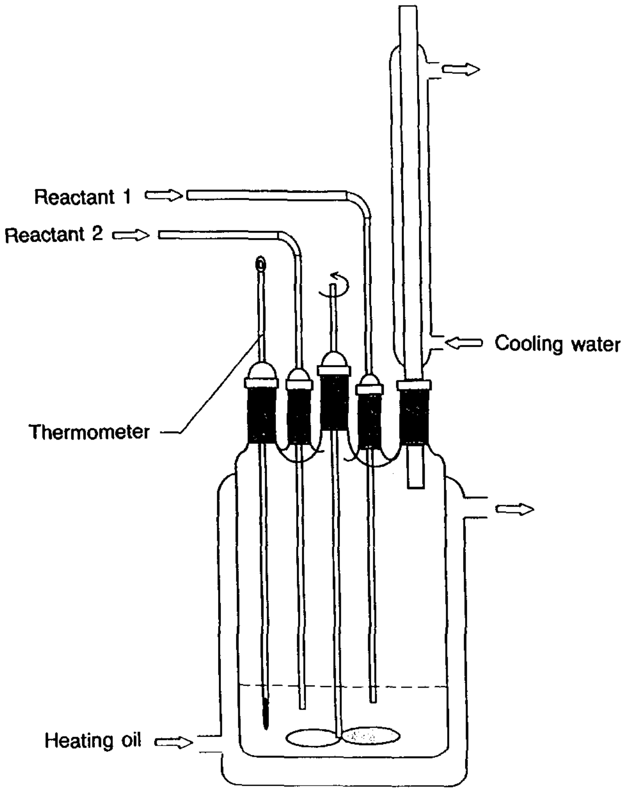

Fig. 4. Schematic presentation of the controlled double-jet precipitation (CDJP) reactor: the 0·50 dm^3 container is equipped with a heating jacket, into reactant solutions are introduced simultaneously by means of peristaltic pumps, under stirring rate of 500 rpm.[35]

the precipitated solids could be achieved. These powders yielded on sintering green bodies with a uniform grain size of 2–3 μm.

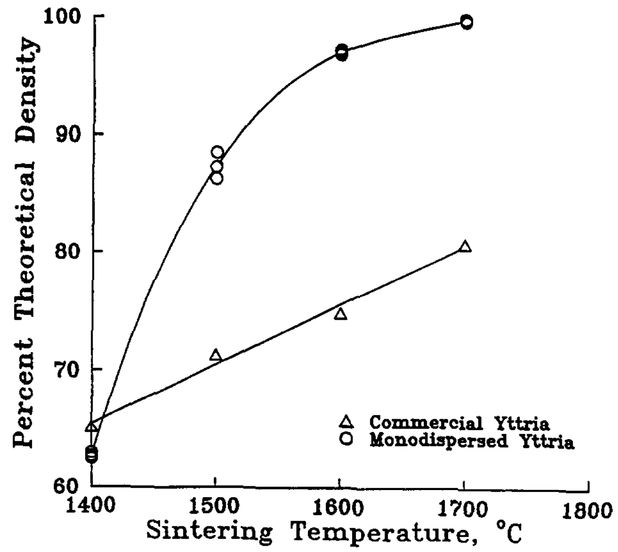

Fig. 5. Plot of the density of sintered pellets as a function of the sintering temperature of (○) the monodispersed spherical yttria particles 90·2 μm in diameter and (△) a commercial yttria powder consisting of irregular particles of broad size distribution.[32]

The calcined powders showed superior dielectric properties. Thus, the solid in Fig. 9 has characteristics suitable for multilayer capacitors, while that in Fig. 10 is a good candidate for thermal IR detectors.[37]

3.2 Catalysts

It is well known that various inorganic compounds, and especially metals, in the finely dispersed state act as catalysts.

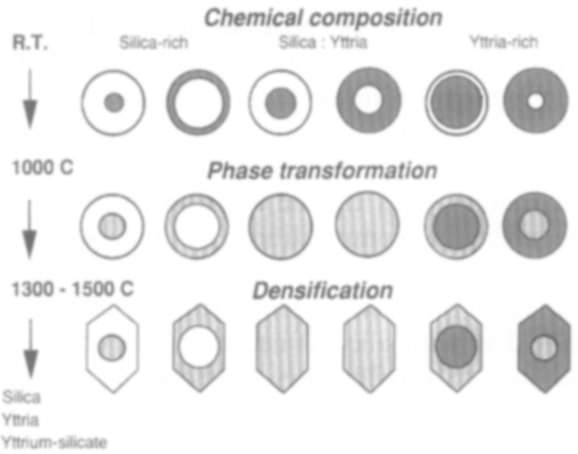

Fig. 6. Schematic drawing of the phase transformation and densification behavior of the silica-yttria system during the sintering process of coated powders of various core and coating thicknesses.[39]

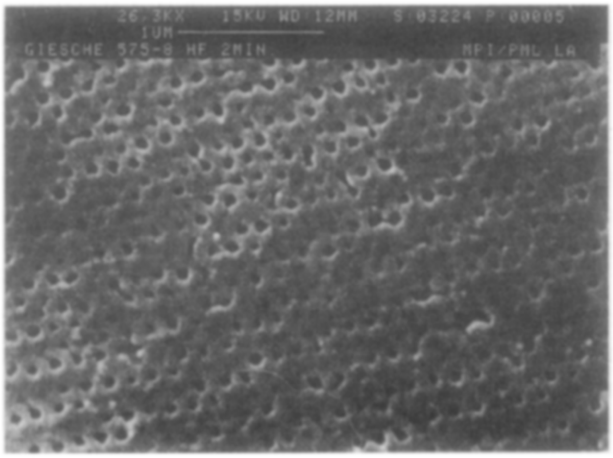

Fig. 7. SEM of a cross-section of a ceramic pellet, prepared by using a powder consisting of silica cores (86 μm in diameter) coated with yttria shells (30 μm thick), which was sintered at 1300°C for 1 h, then cleaved, polished, and finally etched with 4% HF for 2 min.[39]

Recently, nanosized PdS (20–30 nm) was prepared by the CDJP technique by reacting $PdCl_2$ or $Na_2(PdCl_4)$ with Na_2S solutions in the presence of an anionic surfactant (Fig. 11). The so prepared particles adhere well to an epoxy surface treated with a cationic conditioner and efficiently catalyze the electrolytic deposition of copper on the walls of circuit board holes of different sizes.[33]

Another example is the Pd/Sn catalyst for electroless plating. After much controversy regarding the nature of this material, it was established without a doubt that nanosized particles show the catalytic activity, rather than solute complexes formed on reacting $PdCl_2$ with $SnCl_4$ solutions.[40]

3.3 Pigments

The color of a given pigment depends in a sensitive manner on the size and shape of its particles. If the latter consist of spheres of known refractive index, the optical properties can be exactly calculated. Figure 12 illustrates the dependence of the adsorption and scattering coefficients of uniform colloidal spheres having the refractive index of hematite.[41] It

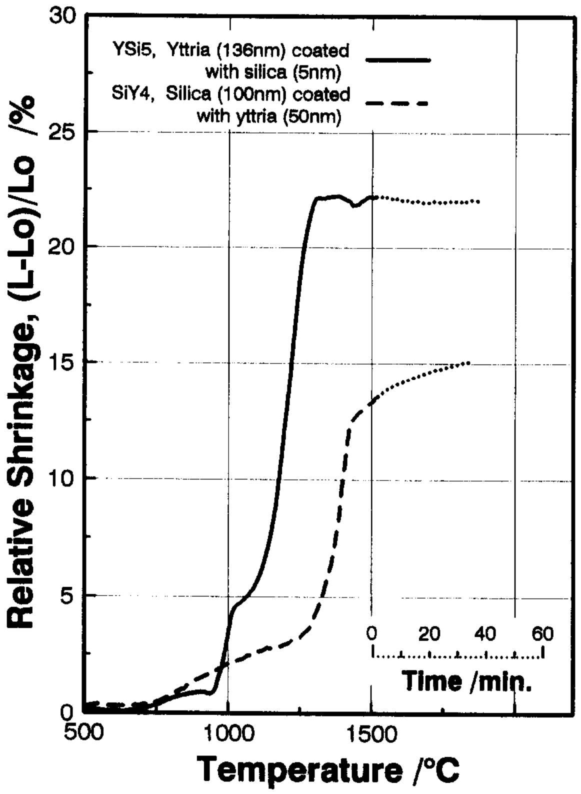

Fig. 8. Dilatometry data for two powders of close molar ratios $[SiO_2]/[Y_2O_3]$, but of opposite cores and shells (precalcined at 600°C for 24 h) as a function of temperature. Samples were heated at a rate of 10°C min^{-1} up to 1500°C in a flowing Ar atmosphere, followed by an isothermal hold at 1500°C for the lengths of times indicated by the scale in the inset (···).[39]

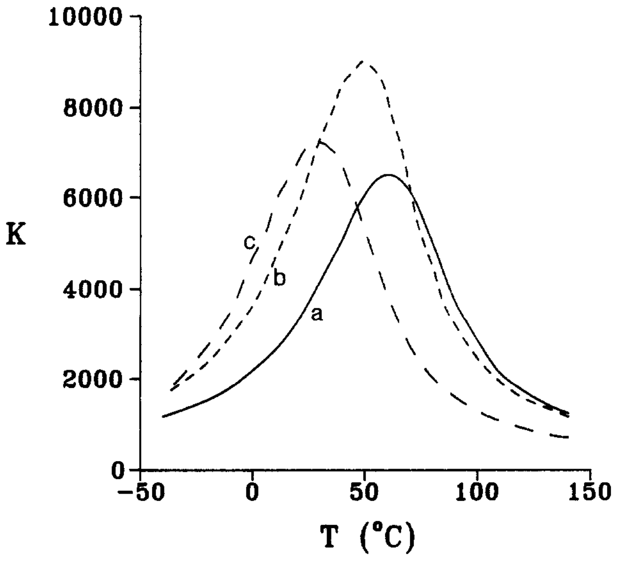

Fig. 9. Plots of the relative dielectric constant (K) as a function of temperature for Zr-doped barium titanate synthesized by the controlled double jet precipitation (CDJP), and sintered at 1275°C with different Zr contents: (a) 17%, (b) 20%, and (c) 23% of Ti atoms substituted by Zr.[37]

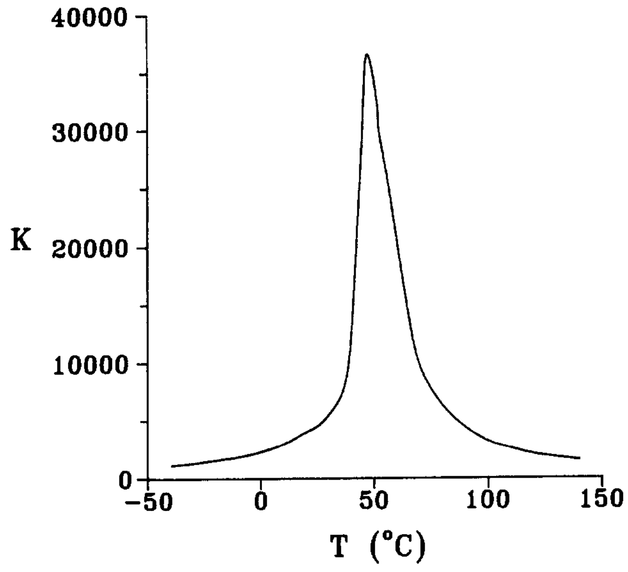

Fig. 10. Plot as in Fig. 9 for Sr- and Zr-doped barium titanate sintered at 1275°C of the solid composition (Ba + Sr)/(Ti + Zr) = 0.996 ± 0·005, Sr/Ba = 0·061 ± 0·005, and Zr/Ti = 0·184 ± 0·005.[38]

should be noted that a small change in particle size has a significant effect on its optical properties. This dependence has indeed been experimentally confirmed with hematite, which is a common red pigment.[42]

Since a vast majority of commercial colored powders consists of irregular polydispersed particles, it is obvious that their optical characteristics cannot be reproducible. Additional difficulty is that these pigments are, as a rule, insoluble in any solvent and they decompose on melting, making it difficult, if not impossible, to produce them as uniform particles. To circumvent this problem, pigments have been prepared by interacting dyes with monodispersed spherical particles.[43,44] By selecting the core materials of a given refractive index and size, and combining them with specific dyes, it is possible to produce, in a controlled manner, pigments of any desirable color, purity, transparency, etc. The dye can be incorporated into the core, if the latter is precipitated in the presence of the color molecules. Alternately, dyes can be adsorbed, in which case the chemical compositions of the solids and solutes play a dominant role. Thus, acidic dyes interact with basic surfaces, such as alumina, and basic dyes with silica. If necessary, the cores can be modified to provide sites for bonding. For example, acid dyes will interact with silica surface modified with specific silanolic groups or coated with alumina.

Figure 13 illustrates a series of so synthesized pigments using different cores,[44] while Fig. 14 shows examples of spectra using the same silica and different dyes.[43] With very small cores (several nanometers), it is possible to achieve exceedingly high transparency. A polymer film, 5 μm thick, containing 55 wt% of such a pigment, synthesized with nanosized (10–15 nm) TiO_2 particles and coated with the Red Dye #6, shows 100% transparency (Fig. 15). Photoresists prepared with these materials had a 150% higher constrast than the best commercial films.

The optical properties of concentric spheres are also fully understood, offering another avenue in the design of pigments for specific applications. For example, uniform silica particles coated with titania can be used to synthesize paper whiteners of desired optical characteristics, which can be controlled by the size of the core and the thickness of the shell. The so prepared coated powders showed high and reproduce reflectance.[46]

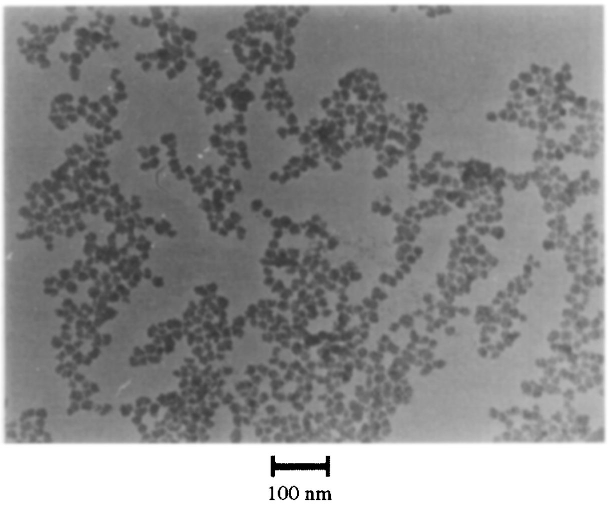

Fig. 11. TEM of a PdS catalyst prepared by the CDJP process by mixing 50 cm^3 solutions each of 2×10^{-3} mol dm^{-3} acidified $PdCl_2$ (HCl) and 2×10^{-3} mol dm^{-3} Na_2S.[33]

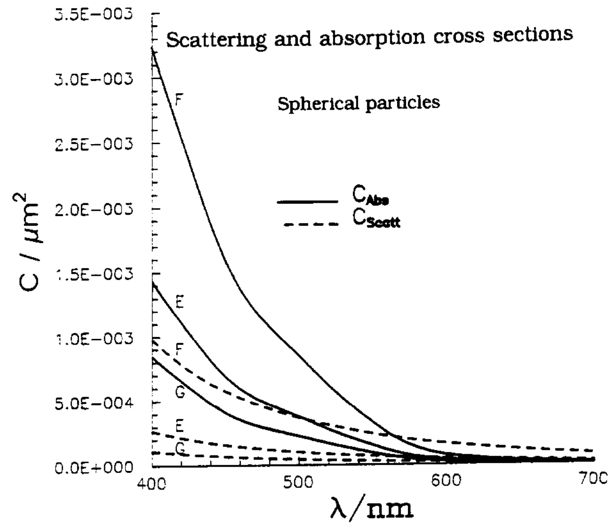

Fig. 12. Calculated scattering and absorbance cross-sections for a single spherical particle having refractive index of hematite. Particle diameters: G, 53 μm, E 61 μm, F 74 μm.[41]

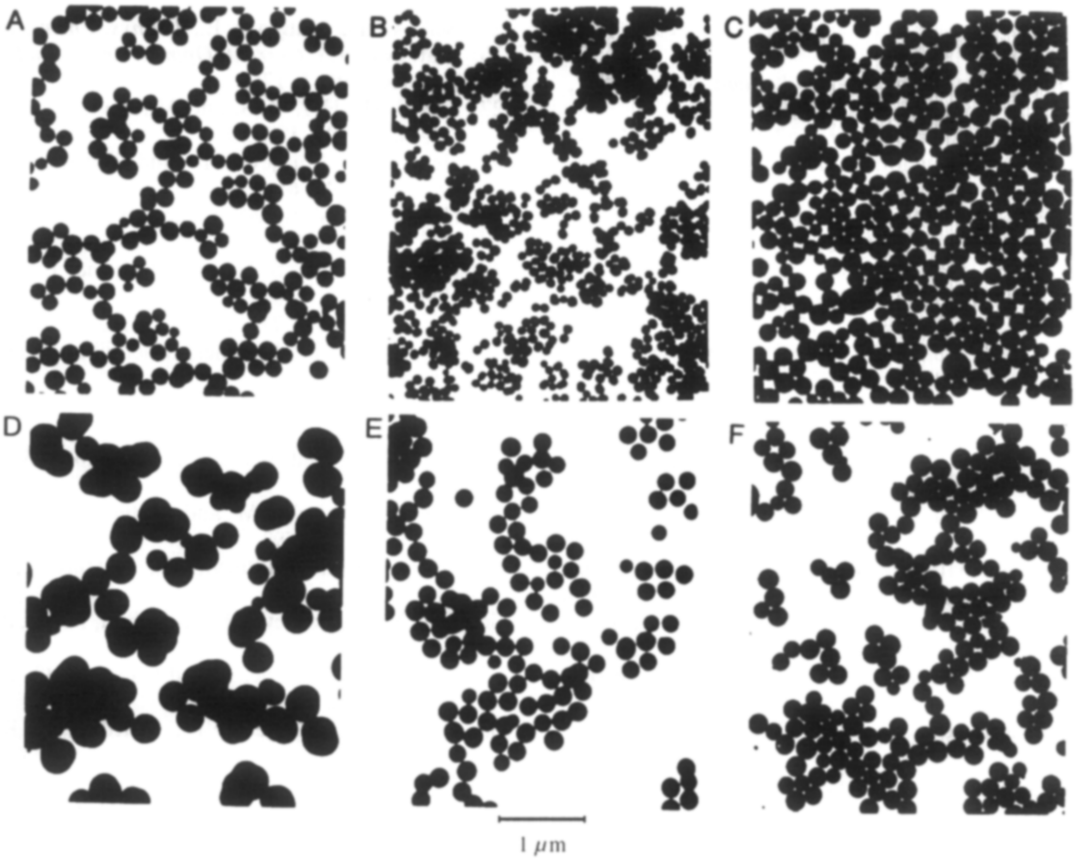

Fig. 13. TEM of pigment particles obtained by interacting water soluble dyes with spherical inorganic particles: (A) Aniline Blue/$Y(OH)CO_3$; (B) Acid Black 3/$Y(OH)CO_3$; (C) Acid Yellow 99/$Y(OH)CO_3$; (D) Naphthol Green B/$Y(OH)CO_3$; (E) Acid Red 183/$Y(OH),CO_3$; (F) Acid Red 183/$Al(OH)_3$.[44]

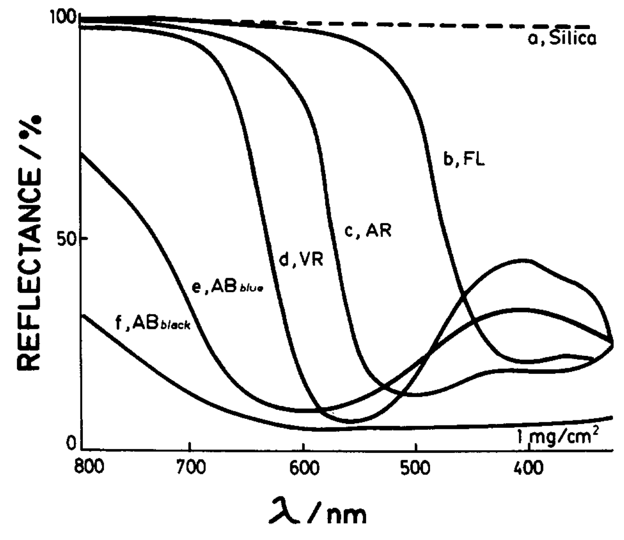

Fig. 14. Reflectance spectra of powder samples of different dyes coupled to amino-modified silica particles of ~100 μm in diameter. (a) silica, (b) Flavoxin L; (c) Acid Red 183; (d) Violamin R; (e) and (f) Acid Blue 45 interacted with differently modified cores.[43]

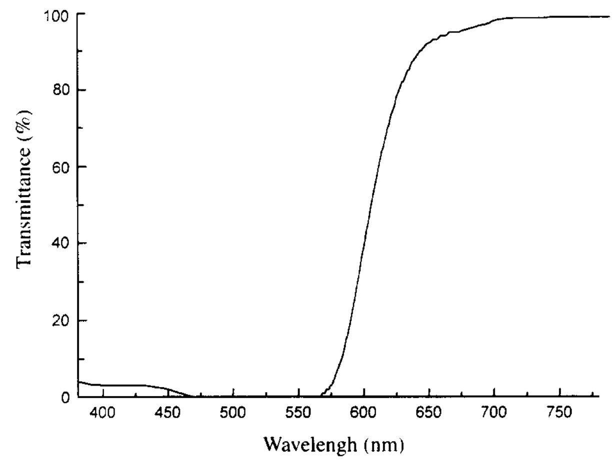

Fig. 15. Transmittance spectrum of a polymer film containing 55% by wt of a nanosized pigment prepared by interacting Red Dye #6 with titania particles 10–15 μm in diameter.[45]

4 Concluding Remarks

The intention of this review is to demonstrate that a large number of monodispersed simple and composite inorganic colloids can now be prepared. These dispersions may be designed to meet rather stringent specifications for various application, resulting in superior products. Examples in different areas of materials are offered to substantiate these claims.

Acknowledgement

Supported by the NSF grant CHE-9423163.

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