SCIENCE AND ART OF FINE PARTICLES

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Without science we should have no notion of equality, without art no notion of liberty.
W.H. Auden

INTRODUCTION

This presentation deals with an area of materials science, which is causing a great deal of excitement for academic and practical reasons, i.e. with the so called monodispersed colloids. While the subject is an old one, dating back to Faraday's gold sols described in 1857, it has become a topic of wide-spread interest only relatively recently.

There are some intriguing aspects of this field of science and technology which justify some comments. First, it is obvious from the title, that the size of the "fine particles" to be discussed is missing. Presently we have two groups of scientists interested in finely dispersed matter, some dealing in the nanometer and the other in the micrometer range. In many cases these systems are treated as separate worlds, yet it will be shown that they are closely connected, especially when these dispersions are prepared by chemical reactions in solutions.

Another interesting aspect is that the uniformity of particles has seldom been encountered in natural environments. Indeed, there are only a few examples of indigenous monodispersed systems, opal being probably the best known. Yet scientists have produced a large number of such solids over a broad range of modal sizes, of simple or mixed (internally or externally) compositions, of different structures, and in a variety of shapes. The reasons for the discrepancy between the natural occurrences and research achievements will be addressed in the presentation.

It will also be shown that, despite this progress, many questions remain to be resolved, which represent major challenges to the workers in the field. One of the problems is the actual mechanism (or mechanisms) by which uniform particles are formed. A recent development on the subject will be described. Another aspect is the predictability of shapes and structures of monodispersed colloids, to which there is still no answer.

Finally, the title of the lecture requires further explanation. The word "art" has two meanings in the English language: it is used to describe skilled craftsmanship or something of beauty. In dealing with well defined particles there is room for both of these interpretations.

EXAMPLES OF UNIFORM PARTICLES

There are many different techniques, which may yield particles of uniform size and shape, but none can be used to produce every kind of dispersions of desired properties. Due to the simplicity, versatility, and practicality, the precipitation from solutions is the method of choice. In the past this procedure yielded a number of monodispersed systems, although mostly by serendipity. About a quarter of a century ago systematic studies were initiated, which resulted in a multitude of well defined dispersions as reviewed in several articles[1-3]. In most instances the processes have involved either mixing reactants or decomposing complexes, normally under mild temperatures and in moderate concentrations. A few examples of uniform particles of simple chemical compounds are illustrated by the electron micrographs in Figure 1.

Using the same technique, it is also possible to precipitate composite particulates. The latter can be homogeneous of exact stoichiometry, as exemplified by pure or doped barium titanates. To achieve these conditions rapid mixing is required, such as by using the controlled double jet precipitation process. In contrast, slow precipitation results, as a rule, in internal inhomogeneity, i.e., the composition changes from the center to the periphery, although the particles may still be perfectly spherical, as observed with mixed alumina/silica, or copper/lanthanum, or copper/yttrium oxides.

Another major area of interest are coated particles. Again, it is possible to produce uniform surface layers of varying thickness on inorganic cores with either inorganic or organic coatings or organic cores with inorganic coatings. It is interesting that the shell of the same material can be deposited on different cores. For example, yttrium basic carbonate coatings were produced on silica, hematite, and latex!

It is essential to note that conditions needed to obtain a given material as a uniform dispersion are sensitive to a great degree to the experimental parameters, such as the temperature, concentration of reactants, pH, ionic strength, solvent composition, etc. In some cases even a small change in these conditions can not only affect the particle uniformity, but it may yield solids of different chemical composition, structure, or morphology. This sensitivity

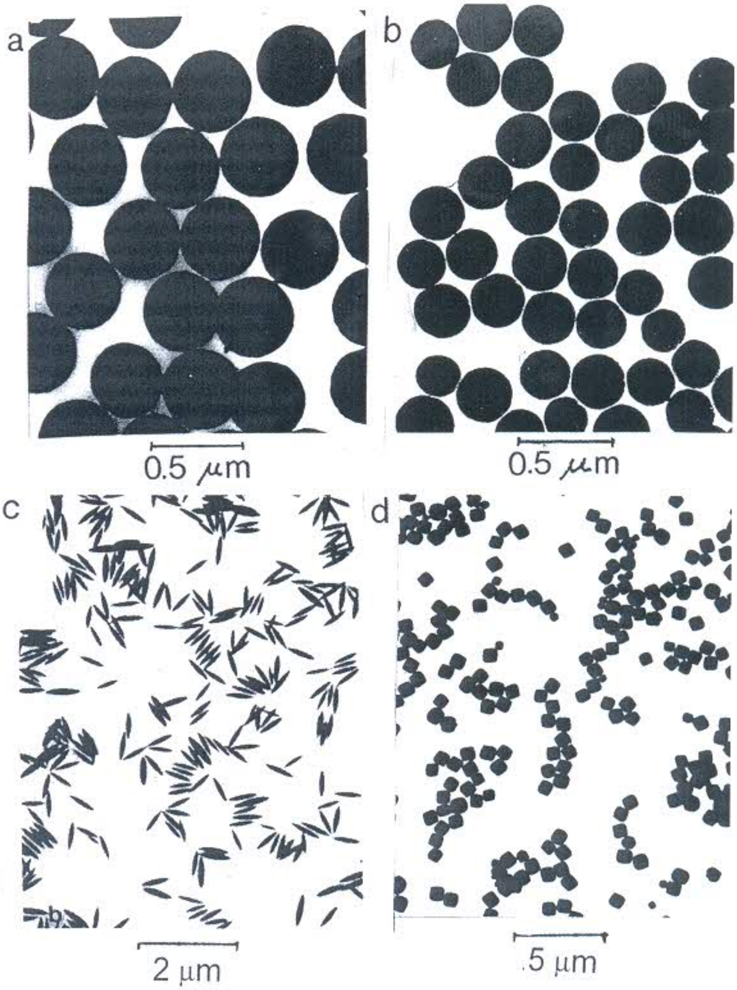

FIGURE 1 - Transmission electron micrographs (TEM) of (a) zinc sulfide, (b) manganese(II) phosphate, (c) and (d) hematite (Fe_2O_3) particles.

explains the paucity of naturally occurring monodispersed particles. It should also be noted that the laboratory preparations require minutes or hours, while the processes in nature extend over geological times.

A final comment in this section refers to scaling up the production of well defined powders. Interestingly, the two materials first obtained in large quantities are the polymer latex and silica. The first is not a subject of this presentation, while silica will be exemplified in connection with some applications.

One important aspect of scaling up precipitation processes, which yield uniform particles, is the necessity that any engineering design must consider the optimum conditions established in small batches. Much success has been achieved by using a plug-flow type of a reactor for continuous precipitation of a variety of uniform colloid dispersions, such as yttria, silica, aluminum hydroxide, and barium titanate[4]. The schematic presentation of this equipment is given in Figure 2.

MECHANISM OF THE FORMATION OF MONODISPERSED PARTICLES

As one would expect, the understanding of the mechanism of the formation of monodispersed colloids by precipitation has been of major concern to workers in the field. For a long time the concept developed by LaMer was generally accepted; i.e., such dispersions should be generated, if a short lived burst of nuclei in a supersaturated solution is followed by controlled diffusion of constituent solutes onto these nuclei, resulting in the final uniform particles. This mechanism is indeed operational in some, albeit limited cases, and more often only at the initial stage of the precipitation process.

For a long time the writer of this article has been puzzled by some

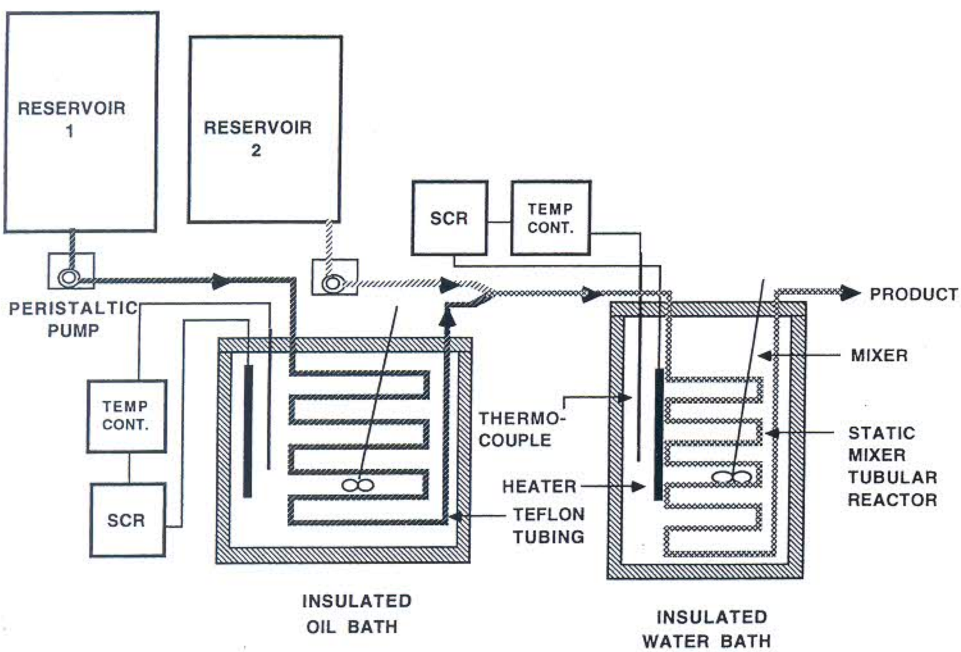

FIGURE 2 - Schematic presentation of the apparatus for continuous flow precipitation.

experimental observations, one of which is illustrated by the electron micrograph of zinc sulfide in Figure 1a. These perfectly spherical particles, obtained by precipitation in ionic solutions, exhibit X-ray characteristics of a known mineral (sphalerite). Obviously, it is not easily understood why would such homogeneously precipitated perfect spheres have crystalline characteristics. Importantly, low angle X-ray measurements showed these particles to be made up of essentiality identical nanosized subunits. Electron microscopy and other methods of evaluation demonstrated on numerous other dispersions, that particles of different morphologies and chemical compositions clearly exhibited particulate substructures.

Based on the illustrated samples and many others, it is now firmly established that the prevailing mechanism in the formation of monodispersed particles proceeds in several stages: (*1*) nucleation, (*2*) growth to nanosize particles, and (*3*) aggregation of nanosize particles to uniform final colloids. Extensive studies have indeed documented the existence of the aggregation stage[5]. For example, the electron micrographs, X-ray analysis, and independently prepared precursor particles all yielded the average diameter of crystallite subunits of 35±5 nm of spherical gold particles displayed in Figure 3[6].

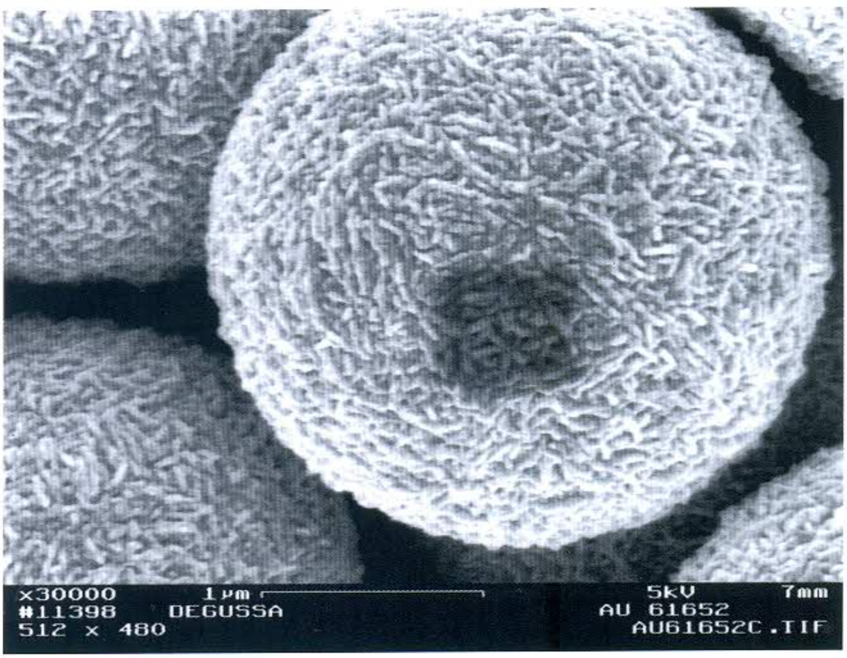

FIGURE 3 - Colloidal gold particle.

It was then necessary to derive a mechanism, which would account for the aggregation of a huge number of nanosized particles into identical larger colloids. Recently a kinetic model has been developed that explains this size selection mechanism [7]. The latter is based on the assumption that the nucleation is followed by a rapid formation of singlets, i.e. primary (nanosized) particles, which are sufficiently sparsely populated, and once formed are not further generated. Thus, their concentration decays by aggregation, when the conditions in the system eliminate repulsion between them. The latter can be due either to an increase in the ionic strength or to a change in the pH in course of the process. It is also assumed that the diffusion constant of singlets is larger than that of aggregates. The dominance of the irreversible singlet capture in the growth process can, under certain set of conditions, result in the size selection (i.e. uniformity) of the final particles.

The calculated size distributions of the secondary (final) spheres for three reaction times, using the parameters for the precipitation of the displayed gold sol, are given in Figure 4. The model describes reasonably well the experimental observations, considering the simplification used in the calculations.

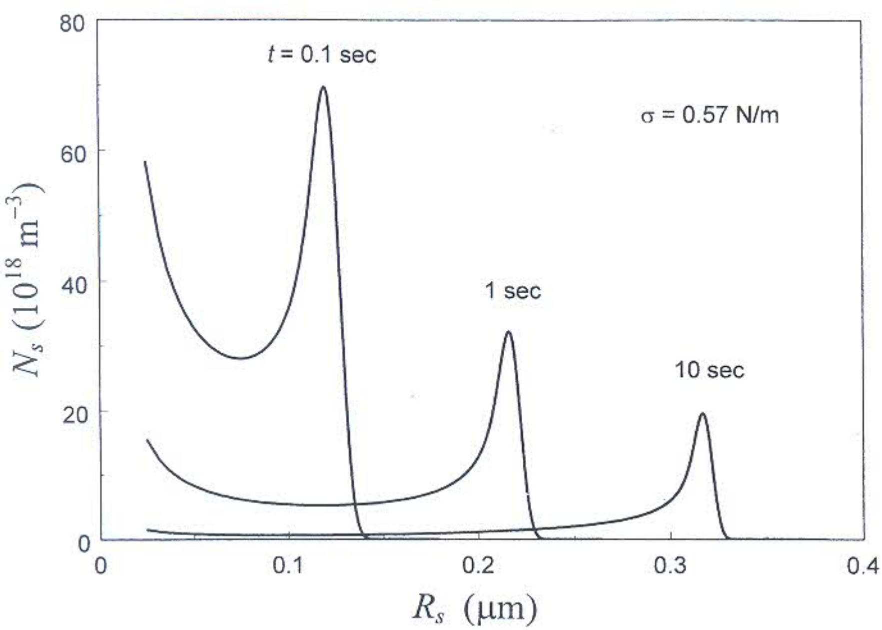

FIGURE 4 - Distribution of secondary particles by their sizes at 0.1, 1, and 10 sec., calculated for the precipitation of spherical gold particles, using the model described in ref. 7.

An interesting consequence of the newly established mechanism, is the fact that precipitation in solutions yields, as a rule, nanosized particles. If the process is arrested at this stage by additives, such as surfactants or microemulsions, one obtains stable nanosystems. However, in the absence of stabilizers, these particles aggregate (rather than to grow) into larger final products, which under appropriate conditions consist of monodispersed colloids. Thus, here we have found the "bridge" between the two "worlds" mentioned earlier!

NANOSIZED PARTICLES

The understanding of the mechanism of the formation of colloids throws new light on the possible preparation procedures of nanosized particles. Normally, wet routes involve precipitation in the presence of large amounts of surfactants (e.g. microemulsions, vesicles, etc), which affect the nucleation stage, but also stabilize the resulting finely dispersed matter. These processes make it difficult to separate solids from the additives.

Obviously it is of interest to produce monodispersions in quantities with a minimum amount of stabilizers. One such process is based on the recognition that larger particles are aggregates of much smaller precursors. Should it be possible to peptize such colloids, one would have a new avenue of approach in the generation of nanoparticles. This method was indeed proven possible in some cases. Thus, monodispersed colloidal indium hydroxide was prepared in ethylene glycol. On addition of water the original organic solvent was leached out and the precipitated solids fell apart into constituent subunits of nanometers in size.

Another useful technique proves to be the controlled double jet precipitation (CDJP), which can yield in larger quantities nanoparticles in the presence of moderate amounts of surfactants, as demonstrated on a variety of systems, including ZnO, PbS, $BaTiO_3$, etc.

"ART" AND SCIENCE

The new developments in the understanding of the mechanisms of formation of monodispersed colloids have greatly advanced the scientific aspects of this area of materials. Yet in actual preparations the art, i.e. skills, still play an essential role, especially since we do not know how to predict and control some properties, such as the shape or even the composition of the resulting particles.

The finely dispersed matter offers much in terms of the other aspect of art, i.e. the beauty. The latter can be affected by shape or color or both.

Examples of such artistic impressions will be offered using electron micrographs of monodispersed particles and their surfaces. Even more importantly, pigments, marbles, metals, etc. are made of fine particles, without which we would have no paintings, sculptures, and other works of art, which so much embellish our lives.

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