Chapter 3

Dispersions and Coatings

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INTRODUCTION

The object of the controlled assembly of nanoparticulates is to make materials with new properties and assemble them with practical applications. A unique value of nanoparticulates is their extremely high particle surface area; having many more sites for achieving property enhancements makes them ideal for a wide variety of applications as dispersions and coatings. Dispersive and coating applications of nanoparticles include optical, thermal, and diffusion barriers. Significant work on nanoscale dispersions and coatings is underway worldwide in the areas of ceramics, cosmetics, biosensors, colorants, and abrasion-resistant polymers. Other applications include imaging ink jet materials, electrophotography, pharmaceuticals, flavor enhancers, pesticides, lubricants, and other proprietary applications specific to industry. Still another application is in a new, post-silicon generation of electronic devices that includes nanotubes and fullerenes as constituent units of carbon nanoelectronic devices; here, dispersion takes on a more quantum consideration in which the number of atoms in a cluster is compared to the number of surface atoms to determine its dispersion function. Also in the semiconductor industry, a monolayer or thin film coating of atoms or molecules is deposited on foils, metal sheets, or glass to enhance storage capacity and accelerate responses from the electronic component.

All these applications deal with dispersions or coatings of particles that enhance specific features. Also, ability to manufacture smaller functional systems enhances performance, cost, and efficiency. These considerations power the drive towards miniaturization and precision finishing.

PROPERTY AMPLIFICATION

What's particularly exciting in the study of nanoparticles, nanostructured materials, and nanodevices is their ability to also add value to materials and products through enhancement of specific properties, such as the following:

- Mechanical strength. Nanostructured powders have been produced by plasma processing where the reactor vaporizes coarse metal particles (Froes 1998, 105-6); by combustion synthesis where redox reactions take place at elevated temperatures, followed by quenching; and by mechanical alloying with gas atomization. When nanocrystalline powders achieved by these means are compacted and applied as a coating, they lend significant strength and ductility to a variety of conventional materials such as ceramic, composites, and metal alloys.
- Superconductivity. Brus (1996) describes the nature of the superconductivity effect in detail. It involves a deposition of nanocrystals on substrates, leading to improved optical and electrical properties.
- Covering power. Because nanostructuring increases the number of active sites—there are many more atoms per grain boundary—the enhanced surface area leads to a reduced material requirement, which in turn can lower cost (Solomaon and Hawthorne 1983).
- Ability to incorporate high cost materials. Expensive materials such as colorants and drugs may be effectively dispersed in small and controlled quantities through nanostructuring (Schnur 1994).
- Environmental value. Improvements in environmental impact are achieved by utilizing nanostructure particulates in coatings and thus eliminating the requirement for toxic solvents. By eliminating hazardous wastes, nanocoatings can both reduce a company's disposal costs and improve its environmental position.

Thus, nanostructured dispersions and coatings can significantly reduce material costs and improve performance and functionality in a large variety of applications. In all of the sites the WTEC panel visited in Europe, Russia, and Japan, research groups were interested in achieving one or more of the properties listed above.

ENABLERS

For nanoparticulate dispersions and coatings, certain enablers must be present to achieve success: (1) effective particle preparation, (2) stabilization of the dispersed phase, (3) scaleup and control of the process, and (4) the existence of excellent analytical capabilities. The main methods or issues for each are described below.

1. Particle preparation. Wet chemical methods such as liquid phase precipitation or sol-gel methods are of high interest in particle preparation (Friedlander 1993). In the area of hybrid methods, both spray pyrolysis and flame hydrolysis are utilized. Numerous physical methods such as mechanical size reduction are also often employed.

2. Stabilization of the dispersed phase. For stabilization of the dispersed phase, it is necessary to understand how particles can be kept as distinct entities. Either a charged stabilized system or a sterically stabilized approach is required. A successful preparation for use as a dispersion should be free from agglomeration in the liquid state so as to maintain particle integrity. The dry-coated format of nanoparticles should also minimize any presence of particle aggregation

3. Scaleup and control of the process. The scaleup and control of nanoparticle processing is well described by Kear (1998). Here, the issue in achieving a high rate of production of powder is the effective pyrolysis of the gas stream containing the precursor. Issues such as scaling and reproducibility from one run of nanoparticle material or dispersions to another are all inherent in the concept of precision engineering or invariant process control.

4. Analytical capabilities. Analytical capabilities are absolutely essential for characterizing dispersions and coatings (Angstrom 1995). Particle size determinations, assay analysis, and interfacial properties are all important. Transmission electron microscopes, atomic force microscopy, nuclear magnetic resonance, and scanning tunneling microscopy are just some of the tools utilized in characterizing nanoparticle dispersions and coatings, particularly at the very small end of the nanoscale.

APPLICATIONS

Below are some general examples of the vast array of applications of nanoparticulate dispersions and coatings. There are a number of applications in all of the categories below that are already in the public domain; however, most are still highly proprietary, especially drug delivery applications.

Cosmetics. An area of nanoparticle technology that has incredible commercial potential is the cosmetic industry (Crandall 1996, 251-267). Here there is a great demonstrated demand, and the technology can be made simple, since properties of color and light fastness are achieved by component mixing in the cosmetic preparation. A survey in 1990 indicated a worldwide gross volume of $14-18 billion for toiletries (Crandall 1996, 61), i.e., traditional hygiene products such as powders, sprays, perfumes, and deodorants. The large markets for sunscreens and skin rejuvenation preparations promise additional revenues.

The diet industry is said to gross $33 billion annually (Crandall 1996, 61). One way that nanoparticle technology is addressing this market is through introducing nanoparticulate taste enhancers into low-calorie substrates.

Medicine/Pharmacology. In the area of medical applications, finely dispersed pharmaceuticals offer rapid drug delivery and reduced dosages for patients (POST 1995). Dispersions of strong and resilient biocompatible materials suggest opportunities for artificial joints. These generally are ceramic materials containing nanoparticulates.

Overall, much of the demand for nanoparticulate dispersions and coatings comes from the cosmetic and pharmaceutical industries; in particular, liquid dispersion preparations will be widely used to apply topical coatings to the human epidermis because they can be absorbed faster and more completely than conventional coatings.

Microelectromechanical systems (MEMS). Although MEMS technologies will support the semiconductor industry in particular, there are many other applications being explored, such as in medicine, ceramics, thin films, metal alloys, and other proprietary applications. In the United States a particular focus is applying sputtering coatings to achieve MEMS technology in concert with these applications.

Printing. In the areas of image capture/image output addressed by ink jet technology, nanoscience can help control the properties of the inks themselves. The production and use of nanoengineered ink products benefits from such complimentary technology as laser-assist delivery of the ink jet droplet to maintain an accurate deposit of the ink on its target (POST 1996). Another application in this field is using nanoscale properties to tailor the inks to achieve ideal absorption and drying times for desired color properties and permanency.

Semiconductors. One form of “bottom up” technology that is receiving considerable attention is thin films for the semiconductor industry (POST 1996). Here single atoms or molecules are deposited by physical vapor deposition, which could be achieved through sputtering, molecular beam epitaxy, or chemical vapor deposition. Sputtering is used on a large scale to coat metal sheets, glass, polymer substrates and other receptive materials in order to produce enhanced electronic properties for information storage and processing speed.

Sensors. Chemical or physical sensors often use nanoparticles because they provide high surface area for detecting the state of chemical reactions, because the quality of detection signals is improved, and because earlier and more accurate determination of leakage reduces waste. Some commercial sensors and actuators composed of thin films are already used for environmental vapor monitoring in reactors, for example.

Other likely applications of nanotechnology involving dispersions and coatings include nanofabricated surface coatings for keeping windows and surfaces clean (POST 1996). Here, the transparent nanocoating on a surface prevents fog and dirt particles from depositing on the substrate. Commercial products (achieved through gas phase condensation) also include aluminum oxide/epoxy dispersions yielding 19 times more wear resistance than conventional products.

ONGOING R&D / PREPARATION ISSUES

During the course of this study, the WTEC panelists were privileged to hear of and to observe a wide variety of current work on nanostructured dispersions and coatings in various laboratories around the world. Descriptions follow of a number of research projects and the preparation issues being addressed in the United States and in some of the foreign laboratories that panelists visited. Table 3.1 outlines some of the nanoparticle preparation techniques that are currently in use, many of which will be discussed in the paragraphs that follow.

Work in the United States

Significant work on coatings of dispersions is underway in the United States, as described in the proceedings of the 1997 WTEC workshop report, *R&D status and Trends in Nanoparticles, Nanostructured Materials, and Nanodevices in the United States* (Siegel et al. 1998). Some of the highlights of that volume are summarized below. Similar work is ongoing in other countries.

TABLE 3.1. Nanoparticle Preparation for Dispersions/Coatings

Liquid Chemical Methods	Physical Methods	Elevated Temperature Methods
Sol-Gel *	Size reduction by mechanical means (low energy)	Aerosol
Chemical Precipitation		Flame
Ag-X (Eastman Kodak) †		
Colloidal Micelles *		Vapor phase condensation

* Wiltzius 1998; † Trivelli and Smith 1930.

I.A. Aksay describes a ceramic thin film structure that would mirror-image a self-assembly process in many materials (Aksay et al. 1992). Here silica precursors when mixed with surfactants yield polymerized templates having structures similar to surfactant-water liquid crystals; what results are highly controlled pores on the 10 to 100 Å scale. Controlling the pore structure and synthesizing the building blocks are two technical challenges facing future work in this area. However, Aksay has shown that he can grow silicate films onto a wide variety of substrates. The layer structure of the bound surfactant molecules is key. Atomic force microscopy can reveal some details on the morphology of these films. The nanostructural patterns obtained in processing ceramics that contain organic/inorganic composites allow self-assembly to take place at lower temperatures.

Another example of thin films or coating is the work of Gell (1998, 124-130), focused on improving both the physical and the mechanical properties of materials. Nanostructured coating can lead to high diffusivity, improved toughness and strength, and better thermal expansion coefficients, with lower density, elastic modulus, and thermal conductivity. In comparisons of nanostructures and conventional materials, use of nanostructured WC/cobalt composites have resulted in as much as a two-fold increase in abrasion resistance and hardness. Deposition is often accomplished by utilizing a sputtering chamber where the nanomaterial is coated on substrates. This can lead to such benefits as resistance to oxidation and cracks in addition to resistance to wear and erosion.

An area that offers exciting possibilities in the area of dispersions is the sol-gel process described by P. Wiltzius (1998, 119-121). Here, a concentrated dispersion of colloids is chemically converted into a gel body. Drying followed by sintering produces a ceramic or glass product. This process can create nanoparticles, fibers, film, plates, or tubes. All processing is at low temperatures. Lucent Technologies has developed a silica casting process that is reproducible for making tubes of pure silica of one meter in length for use in manufacturing optical fibers. Technical challenges include obtaining pure starting materials, removing refractory particles that lead to breakage in the fiber drawing process, and achieving very tight dimensional tolerances. Colloidal dispersions of this type play a critical role in chemical mechanical polishing. To obtain good yield and high quality, it is necessary to achieve very tight process control.

R. Brotzman at Nanophase Technologies Corporation describes the gas phase condensation process for synthesizing inorganic and metallic powders (Brotzman 1998, 122-123). Such a process was invented by R. Siegel and his colleagues at Rensselaer Polytechnic Institute in New York (Siegel et al. 1994). The process involves production of physical vapor from elemental or reacted material followed by sudden condensation and reaction of the vapor into small nanometer particles. The condensation process is rapid and involves dilution to prevent the formation of hard agglomerates and coalescence.

Nanophase Technologies has developed a production system where forced convection flow controls the particle/gas stream and enhances particle transport from the particle growth region so as to generate more metal vapor (Parker et al. 1995). The convection flow helps in forming oxides and nitrides from metal crystallites. This process produces commercial quantities of nanosized inorganic powders that have a spherical shape with narrow size distributions. Table 3.2 shows some properties of these particles, and Figure 3.1 shows their transparency as a function of particle size.

Nanophase Technologies Corporation has developed a coating process that encapsulates nanoparticles with a surface treatment that ensures individual integrity of the particles in subsequent coating steps. Applications span their use in low dielectric media all the way to water and, if needed, steric stabilizers.

Nanophase also has directed efforts in the electronics and industrial catalyst areas. Friedlander (1998, 83-8) describes in good detail aerosol reaction engineering where attention is paid to design of the process and the importance of material properties and process conditions. Key process parameters include time, temperature, and volume concentration. Most commercially produced particles have polydispersity. Important full-scale processes are flame reactors for preparing pigments and powdered materials for optical fibers. Pyrolysis reactors have long been used to prepare carbon blacks.

Kear and Skandan (1998, 102-4) have discussed two divergent approaches toward fabrication of bulk materials. The first is a powder processing route involving preparations by physical or chemical means followed by condensation and sintering. Materials for cutting tools such as tungsten carbide/cobalt powders were prepared in a controllable way to about 50 nm. Liquid phase sintering completes the formation of the solid dispersion phase. However, a gap in fabrication technology remains that of controlling grain growth during liquid phase sintering.

A second approach to fabrication of bulk materials is spray forming. This procedure avoids contamination and coarsening of the dispersion and its particles when the process has a controlled atmosphere of inert gas at low pressure. In this approach there is need to establish process/product co-design where we understand cause-effect relationships between processing parameters and properties of nanophase spray/deposited materials.

TABLE 3.2. Particle Properties

Particle Properties	TiO_2	ZnO	Fe_2O_3
Refractive Index	2.40	2.01	3.01
Density (gm/cc)	3.95	5.61	5.30
Molecular Weight (µ)	80	81	160
Particle Sizes (see Figure 3.1 below)			
Optical Density (D) = Absorbance (A) = log 10 (lo/l = ε Cl) C = concentration l = optical path length ε = molar absorption coefficient/2.303			

Source: R. Brotzman, Nanophase Technologies

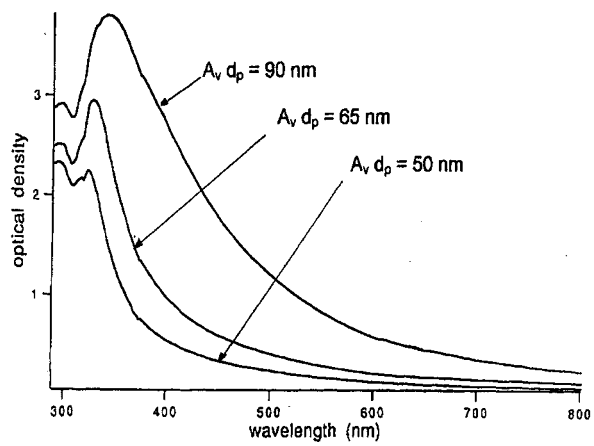

Figure 3.1. Transparency as a function of particle size (Nanophase).

In summary, particle preparation in the United States utilizes a wide variety of methods—both chemical and physical, at both high and low temperatures—all having unique considerations for scale-up and process control. Researchers in other countries are tackling many of these same issues.

Work in Europe and Japan

Due to time constraints, the WTEC panel was able to visit only a few labs in Europe and Japan that deal with issues associated with dispersions and coatings. Cited below are a visit to the Institute for New Materials at Saarbrücken in Germany and a visit to Japan's Industrial Research Institute of Nagoya, both of which are exploring direct applications of nanostructured dispersions and coatings.

Drs. Rudiger Nass and Rolf Clasen at the Institute for New Materials at Saarbrücken make specific use of the sol-gel process in which liquid starting materials are utilized at low temperatures for nanoscale metal, ceramic, glass, and semiconductor nanoparticles (Clasen 1990). The advantages, besides temperature, include the isolation of high purity powders. The institute has focused on four basic areas for spin-off and adaptation towards commercialization:

1. New functional surfaces with nanomers. Properties such as corrosion protection, wettability, coloration, micropatterned surfaces, porosity, and the ability for selective absorption of molecules produce multifunctionality.
2. New materials for optical applications. This area combines properties of lasers and ceramics with polymers. Such features as optical filters, transparent conducting layers, materials for optical telecommunications, photochromic layers, and holographic image storage are under investigation.
3. Ceramic technologies. In this area, a simple precipitation process such as sol-gel provides for pilot-scale production of agglomerate-free powder.
4. Glass technologies. Chemical incorporation of metal colloids with intelligent properties into glasslike structures is clearly possible.

During the WTEC team's site visits to the Industrial Research Institute of Nagoya, S. Kanzaki and M. Sando described methods for preparing synergy ceramics using nanoporous silica particles that are used to fabricate thin films with one-dimensional throughput channels (Kanzaki et al. 1994). The channels had 10-20 nm sizes. High temperature Fe_2SiO_4 oxides were prepared as both molecular sieves and particulate fibers. Japan plans to pursue the preparation of nanoporous materials for absorbing oil and identified particulates.

ALTERNATIVE PREPARATION METHODS

The quest for low temperature nanoparticle preparation methods has spanned a wide range of systems. One that has been in existence for decades but has not been put into use in other industries is the method of preparing silver halide particles. Eastman Kodak in France, England, and the United States has utilized solution precipitation technology with well-controlled mixing and nucleation control to produce a wide range of grain sizes. "Lippmann"-type grains have a size of about 50 nm. Some of the properties of these fine-grain systems are discussed by Trivelli and Smith (1939).

There are other methods of creating nanoparticles of organic materials such as filter dye applications in photographic films and spectral sensitizing dyes for use in silver halide grains. Ultrafine grinding media are used to almost sandpaper organic crystals to nanoparticle ranges of 20-80 nm (Czekai et al. 1994). Similar technology by Bishop has been utilized in both pharmaceutical preparations and ink jet applications with good success (Bishop et al. 1990).

One other exciting area is in polymer science, where dendrimer molecules, often 10 nanometers in diameter, are prepared synthetically. These molecules have been studied in gene therapy, as aids in helping to detect chemical or biological agents in the air, and as a means to deliver therapeutic genes in cancer cells (Henderson 1996). The preparation of dendritic starburst molecules is described by Salamone (1996, 1814). One can imagine applications for coatings in which these molecules with their highly reactive surfaces participate in either classical (sub-nanoscopic chemistry) or novel nanoscopic conversions.

OPPORTUNITIES AND CHALLENGES

There are some outstanding opportunities and challenges that face the nanoscience community. For dispersions and coatings these include four areas:

1. The foremost area of opportunity is controlling the particle preparation process so that size is reproducible and scaleable. This requires creation of narrow size range particles that can be prepared by processes mentioned in the study such as vapor phase condensation, physical size reduction, or flame and pyrolysis aerosol generators. These same processes must respond to good reproducibility and scaling. In most studies to date, the size of primary particles depends on material properties and the temperature/time history. Two processes, collision and coalescence, occur together, and the processes need to be controlled in order to favorably influence final particle size distribution (Wu et al. 1993).
2. The second area of opportunity is process control (Henderson 1996). In the concept of a process control methodology, the nature of chemical processes makes it imperative to have means of effectively monitoring and initiating change in the process variables of interest. Accordingly, those involved with production of nanoparticles would monitor outputs, make decisions about how to manipulate outputs in order to obtain desired behaviors, and then implement these decisions on the process. Control system configuration will necessarily have a feeding process from the output such that information can be fed back to the controller. It may also have an

opportunity to base controller decision-making on information that is being fed forward; decisions could be made before the process is affected by incoming disturbances. Such would apply to process parameters like temperature, flow rate, and pressure.

In many chemical setups, product quality variables must be considered, and such measurements often take place in the laboratory. An objective analysis is needed of any observed deviation of a process variable from its aim, and an objective decision must be made as to what must be done to minimize any deviation. Here process understanding leads to well behaved reactors in manufacturing that allow for true process verification with data feedback and analysis. This concept of process control requires the application of statistical methodologies for product and process improvements. Current interest in statistical process control (SPC) is due to several factors, in particular, interest in realizing consistent high quality so as to sustain the business and obtain greater market share. Most manufacturing zones are moving toward inline/online sensor technologies coupled with process software and user-friendly computer hardware for factory operators.

The benefits of process control are many. They include achieving reduced variability and higher quality, safety enhancement, reduction of process upsets, and in many cases, environmental improvements due to achieving mass balance in processes with material in/product out. Poor process design can be inherently overcome through SPC. Reduction in sampling and inspection costs results.

3. A third area of opportunity is the process/product relationship that leads to continuous uniformity—that is, the specification setting by product users that must be available to relate to process control in manufacturing. Here, nanoparticle formulation and the process used to prepare the particles must be linked and interactive.

4. A fourth technical opportunity is to develop process models for various dispersions and coatings that lead to shorter cycle time in manufacturing. Table 3.3 shows a comparison of enablers and opportunities in Europe, Japan, and the United States.

These four areas of opportunity, then, represent what lies ahead for advancement in nanotechnology with respect to dispersions and coatings. Achieving implementation in the industrial market will require close attention to resolving the challenges in the four areas summarized above. In addition, there remains a large gap between the cost of preparing conventional materials and the cost of preparing nanoparticles. This will remain a challenge for the future if nanomaterials are to be competitive.

TABLE 3.3. Dispersions and Coatings—Nanotechnology Comparisons Between the United States, Europe, and Japan

LEVEL	1 (Highest)	2	3	4
Enablers				
Particle Preparation	U.S./Europe	Japan		
Stabilization	U.S./Europe	Japan		
Scaleup				
Characterization	U.S./Europe	Japan		
Coating	U.S./Japan/ Europe			
Opportunities				
Process Control			U.S.	Japan/Europe
Process/Product Co-Design			U.S.	
Modeling		U.S./Japan		

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