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The Importance of Particle Analysis in Formulating Both Fine and Specialty Chemicals

White paper

The global chemical industry can be classified into three main categories: commodity chemicals, fine chemicals, and specialty chemicals. Commodity – or bulk – chemicals are manufactured in large quantities. Some examples include ammonia, sulfuric acid, and sodium hydroxide.[1] Despite being manufactured by different chemical suppliers, commodity chemicals are generic enough in formulation that they are interchangeable.

Alternatively, fine chemicals and specialty chemicals are produced in limited quantities and in small batches using many complex steps. Their formulations are unique to each manufacturer and make up the "special sauce" in end products across a range of markets, including industrial, agriculture, biotech, electronics manufacturing, consumer, and more, Figure 1.

Commodities	Fine chemicals	Specialties
Single pure chemical substances	Single pure chemical substances	Mixtures
Produced in dedicated plants	Produced in multi-purpose plants	Formulated
High volume/ low price	Low volume (<1000 mt) High price (>$10/kg)	Undifferentiated
Many applications	Few applications	Undifferentiated
Sold on specifications	Sold on specifications "What they are"	Sold on performance "What they can do"

Figure 1. Chemical categories defined.[2]

In this white paper, we will investigate the importance of particle analysis in the manufacture of specialty chemicals and fine chemicals. While these chemicals come in both powder and liquid form, this paper focuses on how fine chemicals are used to formulate liquid specialty chemicals that are two-phase dispersions: suspensions and emulsions. We will discuss why particle analysis is critical to achieving the highest-value formulations and will discuss approaches to particle analysis and the special instrumentation used in the process.

FINE CHEMICALS VS. SPECIALTY CHEMICALS

While fine chemicals and specialty chemicals are often referred to interchangeably, they are each a separate classification of chemical product. Both are formulated in small batches according to specific formulations and require specialized knowledge to manufacture, but they have different purposes. Together, they compose the high-value end of the chemicals market.

Fine chemicals provide the active ingredients in many products and are custom-made to provide unique properties or performance effects. They can be novel molecules, such as specialty polymers or additives, or a mixture of molecules and phases, such as a coating formulation. While complex to formulate, fine chemicals exist in a pure state. They are generally combined with other chemicals and substances to reach their full potential as commercial products.

Examples of fine chemicals include precursors to pharmaceutical products, biocides, fragrances, additives, and pigments.[3] Zinc oxide (ZnO) is a fine chemical used in cosmetics. Carbon black is one of the oldest existing fine chemicals and is used in a variety of specialty chemicals, from tires to printer ink. Fumed silica is a good example of a fine chemical that is used in creating CMP slurry, a specialty chemical suspension used in semiconductor manufacturing.

Specialty chemicals are evaluated based on performance rather than composition. They contain one or more fine chemicals as active ingredients and are formulated to have only one or two core applications.[4] Generally sold under brand names, specialty chemicals are often considered to be high-value products.

Examples of specialty chemistry products include adhesives, agrochemicals, cleaning materials, colors, cosmetic additives, construction chemicals, elastomers, flavors, food additives, fragrances, industrial gases, lubricants, paints, polymers, surfactants, and textile auxiliaries.[5]

Ultimately, fine chemicals are sold primarily based on chemical composition, or what they are. Specialty chemicals are sold based on performance, or what they can do.[6] For example, carbon black or titanium dioxide (TiO_2) are fine chemical pigments that when formulated with other additives create the specialty chemical of ink. It includes pigment, water carrier, resin, surfactants, and co-solvents.

FORMULATING TWO-PHASE DISPERSIONS

Like all fine and specialty chemicals, dispersions are made using batch processes to make a finite amount of product. The processes take anywhere from a few hours to a few days and follow the following steps:

1. Measured amounts of starting materials are placed in a vessel.
2. These materials undergo a series of scheduled processes (mixing, heating, distilling, etc.).
3. Products, by-products, and waste streams are removed and stored.
4. The equipment is cleaned and prepped for the next process cycle.[4]

Two-phase dispersions comprise a continuous phase and a dispersed phase. Examples include liquid/solid suspensions and liquid/liquid emulsions. Creating stable dispersions requires careful consideration of two key properties: particle size and surface charge. In both suspensions and emulsions, a solvent creates the continuous phase. Particles constitute the dispersed phase of a suspension, while emulsion droplets constitute the dispersed phase of an emulsion. Suspension examples include sunscreen, latex paint, printer ink, and many over-the-counter medications. Emulsion examples include lotions, creams, and the most common, salad dressing. All are formulated from fine and specialty chemicals.

THE ROLE OF PARTICLES IN EMULSION AND SUSPENSION STABILITY

Stability of a suspension or emulsion impacts the product's shelf life and overall performance. Consider salad dressing that does not emulsify regardless of how much it is shaken, or a can of paint that phase-separates into its solvent and particles, which impacts its application, adhesion, and overall appearance on the surface to which it is applied.

Creating stable dispersions involves controlling the chemistry and physical properties of both the continuous and dispersed phases. The chemistry of the continuous phase can be optimized by varying surfactant selection and concentration, changing the salt concentration, controlling the pH, and a combination of all these factors. The dispersed phase can be made more stable by adding a polymer coating to the surface (steric stabilization), by increasing the charge on the surface (electrostatic stabilization), or by a combination of both.[6]

Before a formulation can be optimized, it is important to understand the relationship between its components. Particle size affects behavior and performance several ways including settling rate, stability, appearance, and flow properties like viscosity. Surface charge also comes into play, as a build-up of surface charge repels particles from each other so that they never touch. Tweaking the size of the particles and adjusting the surface charge extends the stability of the end product, often enhancing its shelf life. Therefore, particle measurement is a critical step in fine and specialty chemical formulation.

PARTICLE CHARACTERIZATION

Particle characterization is important for evaluating product performance and optimizing a formulation for stability. It can determine whether a product has been formulated correctly or incorrectly.

Several analytical methods can be used to measure particle size as well as determine the surface charge, or zeta potential, to understand the relationship between them. The zeta potential refers to the potential in mV (millivolts) a short distance from the particle, Figure 2.

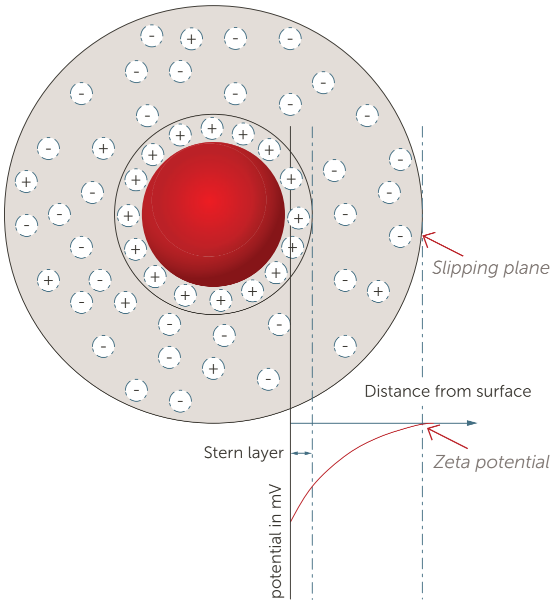

Figure 2. The Zeta potential determines the surface charge of a product.

When there is no charge on the particle surface, the particles can approach each other closely enough that there is no barrier keeping them from aggregating, reducing dispersion stability. But if sufficient charge is present on the surface, the particles repel each other like magnets and never get close enough to aggregate, Figure 3.

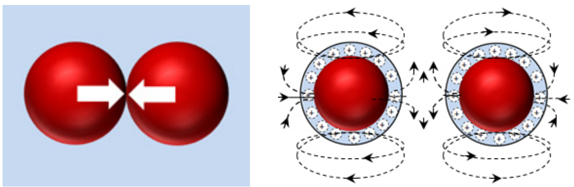

Figure 3. Attractive particles aggregate (left), repulsive particles separate (right).

Zeta potential measurement is performed by applying an electric field to the suspension and detecting the motion of the particles by electrophoretic light scattering. The direction the particles move determines the sign (+ or -) and the velocity determines the magnitude of the charge. The motion can be analyzed either by detecting the frequency shift (phase Doppler) or the phase shift (phase analysis light scattering, or PALS).[7]

A higher zeta potential value is an indicator of improved dispersion stability. Chemists can optimize new products by varying the surface chemistry to achieve the zeta potential required to stabilize the sample. Chemical factors that can alter zeta potential include pH, salt concentration, and surfactants. Combining particle size measurement, zeta potential, and other tests, such as pH, facilitates the formulation of new products for optimal performance and shelf life.

USING THE CORRECT INSTRUMENTATION

Three particle size distribution characteristics provide insight into dispersion stability: the mean, width, and percentage of large particles at the tail. Different analytical techniques are used to determine these various distribution features. Dynamic light scattering (DLS) is the preferred analytical technique to determine mean and width of the distribution in submicron samples. DLS systems are also often equipped with zeta potential capability to measure surface charge. However, because the resolution of DLS is limited for quantifying the percentage of large particles at the tail, it is not suitable for obtaining concentration data.

Single Particle Optical Sizing (SPOS) is a higher resolution technique used to measure and count each individual particle to provide concentration data. SPOS technology makes it possible to quantify the large particles at the tail of the distribution. Its accuracy for this measurement requirement is so precise that it forms the basis for the USP <729> test for lipid emulsions, used to predict emulsion stability. Many fine and specialty chemical products like inks and flavor emulsions use SPOS to predict and assure stability. The combination of DLS, zeta potential, and SPOS provides a comprehensive characterization for formulating and testing dispersion stability.

CASE STUDY #1 ZINC OXIDE

In one example, a sunscreen formulation, DLS can be used to measure the size of the base, zinc oxide (ZnO), to find the optimum size for product performance. The smaller size of these mineral particles increases their cosmetic acceptability by users because they are much less visible after application. Figure 4 shows the change in particle size from monomodal to bimodal distribution. In this example, monomodal peaked at 198 nm at pH 6.9, while bimodal peaked at 204 and 573 nm at pH 11.2. As the zeta potential approached zero, the suspension destabilized and began to aggregate. The pH where the zeta potential of a suspension becomes zero is called the isoelectric point (IEP). The IEP for ZnO is near pH = 9-10, the pH range where the suspension destabilized and started to agglomerate. Here both size and zeta potential were used to optimize the formulation for stability.

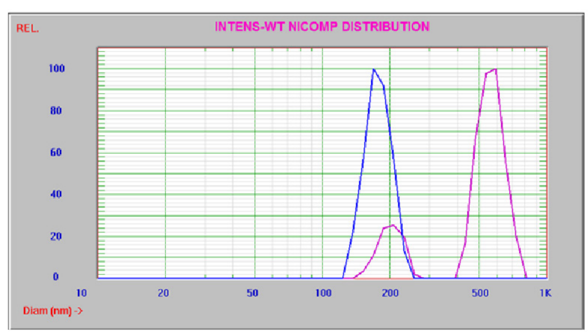

Figure 4. ZnO particle size at pH 6.9 (blue) and 11.2 (pink).

CASE STUDY #2 TITANIUM DIOXIDE

Titanium dioxide (TiO_2) can be used for many purposes including sunscreens, pigments, and food coloring. Two samples of anatase TiO_2 (sample A and B) were purchased from a chemical supplier and dispersed in DI water. Size measurements were made before and after 30 and 60 seconds of ultrasonication to reduce agglomeration. The sample was then titrated using 0.01 M HCl to reduce the pH below the IEP of 3.5. The results from the size and zeta potential measurements as a function of pH are shown in Figures 5 and 6. This is another example where particle size and zeta potential can help formulate the most stable dispersion by selecting surface chemistry conditions away from the IEP.

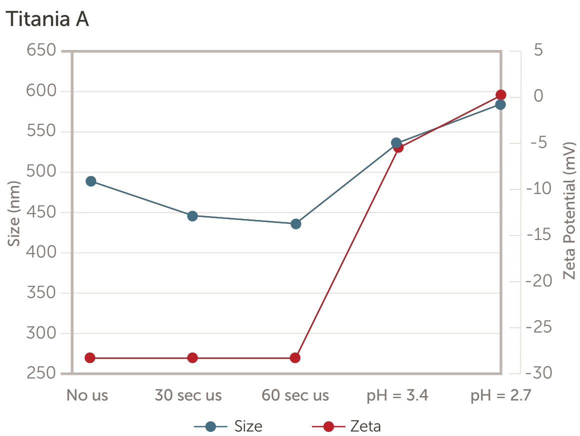

Figure 5. TiO_2 sample A.

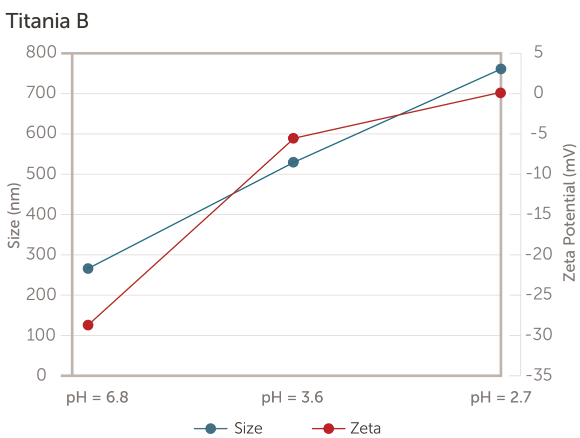

Figure 6. TiO_2 sample B.

CASE STUDY #3 BLACK INKJET INK

Carbon black has been used as a pigment throughout human history and remains in use for inkjet inks. In this example the fine chemical is carbon black, and the inkjet ink is the specialty chemical. A commercial black inkjet ink was analyzed using DLS to determine the mean size and SPOS to quantify the large particle tail. The mean size as measured by DLS is 75.1 nm as shown in Figure 7. The large particle tails as measured by SPOS is shown as particles counts/mL and volume % on the Y axis in Figures 8a and 8b.

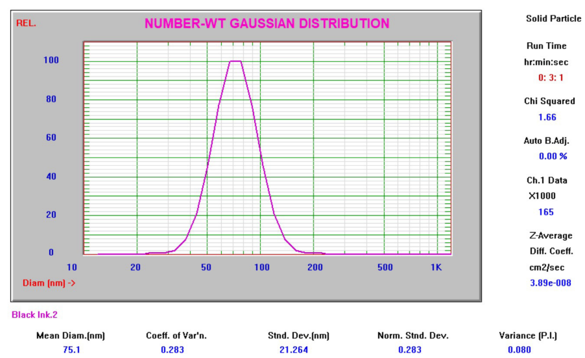

Figure 7. Black inkjet ink mean size by DLS.

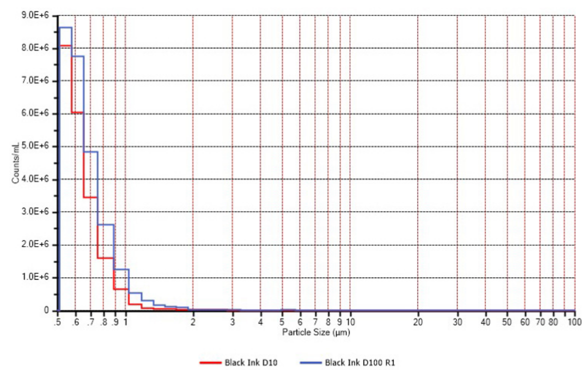

Figure 8a. Black inkjet ink large particle tail, counts/mL.

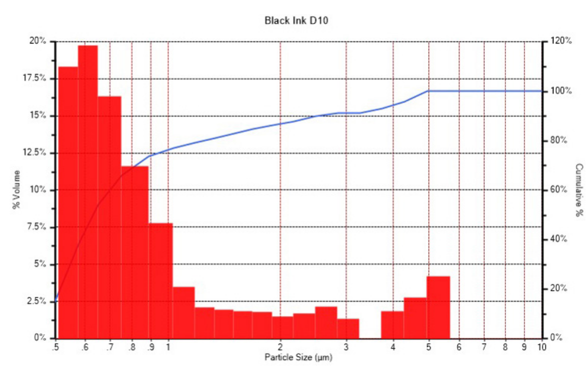

Figure 8b. Black inkjet ink large particle tail, volume %.

CASE STUDY #4 INKJET INK FILTRATION

The number and size of large particles in the tail of the distribution can reduce the performance of the inkjet by causing print defects and plugging the channels and jets. Filtering out the large particles can assure proper performance and testing the ink using SPOS is the best method for determining the optimum filtration method. A commercially available magenta inkjet ink sample was tested before and after syringe filtration using the SPOS technique. The results shown in Figure 9 show the particle counts/mL vs. size of the magenta ink sample before filtration, after two passes through a 0.8/0.2 µm two stage syringe filter, and after one pass through a 0.02 µm filter.

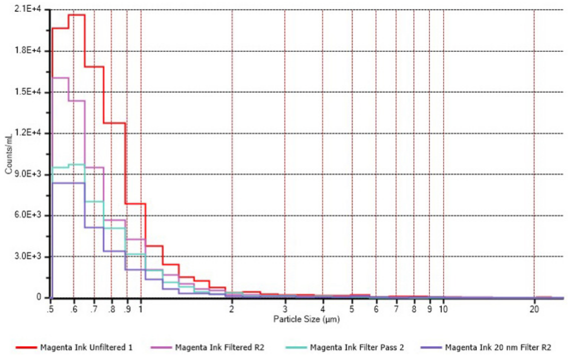

Figure 9. Magenta inkjek ink large particle tail in counts/mL.

CASE STUDY #5 OIL IN WATER EMULSION

In an oil/water dispersion, DLS can be used to measure mean size of the emulsion droplets as well as the zeta potential. The results from the DLS measurements are reported as mean size and polydispersity. The SPOS system is then used to measure the large-diameter droplet tail, an indication of emulsion stability.

Figure 10 shows the DLS result from an oil in water emulsion. The mean size is 116 nm, with a polydispersity index of 0.333. This is larger than ideal for stable emulsions. The DLS result indicates large droplets extending beyond 500 nm, or 0.5 µm. This tail can indicate poor formulation and potential instability.

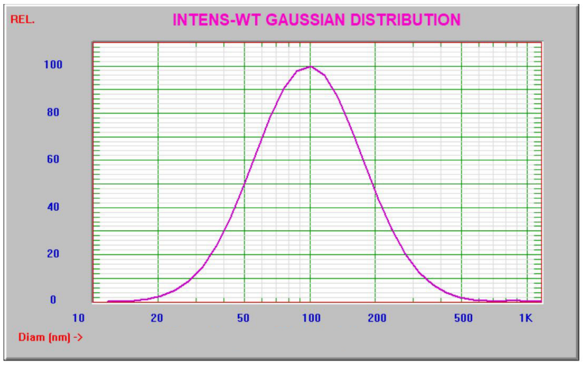

Figure 10. DLS result of an oil in water emulsion.

The tail of the distribution greater than 0.5 µm for this sample was analyzed using SPOS ten minutes after the emulsion was first created and again after four hours, Figure 11.

Figure 11. SPOS result for an oil in water emulsion after 10 minutes and four hours.

This is an extreme example where the tail quantified by the SPOS technique is used both to predict and track emulsion instability.

SUMMARY AND CONCLUSION

Fine and specialty chemicals are unique, by design, and have a higher value-add than commodity chemicals because they are manufactured using batch processes in limited quantities. Also, unlike commodity chemicals, they are not interchangeable between manufacturers. While fine chemicals stand alone as products, they are also integrated into specialty formulations, which means their performance and stability are critical to a host of markets and applications.

Particle characterization is essential to understanding key formulation properties including particle size and surface charge. By using DLS and SPOS measurement systems to measure particle size and zeta potential across the dispersion, formulation adjustments can be made to improve the shelf life and performance of a product, thereby increasing its value.

Learn more about DLS instrument systems.
Learn more about SPOS instrument systems.

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