



Combined Use of Dynamic Light Scattering, Laser Diffraction, Imaging and Zeta Potential for Characterization of Nanoparticles with Special Emphasis on Inks.

APPLICATION NOTE

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Application Note

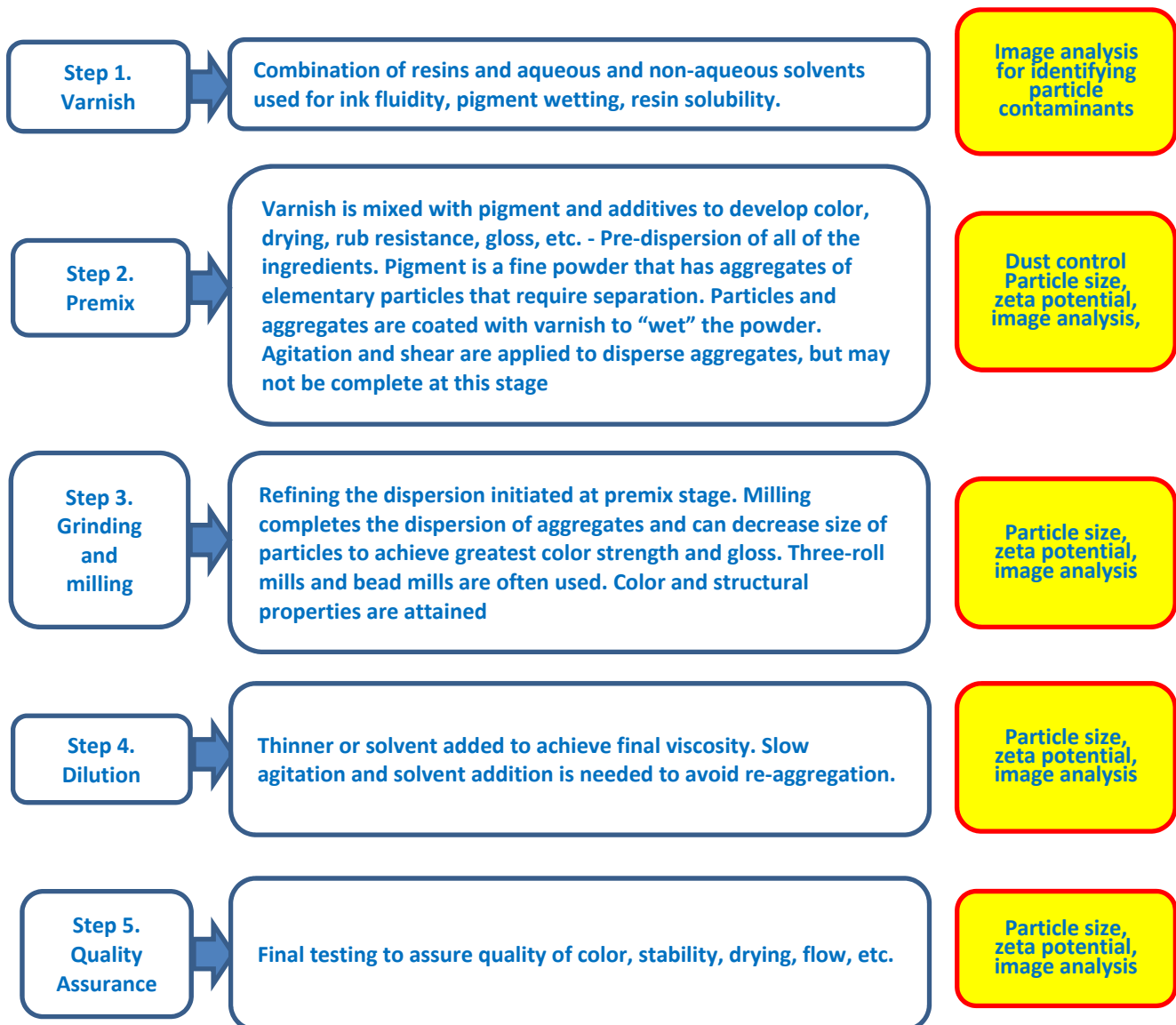
SL-AN-36 Revision A

Provided By:
Microtrac, Inc.
Particle Size Measuring Instrumentation



General: There are many attributes to consider when evaluating the properties of a particle system for specific processes and final use. These can include, but are not limited to, particle size distribution, surface area, porosity, shape factors, and particle charge. In practice, each of these provides a piece to the “particle size puzzle” of full characterization that result in the properties of the particle mass. The properties that can be ascribed to or evaluated by particle characterization include powder flow, dispersion, pharmaceutical efficacy, dry coating quality, suspension stability, printing ink quality, structural strength of metal powders and composites, tableting issues, identification of contaminants, particle packing behavior, aggregation, reflectivity effects, sphericity, and injection molding. This writing applies to all materials, but as an example, the production of ink will be used since it includes nanoparticles (ISO definition for nanoparticles is particles smaller than 100nm. For this discussion, the general range of particles smaller than 1000nm is being used). The various process steps for ink manufacture include chemical mixing, colloidal stability, grinding/milling and dilution which allow demonstration of the utility of using a variety of technologies to elucidate process control information from the incipient R& D efforts through to final quality.

There are several processing steps in the manufacture of ink each of which can impact the quality and are intimate with particle characteristics. The many types of inks include conventional offset inks, lithographic, inkjet, flexographic and gravure. In general the steps to manufacturing are very similar as shown in the diagram below that includes any particle characterization tests of importance. Note that variations of many of these steps are applied in many other products and processes. One or more analysis types may be necessary for process control, quality control or R&D development.



As shown above, full characterization of materials may entail more than one technique or method to elucidate particle characteristics. The selection as to which techniques to employ depends on the purpose of measurement. R&D efforts are an operation that might take full advantage of all the different types of technology to gain full perspective of a new product. With full knowledge of the product (including chemical and other characteristics) a firm definition of the product can be established. It also affords the opportunity to examine and establish specifications while compiling information on potential manufacturing issues and solutions. Manufacturing may select those test methods that provide best process control based on information from R&D. As part of these efforts, dust control, chemistry, upgraded process equipment, government regulations and product improvements can be explored and addressed. Below is an example of the various types of information that can be gleaned by different technologies.

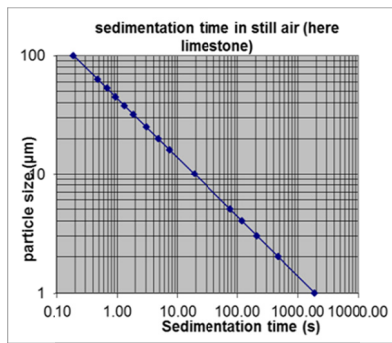
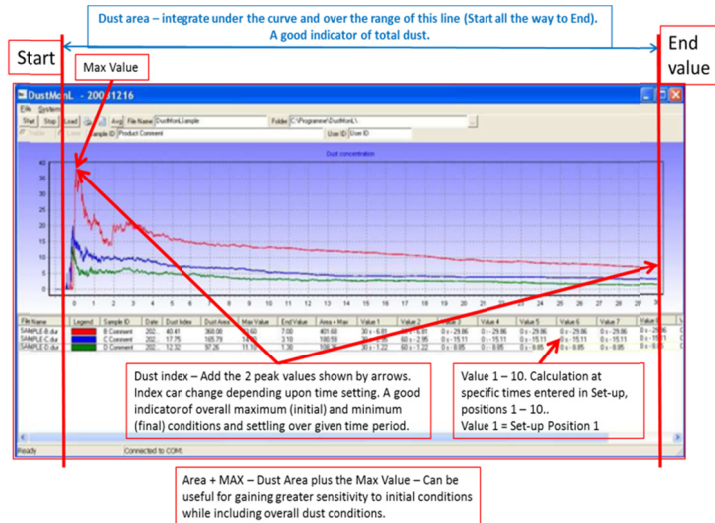
Example of application of instrumental analysis: The example below uses ink manufacturing, but the concepts are applicable to any process where powders or suspensions are involved. Ink manufacture includes many ingredients that impact the final product and provides a sample approach to characterization steps that can be included for the many types of materials used in manufacturing various products including ceramics, cement, suspension stability, pharmaceuticals, plastics, etc.

Varnish –

In general the quality of the components used is very pure but extraneous particle contaminants can cause streaks or other final use issues causing customer concern. Using image analysis affords an opportunity to evaluate incoming raw materials for contaminating materials.

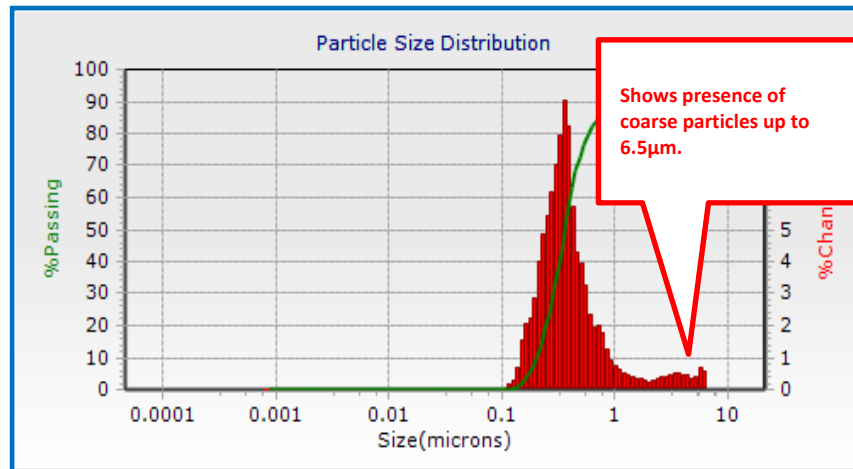
Premix –

Dust control is becoming an important aspect of handling powders due to potential inhalation by manufacturing personnel and global government regulatory review. The **Microtrac Dustmon** affords an opportunity to evaluate dust content for respirable particles, environmental settling characteristics and particle size. Measurements require less than 3 minutes and are easily performed instrumentally. Various values are available to examine the exposure time based on settling in air as well as sedimentation time including dust particle size.

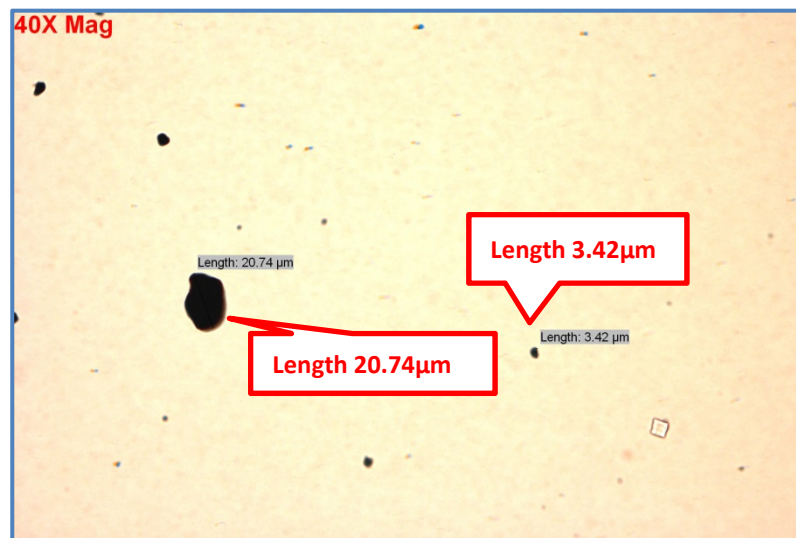


Evaluation of the premix and resulting dispersion characteristics of the suspension is of special importance that can include particle size measurements, zeta potential and image analysis. In the following example, these techniques are used to evaluate the progress of the mix.

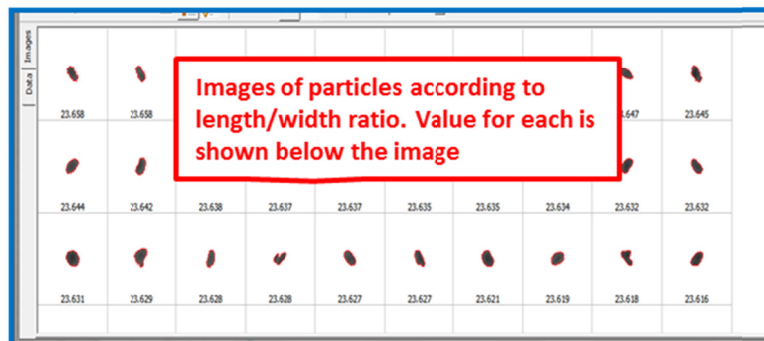
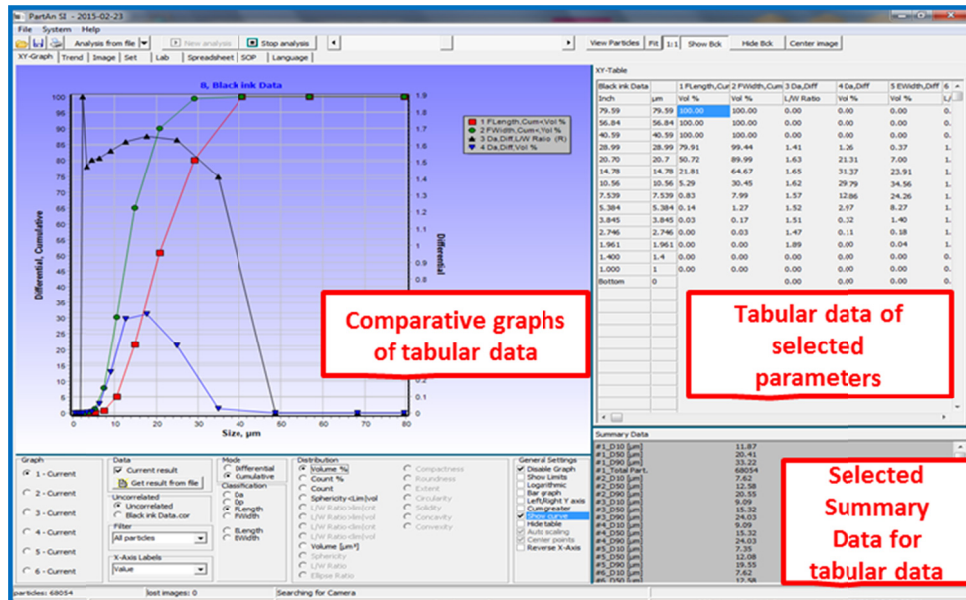
Dynamic light scattering using the Microtrac Wave II showed the presence of a small amount of coarse particles in a suspension of black ink. The presence of the coarse particles is expected but assurance that maximum dispersion of aggregates or agglomerates by this step in the process (premix) is important before proceeding to the next manufacturing step of grinding.



Microscopy confirmed the presence of coarse particles.

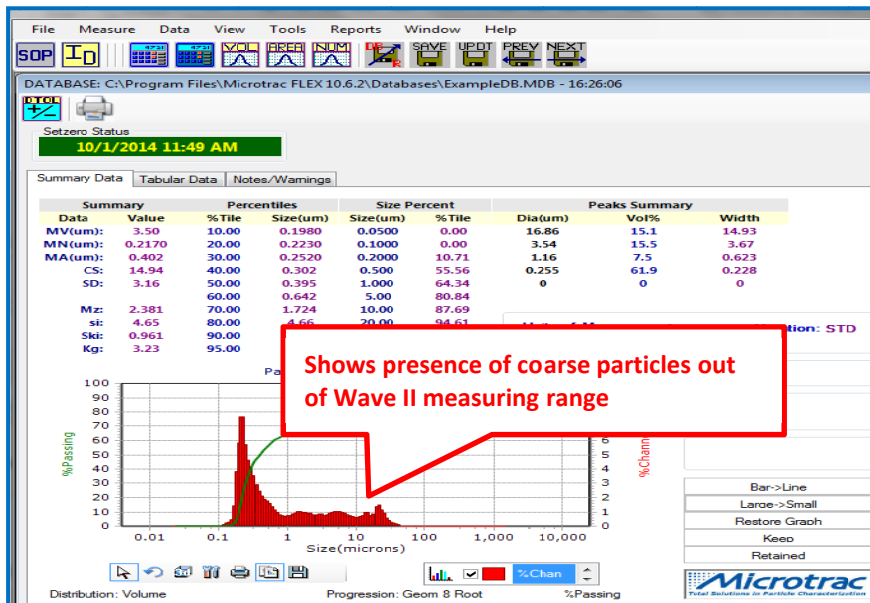


However, microscopy provides a limited number of particles that can be examined. Thus, to gain the best possible information on the particles present, a greater number of particles should be examined. This issue is addressed by using Dynamic Image Analysis (DIA) where particles are flowing and in motion. This technology assures the best knowledge of the larger particles in the ink when ascertaining whether they are aggregates, agglomerates or individual large particles. To satisfy this need, PartAn SI image analysis was performed *simultaneously* with the S3500 diffraction measurement.



PartAn Imaging shows the particle distribution and provides shape information. However, the lower size range is limited whereas diffraction (S3500/Bluewave and Tribblue) and DLS (Wave II and NanoFlex) can measure much smaller particles. Particles are not perfect spheres since length and width are somewhat different. Da L/W ratio shows size of particles according to L/W and that there is a distribution of these ratios and shapes. Da, Diff shows size range without concern to the aspect ratio. Very useful when monitoring the shape of particles and effect of milling process.

To obtain full distribution, Microtrac S3500 diffraction measurement was performed over the range .020µm to 2000µm.

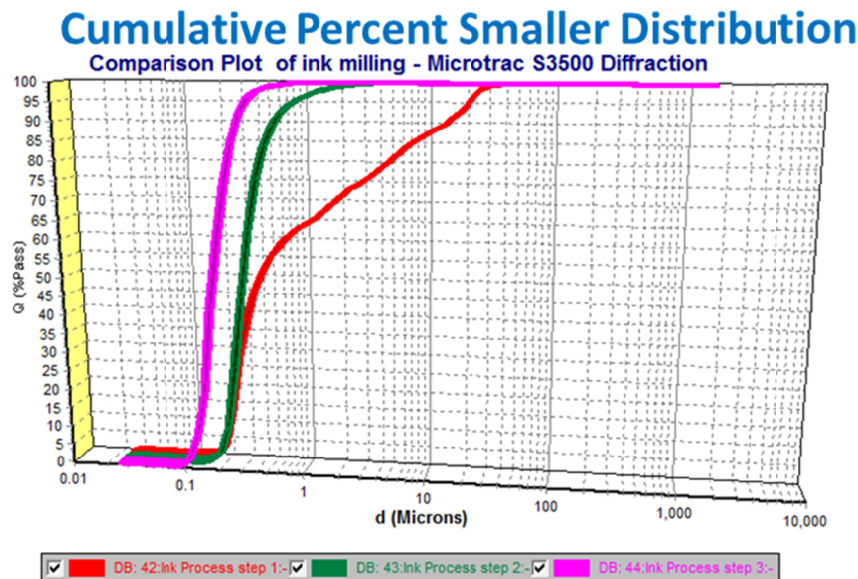
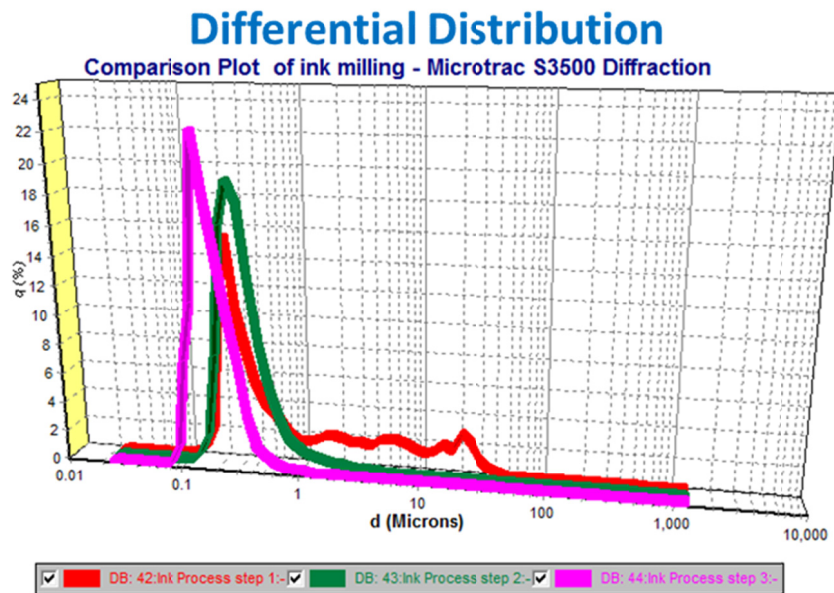


The combination of imaging and diffraction provides information over the entire range while providing pictorial information on the coarse particles.

At this point zeta potential measurements can be performed to assure that the chemistry is performing properly to promote stability of the particle system.

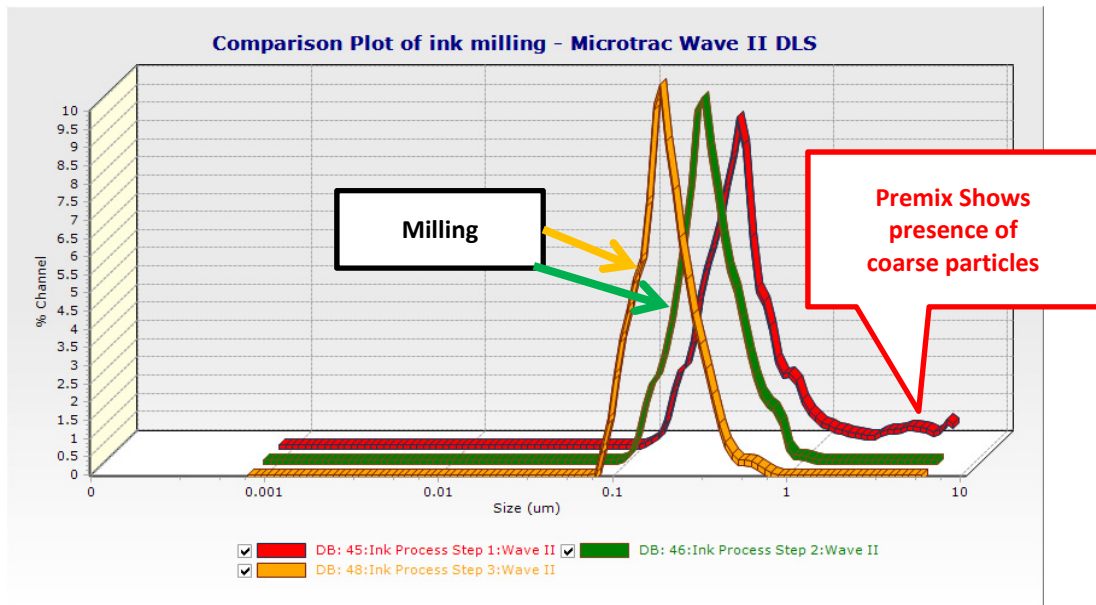
Milling/Grinding –

Microtrac S3500 diffraction data for two of the milling periods was compared to the premix. As indicated, particle aggregates and coarse particles were eliminated by grinding the premix. Note that Microtrac FLEX 3-D software features allow modifications to turn graphs that allow better separation and comparison of the graphs.

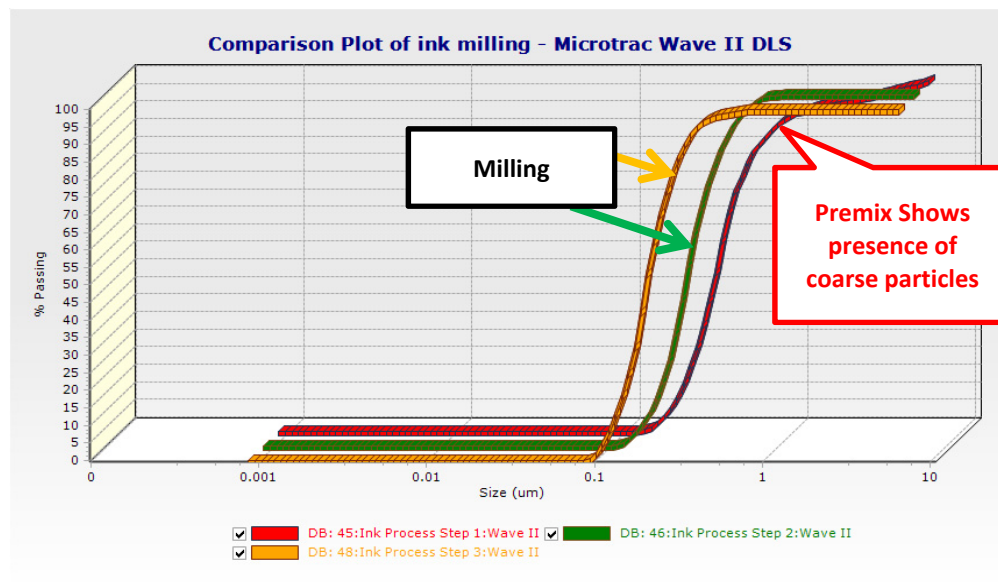


In addition to the diffraction data which required dilution, high concentration Wave II dynamic light scattering data were obtained and compared to the premix. High concentration measurement under the quiescent measurement of Wave II is important, since (1) dilution for diffraction may cause agglomeration errors in data and (2) quiescent conditions eliminate the possibility that sample flow turbulence and dispersion effects of diffraction flow systems may hide the presence of agglomerates. Wave II as with all DLS measurements requires no flow of material as a basis for Brownian motion to ensue.

Differential Distribution



Cumulative Percent Smaller Distribution

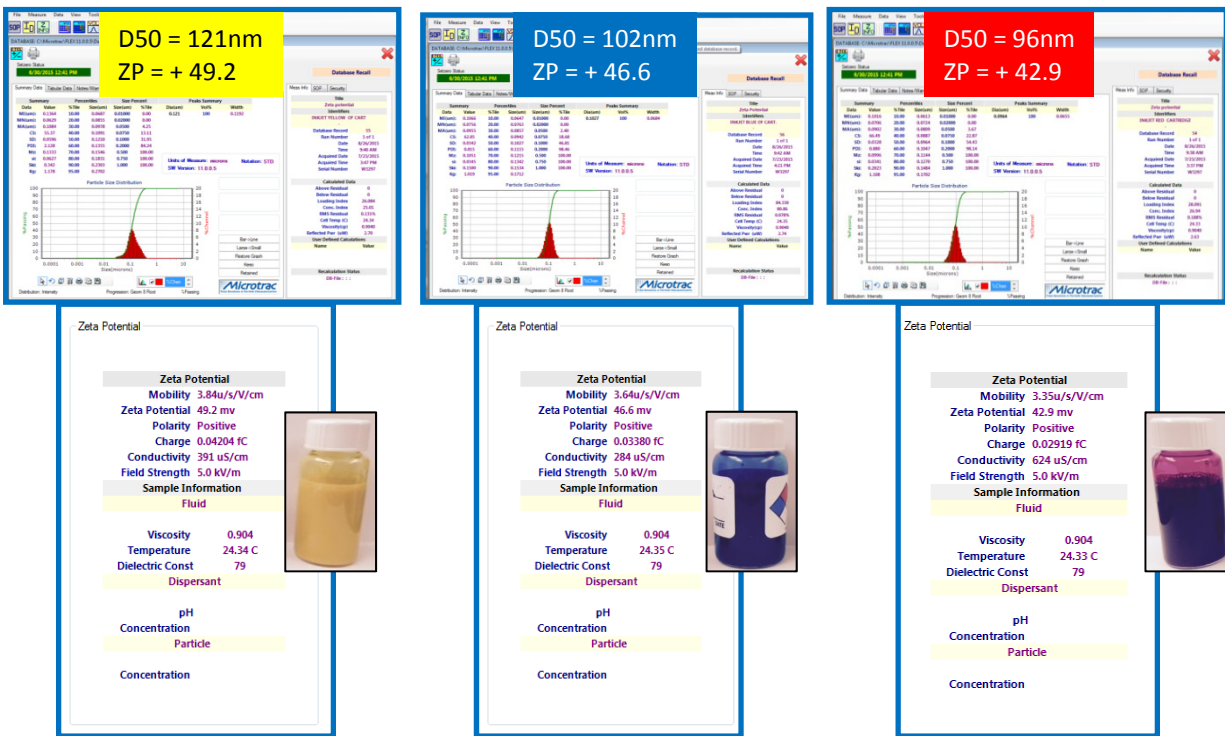


Dilution –

Dilution is performed to obtain final properties of the ink suspension just prior to packaging/filling operations. Dilution of suspensions can cause agglomeration. Thus, it is prudent to evaluate the material by diffraction and high concentration Wave II measurements. Image analysis will also provide insight to the presence of large agglomerated particles should they occur at this step. Following dilution and prior to packaging, quality assurance evaluation and checks are performed and may occur as part of the dilution.

Zeta Potential –

While preparing the premix where addition of additives is performed, zeta potential can provide information on the stability of the mixture. In addition, dilution also can cause a large shift of the zeta potential developed by various additives to gain and maintain colloidal stability. Wave II with zeta potential capability can provide information as to the stability of the final product or during various process steps. The diagram below shows the zeta potential and particle size information for finished inks of three colors. The values are greater than 25mV (either plus or minus this value can indicate emulsion stability) indicating that the colloids/suspensions should be quite stable prior to packing and final use. Wave II particle size provides assurance of the final size since both measurements (size and zeta potential) were performed at final concentrations without dilution or other preparation of the suspension for measurement. Note that the inks were *estimated* to have a particle concentration of 15% w/w.



Application Summary – Under what conditions each instrument should be used?

1. Wave II dynamic light scattering:
 - a. When only the presence of coarse particle information above 6.5um is NOT needed
 - b. When final product QC data are needed. High concentration capability.
 - c. Requirement for high concentration measurement due to potential agglomeration when diluting for diffraction. Agglomeration due to dilution may be misleading.
 - d. Note: Many DLS units use various calculations of the DLS phenomenon. These tend to have very low resolution (cumulants) or require previous knowledge of the distributions and special settings (NNLS and others). Only Wave II provides highest **resolution and sensitivity** to large and small particles simultaneously without assumptions or curve-fitting to report data.

2. Microtrac S3500 Diffraction
 - a. When entire process must be followed for particles beyond measuring range of Wave II DLS.
 - b. When stepwise milling or other process is involved where certain maximum size must be attained before going to the next step, e.g., change of mill type or milling material
 - c. Caution: Dilution may cause agglomeration which may be false. Wave II data may be useful to interpret.
3. PartAn SI Image analysis and microscopy
 - a. Diffraction and Wave II DLS cannot provide shape information. PartAn SI image analysis provides information simultaneously with diffraction to understand large particle shapes present.
 - b. Determine the type of particles undergoing size reduction – resulting shapes may provide indication of milling effects batch to batch or step to step.
 - c. Determine whether large particle information from diffraction is due to agglomerates or individual particles. Agglomerates may be artifacts of any dilution, insufficient additive concentrations or less than desirable chemical conditions.. Individual particles may indicate poor performing milling media or settings.
 - d. Assures that the diffraction measurements are free of unwanted bubbles that can produce erroneous data reports.
 - e. Validates diffraction data.
4. Microtrac Zeta Potential
 - a. During premix stage to assure chemistry is correct for dispersing agglomerates.
 - b. During dilutions to monitor effects of potential changes to emulsion and colloid stability.
 - c. Determination of final stability chemistry
5. Why it is useful to employ more than one method of particle characterization.
 - a. Each instrument has a certain size range capability based upon specific physical concepts.
 - b. DLS (Wave II, NanoFlex) – Group of particles that must remain in suspension that produce fluctuations of light that are frequency shifted. Frequency spectrum analysis allows computation of sizes and amounts. High frequency shift is related to small particles; low frequency shift is related to large particles.
 - c. Diffraction (Microtrac S3500, Bluewave and Triblue) – Group of particles produces a fingerprint of scattered light having a characteristic pattern based on angles and intensities measured by a series of detectors. Size= angles; Amount = intensity
 - d. Image analysis (PartAn SI) – image photography of each particle is followed by special calculations on each particle to discern shape characteristics.

General Summary: Full examination and elucidation of the characteristics of particle processes is possible using a combination of technologies. For particle system characterization, Dynamic Light Scattering (Wave II), S3500/Bluewave/Triblue diffraction, PartAn SI image analysis, microscopy and Wave II zeta potential afford the opportunity to accumulate information during R&D through to final packaging and use. The use of the technologies allows setting specifications at the R&D stage. It also allows development of baseline information that can be used as comparison during scale-up and full production to maintain process control and product quality.