Lab and Online Particle Size Analysis of Silicas

Nicomp® DLS system and AccuSizer® SPOS system

INTRODUCTION

Silicon oxides such as SiO_2 are the most abundant component of the earth's crust. It can be found in nature in crystalline form and is industrially manufactured in many forms including colloidal silica, fumed silica, precipitated silica, and silica gels. Table 1 details a range of silica processes and the typical particle size.

Colloidal silica dispersions are dense (2.1 – 2.3 g/cm3), amorphous particles with an alkaline pH of 9 – 11 and a viscosity near water. The particle size range is typically from 5 – 150 nm with varying width from very narrow to broad; PDI values from 0.008 – 0.350.[1] The smaller size dispersions typically require some form of stabilization.

Controlling particle size in silica suspensions is crucial for tailoring their properties to meet the specific requirements of different applications and industries for various reasons including:

- Uniformity and stability: Consistent particle size distribution ensures stability and uniformity in the suspension. It prevents settling and agglomeration, maintaining a homogeneous mixture, which is crucial for the performance and properties of the final product.
- Rheological properties: Smaller particles tend to increase viscosity, impacting flow characteristics. Controlling particle size aids in managing viscosity, which is vital in applications such as coatings and printing inks.
- Surface area and reactivity: Finer particles result in a higher surface area. This increased surface area enhances reactivity, making it beneficial for catalysis, adsorption, and other chemical processes.
- Processability: Smaller particles might enhance properties but could complicate manufacturing processes due to increased surface area and potential difficulties in handling.

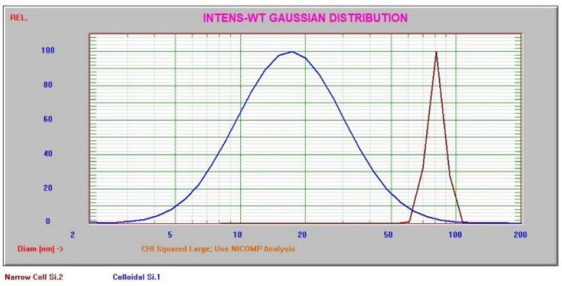
Silicas are used in a wide range of industrial applications including desiccants, binders, papermaking, catalysts, and as an abrasive in CMP slurries, where Entegris has extensive experience. Entegris also uses silica suspensions for filter retention testing. Entegris is in the unique position of having expertise in formulating silica CMP slurries, performing particle size testing, and also designing and manufacturing the particle size analyzers used (Nicomp and AccuSizer product lines).

Table 1. Colloidal Silicas

	FUMED SILICA	PRECIPITATED SILICA	SILANE-BASED	WATERGLASS
Process	Flame pyrolisis	Precipitation	Stoeber	Ion exchange
Raw material	Chlorosilane	Sodium silicate	Tetraalkoxysilane	Metal silicate
Particle size	5-50 nm	5-100 nm	10-1000 nm	5-50 nm
Form	Aggregates	Aggregates	Discrete	Discrete

Mean Size and Zeta Potential by DLS

Both particle size and the surface charge (the zeta potential), are important physical characteristics that affect dispersion stability. 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 either adding a coating of polymer to the surface (steric stabilization), by increasing the charge on the surface (electrostatic stabilization), or by a combination of both. The mean size and zeta potential of silica suspensions[1] can be analyzed using dynamic light scattering (DLS). The size distribution and zeta potential of two very different colloidal silicas measured on the Nicomp DLS system is shown in Figure 1. The zeta potential of the narrow distribution silica was -18.4 mV and -22.1 mV for the wide distribution silica.



Sample	Mean	PI	Zeta potential
Narrow	80.9 nm	0.008	-18.4 mV
Wide	20.1 nm	0.325	-22.1 mV

Figure 1. Nicomp DLS mean size and zeta potential of colloidal silicas.

Figure 2 shows four Nicomp results of a mixture of two colloidal silicas with mean diameters near 8 and 50 nm. These results show the ability of the Nicomp algorithm to effectively split a bi-modal silica mixture.

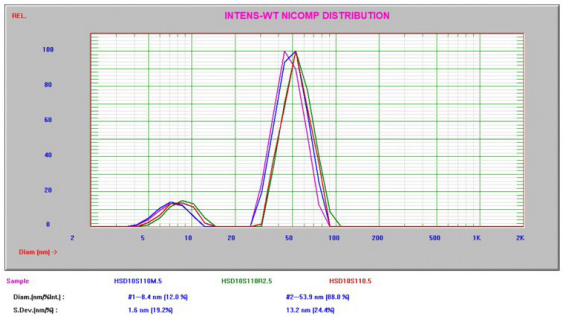


Figure 2. Bimodal Nicomp result.

Large Particle Size & Count by SPOS

Even a small concentration of large particles (tails) in silica suspensions can cause troubles such as reduced stability, changes to optical properties, surface roughness, and mechanical properties. In CMP slurries large particle counts (often defined as particles/mL > 1 micron) can cause defects on silicon wafers, reducing semiconductor yields.

The tails of silica suspensions are typically measured using the technique of single particle optical sizing (SPOS), the operating principle of the Entegris AccuSizer product line[2]. The AccuSizer range used includes the AccuSizer AD, AccuSizer APS, and AccuSizer FX Nano systems. The choice of instrument is determined by size range of interest and dilution fluidics design. The AccuSizer AD and APS couple single and two-stage dilution fluidics and the LE400 sensor with a dynamic range of 0.5-400 µm. The AccuSizer APS is the most automated dilution system capable of accurately diluting samples up to 1 million to one. Figure 3 shows the large particle tail results for three different silica CMP slurries above, and the reproducibility of two individual measurements below.

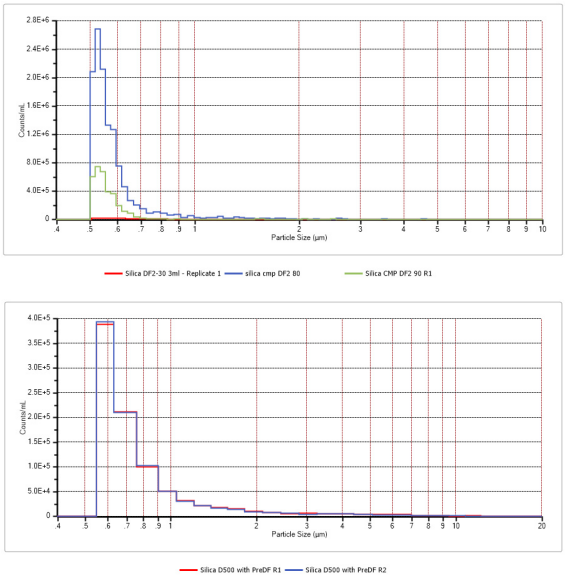


Figure 3. AccuSizer APS silica CMP LPC results.

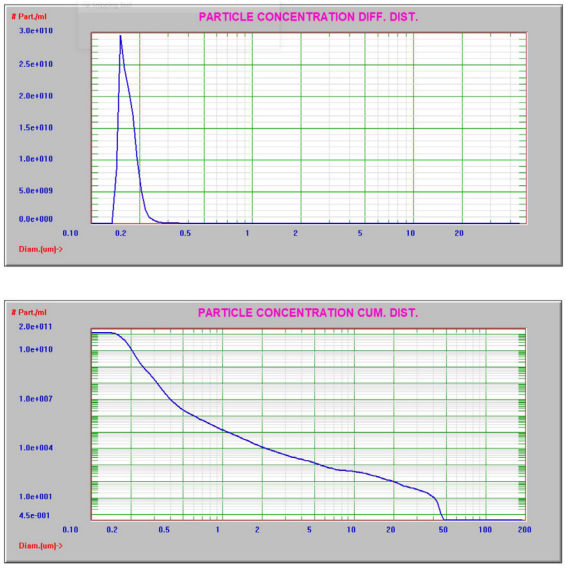


Figure 4. AccuSizer FX Nano silica CMP LPC results.

AccuSizer FX Nano Results

Some newer, cleaner silica CMP slurries have very few particles/mL greater than 0.5 µm, so measuring at smaller particle size is required. The AccuSizer A9000 FX Nano can measure down to 0.15 µm, or 150 nm. This is still the mostly the tail of the distribution, but in some samples the "working particles" can also be present in this size range. This instrument combines the LE400 sensor with the FX Nano to cover a wide dynamic range of 0.15 – 20+ µm. Because of the wide dynamic range, the AccuSizer FX Nano needs to measure a sample in three measurement ranges (FX Nano high gain, FX Nano low gain, and LE400) and then combine these into the final result.

AccuSizer A9000 FX Nano results for a colloidal silica CMP slurry are shown in Figure 4. The result above shows the differential distribution with particle counts on the X axis using a linear scale and the result below shows the X axis using a log scale. The log scale provides a better visual portrayal the tail of larger particles tail.

Entegris is a leading supplier of CMP filter solutions provided to the semiconductor industry. Particle retention tests for these filters are performed using the AccuSizer FX Nano because of its extended dynamic range. Figure 5 shows filter retention results from 0.15 – 1+ µm for several conditions after 5 (solid lines) and 15 minutes (dashed lines) of recirculation time.

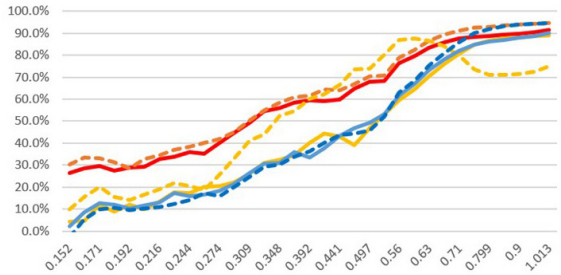


Figure 5. AccuSizer FX Nano filter retention data.

IN-PROCESS PARTICLE SIZE MEASUREMENTS

Mean size by Mini DLS System

The Mini DLS system[3] is a flexible and elegant solution that can be adapted to a wide range of nanoparticle manufacturing processes including milling, homogenizing, or microfluidizers. A pressurized stream of suspension product connects to the Mini DLS system. This sample is then automatically diluted to achieve an appropriate light scattering intensity for the measurement. The particle size distribution is determined and the system is automatically flushed and cleaned before the measurement sequence is repeated.

Two silica suspension samples were analyzed using the Mini DLS system mimicking in-process monitoring: Ludox TM 50 and a silica CMP slurry. The results are shown in Figure 6.

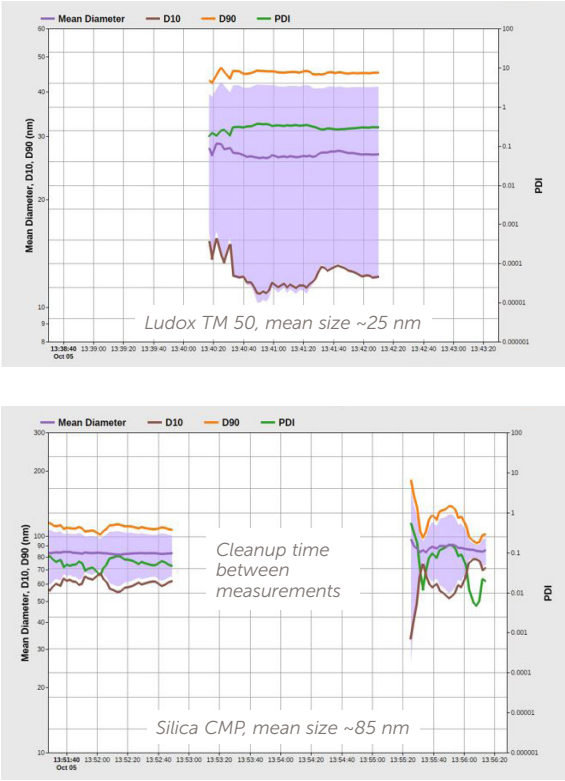


Figure 6. In-process Mini DLS results of silica samples.

Large Particle Size and Count by AccuSizer Mini

Hundreds of AccuSizer Mini systems are installed in slurry delivery systems to continuously monitor LPC concentration in semiconductor fabs. These Mini systems combine a choice of sensor (LE400, FX, and FX Nano) with various dilution fluidics matched to specific CMP slurries. The Mini LE (LE400 sensor) is typically used for standard silica-based slurries and the Mini FX Nano is used for extremely clean colloidal silica slurries. Results from the Mini LE and Mini FX Nano for silica CMP slurries are shown in Figure 7.

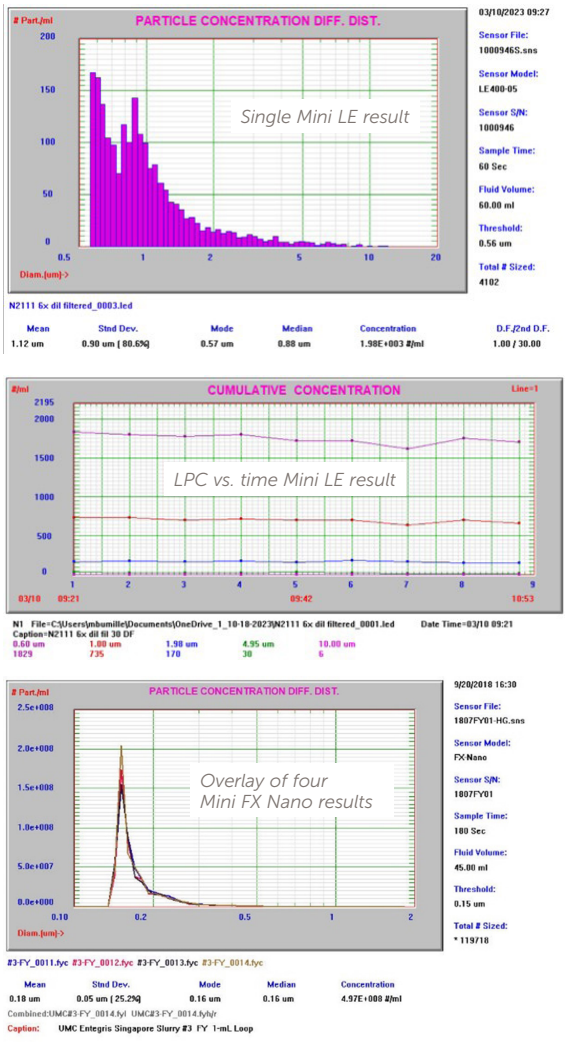


Figure 7. Mini LE (above & middle) and Mini FX Nano silica CMP results.

CONCLUSIONS

Entegris provides a wide range of particle size and count solutions to any business manufacturing or using silica suspensions. The mean size can be analyzed in the lab using the Nicomp system and in-process using the Mini DLS system. The large particle count (tail) is best analyzed using the AccuSizer lab system or Mini in-process analyzer. Our expertise in manufacturing and testing instrumentation, CMP slurries, and filters positions Entegris as a premier partner for any customer manufacturing silica suspensions.

References

[1] Entegris application note Mean Particle Size and Zeta Potential Analysis of CMP Slurries

[2] Entegris application note Detecting Tails in CMP Slurries

[3] Entegris Mini DLS data sheet

FOR MORE INFORMATION

Please call your Regional Customer Service Center today to learn what Entegris can do for you. Visit entegris.com and select the Contact Us link to find the customer service center nearest you.

TERMS AND CONDITIONS OF SALE

All purchases are subject to Entegris' Terms and Conditions of Sale. To view and print this information, visit entegris.com and select the Terms & Conditions link in the footer.

Entegris

Corporate Headquarters
129 Concord Road
Billerica, MA 01821
USA

Customer Service
Tel +1 952 556 4181
Fax +1 952 556 8022
Toll Free 800 394 4083