Aqueous Pre-dispersions of Fumed Silica to Enhance Waterborne Adhesives and Sealants

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October 18, 2016
Agenda

1. Fumed Silica Physical Properties and Capabilities
2. Fumed Silica Powder Process of Dispersion
3. Aqueous Pre-dispersions of Fumed Silica in Waterbased Adhesives
4. Aqueous Pre-dispersion of Hydrophobic Fumed Silica Potential in Waterbased Adhesives
5. Q&A – Session and Discussion Round
Initially germ free; incidence of microbial contamination very low
Inert toward most active ingredients and excipients
Non-irritant and nontoxic
Regulatory Status: (Powder form only)
• Pharmacopoeias: BP, Ph.Eur., USP/NF, JP,....
• Included in the FDA Inactive Ingredients Guide
INCI name: Silica
Particle growth and formation of aggregates

Production process:
Controlled Surface Area

Burner

Flame tube

SiCl\textsubscript{4} + H\textsubscript{2} + O\textsubscript{2} → SiO\textsubscript{2}

Reaction and nucleation zone.

Collision of aggregates, formation of agglomerates.

- Formation of aggregates due to delayed fusion.
- Collision of molten spherical primary particles.
- Surface area range from 50 – 380 m\textsuperscript{2}/g

Down Stream Processes:
Surface Treatment – DDS, D4, HMDS, PDMS, etc.
Structure Modification -  Reduced branching, High filler loading, Higher Tap Density and Reinforcement
Primary Particle Determines the Surface Area

<table>
<thead>
<tr>
<th>BET Surface Area, m²/g</th>
<th>Theoretical Primary Particle Size, nm</th>
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<tbody>
<tr>
<td>50</td>
<td>90</td>
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<tr>
<td>40</td>
<td>20</td>
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<tr>
<td>150</td>
<td>14</td>
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<tr>
<td>200</td>
<td>12</td>
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<tr>
<td>300</td>
<td>7</td>
</tr>
<tr>
<td>380</td>
<td>7</td>
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- Most common base type
- Balanced thickening and dispersibility
- Higher surface area gives better transparency
- Lower surface area allows for higher filler loading
Structure of Fumed Metal Oxides

Primary particles (7-40 nm)

Aggregates (ca. 80-300 nm)

Agglomerates (up to >100 Microns)

Energy input

at rest

in process
Particle Modification of Fumed Oxides
Surface treatment

Hydrophilic Fumed Silica Aggregate
hydrophilic

Hydrophobic Fumed Silica Aggregate
hydrophobic

Silanol groups

Surface treatment

Organic group
Fumed Silica Powder Incorporation to Optimize Rheology and Suspension
When insufficient energy is put into the system, the effect is a drastic reduction in efficiency of fumed silica powder and the consistency of the final product.

Higher shear rate leads to improved shelf stability with a low drop in viscosity after 4 weeks.

The lower energy mixing will experience a higher drop in viscosity after 4 weeks.

Note:
1- Fumed Silica should be wet in before high shear is used.
2- The use of high energy allows for shorter mixing time.
The final products exhibit specks and/or other surface flaws. The amount of Fumed Silica Powder used does not achieve the desired thixotropic effect.

The thickened resin exhibits poor storage stability:
- sedimentation of fumed silica may occur
- viscosity deteriorates the longer the product is stored.
- Separation/ syneresis of additives and fillers under pressure and long storage
Factors Influencing the Dispersion of Fumed Silica Powder

Proper Use Suggestions

- **Equipment & Design Features**
  (Blade-Vessel = 1:2 – 1:3 observing a strong vortex. At 1:4 ratio material clings to vessel sides)

- **Tip Speed Considerations**
  (26 - 32 ft/sec)

- **Length of Shearing Time**
  (Minimize to prevent heat build-up, RPM more critical than time)

- **Temperature Build-up**
  (Lowers mixing viscosity)

- **Sequence of Addition**
  (Add after oil/resin. Add preferably to film forming liquid – do not pre-disperse in solvent)

- **Grind vs. Post-add**
  (Post add not recommended for Fumed Silica Powders)

- **Hegman Grind vs. Dispersion**
  (Poor grinds – high values indicate silica is poorly dispersed)

- **Preventing Under/Over Shear**
  (Under shear more common. Over shear can result in low viscosity/no thixotropy rebound)
Aqueous Pre-dispersion of Fumed Silica in Waterbased Adhesives and Sealants
Aqueous Pre-dispersions of Fumed Silica enhances the cohesive properties of the film thus building a more integrated bond line for adhesion.

Aqueous Pre-dispersions of Fumed Silica eliminate the dispersing step that is required when working with powder fumed silica. (Some waterborne polymer systems are sensitive to shear)

Aqueous Pre-dispersions of Fumed Silica also impart the combined properties of:

- Reinforcement
- Viscosity Control
- Suspension Properties
- Improved Film Formation
Aqueous Pre-dispersions of Fumed Silica Efficiency

The Aqueous Pre-dispersion of Fumed Silica does not require additional mixing/dispersion unlike the Fumed Silica Powder.

Aqueous Pre-dispersions of Fumed Silica are best added last in the preparation of waterbased adhesives and sealants.

High shear mixing is not needed for effective distribution of Aqueous Pre-dispersions of Fumed Silica.

**FS D** – Represents Aqueous Pre-dispersion of Fumed Silica

**FS P** – Represents Powder fumed silica
Interaction of Aqueous Pre-dispersion of Fumed Silica with Latex promotes formation of a nano-structured composite film which improves reinforcement.
Improved Film Formation leads to better adhesion

Improved Film Formation:
Reduced Cracking Tendency with Aqueous Pre-dispersion of Fumed Silica

Images of Film on Temperature Gradient Bar

EL2000 – Noveon With 5% Aqueous Pre-dispersion of Fumed Silica 200 m²/g at 20% Solids

EL2000 – Noveon Resin Only

5°C  7°C  11°C  15°C  17°C

Information Provided by The University of Minnesota
Conclusions Based on University of Minnesota research:

- Aqueous Pre-dispersion of Fumed Silica reduce cracking tendency during film formation.
- Fumed Silica causes more energy to be required to form a crack.
- Lower MMFT with Aqueous Pre-dispersion of Fumed Silica and reduction of crack formation.
- Most noticeable effect in resins softer particles – MMFT <15°C
  - Poor film formation in these systems is due to cracking
  - Resins with harder particles exhibited lack of coalescence and therefore require addition of co-solvent
- Films with Aqueous Pre-dispersion of Fumed Silica have higher König Hardness
- Ability to reduce or replace co-solvents with Aqueous Pre-dispersion of Fumed Silica provides potential to lower VOC’s
Fumed Silica improves shear strength of adhesives by increasing the cohesive properties of the film.

As with any shear adhesion test, the total force is a sum of adhesive and cohesive properties.
Shear adhesion for UCAR Latex improved when using both the Aqueous Pre-dispersion of Fumed Silica (FS Dispersion 200 m²/g) and the Fumed Silica Powder (FS Powder 200 m²/g).

The improvement was more pronounced when using the Aqueous Pre-dispersion of Fumed Silica.
Flexcryn® emulsion polymers
- PSTC 107 180° Shear Adhesion

Flexcryn also shows an improvement in 180° Shear time with the Aqueous Pre-dispersion.

In this case, the Fumed Silica Powder does not add to adhesion. This may be due to a number of factors, including shear sensitivity of the emulsion resulting in aggregates that are much larger than the Aqueous Pre-dispersion of Fumed Silica.

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<tr>
<th>silica [%]</th>
<th>Shear [minutes]</th>
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<tbody>
<tr>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
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<tr>
<td>2</td>
<td>15</td>
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<td>4</td>
<td>25</td>
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<tr>
<td>5</td>
<td>30</td>
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FS Dispersion 200 m²/g  FS Powder 200 m²/g
Fumed Silica improves shear strength of adhesives by increasing the cohesive properties of the film.

Formulation changes that negatively impact the tack properties can also affect the adhesive properties.

However, the addition of a fumed silica can balance these properties.
Aqueous Pre-dispersion of Fumed Silica results in better retention of inherent adhesive properties when compared to Fumed Silica Powder.
Flexcryl® was designed for clear label applications.

Use Aqueous Pre-dispersion of fumed Silica shows a lower decrease in peel adhesion compared to Fumed Silica Powder.
The addition of any powder into a PSA film has the potential to severely impact the tack.

The use of Aqueous Pre-dispersions of Fumed Silica reduce this impact.

This effect is resin/formulation dependent and the use of Aqueous Pre-dispersion of Fumed Silica can balance these properties.
The UCAR Latex shows only a moderate drop in tack with the Fumed Silica Dispersion 200 m²/g over the full range of loading tested.

The Fumed Silica Powder begins to show a significant loss of tack at higher loading levels.
With Flexcryl, the loss of tack for both materials was about even with a slight advantage to the dispersion.
Aqueous Pre-dispersion of Hydrophobic Fumed Silica (20% solids)

- Environmentally-friendly Aqueous Pre-dispersion using hydrophobic (DDS treated) Fumed Silica at 20 % solids
- Customized structuring eliminates need for high energy mixing.
- Dispersion exhibits high stability
- Good compatibility with many coating and adhesive systems
- Efficient thickening and thixotropic agent
- Efficient anti-settling agent
- Minimal effect on the optical properties of water-based clear coats
Rheological effectiveness of Aqueous Pre-dispersion of hydrophobic fumed silica in a water-based filler for coatings; 1 % silica

- **without Fumed Silica**
- **Hydrophobic Fumed Silica Powder:** added using bead mill
- **Aqueous Pre-dispersion of Hydrophobic Fumed Silica:** added under agitation

![Graph showing rheological properties of different dispersions](image)
Aqueous Pre-dispersion of Hydrophobic Fumed Silica Thixotropy and Suspension

Simulation of the spraying process and simulation of the situation shortly after application

- Hydrophobic fumed silica as powder
- Hydrophobic fumed silica as powder + additives
- Hydrophobic fumed silica dispersion
- Control

![Graph showing viscosity over time for different samples.](image)
• Fumed Silica enhances the cohesive properties of the film thus building a more integrated bond line with improved reinforcement.

• Aqueous Pre-dispersions of Fumed Silica eliminate the dispersing step that is required when working with Powder Fumed Silica simplifying the process while reducing mix time. It also enables the use of fumed silica in shear sensitive waterborne polymers systems.

• Aqueous Pre-dispersions of Fumed Silica also impart the combined properties of reinforcement with viscosity control and suspension properties.

• Aqueous Pre-dispersions of Fumed Silica result in better retention of inherent adhesive properties, showing a less impact on tack and peel performance compared to Fumed Silica Powder.

• The results also indicate that each adhesive system must be studied as results may vary based on chemistry and polymer sensitivity.
Aqueous Pre-dispersions of Fumed Silica to Enhance Waterborne Adhesives and Sealants