Precipitated Silica: Technology, Production, Compounding & Applications

VKRT Seminar 2/14/19

Jared Rueby
Overview

• Background
• Typical Silica Manufacturing Process
• Silica Characterization
• Factors Influencing Reinforcement
• Agilon® Performance Silica
Filler Classification

- **Non-Reinforcing**
- **Semi-Reinforcing**
- **Reinforcing**

**Particle Size**
- microns
- nm

- Dry Ground Marble
- Whiting CaCO₃
- Wet Ground CaCO₃

**TALCS**
- Precipitated CaCO₃
- Al & Ca Silicates

**CLAYS**
- N990
- N700
- N550
- N330
- N110

**Silica:** Precipitated and Fumed
Forms of Silicon Dioxide

Silica
7631-86-9

Amorphous Silica
7631-86-9

- Natural
  - Kieselguhr (Diatomite)
    61790-53-2
  - Calcined
    91053-39-3
  - Flux-Calcined
    68855-54-9

- By-Products
  - Fused Silica
    60676-86-0
  - Silica Fume
    69012-64-2

- Synthetic Amorphous Silica
  7631-86-9
  - Pyrogenic Silica
    112945-52-5

- Crystalline Silica
  7631-86-9
  - Cristobalite
    14464-46-1
  - Quartz
    14808-60-7
  - Tridymite
    15468-32-3

- Precipitated Silica
  112926-00-8

Surface Treated Silica
[67762-90-7]/[68611-44-9]/[68909-20-6]
Precipitated Silica End-use Applications

**Rubber (Reinforcement) Applications**
- Tires
- Industrial Rubber
- Silicone Rubber
- Footwear

**Non-Rubber Applications**
- Microporous
- Carrier
- Coatings, Adhesives, Sealants, Etc.
Typical Precipitated Silica Manufacturing Process

- Sand
- Soda ash
- Furnace
- Cullet
- Water
- Sodium silicate aka water glass

\[
mH_2SO_4 + [Na_2O \cdot (SiO_2)_{3.2}]_m \xrightarrow{\text{H}_2\text{O}} mNa_2SO_4 + zH_2O + (m-z)H_2O
\]

Precipitation\[25-95°C\]

Hydrated Amorphous Silica Hi-Sil®, Silene™, Agilon®

- Powder
- Granules
Silica Particle Size

**Primary Particle**
- 5-50 nm

**Aggregate**
- ~500 nm
- = ~0.5 μm

**Agglomerate**
- ~100,000 nm
- = ~100 μm
Silica Particle Size: Surface Area Measurement

- TEM/SEM/AFM for direct particle size measurement
- \(N_2\) BET: Primary Particles + Micropores
- CTAB: Primary Particles Only
When microporosity is constant, BET and CTAB correlate with ultimate particle size, and reinforcement capability correlates with both measurements. Otherwise, correlates with CTAB surface area only.
Silica Porosity: Structure Measurement

N\textsubscript{2} Porosimetry $\rightarrow$ Hg Porosimetry

$\leftarrow$ Oil Absorption

PRIMARY PARTICLE SURFACE ROUGHNESS

INTRA-AGGREGATE PORE VOLUME

INTER-AGGREGATE PORE VOLUME

INTER-AGGLOMERATE VOID VOLUME

INTRA-AGGLOMERATE PORE VOLUME
Silica Porosity: Intra-aggregate Hg Pore Volume

$dV(D)$ vs Diameter

Pore Diameter (Å)
Silica Surface Chemistry: Silanol Types & Water Adsorption

- **GEMINAL**
- **VICINAL**
- **ISOLATED**

WATER ADSORPTION
Silica Surface Chemistry: TGA Curve

“Physically Adsorbed Water”

Difference (2.3%) = “Bound Water”

5.35%  7.65%
Key Precipitated Silica Properties

Surface Area and Particle Shape: The single most important factor for reinforcement

Amorphous Precipitated Silica

Surface Activity: Silanol Groups/TGA

Morphology and Porosity: Mercury Porosimetry/TEM
## Typical Range of Silica Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area:</td>
<td>30 - 300 m²/g</td>
</tr>
<tr>
<td>CTAB Surface Area:</td>
<td>30 - 300 m²/g</td>
</tr>
<tr>
<td>Oil Absorption:</td>
<td>150 - 350 mL/100g</td>
</tr>
<tr>
<td>pH (5% Slurry)</td>
<td>6.0 - 8.5</td>
</tr>
<tr>
<td>Typical Composition:</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>85.5 - 93.0 wt. %</td>
</tr>
<tr>
<td>Absorbed H₂O</td>
<td>4.0 - 7.0 wt. %</td>
</tr>
<tr>
<td>Bound H₂O</td>
<td>2.0 - 4.0 wt. %</td>
</tr>
<tr>
<td>Salt</td>
<td>0.5 - 2.5 wt. %</td>
</tr>
<tr>
<td>Other Impurities</td>
<td>&lt; 1 wt. %</td>
</tr>
<tr>
<td>Form</td>
<td>Powder, Micropearls, Pellets &amp; Granules</td>
</tr>
</tbody>
</table>
### Silene/Hi-Sil® Silica Products

Industrial Rubber Grades

<table>
<thead>
<tr>
<th>Product</th>
<th>Dispersibility</th>
<th>Reinforcing Capability</th>
<th>CTAB (m²/g)</th>
<th>N₂ (BET-5) (m²/g)</th>
<th>pH</th>
<th>Residual Salt Type</th>
<th>Physical Form</th>
<th>Manufacturing Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silene 732D</td>
<td>Classical</td>
<td>Semi</td>
<td>33</td>
<td>33</td>
<td>8.5</td>
<td>Na₂SO₄</td>
<td>Powder</td>
<td>USA</td>
</tr>
<tr>
<td>Hi-Sil 532EP</td>
<td>Classical</td>
<td>Semi</td>
<td>55</td>
<td>55</td>
<td>8.5</td>
<td>Na₂SO₄</td>
<td>Powder</td>
<td>USA</td>
</tr>
<tr>
<td>Hi-Sil EZ90G-D</td>
<td>High</td>
<td>Medium</td>
<td>90</td>
<td>90</td>
<td>6.5</td>
<td>Na₂SO₄</td>
<td>Granule</td>
<td>Netherlands</td>
</tr>
<tr>
<td>Hi-Sil 200 Series</td>
<td>Classical</td>
<td>Medium</td>
<td>135</td>
<td>135</td>
<td>6.9</td>
<td>NaCl</td>
<td>Pd, Gr, Pt</td>
<td>USA</td>
</tr>
<tr>
<td>Hi-Sil HDP320G</td>
<td>Classical</td>
<td>Medium</td>
<td>160</td>
<td>160</td>
<td>6.5</td>
<td>Na₂SO₄</td>
<td>Granule</td>
<td>USA</td>
</tr>
<tr>
<td>Hi-Sil EZ160G</td>
<td>High</td>
<td>Medium</td>
<td>160</td>
<td>160</td>
<td>6.5</td>
<td>Na₂SO₄</td>
<td>Granule</td>
<td>USA &amp; Netherlands</td>
</tr>
<tr>
<td>Hi-Sil 255C(G)-D</td>
<td>Classical</td>
<td>High</td>
<td>167</td>
<td>175</td>
<td>6.5</td>
<td>Na₂SO₄</td>
<td>Pd, Gr</td>
<td>Netherlands</td>
</tr>
<tr>
<td>Hi-Sil 134(G)</td>
<td>Classical</td>
<td>High</td>
<td>160</td>
<td>180</td>
<td>6.3</td>
<td>Na₂SO₄</td>
<td>Pd, Gr</td>
<td>USA</td>
</tr>
<tr>
<td>Hi-Sil 190(G)</td>
<td>High</td>
<td>High</td>
<td>170</td>
<td>195</td>
<td>6.9</td>
<td>Na₂SO₄</td>
<td>Pd, Gr</td>
<td>USA</td>
</tr>
<tr>
<td>Hi-Sil EZ200G</td>
<td>High</td>
<td>High</td>
<td>200</td>
<td>300</td>
<td>7.0</td>
<td>Na₂SO₄</td>
<td>Granule</td>
<td>USA &amp; Netherlands</td>
</tr>
</tbody>
</table>

### Agilon® Performance Silica

<table>
<thead>
<tr>
<th>Product</th>
<th>Dispersibility</th>
<th>Reinforcing Capability</th>
<th>CTAB (m²/g)</th>
<th>N₂ (BET-5) (m²/g)</th>
<th>SH %</th>
<th>Carbon %</th>
<th>pH</th>
<th>Residual Salt Type</th>
<th>Physical Form</th>
<th>Manufacturing Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agilon 400</td>
<td>High</td>
<td>High</td>
<td>140</td>
<td>75</td>
<td>0.5</td>
<td>4.0</td>
<td>6.5</td>
<td>Na₂SO₄</td>
<td>Granule</td>
<td>Netherlands</td>
</tr>
<tr>
<td>Agilon 454</td>
<td>High</td>
<td>High</td>
<td>200</td>
<td>140</td>
<td>0.5</td>
<td>4.0</td>
<td>6.5</td>
<td>Na₂SO₄</td>
<td>Granule</td>
<td>Netherlands</td>
</tr>
</tbody>
</table>
Silica Compounding
Rubber Reinforcement

Reinforcement = rubber tensile strength, abrasion resistance, and tear resistance.

Silica factors influencing rubber reinforcement
  • Primary particle size (surface area)
  • Volume Fraction (Loading + Surviving Silica Structure)
  • Polymer-silica interaction, Coupled or Un-Coupled
Surface Area – Impact on Compound Properties

Hi-Sil® EZ200G -> 190G -> 255G -> 210 -> 315G -> EZ90G

**High Surface Area**
*(Small Ultimate Particle)*
(without silane coupling agents)
- Slower Cure
- Higher Viscosity
- Higher Hardness
- Higher Set
- Higher HBU
- Higher Tear Resistance
- Higher Cut Resistance
- Higher Reinforcement

**Low Surface Area**
*(Large Ultimate Particle)*
- Faster Cure
- Lower Viscosity
- Lower Hardness
- Lower Set
- Lower HBU
- Lower Tear Resistance
- Lower Cut Resistance
- Lower Reinforcement

Reinforcement and Tear/Cut Resistance -> Processing, Resilience and Heat Aging
Silica Mixing: Incorporation & Dispersion

- **Powders vs Granules**: Granules generally incorporate faster due to less air content and higher density.

- **Incorporation vs Dispersion**: Incorporation is to break down agglomerates to > 10µm; while dispersion is to break down silica into aggregates scale <1µm [Macrodispersion vs Microdispersion].

- **Silica Addition**: In the early stage of mixing; split additions are recommended when loading is high (especially for powder).

- **Oil Injection**: Delayed oil injection to facilitate silica dispersion.

- **ZnO addition**: ZnO will interfere with Silica-Silane reaction and has a negative effect on wear.

- **Fly Loss**: Should be determined and adjusted separately from carbon black.
Silica Mixing: Compounding Stages

Mixing Stages (3)
Oil Extended SSBR/BR and 50 PHR Silica

- **Incorporation**
- **Dispersion**
- **Plasticization**

Hi-Sil® 255CG-D
Properties Affected by Dispersion:
- Viscosity
- Cure Profile
- Stress/Strain
- Abrasion
- Dynamic Properties
  - HBU
  - Stiffness
  - Friction

Silica Mixing: Dispersion Energy Requirement

Shear Energy

Median Particle Size (microns) 1.0

Hi-Sil® 210
Hi-Sil® EZ160G
EXPERIMENTAL

Highly Dispersible
Classical
Masterbatch - PDS
Nanocomposite?
One Method to Quantify Friability:
Vol% < 1 um and > 53 um
Silica Surface Chemistry - Affinity for Various Molecules

- Alcohols and Glycols
  - DEG & PEG
- Amines
  - Triethanolamine, Hexa, HMMM, Some accelerators and AOs
- Metal Salts (Zn++)
- Polar hydrocarbons
  - Aromatic Resins, Tall oil (NR)
- Silica particles (agglomeration)
- Silane coupling agents
- Water
Silica Mixing: Silane Coupling Agents

- **Silane Selection:** TESPT, TESPD, Mercaptosilane, etc.
- **Efficiency Control:** Reaction time, reaction temperature, release of VOC
- **Scorch:** impact of temperature on silane stability
- **Impact on downstream processing** (porosity and mold fouling etc.)

<table>
<thead>
<tr>
<th>Silica-Silane Reaction Provides</th>
<th>Reduced</th>
<th>Increased</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td></td>
<td>Bound Rubber</td>
</tr>
<tr>
<td>Filler-Filler Interaction</td>
<td></td>
<td>Modulus</td>
</tr>
<tr>
<td>Elongation</td>
<td></td>
<td>Abrasion Resistance</td>
</tr>
<tr>
<td>HBU/Hysteresis loss</td>
<td></td>
<td>X-Link Density</td>
</tr>
<tr>
<td>Compression Set</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$$[(ROH)_3\text{-Si-(CH}_2)_3\text{-S}_2]_2 + ROH$$
Silica Compound Mixing

- Silica Incorporation & Dispersion
- Silanization
- Heat Treatment
- Batch-Off
On an aggregate scale, silica and carbon black have a similar appearance.
At the atomic scale, silica and carbon black are significantly different.
Silica vs. Carbon Black: Compound Performance

Differences (without Special Compounding)
- Higher Viscosity
- Slower Cure Rate
- Lower Crosslink Density
- Lower Modulus
- Better Heat Aging Resistance
- Neutral Color
- Higher Hardness/Stiffness

Advantages

<table>
<thead>
<tr>
<th>Without Silane Coupling</th>
<th>With Silane Coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tear Resistance</td>
<td>High Resilience</td>
</tr>
<tr>
<td>Cut Growth resistance</td>
<td>Hysteresis/HBU</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Friction</td>
</tr>
<tr>
<td></td>
<td>Abrasion Resistance</td>
</tr>
</tbody>
</table>
Agilon® Performance Silica

- Technology platform comprising numerous products
- Patented chemistry and process for reacting silica with coupling agent and compatibilizer to form unique reinforcing fillers

**Compatibilizer**
- Various chain lengths
- Bonding chemistry

**Silane**
- C1 -> C36
- Mercapto
- Polysulfides
- Vinyl
- Chloropropyl
- Glycidoxy
- Amino
- Propylchloroformate
- Hydroxyalkyl
- PDMS
- Glycols - PEG

**Typical Properties**

<table>
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<tr>
<th>Property</th>
<th>Agilon 400 Silica</th>
<th>Agilon 454 Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB Surface Area, m²/g</td>
<td>140</td>
<td>200</td>
</tr>
<tr>
<td>N₂ (BET-5) Surface Area, m²/g</td>
<td>75</td>
<td>140</td>
</tr>
<tr>
<td>SH, Wt. %</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbon, Wt. %</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

- Mercaptosilane-functionalyzed for sulfur cure
- Long chain hydrocarbon compatibilizer
- Two different levels of reinforcement
**Agilon: Patented Chemistry-Based Solution**

**AGILON INNOVATION**
- Utilizes specialty silane & compatibilizer in unique pre-reaction with silica
- Pre-reacting enables better usage/interaction of these materials, delivering better overall balance of rubber reinforcement properties

<table>
<thead>
<tr>
<th>Rubbe</th>
<th>Short Chain Silane</th>
<th>Stronger coupling bonds to rubber limits heat generation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Compatibilizer**

- Enables compound flexibility that improves abrasion resistance

**Silica**

- Polar silica and non-polar rubber interaction improve tear over carbon black

**Heat Build-Up Resistance**

- Abrasion Resistance
- Tear Strength
Agilon: Enabling Manufacturing Improvement

Manufacturing Benefits

Current In-Situ Silica + Silane Technology

Agilon Silica Technology

Silica + Silane

Agilon

In-situ silica + silane:
- Increases mixing complexity vs. carbon black
- Reduces mixing throughput vs. carbon black
- Increases mixing energy intensity vs. carbon black
- Requires elevated temperature for silica + silane reaction
- Generates alcohol-related VOCs
- Can lead to porosity in extrusion

Agilon addresses many concerns:
- Reduces mixing complexity
- Increases mixing throughput/efficiency
- Allows for lower-temperature mixing
- Reduces mixing energy intensity
- Works in older mixing technology
- Eliminates nearly all alcohol-related VOCs
- Smoother extrusions with less porosity
Summary

- Precipitated silica manufacturing process
- Silica characterization – key properties
  - Silica particle size (and shape)
  - Silica porosity
  - Silica surface activity
- PPG Silica products for industrial rubber
- Rubber Reinforcement – silica surface area effects
- Silica Mixing
  - Incorporation and dispersion
  - Use of silane coupling agents
  - Silica vs. carbon black
- Agilon® performance silica
Q & A

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