LUDOX® Colloidal Silica in Coatings
Lithium Polysilicate in Coatings

Introduction

LUDOX® colloidal silicas are aqueous dispersions of very small silica particles in the low nanometer size range. Many grades are offered in this family, giving broad flexibility for specific performance targets. This bulletin aims to inform the formulator about the unique properties of LUDOX® colloidal silica and to offer starting points for applications such as anticorrosive coatings and architectural paints.

Colloidal silica particles are roughly spherical, non-porous and dispersed in water. They have a dense silica core and a surface covered by silanol (Si-OH) groups.

Because of their small particle size and high surface area, these silanol groups interact strongly with metal substrates, metal oxide fillers commonly found in coatings, and with many polymeric and latex binders. These interactions result in strong binding properties to various substrates, giving the coating higher strength and durability.

Larger particle grades may also be used to modify coatings surface properties such as surface roughness.

LUDOX® Colloidal Silica Grade Description

LUDOX® colloidal silica grades are distinguished by average particle size and stabilization method. In practice, the specific surface area (i.e., surface area per gram of silica) instead of average particle size is used as a specification property in most grades, because of its inverse relationship to average particle size, and because it is more easily measured.

Particle size (or specific surface area) and the method of charge stabilization are key in selecting the optimum grade for a particular application.

Particle Size

Based on proprietary manufacturing processes, LUDOX® colloidal silica grades offer a wide range of particle sizes from 5 nm (or 425 m^2/g SiO_2) to 60 nm (or 90 m^2/g SiO_2). Please refer to *Table 1* for the particle size/specific surface area range offered.

Most of the grades are "monodisperse" with relatively narrow particle size distribution. Grades designated with the letter "P" (e.g., LUDOX® P X-30) are "poly-disperse" and have broader particle size distribution.

LUDOX® Colloidal Silica Grades

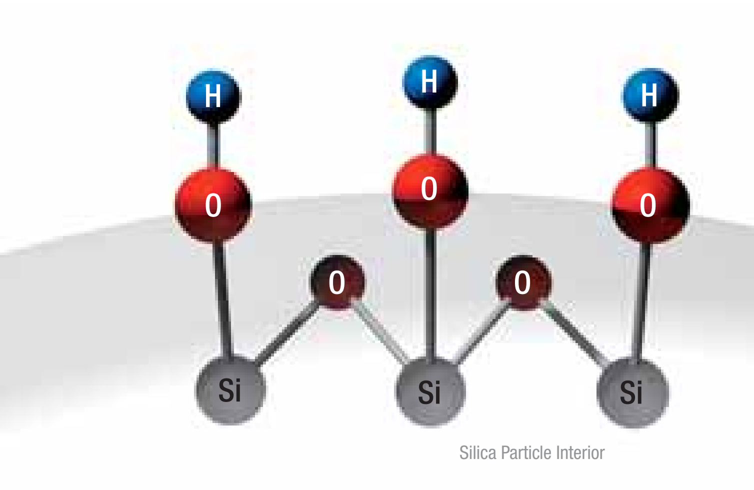
		Anionic Grades									Cationic Grades		
APS (nm)	SSA (m^2/g SiO_2)	Sodium Counter Ion			Ammonium Counter Ion			pH Stable			Chloride Counter Ion		
		Grade	% SiO_2	pH	Grade	% SiO_2	pH	Grade	% SiO_2	pH	Grade	% Solids	pH
Monodisperse Grades													
5	425	**FM**	15	10									
7	350	**SM**	30	10	**SM-AS**	25	9.5						
		HS-30	30	9.7	**AS-30**	30	9.6	**AM**	30	9	**CL**	30	4
12	220	**HS-40**	40	9.7				**HSA**	30	4			
		LS	30	8									
22	140	**TM-40**	40	9	**AS-40**	40	9.2	**TMA**	34	4-7	**CL-P**	42	4
		TM-50	50	9									
Polydisperse Grades													
15	260	**P X-30**	30	10									
20	155	**P T-40**	40	10									
40	80	**P W-50**	50	10									

Table 1

APS = Average Particle Size (diameter) / SSA = Specific Surface Area

Stabilization

Because of their chemical reactivity, the colloidal silica particles must be prevented from reacting with themselves after manufacturing. Colloidal silica products must remain stable during storage, formulation, and until the final coating is applied. All grades within the LUDOX® colloidal silica family are charge stabilized to keep the particles from aggregating and gelling. The following describes the three approaches used to impart charge to the silica surface. Please refer to the figures to visualize the surface structure for each approach.



Colloidal Silica Surface Structure

Alkaline Grades

The easiest method of inducing a charge is by taking advantage of acidic silanol groups on the silica particle surface. By reacting these groups with alkali, the particles become charged. The alkaline compounds of commercial interest are sodium hydroxide and ammonium hydroxide. Chemically, the interaction can be written as:

$$(SiOH) + NaOH \rightarrow (SiO^{\ominus}) + Na^{\oplus} + H_2O$$

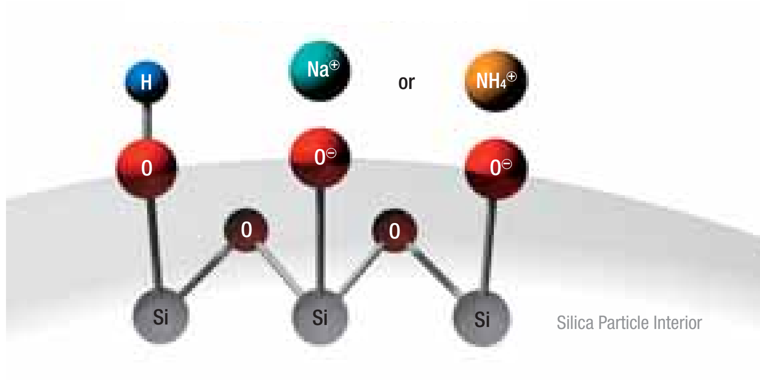
or

$$(SiOH) + NH_4OH \rightarrow (SiO^{\ominus}) + NH_4^{\oplus} + H_2O$$

where (SiOH) and ($SiO^{\ominus}$) denote uncharged and charged silanol groups on the particle surface.

Important features:

- In alkaline LUDOX® colloidal silica grades, the particles are negatively charged. For this reason, these grades are often termed anionic.
- The sodium ($Na^{\oplus}$) or ammonium ($NH_4^{\oplus}$) ions are usually called counter ions and balance the charge induced on the silica particles.

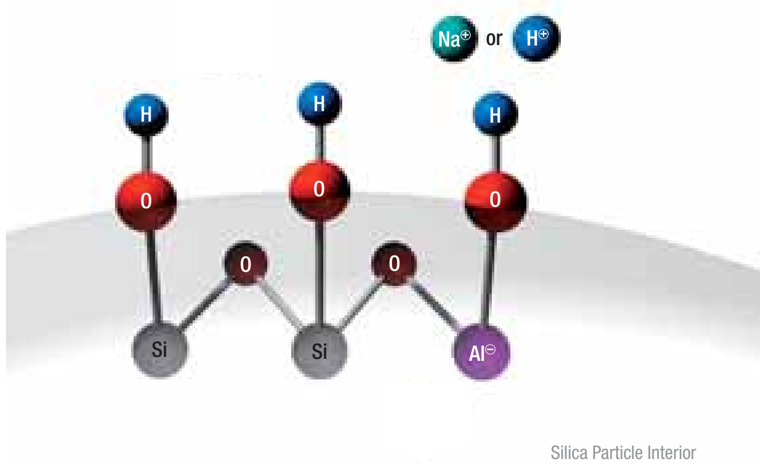


Alkaline Grades

- Typically, grades stabilized this way will be offered at or above pH 8, more commonly at pH 9-10. More alkali is needed for smaller particle sizes. If a grade with sodium counter ions is used in a coating formulation, the sodium will remain in the coating after it is applied and dried. On the other hand, ammonium hydroxide is volatile and will evaporate from the coating during dry down.
- Below about pH 8 the colloidal silica particles do not have sufficient charge density to remain stable at concentrations ≥10% silica. These grades may still be used in acidic or neutral formulations if process throughput is relatively short.

pH Stable Grades

In some cases, the coating formulation must be maintained in the acidic to neutral pH region for various reasons. The alkaline grades discussed above may be unsuitable due to long process throughput.



pH Stable Grades

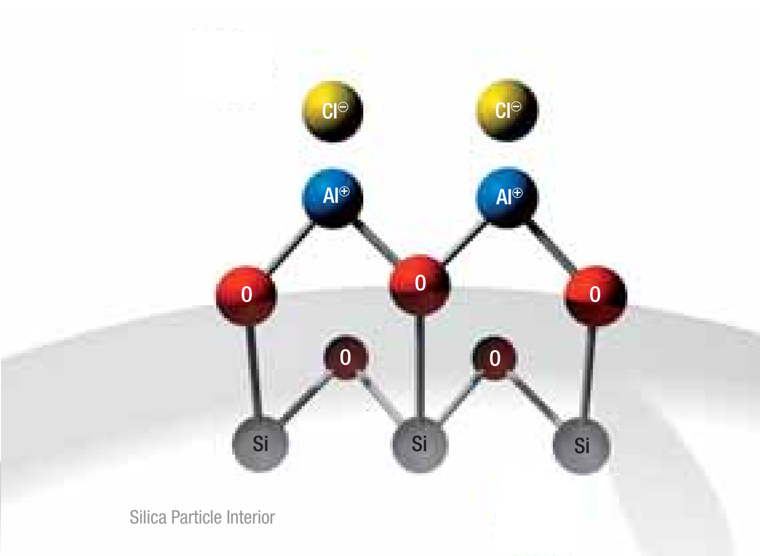
Grades are available in which a small amount of the silica surface is modified with an aluminate compound. The aluminate maintains charge density such that the stability range is extended to about pH 4-10.5.

Important features:

- Since a small amount of the particle surface is modified, the particle chemistry is predominantly that of the silica surface.
- These grades are anionic. The particles are negatively charged.
- The counter ion may be sodium, as in the case of LUDOX® AM, which is offered at about pH 9. For applications in which sodium is not desired, acidic grades are offered in which the counter ion is the acid or hydronium ion.
- Acidic or alkaline grades stabilized in this manner may be added to coating formulations adjusted to the pH 4-10.5 range with good stability.
- Acidic grades are especially compatible with water-soluble polymers such as polyvinyl alcohol and with formulations containing polar organic solvents.

Cationic Grades

In these grades, the silica particles are fully coated with an aluminum hydroxide compound (different from the pH stable grades) such that the net particle charge is positive.



Cationic Grades

The particles may be considered to be a "core-shell" structure in which the core is composed of the silica particle and the aluminum compound is the shell.

Important features:

- These grades are cationic. The particles are positively charged.
- Particle chemistry is dictated by the aluminium hydroxide surface rather than silica.
- The counter ion is chloride.
- pH stability is in the range pH 3.5-6.

Lithium Polysilicate

Although not strictly a colloidal silica, Lithium Polysilicate is a companion grade to our colloidal silica line and was developed specifically for inorganic coating applications.

Lithium Polysilicate is a "high ratio silicate." Typically, silicate grades are characterized by the molar ratio of silica to metal oxide. In the case of sodium silicate, grades with SiO_2:Na_2O ratios above 3.5 are uncommon due to low water solubility. Low ratio sodium silicate grades tend to contain relatively high levels of water that can have deleterious aging effects.

With a proprietary process, Grace Davison can make Lithium Polysilicate at any SiO_2:Li_2O ratio up to 40, at which point the product becomes a true colloidal silica. Commercial experience has focused on Lithium Polysilicate with a molar ratio of 4.8.

Features to note:

- pH ~11. Similar handling to sodium silicate.
- Very compatible with powdered zinc for zinc-rich primers.
- High ratio results in lower levels of water in coatings.

Formulation Guidelines

Because of their small size, colloidal silica particles can play a unique role in many waterborne coating formulations. Grades with smaller particles can be used as binders or co-binders for added strength and durability to the coating. This is due to silica surface reactivity with other silica particles, metal surfaces, fillers or organic polymers. Larger particle grades are mainly used as surface modifiers.

To decide which of the available grades to evaluate, we recommend the following selection process:

1. For alkaline coatings formulations, the alkaline LUDOX® colloidal silica grades are natural fits.
   - 1.1 If sodium poses no problems in the formulation, evaluate a medium particle grade such as HS-40 as a starting point.
     - 1.1.1 If better binding performance is required, try a smaller particle grade such as SM.
     - 1.1.2 If better surface effect or formulation stability is required, try a larger particle grade such as TM-50.
   - 1.2 If sodium poses problems in the formulation, consider a medium particle, ammonia-stabilized grade such as AS-30 as a starting point.
     - 1.2.1 If better binding performance is required, try the smaller particle grade SM-AS.
     - 1.2.2 If better surface effect or formulation stability is required, try a larger particle grade such as AS-40.

2. For acidic coating formulations, the pH stable LUDOX® colloidal silica grades are natural fits.
   - 2.1 Decide whether the colloidal silica concentration in the formulation and process times will allow the use of alkaline grades with pH adjustment. This is often the more cost effective choice. If so, the same evaluation process for alkaline formulations can be used as described under 1.
   - 2.2 If greater pH stability is required, evaluate a medium particle size, pH stabilized grade.
     - 2.2.1 If sodium poses no problem in the formulation, evaluate the medium particle grade AM (with pH adjustment).
     - 2.2.2 If sodium poses a problem, try HSA colloidal silica (with perhaps minor pH adjustment).
   - 2.3 If better surface effect or formulation stability is required, try the larger particle TMA grade (with perhaps minor pH adjustment).
   - 2.4 If the formulation contains significant levels of positively charged cations (from, for example, surfactants, polymers or metal ions) or if greater modification to a substrate surface is desired, evaluate CL-P.
     - 2.4.1 If better performance is required, try the medium particle grade CL.

Lithium Polysilicate may be used as a replacement for sodium silicate in metal pretreatments, zinc-rich primers and silicate paints.

Some applications require the development of special grades. Please contact a Grace Davison representative if you have needs that our current portfolio of grades does not satisfy.

Key Coatings Applications

Architectural Emulsion (Latex) Paints and Parquet Hardcoats

Colloidal silica may be added to many water-borne coating systems to significantly improve durability and anti-soil properties (especially dust retention). Colloidal silica may improve hardness and abrasion resistance in parquet formulations.

The colloidal silica grade must be chosen to be compatible with the other components of the formulation. Anionic grades are compatible with most latex emulsions, nonionic and anionic surfactants and polymers. They are not compatible with cationic surfactants and polymers.

Zinc-Rich Silicate Primers

Zinc-rich silicate primers provide very hard, anti-corrosive coatings on steel and are often used in marine applications. Sodium, potassium, lithium silicates and combinations may be used. These coatings are markedly weather resistant, do not chalk, are resistant to many organic solvents and are used in a broad temperature range.

High ratio silicates are necessary to fill these requirements and to provide good film forming characteristics and faster drying times. With a molar ratio of 4.8, Grace Davison's Lithium Polysilicate ratio is higher than commonly available sodium and potassium silicates. In addition, Lithium Polysilicate coating systems exhibit excellent compatibility with powdered zinc and typically have a longer pot life than sodium and potassium silicates.

A simple zinc-rich primer formulation containing lithium polysilicate consists of:

Component	Parts (by Mass)
Lithium Polysilicate	100
Zinc Powder (medium particle, 5 – 9 µm)	290

Masonry Silicate Coatings

As with zinc-rich silicate primers, sodium, potassium and lithium silicates are used to make waterborne masonry paints. Silicate paints are suitable for indoor and outdoor applications and have excellent adhesion to masonry and cementitious substrates.

Colloidal silica may be added to silicate formulations for faster development of water resistance and faster overall drying times.

Because these coating formulations also favor high ratio silicates, Grace Davison Lithium Polysilicate may offer significant advantages in terms of durability and chemical resistance, either as the principal binder or as a co-binder with sodium and potassium silicates.

Anticorrosive Metal Pretreatments

Metals may be "pretreated" with a formulation to protect the metal against corrosion and to improve adhesion of subsequent organic layers for better film formation. The pretreatment formula typically contains alkaline oxides, chromates and/or phosphates and is used to convert the metal surface to a mixed oxide to "passivate" the metal.

In efforts to replace hexavalent chromium formulations with trivalent chromium, colloidal silica and Lithium Polysilicate have been found to improve trivalent chromium adsorption and to help film formation. Furthermore, colloidal silica's high surface area helps control rheology.

The table below gives a typical formulation used for the treatment of galvanized steel:

Component	%
Phosphoric acid	15 – 20
Aluminum hydroxide $Al(OH)_3$	3 – 6
LUDOX® HS-40, AM or AS-40	40 – 50
Chromic acid	2 – 4
Water	Balance

Electroplating/Galvanization

In this application, a layer of zinc metal is electrodeposited onto a metal substrate. The zinc is then treated with a passivating formula similar to the metal pretreatment formula given above for added corrosion protection and to promote adhesion for subsequent paint applications. If needed, a sealant formula, also containing colloidal silica, may be coated on top of the passivating layer to seal defects and increase protection further.

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