

AEROSIL® Fumed Silica in Waterbased Adhesives & Sealants

Technical Information 1324



1 Introduction

AEROSIL® Fumed Silica has long been used in adhesives and sealants to provide thixotropy and reinforcement. In the area of waterborne systems, the use has primarily been in sealants. The unique combination of properties that AEROSIL® Fumed Silica provides applies to waterborne adhesives as well.

AEROSIL® is a synthetic amorphous silica that modifies flow behavior through its structure of aggregated particles. It increases viscosity and influences the flow, leveling as well as sag. When replacing traditional thickeners such as cellulosics, associative thickeners and clays with AEROSIL®, additional reinforcement properties are achieved. The same structure that controls viscosity also sets up an internal network of inorganic particles that improve the bulk properties of the dried film.

Adhesion of a material is a combination of its cohesive and adhesive properties. Each must be balanced to obtain the desired performance. Poor adhesive or cohesive properties may result in early failure of the adhesive. AEROSIL® Fumed Silica enhances the cohesive properties of the film thus building a more integrated bond line.

Evonik offers AEROSIL® Fumed Silica either as powders (AEROSIL®) or as liquid dispersions under the trade name AERODISP®. Powders are available in various hydrophilic and hydrophobic grades. Surface treated products offer additional unique features. AEROSIL® hydrophobic fumed silica grades are offered in different levels of hydrophobicity and carry the "R" designation. AERODISP® Fumed Silica dispersions eliminate the dispersing step that is required when working with powder fumed silicas. AERODISP® dispersions also impart the combined properties of reinforcement and viscosity.

2 AEROSIL® Fumed Silica in Pressure Sensitive Adhesives

Pressure sensitive adhesives, PSAs, are used to adhere labels, tapes and films to a variety of substrates. They are commonly used in industrial, consumer and medical applications. Strength and tack are key elements of the adhesive performance while the viscosity affects the thickness of the applied film.

The Pressure Sensitive Tape Council (PSTC) has developed a number of test methods to determine adhesion-in-peel, shear strength and tack. These basic tests were used to compare the performance of AEROSIL® 200 and AERODISP® W 7520. Other AEROSIL® fumed metal oxides were tested and may be suitable for specific applications where alternative surface areas or surface treatments may be a benefit.



PSA color tape

A short survey of polymers was made and the study included UCAR® Latex 9037 (acrylic copolymer) from Dow Chemical Company, and Flexcryl® AF 2066 and 260 B (emulsion polymers based on vinyl acetate, ethylene and butyl acrylate) from Air Products and Chemicals, Inc.. To each of these, levels of 1, 2, 3, 4, and 5% of dry fumed silica to polymer solids were added and compared to a control without silica.

2.1 180° Shear Adhesion Results

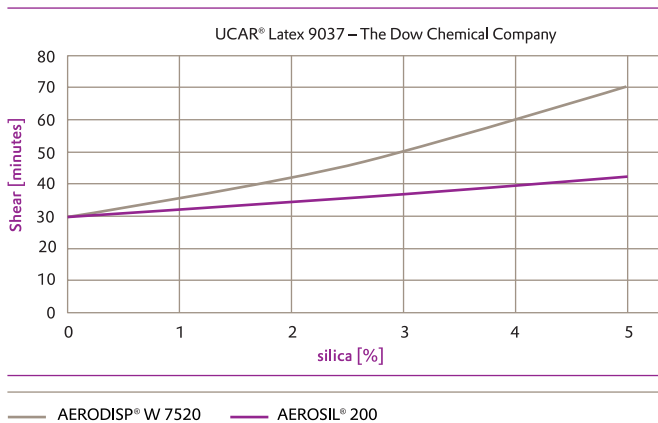
AEROSIL® Fumed Silica improves shear strength of adhesives by increasing the cohesive properties of the film. As with any shear adhesion test, the total force is a sum of adhesive and cohesive properties. The three latexes were tested with the PSTC method's arrangement of a ½ inch x ½ inch x 1000 gram configuration on stainless steel panels.

Shear Adhesion



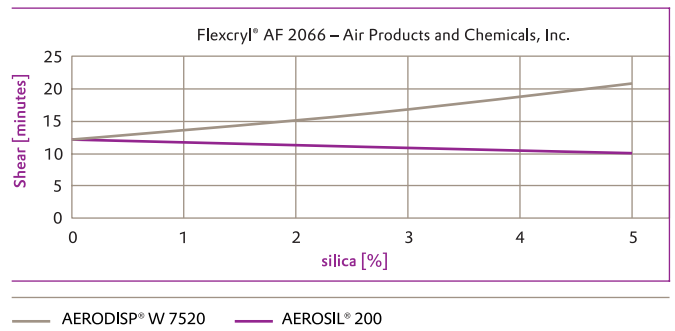
Shear adhesion for UCAR® Latex 9037 improved in both scenarios—when using the powder as well as when using the dispersion. The improvement was more pronounced when using AERODISP® W 7520 instead of the powder.

Shear Adhesion, UCAR® Latex 9037



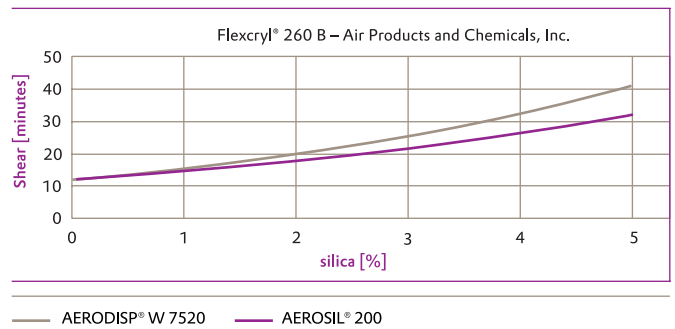
Flexcryl® AF 2066 also shows an improvement in 180° Shear times with the dispersion. In this case, the AEROSIL® 200 does not add to adhesion. This may be due to a number of factors, including shear sensitivity of the emulsion.

Shear Adhesion, Flexcryl® AF 2066



Flexcryl® 260 B also shows improvement for both dispersion and powder forms of fumed silica.

Shear Adhesion, Flexcryl® 260 B

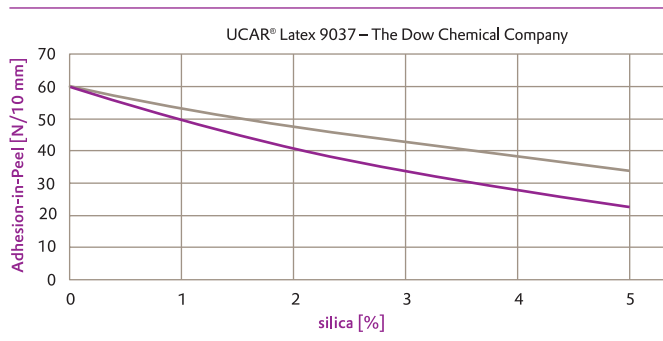


2.2 Adhesion-in-Peel Results

Adhesion-in-peel is related both to the adhesive and cohesive properties of the film. Formulation changes that negatively impact the tack properties (see below) can also affect the adhesive properties. However, the addition of a fumed silica improving shear (see above) can balance these properties out.

Dow Chemical's acrylic UCAR® Latex 9037 is intended for clear decal applications. One application is for screen printed signs for the side of trucks. Clarity is obviously important as is strength to prevent peeling. AERODISP® 7520 results in better retention of inherent adhesive properties when tested in peel than AEROSIL® 200.

Adhesion-in-Peel, UCAR® Latex 9037

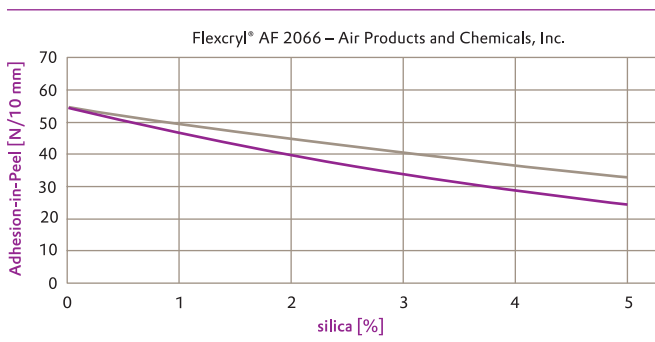


— AERODISP® W 7520 — AEROSIL® 200

Adhesion-in-Peel



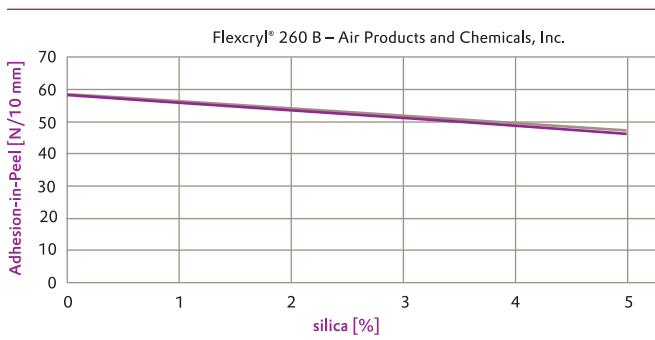
Adhesion-in-Peel, Flexcryl® AF 2066



— AERODISP® W 7520 — AEROSIL® 200

Air Products' Flexcryl® AF 2066 was also designed for clear label applications. Use of AEROSIL® 200 and AERODISP® W 7520 show a steady decrease in peel adhesion, but less with the dispersion. Finally, Flexcryl® 260 B from Air Products was also tested. This is a general purpose adhesive designed for paper and label applications. For this latex, both powder and dispersion perform similarly with a slight decrease at higher loading levels.

Adhesion-in-Peel, Flexcryl® 260 B



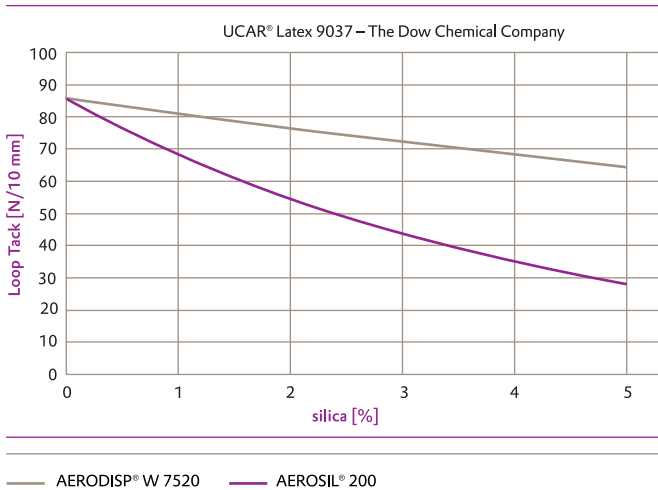
— AERODISP® W 7520 — AEROSIL® 200

2.3 Loop Tack

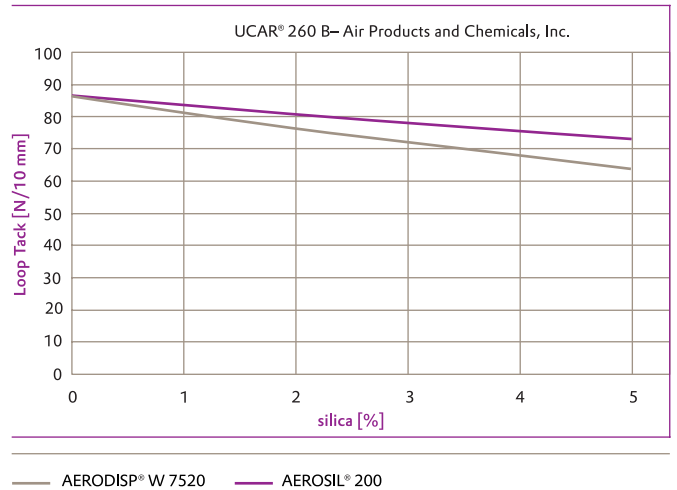
The addition of any powder into a PSA film has the potential to severely impact the tack.

The UCAR® Latex 9037 shows only a moderate drop in tack with the dispersion over the full range of loading tested. The powder begins to show a significant loss of tack at higher loading levels.

Loop Tack, UCAR® Latex 9037



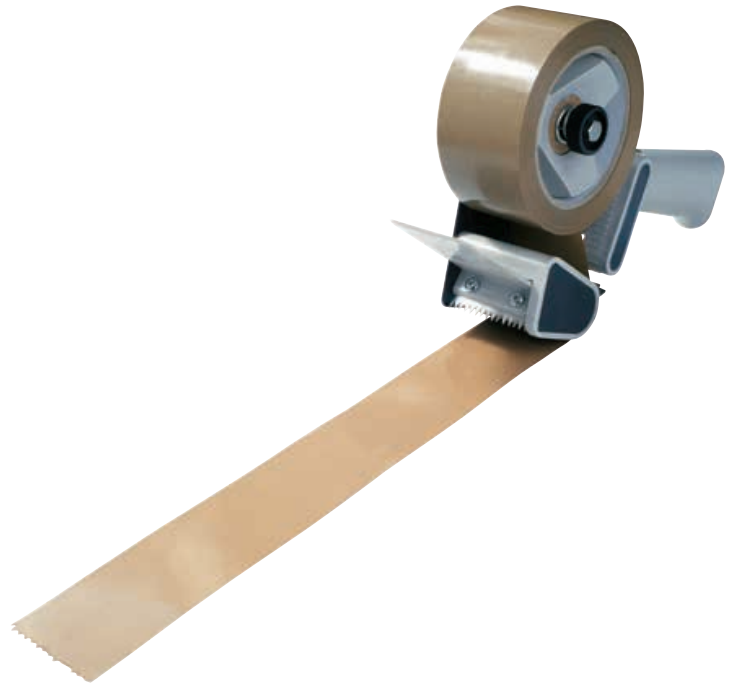
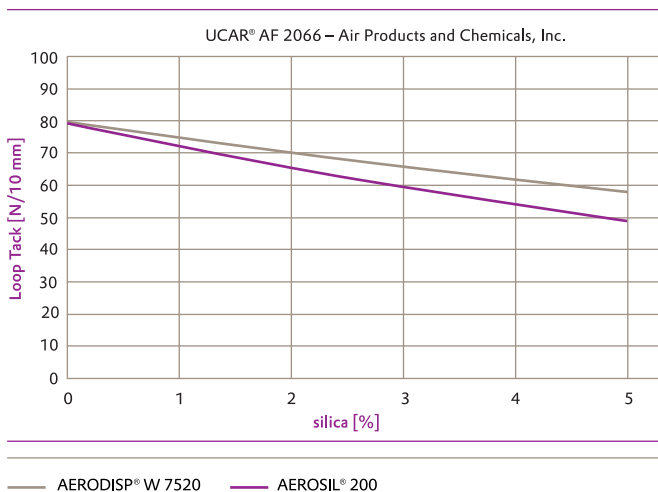
Loop Tack, Flexcryl® 260 B



With Flexcryl® AF 2066, the loss of tack for both materials was about even with a slight advantage to the dispersion.

Again, both powder and dispersion show a decline in tack, but less with Flexcryl® powder in this case.

Loop Tack, Flexcryl® AF 2066



Loop Tack Test



2.4 Conclusions

In pressure sensitive adhesives, the use of AERODISP® Fumed Silica dispersion is generally better than using the equivalent AEROSIL® Fumed Silica. The results also indicate that each latex must be studied as results may vary. While improving shear results, fumed silica does slightly diminish the tack and adhesion-in-peel results so care must be taken when these properties are important.

3 Subfloor Construction Adhesive

In the construction industry, solvent based adhesives make up a large portion of the market, in particular the subfloor adhesive. The performance requirements of this type of adhesive are such that wet and frozen lumber must be adequately bonded. The American Plywood Association has written a specification to cover this, *AFG-01 Adhesives for Field-Gluing Plywood to Wood Framing*, and is often cited. ASTM International's Committee D 14 Adhesives has developed *D 3498 Standard Specification for Adhesives for Field-Gluing Plywood to Lumber Framing for Floor Systems*. However, for everyday development of adhesives, wood lap shears are most commonly used to evaluate tensile strength.



A formulation was obtained from BASF for a subfloor construction adhesive that claims performance that meets the two standards mentioned. It is based on Acronal® DS 2159, a 50% solids emulsion and contains Acrysol® ASE-60 as a thickener. All formulations were made in a double planetary mixer and were vacuum deaired prior to transfer.

Wood Sub Floor Sample Preparation



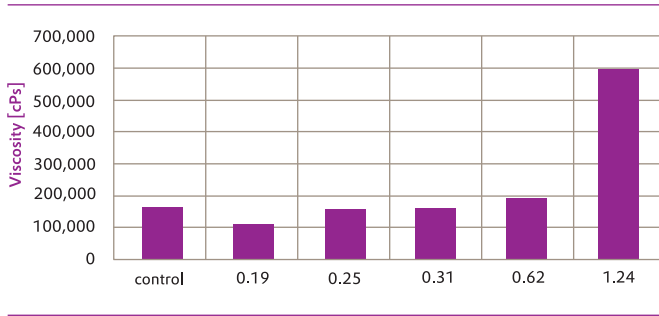
Raw Material		Supplier	Pct. Weight (wet)
Acronal® DS 2159	Styrene-acrylic copolymer	BASF	56.7
Sodium Tripolyphosphate	Dispersant	various	0.1
Pigment Disperser N	Dispersant	BASF	0.1
Foamaster NXZ	Defoamer	Cognis	0.05
Snowtack 301 A	Tackifying resin dispersion	Eka Nobel	3.6
Ethylene glycol	Freeze-thaw stabilizer	various	3.0
Eastman DBA	Cosolvent	Eastman Chemical	2.3
Duramite	CaCO ₃ , 6 micron	IMERYS	11.4
Nuclay	Kaolin clay	BASF	22.7
Acrysol® ASE-60	Polyacrylic acid thickener, 28% solids	Rohm and Haas	0.3

AEROSIL® R 972 was used to replace the Acrysol® ASE-60 for rheology and for the added benefit of reinforcement. A loading level of 0.25 to 0.31 % on the total, 0.88 to 1.09 % on the polymer solids was found to be sufficient to optimize the rheological and adhesive properties.

3.1 Viscosity Testing

Viscosity using a Brookfield HA-T spindle E at 5 rpm was taken 24 hours after the material was compounded and compared. The control (Acrysol® ASE-60) had a viscosity of 160,000 cPs.

Subfloor Adhesive Viscosity (cPs) by Silica Amount



Loading levels up to 0.62% AEROSIL® R 972 ranged from 110,000 to 190,000 cPs. At 1.24% loading, the viscosity climbed to 590,000 cPs. This indicates that AEROSIL® R 972 may be used in the same relative amounts as an alkali swellable thickener and even to twice the amount without serious impact to the viscosity of the system.

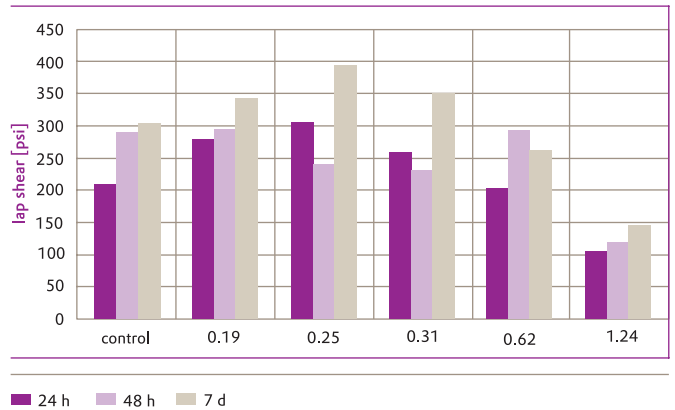
Wood Floor Preservation is a function of Adhesive Water Resistance



3.2 Lap Shear Adhesion and Water Resistance

Adhesion was compared using lap shears similar to ASTM D 1002 but made of poplar. A 1 x 2 inch area (25 by 50 mm) was adhered and tensile strength determined by dynamic loading. A crosshead speed of 0.05 in/min (1.27 mm/min) was used and the peak load noted with the final results reported in psi (MPa). Strength development was determined by testing at intervals of 24 hours, 48 hours and 7 days.

Subfloor Adhesive ASTM D 1002 Lap Shear Strength



With AEROSIL® R 972 loading up to 0.31%, strength development is as good as or better than the control (ASE-60). Above that loading, the shear strength begins to decline. This is likely due to too much of the polymer being tied up with wetting the fumed silica. At 0.25% loading, the 7 day results are the highest at 398 psi (2.74 MPa) compared to 307 psi (2.12 MPa) for the control, an almost 30% increase in shear strength. Additionally, several samples were cured for 14 days at room temperature and then immersed in water for 72 hours prior to testing to determine relative water resistance. The same lap shear assembly and test speed was used.

Subfloor Adhesive D 1002, 72 hour Water Soak

	Shear Strength	
	psi	MPa
Control (ASE-60)	26.5	0.18
AEROSIL® R 972, 0.31 %	62.1	0.43
AEROSIL® R 972, 0.62 %	42.2	0.29
AEROSIL® R 972, 1.24 %	35.0	0.24

3.3 AEROSIL® and Dynasylan® Synergy

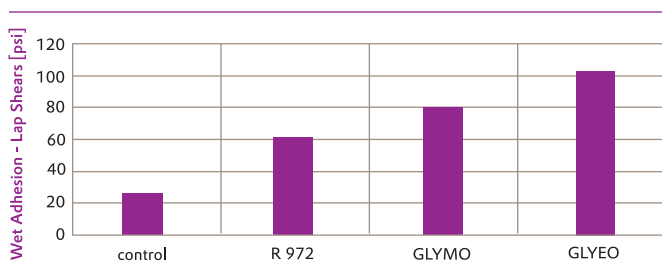
Dynasylan® Silanes are known to add value to latex sealant formulations. US Patent 4,340,524–Bullman, 1982, specifically discusses the use of γ -glycidioxypropyltrimethoxysilane (Dynasylan® GLYMO silane) and its benefits. In the area of waterborne adhesives, the use has been limited primarily due to the traditional methods of rheology control. More often, an alkali swellable thickener is used that requires the pH range of the system to be between 8 and 10 for optimal viscosity build. This detracts from the useful shelf life of silane coupling agents as the hydrolysis rate is accelerated in this pH range.

With the use of AEROSIL® Fumed Silica for rheology and reinforcement, the pH of the adhesive can be controlled more precisely and adjusted to more neutral conditions. This increases the stability of the silane in the system. Additionally, the use of ethoxy-functional silanes may further enhance shelf-life properties.

3.4 Conclusions

AEROSIL® R 972 fumed silica can effectively replace alkali swellable polymer thickeners and provide the added benefit of improved water resistance. With this replacement, the pH of the system is not as critical and can be reduced to the range in which silane adhesion promoters can be used to further enhance the formulation.

Subfloor Adhesive ASTM D1002 Lap Shears with Silane



AEROSIL® R 972 was used again, at a loading level of 0.25 %, along with 0.50 % silane on the total formulation (2 % on polymer solids). Dynasylan® GLYMO and GLYEO were the silanes chosen for this evaluation. Poplar lap shears were made with 2 inch² surface area overlap, allowed to dry at room temperature for 14 days, and then submerged in deionized water for three days prior to testing. The results showed improvements when using silane, especially the Dynasylan® GLYEO.

ASTM D 3498 testing of these four formulations show that they all pass the 150 psi minimum requirement for the specification.

4 AEROSIL® Fumed Silica in Waterborne Sealants

AEROSIL® Fumed Silica is well known for its performance in waterborne sealants. Chang's patent (U.S. Patent 4,626,567) granted in 1986 includes the use of hydrophilic or hydrophobic fumed silica in water-resistant, clear and color acrylic sealants. In 1992, Goldstein (5,124,384) discusses improvements in clarity of transparent latex caulks when matching refractive indices of fumed silica with those of the other formulation components. Even better clarity can be achieved with AERODISP® Fumed Silica dispersions.



Clarity of waterborne sealants is predominantly affected by the fumed silica and how well it is dispersed. High speed dispersing equipment is required to break up the agglomerates and reduce the fumed silica to its aggregate structure. This structure improves the cohesive properties of the sealant but, depending on the particle size, may negatively impact the light transmission through the sealant.

As light travels through the sealant, it strikes the fumed silica particles and is reflected back to the observer, creating a translucent effect. This effect can be minimized by optimizing the size and thus, the refractive index of the particles through proper dispersion. High energy is required to disperse fumed silica in powder form. The mechanical shear can destabilize the emulsion polymer, thus "breaking" the emulsion during the manufacturing process. Surfactants can prevent destabilization but have a negative impact on water resistance, adhesion & blushing.

The use of AERODISP® Fumed Silica dispersions eliminates the high energy dispersing process and reduces cycle times. Special milling procedures and pH control make these products stable. Their solids content is a function of the surface area of the fumed silica they contain and is inversely proportional. AERODISP® Fumed Silica dispersions are commercially available in solids contents ranging from 15 to 30%. For example, AERODISP® W 7330 N is offered at a 30% weight solids and an approximate pH of 10, and AERODISP® W 7520 at 20% weight solids.

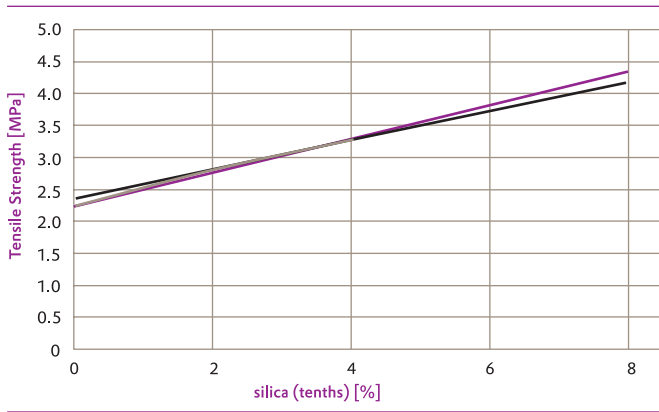
Tests were performed with a clear sealant formulation based on UCAR® Latex 9192, a high solids acrylic emulsion polymer. While the formulation mainly consists of latex, it also contains other ingredients to improve processing, UV stability, freeze-thaw characteristics, rheology and adhesion. Additional ingredients may also be added to improve flexibility, tooling and application. When using dispersions, it is important to keep in mind that the water is a volatile component that needs to be accounted for in the formulation. This may require replacing ingredients such as mineral spirits, with less volatile organic compounds that will aid in tooling and open time properties.

Raw Material		Weight (g)	Weight Percent
UCAR™ Latex 9192	Acrylic copolymer, 65 % solids	895.0	92.98
TERGITOL™ NP-4 Nonionic Surfactant	Nonylphenol ethoxylate	1.4	0.15
Foamaster NXZ Defoamer		3.2	0.33
Propylene Glycol		26.0	2.70
UCAR™ Filmer IBT	2,2,4-trimethyl-1,3-pentanediol monisobutyrate	7.7	0.80
Mineral Spirits		15.0	1.56
Tinuvin 1130 UV Stabilizer	50%: α -[3-[3-(2H-Benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]- ω -hydroxypoly(oxo-1,2-ethanediyl); 38%: α -[3-[3-(2H-Benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]- ω -[3-[3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]poly(oxy-1,2-ethanediyl);	0.6	0.06
Tinuvin 292 UV Stabilizer	Hindered amine light stabilizer	0.6	0.06
Dynasylan® GLYMO silane	γ -glycidyoxypropyltrimethoxysilane	0.6	0.06
AEROSIL® 200 Fumed Silica	SiO ₂	2.0	0.21
Ammonium Hydroxide (28 %)	NH ₄ OH	10.5	1.09
Total		962.6	100.00

Based on this formulation, AERODISP® W 7520 and AERODISP® W 7330 N fumed silica dispersions were compared to the standard AEROSIL® 200 at various loading levels. Of most interest are the properties of tensile elongation and clarity. Commonly, ASTM D 412 *Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension* is used to study the differences in tensile elongation properties of Elastomeric sealants. A specimen is cut in the shape of a dumb-bell or “dog bone” and elongated at strain rate of 10 in/min. Peak stress is reported along with the elongation at break as a function of a percentage of the original length. Clarity is compared visually by applying a layer of sealant on a black background, such as on a Leneta™ Chart.

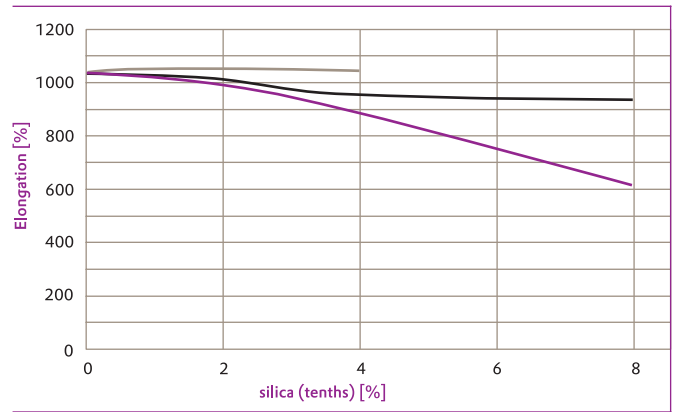


Clear Latex Sealant Tensile Strength



— AERODISP® W 7520 — Linear AEROSIL® 200
 — Linear AERODISP® W 7330 N

Clear Latex Sealant % Elongation at Break



— AERODISP® W 7520 — AEROSIL® 200
 — AERODISP® W 7330 N

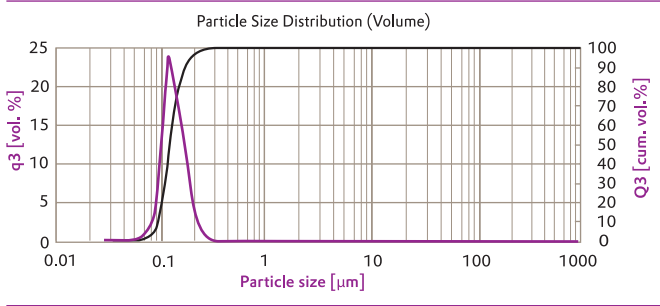
Tensile strength was compared with loading levels of 0, 0.2 (as called for), 0.4 and 0.8% total loading on a solid fumed silica basis. The formulations with AEROSIL® 200 included no additional water. Over this range of loading, the three products performed similarly. Higher loading levels are usually not used because of potentially higher viscosities.

Due to the nature of fumed silica's reinforcing properties, elongation at break is typically reduced with increased loading. This is visible in the graph where products made with AEROSIL® 200 did not perform as well as those made with AERODISP® dispersions. This is most likely a result of the improved dispersion of the fumed silica particles. A visual comparison of the three products/systems indicates that the AERODISP® Fumed Silica dispersions also result in better clarity than powdered products. In this particular formulation, AERODISP® W 7520 performed slightly better than AERODISP® W 7330 N, most likely because of the lower specific surface area of AERODISP® W 7330 N.

Overall, the use of fumed silica dispersion such as AERODISP® W 7330 N or AERODISP® W 7520 can improve clarity without sacrificing physical properties.

The data above also demonstrate that AERODISP® products improve the mechanical properties for elongation.

Particle Size Distribution of AERODISP® W 7330 N



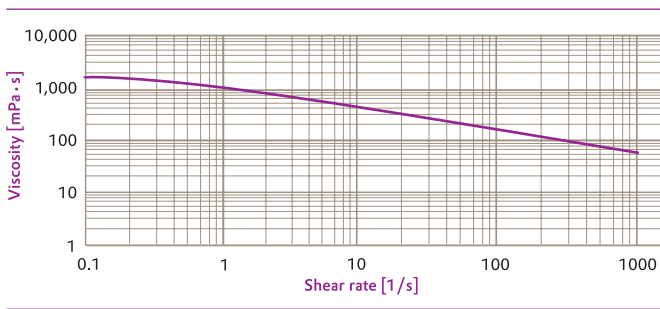
— q3 = Volume at the particular particle size
 — Q3 = Accumulative volume at the particular particle size

Conclusion:

„Overall, the inclusion of fumed silica dispersion such as AERODISP® W 7330 N can provide for a clearer film without sacrificing physical properties.“

The above data also demonstrates that the dispersed form provides better mechanical properties for elongation than the corresponding powder version. Additionally, an improvement in the cohesive properties of the sealant as well as tensile strength of the elastomeric polymer used for the sealant were noted when using AERODISP® W 7520, AERODISP® W 7330 N and AEROSIL® 200.

Viscosity Curve—AERODISP® W 7330 N



Physical properties of AERODISP® W 7330 N

Properties	Unit	Typical Value
SiO ₂ -Content	Wt. %	30 ± 1.0
Stabilizing Agent		Sodium Hydroxide
pH (DIN EN ISO 787/9)		9.5–10.5
Viscosity (DIN EN ISO 3219, 100 s ⁻¹ , 23 °C)	mPa · s	≤ 1000
Mean aggregate size (d ₋₅₀ value, volume)	µm	0.15
Density (20 °C)	g/cm ³	1.20

Appendix –Testing Procedures

Several ASTM International documents are referenced in this document. These are under copyright by ASTM and are available either as individual documents or in a collection of standards under the responsible committee. ASTM Committee D 14, Adhesives, publishes the referenced documents in Book 15.06. ASTM Committee C 24, Building Seals and Sealants, publishes the referenced documents in Book 04. 07.

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The Pressure Sensitive Tape Council (PSTC) publishes *Test Methods for Pressure Sensitive Tapes*. This is a collection of relevant test methods developed by the Council and some ASTM methods.

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