

A Guide to Silicone Dispersions

Strategies for processing and Troubleshooting

Application Note

“Dispersion” is a term used to describe silicone elastomer systems that are suspended or dissolved in a solvent carrier. They are complex solutions that contain silicone polymers of various molecular weights and reinforcing fillers. Silicone dispersions typically have a low viscosity which is beneficial for applications where a thin film coating is needed, and they can easily be used in dipping and spraying processes. NuSil uses a variety of solvents such as xylene, tert butyl acetate, heptane, hexane and naphtha for manufacturing silicone dispersions. The rheology of a silicone dispersion can range from water-like to thick and not self-leveling.

While dispersions allow certain silicone rubbers to be processed easily, they require a deeper understanding of their inherently complex structure and consequently their behavior during coating. This application note will summarize important properties and characteristics of dispersions, present guidelines for applying a dispersion and offer suggestions for troubleshooting.

Important Properties of Dispersions

Dispersions can vary based on the properties listed below. These properties define the characteristics of dispersions and their behavior during application.

- Cure mechanism- addition cure or moisture cure
- May be supplied as one or two part systems
- Polymer back bone structure/substituent groups: Polydimethylsiloxane, Dimethyl Diphenyl copolymer, Fluoro homo polymer or copolymer
- Molecular weight of the polymer can vary from very low (oil like) to high (clay like). This affects the dispersion viscosity and cured mechanical properties.
- Solvent Type- Some properties of common solvents are shown in Appendix A
- Viscosity and Rheology of dispersion- Important since most dispersions are “thixotropic” where the viscosity decreases with increase in shear and are non-Newtonian. This directly influences how the dispersion will coat the substrate.
- Solids content- Silicone to solvent ratio
- Fillers- Reinforcing silica, electrically and/or thermally conductive fillers, etc.

NuSil's silicone dispersions are summarized in Appendix B.

Dispersion Basics

Viscosity vs. Solids Content

- Viscosity of a dispersion will increase with increasing solids content
- Not a linear relationship
- It is important to compare viscosities at similar solids content

Shear Thinning Index (STI)

- Not equal to thixotropic index
- Can be influenced by the formulation, such as solvent used and/or type of silicone dispersed, especially the backbone constituents.
- Viscosity will change with shear rate change
- Shear Thinning index (STI) shows the viscosity change over time at same shear. The closer the STI is to "1", the more self leveling the dispersion will be.

$$STI = V1/V2$$

V1: Low rpm (shear) viscosity

V2: High rpm (shear) viscosity

- Depending on the application, low or high STI might be desired
 - High STI dispersions tend to give thicker coats
 - Low STI dispersions result in smoother coatings

Characterizing Dispersions

Rheology of the dispersions

A silicone dispersion is a viscoelastic material and in addition to its physical properties, its performance is significantly related to how it flows during the application process. Formulation, processing and application conditions are significant parameters that affect the rheological properties of a dispersion.

Dispersions are defined by both their viscosity and their solids content, which is a common parameter to describe how flowable the material is. The shear thinning index is derived from viscosity measurements and is also commonly used to describe a dispersion. For both properties (viscosity and shear thinning index) the solids content of the dispersion is important.

Measuring Viscosity

Viscosity can be measured by

- Rotational Viscometer. (Brookfield is a commonly used brand in the industry LV or RVT).
 - Unit = cPs
 - Spindle size and RPM are very important for comparing results
- Zahn cup
 - Measures the flow with gravity.
 - Unit = seconds
 - The higher the seconds, the higher the viscosity
 - Zahn cup sizes are very important
 - Difficult to correlate to Brookfield viscosities
- Controlled stress or strain rheometers
 - Allows users to study and understand complex viscoelastic structure of silicone dispersions
 - Measures viscoelastic properties at different strain, stress and temperature settings
 - Helps to predict the dispersion's performance by simulating the application

Processing Dispersions

Every stage in processing may be defined differently dependant on the application method. It is essential to know the details of these processing steps in order to choose the right dispersion to maximize the performance and processing efficiency.

Storage

Most dispersions are stored prior to application. It is important to note that NuSil recommends keeping the dispersion in its original container when possible, tightly sealed and stored below 40° C.

Contamination:

The dispersion should be protected from contaminants for both long term and short term storage. Covering or sealing the container can help to prevent contamination. Care should be taken to prevent solvent evaporation during long or short term storage.

Preparation

Most dispersions need additional processing prior to application, such as combining Part A and B. These steps can have a significant affect later in the coating performance and are outlined below.

Mixing or Blending

- Dispersions need to be mixed adequately to get a homogeneous blend. When possible the dispersion material should be mixed prior to use. Pre-mixing is recommended but is not required. For further information on mixing and de-airing, please reference NuSil's *Mixing and De-airing Addition Cure Silicones* Application Note.
- Mixer design/size/type, blade/propeller type, shear/RPM levels, speed of mixer, and heat created from the mixer are all important parameters in mixing the material and should be addressed in order to have an adequately mixed dispersion.
- It is important to ensure dedicated tools and clean pots are used to prevent contamination. Tools used to mix moisture cure dispersions can introduce poisons to platinum catalyzed addition cure dispersion. Please see NuSil's *Avoiding Inhibition When Working with Platinum Catalyzed Silicones* tear sheet for more information on inhibition.
- For 2 part, platinum catalyzed dispersions, mixing Part A into Part B (instead of Part B into Part A) is important especially when using a dispersion with high solids content. With lower solids content, the crosslinker and catalyst are far apart from each other and the pot life is generally longer. This eliminates any possibility of high catalyst content in Part A reacting with a small amount of crosslinker in Part B when it is initially introduced.
- Blending- For some automated systems it may not be possible to have only one lot in the system. Generally, when the reservoir level is low, it is filled with the lot next in line. The dispersion can be a blend of two lots, in different ratios. The blends can be added during the transitions or at any given time, depending on the process details. This could affect cure time and other processing parameters and may prevent an accurate evaluation of a lot if problems occur. If possible, purging the system with a new lot of material prior to the run is recommended.

De-airing

De-airing is a vital step in eliminating bubbles in the material. Below is a list of possible reasons why de-airing may not work effectively.

- De-airing instruments and accessories:
 1. Vacuum chamber- Size, design and placement of the vacuum outlet may be incorrect causing decreased pressure for the specified de-airing time
 2. Pump- Capacity and ultimate vacuum rating of the pump may not be sufficient
 3. Plumbing- Leaks can cause vacuum loss
- Ultimate vacuum- Vacuum should be checked when the chamber is empty to ensure maximum vacuum can be reached.
- De-airing time: If de-airing time is too short it may leave bubbles in the dispersion. If it is de-aired for too long, the solids content can increase.
- Centrifuging just before application might change the dispersion's rheology so the time should be monitored and to ensure viscosity stays in the needed range.

For additional questions about de-airing, please reference NuSil's *Mixing and De-airing Addition Cure Silicones* Application Note.

Waiting period prior to application

Some processes will require a waiting period before the material is used for its intended application. During this period the following parameters may influence the dispersion's performance.

- Time:
 - Too long- Solvent may evaporate changing the dispersion's rheology and causing increased solids and therefore higher viscosity. This tends to produce thicker layers which may not be desirable.

Too short- If high shear was used to mix the dispersion, it may not have sufficient time to return to its rest properties due to shear thinning. This results in thinner layers.

Coating

Dispersions are used for coating objects with a thin layer of silicone where there is typically more than one coat applied. There are many different ways to apply dispersions as coatings. Some of them are:

- Dipping- Manual or Automated
- Slush Molding- The inside of a mold cavity is coated
- Knife Coating
- Spraying
- Casting

Coating Basics

Silicone dispersions make tough coatings once cured. In most cases, more than one layer of dispersion is needed to achieve the best results and the toughest coating. This involves a delicate balance between curing and allowing the solvent to evaporate at a rate which does not leave surface defects. The quality of the coating will depend significantly on the coating process parameters provided below.

- Number of the coats- The more coats applied, the thicker the coating
- Device geometry- Large surfaces at the same direction as the applied force will result in thin layers and surfaces perpendicular to the applied force will contribute to thicker layers.

- Size of the device- Larger sizes tend to have thicker layers due to the dispersion volume they can hold if the container only fits the part.
- Parameters of coating sequence- Speed, direction of the device and time between coats
- Environmental conditions- Temperature, humidity, air flow speed and placement of diffusers
- Coating techniques:
 - Manual dipping: Most flaws are created or can be avoided by dipping techniques.
 - Automated dipping: Automated dipping processes can use a wider range of dispersions, however some details of the process can cause defects that otherwise may not be seen with manual dipping. The product should be carefully evaluated for an automated process. A uniquely formulated product might be needed.
 - Spray processes may reach a very high shear which can not be seen during manual dipping. The dispersion rheology and structure needs to be evaluated for spray conditions resulting maximum performance. A new formulation may be needed for a better performance.

Most of the parameters above will have an affect on how and when the material flows.

Solvent Evaporation (also known as Devolatilization or Devol)

One of the most important processing steps of silicone dispersion is the devolatilization step. Each application may use a different formulation based on the required chemistry of the application (fuel resistance, permeability, etc.)

- The quality and thickness of the coating can be manipulated by:
 - Length of Devol process
 - Time between coats
 - Temperature
 - Air flow

Crosslinking during Devolatilization

Crosslinking during devolatilization depends on the length of time, temperature and number of the devol steps. If it does not happen during devolatilization, it can produce thinner layers.

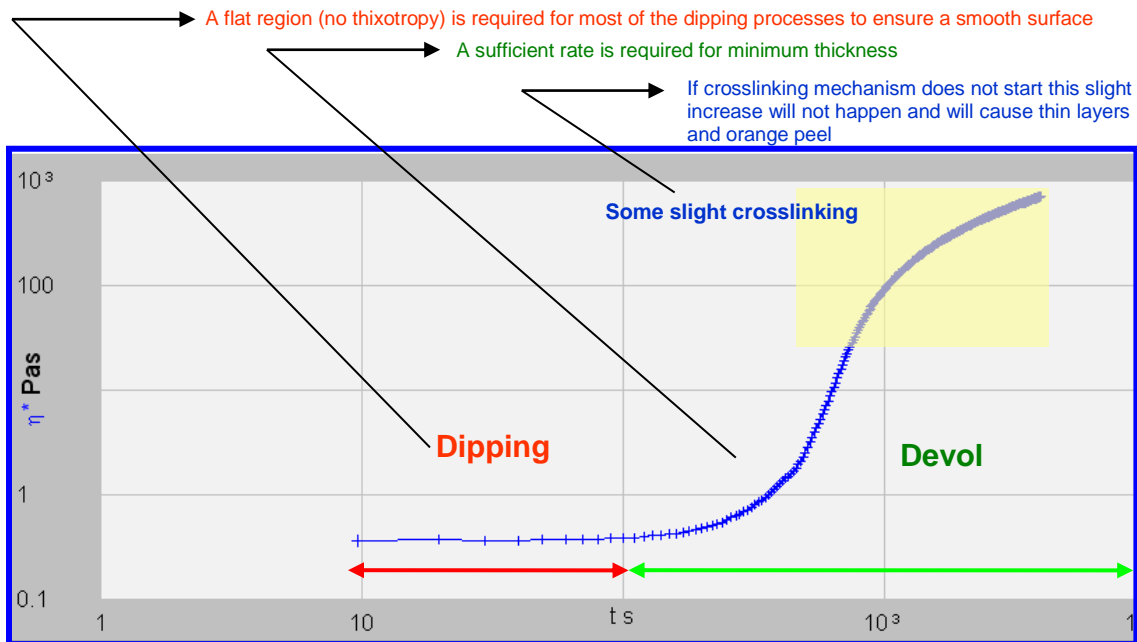


Figure 1. Schematic of rheology over time with an addition cure dispersion applied during dipping and a Devol at constant temperature.

Cure

- The cure schedule will vary depending on the application and solids content
- NuSil establishes a ramp cure, also known as “step cure” to cure dispersions. The cure profile will typically need to be adjusted to give the best results based on the curing environment and device configuration.
- The elastomer might have more than one cure schedule depending on assembly.
- Deviations in cure schedules (temperature and time) may cause different elastomeric properties therefore, controlling the process once it has been established is recommended.
- Shrinkage – can be caused by evaporation of solvents and/or cure chemistry (i.e. leaving group from a moisture cure reaction).

Additional Processing (may or may not be necessary for every application)

Additional processing can include sterilization, removal from the mold or mandrel, adhering additional components, marking, etc. NuSil recommends customers test the device to ensure it still meets the mechanical and physical properties required if it undergoes the following additional strains that may induce some defects. Strains may include:

- Thermal- Extra heating or higher temperatures
- Physical- Pulling, poking, vacuum
- Chemical- Washing with solvents

Sterilizing Dispersions (may or may not be necessary for every application)

- Thermal- Dry heat or Steam Autoclave
 - Very little effect on silicone elastomers
 - May have a slight effect on elastomeric properties depending on very high temperatures or length

- Some remaining solvent can come out in closed package
- Chemical- ETO, Peroxide
 - Usually no effect is observed
 - Any defect that might happen would depend on the dose and time
- Radiation- Gamma and E-Beam
 - Minor changes in physical properties and color depending on the dose and time

Causes of Most Common Defects

Defects are caused by two main reasons:

- Dispersion related defects
- Process related defects
- There might also be instances where both cases exist
- May occur for both addition and moisture cure dispersions

Thin layers

- Directly related to the slope and size of the device coated
- Can be eliminated by increasing
 - viscosity and/or solids content
 - number of coatings
 - devol temperature & time
 - Evaporation of the solvent by changing air flow, temperature and moisture content (when using moisture) in the devol environment
- Spray Equipment
 - Adjust Atomizer
 - Pot pressure is too low
 - Pass time/spray speed is too fast

Thick layers

- Directly related to the size of the device coated
- The location of the thick layer is important. It can be fixed by decreasing
 - viscosity and/or solids content
 - the number of the coats
 - devol time and temperature
- Dispersions with high shear thinning indices tend to result in increased thicknesses
- This defect might be accompanied with ripple, crown, ridge, large cutting hole size and bubbles
- Spray Equipment
 - Adjust Atomizer
 - Pot pressure is too high
 - Pass time/spray speed is too slow

Orange Peel

By itself

- Both dispersion and process related
 - Too much crosslinking and drying might be happening on the surface of the material while below the surface it is not crosslinking and drying at same rate
 - Too much air flow, air is too dry and high temperatures
 - Too much applied per layer

Accompanied by thin layers

- The catalyst may not be active at lower temperatures, or it may not be the right amount due to off ratio during mixing.

Bubbles

Mostly process related

- Caused by the dipping/coating technique
- Not dipping onto a bubble is important
- Can be avoided by careful evaluation of coating process
- Right vacuum is needed to eliminate the bubbles
- The deairing instruments and the system should be evaluated for ultimate vacuum achieved, leaks and capacity

It could be also dispersion related due to viscosity and thixotropy of the dispersion. It can be accompanied by thick layers.

- Decreasing viscosity helps to eliminate bubbles in the dispersion.
- Dispersions with higher shear thinning indices tend to be more sensitive to the de-airing process and trap air.

Ripple, crown, ridge, thick base

- The location of the defect is important to evaluate the root cause
- Thick layer remedies can be applied
- Large cutting hole size is caused by cutting a larger hole to eliminate material being too thick at the base.
- Different cure rates applied to each layer

Slides / Separations

- Very rarely seen
- Dispersion may not be mixed well

Spray bubbles

- Mostly process related
- If it is following a barrier layer, the barrier layer might be too dry
- Dipping directly onto a bubble also causes spray bubbles
- Material needs to be de-aired well
- Dispersion should be particle free

Drips / Sagging

- Could be process and material related
- Low solids content
- Material is not suitable for the coating conditions
- Too much material is applied per layer/pass

Pull Marks / Stretch Marks

- Too much force is applied
- May not be curing properly. Duration of cure, temperature and moisture may not be at right levels
- Material has a high tensile set

Surface Marks

- The device is left on a textured surface during cure
- Ensure the elastomer is cured properly (Time, temperature, moisture).
- Ensure the surface and the shape of the mold is right for the shell

Tears

If they appeared during un-casting

- Elastomer may not be cured properly. Duration of cure, temperature and moisture may not be at correct levels
- Excessive force might have been applied for un-casting

If coating is not easily peeled

- Device surface might have been contaminated
- Crosslinking mechanism may not be working properly

Mud Cracking

- Moisture content
- Solvent concentration in the environment
- Temperature
- Air flow
- Too much material is applied per layer/pass

This application note is to provide general guidelines and is for reference only. For specific questions on products or applications please contact NuSil Technology.

Appendix A

Common Solvents – Can be purchased separately by NuSil Technology for further dilution. If you need assistance with selecting the appropriate grade or purity, please contact NuSil.

Table 1. Solvent Evaporation Rates

Solvent Name	NuSil Product Number	Boiling Point °C / °F @ 1 Atm.	Evaporation Rate	Polar	Flash Point °C/ °F
Xylenes	R1-1001	137/278.6	0.86	Slightly	27/80.6
Tert Butyl Acetate**	R2-1001	98/208.4	2.8	Yes	(17-22)/(62-72)
Naphtha	R-1001	85/185	3.5	No	10/50
Hexane	-	(65-75)/(149-159)	9.0	No	23/73.4
Acetone	-	56/132.8	14.4	Yes	-20/-4
Heptanes	-	98.4/209.1	*	No	-4/24.8.4

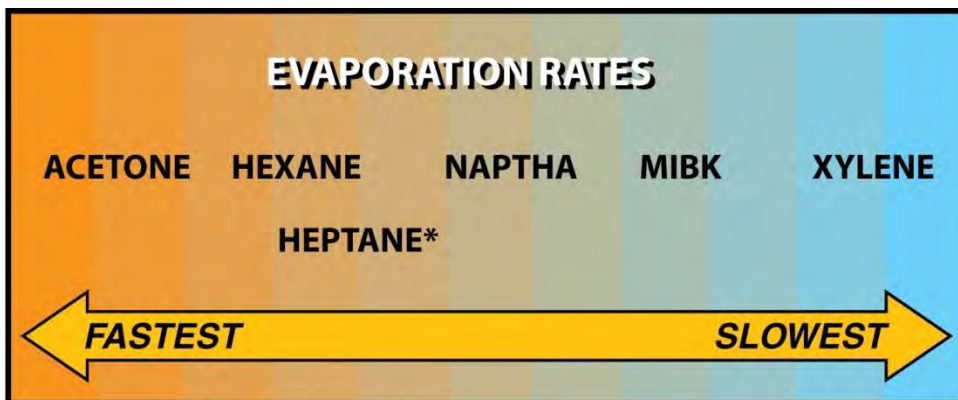
*Evaporation rates for these solvents are undefined.

**Non VOC

Vapor Density: The mass of a unit volume of a vapor.

Vapor Pressure: For a liquid or solid, the pressure of the vapor in equilibrium with the liquid or solid

Evaporation Rates: The scale below is based on evaporation rates as stated in Table 1 and is for comparison purposes only.



* Evaporation rates for these solvents are undefined

Figure 1. Visual representation of evaporation rates of common solvents used for silicone dispersions.

Appendix B

Table 1. Listing of NuSil Technology's dispersion product offerings.

Product Name	Mix Ratio	Catalyst	Solvent
MED-2214	1 Part	Platinum	Xylene
MED-4162	1 Part	Non-Curing	Xylene
MED-6400	2 Part	Platinum	Xylene
MED-6600	2 Part	Platinum	Xylene
MED-6605	1 Part	Acetoxy	Xylene
MED-6607	1 Part	Tin	VM& M Naphtha
MED-6608	1 Part	Tin	Xylene
MED-6613-2	2 Part	Platinum	Xylene
MED-6615	2 Part	Platinum	Heptane
MED-6640	2 Part	Platinum	Xylene
MED-6641	2 Part	Platinum	Xylene
MED-6655	1 Part	Acetoxy	Tert Butyl Acetate
MED-6670	2 Part	Platinum	Xylene
R-1009	1 Part	Tin	VM& M Naphtha
R3-1075	1 Part	Tin	Xylene
R-1082	1 Part	Acetoxy	Xylene
R-2180	2 Part	Platinum	Xylene
R-2180-2	2 Part	Platinum	Xylene
R-2182	2 Part	Platinum	Xylene
R-3930	1 Part	Acetoxy	Tert Butyl Acetate
R-3930-1	1 Part	Acetoxy	Tert Butyl Acetate
R-3975	1 Part	Acetoxy	Tert Butyl Acetate

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