PAINTS, INKS AND COATINGS

Silicone resins and intermediates

Selection guide

DOWSIL™ technologies by Dow

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Discover innovative technology

The use of silicon-based technologies in the coatings market has evolved over the decades, allowing formulators to create differentiated, high-performance protective and decorative coatings.

Silicone resins and resin intermediates have found utility in heat-resistant paint and industrial, marine and protective coatings (1950s); coil coatings (1970s); and, most recently, hybrid resin systems (1990s), creating interpenetrating silicone-organic resins with attributes of both chemistries for premium topcoat finishes.

Paint and coating formulations incorporating DOWSIL™ silicone resins and resin intermediates exhibit improved resistance to:

- Temperature
- Moisture
- Corrosion
- Electrical discharge
- Weathering

With excellent compatibility with many organic resins, silicone resins can provide a wide range of film and performance properties for many high-value applications.

Applications

High temperature

- Barbecue Grills
- Woodstoves
- Fireplace Inserts
- Automotive Mufflers
- Heat Exchangers
- Lighting Fixtures
- Cookware
- Ceramic Composites
- Bakeware

Weathering

- Offshore Rigs
- Wind Turbines
- Bridges
- Tank Farms
- Stadiums
- Ships
- Refineries
- Chemical Processing
- Amusement Park Rides

The chemistry of silicone resins

Silicone resins are polymers comprised of a siloxane (silicon–oxygen) lattice with at least some portion comprised of the silicate ($SiO_{4/2}$) or silsesquioxane ($R\text{-}SiO_{3/2}$) structures, where R represents various alkyl or aryl organic groups (most commonly methyl or phenyl). In comparison to organic resins (with their carbon-carbon backbone), silicone resins exhibit greater resistance to thermal and radiation degradation. The durability of silicone resins is attributed to the bond strength between silicon and oxygen (108 vs. 82.6 kcal/mole for the carbon-carbon bond), transparency to visible and ultraviolet light, and the inherent partially oxidized structure. Evidence supporting this stability claim can be found beneath our feet. The silicon-oxygen bond is the most abundant chemical bond on earth.

With the addition of organic substituents (see "Degree of substitution" in tables 2-4), the siloxane polymer becomes more linear, modifying the physical properties (e.g., flexibility) and performance. The attachment of phenyl to the silicone backbone contributes organic compatibility, toughness and longer thermal stability at moderate temperatures (250°C). In comparison, methyl groups provide fast cure, thermal shock resistance and lower weight loss at extreme temperatures (see "Silicon dioxide content" in tables 2-4).

Silicone resins can be produced by hydrolyzing mixtures of chlorosilanes or alkoxy silanes to form highly reactive silanol groups:

$$\mathbf{RSiCl_3 + 3H_2O \longrightarrow RSi(OH)_3 + 3HCl}$$

$$\mathbf{RSi(OR')_3 + 3H_2O \longrightarrow RSi(OH)_3 + 3R'OH}$$

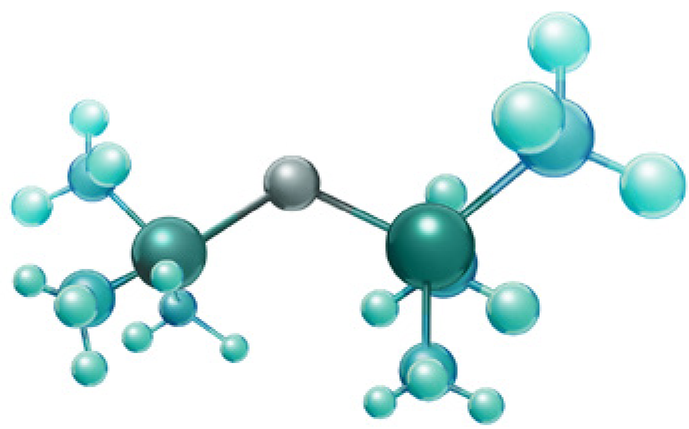
which initially condense to form oligomeric siloxane structures:

$$\mathbf{2\ RSi(OH)_3 \longrightarrow RSi(OH)_2 - O - SiR(OH)_2 + H_2O}$$

Further condensation occurs to form three-dimensional siloxane lattices. Driving the condensation by applying heat and catalysis increases molecular weight and improves physical properties (see DOWSIL™ RSN-0805 Resin, DOWSIL™ RSN-0806 Resin, and DOWSIL™ RSN-0808 Resin) but increases polymer viscosity and solvent-loading requirements.

Similarly, where application performance requires, the silanol and alkoxy functionality can be reacted with hydroxyl groups on organic resins (e.g., polyesters) to form silicone-organic hybrid resins with performance improvements proportionate to the level of siloxane modification (see table 1). Cold-blends of silicone and organic resins require lower additions of application solvent but rely on hotter and longer thermal curing schedules to drive copolymerization and complete cure.

Along with selecting the appropriate silicone resin, the choice of other formulation components plays a critical role in coating performance.



Selecting a resin binder system

The first step in creating a coating prototype is to define the application performance demands and the potential resin binder system. Thermal, chemical and radiation exposure along with required cure schedule and needed physical properties all influence the choice of resin binder.

While silicone resin will contribute to the paint's thermal, chemical and UV radiation resistance, some performance attributes and physical properties will benefit from combinations of silicone and organic binders.

- Hardness: Phenolics and melamines
- Air-dry: Acrylics
- Corrosion resistance: Epoxies
- Toughness: Alkyds

The level of silicone utilization in a paint formulation is dictated by the severity of the application performance requirements and can range from a minimum of 15% to as high as 100% of the resin binder system (see table 1).

Table 1: Resin system selection

Performance temperature range[1]	Resin type	% Silicone	Pigment
121-204°C (250- 400°F)	Silicone-modified organic	15-50	All pigments
204-316°C (400-600°F)	Silicone-modified organic	15-50	Leafing aluminum
	Organic-modified silicone	51-90	All pigments
316-427°C (600-800°F)	Organic-modified silicone	51-90	Black iron oxide, leafing aluminum
	Silicone	100	All pigments
427-538°C (800-1,000°F)	Silicone	100	Black iron oxide, leafing aluminum
538-760°C (1,000-1,400°F)	Silicone	100	Ceramic

[1]1,000 hours minimum

Choosing a silicone resin

Dow offers a diverse line of silicone resins and resin intermediates. Silicone resins are, themselves, good film-formers. Whereas resin intermediates are intended for blending with other silicone, or organic resins to create a film with the required balance of performance properties. Solvent-based, solventless liquid and solid flake options are available, allowing formulators to meet a wide range of performance and regulatory requirements and to achieve the best balance of performance, compliance and economy.

Choosing which DOWSIL™ product to use is influenced primarily by two factors: organic compatibility and desired film hardness.

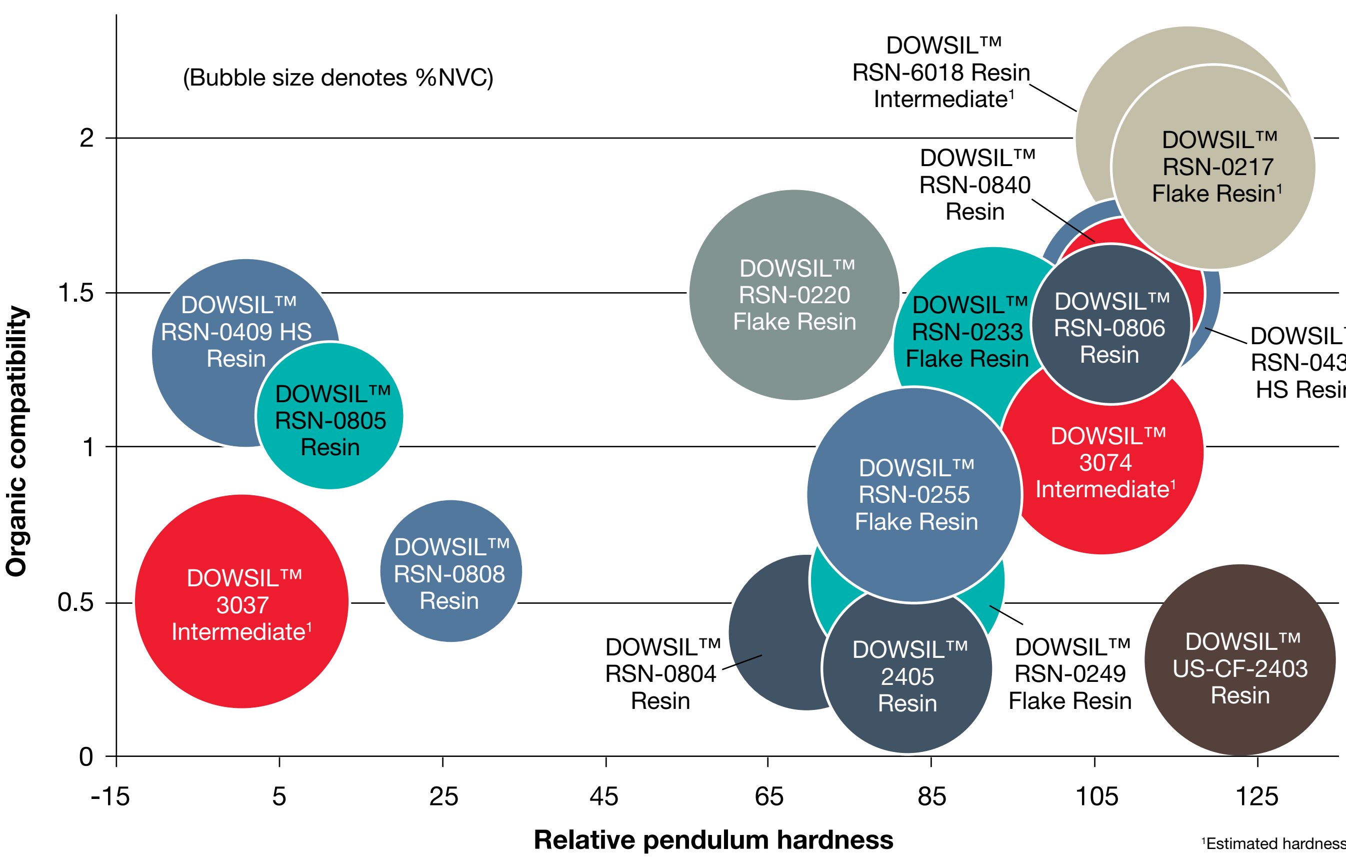
Softer, more flexible resins are recommended for coating formulations required to withstand the thermal expansion and contraction associated with heated metal. Rigid resins provide excellent hot hardness for exposed painted surfaces prone to nicks and scrapes.

A third consideration is the level of residual silicon dioxide produced during the pyrolysis of the resins. As silicone resins oxidize, the remaining silicon dioxide ash reacts with pigments and fillers to create the metalo-silica composite, which provides long-term thermal stability – but this attribute must be balanced with other film properties, particularly flexibility.

Figures 1 and 2 provide the means by which to select a DOWSIL™ resin for your coating prototype.

It is possible that a single resin may not meet the specific needs of your application. In general, DOWSIL™ resins have good intercompatibility and can be blended together at any ratio to achieve a balance of properties. However, resins with a phenyl:methyl ratio below 1:1 tend to be less compatible with organic resin systems. Laboratory testing of resin mixtures should be conducted prior to commercial use.

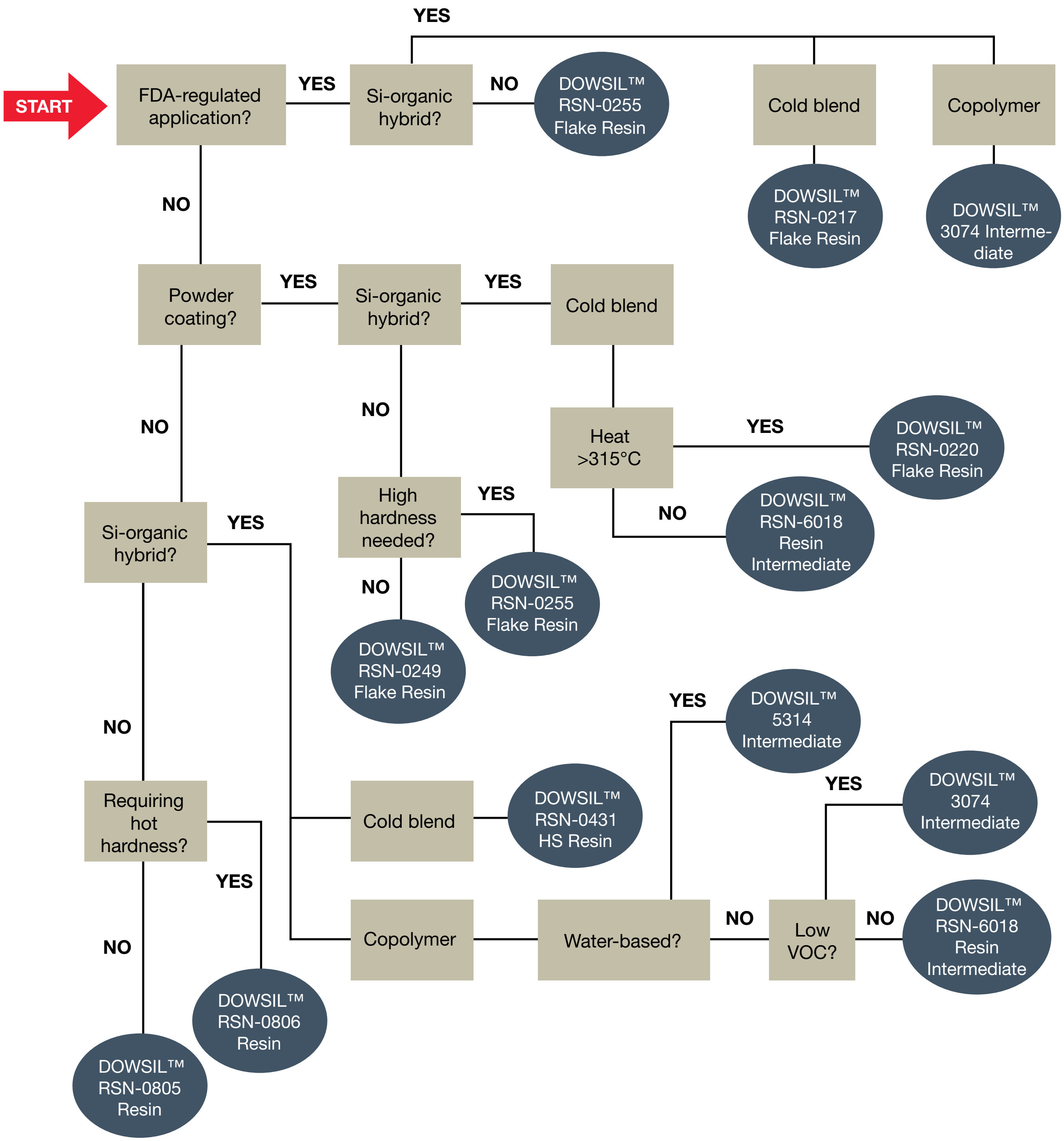
Figure 1: Resin property comparison



[1]Estimated hardness

Figure 2: Decision tree for selecting a DOWSIL™ Resin

Is the intended coating…



Solvent-based resins from Dow

Dow delivers silicone resin solutions that can be used alone, or in combination with organic resins or other silicone resins. They vary in resin content, organic compatibility and molecular weight, allowing formulators to design coatings to meet specific application requirements:

- High-temperature coatings where low VOC content is required
- Maintenance paints for improved UV durability
- Colored baking enamels for wood-burning stoves, space heaters, etc.
- As an additive to improve the flow-out and initial gloss of epoxy coatings

Table 2: Characteristics and properties of solvent-based resins from Dow

	DOWSIL™ RSN-0409 HS Resin	DOWSIL™ RSN-0431 HS Resin	DOWSIL™ RSN-0804 Resin	DOWSIL™ RSN-0805 Resin	DOWSIL™ RSN-0806 Resin	DOWSIL™ RSN-0808 Resin	DOWSIL™ RSN-0840 Resin
Characteristics							
Functionality	Silanol	Silanol	Silanol	Silanol	Silanol	Silanol	Silanol
Silanol content[1]	3	3	3	1	1	1	3
Silicon dioxide content[1]	48	52	64	48	52	57	52
Degree of substitution[2]	1.6	1.4	1.3	1.6	1.4	1.5	1.4
Phenyl:Methyl ratio	1.1:1	1.2:1	0.4:1	1.1:1	1.2:1	0.6:1	1.2:1
Molecular weight[3] (1,000)	2-7	2-7	2-7	200-300	200-300	200-300	2-7
Typical properties							
Resin solids, % by weight[4]	80	80	60	50	50	50	60
Resin solids, % by volume	74	74	51	42	41	42	51
Solvent	Xylene	Toluene	Toluene	Xylene	Toluene/ xylene	Xylene	Toluene
Viscosity, centipoise	200	800	30	100-190	150	125	20
Specific gravity	1.12	1.14	1.07	1.01	1.02	1.01	1.06
VOC[5], g/L (lb/gal)	228 (1.9)	228 (1.9)	431 (3.6)	503 (4.2)	515 (4.3)	503 (4.2)	431 (3.6)
Flash point – Closed cup, °C (°F)	27 (81)	7 (45)	7 (45)	27 (81)	7 (45)	27 (81)	7 (45)

[1]Percent by weight
[2]Organic groups attached per silicon atom
[3]Weight average
[4]0.5 g/1 hr/110°C (230°F)
[5]Volatile organic content, EPA Reference Method 24

Flake Resins from Dow

DOWSIL™ flake resins deliver silicone technology concentrated in dry, pourable flakes, which can either be solvated or used as neat polymers in powder coatings or composites or combined with "softer" solvated silicone resins to improve hardness and reduce VOCs. The flakes also can be cold-blended or copolymerized with organic polymers to improve thermal and weathering resistance.

- High-temperature powder coatings for barbecue grills
- Mica board composites
- Ceramic firings
- Silicone-alkyd copolymers for protective and marine paint
- Silicone-polyester copolymers for coil coatings
- DOWSIL™ RSN-0217 Flake Resin, DOWSIL™ RSN-0233 Flake Resin and DOWSIL™ RSN-0255 Flake Resin are suitable for applications regulated by FDA 21 CFR 175.300

Table 3: Characteristics and properties of flake resins from Dow

	DOWSIL™ RSN-0217 Flake Resin	DOWSIL™ RSN-0220 Flake Resin	DOWSIL™ RSN-0233 Flake Resin	DOWSIL™ RSN-0249 Flake Resin	DOWSIL™ RSN-0255 Flake Resin	DOWSIL™ RSN-6018 Resin Intermediate
Characteristics						
Functionality	Silanol	Silanol	Silanol	Silanol	Silanol	Silanol
Silanol content[1]	6	6	5	5	5	6
Silicon dioxide content[1]	47	51	55	63	62	50
Degree of substitution[2]	1.0	1.2	1.15	1.15	1.05	1.0
Phenyl:Methyl ratio	All phenyl	2.0:1	1.3:1	0.6:1	0.84:1	2.7:1[3]
Molecular weight[4] (1,000)	1.5-2.5	2-4	2-4	2-4	2.5-4.5	1.5-2.5
Typical properties						
Resin solids, % by weight[5]	99	99	99	99	99	99
Tg (°C)	65	49	47	41	56	48
Specific gravity	1.34	1.33	1.32	1.3	1.22	1.31
Flash point – Closed cup, °C (°F)	138 (280)	138 (280)	138 (280)	138 (280)	138 (280)	138 (280)

[1]Percent by weight
[2]Organic groups attached per silicon atom
[3]Phenyl:Propyl Ratio
[4]Weight average
[5]0.5 g/1 hr/110°C (230°F)

Alkoxy resins and intermediates from Dow

The unique reactivity of the silylalkoxy group provides this class of materials with a broad array of utility in the coatings market.

- "Polysiloxane" epoxy and acrylate hybrid topcoats
- Reacted with unsaturated polyesters, oil-free alkyds and other hydroxyl-bearing organic resins for flexible, weather-resistant coil coatings
- DOWSIL™ 5314 Intermediate is used for modification of acrylic and other alkaline pH resin emulsions
- Silicone-polyester copolymers made with DOWSIL™ 3074 Intermediate are suitable for applications regulated by FDA 21 CFR 175.300
- Blended with other silicone resins to reduce VOCs
- When catalyzed with titanates, DOWSIL™ US-CF-2403 Resin can be formulated into ambient tack-free coatings

Table 4: Characteristics and properties of alkoxy resins and intermediates from Dow

	DOWSIL™ US-CF-2403 Resin	DOWSIL™ 2405 Resin	DOWSIL™ 3037 Intermediate	DOWSIL™ 3074 Intermediate	DOWSIL™ 5314 Intermediate
Characteristics					
Functionality	Methoxy	Methoxy	Methoxy	Methoxy	Methoxy
Methoxy content[1]	36	28	15-18	15-18	35
Silicon dioxide content[1]	89	78	65	54	46
Degree of substitution[2]	1	1.05	1.7	1.3	1.3
Phenyl:Methyl ratio	All Methyl	All Methyl	0.25:1	1.0:1	3.3:1
Molecular weight[3] (1,000)	0.7	4	0.8-1.3	1-1.5	Monomer Blend
Typical properties					
Resin solids, % by weight[4]	64	72	82-85	82-85	65
Viscosity, centipoise	25	200	14	120	1.87
Specific gravity	1.15	1.11	1.07	1.16	1.04
Flash point – Closed cup, °C (°F)	39 (102)	39 (102)	106 (223)	120 (248)	28 (83)
Suitable for FDA 21 CFR 175.300	No	No	No	Yes	No

[1]Percent by weight
[2]Organic groups attached per silicon atom
[3]Weight average
[4]Cured resin solids, delivered solventless

Other formulation components

Catalysts

Silanol-functional resins will heat-cure without the addition of catalyst, but the addition of metallic driers (e.g., zinc, iron or cobalt octoate) will accelerate the rate of cure. Typical catalyst level is 0.1 to 0.2% metal on resin solids.

DOWSIL™ RSN-0805 Resin, DOWSIL™ RSN-0806 Resin and DOWSIL™ RSN-0808 Resin are supplied pre-catalyzed.

Silylalkoxy resins require the addition of a hydrolysis or condensation catalyst to promote full-cure properties. Typical use level is 0.5-3% on resin solids, depending on the resin, desired cure profile, and final performance requirements.

Leaching of metals (e.g., iron or lead) from unlined storage containers can catalyze the condensation of silicone resins and cause a viscosity increase or gelation.

Application

Film thickness varies depending upon application and specific formulation, but typical high temperature paints are applied at film thicknesses ranging from three to four mils (75 to 100 microns). Thicker films can result in delamination.

Curing schedules

Coatings formulated with silanol-functional silicone resins typically require thermal curing to achieve optimum film properties, but curing cycles vary depending upon the level of silicone content and the cure chemistry of other primary components. A typical cure for a 100% silicone resin system is 30 minutes at 232°C (450°F) or 60 minutes at 204°C (400°F). For silicone-organic blends in which silicone is not the primary component, follow the cure recommendation for the primary resin.

Solvents and thinners

The resins described in this selection guide can be solvated with aromatic hydrocarbons (e.g., toluene and xylene), most ketones, esters, acetates and chlorinated solvents.

Aliphatic hydrocarbons (e.g., VM&P Naphtha and mineral spirits) are reasonable diluents but should be combined with stronger solvents.

Glycol ethers and alcohols (e.g., butanol), at low levels (<5%), improve resin stability.

Pigments and fillers

Traditional pigments used with organic binder systems can be employed with silicone resins for those applications exposed to low or moderate heat (121 to 204°C [250 to 400°F]). For higher temperatures, only heat-stable inorganic pigments should be utilized. Consideration also should be given to weather and chemical exposure. Leafing aluminum pastes and metal oxides, particularly iron and titanium, are useful. Hydroxyl reactivity on the pigment surface reacts with the silicone resin during curing and pyrolysis to form metalo-silicone composites. Typical pigment-to-binder ratios range from 0.6 to 1.0.

Unreactive pigments (carbon black) and fillers (calcium carbonate) should be used sparingly (<10%), as these materials do not integrate into the composite structure and will detract from long-term performance.

Reactive (hydroxyl-bearing) reinforcing fillers (e.g., silica, mica or wollastonite [2 to 20 weight % loading]) can improve the physical properties and long-term durability of a coating.

Product information and technical support

Our website, **www.dow.com**, gives you immediate access to:

- Product samples
- Product literature and technical data sheets
- Technical articles
- Customer and technical service
- The name of a Dow distributor near you

More than materials … solutions

Available worldwide, the products listed in this guide meet the majority of global industry requirements. However, they represent only a portion of Dow's total resin technology offering. Our extended product line includes options designed especially to meet the needs of your local market. Contact Dow for tailored recommendation.

Limitations

These products are neither tested nor represented as suitable for medical or pharmaceutical uses.

Your global connection

At home or abroad – wherever your business takes you– you will find the product supply, customer service and technical support you need to succeed available locally from Dow.

Whether you are facing a challenge that could benefit from Dow's international business and market experience or you need a reliable, local source of supply for innovative paints, inks and coatings solutions, contact your Dow representative. Product samples, technical information and assistance also are available online at **dow.com**.

Important information on storage, handling and flammability

Storage and shelf life

DOWSIL™ silicone resins should be stored at room temperature in sealed containers, away from heat and open flame. DOWSIL™ solid flake products should be stored below 22°C (72°F).

Refer to individual products' technical data sheets or contact Dow for the shelf life (from date of manufacture) of the DOWSIL™ resins and intermediates discussed in this brochure.

Handling precautions

Product safety information required for safe use is not included. Before handling, read product and safety data sheets and container labels for safe use, physical and health hazard information. The material safety data sheet is available on the Consumer Solutions website at www.dow.com. You also can obtain a copy from your local Dow sales representative or distributor.

When working with DOWSIL™ silicone resins formulated with flammable solvents, the following safety precautions should be taken:

- Keep away from heat and open flame
- Use only with adequate ventilation
- Avoid prolonged breathing of vapor
- Avoid prolonged or repeated skin contact
- Avoid eye contact

DOWSIL™ solid flake resins are electrically nonconductive and, like plastic in particle form, can generate static charges during transfer operations. For this reason, proper precautions should be taken to safely dissipate any charges possibly generated, particularly when solvents or solvent vapors are present. These two important cautions are detailed as follows:

1. The flake itself will generate an electrical potential, and the user should maintain adequate safeguards to properly handle it. The vessel into which the flake is being poured should be grounded along with the platform on which the operator stands.
2. Avoid the presence of ignitable materials during the transfer operation. If possible, have an inert atmosphere in the kettle and keep the solvent vapor content of the surrounding area at safe levels by providing adequate building area ventilation.

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