

DOW CORNING® Z-6032 Silane

FEATURES

- Improved adhesion
- Good resin wet-out
- Increased wet and dry composite tensile strength

BENEFITS

- Organic and inorganic reactivity

COMPOSITION

- Cationic styrlamine functional silane
- 40% silane in methanol

Coupling agent to improve adhesion of organic resins to inorganic surfaces.

APPLICATIONS

- As a coupling agent, DOW CORNING Z-6032 Silane can be used either as an additive to a polymer or as a pre-treatment on inorganic surfaces.
- This product's special properties include organic and inorganic reactivity, improves chemical bonding, good resin wet-out, increases flexural and tensile strength.

TYPICAL PROPERTIES

Specification writers: These values are not intended for use in preparing specifications. Please contact your local Dow Corning sales representative prior to writing specifications on this product.

| CTM* | Parameter | Unit | Value |
|-------|---------------------------------|------|---|
| | Active ingredients | % | 40 |
| 0176 | Appearance | base | Greenish-yellow changing to Reddish-Amber with time |
| 0004 | Viscosity at 25°C (77°F) | cs | 2.0 |
| 0001A | Specific gravity at 25°C (77°F) | | 0.90 |
| 0022 | Refractive index at 25°C (77°F) | | 1.395 |
| 0021A | Flash point - closed cup | °C | 13 |
| | | °F | 55 |
| | Solubility | | Self emulsifying in water, soluble in alcohols |

* CTM: Corporate Test Method, copies of CTMs are available on request.

DESCRIPTION

DOW CORNING Z-6032 contains a vinylbenzyl and amine organic and a trimethoxysilyl inorganic group. The product is supplied in methanol.

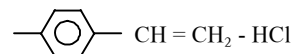
Possessing both organic and inorganic reactivity, DOW CORNING Z-6032 Silane can react with organic polymers and inorganic mineral surfaces such as glass. As a coupling agent, it can be used as either an additive to a polymer or as a pretreatment on organic surfaces.

DOW CORNING Z-6032 Silane is designated as the reaction product of vinylbenzyl chloride and ethylene diaminopropyltrimethoxysilane.

Figure 1: General chemical formula for DOW CORNING Z-6032 Silane.



where R is either hydrogen or



This vinylbenzylamine functional silane is one of a series of DOW CORNING organofunctional silane chemicals.

Other reactive silanes include the amines (DOW CORNING® Z-6020 and DOW CORNING® Z-6026

Silanes), methacrylate (DOW CORNING® Z-6030 Silane), epoxy (DOW CORNING® Z-6040 Silane), vinyls (DOW CORNING® Z-6075 and DOW CORNING® Q9-6300 Silanes) and chloroalkyl (DOW CORNING® Z-6070 Silane). Other experimental silanes may also be available for testing purposes.

HOW TO USE

DOW CORNING Z-6032 is used as an additive to polymers or as a pre-treatment on inorganic surfaces to improve adhesion of organic resins to inorganic surfaces.

DOW CORNING Z-6032 can be applied to inorganic surfaces such as fiberglass from dilute aqueous dispersions of 0.1 to 1.0% active silane content by weight. Most silicious particulate minerals are treated directly by first diluting one part of the silane with four parts of an ether alcohol solvent, such as Dowanol® PM, and blending in a high shear mixer.

(Dowanol® is a registered trademark of the Dow Chemical Company).

The total concentration of silane should be varied according to the surface area of the inorganic substrate. For example, fillers with high surface areas require more silane than those with relatively low surface areas. Typical concentrations range from 0.1 to 1.0% active ingredients based on the weight of the inorganic material.

After applying the silane, the mineral or inorganic material can be dried briefly at 100 to 120°C (212 to 250°F). This drying promotes silanol condensation of the coupling agent with the inorganic surface to give a strong bond between those two materials.

If silane treatment of the inorganic surface is not feasible or requires costly processing, DOW CORNING Z-6032 can be used as a resin additive. The level of silane necessary as an additive will vary according to filler loading. Typical concentrations range from 0.05 to 1.0% silane by weight of resin.

The organic group of DOW CORNING Z-6032 Silane polymerizes in air at approximately 175°C (350°F). Consequently, prolonged exposure above this temperature should be avoided

For treatment from dilute aqueous solution, DOW CORNING Z-6032 Silane can be added directly to water in low concentrations, but it does not form a true solution. Instead, it forms a milky white emulsion that is a very effective coupling agent, but may cause trouble with bath stability. Stable aqueous solutions may be obtained by prehydrolyzing DOW CORNING Z-6032 Silane in methanol under acid conditions¹ (see reference section pg. 5). A prehydrolyzed concentrate can be made that is ready to dilute with water within an hour. The concentrate is stable for about a week. It is recommended that prehydrolyzed concentrate be prepared as needed and not stored for more than a few days.

Prehydrolyzed concentrate formulation:

100 parts Z-6032 Silane
5 parts glacial acetic acid
25 parts water

The silane becomes completely soluble in less than an hour and may be considered as 30% active DOW CORNING Z-6032 Silane equivalent. This solution is diluted with water to 0.1 to 0.5% active ingredient and is particularly useful for application to fiberglass. The dilute aqueous solutions are stable for long periods of time.

Performance in Thermoset Composites

DOW CORNING Z-6032 Silane is universally effective for common thermoset resins such as polyester, epoxy and phenolics. The performance data of DOW CORNING Z-6032 Silane as a fiberglass finish in epoxy, polyester and phenolic laminates is listed in Table 1.

Performance in Thermoplastic Composites

As a mineral surface treatment, DOW CORNING Z-6032 Silane improves the composite strength of mineral filled polyolefins. The performance of DOW CORNING Z-6032 Silane in a variety of mineral polypropylene composites is listed in Table 2. This silane has been shown to be a very effective coupling agent and dispersion aid in mica-polypropylene composites² (see reference section pg. 5). It is also an effective coupling agent for other thermoplastics such as PVC, nylons 6 and 66, polybutyleneterephthalate, and polycarbonate³⁻⁴ (see reference section pg. 5).

PRIMER

DOW CORNING Z-6032 Silane can also be diluted to 5 to 15% solids and used as a primer for binding organic materials to inorganic surfaces. This silane is particularly useful for bonding polypropylene to aluminum panels. For this application, DOW CORNING Z-6032 Silane is diluted to 15% solids with methanol, and dicumyl peroxide is added at a concentration of 0.15%. The primer solution can then be applied by dipping or brushing and dried by heating at 100°C (212°F) for 10 minutes or less. The polypropylene can then be bonded to the primed surface by molding the resin against the surface briefly at 290°C (554°F).

While acid-prehydrolyzed DOW CORNING Z-6032 Silane is recommended for coupling applications from dilute aqueous solutions, a neutral prehydrolyzed DOW CORNING Z-6032 Silane is very effective in many primer application¹ (see reference section pg. 5). Acid hydrolysis provides a monomeric silanetriol with maximum reactivity, while neutral hydrolysis provides a cyclic oligomer siloxane with improved flexibility and compatibility for primer applications.

1. Add 5% water by total weight of silane solution as supplied.
2. Allow the material to reach a hydrolysis / condensation equilibrium (age for approximately 24 hours).
3. Dilute the prehydrolyzed material with an organic solvent, such as an alcohol or glycol, to the desired treatment concentration.

Nonporous surfaces are typically treated with a primer of approximately 1 to 10% active ingredient. Porous surfaces require higher concentrations.

Prehydrolyzed DOW CORNING Z-6032 Silane prepared in this manner is not recommended for coupling agent applications such as filler treatment. 1% dicumyl peroxide may also be added to prehydrolyzed primer (based on active silane) to

improve bonding to polymers. This primer will bond most thermosetting and thermoplastic polymers to metals and silicious surfaces.

The performance of primers is generally related to a variety of factors such as the reactivity or nature of the resin, condition of the metal or glass surface, and the environment of the organic/inorganic interface. Consequently, it is strongly recommended that this silane be thoroughly tested at a variety of concentrations and over a range of other application parameters before it is used in a commercial application.

CHEMISTRY

Two types of reactivity must be considered with an organofunctional silane such as DOW CORNING Z-6032 Silane: the vinylbenzylamine group and the trimethoxysilyl group.

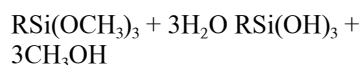
Vinylbenzylamine Reactivity

The vinylbenzylamine reactivity of DOW CORNING Z-6032 Silane is similar to other styrenics in its ability to participate in free radical polymerization of unsaturated resins such as polyesters. In addition, the vinylbenzyl group also appears to be sufficiently reactive to generate a free radical when heated to temperatures in the range necessary to mold polyolefins. The amine moiety of the organic group, based on performance in resin fiberglass composites, is capable of participating in reactions with epoxies, phenolics, nylons and other polymers.

Trimethoxysilyl Reactivity

The trimethoxysilyl portion of DOW CORNING Z-6032 Silane undergoes the typical chemistry of alkoxysilanes. The methoxysilyl group is subject to hydrolysis in water or water/alcohol solutions.

The initial product of hydrolysis is a silanetriol:



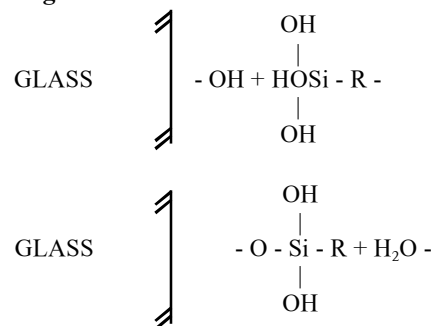
Silanetriols are moderately stable at dilute concentrations in polar solvents

such as water and alcohols.

Dispersions of DOW CORNING Z-6032 Silane are more stable, and have more favorable orientation on silicious surfaces if they are applied from a slightly acid solution. Mineral acids form amine salts that leave a hydrophilic residue on the treated surface. To avoid this residue, the dispersions are acidified with volatile organic acids such as acetic acid or carbon dioxide. These amine acid salts are stable in solution but lose the acid as the film dries. This treatment provides bonds to polymers with maximum water resistance.

Silanol groups are capable of condensing with hydroxyl groups at the surface of glass and silicious minerals as shown in Figure 2.

Figure 2: Silanol groups condensed with hydroxyl groups at the surface of glass and silicious minerals.



After condensing with the mineral surface, the remaining silanol groups are capable of hydrogen bonding or condensing with adjacent silanol groups. By this combination of covalent and hydrogen bonding, the coupling agent is bonded to the inorganic surface, and modifies it so that it is organoreactive.

USABLE LIFE AND STORAGE

When sealed in original containers and stored at ambient temperatures, this product has a usable life of 18 months from the date of production.

If material is transferred from the original container, it should not be stored in glass or metal. To obtain maximum storage stability, polyethylene containers are recommended.

FLAMMABILITY

DOW CORNING Z-6032 Silane is supplied in methanol, a flammable solvent. Keep away from heat and open flame. In case of fire, extinguish with CO₂ or foam.

LIMITATIONS

Shipping: DOT Classification: flammable.

This product is neither tested nor represented as suitable for medical or pharmaceutical uses.

PACKAGING

DOW CORNING Z-6032 Silane is supplied in 30-lb/13.6kg (5gal) and 330-lb/149.7kg (55gal) containers. All weights, net.

HANDLING PRECAUTIONS

Caution: Contact with DOW CORNING Z-6032 Silane can cause severe burns to eyes and irritation to skin. In case of contact with eyes, immediately flush with large amounts of water for at least 15 minutes and get prompt medical attention. Confined or prolonged skin contact can cause superficial burns. In case of skin contact, flush with large amounts of water.

Overexposure to the methanol solvent vapors of DOW CORNING Z-6032 Silane can cause serious injury. If swallowed, the solvent can cause blindness or death.

DOW CORNING Z-6032 Silane may cause skin sensitization. Prolonged or repeated skin contact should be avoided.

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 Dow Corning website at www.dowcorning.com. You can also obtain a copy from your local Dow Corning sales representative or Distributor or by calling your local Dow Corning Global Connection.

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REFERENCES

1. E.P. Plueddemann, Proc. 39th Ann.Tech. Conf., SPI/Reinforced Plastics Div., 4-C (1984).
2. M.S. Boaira and C.E. Chaffey, "Effects of Coupling Agents on the Mechanical and Rheological Properties of Mica-Reinforced Polypropylene," Polymer Engineering and Science, Oct 77, Vol. 17, No. 10.
3. W.T. Collins and J.L. Kludt, Proc. 30th Ann. Tech. Conf., SPI/Reinforced Plastic Div., 7D (1975).
4. E.P. Plueddemann, Proc. 27th Ann. Tech. Conf., SPI/Reinforced Plastics Div., 19-A (1969)

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Table 1: Performance of DOW CORNING Z-6032 Silane as a fiberglass finish in various laminates

| | Flexural Strength, psi ² | |
|--|-------------------------------------|------------------|
| | Dry | Wet ³ |
| Epoxy - Fiberglass Laminate, ¹ 125 mil (14 ply) | | |
| Without silane | 68,340 | 38,270 |
| With DOW CORNING Z-6032 Silane | 97,800 | 72,460 |
| Polyester - Fiberglass Laminate, ⁴ 125 mil (14 ply) | | |
| Without silane | 53,310 | 18,220 |
| With DOW CORNING Z-6032 Silane | 86,350 | 45,650 |
| Phenolic - Fiberglass Laminate, ⁵ 125 mil (14 ply) | | |
| Without silane | 69,300 | 19,970 |
| With DOW CORNING Z-6032 Silane | 89,630 | 80,220 |

¹Laminates prepared with D.E.R.[®] 330 epoxy from The Dow Chemical Company, resin cured with metaphenylene-diamine, and 7781 style glass cloth finished with an aqueous solution containing 0.2% silane solids at a solution pH of 4 (adjusted with acetic acid).

²Flexural strength measured according to Dow Corning CTM 0491. Based on ASTM D 790.

³Wet flexural strength measured on laminate after 72 hours in boiling water.

⁴Laminates prepared with Rohm and Haas[™] P43 resin containing 10 pph styrene and 1 pph benzoyl peroxide catalyst, and 7781 style glass cloth finished with an aqueous solution containing 0.2% silane solids at a solution pH of 4 (adjusted with acetic acid).

⁵Laminates prepared with Monsanto[®] Resinox SC-1008 phenolic resin, and 7781 style glass cloth finished with an aqueous solution containing 0.2% silane solids at a solution pH of 5.8.

Table 2: Physical properties of polypropylene reinforced with 35% mineral¹

| | Tensile strength, psi ² | | Flexural strength, psi ³ | | Flexural modulus x 10 ⁵ | |
|---|------------------------------------|--------------------------------|-------------------------------------|--------------------------------|------------------------------------|--------------------------------|
| | Without Silane | With DOW CORNING Z-6032 Silane | Without Silane | With DOW CORNING Z-6032 Silane | Without Silane | With DOW CORNING Z-6032 Silane |
| Novacite [®] 207A ⁴ | 3,227 | 4,250 | 6,610 | 8,150 | 3.15 | 3.10 |
| Wollastonite F-1 ⁵ | 3,780 | 4,900 | 7,810 | 10,260 | 5.00 | 6.44 |

¹Minerals treated with silane by dry blending with 0.5% DOW CORNING Z-6032 Silane solids at high shear. Before compounding, minerals were dried at 100°C (212°F).

²Tensile strength measured according to Dow Corning CTM 0501. Based on ASTM 0638.

³Flexural strength and modulus measured according to CTM 0491. Based on ASTM D 790.

⁴Novacite is a registered trademark of Malvern Minerals Corporation.

⁵F-1 is a grade of wollastonite supplied by Interspace Corporation.

