

INNOVATIVE POLYSILAZANE LIQUID COATING RESINS

Low Viscosity, Solvent Free & Fluorine Free Excellent Adhesion to Most Substrates Super High Hardness (9H+) Extremely High Temp Resistance (up to 1800 °C) Ultra-thin Clear Coat (Dozens of Nanometers to Micrometers) Patented Technology from Europe



About Us

Established in the 1950s, AZ Electronic Materials is a leading producer of high quality and high-purity specialty chemicals listed on the London Stock Exchange with headquarters in Luxembourg. We serve both the electronic and non-electronic markets. Our materials are widely used in integrated circuits (IC) and devices, flat panel displays (FPD), light-emitting diodes (LED), photolithographic printing, adhesives, pre-ceramic polymers, composites, paint and coatings.

Innovation is the lifeblood of our business and the ultimate competitive advantage. AZ has six principal R&D centers in Japan, South Korea, Taiwan, Germany, France and United States. AZ has a very strong intellectual property portfolio with over 2,200 patents granted. In 2012, some 81% of revenue of AZ derived from products with patented technology.

AZ operates polysilazane production facilities in Germany, Japan and India.

C The Only Manufacturer Offering the Entire Range of Polysilazanes at Commercial Scale Globally

AZ DURAZANE Polysilazane Coating Resins

As the only manufacturer in the world offering the entire range of polysilazane resins on a commercial scale, AZ is recognized as a specialty chemicals pioneer. We are known as an innovator in the chemical industry.

We supply DURAZANE polysilazanes for architectural, industrial, OEM and special purpose coatings used in a wide spectrum of industries such as aerospace, automotive, metals, construction, electronics and composites. AZ DURAZANE polysilazanes can be applied on wood, metal, plastic, glasses, ceramics and other surfaces. With manufacturing facilities and research and technology support centers located throughout the world, we provide responsive, local support to our customers, helping them to rapidly bring advanced coating solutions to the market by the utilization of polysilazane resins.

Basic Knowledge of Polysilazanes

Polysilazanes (PSZ) are polymers in which silicon and nitrogen atoms alternate to form the basic backbone. Each silicon atom is bound to two separate nitrogen atoms and each nitrogen atom to two silicon atoms, and both chains and rings of the formula [R1R2Si–NR3]n occur. R1-R3 can be hydrogen atoms or organic substituents. If all substituents R are H atoms, the polymer is designated as Perhydropolysilazane (PHPS) or Inorganic Polysilazane ([H2Si–NH]n). If hydrocarbon substituents are bound to the silicon atoms, the polymers are designated as Organopolysilazanes (OPSZ). Molecularly, polysilazanes [R1R2Si–NH]n are isoelectronic with and close relatives to Polysiloxanes [R1R2Si–O]n (silicones).



Inorganic Polysilazane (PHPS)



Organic Polysilazane (OPSZ)

Organic Polysilazanes (OPSZ) VS. Inorganic Polysilazanes (PHPS)

	Organic Polysilazanes (OPSZ)	Inorganic Polysilaznes (PHPS)		
Polymer	Si-N-H polymer with organic residues (contains carbon)	Pure Si-N-H polymer without carbon		
After curing	SiO2 layer with carbon residues; less carbon residues under high temp baking	Pure SiO2 layer (glass ceramic)		
Cracking Threshold of Resin	30+µm layer	<2µm layer		
Electrical Insulation	Good (carbon contamination)	Excellent (same as glass ceramic)		
Hardness/Flexibility	Soft/bendable	Hard/brittle		
Chemical Barrier (O ₂ , H ₂ O & other gases)	Good	Excellent		
Surface Property	Hydrophobicity	Hydrophilicity		
Application in Coatings	OPSZ, PHPS, blends of PHPS & OPSZ, blends of PSZ with other resins; Various "R"s with or without pigments & extenders, solvents & additives to modify			

properties;

Application in Coatings

Catalysts to reduce curing temperature depending on specific application



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Figure right: Since 2006, German's Deutsche Bahn (DB) Railway has used AZ's Polysilazane-based coatings for both interior and exterior of its trains

Key Facts of Organic Polysilazanes (OPSZ)

- OPSZ can be combined with nanoparticles, pigments, extenders, additives and other organic resins with excellent adherence to metal, glass, mineral, ceramic and organic surfaces
- OPSZ based coatings demonstrate attractive physical characteristics such as super high hardness, UV transparency, corrosion resistance, thermal durability and stability, weather resistance and chemical resistance
- Inactivated sites of OPSZ can be activated to form a cross-linked network through the addition of heat or UV radiation
- Activated sites of OPSZ can be cured through moisture-induced cross-linking at ambient (room) temperature
- OPSZ based coatings are widely used where thermal stability, light weight and corrosion resistance are important
- The highly reactive components of OPSZ can combine with many materials and form silica or polysiloxane coatings that are extremely stable and dense

Applications of Polysilazanes

Industrial Coatings Technology

High temperature Corrosion resistance Fire resistance Non-fouling Water repelling Wear & abrasion resistance Thermal barrier Anti-graffiti Easy-to-clean Mold releases

Adhesives Ceramics Metals Glass Organic material

Pre-Ceramic Polymers

Ceramic binders Ceramic matrix composites Metal matrix composites Ceramic fibers

Hybrid Composites & Coatings

Polyurea Silicone Epoxy Acrylic

Key Organopolysilazane Products & Applications

It is now many years since polyurethanes, polyesters, epoxies and alkyd systems became established as binders for the coatings sector. Other tried and tested systems include those based on silicon such as sol-gels, silicones and fluorine containing materials. But now there is a third attractive option: the class of polysilazanes. These can easily compete with conventional binders in many different applications, and in some areas they have significant advantages. Besides pure polysilazane-based coating systems, there is the possibility of hybrids, opening up a multitude of variations. These coating systems display excellent performance, service life and adhesion to substrates.

AZ offers Organopolysilazanes (OPSZ) polymers with tailor-made properties for coating applications. The resins form flexible and highly cross-linked coatings that are extremely weather resistant, and provide excellent corrosion protection and hydrophobic properties. Moreover, the polymers are solvent-free and fluorine-free. Due to their properties, OPSZ resins are perfectly suitable as durable binders for lacquer systems and coatings.

The materials are available in three different grades.

- **DURAZANE 1500 RC** can be rapidly cured at ambient and high temperatures.
- DURAZANE 1500 SC needs slightly more time for curing at ambient and high temperatures.
- **DURAZANE 1800** needs thermal or radiation curing.

Refer to the table below on the applications, substrates and curing condition of the three products.

	DURAZANE 1500 RC	DURAZANE 1500 SC	DURAZANE 1800
Suggested Application			
Anti-graffiti Coatings			
Easy-to-clean Coatings		•	
Anti-scale Coatings		•	
Transportation Maintenance & Repair Coatings		•	
Transportation OEM Coatings		•	
Coil Coatings			
Non-stick Coatings		•	
Marble & Stone Coatings			
Glass Coatings			•
Thermal Resistant Coatings*		•	•
Plastic Coatings			
Protective Coatings / Anticorrosive Coatings			•
Wood Coatings		•	
Architectural Coatings		•	
Preferred Substrates			
Coatings		•	•
Steel, Stainless steel, Galvanized steel		•	•
Aluminum			
Zinc		•	•
Copper, Brass and Bronze		•	•
Silver		•	•
Polycarbonate		•	
Polymethylmethacrylate		•	
Other Plastics		•	
Marble & Stone			•
Glass		•	•
Ceramic	•	•	•
Minerals		•	•
Carbon		•	•
Wood		•	
Curing Conditions			
Ambient Temp. Curing		•	
Thermal Curing	•	•	•
UV Curing			

*Note:

• Operating temperatures up to 750 °C can be achieved by the use of DURAZANE 1500 RC or DURAZANE 1500 SC

• Operating temperatures up to 1800 °C can be achieved by the use of DURAZANE 1800

Curing of OPSZ

Four different cures are possible based on the intended outcome of OPSZ materials.



Thermal Cure

UV curing in the presence of a UV sensitizer

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Reactive Systems of OPSZ with Other Organic Resins

OPSZ possesses reactive Si-N functionality which enables co-reaction with various organic resins such as epoxies, isocyanates, and phenols.



Reaction with Isocyanates

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Cold-blending Systems of OPSZ with Other Resins

OPSZ can be cold blended with any resins without chemical reaction among the ingredients, such as thermoplastic acrylics, silicones, hybrids of OPSZ and PHPS, etc.



Hardness of the Coatings Film of PSZ

Туре	Substrate	Curing	DFT	Pencil Hardness
PHPS	-	RT x 6d	1.0 um	>9H
PHPS		RT x 2d	1.0 um	8H
PHPS		RT x 1d	1.0 um	7H
PHPS		200 °C x 1hr	1.0 um	7H
OPSZ	Stainless steel	RT X 5d	25-30 um	4-5H
OPSZ		RT X 5d	30-35 um	2-3H
OPSZ		200 °C, 45 min	15-35 um	3H
Car Body Coating		RT X 7d	100 um	1H
Silicone Hard Coating		RT X 7d	30-40 um	2H
Acrylic Hard Coating		RT X 7d	30-40 um	1H
PU Coating		RT X 7d	25-35 um	2H

Ultra-thin Clear Coat (Dozens of Nanometers to Micrometers)

Both Perhydropolysilazanes (PHPS) and Organopolysilazanes (OPSZ) are widely used in clear coatings for Transportation Maintenance & Repair Coatings, Transportation OEM, Coil Coatings, Non-stick Coatings, Marble & Stone Coatings, Glass Coatings, Thermal Resistant Coatings, Plastic Coatings, Protective Coatings & Anticorrosive Coatings, Ceramic Coatings, Wood Coatings and Architectural Coatings. PHPS and OPSZ materials can deliver durability against weathering, UV, chemical, corrosion, staining, graffiti, scratch, and heat.

Based on the in-service performance and the inherent properties of the materials, the typical coating dry film thickness (DFT) of OPSZ-based clear coat is between 2 to 10 um, while the typical coating DFT of PHPS-based clear coat is between dozens of nanometers to 2 um.

- Easy-to-Clean and anti-graffiti:
- Corrosion resistance:
- Scratch resistance:

0.5 to 1 μm 0.5 to 1 μm

0.05 to 0.2 µm

Chemical Resistance of OPSZ



OPSZ: Organopolysilazane system OPSZH: Organopolysilazane hybrid system AM: Alkyd melamine system 2K PU: Polyurethane system

Test Methods:

A cotton ball saturated

with the tested solvent was

placed in a one ounce bottle

(10mm x 75mm test tube).

The container was inverted

on the test material surface

for a period of 24 hours.

Method A:

Method B:

For non-volatile chemicals, five drops (1/4 cc) of the test chemical were placed on the test material surface. The chemical was then covered with a watch glass (25 mm) for a period of 24 hours.

After the 24 hour period the exposed surface areas were then washed with water, then a detergent solution, and finally with isopropyl alcohol. Materials were then rinsed with distilled water and dried with a cloth.

Samples are numerically rated as follows:

- 5: No Effect No detectable change in the material surface.
- 4: Excellent Slight detectable change in color or gloss, but no change in function or life of the surface.
- Good A clearly discernible change in color or gloss, but no significant impairment of surface life or function.
 Fair Objectionable change in appearance due to dis-coloration or etching, possibly resulting in deterioration of function over an extended period of time.
- 1: Fail Pitting, cratering or erosion of the surface. Obvious and significant deterioration.

Weathering Resistance of OPSZ



- DIN EN ISO 11341 Paints and varnishes
- Artificial weathering and
- exposure to artificial radiationExposure to filtered xenon-arc
- radiation (2000 hours)

OPSZ: Organopolysilazane system OPSZH: Organopolysilazane hybrid system AM: Alkyd melamine system 2K PU: Polyurethane system

Thermal Resistance of OPSZ



Silicone PE resin 1 — Silicone PE resin 2
 OPSZ — OPSZ — OPSZ

- Weight loss at high temp
- Comparison between OPSZ and silicone polyesters
- Rate of heating: 5 °C/min

Corrosion Resistance of OPSZ

Aluminum coated with OPSZ-based coatings display no corrosion even after 100 days (2400 hours) in the salt spray test performed in accordance with ISO 7253.

▶ ISO 7253:1996 Paints and varnishes – Determination of resistance to neutral salt spray (fog)

Steel coated with OPSZ-based coatings display no corrosion after 100 days (2400 hours) in the condensed water climate test carried out in accordance with ISO 6270.

ISO 6270-2:2005 Paints and varnishes – Determination of resistance to humidity – Part 2: Procedure for exposing test specimens in condensation-water atmospheres

Hydrophobic Properties of OPSZ

The films of OPSZ resins have a contact angle of around 95° to water, and this level is maintained over a long period. The contact angle to water of OPSZ-based coatings can be raised further, to more than 120°, with appropriate additives. This makes OPSZ resins the binders of choice for easy-to-clean applications, since not only does it adjust to the optimum contact angle, but the systems also have a correspondingly high cross-link density with an outstanding barrier effect. Comprehensive tests have shown that polysilazane binders also contribute to high resistance to weathering. OPSZ resins are unique coatings binders with excellent hydrophobic properties (low surface energy) which deliver excellent adhesion to different substrates.

Hydrophilic Properties of PHPS

Hydrophilic property means that the surface of a substance easily gets wet. The surface with this property produces the state in which dust takes off easily in the rain and with water.

The degree of hydrophilic property is expressed in terms of contact angle formed with water. In the painting industry, materials which have a contact angle of less than approx. 40°, are referred to as "hydrophilic".

The figure in the right shows contact angles of PHPS. In combination with Wetting promoter and Aquanol 50, it is possible to achieve high hydrophilic property quickly with a contact angle less than 10°.



Scratch Resistance of PHPS

The table below shows the results of a scratch resistance test using pencil hardness and abrasive detergent on stainless steel. The excellent scratch resistant performance of PHPS is demonstrated.

There was no cracking, checking or loss of film integrity observed in the sample with PHPS tested at 528 quarts (500 liters) of sand.

Test item	Materials	Application Method	Baking	DFT, µ	Results
Abrasion* (Abrasive detergent)	PHPS	Wipe	200°C for 1 hr	~1	No change
	No coating (control)	-	-	-	Scratched all over
Pencil Hardness	PHPS	Spray	200°C for 1 hr	~1	7H
	No coating (control)	-	-	-	2H

ASTM D 968: Standard Test Methods for Abrasion Resistance of Organic Coatings by Falling Abrasive

Stain Resistance of PHPS

Anti-stain test of PHPS based car coatings with carbon powders

The figure below shows the results of a stain resistance test with carbon powders. The excellent anti-stain performance of PHPS is demonstrated.

*Ant	i-stain ab	ility of Pl	HPS is ter	rific!!
		in the		
PHPS	Glass Coating A	Glass Coating B	Glass Sealant C	Non coating

Substrate:Test period:

Accelerated exposure test by Super-UV (90mW/cm2, 295-450nm) with high humidity (80%RH) & temperature (63°C)

White side door panel of a vehicle

100 hours = around 5 years

Perhydropolysilazanes (PHPS) Products

AZ offers entire range of Inorganic Polysilazanes (PHPS) for coatings applications.

With different additives and solvents used in the formulation, AZ's PHPS resins can be cured under different conditions from room to high temperatures.

After application, PHPS resins will convert to SiO2 (Silica) by reacting (dehydrogenation) with moisture or by heating.

Fundamental Properties of PHPS:

- Super high hardness (9H+)
- ▶ Hydrophilic property with water (< 10°)
- Excellent weather resistance
- ▶ Good acid resistance & barrier property
- Excellent adhesion on various materials
- Transparent fine dense film
- High purity silica
- ▶ High flattening effect (with low viscosity and high yield)

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