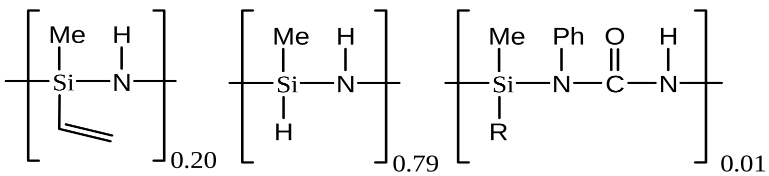
TB1: KiON® Ceraset® Polyureasilazane and KiON® Ceraset® Polysilazane 20

Heat-Curable Resins

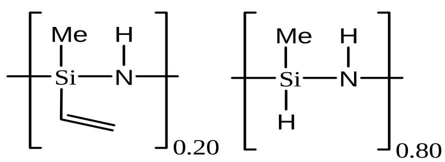
Description:

KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 are versatile, low viscosity liquid thermosetting resins. These patented polymers contain repeat units in which silicon and nitrogen atoms are bonded in an alternating sequence. Both of these polysilazanes contain cyclic and linear features. The distinguishing characteristic that differentiates KiON Ceraset Polyureasilazane from KiON Ceraset Polysilazane 20 is that the former contains a small percentage of urea functionality. In addition, KiON Ceraset Polysilazane 20 contains fewer low molecular weight polysilazane components.



R = -H or -vinyl

KiON Ceraset Polyureasilazane



KiON Ceraset Polysilazane 20

These low viscosity polymers are thermoset (cured) to a solid by heating to 180 - 200°C or at lower temperatures by adding a free radical initiator such as an organic peroxide. Alternatively, these polymers may be cured by exposure to UV radiation in the presence of a UV sensitizer. Both polymers convert to silicon carbide or silicon nitride ceramics at elevated temperatures[1-3]. KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 were specifically designed for CMC, MMC, and other high performance ceramic precursor applications.

Uses:

- Ceramic Matrix Composites (CMCs)
- Metal Matrix Composites (MMCs)
- Corrosion Resistant Coatings
- Infiltrants for Ceramic Performs
- Oxidation Resistant Coatings
- High Temperature Coatings

- Polymer Infiltration / Pyrolysis (PIP)

General Properties of KiON Ceraset Polysilazane Based Resins:

Liquid Resin

- Color: Clear to Pale Yellow Liquid
- Viscosity: 50 - 200 cps @ 25 °C [77 ^{o}F]
- VOC Content: N/A
- Refractive Index of Liquid Polymer: 1.4896 @ 23 °C [73 °F]
- Molar Extinction Coefficient: 0.15 M^{-1} cm^{-1}
- Flash Point: 29 °C [84 °F]
- Specific Gravity: 1.020
- Density: 8.50 lb/gal [1.02 kg/L]
- Amine Equivalent Weight: 64
- DC Electrical Conductivity of Liquid Resin: 1.0 X 10^{-12} mhos
- Solubility: soluble in most aprotic solvents both polar and non-polar

Cured Resin

- Density of Cured Solid: 1.120
- Hardness of Cured Solid: 120 MPa Vickers
- Rockwell M Hardness: 45 to 60
- Pencil Hardness of Cured Film (Coating): 9H
- Volume Shrinkage upon Curing: 6.2 %
- Moisture Absorption of Cured Resin at Room Temp: 0.1 % (boiling water for 24 hr)
- Linear Expansion Coefficient: CTE (25 – 475 °C) = 152.4 ppm/K
  CTE (475 – 975 °C) = -334 ppm/K
- Thermal Expansion Coefficient: 8 X 10^{-5} / °K
- UV Absorption Edge of Cured Resin: 300 nm
- Dielectric Constant of Cured Resin (8.4-12.1 GHz): 2.74 (± 0.005)
- Voltage Breakdown of Cured Resin: 1,000 V
- AC Loss Tangent of Cured Resin: 0.0093
- Solubility: insoluble in most solvents, water, dilute acids and bases

Ceramic

- Linear Shrinkage upon Pyrolysis: 15 – 20 %
- Weight Loss upon Pyrolysis: 15 – 20 %
- Ceramic Mass Yields (900 – 1600 °C):
  Pyrolyzed in **Argon 75-86 %**; in **Nitrogen 75-85 %**; in **Air 95 %**
- Compositions at 1600 °C:
  Pyrolyzed in **Argon; SiC**; in **Nitrogen; SiC/Si_3N_4**; in **Ammonia; Si_3N_4**;
  in **Air; $Si_xO_yN_z$**
- Crystalline Phases at 1600°C: Pyrolyzed in **Argon; beta SiC**; in **Nitrogen; beta SiC, alpha Si_3N_4 , beta Si_3N_4;** in **Ammonia; alpha Si_3N_4, beta Si_3N_4**
  (Note: Crystal seeding influences exact crystalline phase formed.)

- Bulk Density of amorphous Ceramic from Pyrolysis (@1000 °C):   2.4 g/cm^3
- Bulk Density of crystalline Ceramic from Pyrolysis (@ 1600 °C):   3.2 g/cm^3
- Flexural Strength of SiCN Ceramic Generated from Pyrolysis: 600 – 1,000 Mpa
- Young's Modulus of SiCN Ceramic Generated from Pyrolysis: 155 Gpa
- Fracture Toughness of SiCN Ceramic Generated from Pyrolysis: 3.5 $Mpa.m^{0.5}$
- Hardness of SiCN Ceramic Generated from Pyrolysis: 15 Gpa
- Thermal Expansion Coefficient of Ceramic from Pyrolysis: 0.5 X 10^{-5} / °K
- Poisson's Ratio: 0.18

Appearance:

KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 are colorless to pale yellow liquids as prepared and shipped. During handling and with use in air the polymers may become slightly hazy or develop small particulates in the liquid. These changes occur due to slight hydrolysis of the polymers and will not dramatically affect their use and performance.

Use of Solvents:

KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 are hydrolytically sensitive and will slowly generate ammonia upon contact with water or moist surfaces. The polymers will also react with other protic substances such as acids, bases and alcohols to produce ammonia. KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 can be diluted with aprotic solvents such as alkanes, aromatic hydrocarbons, ethers, and chlorocarbons, siloxanes, esters and ketones. Choice of solvent will depend upon application specific criteria with respect to solvent flammability and vapor pressure. *(Note: It is essential that ketone solvents be dry. Limited bench life (days) has been observed in ketone solvents depending upon storage conditions.)*

Thermosetting KiON Polysilazanes:

Liquid KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 are readily thermoset to a solid, through a vinyl crosslinking mechanism, by heating to 180-200 ^{o}C. Cure can be effected at lower temperatures through the addition of a small quantity of a free radical generator, typically a peroxide. Developmental work has demonstrated that a variety of peroxides, including dialkyl peroxides, peroxyketals, diperoxyesters, alkyl peroxyesters and peroxycarbonates are effective cure initiators. Typically 0.1 to 5 wt% of the above peroxides (alone or in combination) are sufficient to initiate cure. Diacyl peroxides such as benzoyl peroxide are not effective initiators. It is important that peroxides not become contaminated during use or storage. *(Note: Please review the manufacturer's MSDS for appropriate safety, health, storage, and handling information for peroxides.)*

Figure 1 *(next page)* displays four specific peroxides that accomplish the cure from liquid to solid in times ranging from 1 to 90 minutes over a temperature range of 90 °C (194 °F) to 190 °C (374°F). The peroxides were dispersed in solvent free polymer samples at 1 wt% based on the weight of KiON Ceraset polysilazane based resins employed.

A representative procedure for curing, using dicumyl peroxide, follows. Dicumyl peroxide is soluble in the liquid polymer and typically about 0.5 – 1wt% peroxide based on the weight of the polymer is used. This peroxide/polymer solution is stable at room temperature for at least six months. Heating the peroxide/polymer solution causes the peroxide to undergo decomposition into radical species which initiate the thermosetting reaction. At temperatures above 150 °C the thermosetting is rapid and may be extremely exothermic. This converts liquid KiON Ceraset polysilazane based resins to a solid, crosslinked polymer. Heating of polymer/peroxide mixtures, if performed in air, must be conducted with adequate ventilation to ensure that no combustible volatiles accumulate. (Caution: Due to the highly exothermic nature of the cure, heating of large quantities of these polymers in an air environment can result in excessive heat generation, charring, and in some instances fire.)

The time/temperature curves in Figure 1 are to be used only as a guide. Cure times of specific samples will vary depending upon the type and loading level of fillers and the level of peroxide. Slight acceleration in the cure rate may occur on using higher levels of peroxide (2-5 wt%).

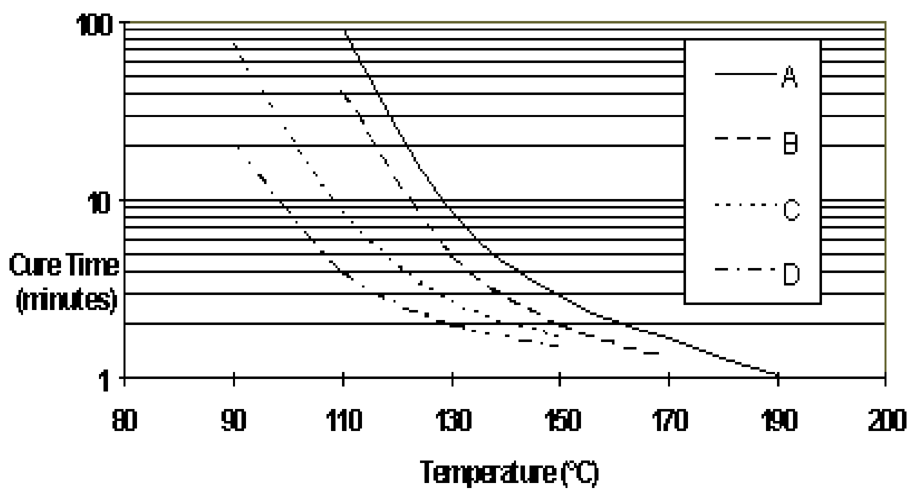


Figure 1. Cure time/temperature relationships for KiON Ceraset Polysilazanes with selected peroxides. Peroxide Key A) 5-Bis(tert-Butylperoxy)-2,5-Dimethyl-3-Hexyne; B) Dicumyl Peroxide; C) 1,1-Bis-(tert-Butylperoxy)-3,3,5-Trimethylcyclohexane; D) 2,5-Dimethyl-2,5-di-(2-Ethylhexanoylperoxy)hexane

Characteristics of Thermoset KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20

Upon curing with a peroxide KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 are rendered as rigid solids, which are insoluble in common organic solvents, water, and dilute acids and bases. The cured material does not melt, flow or slump. The “char yield”, an indication of mass conversion to ceramic material, as measured by thermal gravimetric analysis (TGA), is about 85-85% for KiON Ceraset Polysilazanes in both nitrogen and argon and about 95% in air . Figure 2 *(next page)* shows the TGA curves under different pyrolysis atmospheres.

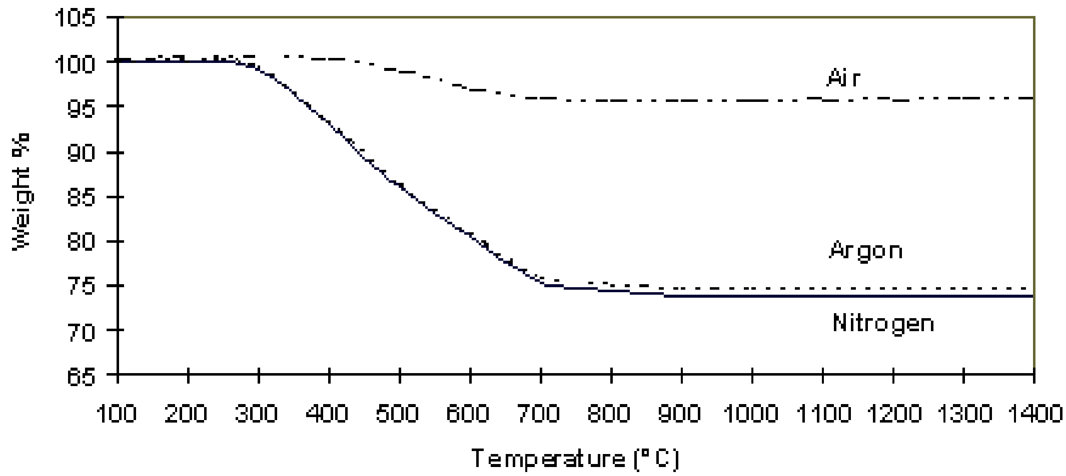


Figure 2. Thermogravimetric Analysis of Cured KiON Ceraset Polyureasilazane

Fillers:

Polymer, metal or ceramic fillers (particulate or fiber) may be added to the polymer/peroxide solution and subsequently thermoset. Such fillers can markedly reduce the bench life of the polymer/peroxide solution. The solid, thermoset polymer has been found to adhere to many surfaces including numerous metals, glasses, ceramics and polymers, so an appropriate release agent should be used. Suitable release agents include silicone and fluoropolymer-based agents. Shaped articles may be directly thermoset in a heated mold.

Storage:

The liquid polymer should be stored in a closed plastic or metal container at or below room temperature to maximize shelf life. Under these conditions the shelf life of the polymer is in two years. Material in unopened original containers has been show to be viable up to five years. Once mixed with a peroxide curing initiator the shelf life will be strongly dependent upon the half-life of the peroxide employed.

Health and Safety:

KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 are listed on the EPA/TSCA (Toxic Substance Control Act) inventory of chemical substances. Please refer to the Materials Safety Data Sheet (MSDS) for details concerning the health hazards of KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20. The toxicity or other hazards of this material, alone or in combination with other substances, are not fully known. Read the health and safety information provided before using this material. These polysilazanes have a musty amine or ammonia-like odor and should be used in a fume hood or with adequate ventilation. The material should be used with appropriate personal protective clothing, safety glasses and/or goggles and impervious gloves.

KiON Corporation Polysilazane Technical Bulletins:

TB1 "KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 - Heat-Curable Resins"
TB2 "KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 - Ceramic Precursor Applications"
TB3 "KiON Polysilazanes: Reactivity with Isocyanates"
TB4 "KiON Polysilazanes: Reactivity with Phenolic Resins"
TB5 "KiON Polysilazanes: Reactivity with Epoxy Resins"

References:

1. Ceraset and KiON are registered trademarks of KiON Corporation.
2. U.S. Patent 4,929,704; 5,001,090; 5,021,533; 5,032,649; 5,155,181; 6,329,487.
3. R.L.K. Matsumoto Mat, Res. Soc. Symp. Proc., 1990, 180, 797-800.

Additional Information:

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