

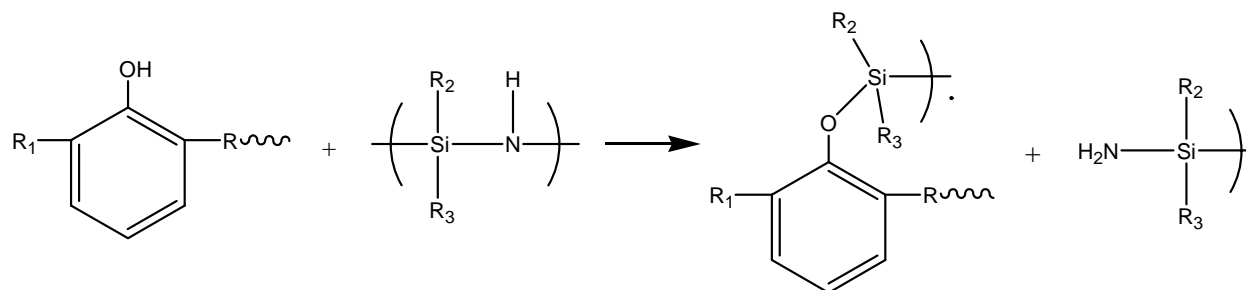
TB4: KiON[®] Polysilazanes - Reactivity with Phenolic Resins

Background:

KiON Polysilazanes are patented polymers which contain repeat units in which silicon and nitrogen atoms are bonded in an alternating sequence. The majority of KiON Polysilazanes are low viscosity liquids. KiON Polysilazanes all possess reactive Si-N functionality which enables co-reaction with various organic resins such as epoxies, isocyanates, and phenols [3].

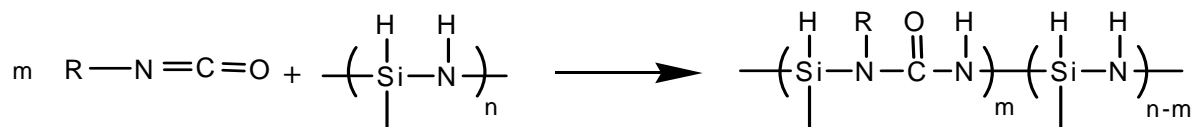
Phenolic Side Reactions:

The reactivity of the Si-N bond with active oxygen systems creates an inherent complication with the use of silazane-based polymers in combination with phenolic resins. The hydroxyl groups react with the Si-N bond to form terminal Si-NH₂ groups. Such groups can further react with either hydroxyl groups or other terminal Si-NH₂ to generate free ammonia, which is evolved during the cure as shown below. The phenolic structure is intended to be generic in nature and not represent a specific type of resin.



We have found, however, that "foaming" (due to ammonia generation) can be ameliorated in following ways: (1) pre-cure the phenolic to powder form and use the cured powder with the KiON Polysilazane resin or (2) form a prepolymer of the phenolic resin and an isocyanate prior to the addition of KiON Polysilazane.

The first route simply uses KiON Polysilazane as a binder or carrier for cured phenolic resin powder. The second route will be described in more detail. The hybrid system combines a phenolic resin with a co-curing system consisting of an aromatic polyisocyanate and a KiON Polysilazane. Although various isocyanates could be employed, methylenediphenyl diisocyanate based resins (MDI) show good compatibility. Representative examples of MDI resins are: e.g. Mondur[®] MR (Bayer Corporation) or Rubinate[®] M (ICI Polyurethanes). In a typical formulation the phenolic resin is mixed with the MDI polyisocyanate and heated to partially react the phenolic with the polyisocyanate. KiON Polysilazane is then stirred into the resulting fluid, allowed to set at ambient or slightly elevated temperature and post-cured at elevated temperature. The prepolymer cure proceeds through the reaction of isocyanate residues in the prepolymer with the Si-N bonds of the polysilazane. The R group of the isocyanate prepolymer in this case incorporates the phenolic groups.



Representative Formulation:

A typical formulation and curing procedure is given below.

Preparation of a KiON Ceraset Polyureasilazane / phenolic hybrid using Durite[®] 5614 resin:

- 80 grams Mondur MR aromatic polyisocyanate
- 15 grams Durite 5614 solid phenolic resin (Borden, Inc.)
- 15 grams KiON CERASET polyureasilazane

The solid Durite 5614 phenolic resin was added to Mondur MR aromatic polyisocyanate and heated with occasional stirring to 110°C for a period of 15 minutes. Over the course of the 15 minute period the reaction mixture foams and, with stirring, eventually becomes a homogeneous, fluid prepolymer. The prepolymer is then cooled to a temperature of 60°C, and the KiON Ceraset Polyureasilazane is added. [Note: the prepolymer is quite viscous at room temperature which complicates mixing with the KiON Ceraset Polyureasilazane inorganic polymer. Consequently, slight warming, e.g. 60°C, aids in resin mixing.] The KiON Ceraset Polyureasilazane is blended into the prepolymer with vigorous stirring and the mixture is then allowed to cure. Setting occurs within a period of about 10 minutes. The set composition can then be post-cured at 125°C for a period of about 2 hours.

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 shown 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. KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20. 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.

All information on KiON Ceraset Polyureasilazane and KiON Ceraset Polysilazane 20 is based on experimental results. Although we believe this information to be reliable, we expressly do not represent, warrant, or guarantee accuracy, completeness, or reliability. NO REPRESENTATIONS OR WARRANTIES, EXPRESSED OR IMPLIED OF MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, OR OTHERWISE ARE MADE OR CONTAINED HEREIN. Each user should conduct a sufficient investigation to establish the suitability of any product for the intended use. User should comply with all applicable safety and environmental standards. Nothing herein is to be construed as advising or authorizing practice of any invention covered by existing patents without license from the owners thereof.

Additional Information:

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