# MOMENTIVE



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## **Product Description**

Silquest and other Momentive silanes are versatile products that can react with a wide variety of organic and inorganic materials. Their unique ability as coupling agents, crosslinking agents, and surface modifiers has been proven in an ever-increasing number of applications, ranging from crosslinking plastics, fuel-saving silica tires, adhesives and coatings for fiberglass reinforced composites. The benefits that Silquest silanes can impart to these end-use applications are highlighted on page 2.

## **Application Guidelines**

The choice of a Momentive silane is specific to resin type and application. We recommend that you contact the nearest Momentive Performance Materials sales office for assistance before selecting a silane for your end-use application. The following selection guide is a starting point when considering a Silquest silane for various polymers (resins). The selection of the preferred silane for a specific end-use application will require experimentation.

| Potential Applications                              | Typical Benefits  |
|---|---|
| Adhesives and Sealants                              | Moisture-initiated crosslinking of resins, improved wet adhesion, primerless adhesion to many substrates, improved chemical resistance, weatherability and durability   |
| Coatings / Inks                                     | Moisture-initiated crosslinking of resins, improved wet adhesion, chemical and corrosion resistance, weatherability, pigment dispersion and scrub resistance  |
| Fiber Reinforced Composites<br>and Glass Insulation | Coupling of resins with fibers for improved resiliency of insulation batts, better wet strength retention and electrical properties of FRP composites, and improved fiber strand integrity, protection and handling         |
| Filler Treatment                                    | Improved coupling of resins with fillers, better filler dispersion and processing ease in thermoset and thermoplastic resins  |
| Polymer Modification                                | Moisture-cure crosslinking for improved environmental and chemical resistance   |
| Rubber and Elastomers                               | Coupling of resins with minerals for improved composite strength, toughness, abrasion resistance, rolling resistance, wet electrical properties and rheology control, fewer mixing steps and better filler dispersion       |
| Thermoplastics                                      | Moisture-curable crosslinked polyethylene for wire & cable and polyethylene crosslinked (PEX) pipe. Mineral and pigment treatment for dispersibility and coupling of resins with fillers in high performance thermoplastics |
| Tires   | Coupling silica in tire compounds to improve the rolling resistance, traction and wear. New generation silanes may facilitate higher-efficiency tire manufacturing while enhancing tire performance.                        |

## Silquest and other Momentive silanes have been shown to enable many end-use properties.

## **Functions, Chemistry and Reaction Mechanisms**

#### **Function**

## Crosslinking

When attached to a polymer backbone, silanes can link together polymer molecules through the formation of siloxane bonds, creating a three-dimensional network. The "crosslinking" is activated by ambient moisture and can take place at ambient temperature. Silquest silanes are excellent candidates to consider for improved thermal stability, creep resistance, hardness and chemical resistance in coatings, adhesives, sealants and composites

#### Adhesion Promotion

Silquest silanes have been shown to provide improved adhesion of adhesives, sealants and coatings to various substrates, especially under hot and humid conditions. Silanes are commonly used to improve adhesion to glass, minerals and metals, and typically show similar benefits on difficult substrates such as polyamide, SMC, acrylics, PVC and others.

## Coupling

Silquest silanes can couple inorganic pigments and fillers to organic resins. Coupling typically improves the moisture and chemical resistance of the coating, adhesive or composite.

#### Dispersion

Silquest silanes can aid in the dispersion of inorganic pigments and fillers in coatings and sealants. Better dispersion typically leads to lower viscosity in the formulated product, higher pigment and filler loading and improved hiding power of coatings.

#### Chemistry

Silquest organofunctional silanes are bi-functional molecules that have two types of reactivity built into their structures - organic and inorganic. Figure 1 shows the common features of a typical organofunctional silane.

#### Figure 1: Anatomy of a Typical Organofunctional Silane



gamma-Aminopropyltrimethoxysilane Silguest A-1110 silane

OCH<sub>3</sub>

#### **Reaction Mechanisms**

#### Reactions at the Functional End of a Silquest Silane

The functional group (Y) is designed for reactivity with an organic resin. The functional group is selected either to react with, to co-polymerize into a resin or to take part in the cure reaction of the resin system. Reactive functional groups include primary and substituted amino, epoxy, methacryl, vinyl, mercapto, urea and isocyanate.

#### • Linking Group in the Center of a Silquest Silane

Between the functional group and the silicon atom is a linking group, referred to as an "alkylene group." The silicon-carbon bond of the linking group is stable in most environmental conditions. The inorganic end of the silane possesses hydrolyzable groups that are attached to the silicon. The hydrolyzable groups are usually alkoxy groups such as methoxy, ethoxy or isopropoxy. Each hydrolyzable group reacts at a different rate and releases a different alcohol when it comes in contact with ambient moisture. In some cases only two hydrolyzable groups are present, although a three-group configuration typically results in more moisture-resistant bonds. Most coupling agents have a single silicon atom, but some Silquest silanes are available with multiple silicon atoms.

#### Reactions at the Silicon End of a Silquest Silane

Silane hydrolysis rates are influenced by the reaction conditions and the "X" groups on the silicon atom. The "X" groups hydrolyze to form silanols that condense with other silanols or other hydroxyl groups. These condensation reactions liberate water. The speed of both hydrolysis and condensation is controlled by pH [Figure 2-effect of pH]. Each of these reactions will be discussed separately.

#### Figure 2: Effect of pH



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## Functions, Chemistry and Reaction Mechanisms (continued)

#### Reactions at the Silicon End of a Silquest Silane (continued)

#### Hydrolysis

In order to become "active" the Silquest or other Momentive silane must first hydrolyze. The reaction of the silicon end of the molecule, as depicted in Figure 3, is initiated by hydrolysis of the alkoxy group, usually after exposure to ambient moisture, but sometimes by the purposeful addition of water. This reaction releases an alcohol and forms a silanol. The speed with which hydrolysis occurs depends on the pH of the formulation (slowest at pH 7) and upon the steric bulk and polarity of the alcohol residue (methoxy > ethoxy > 2-methoxyethoxy > isopropoxy >> t-butoxy). Both bases (such as organic amines) and acids (such as carboxylic acids) will catalyze the reaction. The speed with which hydrolysis occurs depends on temperature conditions.

#### Figure 3: Hydrolysis and Condensation Reactions of Organofunctional Silanes

| Hydrolysis:   |
|---|
| Y-R-Si(OCH <sub>3</sub> ) <sub>3</sub> $\xrightarrow{H_2O}$ Y-R-Si(OH) <sub>3</sub> + 3 CH <sub>3</sub> OH    |
| Silanol Condensation on a Surface (Adhesion/Coupling):  |
| Y− R−Si(OH) <sub>3</sub> + HO−Si−Surface $\longrightarrow$ Y−R−Si−O−Si−Surface + H <sub>2</sub> O             |
| Condensation with Another Silane - (Crosslinking):  |
| 2 Polymer-Y-R-Si(OH) <sub>3</sub> $\longrightarrow$ Polymer-Y-R-Si-O-Si-R-Y-Polymer + H <sub>2</sub> O<br>I I |
|   |

The naturally occurring acidity or alkalinity of most inorganic surfaces is typically sufficient to catalyze silane hydrolysis. The adsorbed water found on these surfaces is generally adequate to complete hydrolysis of a Silquest silane.

#### Silanol Condensation on a Surface (Adhesion/Coupling)

When in the silanol state, the silane condenses with a mineral or substrate surface. This is the first step in the actual coupling process. The silane migrates to the surface, hydrolyzes, hydrogen bonds with the surface and upon release of water forms a direct covalent bond with the surface.

Condensation proceeds slowest at pH 4-5 and is catalyzed by both acids and bases. Each silicon atom possesses up to three hydrolyzable sites but it is unlikely that all three sites will bond with the surface. Many of the silanols that do not react with the surface condense with each other to form an Si-O-Si network on the substrate surface. To complete the adhesion process, the reactive functional group on the silane reacts with the resin or binder of the coating, adhesive or sealant.

## **...** Silane Condensation for Polymer Crosslinking

The most common method for silane crosslinking involves attachment of the silane to a polymer backbone through reaction with the "Y" group. This "silylation" process can involve co-polymerizing the functional group on a methacrylate silane during the production of an acrylic co-polymer, end-capping of a polyurethane with amino or mercapto silanes, or capping polyols with isocyanato silanes.

## Introducing Silquest and Other Momentive Silanes into Polymer-based Systems

There are basically four ways to use a silane in a polymer matrix.

- primer (surface pre-treatment)
- polymer modification
- filler pre-treatment
- integral blending

The optimum method is governed by the benefits sought, variables of the chemistry, nature of the application and cost. Like any moisture-reactive components, silane reaction rates depend on availability of water, the moisture diffusion rate, pH, catalysts and the resins, overall hydrophobicity.

#### Primer (Surface Pre-treatment)

Silane coupling agents have been shown to be effective additives when used as primers for paints, inks, coatings, adhesives and sealants. As a primer, the silane coupling agent is applied to the inorganic substrate before the product to be adhered is applied. In this case, the silane is in the optimum position (in the interphase region), where it can be most effective as an adhesion promoter.

Silane primers typically are applied as "wash" coats very thin layers with no "body". A simple primer formulation is given in Table 1. Primers may contain more than one silane. A small amount of water is added to hydrolyze the silane and bring it into its active state. Often an alcohol is used to help minimize silane condensation prior to use of the primer. The primer can be applied by spraying, dipping or brushing. It is dried before application of the resin at 100-125°C for 10-60 minutes, which helps to complete the reaction with the surface prior to application of the resin. Some applications require only room temperature drying.

#### **Example Silguest Silane Primer Recipe**

| Ingredient              | Parts by Weight |
|-------------------------|-----------------|
| Organofunctional silane | 5               |
| SDA - alcohol           | 40              |
| Distilled water         | 5               |
| Xylene                  | 40              |
| n-butanol               | 5               |
| 2-butoxyethanol         | 4               |

Product formulations are included as illustrative examples only. Momentive makes no representation or warranty of any kind with respect to any such formulations, including, without limitation, concerning the efficacy or safety of any product manufactured using such formulations

Primers are useful for determining Silquest silane efficiency on a surface without interference from other components in the total formulation. Primers generally offer excellent adhesion in coatings. They require extra steps, labor and care. Creating a primer is an effective method to determine which silane provides the best performance.

## Polymer Modification

The functional group of a silane can be used to silvlate polymers by grafting, endcapping or co-polymerization. This can be accomplished with most polymers: acrylics, polyesters, epoxies, urethanes, polyolefins, etc.

Silvlated copolymers offer coupling and crosslinking reactions through the grafted silicon group, without requiring high temperature cure. The result is a moisture-cured, self-crosslinking polymer generally

curable at room temperature. Crosslinking typically gives significant improvements in polymer properties including:

- Durability
- □ Water and chemical resistance
- □ Higher tensile strength and elongation
- □ Tear and crack resistance
- □ Toughness and abrasion resistance
- □ Thermal stability
- □ Creep resistance

Additional silane may be added to the formulation for improved end-use properties.

#### Filler Pre-treatment

Silanes can be used to pre-treat fillers. The method involves adding silanes to the filler, and then blending and mixing the mixture to disperse the silane over the filler surface. Surfactants or solvents can be used to disperse the silane. Various types of mixing equipment are available, which are designed to mix liquids with solids. V-shell blenders, ribbon blenders, roll mills and Herschel blenders are examples of suitable mixing equipment. A mild heat treatment is often employed to remove the solvents if used and the alcohol of hydrolysis.

#### Integral Blending

Integral blending can be the easiest method for using Momentive's silanes because it avoids a separate polymer modification or surface pre-treatment step.

Silguest silanes can be mixed, by any convenient method with the polymer component of most formulations. For good dispersion of the small amount of silane typically involved, it is advisable to prepare a pre-dispersion with a high silane concentration to add to the bulk of the polymer. In solvent-containing systems, the silane can be pre-dispersed in a small amount of the solvent. In latex systems, it can be added to the coalescing solvent.

Because there is enough variety in Silguest silane functionalities, the silane should have reactivity with the resin, to make this possible. Figure 4 shows the adhesion obtained between an epoxy paint and aluminum metal using a mercapto and an amino silane. Generally, the biggest increase in adhesion was achieved after exposure to moisture or humidity.

#### Figure 4: Improved Wet and Dry Adhesion of **Epoxy Paint to Aluminum**



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| Thermoset Resins                             | Water Based Systems  | Non Aqueous Systems   |  |  |  |
|--|--|---|--|--|--|
| Acrylics with carboxyl or<br>hydroxyl groups | CoatOSil* MP 200, Silquest A-187*, A-1871,<br>CoatOSil 2287, CoatOSil 1770           | Silquest A-1100*, A-1110, A-1120,<br>A-Link* 15, A-Link 35, A-Link 25   |  |  |  |
| Ероху  | Silquest A-187, A-1871, CoatOSil MP 200,<br>CoatOSil 2287, Silquest* VS 142 (A-1106) | Silquest A-187, A-1100, A-1110, A-1120,<br>A-Link 15, CoatOSil MP 200   |  |  |  |
| Melamine                                     | Silquest VS 142 (A-1106), A-1524   | Silquest A-1100, A-1110, A-1120, A-1524   |  |  |  |
| Phenolic                                     | Silquest VS 142 (A-1106), A-1524, A-187  | Silquest A-1100, A-1110, A-1120, A-1524   |  |  |  |
| Unsaturated polyesters                       | n.a.   | Silquest A-174*NT, A-178  |  |  |  |
| SPUR <sup>+*</sup> prepolymers               | n.a.   | Silquest A-1100, A-1110, A-1120,<br>A-Link 15, VX 225, Y-15744, A-Link 597  |  |  |  |
| Polysulfide                                  | n.a.   | Silquest A-187, CoatOSil MP 200   |  |  |  |
| Polyurethanes                                | CoatOSil MP 200, Silquest A-187, A-1871,<br>CoatOSil 2287, CoatOSil 1770             | 1K Silquest A-187, A-1524<br>2K Silquest A-1100, A-1170, A-Link 15  |  |  |  |
| Silicone                                     | n.a.   | Addition cure; Silquest A-171*, A-151NT<br>Condensation cure; Silquest A-1100,<br>A-1110, A-1120, A-Link 15, VX 225,<br>Y-15744, A-Link 597 |  |  |  |

## **Reactive Resin Grid**

## **Thermoplastic and Elastomer Grid**

| Thermoplastic Resins | Silquest Silane  |
|----------------------|--|
| Polyamide            | Silquest A-187, A-1100, A-1110, A-1120, A-Link 15, CoatOSil MP 200 |
| Polyester            | Silquest A-1100, A-1110, A-1120, A-1524, Silquest A-186            |
| Polyolefin           | Silquest A-171, A-151NT, A-137                                     |
| PVC / PVB            | Silquest A-1100, A-1110, A-1120, A-1524, Silquest A-186            |
|                      |  |
| Elastomers           | Silquest Silane  |
| Butyl                | Silquest A-174NT, A-178. A-189, A-Link 599                         |
| Neoprene             | Silquest A-189, A-Link 599   |
| Nitrile              | Silquest A-187, A-189, CoatOSil MP 200, A-Link 599                 |
| Silicone             | Silquest A-171, A-151NT, A-174                                     |
| SBR                  | Silquest A-1100, A-1110, A-1120, A-1189, A-Link 599                |



**Decision Tree for SB or HS Systems** 

Integral blend modification (IL Polymer modification (PM)

Each Polymer and Curing technology may have one or several silane possibility for integral blend modification or polymer synthesis

## **Decision Tree for WB Systems**



Each Polymer and Curing technology may have one or several silane possibility for integral blend modification or polymer synthesis

## **Crosslinking Polyethylene with Silquest and Other Momentive Silanes**

Polyethylene has been crosslinked for many years by a number of proven methods. The initial goal was to extend the maximum service temperature. Crosslinking of polymers can deliver many important potential advantages to thermoplastic polymers such as polyethylene and PVC. The typical benefits include:

- Improved temperature stability [long-term service temperature (XLPE = 90°C) and short-time peak temperature (XLPE up to 250°C)]
- Increased aging properties
- Reduced drip phenomena when burning
- Reduced deformation under load, improved creep, and for pipe, improved stress rupture performance
- Improved chemical resistance (e.g., against solvents)
- Increased abrasion resistance
- Memory effect for shrink tubing, shrink film and stretch wrap
- Improved flexural modulus and impact strength

## Momentive's Silane Selection Tree for Polymer Additives and Resins

#### Silane Selection Tree for One-Step, Monosil Process



XL-PEarl silane masterbatch grades are predominantly promoted in North and Latin America.

\*Silquest, XL-PEarl and Silcat are trademarks of Momentive Performmance Materials Inc.

## Silane Selection Tree for Two-Step, Siloplas Process



| Non Organo Reactive |   |  |             |  |  |  |  |  |  |
|---------------------|---|--|-------------|--|--|--|--|--|--|
| A-137               | Octyltriethoxysilane                            | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>   | 276.6       |  |  |  |  |  |  |
| A-162               | Methyltriethoxysilane                           | CH <sub>3</sub> Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>   | 178.3       |  |  |  |  |  |  |
| A-1230              | Proprietary nonionic silane dispersing agent    | _  | Proprietary |  |  |  |  |  |  |
| A-1630A             | Methyltrimethoxysilane                          | CH <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>   | 136.3       |  |  |  |  |  |  |
| A-Link 597          | tris-[3-(Trimethoxysilyl)propyl] isocyanurate   | _  | 615.4       |  |  |  |  |  |  |
| HDTMS               | Hexadecyltrimethoxysilane                       | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>  | 346.6       |  |  |  |  |  |  |
| Vinyl               |   |  |             |  |  |  |  |  |  |
| RC-1                | Coupling agent - proprietary                    | _  | _           |  |  |  |  |  |  |
| A-151NT             | Vinyltriethoxysilane                            | CH <sub>2</sub> =CHSi(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>  | 190.4       |  |  |  |  |  |  |
| A-171*              | Vinyltrimethoxysilane                           | CH <sub>2</sub> =CHSi(OCH <sub>3</sub> ) <sub>3</sub>  | 148.2       |  |  |  |  |  |  |
| A-172NT             | Vinyl- <i>tris</i> -(2-methoxyethoxy) silane    | CH2=CHSi(OCH2CH2OCH3)3   | 280.4       |  |  |  |  |  |  |
| e-free* 172         | Oligomeric vinyl silane                         | _  | 322.6       |  |  |  |  |  |  |
| G-170               | Oligomeric vinyl silane                         | _  | 277.5       |  |  |  |  |  |  |
| Methacryloxy        |   |  |             |  |  |  |  |  |  |
| A-174*NT            | gamma-methacryloxypropyltrimethoxysilane        | (CH <sub>3</sub> O) <sub>3</sub> Si  | 248.4       |  |  |  |  |  |  |
| A-178               | methacrylamido-silane                           | $CH_2 = \begin{array}{c} & \\ CH_2 = C \\ CH_3 \end{array} $   | 274.4       |  |  |  |  |  |  |
| Y-9936              | gamma-methacryloxypropyltriethoxysilane         | (CH <sub>3</sub> CH <sub>2</sub> O) <sub>3</sub> Si  | 290.43      |  |  |  |  |  |  |
| CoatOSil* 1757      | gamma-methacryloxypropyl-tris-(2-propoxy)silane | cryloxypropyl-tris-(2-propoxy)silane   |             |  |  |  |  |  |  |
| Epoxy               |   |  |             |  |  |  |  |  |  |
| A-186               | beta-(3,4-Epoxycyclohexyl)ethyltrimethoxysilane | 0  | 246.1       |  |  |  |  |  |  |
| CoatOSil 1770       | beta-(3,4-epoxycyclohexyl)ethyltriethoxysilane  | (CH <sub>3</sub> CH <sub>2</sub> O) <sub>3</sub> SiCH <sub>2</sub> CH <sub>2</sub>   | 288.1       |  |  |  |  |  |  |
| A-187*              | gamma-glycidoxypropyltrimethoxysilane           | 0<br>0CH2CH2CH2Si(OCH3)3   | 236.1       |  |  |  |  |  |  |
| A-1871              | gamma-glycidoxypropyltriethoxysilane            | Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>   | 278.1       |  |  |  |  |  |  |
| CoatOSil 2287       | 3-glycidoxypropylmethyldiethoxysilane           | 0<br>CH <sub>3</sub><br>I<br>Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>  | 248.4       |  |  |  |  |  |  |
| CoatOSil MP 200     | Epoxysilane oligomer                            | $\begin{array}{c} & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$ | _           |  |  |  |  |  |  |

Typical physical properties are based upon average data and are not to be used as product specifications.

\*Silquest, e-free, Silquest A-187, CoatOSil, A-Link, Silquest A-174 and Silquest A-171 are trademarks of Momentive Performance Materials Inc.

| Silo<br>or (<br>Mo<br>Sila | quest<br>Other<br>omentive<br>ane | Physical<br>Form<br>CL=Clear Liquid<br>L=Liquid | Viscosity<br>at 25°C,<br>cSt | Apparent<br>Specific<br>Gravity, 25°C | Refractive<br>Index,<br>25°C | Flash<br>Point<br>°C (°F | ,<br>-) | Boiling<br>Point,<br>°C | CAS #       | EINECS #    |
|----------------------------|-----------------------------------|---|------------------------------|---------------------------------------|------------------------------|--------------------------|---------|-------------------------|-------------|-------------|
| No                         | n Organo Read                     | ctive   |                              |                                       |                              |                          |         |                         |             |             |
| A-1                        | 37                                | CL  | _                            | 0.876                                 | _                            | 82                       | (180)   | 250 est.                | 2943-75-1   | 220-941-2   |
| A-1                        | 62                                | CL  | _                            | 0.915                                 | 1.382                        | 29                       | (85)    | 143                     | 2031-67-6   | 217-983-9   |
| A-1                        | 230                               | CL  | 37                           | 1.1                                   | _                            | 87                       | (190)   | >150                    | Proprietary | Proprietary |
| A-1                        | 630A                              | CL  | 0.50                         | 0.953                                 | 1.369                        | 12                       | (54)    | 101                     | 1185-55-3   | 214-685-0   |
| A-L                        | _ink 597                          | CL  | ~95                          | 1.170                                 | _                            | 102                      | (216)   | >250                    | 26115-70-8  | 247-465-8   |
| HD                         | TMS                               | CL  | _                            | 0.887                                 | _                            | 104                      | (219)   | >150                    | 16415-12-6  | 240-464-3   |
| Vin                        | ıyl                               |   |                              |                                       |                              |                          |         |                         |             |             |
| RC                         | -1                                | CL  | _                            | 0.950                                 | _                            | 47                       | (116)   | >160                    | Proprietary | Proprietary |
| A-1                        | 51NT                              | CL  | 0.70                         | 0.91                                  | 1.397                        | 44                       | (111)   | 160.5                   | 78-08-0     | 201-081-7   |
| A-1                        | 71*                               | CL  | _                            | 0.967                                 | 1.390                        | 28                       | (82)    | 123                     | 2768-02-7   | 220-449-8   |
| A-1                        | 72NT                              | CL  | 1-2                          | 1.03                                  | 1.427                        | 92                       | (198)   | 285                     | 1067-53-4   | 213-934-0   |
| e-fr                       | ree* 172                          | CL  | 600                          | 1.07                                  | _                            | >100                     | (220)   | 217                     | Proprietary | Proprietary |
| G-1                        | 170                               | CL  | 600                          | 1.07                                  | _                            | 104.4                    | (220)   | 216.7                   | Proprietary | Proprietary |
| Me                         | thacryloxy                        |   |                              |                                       |                              |                          |         |                         |             |             |
| A-1                        | 74*NT                             | CL  | 2                            | 1.045                                 | 1.429                        | 108                      | (226)   | 255                     | 2530-85-0   | 219-785-8   |
|                            |                                   |   |                              |                                       |                              |                          |         |                         |             |             |
| A-1                        | 78                                | L   | _                            | 1.02                                  | _                            | 101                      | (214)   | 322                     | Proprietary | _           |
| Y-9                        | 936                               | CL  | _                            | 0.986                                 | 1.4277                       | 116                      | (241)   | 78                      | 21142-29-0  |             |
|                            |                                   |   |                              |                                       |                              |                          |         |                         |             |             |
| Coa                        | atOSil* 1757                      | CL  | _                            | 0.938                                 | _                            | 59                       | (138)   | >200                    | 80750-05-6  | _           |
| Ep                         | оху                               |   |                              |                                       |                              |                          |         |                         |             |             |
| A-1                        | 86                                | CL  | 5                            | 1.065                                 | 1.448                        | 113                      | (235)   | 310                     | 3388-04-3   | 222-217-1   |
| Coa                        | atOSil 1770                       |   |                              | 1.004                                 |                              | 129                      | (264)   | >300                    | 10217-34-2  | 425-050-4   |
| A-1                        | 187*                              | CL  | 2.7 cSt @ 20°                | 1.07                                  | 1.427                        | 110                      | (230)   | 290                     | 2530-83-8   | 219-784-2   |
| A-1                        | 871                               | CL  | _                            | 1.003                                 | _                            | 118                      | (244)   | >300                    | 2602-34-8   | _           |
|                            |                                   |   |                              |                                       |                              |                          |         |                         |             |             |
| Coa                        | atOSil 2287                       | CL  | 3                            | 0.98                                  | 1.431                        | 104                      | (219)   | 290                     | 2897-60-1   | 220-780-8   |
|                            |                                   |   |                              |                                       |                              |                          |         |                         |             |             |
| Coa                        | atOSil MP 200                     | CL  | 30-40                        | 1.166                                 | _                            | 107                      | (225)   | 290                     | 68611-45-0  | _           |

Typical physical properties are based upon average data and are not to be used as product specifications.

\*Silquest, e-free, Silquest A-187, CoatOSil, A-Link, Silquest A-174 and Silquest A-171 are trademarks of Momentive Performance Materials Inc.

| Silquest<br>or Other<br>Momentive<br>Silane | Chemical Name  | Formula   | Formula<br>Molecular<br>Weight |
|---|--|---|--------------------------------|
| Sulfur                                      |  |   |                                |
| A-189                                       | gamma-mercaptopropyltrimethoxysilane                       | HSCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>  | 196.4                          |
| A-1891                                      | gamma-mercaptopropyltriethoxysilane                        | HSCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>  | 238.4                          |
| A-Link* 599                                 | 3-octanoylthio-1-propyltriethoxysilane                     | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> C(=O)SCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>  | 364.6                          |
| e-free* 189                                 | Oligomer mercaptosilane                                    | -   | 370.6                          |
| NXT*  | 3-octanoylthio-1-propyltriethoxysilane                     | CH3(CH2)6 S -CH2CH2CH2SI(OCH2CH3)3  | 364.6                          |
| NXT Low V                                   | 3-octanoylthio-1-propylalkoxysilane                        | $\begin{array}{c} 0\\ CH_3(CH_2)_6\end{array} \xrightarrow{C} S \xrightarrow{CH_2CH_2CH_2CH_2Si} O \xrightarrow{CH_2} CH_2\\ 0\\ CH_2CH_2CH_2CH_2Si} \xrightarrow{CH_2} CH_2\\ 0\\ 0\\ CH_2CH_3\end{array}$ | _                              |
| Amino                                       |  |   |                                |
| A-1100*                                     | gamma-Aminopropyltriethoxysilane                           | $H_2NCH_2CH_2CH_2Si(OCH_2CH_3)_3$   | 221.4                          |
| A-1102                                      | gamma-Aminopropyltriethoxysilane (Technical Grade)         | $\mathrm{H_2NCH_2CH_2CH_2Si(OCH_2CH_3)_3}$  | 221.4                          |
| A-1106                                      | gamma-Aminopropylsilsesquioxane (aqueous solution)         | (H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SiO <sub>1.5</sub> )n  | Oligomer                       |
| A-1110                                      | gamma-Aminopropyltrimethoxysilane                          | $H_2NCH_2CH_2CH_2Si(OCH_3)_3$   | 179.3                          |
| A-1120                                      | N-beta-(Aminoethyl)-gamma-aminopropyltrimethoxysilane      | H2NCH2CH2NHCH2CH2CH2Si(OCH3)3   | 222.4                          |
| A-1128                                      | Benzylamino-silane (50% in methanol)                       |   | _                              |
| A-1130                                      | Triaminofunctional silane                                  | H2NCH2CH2NHCH2CH2NHCH2CH2CH2Si(OCH3)3   | 265.4                          |
| Y-11699                                     | bis-(gamma-Triethoxysilylpropyl)amine                      | $NH[CH_2CH_2CH_2Si(OCH_2CH_3)_3]_2$   | 383.5                          |
| A-1170                                      | bis-(gamma-Trimethoxysilylpropyl)amine                     | <pre>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)3</pre>   | 342.6                          |
|   |  | H-N   |                                |
| Δ_1387                                      | Polyazamide (50% actives in methanol)                      |   | _                              |
| A-1001                                      | r olyazamide (50% actives in methanol)                     |   |                                |
| Y-19139                                     | Ethoxy based Polyazamide (50% in ethanol)                  | $\begin{array}{c c} H_2 N + H - N - H - H - H - H - H - H - H - H -$  | _                              |
| A-2120                                      | N-beta-(Aminoethyl)-gamma-aminopropylmethyldimethoxysilane | H2NCH2CH2NHCH2CH2CH2SiCH3(OCH3)2  | 206.4                          |
| A-Link 15                                   | N-Ethyl-3-trimethoxysilyl-methylpropamine                  | H<br>N<br>Si(OCH <sub>3</sub> )   | 222.1                          |
| VX 225                                      | Amino-functional oligosiloxane                             | _   | _                              |
| Y-15744                                     | Amino-functional oligosiloxane                             |   |                                |
| Ureido                                      |  | 0   |                                |
| A-1160                                      | gamma-Ureidopropyltrialkoxysilane (50% in methanol)        | іі<br>H <sub>2</sub> NCNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si(OCH <sub>3</sub> ) <sub>X</sub> (OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3-х</sub><br>О   | Mixture                        |
| A-1524                                      | gamma-Ureidopropyltrimethoxysilane                         | II<br>H <sub>2</sub> N CNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>  | 222.4                          |
| Isocyanate                                  |  |   |                                |
| A-Link 25                                   | gamma-Isocyanatopropyltriethoxysilane                      | O=C=NCH2CH2CH2Si(OCH2CH3)3  | 247.3                          |
| A-Link 35                                   | gamma-lsocyanatopropyltrimethoxysilane                     | $O=C=NCH_2CH_2CH_2Si(OCH_3)_3$  | 205.2                          |

Typical physical properties are based upon average data and are not to be used as product specifications.

\*Silquest, e-free, A-Link, NXT, and Silquest A-1100 are trademarks of Momentive Performance Materials Inc.

| Silquest<br>or Other<br>Momentive<br>Silane | Physical<br>Form<br>CL=Clear Liquid<br>L=Liquid | Viscosity<br>at 25°C,<br>cSt | Apparent<br>Specific<br>Gravity, 25°C | Refractive<br>Index,<br>25°C | Fla<br>Po<br>°C ( | ash<br>vint,<br>°F) | Boiling<br>Point,<br>°C   | CAS #       | EINECS #    |
|---|---|------------------------------|---------------------------------------|------------------------------|-------------------|---------------------|---------------------------|-------------|-------------|
| Sulfur                                      |   |                              |                                       |                              |                   |                     |                           |             |             |
| A-189                                       | CL  | _                            | 1.0500                                | 1.440                        | 88                | (190)               | 212                       | 4420-74-0   | 224-588-5   |
| A-1891                                      | CL  | _                            | 0.990                                 |                              | 88                | (190)               | 240                       | 14814-09-6  | _           |
| A-Link 599                                  | CL  | _                            | 0.968                                 | _                            | 110               | (230)               | >400                      | 220727-26-4 | 436-690-9   |
| e-free* 189                                 | CL  | _                            | _                                     | _                            | 110               | (230)               | 227                       | Proprietary | _           |
|   |   |                              |                                       |                              |                   | ( )                 |                           |             |             |
| NXT*  | CL  | -                            | 0.968                                 | -                            | 110               | (230)               | >400                      | 220727-26-4 | 436-690-9   |
| NXT Low V                                   | L   | _                            | 1.04                                  | _                            | >100              | (212)               | >400                      | 676319-97-4 | _           |
| <br>Amino                                   |   |                              |                                       |                              |                   |                     |                           |             |             |
| A-1100*                                     | CI  | 2                            | 0.950                                 | 1 420                        | 93                | (144)               | 220                       | 919-30-2    | 213-048-4   |
| A-1102                                      | CL  | _                            | 0.950                                 | _                            | 49                | (120)               | 217                       | 919-30-2    | 213-048-4   |
| A-1106                                      | CL  | 4                            | 1.076                                 | _                            | 100               | (>212)              | >100                      | 58160-99-9  | 261-145-5   |
| A-1110                                      | CL  | 2 cSt                        | 1.014                                 | _                            | 82                | (180)               | 210                       | 13822-56-5  | 237-511-5   |
| A-1120                                      | CL  | 6                            | 1.030                                 | 1.448                        | 138               | (280)               | 259                       | 1760-24-3   | 212-164-2   |
|   |   |                              |                                       |                              |                   |                     |                           |             |             |
| A-1128                                      | CL  | _                            | 0.942                                 | _                            | 9                 | (48)                | >65                       | 42965-91-3  | 256-023-3   |
| A-1130                                      | CL  | _                            | 1.030                                 | _                            | 125               | (257)               | >250                      | 35141-30-1  | 252-390-9   |
| Y-11699                                     | CL  | _                            | 0.968                                 | _                            | 141               | (285)               | >150                      | 13497-18-2  | _           |
| A 1170                                      | CL  |                              | 1.05                                  |                              | 112               | (225)               | 152 (+ 0.4 mm) (+)        | 82085 35 1  | 280 084 5   |
| A-1170                                      | OL  | _                            | 1.00                                  | _                            | 110               | (200)               | 1 <b>JZ</b> (at 0.4 mmHg) | 02900-00-1  | 200-004-0   |
| A-1387                                      | CL  | _                            | 0.969                                 | _                            | 8                 | (46)                | >65                       | Proprietary | _           |
| Y-19139                                     | CL  | <100 cStk                    | 0.949                                 | _                            | 14 es             | t. (61)             | 78                        | Proprietary | Proprietary |
|   |   |                              |                                       |                              |                   | . ,                 |                           |             | , ,         |
|   |   |                              |                                       |                              |                   |                     |                           |             |             |
| A-2120                                      | CL  | _                            | 0.980                                 | _                            | >93               | (>200)              | 85 (at 0.8 mmHg)          | 3069-29-2   | 221-336-6   |
| A-Link 15                                   |   |                              | 0.954                                 |                              | 92                | (148)               | >217                      | 227085-51-0 |             |
| VX 225                                      | CL  | _                            | 0.990                                 | _                            | 80                | 176                 | 266                       | 749886-39-3 |             |
| Y-15744                                     |   |                              |                                       |                              |                   |                     |                           |             |             |
| Ureido                                      |   |                              |                                       |                              |                   |                     |                           |             |             |
| A-1160                                      | CL  | 2.2                          | 0.920                                 | 1.386                        | 14                | (57)                | >65                       | 116912-64-2 | _           |
|   |   |                              |                                       | '                            |                   | ()                  |                           |             |             |
| A-1524                                      | CL  | _                            | 1.150                                 | 1.386                        | 99                | (210)               | 217                       | 23843-64-3  | 245-904-8   |
| Isocyanate                                  |   |                              |                                       |                              |                   |                     |                           |             |             |
| A-Link 25                                   | CL  | 1.5                          | 0.999                                 | 1.420                        | 77                | (171)               | 238                       | 24801-88-5  | 246-467-6   |
| A-Link 35                                   | CL  | 1.4                          | 1.073                                 | 1.420                        | 99                | (210)               | >200                      | 15396-00-6  | 239-415-9   |

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\*Silquest, e-free, A-Link, NXT, and Silquest A-1100 are trademarks of Momentive Performance Materials Inc. Page 13 of 24

## **Tips For Success With Silanes**

#### **General Tips**

- For good dispersion of silanes in solvents or polymerbased formulations, the unhydrolyzed silane should be mixed well. Intensive agitation and dilution solvent are recommended. pH should be controlled prior to adding silanes to water, and adjusted as necessary throughout the process.
- Since silanes hydrolyze in the presence of water, containers should be kept tightly sealed.
- Ambient humidity is often sufficient for silanes to hydrolyze and to activate silanes for subsequent condensation.
- Hydrolysis is not immediate. To ensure a complete reaction, silanes should be allowed to react for 10-20 minutes at a pH of 4.5.

#### Tips for Water-Based Systems

- Some silanes are not water-soluble. However, when hydrolyzed, silanes are converted to silanols, which are typically water soluble.
- For most silanes, high concentrations in solutions are not possible because competitive condensation results in oligomerization and precipitation. For many silanes, stable solutions can be obtained at concentrations not exceeding 5 to 8%.
- Hydrolysis is ideally run under acidic or basic conditions. Silanes hydrolyze slowly in neutral water. Acid hydrolysis at pH 4-6 in diluted solutions generally optimizes hydrolysis of most silanes (except aminosilanes) without premature formation of oligomers and insoluble polymers.
- Condensation of hydrolyzed silanes is slowest at slightly acidic pH, and the rate is accelerated at elevated temperatures.

## **Tips for Solid Surfaces**

When reacting silanes with hydroxylated surfaces, surface pH and catalytic activity are important parameters. Neutral surfaces (quartz, silica, mica) react slowly. Acidic surfaces (such as kaolin) clays and basic surfaces (glass, aluminum, hydroxide, magnesium hydroxides) react quickly. Solid surfaces at standard atmospheric conditions absorbed enough moisture to promote the reaction without additional water.

## **Reactive Mineral Chart**



The above chart demonstrates typical silane effectiveness with various minerals.

## **Basic Guidelines for Handling Momentive Silanes**

Organofunctional silanes are highly reactive materials, requiring special handling precautions for safe use. As the world's leading supplier of high quality organofunctional silanes, Momentive Performance Materials is presenting the following information to customers as part of our continuing effort and commitment to Product Stewardship. This document contains general safety guidelines only and should in no way be viewed as a substitute for your exercise of all appropriate safety measures. The information contained herein applies only to Momentive's products. Competitive materials may not necessarily be chemical equivalents and, as such, may pose different safety issues and hazards.

#### **Purpose of this document**

This document is intended to provide an overview of the special safety issues and resultant storage and use considerations for organofunctional silanes. **This document is not intended to replace, or act as a substitute for, the material safety data sheet** (MSDS), or to identify all generally accepted industry standards for chemical handling that may be relevant to the use of all potentially hazardous chemicals. Accordingly, Momentive Performance Materials recommends that all laboratory and manufacturing/operations personnel who use or handle organofunctional silanes be well acquainted with the MSDS and other company literature for each specific silane, and also appropriate industry safety practices and standards for chemical management.

If further background is needed regarding the toxicology, safe use, or handling of Momentive Performance Materials organo-functional silanes, we recommend calling our Product Safety and Regulatory Affairs group at 800.295.2392.

#### **Process Safety Reviews and Inspections**

Before using organofunctional silanes at your location, a thorough safety review of all equipment and operational facilities should be conducted. Aspects of facility electrical/hazard classification, equipment operation, operational procedures, personal protective equipment, personnel training, fire safety, emergency equipment, emergency procedures and disposal issues, etc., should be covered in these reviews. Periodic safety inspections are important in maintaining safe operations and should be conducted as deemed appropriate.

#### **Understanding the Reactivity of Silanes**

The reactivity of each specific silane is outlined in its MSDS in Section 10, subtitled "Stability and Reactivity." However, reactions that are common to all alkoxy silanes [silanes which contain groups such as methoxy-, ethoxy-, or isopropoxy- attached to the silicon atom(s)] include hydrolysis and condensation, as described below. In addition to hydrolysis and condensation, each organo-functionality imparts its own specific reactivity characteristics. Momentive Performance Materials manufactures a wide variety of organofunctional silanes, each tailored with different reactivity characteristics. A discussion of each silane with its unique reactivity is beyond the scope of this document. The following overview provides basic input on alkoxy silane group covering hydrolysis, condensation, moisture hydrolyzate reaction and organofunctional group reaction.

#### **The Alkoxy Silane Group:**

#### Hydrolysis/Condensation and Liberation of Alcohol

Organofunctional alkoxy silanes, by nature, react with water (hydrolyze) from humid air, or from water contamination that may occur from hydrous chemicals in wet equipment. Hydrolysis and condensation are necessary for organofunctional silanes to work effectively. However, premature hydrolysis that occurs as a result of careless handling or moisture contamination will reduce product quality, possibly resulting in reduced downstream performance. Therefore, it is important to keep silanes free from moisture contamination throughout storage.

Amino-functional alkoxysilanes are readily soluble in water and hydrolyze very rapidly with noticeable heat generation (exotherm) and the liberation of alcohol. Other silanes hydrolyze more slowly depending upon the functional group, of the specific alkoxy group attached to silicon, the product's solubility in water, and the pH of the water. Upon hydrolysis, the alkoxy groups of all alkoxysilanes [most typically in the form of "methoxy" (-OCH<sub>3</sub>) or "ethoxy" (-OCH<sub>2</sub>CH<sub>3</sub>)] are liberated as the corresponding alcohol (methanol or ethanol, respectively). The amount of alcohol liberated upon hydrolysis can be as high as 70% by weight of the initial silane charge. During hydrolysis, the resulting silane is converted to a silanol (-Si-OH) group. The formation of silanol is key to the function of silane coupling or crosslinking with themselves. Within a short period of time, silanols condense with other silanols and hydroxylated substrates to form siloxanes and silicate-like structures (-Si-O-Si- or -Si-O-[metal atom]). This reaction is referred to as the "condensation" of silanols. The liberation of alcohol from alkoxysilane hydrolysis has an impact on flammability, personnel exposure, worker exposure issues:

a) Flammability: The flammability of the resulting silane mixture will increase following hydrolysis according to the amount of water present. In the simplest case, the flash point of an alkoxysilane is reduced significantly following moisture contamination. With an intentional hydrolysis step during which most of the alcohol by-product is released, an explosive mixture could develop within equipment headspaces assuming sufficient oxygen (air) is present.

b) Worker Exposure: For methoxy-silane hydrolysis, by-product methanol is toxic and can be absorbed through the skin. In addition, the OSHA and ACGIH occupational exposure limit for methanol by inhalation is 200 ppm TWA. For ethoxy- silanes, ethanol is liberated upon hydrolysis. Although ethanol is significantly less toxic than methanol, the MSDS carries the associated warnings appropriate for ethanol exposure. For either methoxy or ethoxy silane esters, additional effects would be observed based on the specific organofunctionality of each silane product.

## The Alkoxy Silane Group: Adventitious Moisture

A nuisance in handling some alkoxysilanes is the undesirable formation of hydrolyzate, or build-up of solids due to premature hydrolysis and condensation of the product. Silane hydrolyzate may appear crystalline or gummy depending upon the original silane and hydrolysis conditions. The solids are actually condensed, crosslinked amorphous polymers of the silane. A typical problem in handling laboratory quantities of alkoxysilanes is the opening of sealed bottles if the caps appear 'frozen'. Leather gloves and extra precautions are recommended when opening glass containers of organofunctional silanes.

Silane hydrolyzate is avoidable or can be minimized with the proper use of a dry nitrogen purge, desiccants, and solvent flushing of equipment and lines.

Hydrolysis and condensation reactions and kinetics for organofunctional silanes have been reviewed by F. D. Osterholtz and E. R. Pohl,<sup>(1)</sup> of Momentive Performance Materials.

## Organofunctional Chemistry Considerations: Reactivity

The organofunctional group of the silane molecule materials is designed to react/interact with organic materials, as for example, in polymeric resins or with polymerizable organic media. The silane is matched with the organic/polymeric matrix to maximize the compatibility and effectiveness for optimum coupling and product performance. The reactivity of crosslinking at the functional end of the silane varies among silanes. Therefore, refer to the MSDS, Section 10 ("Stability and Reactivity") for warnings of incompatibility and specific conditions to avoid.

#### The Organofunctional Group: Methacryloxy Functionality

An organofunctional silane may be susceptible to polymerization and may require extra care during temporary and longer term storage. The polymerization potential is described within the MSDS (Section 10).

In order to prevent unwanted polymerization, certain contaminants must be avoided with methacryloxysilanes (*e.g.*, Silquest A-174\*NT and Silquest Y-9936 silanes, CoatOSil\* 1757 silane). Peroxides and other free radical initiators, oxidants, reducing agents, and transition metal salts or their oxides (even rust) should be avoided. Avoid direct exposure to UV light and excessive heat. Follow storage and handling procedures as dictated in standard vinyl ester and acrylate/methacrylate ester product safety brochures. Do not attempt to remove polymerization inhibitors or treat these products with adsorption media that could lower the concentration of contained inhibitors.

The presence of dissolved oxygen is important in maintaining the stability of methacrylate silanes. Therefore, for methacryloxy-silanes, **do not** purge the headspace of drums or storage containers or sparge the liquid with an inert gas such as pure nitrogen, unless the storage period is very short and at, or below, ambient temperature.

## The Organofunctional Group: Vinyl Silane Reactivity

The potential exists for self-heating reactions of vinyl silanes, especially at elevated temperatures and if peroxides or other free radical initiators are present. Examples of vinyl silanes are Silquest A-151NT, Silquest A-171\*, e-free\* 172 and Silquest G-170 silanes. Follow the precautions specified in the MSDS.

## The Organofunctional Group: Vinyl Silane/Peroxide Blends

The Momentive Performance Materials silanes portfolio includes a series of vinyl silane/peroxide blends (*e.g.*, Silcat\* and XL-PEarl\* blends) available for a number of specific applications. These blends are prepared under carefully controlled conditions in order to prevent runaway reactions. Most simple vinyl silane/peroxide blends have the potential to undergo uncontrolled self-accelerating decomposition (SADT) reaction if heated beyond moderate temperatures (*i.e.*, the SADT may be as low as 50°C/122°F).

SADT Definition (summarized): A self-accelerating decompositon temperature is the lowest ambient air temperature at which a self-reactive substance underwent (or is predicted to have undergone) an exothermic reaction, in a specified commercial package, within a period of seven days or less, from which the container was damaged excessively.

The SADT is the basis for deciding whether a selfreactive substance should be subject to temperature control during transport. The SADT value of a reactive liquid within a container is inversely proportional to the total mass (a larger container has a lower SADT). It is also highly dependent on the configuration and heat transfer properties of the container. The SADT is therefore container-specific. For this reason and because of DOT restrictions, Momentive Performance Materials generally does not supply vinyl silane/ peroxide blends in containers larger than drum size. As a result. Momentive Performance Materials cautions against storing most vinyl silane/peroxide blends in guantities larger than one drum. Likewise, Momentive Performance Materials recommends extra caution to those customers who choose to do their own silane blending with peroxides or other polymerization agents. For a vinvl silane/peroxide blend sold by Momentive Performance Materials, the SADT specifications for the container in which it is sold has been determined to be no lower than 60°C (the legal limit is 50°C).

### The Organofunctional Group: Epoxy Silane Reactivity

CoatOSil MP 200, Silquest A-186, Silquest A-187\*, Silquest A-1871, CoatOSil 1770, and CoatOSil 2287 silanes are common epoxy-functional silanes which have reactivities similar to epoxy monomers. Hydrolysis can occur at both the silyl ester group as well as the epoxy group. Epoxy ring opening can occur when exposed to contaminants such as acids and bases, amines, and ionic chloride. Silquest A-186 silane and CoatOSil 1770 silane are more prone to acid catalyzed ring opening; Silquest A-187, Silquest A-1871 and CoatOSil 2287 silanes are susceptible to base catalyzed ring opening. Polymerization can occur depending upon the specific reagents and conditions. Generally, product degradation or shelf life concerns are not significant provided care is taken to avoid product contamination.

Polysiloxanes are produced by hydrolysis and condensation of the silyl ester group in the presence of controlled amounts of water and alkali or acid catalyst at ambient temperatures. At slightly higher temperatures (~50°C), polyglycols or polyglycol ethers are produced via the epoxy functional group under the same conditions of water concentration and alkali or acid catalyst.

These reactions are exothermic. Furthermore, the heat evolved may be cumulative and greatly accelerate the rate of continued reactions.

*Note:* It is imperative, therefore, that unintentional contamination of the epoxysilanes with water be avoided, and that intentional hydrolysis be properly controlled to avoid hazardous conditions.

#### The Organofunctional Group: Amino Silane Reactivity

Silquest A-1100\*, Silquest A-1102, Silquest A-1110, Silquest A-1120, Silquest A-1130, Silquest A-1170 silanes are common examples of aminofunctional silanes. Aminosilanes are unique in that the rate of hydrolysis is rapid without pH adjustment of the water used in the aqueous premixes. Therefore, aminosilanes are readily soluble in water and the subsequent hydrolysis occurs almost instantaneously. When hydrolysis occurs with these silanes, heat may be noticeable and the alcohol by-product is rapidly generated (methanol or ethanol, depending upon whether the silane contains methoxy- or ethoxy- substituents on the silicon atom).

*Note:* Certain weight ratios of silane and water can lead to the generation of enough heat that the mixture may boil, thereby liberating significant amounts of alcohol.

Due to the inherent affinity of amino-functional silanes with water, extra care should be taken to ensure that moisture contamination does not occur within original containers and temporary storage tanks prior to their intended use. Unintentional water contamination can lead to gels or solids which can cause plugging of equipment and lines. Therefore, nitrogen blanketing and purging of equipment and containers is strongly encouraged for eliminating equipment fouling and for maintaining the integrity of these silanes.

#### **Organofunctional Silanes Manufacturing and Operation Considerations**

#### Flammability Considerations: Specialty Blending and Mixing Operations

Blenders, mixers, and compounding operations may present varying inherent hazards when introducing silanes. In addition to the mechanical hazards associated with mixing units, there are recommended precautionary steps to avoid flammable atmospheres during or following the mixing of silanes with other chemicals, solvents, polymers, mineral fillers, or inorganic substrates.

Operations personnel should be aware of the inherent generation of free alcohol when organofunctional silanes are exposed to water or moisture. Hydrolysis is an inherent characteristic of silanes, and in most applications is intended for the optimum performance of the silane. As noted earlier, hydrolysis occurs when alkoxysilanes react with free water. The water may be 1) a separate ingredient within the mixture, or 2) atmospheric moisture, or 3) present on the surface of the inorganic filler, such as the clay, calcium carbonate, silica, etc. This reaction involves the conversion of alkoxysilanes to silanols and is a necessary step in promoting the chemical bonding of the silane to inorganic substrates. Most silanes will liberate either methanol or ethanol during the intentional silane coupling process in which inorganic fillers are bonded to a polymeric resin. The potential, therefore, exists for flammable vapors to develop within or around mixing units, unless adequate precautions are taken to exclude oxygen and ignition sources. Explosion of air/vapor mixtures can result.

#### The Alkoxy Silane Group: Avoiding Hydrolyzate Formation

a) Use of Desiccants: To avoid premature hydrolysis of silanes during storage and use, desiccants can be utilized. Various disposable desiccating units are currently available from independent distributors and chemical supply companies.

## b) Use of an Inert Gas (e.g., dry nitrogen):

The use of dry nitrogen to blanket the headspaces of silane drums and storage vessels is advantageous for maintaining silane integrity and for minimizing handling problems caused by silane hydrolyzate.

**Exception:** Do not blanket or purge methacryloxysilanes with pure nitrogen since oxygen necessary for stabilization would be removed – see discussion below entitled "Dissolved Oxygen Requirement."

**Note:** Do not pressurize drums or other non-rated vessels/containers with nitrogen or any other gas; the container could rupture. Nitrogen gas can be dangerous due to the displacement of oxygen in the work area, which can potentially cause asphyxiation. In any operating area where nitrogen is used, adequate ventilation must be ensured. The atmosphere of the work area should be checked periodically to be certain adequate oxygen is present. Be aware of potential "confined spaces" and use proper testing and entry procedures, if applicable.

## c) Solvent Flushing Techniques:

Hydrolyzate build-up can be a particular problem at equipment nozzles and valves, and in transfer lines, pipes and tubing. Lines, valves and nozzles should be dry and pre-purged with nitrogen before introducing silanes. The appropriate solvent should be used to flush equipment after shutting down a processing line or operation. Selection of solvent is important. It should be non-reactive, free from water contamination, and compatible with the specific process.

#### **Static**

Often, static can be generated in mixing vessels and compounding operations. Although all mechanical equipment should be properly grounded, static discharges may not be completely eliminated, especially in certain intensive mixing operations. Another consideration is the conductivity of the medium being mixed. Since the fuel source (alcohol) and an ignition source (static) might be unavoidable in some cases, the only controllable factor is the elimination of oxygen. The blanketing of mixing and compounding units with an inert gas, such as nitrogen, is one of the most effective options in the removal of the remaining (third) side of the "fire triangle" (see "Grounding and Purging...").

EPDM, a non-polar rubber compound, is particularly prone to the generation of static sparks, especially during compounding. This is often the case when a Banbury mixer (or equivalent) is undercharged, which is sometimes standard procedure in second stage mix cycles. Wire- and cable-grade EPDM compositions often generate static sparks during compounding because they typically contain low levels of plasticizing oils and use calcined (anhydrous) clays.

# Grounding and Purging of Silanes Drums and Pails

To minimize flammability potential during transfer, mixing, compounding, and blending operations, all equipment and tanks should be properly grounded. Grounds should be periodically tested for electrical continuity. Purge and blanket all mixing, compounding, blending, and storage units and vessels with an inert gas, such as dry nitrogen, to reduce the oxygen concentration to a safe level prior to the addition of silane. The inert blanketing should be maintained throughout the entire operation and storage. As described earlier, inerting also helps to maintain a moisture-free atmosphere, and thus helps to ensure the quality of the product. This is especially true with aminofunctional silanes that hydrolyze rapidly in the presence of moist air.

**Note:** An exception to the purging/inert blanketing requirement is the (meth)acrylate functional silane group, including Silquest A-174\*NT silane, Silquest Y-9936 silane, CoatOSil\* 1757 silane or any other methacryloxy silane (see MSDS for compositional information). The inhibitors in these silanes require the presence of oxygen to help retard premature polymerization. Therefore, these silanes should be maintained with a headspace of dry 3% oxygen in nitrogen, rather than pure nitrogen.

**To minimize oxidation:** In addition to reducing flammability concerns, inert blanketing also helps reduce air oxidation that can lead to color formation, especially with the aminosilanes (Silquest A-1100\* silane, Silquest A-1102 silane, Silquest A-1120 silane, Silquest A-1130 silane and Silquest A-1170 silane). In order to maintain the quality of the aminoalkylsilane, purge the headspace of all partial drums with nitrogen. Do not transfer unused silane back into the original drum. Do not use silane drums as mixing containers. Dispose of all empty drums properly, utilizing an environmentally responsible drum disposal company or reclaimer.

## Volatile Organic Compounds (VOCs)

It is difficult to determine the volatile organic compound value for silanes using ASTM method #D2369 (EPA Method #24), due to the propensity of the alkoxysilane to hydrolyze during the test procedure. Once hydrolysis takes place, a loss of alcohol results, which affects the gravimetric determination of low boiling materials.

## **Personal Protective Equipment**

The minimum recommended personal protective equipment (PPE) is outlined in the applicable MSDS. Be particularly sensitive to the potential for eye and skin contact. The correct glove must be worn if contact is likely. Safety goggles/monogoggles are mandatory when working with silanes. For inhalation concerns, use adequate ventilation, including local exhaust hoses, to minimize the need for respirators and full-face suppliedair systems (required for high vapor concentrations). Note that the use of organic vapor cartridges are not recommended for methoxy-silanes, due to the poor warning properties of methanol (by-product from hydrolysis).

## **Toxicity of Organofunctional Silanes**

Refer to the MSDS and Toxicology Summary for each product for a review of the toxicity testing that has been conducted to date.

#### Fire Safety (Storage) Considerations

Refer to the Appendix for fire safety considerations, particularly if assessing design for the storage of silanes.

## **Materials of Construction (MOC)**

The recommended material of construction for pump and Teflon<sup>®</sup> seals in general is 316 stainless steel. Silanes in general have exceptionally good solvating properties. For this reason, many elastomers are not suitable for use as seals and transferring with silanes.

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# Maintaining the Integrity of Partial Drums of Silanes

The purging of drum headspaces with dry nitrogen is critical to maintaining the quality integrity of alkoxysilanes. The exception to nitrogen purging is Silquest A-174\*NT silane, Silquest Y-9936 silane and CoatOSil\* 1757 silane or any other (meth)acryloxy functional silane (see discussion earlier).

If piped nitrogen is not available, a simple rack of exchangable nitrogen cylinders can be arranged into a regulated manifold delivery system. As a secondary approach, desiccated air lines can be used to purge the headspaces of silanes provided the silanes have a flash point greater than 150°F.

#### **Environmental Considerations** (Including Disposal)

#### **Clean-Up Procedures**

Equipment and transfer line clean-ups are necessary to avoid hydrolyzate build-up and to reduce the potential for plugging. Due to the hydrolytic instability of most alkoxysilanes, solvent flushing at ambient temperature is recommended following silane contact, especially if inert purging is not possible. The solvent(s) selected for clean-up should be non-reactive, free of water contamination, and compatible with the rest of the process chemistry. The appropriate fire safety precautions should be taken if flammable solvents are selected. For assistance in selecting the appropriate solvent for your purposes, contact your Momentive Performance Materials Technical Service representative or our Product Safety and Regulatory Affairs group.

## **Spills**

For spills, refer to the MSDS. Contain spills by barricading the area and use temporary diking, if possible, to avoid run-off to sewers and waterways. Be certain that clean-up or emergency personnel use the proper protective equipment as specified in the MSDS. Be aware of potential ignition sources. Remember that organofunctional silane esters readily generate the corresponding alcohol when in contact with moisture. The flash point will be lowered dramatically. For small spills, we recommend absorbant products and equipment commonly used in the chemical industry. Collect absorbed product and dispose of in accordance with federal, state, and local regulations. Large spills must be dealt with very carefully on a case-by-case basis. Immediate action must be taken to minimize the potential for fire, personnel exposure, and a threat to the environment. Contact CHEMTREC or other emergency numbers provided in the MSDS.

#### **Disposal Issues**

The proper disposal method for waste silane or silane mixtures may vary depending upon the state or province. Definitions of "hazardous waste" vary. Waste disposal firms have different capabilities and permits that may influence the mode of disposal.

Be certain that the clean-up and containment procedures for the waste are safe and appropriate. For emergency assistance, contact CHEMTREC or emergency phone numbers provided on the specific MSDS.

Consult local, municipal and state regulatory agencies for proper classification of the waste(s). Under the federal RCRA rules (40CFR 261), the following characteristic properties are indicative of hazardous wastes:

- D001: Flash point less than 140°F (PMCC)
- D002: pH <2 or >12.5, or corrodes steel at >0.25 in. per year.
- D003:Reacts violently with water, forms potentially explosive mixtures with water, or when mixed with water generates toxic gases, vapors, or fumes, or releases over 500 ppm of sulfides/ cyanides.

If the silane has been blended or reacted with another material, additional waste codes may apply. If you have questions on the regulatory status of your waste, consult your state or province environmental authorities.

## **Disposal of Empty Containers**

Empty containers may be subject to hazardous waste management and disposal requirements, depending upon the characteristics and amount of residue in the container. Empty containers must be disposed of or reclaimed only by reputable and properly licensed facilities. Please refer to state, national and local waste requirements. Due to the exposure and reactivity potential of residual silanes, "empty" containers should never be given to the public, or sold for reuse by the public or by non-reputable firms.

## References

1. Osterholtz, F. D., Pohl, E. R., "Kinetics of the Hydrolysis and Condensation of Organofunctional Alkoxysilanes: A Review," Journal of Adhesion Science and Technology, Volume 6, No.1, pp.127-149 (1992).

## **Appendix**

#### Safety Considerations for Storing and Using Organosilicones and Silanes

Various criteria should be taken into consideration when assessing safety and design for chemical storage and use in industrial settings. The raw material supplier cannot specify safety standards to the customer since these standards vary with differing state and local regulations, corporate policies, and insurance carriers. The supplier can only give general guidance based on experience and knowledge of the physical properties and characteristics of the product. It is up to the customer to use this guidance, together with other appropriate information, to evaluate all the applicable safety criteria for the customer's area and situation, including local codes, specific operating conditions, building design, equipment design, storage conditions, insurance requirements, and corporate policies. The following outline may be used as a checklist (not intended to be exhaustive) for evaluating what safety criteria should be considered when storing and using organosilicones and silanes. One of the most obvious safety concerns for chemical use and storage is fire safety, an emphasis of this outline.

# Outline and Checklist of Potentially Relevant Safety Criteria

#### A. Building Design/Classification

- Structural design of room/building (metal, concrete, wood vs. synthetic)
- Design for flammable or combustible liquid storage/ handling (NFPA-30 Code)
- Fire protection (NFPA-3, -15, -16 Codes; OSHA 29CFR1910 Subpart L)
  - Automatic Sprinkler protection (29CFR1910.159)
    Fixed vs. portable extinguishing system requirements (29CFR1910.160-.163)
    Water spray, foam, dry chemical, general or gaseous agents
    Remote spray monitors

Electrical classification of operating area (classified vs. non-classified)

- (See NFPA-70 National Electric Code: illustrates provisions, equipment and installation requirements for classified vs. non-classified areas.)
- Height of non-explosion proof electrical equipment and other ignition sources off floor level Ventilation, HVAC, static air volume in building Diking, curbing, drainage, emergency containment

## Appendix (continued)

- General layout of operating or storage areas /
  - access and egress (NFPA-30 restrictions) - Storage [general guidance: NFPA-231 (231C covers rack storage)] based on physical properties of the materials
  - Minimum aisle space; separation between storage containers and portable tanks
  - Minimum distance between storage and use areas

Potential for ignition sources

Temperature of equipment in vicinity Vehicular traffic limitations Explosion proof equipment requirements

Spark producing devices or open flame in area Grounding and inerting (purging) practices (also see procedures)

Consultation with Engineering Dept./contractor or architect knowledgeable in industrial fire codes and design classifications

## **B. Equipment Design/Classification**

Electrical classification Equipment electrical rating Equipment supplier's recommendations Engineering controls

#### C. Raw Material Characteristics: Physical Properties, Reactivity, etc.

Flash point of organosilicone/silane (impacts NFPA classification) Boiling point of organosilicone/silane (impacts NFPA classification) Reactivity of organosilicone/silane Keeping equipment and raw materials dry Maximum volume of material Delivery rate of material Delivery rate of material Open vs. closed transfer operations (hard-piped vs. temporary connections) Materials of construction and compatibility of equipment

Transfer equipment, reaction/treatment equipment, and storage equipment

# D. Corporate Health, Safety & Environmental Policy / Procedures (*e.g.*, for design criteria)

Corporate manual/standards Fire Safety Group/Skills Center availability within organization Standard Operating Procedures **General Process Operation Emergency Procedures** Life Critical Procedures Hazardous Work Procedures Confined Space Entry Use of Ignition Sources in Classified Areas Breaking or Cutting of Lines or Opening Equipment Facilities and Operational Change **Review Procedures** Grounding and Inerting Procedures Vessel to Vessel Transfer Procedures Flammable Liquid Dispensing Procedures Administrative Controls Process Safety Management OSHA 29CFR1910 (1910.119)Safety Review Process **Process Hazard Analysis Risk Assessments** Internal Audits Safe Operating Envelope for the Process Personnel Safety Personnel Training Hazardous Materials: OSHA 29CFR1910, Subpart H Personal Electrical Safety: 29CFR1910, Subpart S (coincides with NFPA-70) Toxic and Hazardous Substances: 29CFR1910, Subpart Z IH Monitoring Environmental Safety Issues Hazardous Waste Operations and Emergency Response (1910.120) Environmental Monitoring

## E. Local/State Codes

OSHA and NFPA requirements (Note: not all states are subject to NFPA requirements) Local laws and regulations State laws and regulations Fire Marshall requirements

#### **F. Insurance Carrier Requirements**

Consultation prior to design Liability perspective Review of hazards with local fire companies On-site fire brigade availability SMT April 2000

## **Patent Status**

Nothing contained herein shall be construed to imply the nonexistence of any relevant patents or to constitute the permission, inducement or recommendation to practice any invention covered by any patent, without authority from the owner of the patent.

## **Product Safety, Handling and Storage**

Customers should review the latest Material Safety Data Sheet (MSDS) and label for product safety information, safe handling instructions, personal protective equipment if necessary, emergency service contact information, and any special storage conditions required for safety. Momentive Performance Materials (MPM) maintains an around-the-clock emergency service for its products. MSDS are available at www.momentive.com or, upon request, from any MPM representative. For product storage and handling procedures to maintain the product quality within our stated specifications, please review Certificates of Analysis, which are available in the Order Center. Use of other materials in conjunction with MPM products (for example, primers) may require additional precautions. Please review and follow the safety information provided by the manufacturer of such other materials.

#### Limitations

Customers must evaluate Momentive Performance Materials products and make their own determination as to fitness of use in their particular applications.

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