SILANE-CONTAINING ADHESION PROMOTER COMPOSITION AND SEALANTS, ADHESIVES AND COATINGS CONTAINING SAME

Inventors: Remy Gauthier, Aire (CH); Christine Lacroix, Ornex (FR)

Assignee: Momentive Performance Materials Inc., Waterford, NY (US)

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 581 days.

Prior Publication Data

Related U.S. Application Data
Provisional application No. 60/717,721, filed on Sep. 16, 2005.

Int. Cl.
C08G 77/04 (2006.01)

U.S. Cl.
USPC 528/34; 528/901; 528/33; 528/17; 428/447

Field of Classification Search
USPC 528/33; 34; 17; 901

See application file for complete search history.

References Cited

U.S. PATENT DOCUMENTS
4,483,973 A 1/1984 Lucas et al.
4,483,974 A 1/1984 Grogler et al.
4,602,078 A 7/1986 Joseph et al.
4,797,446 A 1/1989 Dietlein et al.
4,978,704 A 12/1990 Perrin
5,554,688 A 9/1996 Frisch et al. 524/588
5,786,032 A 7/1998 Hughes
6,013,754 A 1/2000 Fillion et al.
6,034,171 A 3/2000 Leemopel 524/730
6,258,914 B1 7/2001 Su et al. 528/15
6,395,858 B1 5/2002 Mack et al. 528/18
6,602,964 B2 8/2003 Huang et al. 525/477
7,345,120 B2 3/2008 Ho et al. 526/220
7,605,203 B2 10/2009 Feng et al. 524/268
2004/0138939 A1 7/2004 Stevin

FOREIGN PATENT DOCUMENTS
DE 3903338 A1 8/1990
EP 0 950 115 B1 12/1994
WO WO 01/12693 A1 2/2001
WO WO 03/00775 A2 1/2003

OTHER PUBLICATIONS

Primary Examiner — Margaret Moore
Attorney, Agent, or Firm — Dominick G. Vicari; Joseph S. Ostroff

ABSTRACT
An adhesion promoter composition which comprises an oligomer of a functional alkoxy silane and a specific alkyl alkoxy silane is advantageously employed to improve the bonding of sealants/adhesives/coatings such as moisture curable siloxane polymers or various substrates such as wet or dry concrete. In a preferred embodiment the adhesion promoter contains an octyltrialkoxy silane and an oligomer prepared from an epoxy or polyethylene oxide functional alkoxy silane.

14 Claims, No Drawings
SILANE-CONTAINING ADHESION PROMOTER COMPOSITION AND SEALANTS, ADHESIVES AND COATINGS CONTAINING SAME

CROSS REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. provisional application Ser. No. 60/717,721 filed Sep. 16, 2005, which is herein incorporated by reference.

BACKGROUND OF THE INVENTION

The present invention relates to compositions of monomeric silanes with, for example, oligosilanes, aminofunctional oligosiloxane, or silicone polymers. These compositions are useful, for example, as adhesion promoters for moisture-curable silylated resins to improve bonding of sealants or adhesives or coatings to many difficult substrates, especially dry and wet concrete.

To fulfill building construction requirements (e.g., ISO-standard specifications and the comparable DIN-EN standard specifications or ASTM standard specification), sealants, adhesives or coatings need to be applied on concrete substrates that have been already pretreated with special primer (mainly epoxy based). It is very difficult with the currently available organofunctional silane adhesion promoters to provide cohesive or strong adhesive bonding of the moisture-curable silylated sealant or adhesive on concrete after water immersion without pre-treatment of the concrete.

Concrete is made up of cement, sand, aggregate and water. The surface of the concrete is highly alkaline (pH -12) and any absorbed water has a detrimental influence on the adhesion of the sealant or adhesive on the surface of the concrete. Concrete substrates are manufactured according to ISO 13640 but the final preparation of the cast samples can be different (ISO 13640 method 1 and method 2) and can result in different surface textures ranging from relatively smooth, flat surfaces to rough surfaces. It is more difficult to get good wettability or adhesion of the sealant on rough concrete surfaces.

SUMMARY OF THE INVENTION

A composition is provided herein for promoting adhesion of sealants, adhesives, or coatings onto a substrate. The composition comprises:

a) at least one compound having the formula 1:

R−Si(R1)3

wherein:

each R1 is independently selected from alkoxy, preferably methoxy or ethoxy, or C1-C5 alkyl such as methyl, ethyl or propyl; with the proviso that at least two of the R1 groups is alkoxy;

R is alkyl having from 1 to about 20 carbon atoms or an organic group containing amine, epoxy, vinyl, sulfur, methacryl, acetoxy, ureido, isocyanurate, or polyethylenoxide functionality; and,

b) at least one of an oligomeric silane or a silicone.

The adhesion promoter composition is useful for the preparation of high quality sealants, adhesives or coatings with improved processability. This invention enables sealants/adhesives/coating manufacturers and construction end users to apply moisture-curable silylated polymer compositions to concrete under virtually any condition, wet or dry, without concern about concrete pre-treatments, which allows for more robust use of these sealants/adhesives/coatings, eliminates an application step and avoids delays in application due to weather conditions.

DETAILED DESCRIPTION OF THE INVENTION

In the description below all composition percentages or parts are by weight unless stated otherwise. Numerical values should be understood as being modified by the term "about".

In an embodiment, the present invention comprises compositions of monomeric silanes with oligosilanes or silicone polymers, which are useful as adhesion promoters for moisture-cure silylated polymer to improve bonding of sealants, adhesives or coatings to many difficult substrates, especially dry and wet concrete.

In an embodiment of the invention, the silane composition includes at least one monomeric silane, or mixture of silanes, (e.g., an amino or nitrogen-containing silane) in the range of 40-95% by weight and 5-60% by weight of one or more oligomeric silane and/or one or more silicone polymers.

More particularly, in one embodiment the present invention is directed to a sealant or adhesive or coating composition blend comprising:

a) a moisture-curable silylated polymer resin; and

b) an adhesion promoter comprising one or more compound of formula 1:

R−Si(R1)3

wherein:

each R1 is independently selected from alkoxy, preferably methoxy or ethoxy, or C1-C5 alkyl such as methyl, ethyl or propyl; with the proviso that at least two of the R1 groups is alkoxy;

R is alkyl having from 1 to about 20 carbon atoms or an organic group containing amine, epoxy, vinyl, sulfur, methacryl, acetoxy, isocyanurate, or polyethylenoxide functionality.

Suitable organic groups for R include, but are not limited to, methyl, ethyl, propyl, octyl, aminoethyl, aminopropyl, ureidopropyl, aminodimethylbutyl, aminoisobutyl, epoxycyclohexyl, glycidoxypropyl, vinyl, mercaptoethyl, octanoylthiopropyl, methacryloxy, methacrylaminopropyl or hexadecyl.

In an embodiment of the invention, the adhesion promoter includes an aminosilane and one or more compounds of formula 1 wherein R includes epoxy, vinyl, sulfur, methacryl, acetoxy, isocyanurate or polyethylenoxide functionality.

In another embodiment the present invention is directed to a sealant/adhesive/coating composition blend comprising:

a) a moisture-cure silylated polymer resin; and

b) an adhesion promoter, an oligomer prepared from a compound of formula 1 optionally with tetraethyl orthosilicate (TEOS), optionally including one or more compounds of formula 1.

In another embodiment the present invention is directed to a sealant/adhesive/coating composition blend comprising:

a) a moisture cure silylated polymer; and

b) as an adhesion promoter a mixture of silicone and nitrogen-containing monomeric silanes, optionally including one or more compounds of formula 1.

In an embodiment of the invention the adhesion promoter can be blended into a sealant composition in accordance with the following preferred composition percentages. Composition percentages outside the given ranges may alternatively be used when appropriate:
<table>
<thead>
<tr>
<th>Component</th>
<th>Preferred range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture curable silylated polymer</td>
<td>20% to 50% and all ranges therebetween.</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>10% to 30% and all ranges therebetween.</td>
</tr>
<tr>
<td>Filler</td>
<td>30% to 60% and all ranges therebetween.</td>
</tr>
<tr>
<td>UV stabilizer</td>
<td>0.2% to 1.0% and all ranges therebetween.</td>
</tr>
<tr>
<td>Thixotrope</td>
<td>0.1% to 2.0% and all ranges therebetween.</td>
</tr>
<tr>
<td>Whitener or colorant</td>
<td>0.5% to 4.0% and all ranges therebetween.</td>
</tr>
<tr>
<td>Moisture scavenger</td>
<td>0.2% to 3.0% and all ranges therebetween.</td>
</tr>
<tr>
<td>Catalyst</td>
<td>0.01% to 2.0% and all ranges therebetween.</td>
</tr>
<tr>
<td>Adhesion Promoter</td>
<td>0.2% to 2.0% and all ranges therebetween.</td>
</tr>
</tbody>
</table>

The polymer used as the sealant, adhesive or coating material can be based on any organic or inorganic backbone provided that the polymer has at least two pendant or terminal alkoxysilyl, arylalkoxysilyl or alkylalkoximinosilyl groups thereof. Such systems are known. Organic backbone polymer systems include silylated acrylates, silylated polyurethanes, silylated polyethers, silylated polyesters, silylated polyolefins and others. Inorganic backbone systems are exemplified by polyorganosiloxanes, for instance RTV silicones. In an embodiment of the invention the sealant, adhesive or coating material is made from polymers having an organic backbone such as a polyurethane or a polyether.

In an embodiment, the present invention employs silylated polyurethane resin (SPUR). In another embodiment, modified siloxane polymer can be employed as the sealant/adhesive/coating material. Modified silicone polymers include polyethers functionalized with terminal alkoxysilanes, as in MS Polymer referred to below. Optionally, the modified silicone polymer can be obtained by the hydrolysislation of a silane endgroup onto a vinyl terminated polyether. The following components can be used in blending adhesion promoters for use with the sealant/adhesive/coating material.

### Amino

- Gamma-aminopropyltrimethoxy-silane (20% to 40%)
- N-(beta-aminoethyl)-gamma-aminopropyltrimethoxy-silane (10% to 30%)
- Bis(gamma-trimethoxysilylpropylamine) (10% to 30%)
- Gamma-ureidopropyltrimethoxysilane (10% to 30%)

### Proprietary polysulfide silanes

- Methacryl Gamma-methacryloxypropyltrimethoxysilane
- Gamma-methacryloxypropyltriethoxysilane
- Gamma-methacrylamidopropyltrimethoxysilane
- Gamma-methacryloxypropyltriisopropoxysilane

### Alkyl

- Ocy1triethoxysilane
- Propyltriethoxysilane
- Methyl triethoxysilane
- Methyl trimethoxysilane

### Oligomeric structures:

- Oligomer aminodiallylalkoxy silane
- Oligomer aminalkylalkoxy silane
- Epox silicon oligomer disclosed in U.S. patent application
- Ser. No. 11/100,840 filed Apr. 7, 2005, which is herein incorporated by reference.
- NXTM Ultra-Low V Silane (Available from General Electric Co.)

### Silicones

- Aminofunctional oligosiloxane
- Methacryl endcapped silicone
- Blends of trisiloxanes
- Epoxy silicone
- Linear aminosilicone polyether copolymer
- Aminoethylaminopropyl cyclic oligosiloxane
- Phenylethyl modified siliconoxane
- Octyl functional trisiloxane

### Other:

- 4-acetoxy-3-methoxyphenylpropyltrimethoxysilane
- Tris[3-trimethoxysilylpropyl]isocyanurate
- Poly(ethyleneoxide)trimethoxysilane
- Hexadecyltrimethoxysilane
- Bis[3(trimethoxysilyl)ethane

The following compositions are non-limiting examples of blends which are suitable for use in the invention.

<table>
<thead>
<tr>
<th>Composition</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Gamma-aminopropyltrimethoxysilane (60% to 95%)</td>
<td>Aminosiloxane (5% to 40%)</td>
</tr>
<tr>
<td>2 Gamma-aminopropyltrimethoxysilane (30% to 50%)</td>
<td>Bis[gamma-trimethoxysilylpropylamine] (30% to 50%) Octyltriethoxysilane (5% to 30%)</td>
</tr>
<tr>
<td>3 Gamma-aminopropyltrimethoxysilane (10% to 30%)</td>
<td>Bis[gamma-trimethoxysilylpropylamine] (50% to 70%) Octyltriethoxysilane (5% to 30%)</td>
</tr>
<tr>
<td>4 Gamma-aminopropyltrimethoxysilane (30% to 50%)</td>
<td>Tris[3-(trimethoxysilyl)propyl]isocyanurate (30% to 50%) Aminosiloxane (10% to 30%)</td>
</tr>
<tr>
<td>5 Gamma-aminopropyltrimethoxysilane (50% to 70%)</td>
<td>Bis[gamma-trimethoxysilylpropylamine] (10% to 30%) Octyltriethoxysilane (5% to 30%)</td>
</tr>
<tr>
<td>6 Gamma-ureidopropyltrimethoxysilane (40% to 60%)</td>
<td>Tris[3-(trimethoxysilyl)propyl]isocyanurate (40% to 60%)</td>
</tr>
<tr>
<td>7 Gamma-aminopropyltrimethoxysilane (30% to 50%)</td>
<td>Bis[gamma-trimethoxysilylpropylamine] (30% to 50%) Tris[3-(trimethoxysilyl)propyl]isocyanurate (5% to 20%) Silicone Polymers modified with alkylene oxide polymers (5% to 20%)</td>
</tr>
<tr>
<td>8 Gamma-aminopropyltrimethoxysilane (30% to 50%)</td>
<td>Tris[3-(trimethoxysilyl)propyl]isocyanurate (5% to 50%)</td>
</tr>
</tbody>
</table>
Aminosilicones, aminoethyl-aminopropyl, methyl functionality (5% to 30%)  
9 Gamma-aminopropyltrimethoxysilane (30% to 50%)  
Bis(gamma-trimethoxysilylpropylamine) (30% to 50%)  
Poly(ethyleneoxide) trimethoxysilane (5% to 20%)  
Silicone Polymers modified with alkenyle oxide polymers (5% to 20%)  
10 Gamma-aminopropyltrimethoxysilane (10% to 30%)  
Bis(gamma-trimethoxysilylpropylamine) (50% to 70%)  
Poly(ethyleneoxide) trimethoxysilane (5% to 20%)  
Silicone Polymers modified with alkenyle oxide polymers (5% to 20%)  
11 Gamma-aminopropyltrimethoxysilane (10% to 30%)  
Bis(gamma-trimethoxysilylpropylamine) (30% to 70%)  
Poly(ethyleneoxide) trimethoxysilane (10% to 30%)  
12 Gamma-aminopropyltrimethoxysilane (30% to 50%)  
Bis(gamma-trimethoxysilylpropylamine) (50% to 70%)  
Poly(ethyleneoxide) trimethoxysilane (5% to 30%)  
13 N-(beta-aminosilyl)-gamma-aminopropyltrimethoxysi-lane (10% to 90%)  
Aminosiloxane (5% to 30%)  

The plasticizers customarily employed can also be used in the invention to modify the properties and to facilitate use of higher filler levels. Exemplary plasticizers include, but are not limited to, phthalates, dipropylene and diethylene glycol dibenzoates and mixtures thereof, epoxidized soybean oil and the like. Useful sources of dioctyl and diisodecyl phthalate include those available under the tradenames “Jayflex DOP” and “Jayflex DIDP” from Exxon Chemical. The dibenzoates are available as “Benzoflex 9-88”, “Benzoflex 50” and “Benzoflex 400” from Velsciol Chemical Corporation. The plasticizer typically comprises up to 100 parts per hundred parts of the silylated polymer with 40 to 80 parts per hundred being preferred.

Typical fillers suitable for formulation of the sealants include, but are not limited to, reinforcing fillers such as fumed silica, precipitated silica and calcium carbonates. To further improve the physical strength of the formulations, reinforcing carbon black can be used as a main filler, leading to black systems. Several commercial grades of carbon black useful in this invention are available, such as “Cronax” products (Degussa). To obtain translucent formulations, higher levels of fumed silica or precipitated silica should be used as the main filler, without carbon black.

Treated calcium carbonates having particle sizes from 0.07 microns to 4 microns are preferred fillers and are available under several trade names, such as: “Ultra Pilex” and “Hi Pilex” from Specialty Minerals; “Winnoil SPM” and “Winnoil SPI” from Zeneca Resins; “Hubercarb 1Qt”, “Hubercarb 3Qt” and “Hubercarb W” from Huber and “Kotomite” from ECC. These fillers can be used either alone or in combination. The fillers generally comprise up to 300 parts per 100 parts of the silylated polymer with 80 to 150 parts being the more preferred loading level.

UV stabilizers and/or antioxidants can be incorporated into the sealant formulations of this invention in an amount from 0 to 5 parts per hundred parts of silylated polymer with 0.5 to 2 parts being preferred. These materials are available from companies such as, for example, Great Lakes and Ciba Specialty Chemicals and include, but are not limited to, additives commercially available under the tradenames “Anox 20” and “Uvasil 299 HM/LM” (Chemtura), and “Irganox 1010,” “Irganox 1076,” “Titinov 770,” “Titinov 327,” “Titinov 213” and “Titinov 622 LD” (Ciba), respectively. The sealant formulations can include various thixotropic or anti-sagging agents. This class of additives is typified by various castor waxes, fumed silica, treated clays and polyamides. These additives typically comprise 1 to 10 parts per hundred parts of silylated polymer component with 1 to 6 parts being preferred. Useful thixotropes include, but are not limited to, those available as: “Aerosil” from Degussa, “Cab-O-Sil” from CAB, “Castorwax” from CasChem, “Thixatrol” and “Thixcin” from Rheox, and “Disparon” from King Industries.

Suitable catalysts include, but are not limited to, bismuth carboxylate, zirconium, aluminum or titanium chlorides, dialkyltin dicarboxylates salts or oxide, such as dibutyltin dilaurate, dibutyltin acetate, and di-n-butyltin oxide, the stannous salts of carboxylic acids such as stannous octoate and stannous acetate, and the like.

The sealant/adhesive/coating compositions can be applied to any suitable substrate such as metal, wood, asphalt, brick, stone, concrete and the like. The compositions are particularly suitable for application to concrete surfaces. Concrete can be highly alkaline (pH>7), ≥10, and usually about 12). Moreover, the surface can be wet, for example, after a rainfall before the surface has had time to dry.

The following examples illustrate features of the invention.

**EXAMPLES**

Samples of concrete substrates used in the examples consisted of concrete blocks of 75x12x25 mm, having a testing surface of 75x12 mm. They were manufactured according to the standard ISO 13640. Both of the two methods of concrete preparation set forth in the ISO standard were employed for evaluation. The concrete itself was manufactured according to the same recipe for both methods. However, the final preparation of the cast samples differed so as to provide samples with different surface texture.

In accordance with ISO 13640 Method 1 the testing surface of the concrete samples was wet cut so as to provide a smooth and flat testing surface.

In accordance with ISO 13640 Method 2 the testing surface was brushed with a metallic brush to create surface roughness by exposing sand grains.

Once formulated, the sealant was applied onto the different substrates. Three conditioning methods were used:

“Dry” concrete: the samples were tested dry after the standard curing cycle of 2 weeks at 23°C, 50% relative humidity (RH).

“Pre-rinsed” concrete: the substrates were stored under water and wiped with a tissue just before use. The sealant was applied to the concrete surface while it was still humid, 3 minutes after taking it out of water. This test was useful to determine whether the sealant can be applied to the substrate before the substrate was fully dry, for example after a rain fall.

“Wet” concrete: The sealant was applied to the dry concrete; assemblies were immersed into water for one to four days and allowed to stand for one day at room temperature before the test evaluation after a standard two-week curing cycle.

The pH of the different concretes has been measured and found to be about 12.

The following tests were employed for performance evaluation.

A hard peel test was employed in which, for each sample, the sealant was peeled off by hand. The adhesion of the sealant was determined, wherein the adhesion was measured by the percentage of the surface of the concrete sample still covered with sealant after the test, divided by the area of the surface originally covered.
Since all samples resulted in 0% adhesion when tested after one-week immersion into water, the immersion time was reduced to one day or 4 days, followed by maintaining the sample one day at room temperature before testing. The results from both tests (hand peel at 90°C and at 180°C) were compared. The percentage of the sealant remaining on the concrete was evaluated visually on the concrete after the peeling by a Zwick machine.

The blends which gave the highest value in hand peel test were evaluated with the peel strength test.

On the concrete sample, first a silylated polyurethane resin ("SPUR") or modified silicone polymer ("MSP") sealant was applied followed by the application of a wire-netting treated with Silquest® Primer AP 134, a commercially available reactive silicone, and a second layer of SPUR or MSP sealant was applied. The wire-netting was slightly smaller than the concrete sample (by about 1 mm on each side). The total thickness of the system was between 5 and 8 mm. Preferably, the SPUR or MSP layer should recover wire-netting.

After the samples were aged for two weeks at 23°C and 50% relative humidity, the samples were placed on a Zwick machine for the Peeling test ASTM D 98 (ASTM C794: Standard Test Method) for Adhesion-in-Peel of Elastic/semi-elastic Joint Sealants at 10 mm per minute up to 50 mm. The peeling force was recorded and the average force was calculated.

Additionally, to compare results from both tests (hand peel at 90°C and at 180°C). The percentage of the sealant remaining on the concrete was evaluated visually on the concrete after the peeling by a Zwick machine.

SPUR Sealant Formulations

The SPUR based sealant formulation used Witton WSP 725-80 (SPUR® 1010L, M available from General Electric Co.) as base isocyanate terminated prepolymer with different batches of the same type of Witton resin.

Silylated polyurethane designated herein as SPUR 1 was made with a first batch of Witton WSP 725-80 prepolymer. SPUR 4, 5 and 6 were made with a second batch of Witton WSP 725-80 base prepolymer. SPUR 7, 8, 9 and 10 formulations were made with a third batch of Witton WSP 725-80 prepolymer. SPUR 13 formulation was made with a fourth batch of Witton WSP 725-80 base prepolymer. SPUR 27 formulation was made with a sixth batch of Witton WSP 725-80 prepolymer.

The following components were used to prepare the moisture curable polymer composition:

- Silquest® A-171 (moisture scavenger) up to 3%
- Adhesion promoter up to 3%
- Tin catalyst up to 3%

Sealant Preparation

Using a clean, dry, disposable metal mixing can, the siloxane containing polymer (SPUR/MSP) and the plasticizer (e.g., diisodecyl phthalate (DDP)) were mixed by hand using a tongue blade or spatula. Thixotrope (SiO2), whiteners (TiO2) and UV stabilizers were added and mixed in the blend, followed by addition of fillers (e.g., CaCO3). The blend was then placed in a mixer for 5 minutes at a slow speed (<0.5 dial setting). The mixer was then opened to scrape down any material accumulated on the scraper and stirrers. The blend was then mixed at a moderate speed (dial setting: 2.0-3.0) for 1 hour at 80°C under vacuum until the sealant appeared smooth and uniform. The sealant mixture was then cooled down to not more than 50°C, and a dehydrating agent (Silquest® A-171) was added with mixing for 5 minutes. The vacuum was substituted with a nitrogen atmosphere and the sealant was transferred to the test boxes at about 85 g per box.

Two different methods were employed for the addition of the adhesion promoter to the SPUR formulations. For the SPUR 4, 5, 6, 7 formulations, the adhesion promoter and catalyst were added together, followed by mixing with SPUR in a Hauschild mixer for 1 minute 30 seconds. For all other formulation the adhesion promoter was added to SPUR and mixed into the Hauschild mixer for one minute. A minimum of five minutes was allowed to cool the mixture before adding the catalyst and the formulation was mixed again for one minute in the Hauschild mixer.

### Modified Silicone Polymer (MSP) Sealant Formulations

The MSP sealant formulation (available from Kaneka Belgium Co.) was based on a pre-formulation to which the following ingredients were added:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sililated polyurethane (SPUR)</td>
<td>125</td>
</tr>
<tr>
<td>Plasticiser (DDP)</td>
<td>55</td>
</tr>
<tr>
<td>CaCO3 (lise Wintonsil SP)</td>
<td>192</td>
</tr>
<tr>
<td>CaCO3 coarse (Omya BL1B)</td>
<td>48</td>
</tr>
<tr>
<td>UV stabilizers (Tinvezin 213A)</td>
<td>2</td>
</tr>
<tr>
<td>SiO2 (Cabosil TS-720)</td>
<td>1</td>
</tr>
<tr>
<td>TiO2 (Tit-Pure R-902)</td>
<td>5</td>
</tr>
<tr>
<td>Silquest® A-171 (Moisture scavenger)</td>
<td>1.5</td>
</tr>
<tr>
<td>Adhesion promoter</td>
<td>2.5</td>
</tr>
<tr>
<td>Catalyst (DHTDL)</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Example 1: SPUR 1 blended with gamma-amino-propyltrimethoxysilane (designated herein as A-1101).

Example 2: SPUR Formulations 1, 25, and 27 blended with gamma-amino-propyltrimethoxysilane (A-1110).


Example 4: SPUR formulations 14, 19 and 20 individually blended with adhesion promoter comprising: 40% gamma-amino-propyltrimethoxysilane 40% bis[gamma-trimethoxysilyl] propylamine, 20% octyl-trimethoxysilane.

Example 5: SPUR formulations 14, 19 and 22 individually blended with an adhesion promoter comprising: 20% gamma-amino-propyltrimethoxysilane 60% bis[gamma-trimethoxysilyl] propylamine, 20% octyl-trimethoxysilane.

Example 6: SPUR formulations 14, 15 and 23 individually blended with an adhesion promoter comprising: 40% gamma-amino-propyltrimethoxysilane 40% bis[gamma-trimethoxysilyl] propylamine, 20% Aminosilicone.

Example 7: SPUR formulations 14 and 15 individually blended with an adhesion promoter comprising: 60% Gamma-amino-propyltrimethoxysilane 20% Bis[gamma-trimethoxysilyl] propylamine, 20% Octyl-trimethoxysilane.

Example 8: SPUR formulations 16, 25 and 26 individually blended with an adhesion promoter comprising: 50% Gamma-amino-propyltrimethoxysilane 50% Bis[gamma-trimethoxysilyl] propylamine, 10% Tris[(trimethoxysilyl)propyl]isocyanurate.

Example 9: SPUR formulation 27 blended with an adhesion promoter comprising: 40% Gamma-amino-propyltrimethoxysilane 40% Bis[gamma-trimethoxysilyl] propylamine, 10% Tris[(trimethoxysilyl)propyl]isocyanurate, 10% Silicone Polymers modified with alkylene oxide polymers.
Example 10: SPUR formulation 27 blended with an adhesion promoter comprising:
- 40% Gamma-aminopropyltrimethoxysilane
- 40% Tra [3(trimethoxysilylpropyl)isocyanurate
- 20% Aminosiloxanes, aminoisopropyl, methyl functionality

Example 11: SPUR formulations 26 and 27 individually blended with an adhesion promoter comprising:
- 40% Gamma-aminopropyltrimethoxysilane
- 40% Bosgamma-trimethoxysilylpropylamline
- 10% Poly(ethyleneoxide)trimethoxysilane
- 10% Silicone Polymers modified with allylene oxide polymers

Example 12: SPUR formulation 27 blended with an adhesion promoter comprising:
- 20% Gamma-aminopropyltrimethoxysilane
- 60% Bosgamma-trimethoxysilylpropylamline
- 10% Poly(ethyleneoxide)trimethoxysilane
- 10% Silicone Polymers modified with allylene oxide polymers

Example 13: SPUR formulations 18, 26, and 27 individually blended with an adhesion promoter comprising:
- 20% Gamma-aminopropyltrimethoxysilane
- 60% Bosgamma-trimethoxysilylpropylamline
- 20% Poly(ethyleneoxide)trimethoxysilane

Example 14: SPUR formulation 27 blended with an adhesion promoter comprising:
- 20% Gamma-aminopropyltrimethoxysilane
- 60% Bosgamma-trimethoxysilylpropylamline
- 15% Poly(ethyleneoxide)trimethoxysilane
- 5% linear aminosilicone polyether copolymer

Example 15: SPUR formulation 13 blended with an adhesion promoter comprising:
- 80% Gamma-aminopropyltrimethoxysilane
- 20% aminosiloxane

The tables below illustrate the test results for the blends of the following examples.

Comparative Examples 1, 2 and 3 are presented for comparison purposes only and do not exemplify the invention. Examples 4-15 exemplify the invention.

Wherein multiple SPUR formulations are tested in an example, each SPUR formulation is individually blended and with the identified adhesion promoter and tested. The test results indicated in the Table are the averaged values of the individual formulations.

The blends employed for Comparative Examples 1 and 2 were blends prepared with Silquest A-1110 and SPUR formulations as indicated in Table 1. The results of the hand peel test of Comparative Example 1 showed poor cohesion with only 5% of the SPUR remaining on the dry concrete sample as a result of the peel test. When tested on pre-rinsed concrete in accordance with ISO 13640 Method 1 (smooth concrete surface), the percentage of SPUR remaining was 80%. However, when tested on pre-rinsed concrete in accordance with ISO 13640 Method 2 (rough concrete surface), the percentage of SPUR remaining on the surface dropped to 5%. These ISO 13640 methods are referred to below as simply "method 1" or "method 2". With respect to the wet concrete tests (concrete with sealant immersed in water for one to four days with one day at room temperature), both smooth and rough concrete surfaces resulted in 0% adhesion.

In Comparative Example 2, SPUR formulations 1, 23 and 27 were employed with Silquest® A-1110 adhesion promoter. An average of the results are given in Table 1. The blends of Example 13 provided better test results than that of Example A.

Comparative Example 3 employed a blend of Silquest A-1110 and SPUR 27 with Silquest® Primer AP 134, which provided excellent results.

The blends of Example 4 prepared with SPUR formulations 14, 19 and 20 and adhesion promoter demonstrated good performance on dry and immersed concrete.

The blends of Example 5 prepared with SPUR formulations 14, 19 and 22 and adhesion promoter showed good results with dry concrete and pre-rinsed concrete as well as immersed concrete.

The blends of Example 6 prepared with SPUR formulations 14, 15 and 23 and adhesion promoter provided very good average results with excellent results for concrete (rough surface) and pre-rinsed concrete (smooth surface).

The blends of Example 7 prepared with SPUR formulations 14 and 15 and adhesion promoter showed very good results with dry and pre-rinsed concrete, but showed weaker adhesion in the immersion test.

The blends of Example 8 prepared with SPUR formulations 16, 25, and 26 and adhesion promoter provided very good results.

The blend of Example 9 with SPUR formulation 27 and adhesion promoter generally provided good results.

The blend of Example 10 with SPUR formulation 27 and adhesion promoter only showed good results for the pre-rinsed concrete test using smooth surface concrete (method 1).

The blends of Example 11 with SPUR 26 and 27 and adhesion promoter showed good average performance, with some weakness for the smooth surface dry concrete test (method 1).

The blend of Example 12 with SPUR formulation 27 and adhesion promoter showed weak results except for the excellent adhesion on pre-rinsed smooth surface concrete (method 1) and good results for the immersed rough surface concrete.

The blends of Example 13 with SPUR formulations 18, 26 and 27 and adhesion promoter showed good average results overall.

The blend of Example 14 with SPUR formulation 27 and adhesion promoter showed good results for the dry concrete and pre-rinsed smooth surface concrete.

The blend of Example 15 with SPUR formulation 13 and adhesion promoter showed excellent results on dry concrete and pre-rinsed smooth surface concrete.

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Percentage of SPUR remaining on concrete at 90°C, with selected adhesion promoter compositions, hand peeling test)</td>
</tr>
<tr>
<td><strong>EXAMPLE</strong></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>1 (Comparative)</td>
</tr>
<tr>
<td>2 (Comparative)</td>
</tr>
<tr>
<td>3 (Comparative)</td>
</tr>
</tbody>
</table>
The percent of SPUR remaining on concrete at 90° and 180°, and the adhesion force after the peeling test at 180° was determined for several blends of SPUR and adhesion promoters. The results are shown in Table 2. Two of the blends, labeled as “comparative” do not illustrate the invention but are provided for comparison purposes only.

Examples 16-19 are directed to tests of adhesion on dry concrete with smooth (method 1) or rough (method 2) surfaces. The peeling angles employed were 90° and 180° as indicated.

## Table 2

<table>
<thead>
<tr>
<th>EXAMPLE</th>
<th>SPUR blend with Siliquent A 1110 (comparative)</th>
<th>SPUR/ adhesion promoter blend of Example 6</th>
<th>SPUR/ adhesion promoter blend of Example 8</th>
<th>SPUR/ adhesion promoter blend of Example 11</th>
<th>SPUR/ adhesion promoter blend of Example 13</th>
<th>SPUR/ adhesion promoter blend of Siliquent A 1110/SPUR 1 only at 90° (comparative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Dry concrete method 1. Peeling 180°</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
</tr>
<tr>
<td>17</td>
<td>Dry concrete method 1. Peeling 90°</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
</tr>
<tr>
<td>18</td>
<td>Dry concrete method 2. Peeling 180°</td>
<td>80%</td>
<td>80%</td>
<td>80%</td>
<td>80%</td>
<td>80%</td>
</tr>
<tr>
<td>19</td>
<td>Dry concrete method 2. Peeling 90°</td>
<td>80%</td>
<td>80%</td>
<td>80%</td>
<td>80%</td>
<td>80%</td>
</tr>
<tr>
<td>20</td>
<td>Pre-rinsed concrete method 1</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
</tr>
<tr>
<td>21</td>
<td>Pre-rinsed concrete method 1. Peeling 90°</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
</tr>
<tr>
<td>22</td>
<td>Pre-rinsed concrete method 2</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
</tr>
<tr>
<td>23</td>
<td>Pre-rinsed concrete method 2. Peeling 90°</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
</tr>
<tr>
<td>24</td>
<td>Water immersion concrete method 1</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
</tr>
<tr>
<td>25</td>
<td>Water immersion concrete method 1</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
</tr>
<tr>
<td>26</td>
<td>Water immersion concrete method 2</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
</tr>
<tr>
<td>27</td>
<td>Water immersion concrete method 2</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
</tr>
</tbody>
</table>

## Table 1-continued

<table>
<thead>
<tr>
<th>EXAMPLE</th>
<th>dry concrete 1</th>
<th>dry concrete 2</th>
<th>p-rins. concrete 1</th>
<th>p-rins. concrete 2</th>
<th>concrete 1 immers (1 day)</th>
<th>concrete 2 immers (1 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>40%</td>
<td>80%</td>
<td>90%</td>
<td>90%</td>
<td>5%</td>
<td>30%</td>
</tr>
<tr>
<td>5</td>
<td>30%</td>
<td>90%</td>
<td>70%</td>
<td>70%</td>
<td>5%</td>
<td>30%</td>
</tr>
<tr>
<td>6</td>
<td>50%</td>
<td>95%</td>
<td>90%</td>
<td>90%</td>
<td>5%</td>
<td>40%</td>
</tr>
<tr>
<td>7</td>
<td>70%</td>
<td>70%</td>
<td>70%</td>
<td>70%</td>
<td>5%</td>
<td>40%</td>
</tr>
<tr>
<td>8</td>
<td>70%</td>
<td>90%</td>
<td>80%</td>
<td>80%</td>
<td>5%</td>
<td>30%</td>
</tr>
<tr>
<td>9</td>
<td>50%</td>
<td>50%</td>
<td>70%</td>
<td>70%</td>
<td>5%</td>
<td>20%</td>
</tr>
<tr>
<td>10</td>
<td>5%</td>
<td>20%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>11</td>
<td>25%</td>
<td>70%</td>
<td>50%</td>
<td>50%</td>
<td>5%</td>
<td>30%</td>
</tr>
<tr>
<td>12</td>
<td>5%</td>
<td>20%</td>
<td>95%</td>
<td>95%</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>13</td>
<td>45%</td>
<td>47%</td>
<td>70%</td>
<td>70%</td>
<td>5%</td>
<td>25%</td>
</tr>
<tr>
<td>14</td>
<td>20%</td>
<td>70%</td>
<td>50%</td>
<td>50%</td>
<td>5%</td>
<td>25%</td>
</tr>
<tr>
<td>15</td>
<td>70%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>5%</td>
<td>10%</td>
</tr>
</tbody>
</table>
TABLE 2-continued

<table>
<thead>
<tr>
<th>Concrete Meth 1</th>
<th>Concrete Meth 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Example</strong></td>
<td><strong>MSP with adhesion promoter</strong></td>
</tr>
<tr>
<td>34 (Comparative)</td>
<td>MSP without Silane</td>
</tr>
<tr>
<td>35 (Comparative)</td>
<td>MSP with Silquest A-1110</td>
</tr>
<tr>
<td>36 (Comparative)</td>
<td>MSP with Silquest A-1110 + primer AP 134</td>
</tr>
<tr>
<td>37</td>
<td>MSP with adhesion promoter of Ex. 10</td>
</tr>
<tr>
<td>38</td>
<td>MSP with adhesion promoter of Ex. 8</td>
</tr>
<tr>
<td>39</td>
<td>MSP with adhesion promoter of Ex. 11</td>
</tr>
<tr>
<td>40</td>
<td>MSP with adhesion promoter of Ex. 14</td>
</tr>
<tr>
<td>41</td>
<td>MSP with adhesion promoter of Ex. 13</td>
</tr>
</tbody>
</table>

The above results demonstrate the effectiveness of the adhesion promoters of the invention used in conjunction with moisture-curable silicon-containing polymers such as, e.g., silylated polyurethane resins and silicone polymers.

While the above description contains many specifics, these specifics should not be construed as limitations of the invention, but merely as exemplifications of preferred embodiments thereof. Those skilled in the art will envision many other embodiments within the scope and spirit of the invention.

What is claimed is:

1. A composition comprising:
   a) a moisture-curable silylated polymer selected from the group consisting of a silylated polyurethane polymer and polyether functionalized with terminal alkoxysilane groups; and,
   b) an adhesion promoting amount of at least one adhesion promoter consisting of:
      i) at least one compound having the formula 1:
         \[ R - Si(R^1)_3 \]  \[ \text{[1]} \]
      wherein each \( R^1 \) is independently selected from alkoxyl, and \( R \) is an alkyl group having 8 carbon atoms; and,
      ii) at least one oligomer prepared from a compound having formula 1:
         \[ R - Si(R^2)_3 \]  \[ \text{[1]} \]
wherein
  each R² is independently selected from alkoxy, or C₁₋₃ alkyl, with the proviso that at least two of the R¹ groups are alkoxy, and R is an organic group containing epoxy or polyethyleneoxide functionality, wherein said composition is applied to or is on a concrete substrate.

2. The composition of claim 1 wherein the moisture-curable silylated polymer is a silylated polyurethane polymer.

3. The composition of claim 1 wherein the moisture-curable silylated polymer is polyether functionalized with terminal alkoxyalkyl groups.

4. The composition of claim 1 wherein the R group of the oligomer (ii) is epoxyoctylhexyl or glycidoxypropyl.

5. The composition of claim 4 wherein the R group is glycidoxypropyl.

6. The composition of claim 1 wherein the compound (i) is octyltriethoxysilane.

7. The composition of claim 1 wherein the R¹ groups of compound (i) or oligomer (ii) are methoxy or ethoxy.

8. The composition of claim 1 wherein the oligomer (ii) is prepared from a compound selected from the group consisting of beta (3,4-epoxyoctylhexyloxy)ethyltriethoxysilane, gamma-glycidoxypropyltriethoxysilane, gamma-glycidoxypropyl triethoxysilane, gamma-glycidoxypropylmethyldiethoxysilane and poly(ethyleneoxide)trimethoxysilane.

9. The composition of claim 1 wherein the adhesion promoter composition consists of at least one compound (i) in the range of 40 to 95 weight percent and the oligomer (ii) in the range of 5 to 60 weight percent based upon the total weight of components (i) and (ii).

10. The composition of claim 1 further comprising one or more component selected from the group consisting of plasticizers, fillers, UV stabilizers, thixotropes, colorants, moisture scavengers and catalysts.

11. A method for treating a substrate comprising:
   a) providing a composition containing a moisture-curable silylated resin selected from the group consisting of a silylated polyurethane polymer and polyether functionalized with terminal alkoxyalkyl groups and an adhesion promoter, the adhesion promoter including:
   i) at least one compound having the formula 1:
      \[ R - Si(R^1)_3 \] [1]
   wherein
      each R¹ is alkoxy, and
      R is alkyl having from 8 carbon atoms; and,
   ii) at least one oligomer prepared from a compound having formula 1:
      \[ R - Si(R^1)_3 \] [1]
   wherein
      each R² is independently selected from alkoxy, or C₁₋₃ alkyl, with the proviso that at least two of the R¹ groups is alkoxy, and R is an organic group containing epoxy or polyethyleneoxide functionality; and
   b) applying said composition to a surface of the substrate, wherein said substrate is concrete.

12. The method of claim 11 wherein the substrate has a pH of above 10.

13. The composition of claim 1 wherein the composition is a sealant, coating or adhesive.

14. A sealant, adhesive or coating composition comprising:
   a) a moisture-curable moisture-curable silylated polymer selected from the group consisting of a silylated polyurethane polymer and polyether functionalized with terminal alkoxyalkyl groups; and,
   b) an adhesion promoting amount of at least one adhesion promoter consisting of:
      i) 40% to 95% by weight based upon the total weight of components (i) and (ii) of at least one compound having the formula 1:
      \[ R - Si(R^1)_3 \] [1]
   wherein
      each R² is independently selected from alkoxy, or C₁₋₃ alkyl, with the proviso that at least two of the R¹ groups is alkoxy, and R is an alkyl group having from 8 to 20 carbon atoms; and,
   ii) 5% to 60% by weight based upon the total weight of components (i) and (ii) of at least one oligomer prepared from a compound having formula 1:
      \[ R - Si(R^1)_3 \] [1]
   wherein
      each R¹ is independently selected from alkoxy, or C₁₋₃ alkyl, with the proviso that at least two of the R¹ groups are alkoxy, and R is an organic group containing epoxy or polyethyleneoxide functionality, wherein said sealant, adhesive or coating composition is applied to or is on a concrete substrate.