

1

POLYSILOXANE POLYURETHANE COMPOSITIONS

5

Field of the Invention

The invention relates to moisture-curable urethane compositions and, more particularly to polysiloxane polyurethane compositions having improved chemical resistance and weatherability, improved film build capability, and having high tensile strength, elastomeric properties and elongation when compared to conventional urethane compositions.

10

Background of the Invention

15

Urethane compositions are known to have outstanding abrasion, impact, weather and chemical resistance, combined with excellent tensile and tear strength and high elongation. The combination of such properties has made such compositions commercially accepted as specialty coatings for applications in the textile, paper, automotive, sports and recreation, wood, civil engineering and construction, marine and industrial maintenance coatings markets.

20

The basic raw materials used to prepare conventional binders for a two-component or two-package elastomeric polyurethane coating system includes: (a) an aliphatic or aromatic di- or polyisocyanate; and (b) a coreactant or curative component having active hydrogen containing groups, e.g., hydroxyl, amine groups, or latent active hydrogen containing groups, e.g., oxazolidines or ketimines. Typically, the coreactant is an oligomer having at least one hydroxyl group and is selected from the general classes of polyesters, polyethers, alkyd resins and acrylics. The coreactant is usually the vehicle chosen for pigment grinding and may also contain other additives such as catalysts, plasticizers, antioxidants and ultra-violet (UV) stabilizers, bituminous extenders, suspending agents, antiskinning agents, surfactants and rheological modifiers.

25

A disadvantage of using an amine cured binder is the inherent high reactivity of isocyanate, particularly aromatic isocyanate, with amine containing materials. Accordingly, coating systems formed using an amine-cured binder often react so quickly that application can be accomplished only with specialized plural component spray equipment. Additionally, amine cured systems have a tendency to yellow upon exposure to sunlight, which precludes their use in applications where color stability is required.

30

A disadvantage of using a hydroxyl cured binder to prepare the coating system is that the oligomer containing the hydroxyl group and any water present in the system have similar reactivity with the di- or polyisocyanate ingredient. Accordingly, any moisture on the substrate to be coated, atmospheric moisture in the coating environment compete with the oligomer for the available isocyanate groups. Moisture can, therefore, inhibit the cure

35



1 process of the coating, resulting in slow or partial cure, reduced surface gloss, and
compromised performance. The reaction of di-or polyisocyanates with water also produces
carbon dioxide gas which can cause bubble formation in the coating. Bubbles formed in the
coating are typically unable to travel to the coating surface and are entrapped, creating micro
5 voids in the coating structure. These micro voids are undesirable because they increase the
coating's permeability to water and, thus reduce its corrosion protection. The microvoids
also compromise the physical integrity of the coating, resulting in lower tensile strength,
decreased elongation and reduced abrasion resistance. Limited pot-life is another
disadvantage of using a hydroxyl cured binder.

10 Binders used to form one-component or one-package moisture-cured elastomeric
polyurethane coating systems are known in the art and generally comprise
isocyanate-terminated prepolymers or quasi-prepolymers. These polymers are prepared by
reacting an aromatic or aliphatic di-or polyisocyanate with an oligomer of the type described
above. Moisture scavenging agents, plasticizers and other additives are added to obtain a
15 very low moisture content and, thereby obtain optimum package stability.

Binders used to one-component moisture cured-elastomeric urethane coatings are
believed to cure by the reaction of water with the isocyanate which liberates carbon dioxide
gas. While this reaction is of importance in the formation of foamed microcellular urethane
products, it makes it difficult to obtain a continuous, bubble free protective coating, and
20 generally limits applied dry film thickness to less than about eight millimeters.

Both the one-component and two-component elastomeric urethane coating systems
often include volatile organic solvents to lower the coating viscosity and, thereby, provide
a consistency suitable for spray application with conventional air, airless and electrostatic
spray equipment.

25 Known methods have been used to reduce carbon dioxide generated bubble formation
in both one-and two-component elastomeric urethane coating systems. One such method has
been to incorporate a ketimine, aldimine or oxazolidine ingredient. The ketimines and
aldimines are Schiff's bases derived from a ketone or aldehyde, respectively. Mono, di-or
polyoxazolidines are also used. Upon exposure to moisture, oxazolidines hydrolyze to form
30 a hydroxylamine, while ketimines and aldemines produce amine and the corresponding ketone
or an aldehyde. The hydroxylamine and amine thus produced react with the di-or
polyisocyanate to form the polyurethane and poly(urea)urethane. Hydrolysis of ketimine,
aldimine and oxazolidine, and subsequent reaction of amine or hydroxylamine with
isocyanate, is inherently faster than the reaction of isocyanate with water which thus
35 eliminates or reduces carbon dioxide generation and bubble formation. Very thick coatings
with a wide range of properties can be prepared in this manner.

While use of ketimines, aldemines and oxazolidines may be regarded as an
improvement in conventional one-and two-component urethane elastomeric coating system,

1 they do have some inherent disadvantages. Use of ketimines and aldimines often produce
coatings that have a tendency to yellow upon exposure to sunlight, and that have an increased
time to achieve complete cure and retain slow evaporating ketones or aldehydes in the film
for some time. Oxazolidine modification can also result in some yellowing and reduced
5 chemical resistance to some acids. Another method used to reduce carbon dioxide
generation and bubble formation has been to end cap isocyanate-terminated prepolymers or
quasi-prepolymers with an amino-functional alkoxysilane. Carbon dioxide generation and
bubble formation in the coating is precluded since the isocyanate group is prereacted. These
coatings cure by hydrolysis of the alkoxysilane end capped urethane to form the
10 corresponding silanols and an alcohol, with subsequent condensation of silanol end capped
urethane to form polyurethane-polysiloxane polymer and water. The polyurethane-
polysiloxane coatings so produced generally have good tensile and tear strength, good
chemical resistance and excellent adhesion to many substrates. However, because of the
relatively large amount of amino alkoxysilane used to end cap the isocyanate, these coatings
15 have an inherent tendency to yellow on exposure to sunlight and have an high degree of cross
linking which results in limited elongation.

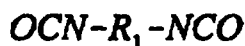
Another disadvantage of both the one-and two-package elastomeric urethane coatings
is the presence of isocyanate. Health hazards associated with exposure to isocyanates include
severe irritation of the skin, eyes, gastrointestinal tract and respiratory systems. Many
20 isocyanates have high chronic inhalation toxicity and, as a result, airborne threshold limit
values in the 0.01 ppm range have been established for many isocyanates. Thus, spray
application of isocyanate based coating materials presents a health hazard which may require
the use of air supplied respirators or other specialized equipment in cretin instances.
Additionally, certain isocyanates are now considered suspect carcinogens. Further, Title III
25 of the 1990 Clean Air Act Amendments lists certain isocyanates among 190 materials that
the EPA has labeled Hazardous Air Pollutants (HAPS) for which emissions must be reduced.
None of the modified elastomeric urethane coatings discussed above eliminate isocyanate and,
therefore, present the same health hazards associated with conventional elastomeric urethane
coatings.

30 In view of the foregoing problems, it is desirable to provide a moisture-curable
urethane composition that, when used as a coating, does not yellow upon exposure to
sunlight, and that eliminates any isocyanate related health hazard. It is also desirable to
provide a moisture-curable urethane composition having improved resistance to chemical and
weather exposure and which also exhibits high tensile and tear strength and high elongation.
35 It is further desirable to provide a moisture-curable urethane composition which eliminates
carbon dioxide generated bubble formation and entrapment to permit application film
thicknesses greater than previously possible using prior known moisture-curable elastomeric
urethanes.

1 Summary of the Invention

2 This invention comprises a moisture-curable polysiloxane polyurethane composition
 3 prepared by combining in the presence of water an organic di-or polyisocyanate, a polyol,
 4 a hydroxyl-containing silicon material having the hydroxyl groups attached directly to a
 5 silicon atom, an organotin catalyst, an amine catalyst, a methoxy-functional silicone
 6 intermediate, and a carbinol. If desired, various different fillers, pigments, solvents, and
 7 additives for enhancing pigment wetting and flow control and the like can also be used to
 8 prepare the composition.

9 The organic di-or polyisocyanate ingredient useful in preparing the composition has
 10 the general formula



15 where R_1 may be selected from the group including aliphatic, cycloaliphatic, or
 16 aromatic groups, where the di- or polyisocyanate ingredient has a weight average molecular
 17 weight in the range of from about 200 to 2,000.

18 The polyol ingredient useful in preparing the composition has the general formula

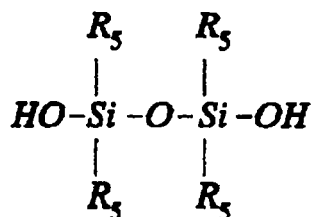


21 where the R_2 group may be selected from the group including polyester, polyether,
 22 polyalkyldiene, and glycol groups, and where the polyol has a molecular weight in the range
 23 of from about 200 to 5,000.

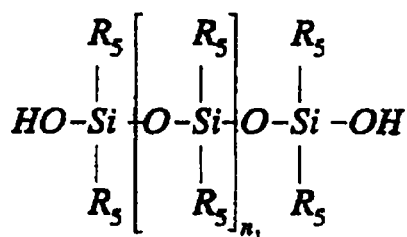
24 Hydroxyl-containing silicon material may be selected from the group consisting of: (a)
 25 silanol materials having the formulas



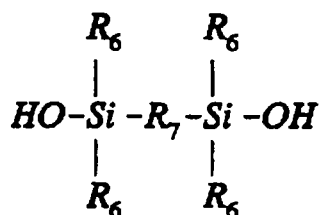
35 where R_3 may comprise organic radicals selected from the group including allyl, alkyl,
 36 cycloalkyl, aryl, alkaryl or araryl radicals; (b) siloxanol materials having the formulas



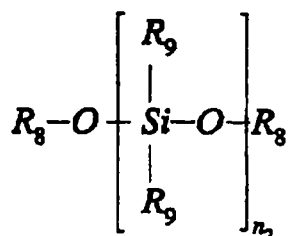
and



where each R_5 group may comprise a hydrocarbon radical selected from the group including alkyl, alkenyl, cycloalkyl, aryl, alkaryl, or aralkyl radicals, and where n_1 may be an integer in the range of from one to about thirty; (c) silicon materials having two or more silicon atoms attached through divalent organic radicals such as those having the formula



where each R_6 group may comprise another OH group or may comprise a hydrocarbon radical selected from the group including alkyl, cycloalkyl, aryl, alkaryl, and aralkyl radicals, where R_7 may comprise a divalent organic radical selected from the group including methylene, polymethylene, arylene, polyarylene, cycloalkylene, and polycycloalkylene; and (d) silanol-functional silicone intermediates having the formula

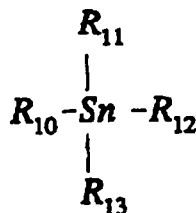


WO 97/11983

PCT/US96/15094

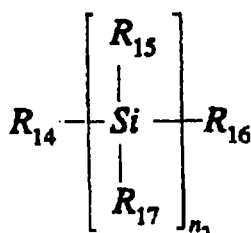
where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of the hydroxy, alkyl, and aryl groups having up to about six carbon atoms, and where n_2 is selected so that a weight average molecular weight is in the range of from about 500 to 15,000.

The organotin catalyst has the general formula



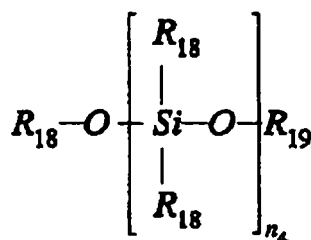
where R_{10} , R_{11} , R_{12} , and R_{13} are selected from the group including alkyl, aryl, and alkoxy groups having up to about eleven carbon atoms, and where any two of R_{10} , R_{11} , R_{12} , and R_{13} are also selected from a group of inorganic atoms including halogens, sulfur, and oxygen.

The amine catalyst is selected from the group including tertiary amines and aminosilanes having the general formula



where R_{14} is selected from the group including aliphatic and aromatic amines comprising in the range of from one to six nitrogen atoms and in the range of from one to six carbon atoms, where R_{15} , R_{16} , and R_{17} are independently selected from the group including alkoxy and aryloxy groups having up to about twelve carbon atoms, and where n_3 is in the range of from one to six.

The methoxy-functional silicone intermediates have the general formula



where each R_{18} group is independently selected from the group including alkyl, aryl, and alkoxy groups having up to about six carbon atoms, where each R_{19} is independently selected from the group including hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, and where n_4 is selected so that the weight average molecular weight of the silicone intermediate is in the range of from about 500 to 6,000.

The chemical ingredients are combined together and react to form silanol-functionalized urethane prepolymers that cure at ambient temperatures in the presence of moisture to form polysiloxane polyurethane compositions of the present invention. The resulting polysiloxane polyurethane composition does not present an isocyanate related health hazard, has improved resistance to chemical and weathering exposure, exhibits high tensile and tear strength, and high elasticity and elongation. The composition, prepared in this manner, eliminates carbon dioxide generated bubble formation and entrapment and is, therefore, capable of being applied as a coating at much greater thicknesses than prior known moisture-curable urethane compositions.

Brief Description of the Drawings

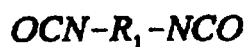
These and other features and advantages of the invention will become appreciated as the same becomes better understood with reference to the specification, claims and drawings wherein:

FIG. 1 is an isometric view of a flexible hose comprising a polysiloxane polyurethane binder composition prepared according to principles of this invention.

Detailed Description of the Invention

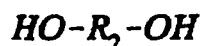
Polysiloxane polyurethane compositions for providing enhanced chemical resistance, weatherability, abrasion resistance, and impact resistance to the surface of a substrate, when applied as a coating, and to the body of a device, when used to form a composite, may have as significant ingredients an isocyanate-terminated urethane prepolymer and a hydroxyl-containing silicon material. A preferred polysiloxane polyurethane composition may be prepared according to the principles of this invention by combining:

- (a) an organic di- or polyisocyanate having the general formula



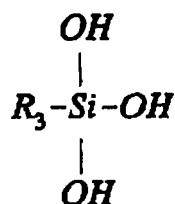
where the R_1 group may be selected from the group including aliphatic, cycloaliphatic, or aromatic groups, and where the di-or polyisocyanate ingredient has a weight average molecular weight in the range of from about 200 to 2,000; with

(b) a polyol having the general formula



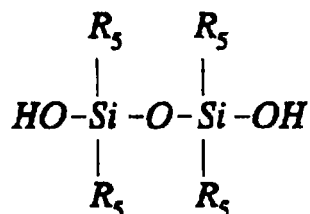
where the R_2 group may be selected from the group including polyester, polyether, polyalkyldiene, and glycol groups, and where the polyol has a weight average molecular weight in the range of from about 200 to 5,000; with

(c) a hydroxyl (OH) containing silicon material including those materials wherein the OH group or groups are attached directly to the silicon atom, such as the silanol materials having the general formulas

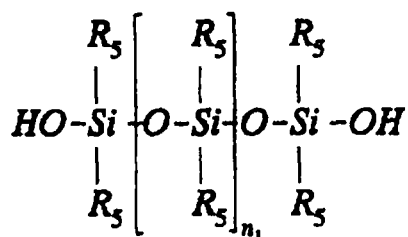


where R_3 may comprise organic radicals selected from the group including allyl, alkyl, cycloalkyl, aryl, alkaryl or araryl radicals.

Another preferred group of hydroxyl-containing silicon materials are silicon materials having two or more OH groups attached directly to the silicon atom such as the siloxanol materials having the general formula

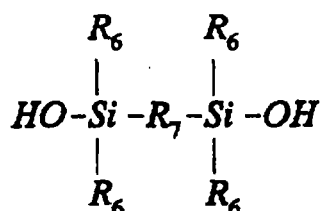


and



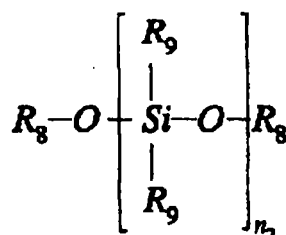
where each R_5 group may comprise a hydrocarbon radical selected from the group including alkyl, alkenyl, cycloalkyl, aryl, alkaryl, or aralkyl radicals, and where n_1 may be an integer in the range of from one to about thirty.

Another preferred group of hydroxyl-containing silicon materials are materials comprising two or more OH groups attached to a silicon atom that have two or more silicon atoms attached through divalent organic radicals such as those having the general formula



where each R_6 group may comprise another OH group or may comprise a hydrocarbon radical selected from the group including alkyl, cycloalkyl, aryl, alkaryl, and aralkyl radicals, where R_7 may comprise a divalent organic radical selected from the group including methylene, polymethylene, arylene, polyarylene, cycloalkylene, and polycycloalkylene.

A particularly preferred class of hydroxyl-containing silicon materials are silanol-functional silicone intermediates having the general formula

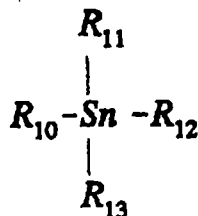


where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of the hydroxy, alkyl, and aryl groups having up to about six carbon atoms, and where n_2 is selected so that the weight average molecular weight is in the range of from about 500 to 15,000; with

WO 97/11983

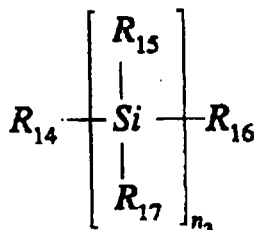
PCT/US96/15094

(d) an organotin catalyst having the general formula



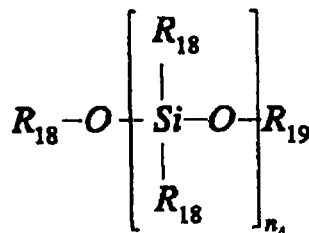
where R_{10} , R_{11} , R_{12} , and R_{13} are selected from a group including alkyl, aryl, and alkoxy groups having up to about eleven carbon atoms, and where any two of R_{10} , R_{11} , R_{12} , and R_{13} are also selected from a group of inorganic atoms including halogens, sulfur, and oxygen; with

(e) a tertiary amine catalyst or an aminosilane having the general formula



where R_{14} is selected from the group including aliphatic and aromatic amines comprising in the range of from one to six nitrogen atoms and in the range of from one to six carbon atoms, where R_{15} , R_{16} , and R_{17} are independently selected from the group consisting of alkoxy and aryloxy groups having up to about twelve carbon atoms, and where n_3 is in the range of from one to six; with

(f) methoxy-functional silicone intermediates having the general formula



where each R_{18} group is independently selected from the group including alkyl, aryl, and alkoxy groups having up to about six carbon atoms, where each R_{19} group is independently selected from the group including hydrogen, alkyl, and aryl groups having up

1 to about twelve carbon atoms, and where n_4 is selected so that the average molecular weight is in the range of from about 500 to 6,000; with

- 5 (g) a carbinol having an average of at least two carbon bonded hydroxy groups per carbinol and a weight average molecular weight in a range of from 60 to 10,000; with
(h) fillers and pigments; with
(i) a solvent such as a non-alcoholic solvent; with
(j) various different types of additives for enhancing pigment wetting, flow control and the like.

10 With respect to the organic di-or polyisocyanate ingredient, it is desired that the weight average molecular weight be within the above identified range to facilitate the reactions between the polyisocyanate and the polyol. The polysiloxane polyurethane composition prepared according to principles of this invention may comprise in the range of from two to fifty percent by weight of the polyisocyanate ingredient. The polyisocyanate ingredient serves to enhance the chemical and weathering resistance of the composition. A composition
15 comprising less than about two percent by weight of the polyisocyanate has been shown to produce a composition that does not display the desired degree of chemical or weathering resistance. A composition comprising more than about fifty percent by weight of the polyisocyanate has been shown to produce cured product that may be too brittle for such applications as a coating, composite binder or the like. The preferred amount of
20 polyisocyanate ingredient used to form compositions of this invention depends on the particular application. For example, when used as a coating to form a membrane for concrete, it is desired that the composition have a low hardness of approximately 30-50 Rockwell A, formed by using in the range of from three to five percent by weight of the polyisocyanate ingredient. As another example, when used as a coating to form an abrasion
25 resistant hopper car lining, it is desired that the composition have a hardness of approximately 80 Rockwell A to 50 Rockwell D, formed by using in the range of from six to eight percent by weight of the polyisocyanate ingredient. As another example, when used to form an elastomeric concrete coating for exterior resistance, the composition is formed by using in the range of from ten to twelve percent by weight of the polyisocyanate ingredient.

30 As another example, compositions of this invention can be used as a binder for reinforcing particles, members, or elements in composite articles. In one embodiment, the composition can be used as a binder for fiberglass, chopped glass fiber and the like to form a hose 10 having improved flexibility, impact resistance, chemical resistance, weatherability, and elasticity when compared to conventional hoses. In such an embodiment, the hose 10
35 may comprise in the range of from about 60 to 80 percent by weight reinforcing material 12, and in the range of from about 20 to 40 percent by weight binder 14. The hose can be formed using conventional manufacturing techniques by molding process, extrusion process, or the like.

1 Although compositions of this invention have been specifically described and illustrated
as being used to form a composite article comprising a flexible hose, it is to be understood
within the scope of this invention that applications of the composition in forming composites
are not limited to flexible hoses, and can include any type of composite article where
5 improved properties of flexibility, impact resistance, weatherability, chemical resistance, and
elasticity is desired.

Any suitable organic di- or polyisocyanate, either aliphatic, cycloaliphatic or aromatic,
may be used to form the composition. Suitable organic polyisocyanates include
10 polymethylene polyphenyl isocyanate, 2,4 and 4,4-diphenylmethane diisocyanate (MDI) and
liquid carbodiimide and uretonimine modified MDI variants, 2,4 and 2,6-toluene diisocyanate
(TDI), paraphenylene diisocyanate, naphthylene diisocyanate, dianisidine diisocyanate,
xylylene diisocyanate (XDI), lysine diisocyanate, tetramethyl-meta-xylylene diisocyanate (M-
TMSDI), dimeryl diisocyanate (DDI), 3-isocyanatomethyl 3,5,5-trimethylcyclohexyl
isocyanate (IPDI), bis (4-isocyanatocyclohexyl) methane (Desmodur W), hexamethylene
15 diisocyanate, and hexamethylene diisocyanate biurets and isocyanurates, i.e., Desmodur N-
100, Desmodur N-3200 and Desmodur N-3300 from Miles, Inc., Pittsburgh, PA.

Aromatic di- or polyisocyanates are preferred for compositions where optimum
chemical resistance is desired. Preferred aromatic di- or polyisocyanates are toluene
diisocyanate, paraphenylene diisocyanate, polymethylene polyphenyl isocyanate and 2,4' and
20 4,4'-diphenylmethane diisocyanate (MDI) and liquid carbodiimide and uretonimine modified
MDI variants.

Aliphatic di- or polyisocyanates are preferred for compositions where optimum
weathering resistance is desired. Preferred aliphatic di- and polyisocyanates include 3-
isocyanatomethyl 3,5,5-trimethylcyclohexyl isocyanate (IPDI), bis (4-isocyanato cyclohexyl)
25 methane (Desmodur W), tetramethyl-meta-xylylene diisocyanate (M-TXMDI) and
hexamethylene diisocyanate biurets and isocyanurates i.e. Desmodur N-100, Desmodur N-
3200, and Desmodur N-3300. A preferred polyisocyanate is 3-isocyanatomethyl 3,5,5-
trimethylcyclohexyl isocyanate produced by Huls America of Piscataway, New Jersey,
under the product name Vestamin IPDI.

30 With respect to the polyol ingredient, it is desired that the polyol have a weight
average molecular weight as described above to facilitate reaction with the polyisocyanate.
A composition prepared according to principles of this invention may comprise in the range
of from two to sixty percent by weight polyol. The polyol ingredient enhances the percent
elongation, modulus of elasticity, resilience, chemical resistance, weatherability, and
35 hydrolytic stability of the composition. Using less than about two percent by weight of the
polyol will produce a composition having high levels of isocyanate and silanol, causing the
composition to be too brittle for application as an elastomeric coating. Using greater than
about sixty percent by weight of the polyol will produce a cured composition that is soft and

1 not well suited for most applications.

The polyisocyanate and polyol are reacted to form an isocyanate-terminated polyurethane prepolymer useful in the present invention. As used herein, an isocyanate-terminated urethane prepolymer refers to compounds having at least one
5 isocyanate group per molecule which yields polyurethane and/or poly(urea)urethane linkages upon reaction or curing. A summary of prepolymer chemistry and technology can be found in *Polyurethanes: Chemistry and Technology*, Saunders and Frisch, Interscience Publishers, New York, 1963 (Part I) and 1964 (Part II) and *Polyurethanes Handbook*, Gunther Oertel, Hanser Publishers, New York, 1985.

10 Polyols used to make the isocyanate-terminated urethane prepolymers or quasi-prepolymers may include polyoxyalkylene ether glycols, polyester glycols, polycaprolactone glycols, polycarbonate glycols, castor oils, polybutadiene glycols, acrylic polyols and glycols and polyetherthioether glycols of which the following are mentioned as non-limiting examples:

15 polytetramethylene ether glycols, MW 650-2900,
polypropylene ether glycols, MW 400-4000,
castor oil and castor oil derivatives, MW 300-1000,
polycaprolactone glycols, MW 300-2000,
hydroxyl terminated bisphenol A polyols, MW 400-1000,
20 polycarbonate glycols, MW 500-2500,
polyetherthioether glycols, MW 400-2000,
hydroxyl-containing polyacrylates and polymethacrylates, equivalent weight 400-4000,
polybutylene ether glycols, MW 400-4000, and
25 polyoxyethylene-propylene copolymer ether glycols, MW 400-4000.

Polyester glycols are reaction products of polyhydric alcohols, such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, 1,4-butanediol, 1,3-butanediol, pentanediol, 1,6-hexanediol, dodecanediol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, neopentyl glycol, 2,2,4-trimethylpentanediol, hydrogenated
30 bisphenol A, propylene oxide addition products of bisphenol A, glycerin, trimethylolpropane, trimethylolpropane, pentaerythritol, and trishydroxyethyl isocyanurate, and a polycarboxylic acid, polycarboxylic acid anhydride, or alkyl ester of a polycarboxylic acid, such as phthalic anhydride, isophthalic acid, terephthalic acid, dimethyl terephthalic acid, succinic acid, adipic acid, azelaic acid, dimer acid, maleic anhydride, fumaric acid, itaconic acid,
35 tetrahydrophthalic acid, anhydrous hexahydrophthalic acid, methyl nadic acid anhydride, trimellitic anhydride, pyromellitic anhydride, and butanetetra-carboxylic acid, in a mixing proportion where the hydroxyl groups are in excess.

Also permissible in combination are, e.g., monobasic acids such as fatty acids, benzoic

1 acid, and tertiary butyl benzoic acid, monoalcohols such as octanol, lauryl alcohol, and oleyl
alcohol, hydroxycarboxylic acids such as hydroxystearic acid, parahydroxybenzoic acid, and
metahydroxybenzoic acid. Monomeric glycols may be blended with polyols and include
ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol,
5 trimethylene glycol, 1,3- and 1,4-butanediol, 1,5-pentanediol, 1,2-hexylene glycol, 1,10-
decandiol, 1,2-cyclohexanediol, 3-cyclohexane-1,1-dimethanol, 4-methyl-3-cyclohexane-
1,1-dimethanol, 3-methylene-1, 5-pentanediol, (2-hydroxypropoxy) 1 propanol, 4-(2
hydroxyethoxy)-butano, 5-(2hydroxypropoxy)-1-pentanol, 1-(2-hydroxy-methoxy)2-hexanol,
1-(2-hydroxypropoxy)-2-octanol, 3-allyloxy-1, 5-pentanediol, glycerin 1,2,6-hexanetriol,
10 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, pentaerythritol, sorbitol, sucrose, lactose,
c-methyl glucoside, novolac resins and hydroxy-terminated caprolactone.

Preferred polyols used in making isocyanate-terminated polyurethane prepolymers of
the present invention included polyoxyethylene propylene copolymer ether glycols (Olin
Chemical, Stanford, CT), polybutylene ether glycols (Dow Chemical, Midland, MI), castor
15 oil and castor oil derivatives (Caschem, Inc., Bayonne, NJ), polyester polyols (Miles, Inc.,
Pittsburgh, PA and Witco Chemical, Chicago, IL) polycaprolactone glycols (Union Carbide,
Danbury CT) and hydroxyl-terminated bisphenol A polyols (Milliken Chem). A particularly
preferred polyol is polyethylene propylene ether glycol produced by ARCO Chemical of
Philadelphia, PA under the product name ARCO 1025.

20 Isocyanate-terminated urethane prepolymers and quasi-prepolymers are also available
from a number of commercial sources including Miles, Inc., Air Products (Ambler, PA,) Hexcel
(Dublin, CA), Uniroyal (Naugatuck, CT), Dow Chemical, Essex Specialty Products
(Clifton, NJ) and Polyurethane Corporation of America (Everett, MA).
Isocyanate-terminated urethane prepolymers from Air Products available under the product
25 name Airthane are preferred because of their low free monomeric isocyanate content and low
viscosities.

With respect to the hydroxyl-containing silicon material, it is to be understood that the
composition of this invention can be prepared using a silanol material, a siloxanol material,
a silicon material having two or more silicon atoms attached through divalent organic
30 radicals, a silanol-functional silicone intermediate, and combinations thereof.

With respect to the silicon material, suitable silanol materials include
diphenyldihydroxy silane, dicyclohexyldihydroxy silane and phenyltolylidihydroxy silane,
xylyltrihydroxy silane and phenyltrihydroxy silane. With respect to the hydroxyly-containing
silicon material comprising siloxanol, suitable materials include tetramethyldisiloxane diol,
35 tetra phenyldisiloxane diol, diphenyldimethyldisiloxane diol, dibutyldiphenyl disiloxane diol
and the like. A preferred siloxanol is diphenyldimethyldisiloxanediol produced by Huls
America.

With respect to the hydroxyl-containing silicon material having two or more silicon

1 atoms attached through divalent organic radicals, suitable materials include ethylenebis
(trihydroxysilane), p-phenylene-bis-(dimethyl) hydroxysilane, p-cyclohexylene-bis(dibutyl)
hydroxysilane and 1,6-hexamethylene-bis-(dimethylhydroxysilane). The preparation of many
5 of these compounds is illustrated in U.S. Patent No. 2,561,429, which is herein incorporated
by reference. A preferred hydroxyl-containing silicon material is p-phenylene-bis-(dimethyl)
hydroxysilane produced by Huls America.

With respect to the hydroxyl-containing material comprising silanol-functional silicone
intermediates, a silanol-functional silicone intermediate having a weight average molecular
weight of less than about 1,000 are not readily available. A silanol-functional silicone
10 intermediate having a weight average molecular weight greater than about 15,000 is
undesirable because the resulting composition will contain a predominate amount of silicone,
rather than polyurethane, and be too soft and gummy for use in such applications as coatings
and binders in composites. Suitable silanol-functional silicone intermediates have a silanol
content in the range of from one to six percent and are exemplified by such commercially
15 available products as Dow Corning's DC-Z6018, DC-6-2230 and DC-1-2530. A preferred
silanol-functional silicone intermediate is manufactured by Dow Corning Corp. of Midland,
Michigan, under the product name DC-1-2530, which is a silanol-functional intermediate
having a weight average molecular weight of approximately 10,000, and comprising
approximately eighty percent solids and three percent silanol.

20 A composition prepared according to principles of this invention may comprise in the
range of from fifteen to sixty percent by weight of the hydroxyl-containing silicon material.
The composition can be prepared using either a single type of silicon material or by using
a combination of different silicon materials. The hydroxy-containing silicon material reacts
with the di- or polyisocyanate ingredient to eliminate the disadvantages associated with
25 conventional isocyanate based coating compositions, e.g., to prereact the isocyanate to
prevent reaction with water and eliminate carbon dioxide bubble formation and entrapment.
Using less than about fifteen percent by weight of the hydroxyl-containing silicon material
produces a soft or gummy composition that is unsuited for most coating and composite
applications. Using greater than about sixty percent by weight of the hydroxyl-containing
30 silicon material produces a composition that is too hard and brittle for most elastomeric
coating and composite applications. A preferred composition for use as a coating comprises
approximately thirty percent by weight of the hydroxyl-containing silicon material.

The isocyanate-terminated urethane prepolymer created by the reaction of the
isocyanate and the polyol are reacted with a hydroxyl-containing silicon material having two
35 or more OH groups attach directly to a silicon atom, an SiOH percent of from about 0.5 to
about 20, and a weight average molecular weight of about 1,000 to about 15,000. The
hydroxyl-containing silicon material is reacted with the isocyanate-terminated urethane
prepolymer at an OH to NCO equivalent ratio of from about 2:1 to about 6:1 to form a

1 silanol-functionalized urethane polymer.

The reaction between the isocyanate and the hydroxyl-containing silicon material is conducted in the presence of a catalyst to accelerate the hydrolytic polycondensation reaction between the reactants. The catalyst may comprise an organotin compound. With respect to
5 the organotin catalyst, suitable organotin catalysts may be selected from the group including dibutyltin dilaurate, dibutyltin diacetate, dibutyltin mercaptide, and the like. Preferred organotin catalysts are dibutyltin dilaurate and dibutyltin diacetate and are commercially available from Air Products of Allentown, Pennsylvania under the product names T-1 and T-12, and by Witco Chemical Corp. of New York, New York under the product name SUL-
10 3.

A composition prepared according to principles of this invention may comprise in the range of from 0.02 to 2 percent by weight organotin catalyst. The organotin catalyst serves to accelerate the hydrolytic polycondensation of the hydroxyl-containing silicon material and the isocyanate-terminated urethane prepolymer by promoting the reaction of the hydroxyl
15 group with the isocyanate and minimizing side reaction, e.g., the reaction of the isocyanate with water and/or urethane. Using less than about 0.02 percent by weight of the organotin catalyst does not provide an effective amount of the organotin catalyst helpful in accelerating hydrolytic polycondensation and, thus does not prevent the occurrence of undesirable side reactions with the isocyanate. Using greater than about 2 percent by weight of the organotin
20 catalyst provides more of the organotin catalyst than needed to accelerate the hydrolytic polycondensation and, therefore is economically undesirable. A preferred composition useful as a coating comprises approximately 0.5 percent by weight organotin catalyst.

The composition can be prepared by using, in addition to the organotin catalyst, a tertiary amine catalyst. Exemplary amines include dimethylethanolamine,
25 dimethylpropanolamine, dimethylbutanolamine, methylethylmethanolamine, methylpropylmethanol amine, methylethylethanolamine, monoisopropylamine, methyldiethanolamine, triethanolamine, diethanolamine and ethanolamine. Preferred amines include dimethylethanol-amine and ethanolamine. Like the organotin catalyst, the tertiary amine catalyst also serves to accelerate the hydrolytic polycondensation of the
30 hydroxyl-containing silicon material and the isocyanate-terminated urethane prepolymer.

Compositions prepared according to principles of this invention may comprise in the range of from 0.1 to 4 percent by weight tertiary amine. Using less than about 0.1 percent by weight of the tertiary amine will provide an insufficient amount of catalyst to effect the acceleration of the hydrolytic polycondensation. Using greater than about 4 percent by
35 weight of the tertiary amine will provide an amount of catalyst greater than that necessary to effect the acceleration of the hydrolytic polycondensation and, thus is economically undesirable. A preferred composition useful as a coating comprises approximately two percent by weight of the tertiary amine.

1 With respect to the aminosilane ingredient, it may be used in lieu of the tertiary amine
in combination with the organotin catalyst to accelerate the hydrolytic polycondensation
reaction between the hydroxyl-containing silicon material and the isocyanate-terminated
urethane prepolymer. A composition prepared according to the principles of this invention
5 may comprise in the range of from one to four percent by weight aminosilane. Like the
tertiary amine catalyst, the aminosilane also serves to accelerate the hydrolytic
polycondensation of the hydroxyl-containing silicon material and the isocyanate-terminated
urethane prepolymer. However, unlike the organotin and tertiary amine catalyst, the
aminosilane becomes part of the SFUP polymer backbone during the polycondensation
10 reaction.

Using less than about one percent by weight of the aminosilane will provide an
inefficient amount of the aminosilane to effect the desired acceleration of the hydrolytic
polycondensation reaction. Using greater than about four percent by weight of the
aminosilane will provide an amount greater than needed to effect the desired hydrolytic
15 polycondensation and, thus is economically undesirable. A preferred composition useful as
a coating comprises approximately two percent by weight aminosilane. Preferred
aminosilanes include aminoethylaminopropyl, trimethoxysilane and aminopropyl
triethoxysilane.

With respect to the methoxy-functional silicone intermediate, preferred
20 methoxy-functional silicone intermediates have a weight average molecular weight of about
1400 and are exemplified by such commercially available products as Dow Corning's 3074
and 3037, SY-231 manufactured by General Electric Co. of Pittsfield, Massachusetts, and
SR-191 manufactured by Wacker. The methoxy-functional silicone intermediate lowers the
viscosity of the coating composition. Compositions prepared according to principles of this
25 invention may comprise up to about twenty percent by weight of the methoxy-functional
silicone intermediate. Using greater than about twenty percent of the methoxy-functional
silicone intermediate produces a composition that, when used as a coating, has a high solvent
content that increases drying time and reduces film. A preferred composition useful as a
coating comprises approximately ten percent by weight of the methoxy-functional silicone
30 intermediate.

With respect to the carbinol ingredient, carbinols particularly useful in the polymer are
at least difunctional. Accordingly the terms glycol and polyol are used herein as being
interchangeable with carbinol. Exemplary glycols may include ethylene glycol, propylene
glycol, glycerol, diethylene glycol, trimethylene glycol, triethylene glycol, dipropylene
glycol, tripropylene glycol, polyethylene glycols, trimethyl propanol, 1,6- or 2,6-hexanediol,
35 neopentyl glycol, 1,3-butylene glycol, pentaerythritol, hexylene glycol, partially-esterified
polyols, cyclopentanediol and the like.

Preferred carbinols include hydroxyl-functional acrylic resins, polyoxyalkaline ether

1 glycols, polyester glycols, polycarbonate glycols, castor oil and its derivatives, polybutadiene
glycols and polycaprolactone polyols and the like. The choice of carbinol will affect the
mechanical properties of the cured product. For instance, if high molecular weight carbinols
5 are used, the tensile and tear strength and percent elongation of the resulting elastomer will
be lower. The addition of a high molecular weight carbinol may improve apparent drying
times or improve adhesion or weatherability. The addition of a glycol or lower molecular
weight carbinol will lower viscosity and may increase cure or drying time. A preferred
carbinol is polyoxypropylene manufactured by ARCO under the product name Arcol 1025,
10 which has a weight average molecular weight of approximately 1000.

10 Compositions prepared according to principles of this invention may comprise up to
ten percent by weight of the carbinol. Using greater than ten percent by weight of the
carbinol will produce a composition having a reduced isocyanate to polyol ratio and, thus
having a reduced cross-link density. A reduced cross-link density causes a reduction in such
desired physical properties as tensile strength and tear strength. A preferred composition
15 useful as a coating comprises approximately ten percent by weight carbinol.

With respect to the fillers, conventional fillers can be used to prepare the composition
including fillers such as silica powder, talc (magnesium silicate), clays such as china clay
(aluminum silicate), wollastonite (calcium silicate), calcium carbonate, barites (barium
sulfate, barium metaborate), aluminum trihydrate, graphite, zinc, aluminum, copper and the
20 like. The composition may comprise up to about twenty percent by weight fillers. A
preferred composition useful as a coating comprises approximately five percent by weight
fillers.

With respect to the pigments, pigments such as iron oxide, titanium dioxide,
phthalocyanine green and blue, hansa yellow and the like may be used to color the cured
25 composition. The composition may comprise up to about twenty percent by weight pigment.
A preferred composition useful as a coating comprises approximately five percent by weight
pigment.

Some of the compositions of this invention require the addition of solvent to improve
application by spray, roll, brush, dip and the like. Non-alcoholic solvents are preferred and
30 include ethers, esters, aromatics and the like. Specific solvents include, for example, MEK,
MIBK, n-propyl ketone, methyl isoamyl ketone, methyl amyl ketone, isobutyl acetate, butyl
acetate, ethyl 3 ethoxy propionate, xylene and higher boiling aromatic solvents such as
Chevron 25, hexyl acetate, heptyl acetate and the like. The amount of solvent that can be
added to the composition is currently regulated by various state and federal environmental
35 agencies to maximum of 420 grams per liter. A particularly preferred solvent is butyl
acetate.

Compositions prepared according to principles of this invention may comprise
additives such as pigment wetting agents, surfactants, defoamers, flow control agents,

1 thixotropes and UV stabilizers as well as bituminous and hydrocarbon extenders and plasticizers. A composition may comprise up to about five percent by weight additives.

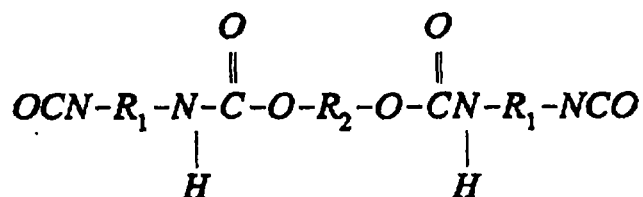
5 The composition is prepared by combining the preferred polyisocyanate, organotin catalyst, and polyol ingredients according to the previously described proportions, raising the temperature to approximately 70°C and blending the mixture together for approximately three hours. While not wishing to be bound by any particular theory or mechanism, it is believed that the polyisocyanate and polyol react to form an isocyanate-terminated urethane prepolymer, as represented in Reaction (1) below. The reactions provided below are not intended to illustrate the entire range of chemical reactions that may occur between reactants but is only intended to illustrate and clarify the general type of chemical reaction believed to occur. Accordingly, it is to be understood that chemical reactions other than those specifically described and illustrated are within the scope of this invention.

Reaction No. 1

15



20



25

A silanol-functionalized urethane prepolymer (SFUP) is prepared, as represented in Reaction (2) below, by combining the preferred hydroxyl-containing silicon material with the organotin catalyst, the amine catalyst, and the isocyanate-terminated urethane prepolymer according to the previously described proportions, and blending the mixture together at a temperature of approximately 70°C for approximately four hours. It is believed that the hydroxyl-containing silicon material and the isocyanate-terminated urethane prepolymer undergo hydrolytic polycondensation to form silanol-functionalized urethane prepolymers.

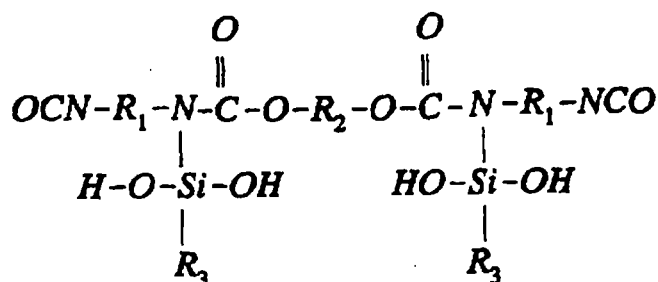
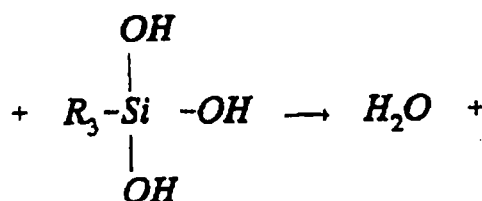
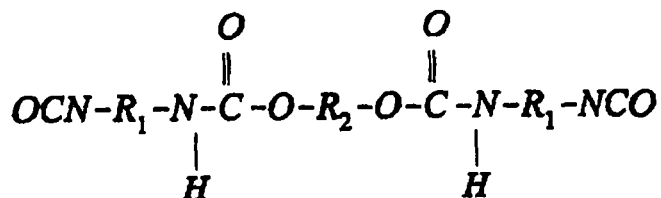
30

35

WO 97/11983

PCT/US96/15094

Reaction No. 2



The reaction is typically conducted in a heated vessel equipped with an agitator, nitrogen inlet and condenser. The catalyst ingredients and hydroxyl-containing silicon compound are charged to the vessel and the isocyanate-functional urethane prepolymer is then added with continuous mixing and nitrogen blanketing. A sample is withdrawn from the vessel periodically and analyzed for unreacted isocyanate with an FTIR spectrophotometer. The reaction is complete when the FTIR spectrum shows no evidence of isocyanate of at least 2,250 centimeters⁻¹.

The silanol-functionalized urethane prepolymers of the present invention cure at ambient temperatures in the presence of moisture by condensation of the silanol groups to form polysiloxane polyurethane elastomers. If desired, pigments, solvents, additives and fillers can be added to the silanol-functionalized urethane prepolymer according to the previously described proportions and blended together until the mixture is uniform.

The silanol-functionalized urethane prepolymer, amine/organotin and/or aminosilane catalyst, pigments, solvents and additives are combined to produce a single package composition system. Optionally, the amine/organotin and/or aminosilane catalyst may be

1 packaged in moisture proof containers, typically epoxy or phenolic lined cans and drums.

Moisture-cured polysiloxane polyurethane compositions of this invention are useful in many different applications, such as surface coatings, composite binders or the like. The isocyanate-terminated urethane prepolymer and silanol-functional silicone intermediate used
5 to make the silanol-functionalized urethane prepolymer are selected for a particular application based on the desired physical and chemical characteristics of the polysiloxane polyurethane composition that they produce. For example, composition systems based on aromatic isocyanate urethane prepolymers have good chemical resistance while aliphatic isocyanate-based urethane prepolymers have better resistance to weathering.
10 Isocyanate-terminated urethane prepolymers prepared from polyesters generally have better chemical and abrasion resistance. Polyether-based urethane prepolymers have good hydrolytic stability. Silanol-functional intermediates having an SiOH content of four to eight percent cure fast and have high tensile strength and hardness, while Silanol-functional intermediates having a lower SiOH content have higher elongation and lower hardness.

15 Compositions of this invention have several advantages compared to prior known elastomeric urethane compositions. For example, compositions prepared according to principles of this invention eliminate any isocyanate related health hazards to the end user by reaction with the hydroxyl-containing silicon material and are, therefore, more toxicologically acceptable. Compositions of this invention also eliminate the problem of
20 carbon dioxide bubble generation and entrapment due to the prereaction of the isocyanate ingredient with the hydroxyl-containing silicon material, thereby precluding reaction of the isocyanate ingredient with water. Elimination of bubble entrapment allows for greater film build thicknesses than allowable using prior known isocyanate-based coating compositions. Moisture-cured polysiloxane polyurethane compositions of the present invention display better
25 weatherability and chemical resistance than prior known elastomeric polyurethanes and have surprisingly high tensile and tear strength and high elongation.

These and other features of the present invention will become more apparent upon consideration of the following nonlimiting examples. Table 1 includes a description of the ingredients used in each example.

30

35

1	<u>MATERIAL</u>	<u>SUPPLIER</u>	<u>TABLE I</u> <u>DESCRIPTION</u>
	DC-Z6018	Dow Corning	silanol-functional phenylpropyl silicone intermediate with 6% SiOH, and a weight average molecular weight of 3000.
5	DC-6-2230	Dow Corning	silanol-functional silicone intermediate with 5% SiOH, a weight average molecular weight of 3000.
	Isophorone diisocyanate (IPDI)	Huls	Cycloaliphatic diisocyanate, MW=222.3
	Arcol 1025	Arco	1000 MW polyoxypropylene ether diol
	Arcol 425	Arco	425 MW polyoxy propylene ether diol
10	T-12	Air Products	dibutyl tin dilaurate
	Sul-3	Witco	dibutyl tin diacetate
	BYK-077	Byk-Chemie	defoamer
	BYK-080	Byk-Chemie	defoamer
	Nuosperse 657	Huls	pigment wetting agent
	R-960	Dupont	titanium dioxide
	Lampblack #6	General Carbon	lamp black
	XAPC-722	Air Products	IPDI/polytetramethylene ether glycol urethane prepolymer, 5.75%NCO
15	butyl acetate	Union Carbide	solvent (urethane grade)
	PM Acetate	Arco	solvent (urethane grade)
	Dabco T-120	Air Products	moisture cure catalyst
	DC-Z6020	Dow Corning	amino silane
	Vestamin A-139	Huls	cycloaliphatic amine
	Epalloy 8250	CVC	epoxy novalac resin
20	DC3074	Dow Corning	methoxy-functional silicone
	Imsil A-10	Illinois Minerals	silica
	Dilson 6500		polyamide wax thixotropic agent

Example 125 Preparation of isocyanate-terminated urethane prepolymer

200.46 grams (g) of isophorone diisocyanate (IPDI), 0.17 g T-12 and 8.5 g of BYK-077 were charged to a resin flask equipped with heating mantle, agitator, nitrogen inlet, thermometer and condenser. A solution of 302.24 g Arcol 1025, 66.47 g Arcol 425, 70.14 g butyl acetate and 175 g Arco PM Acetate was prepared in another vessel and then added to the resin flask containing IPDI over a two minute period. The temperature was then raised to 70°C and held at constant temperature for three hours and 15 minutes with continuous agitation and nitrogen blanketing. The resulting isocyanate-terminated prepolymer had a solids content of approximately 70 weight percent, an isocyanate content of approximately 4.40 weight percent and a Brookfield viscosity of approximately 2480 centipoise (cP).

Preparation of silanol-functionalized urethane prepolymer

339.9 g of DC-Z6018 was dissolved in 183 g of butyl acetate in a resin flask equipped with heating mantle, agitator, nitrogen inlet, thermometer and condenser. When the DC-

- 1 Z6018 was completely dissolved, 0.4 g of T-12 was added and mixed until uniform.
Approximately 477.3 g of the isocyanate-terminated urethane prepolymer prepared above was
added to the DC-Z6018 solution over a two minute period. The temperature was raised to
70°C, then held for four hours at the same temperature with continuous stirring and nitrogen
5 blanketing. The FTIR spectrum of the resulting silanol-functionalized urethane prepolymer
showed no evidence of isocyanate. The Brookfield viscosity was approximately 3200 cP and
the solids content was approximately 67.4 weight percent.

Preparation of pigmented silanol-functionalized urethane prepolymer

- 10 Approximately 150 g of the silanol-functionalized urethane prepolymer prepared
above, 4 g Nuosperse 657, and 6 g BYK-080 were charged to a 1 quart can. Approximately
60 g of R-960 titanium dioxide and 3 g Lampblack #6 were added and the mixture was
dispersed to 3 Hegman fineness of grind using a Cowles dissolver. This required about ten
minutes. An additional 450 g of silanol-functionalized urethane prepolymer was added and
15 the composition was mixed until uniform.

Example 2

- Airthane XAPC-722, a commercially available isocyanate-terminated urethane
prepolymer supplied by Air Products was used in this example. Airthane XAPC-722 is based
20 on isophorone diisocyanate and polytetramethylene ether glycol. It is 100 percent solids and
has an isocyanate content of 5.75 percent.

Preparation of silanol-functionalized urethane prepolymer

- 25 245.9 g of DC-Z6018 was dissolved in 158 g of butyl acetate in a resin flask equipped
as described above. 2 g of Sul-3 and 8 g of BYK-080 were added and mixed until uniform.
A solution of 219.1 g of XAPC-722 and 158 g of butyl acetate was prepared in another resin
flask and then added to the DC-Z6018 solution over a two minute period. The temperature
was raised to 49°C and held at constant temperature for eight hours with continuous agitation
and nitrogen blanketing. The resulting silanol-functionalized urethane prepolymer had a
30 Brookfield viscosity of approximately 4000 cP and a solids content of approximately 60
weight percent. The FTIR spectrum showed no evidence of isocyanate.

Preparation of Pigmented Silanol-functionalized Urethane Prepolymer

- 35 A pigmented composition was prepared as follows: 150 g of the silanol-functionalized
urethane prepolymer, 4 g of Nuosperse 657, and 6 g BYK-080 were charged to a one quart
can. Approximately 60 g of R-960 titanium dioxide and 3 g Lampblack #6 were added and
the mixture was dispersed to 3 Hegman fineness of grind using a Cowles dissolver. An
additional 450 g of the silanol-functionalized urethane prepolymer was added and the

1 composition was mixed until uniform.

Example 3

5 Example 3 was prepared in the same manner as Example 2. The materials used were 306 g of DC-6-2230, 350.1 g of butyl acetate, 4 g of T-12 and 219.1 g of XAPC-722. The resulting silanol-functionalized urethane prepolymer had a solids content of approximately 60 weight percent and a Brookfield viscosity of approximately 3800 cP. The FTIR Spectrum showed no evidence of isocyanate.

10

Comparative Example 4

500 g of XAPC-722 was dissolved in 125 g of xylene in a one quart can using a paddle type mixer. The mixture had a Brookfield viscosity of approximately 1000 cP and a calculated isocyanate content of 4.6 weight percent.

15

Comparative Example 5

Comparative Example 5 uses the same urethane prepolymer solution described in comparative Example 4.

20 Examples 1 through 5 were combined with the catalysts and/or curatives and solvents as shown in Table 2. The compositions were spray applied as a coating on 3" x 8" x 1/16" hot-rolled steel panels with Bonderite 1000 treatment using a Devilbiss suction gun. Each panel was allowed to cure at 70°F (21 °C) and 50% RH for two weeks before measuring 60° gloss and conducting QUV accelerated weathering tests. Free films of each example were prepared using 20 mil and 40 mil Leneta drawdown bars on polyethylene sheet. After two
25 days, each film was removed from the polyethylene sheet and allowed to cure for two weeks at 70°F (21 °C) and 50% relative humidity before conducting chemical resistance tests and measuring hardness, tensile strength and percent elongation. A summary of the test methods is shown in Table 3.

30

35

1

TABLE 2

<u>COATING COMPOSITION</u>		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
5	Example 1	100	--	--	--	--
	Example 2	--	100	--	--	--
	Example 3	--	--	100	--	--
	Comparative Example 4	--	--	--	100	--
	Comparative Example 5	--	--	--	--	100
10	butyl acetate	10	20	10	5	10
	DC-Z6020	2	2	2	--	--
	T-12	1	1	1	--	--
	Dabco T-120	--	--	--	2	--
	Vestamin A-139	--	--	--	--	14.5
15	Dry to touch @ 20 mils (hrs)	4	3	4	6	3
	Dry through @ 20 mils (hrs.)	30	24	24	36	12
	Hardness, Shore A	60	80	75	50	80
	Tensile strength, psi	1500	2100	1800	1000	3000
	Elongation, %	400	205	170	500	260
<u>QUV Accelerated Weathering</u>						
20	60° Gloss - initial	55	62	91	94	95
	- 4 weeks	40	45	70	50	45
	- 8 weeks	24	35	55	20	15(1)
20	Appearance (40 mil drawdowns)	(a)	(a)	(a)	(b)	(c)
	<u>Chemical resistance, 24 hour spot tests</u>					
25	sodium hydroxide (50%)	10	10	10	10	10
	hydrochloric acid (37%)	8	8	8	8	8
	sulfuric acid (98%)	4	8	4	2	2
	phenol (89%)	4	4	4	2	2
	phosphoric acid (85%)	6	8	6	4	4
	acetone	10	10	10	10	10
	ammonium hydroxide (28%)	10	10	10	10	10
	ethyl alcohol (95%)	8	8	8	8	8
	acetic acid (99%)	4	6	6	2	2
	cumene	10	10	10	10	10
30	(a) continuous, bubble free film					
	(b) bubble entrapment, foamy					
	(c) some bubble formation					
	(1) yellowing, cracking, crazing					

35

TABLE 3

TEST	TEST METHOD
Dry times	ASTM D1640
QUV accelerated weathering	ASTM G53 (UV 313B BULB)
Hardness, Shore A	ASTM D2240
Tensile strength	ASTM D412
Elongation	ASTM D412
Impact resistance	ASTM D2794
Taber abrasion	ASTM D4060
Chemical resistance	ASTM D1308
10 = No change	4 = Major change
8 = Slight change	2 = Partial failure
6 = Definite change	0 = Complete failure

A comparison of the data presented in Table 2 clearly indicates that compositions of the present invention have improved weatherability and chemical resistance compared to prior known moisture-cured urethane coating compositions, and also have high tensile strength and elongation.

The bubble entrapment and foamy appearance of the 40 mil draw downs of Comparative Examples 4 and 5 clearly indicates that the compositions of the present invention are capable of being applied in thicker section than conventional moisture-cured isocyanate based urethane coating compositions.

The silanol-functionalized urethane prepolymers of the present invention may also be used to toughen silicone and polysiloxane compositions. The flexibility, impact and abrasion resistance of such compositions can be improved by partial replacement of (or addition to) the silanol-functional silicone resin component(s) with silanol-functionalized urethane prepolymer.

Example 6 is an aminosilane cured polysiloxane epoxy coating comprising the ingredients shown in Table 4. Example 7 is the same coating with fifteen weight percent addition of the silanol-functional urethane prepolymer of Example 2.

Example	6	7
Epalloy 8250	437.1	437.1
BYK-080	12.9	12.9
R-960	233.4	233.4
Imsil A-10	146.8	146.8
Dislon 6500	10.0	10.0
DC3074	374.4	374.4
Example 2*	--	18.2

*Silanol-functionalized urethane prepolymer from Example 2.

1 The ingredients were dispersed to 3 Hegmen fineness of grind with a Cowles
dissolver. One hundred grams of each example was mixed with 18.1 grams of Dow
Corning's Z6020 aminosilane and applied at 20 mils wet film thickness on 4 1/2" x 7 1/2" x
1/32" sandblasted steel panels using a Leneta drawdown bar. Taber abrasion panels of
5 Example 6 and Example 7 were prepared by spray application after thinning each formula
twenty percent by weight with butyl acetate.

 After two weeks cure at 70°F (21°C) and 50% relative humidity, Example 6 had a
direct impact resistance of 34 in./lbs and 119 milligrams weight loss in the Taber (abrasion)
test compared to 52 in./lbs impact resistance and 85 milligrams weight loss in the Taber
10 (abrasion) test for Example 7. This data indicates the utility of the silanol-functional urethane
prepolymers of the present invention in improving the impact and abrasion resistance of
polysiloxane based compositions.

 Although limited embodiments of polysiloxane polyurethane compositions have been
described herein, many modifications and verifications will be apparent to those skilled in
15 the art. Accordingly, it is to be understood that, within the scope of the appended claims,
polysiloxane polyurethane compositions according to principles of this invention may be
prepared other than as specifically described herein.

20

25

30

35

WHAT IS CLAIMED IS:

1. A silanol-functionalized urethane prepolymer composition prepared by combining:

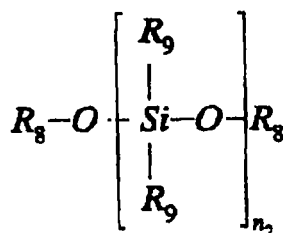
an organic di- or polyisocyanate having the formula



where the R_1 group is selected from the group consisting of aliphatic, cycloaliphatic, and aromatic groups, and where the organic di- or polyisocyanate has a weight average molecular weight in the range of from 200 to 2,000; with

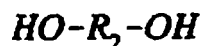
a polyol that can react with the organic di- or polyisocyanate to form an isocyanate terminated urethane prepolymer, and combining with the isocyanate terminated urethane prepolymer;

a silanol-functional silicone intermediate having the formula



where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of hydroxy, alkyl, and aryl groups having up to about six carbon atoms, and where n_2 is selected so that silicone intermediate has a weight average molecular weight in the range of from about 500 to 15,000.

2. The silanol-functionalized urethane prepolymer composition as recited in claim 1 wherein the polyol has the formula



where the R_2 group is selected from the group consisting of polyester, polyether, polyalkyldiene, and glycol groups, and where the polyol has a weight average molecular

WO 97/11983

PCT/US96/15094

1 weight in the range of from about 200 to 5,000.

3. The silanol-functionalized urethane prepolymer composition as recited in claim
1 further comprising an organotin catalyst selected from the group consisting of dibutyltin
5 dilaurate, dibutyltin diacetate, and dibutyltin mercaptide.

4. The silanol-functionalized urethane prepolymer composition as recited in claim
1 further comprising an amine catalyst.

10 5. The silanol-functionalized urethane prepolymer composition as recited in claim
4 wherein the amine catalyst is selected from the group consisting of tertiary amines and
aminosilanes, wherein the aminosilanes having the formula



20 where R_{14} is selected from the group consisting of aliphatic and aromatic amines
comprising in the range of from one to six nitrogen atoms and in the range of from one to
six carbon atoms, where R_{15} , R_{16} , and R_{17} are independently selected from the group
consisting of alkoxy and aryloxy groups having up to about twelve carbon atoms, and where
25 n_3 is in the range of from one to six.

6. The silanol-functionalized urethane prepolymer composition as recited in claim
1 further comprising a methoxy-functional silicone intermediate having the formula



where each R_{18} group is independently selected from the group consisting of alkyl,
aryl, and alkoxy groups having up to about six carbon atoms, where each R_{19} group is

WO 97/11983

PCT/US96/15094

1 independently selected from the group consisting of hydrogen, alkyl, and aryl groups having
up to about twelve carbon atoms, and where n_4 is selected so that a weight average molecular
weight of the silicone intermediate is in the range of from 500 to 6,000.

5 7. The silanol-functionalized urethane prepolymer composition as recited in claim
1 further comprising fillers and pigments.

8. The silanol-functionalized urethane prepolymer composition as recited in claim
1 further comprising solvents and additives selected from the group consisting of pigment
10 wetting agents, surfactants, defoamers, flow control agents, thixotropes, UV stabilizers,
bituminous and hydrocarbon extenders, and plasticizers.

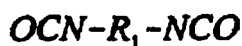
9. A composite comprising a binder formed from the silanol-functionalized
urethane prepolymer composition recited in claim 1, and having a reinforcing material placed
15 in contact with the binder.

10. The silanol-functionalized urethane prepolymer composition as recited in claim
1 comprising in the range of from two to fifty percent by weight di- or polyisocyanate, and
in the range of from two to sixty percent by weight polyol.

20 11. A silanol-functionalized urethane prepolymer composition prepared by
combining:

an organic di- or polyisocyanate having the formula

25



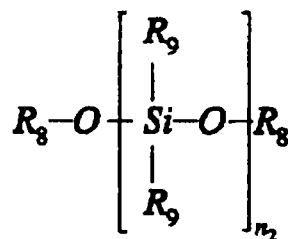
30 where the R_1 group is selected from the group consisting of aliphatic, cycloaliphatic,
and aromatic groups, and where the organic di- or polyisocyanate has a weight average
molecular weight in the range of from 200 to 2,000; with

a polyol that can react with the organic di- or polyisocyanate to form an isocyanate
terminated urethane prepolymer, and combining with the isocyanate terminated urethane
prepolymer;

35 a silanol-functional silicone intermediate having the formula

WO 97/11983

PCT/US96/15094



where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of hydroxy, alkyl, and aryl groups having up to about six carbon atoms, and where n_2 is selected so that silicone intermediate has a weight average molecular weight in the range of from about 500 to 15,000, in the presence of;

an organotin catalyst; and

an amine catalyst to form the silanol-functionalized urethane prepolymer.

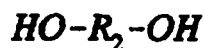
12. The silanol-functionalized urethane prepolymer composition as recited in claim 11 wherein the organic di- or polyisocyanate has the formula



where the R_1 group is selected from the group consisting of aliphatic, cycloaliphatic, and aromatic groups, and where the di- or polyisocyanate has a weight average molecular weight in the range of from 200 to 2,000.

13. The silanol-functionalized urethane prepolymer composition as recited in claim 12 comprising in the range of from two to fifty percent by weight of the organic di- or polyisocyanate.

14. The silanol-functionalized urethane prepolymer composition as recited in claim 11 wherein the polyol has the formula



where the R_2 group is selected from the group consisting of polyester, polyether, polyalkyldiene, and glycol groups, and where the polyol has a weight average molecular

THIS SHEET HAS BEEN
REPLACED

WO 97/11983

PCT/US96/15094

1 weight in the range of from about 200 to 5,000.

15. The silanol-functionalized urethane prepolymer composition as recited in claim
14 comprising in the range of from two to sixty percent by weight of the polyol.

5

16. The silanol-functionalized urethane prepolymer composition as recited in claim
11 comprising in the range of from fifteen to sixty percent by weight hydroxyl-containing
silicon material.

10

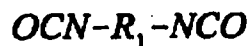
17. The silanol-functionalized urethane prepolymer composition as recited in claim
11 comprising in the range of from two to fifty percent by weight organic di- or
polyisocyanate, in the range of from two to sixty percent by weight polyol, and in the range
of from fifteen to sixty percent by weight silanol-functional silicone intermediate.

15

18. A composite having a binder formed from the silanol-functionalized urethane
prepolymer composition as recited in claim 11, and having a reinforcing material placed in
contact with the binder.

20

19. A silanol-functionalized urethane prepolymer that is prepared by combining;
an organic di- or polyisocyanate having the formula

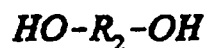


25

where the R_1 group is selected from the group consisting of aliphatic, cycloaliphatic,
and aromatic groups, and where the di- or polyisocyanate has a weight average molecular
weight in the range of from 200 to 2,000; with

30

a polyol that reacts with the di- or polyisocyanate to form an isocyanate terminated
urethane prepolymer, the polyol having the formula



35

where the R_2 group is selected from the group consisting of polyester, polyether,
polyalkyldiene, and glycol groups, and where the polyol has a weight average molecular
weight in the range of from about 200 to 5,000, and combining with the isocyanate
terminated urethane prepolymer;

WO 97/11983

PCT/US96/15094

1 a silanol-functional silicone intermediate having the formula



10 where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of hydroxy, alkyl, and aryl groups having up to about six carbon atoms, and where n_2 is selected so that silicone intermediate has a weight average molecular weight in the range of from about 500 to 15,000, in the presence of;

15 an organotin catalyst selected from the group consisting of dibutyltin dilaurate, dibutyltin diacetate, and dibutyltin mercaptide; and

an amine catalyst selected from the group consisting of tertiary amines and aminosilanes having the formula

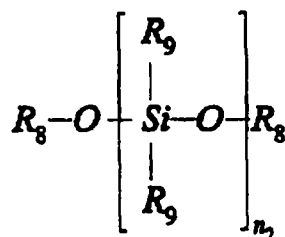


30 where R_{14} is selected from the group consisting of aliphatic and aromatic amines comprising in the range of from one to six nitrogen atoms and in the range of from one to six carbon atoms, where R_{15} , R_{16} , and R_{17} are independently selected from the group consisting of alkoxy and aryloxy groups having up to about twelve carbon atoms, and where n_3 is in the range of from one to six, to form the silanol-functionalized urethane prepolymer.

35 20. A silanol-functionalized urethane prepolymer prepared by combining:
an isocyanate-terminated urethane prepolymer; with
a silanol-functional silicone intermediate having the formula

WO 97/11983

PCT/US96/15094



where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of hydroxy, alkyl, and aryl groups having up to about six carbon atoms, and where n_2 is selected so that silicone intermediate has a weight average molecular weight in the range of from about 500 to 15,000.

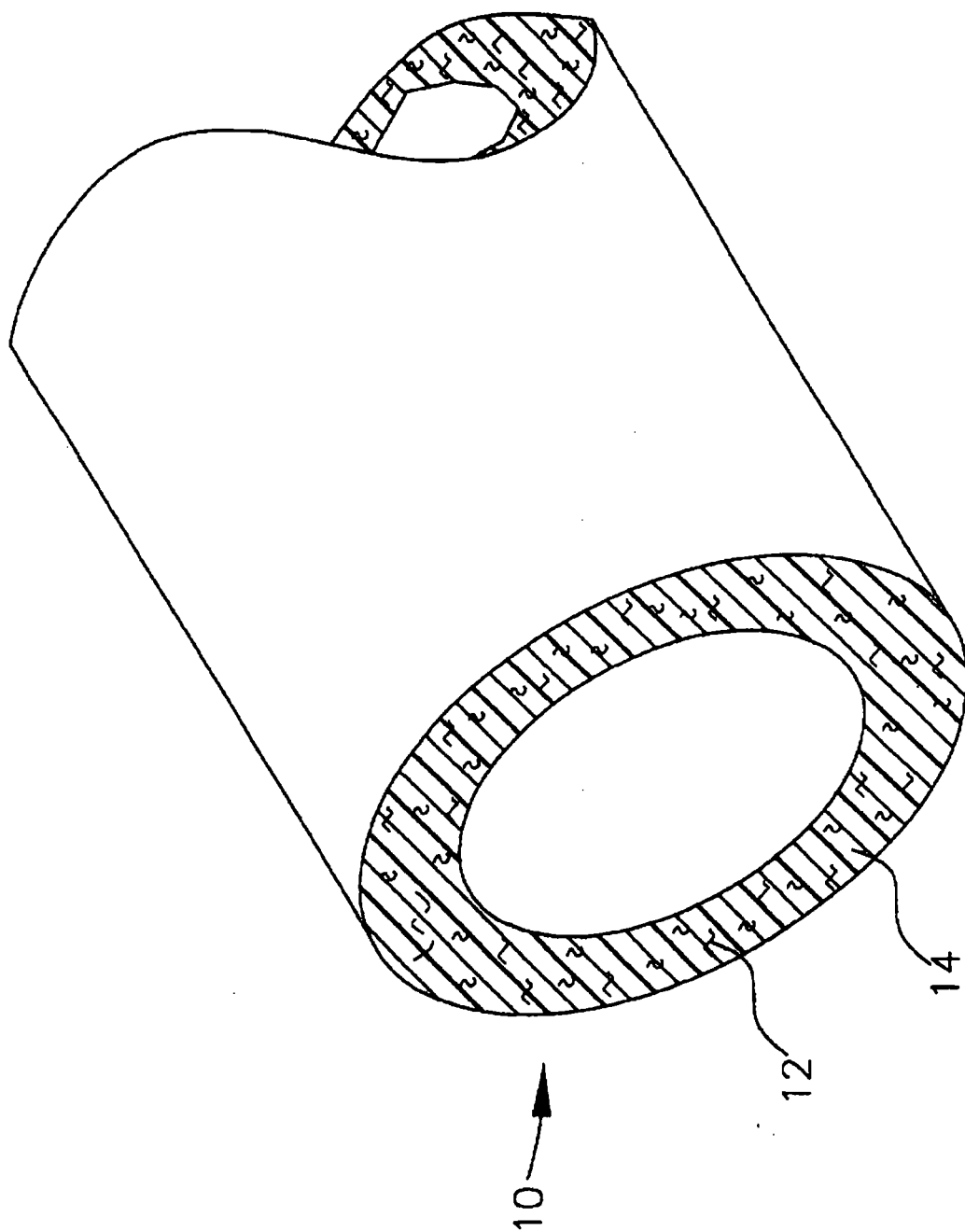
21. A method for forming a an ambient temperature moisture curable silanol-functionalized urethane prepolymer comprising the steps of:

combining an organic di- or polyisocyanate, a polyol, and an organotin catalyst to form a first mixture;

reacting the first mixture under heated temperature conditions to form an isocyanate terminated urethane prepolymer;

combining a silanol-functional silicone intermediate with the isocyanate terminated urethane prepolymer to form a second mixture; and

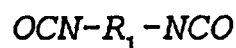
reacting the second mixture under heated conditions to form the silanol-functionalized urethane prepolymer.



WHAT IS CLAIMED IS:

1. A silanol-functionalized urethane prepolymer composition prepared by combining:

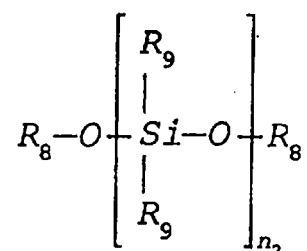
an organic di- or polyisocyanate having the formula



where the R_1 group is selected from the group consisting of aliphatic, cycloaliphatic, and aromatic groups, with

a polyol that can react with the organic di- or polyisocyanate to form an isocyanate terminated urethane prepolymer, and combining with the isocyanate terminated urethane prepolymer;

a silanol-functional silicone intermediate having the formula

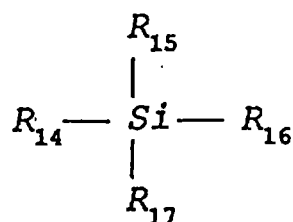


where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of hydroxy, alkyl, and aryl groups having up to about six carbon atoms.

2. The silanol-functionalized urethane prepolymer composition as recited in claim 1 further comprising an amine catalyst selected from the group consisting of tertiary amines and aminosilanes, wherein the aminosilanes having the formula

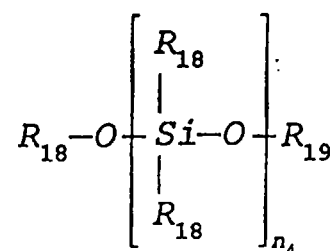
04 JUN 1998

29



where R_{14} is selected from the group consisting of aliphatic and aromatic amines comprising in the range of from one to six nitrogen atoms and in the range of from one to six carbon atoms, where R_{15} , R_{16} , and R_{17} are independently selected from the group consisting of alkoxy and aryloxy groups having up to about twelve carbon atoms.

3. The silanol-functionalized urethane prepolymer composition as recited in claim 1 further comprising a methoxy-functional silicone intermediate having the formula

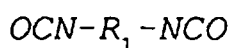


where each R_{18} group is independently selected from the group consisting of alkyl, aryl, and alkoxy groups having up to about six carbon atoms, where each R_{19} group is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms.

4. The silanol-functionalized urethane prepolymer composition as recited in claim 1 comprising in the range of from two to fifty percent by weight di- or polyisocyanate, and in the range of from two to sixty percent by weight polyol.

5. A silanol-functionalized urethane prepolymer composition prepared by combining:

an organic di- or polyisocyanate having the formula

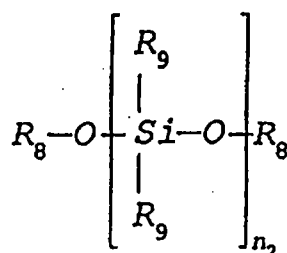


04 JUN 1993

where the R_1 group is selected from the group consisting of aliphatic, cycloaliphatic, and aromatic groups, with

a polyol that can react with the organic di- or polyisocyanate to form an isocyanate terminated urethane prepolymer, and combining with the isocyanate terminated urethane prepolymer;

a silanol-functional silicone intermediate having the formula

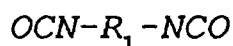


where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of hydroxy, alkyl, and aryl groups having up to about six carbon atoms, in the presence of;

an organotin catalyst; and

an amine catalyst to form the silanol-functionalized urethane prepolymer.

6. The silanol-functionalized urethane prepolymer composition as recited in claim 5 wherein the organic di- or polyisocyanate has the formula

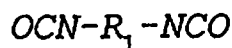


where the R_1 group is selected from the group consisting of aliphatic, cycloaliphatic, and aromatic groups, and where the di- or polyisocyanate has a weight average molecular weight in the range of from 200 to 2,000.

7. The silanol-functionalized urethane prepolymer composition as recited in claim 5 comprising in the range of from two to fifty percent by weight organic di- or polyisocyanate, in the range of from two to sixty percent by weight polyol, and in the range of from fifteen to sixty percent by weight silanol-functional silicone intermediate.

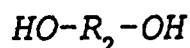
04 JUN 1998

8. A silanol-functionalized urethane prepolymer that is prepared by combining;
an organic di- or polyisocyanate having the formula



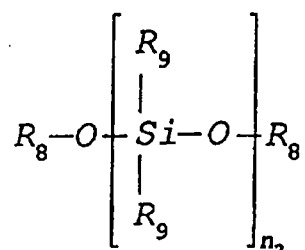
where the R_1 group is selected from the group consisting of aliphatic, cycloaliphatic, and aromatic groups, and where the di- or polyisocyanate has a weight average molecular weight in the range of from 200 to 2,000; with

a polyol that reacts with the di- or polyisocyanate to form an isocyanate terminated urethane prepolymer, the polyol having the formula



where the R_2 group is selected from the group consisting of polyester, polyether, polyalkyldiene, and glycol groups, and where the polyol has a weight average molecular weight in the range of from about 200 to 5,000, and combining with the isocyanate terminated urethane prepolymer;

a silanol-functional silicone intermediate having the formula

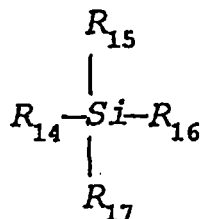


where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of hydroxy, alkyl, and aryl groups having up to about six carbon atoms, and where n_2 is selected so that silicone intermediate has a weight average molecular weight in the range of from about 500 to 15,000, in the presence of;

an organotin catalyst selected from the group consisting of dibutyltin dilaurate, dibutyltin diacetate, and dibutyltin mercaptide; and

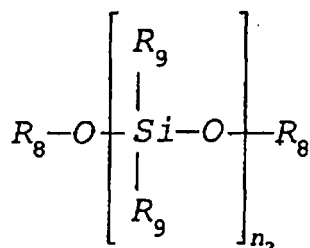
C 4 JUN 1998

an amine catalyst selected from the group consisting of tertiary amines and aminosilanes having the formula



where R_{14} is selected from the group consisting of aliphatic and aromatic amines comprising in the range of from one to six nitrogen atoms and in the range of from one to six carbon atoms, where R_{15} , R_{16} , and R_{17} are independently selected from the group consisting of alkoxy and aryloxy groups having up to about twelve carbon atoms, and where n_3 is in the range of from one to six, to form the silanol-functionalized urethane prepolymer.

9. A silanol-functionalized urethane prepolymer prepared by combining:
an isocyanate-terminated urethane prepolymer; with
a silanol-functional silicone intermediate having the formula



where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of hydroxy, alkyl, and aryl groups having up to about six carbon atoms.

04 JUN 1998

10. A method for forming a an ambient temperature moisture curable silanol-functionalized urethane prepolymer composition comprising the steps of:

combining an organic di- or polyisocyanate, a polyol, and an organotin catalyst to form a first mixture;

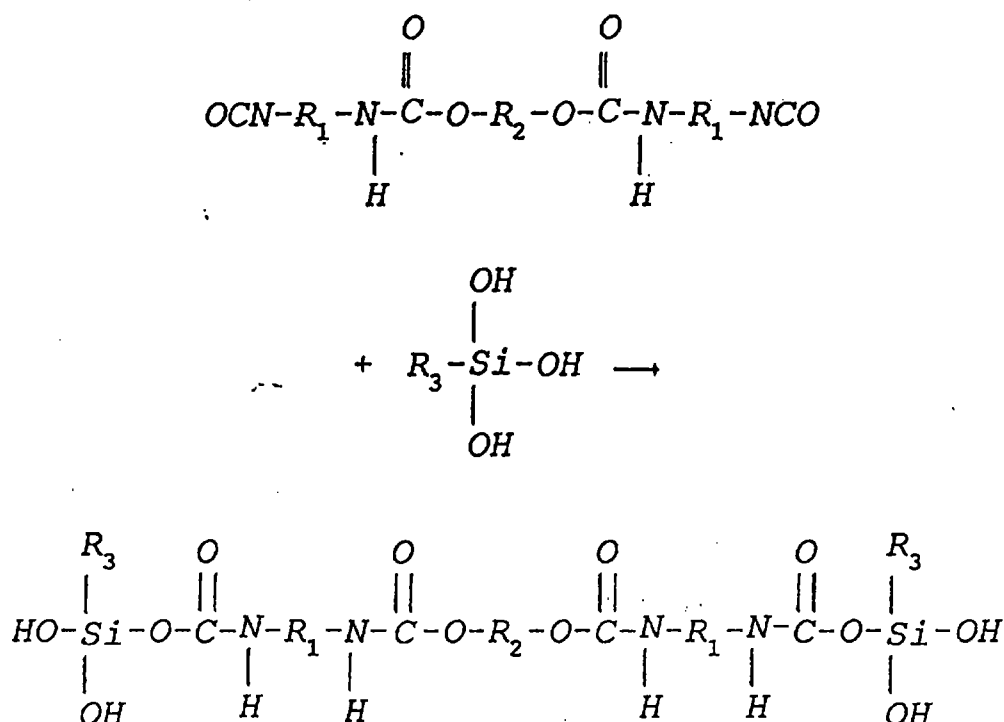
reacting the first mixture under heated temperature conditions to form an isocyanate terminated urethane prepolymer;

combining a silanol-functional silicone intermediate with the isocyanate terminated urethane prepolymer to form a second mixture; and

reacting the second mixture under heated conditions to form the silanol-functionalized urethane prepolymer.

04 JUN 1998

20

Reaction No. 2

The reaction is typically conducted in a heated vessel equipped with an agitator, nitrogen inlet and condenser. The catalyst ingredients and hydroxyl-containing silicon compound are charged to the vessel and the isocyanate-functional urethane prepolymer is then added with continuous mixing and nitrogen blanketing. A sample is withdrawn from the vessel periodically and analyzed for unreacted isocyanate with an FTIR spectrophotometer. The reaction is complete when the FTIR spectrum shows no evidence of isocyanate of at least 2,250 centimeters⁻¹.

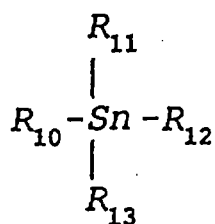
The silanol-functionalized urethane prepolymers of the present invention cure at ambient temperatures in the presence of moisture by condensation of the silanol groups to form polysiloxane polyurethane elastomers. If desired, pigments, solvents, additives and fillers can be added to the silanol-functionalized urethane prepolymer according to the previously described proportions and blended together until the mixture is uniform.

The silanol-functionalized urethane prepolymer, amine/organotin and/or aminosilane catalyst, pigments, solvents and additives are combined to produce a single package composition system. Optionally, the amine/organotin and/or aminosilane catalyst may be

04 JUN 1998

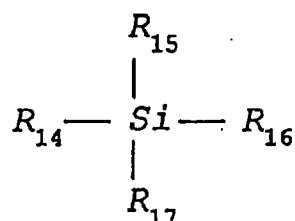
10

(d) an organotin catalyst having the general formula



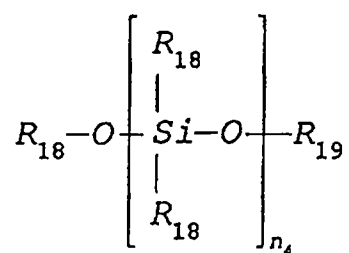
where R_{10} , R_{11} , R_{12} , and R_{13} are selected from a group including alkyl, aryl, and alkoxy groups having up to about eleven carbon atoms, and where any two of R_{10} , R_{11} , R_{12} , and R_{13} are also selected from a group of inorganic atoms including halogens, sulfur, and oxygen; with

(e) a tertiary amine catalyst or an aminosilane having the general formula



where R_{14} is selected from the group including aliphatic and aromatic amines comprising in the range of from one to six nitrogen atoms and in the range of from one to six carbon atoms, where R_{15} , R_{16} , and R_{17} are independently selected from the group consisting of alkoxy and aryloxy groups having up to about twelve carbon atoms; with

(f) methoxy-functional silicone intermediates having the general formula



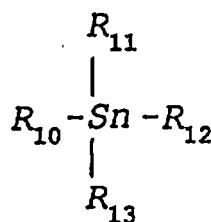
where each R_{18} group is independently selected from the group including alkyl, aryl, and alkoxy groups having up to about six carbon atoms, where each R_{19} group is independently selected from the group including hydrogen, alkyl, and aryl groups having up

04 JUN 1998

Spare copy

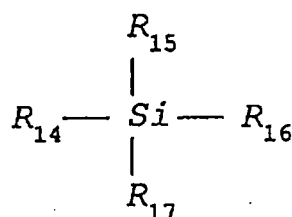
where each R_8 is independently selected from the group consisting of hydrogen, alkyl, and aryl groups having up to about twelve carbon atoms, where each R_9 is independently selected from the group consisting of the hydroxy, alkyl, and aryl groups having up to about six carbon atoms, and where n_2 is selected so that a weight average molecular weight is in the range of from about 500 to 15,000.

The organotin catalyst has the general formula



where R_{10} , R_{11} , R_{12} , and R_{13} are selected from the group including alkyl, aryl, and alkoxy groups having up to about eleven carbon atoms, and where any two of R_{10} , R_{11} , R_{12} , and R_{13} are also selected from a group of inorganic atoms including halogens, sulfur, and oxygen.

The amine catalyst is selected from the group including tertiary amines and aminosilanes having the general formula



where R_{14} is selected from the group including aliphatic and aromatic amines comprising in the range of from one to six nitrogen atoms and in the range of from one to six carbon atoms, where R_{15} , R_{16} , and R_{17} are independently selected from the group including alkoxy and aryloxy groups having up to about twelve carbon atoms.

The methoxy-functional silicone intermediates have the general formula