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(54) Titre : REVETEMENTS EN COPOLYMERE AU SILANE
(54) Title: SILANE COPOLYMER COATINGS

(57) **Abrégé/Abstract:**

The invention is drawn to silane copolymers prepared from the reaction of one or more polyisocyanates with one or more lubricious polymers having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group and with one or more organo-functional silanes having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group and at least one functional group reactive with a silicone rubber substrate. The silane copolymer coatings of the invention are elastic, lubricious, and resist wet abrasion. They are useful as coatings for polysiloxane (rubber) and other difficult to coat substrates, especially for medical devices, such catheters.

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(21) International Application Number: PCT/US99/26155 (22) International Filing Date: 5 November 1999 (05.11.99) (30) Priority Data: 09/189,240 10 November 1998 (10.11.98) US (71) Applicant: C.R. BARD, INC. [US/US]; 730 Central Avenue, Murray Hill, NJ 07974 (US). (72) Inventors: TERRY, Richard, N.; 1728 Little Brook Drive, Conyers, GA 30094 (US). WALSH, Kevin; 1355 Euclid Avenue, #24B, Atlanta, GA 30307 (US). (74) Agents: PRIOR, Kimberly, J. et al.; Jones & Askew, LLP, 2400 Monarch Tower, 3424 Peachtree Road, Atlanta, GA 30326 (US).		(81) Designated States: AU, CA, JP, MX, NZ, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> (88) Date of publication of the international search report: 27 July 2000 (27.07.00)
(54) Title: SILANE COPOLYMER COATINGS (57) Abstract <p>The invention is drawn to silane copolymers prepared from the reaction of one or more polyisocyanates with one or more lubricious polymers having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group and with one or more organo-functional silanes having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group and at least one functional group reactive with a silicone rubber substrate. The silane copolymer coatings of the invention are elastic, lubricious, and resist wet abrasion. They are useful as coatings for polysiloxane (rubber) and other difficult to coat substrates, especially for medical devices, such catheters.</p>		

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SILANE COPOLYMER COATINGS

FIELD OF THE INVENTION

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The invention relates generally to biocompatible, hydrophilic coatings, their manufacture, and their use for coating silicone and other difficult to coat medical devices. More specifically, the invention relates to hydrophilic coatings which are elastic when dry and resist wet abrasion, and to their use as coatings for polydimethylsiloxane (silicone) rubber substrates.

BACKGROUND OF THE INVENTION

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In the practice of medicine there are many diagnostic and therapeutic procedures which require the insertion of a medical device into the human body through an orifice or tissue or contact of a medical device with blood or tissue. Such devices include guidewires; catheters, including Foley, angioplasty, diagnostic, and balloon catheters; implant devices; contact lenses; IUDs; peristaltic pump chambers; endotracheal tubes; gastroenteric feed tubes; arteriovenous shunts; condoms; and oxygenator and kidney membranes. It is necessary for the surface of these medical devices to have a low coefficient of friction to prevent injury, irritation, or inflammation to the patient and to facilitate medical and surgical procedures.

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There is a need in the art for medical devices with the appropriate degree of slipperiness. The appropriate level is one at which the device is very slippery when contacted with the patient's moist tissue, but is not so slippery when dry that it is difficult for medical personnel to handle. Current materials from which such medical devices are made include silicone rubber, Teflon®, polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyurethane (PU), polytetrafluoroethylene (PTFE), Nylon®, polyethylene terephthalate (PET), and glass. These materials, however, lack the desired degree of slipperiness.

One approach to providing medical devices with more desirable surface characteristics is to coat the devices made from existing materials with various coating compositions. These coatings may be applied by spraying or painting the coating on the device or by dipping the device in a solution of the coating. Some substances which have been employed as coatings are Teflon®, silicone fluid, glycerin, mineral oils, olive oil, K-Y jelly, and fluorocarbons. However, these substances have not been entirely satisfactory because they lack hydrophilicity, are not retained on the device surface during the period of use, are non-durable, or exhibit inadequate retention of lubricity.

Hydrophilic polymer and hydrogel coatings were an improvement to the art and have been used successfully to provide coatings for many of the easier to coat substrates, such as polyurethane and latex rubber. These coatings, however, are poorly adherent to silicone rubber and wash off when the device is wetted.

Many medical devices such as guidewires, catheters, implant devices, contact lenses, IUDs, peristaltic pump chambers, endotracheal tubes, gastroenteric feed tubes, arteriovenous shunts, condoms, and oxygenator and kidney membranes are made from silicone rubber or other difficult to coat materials, such as Teflon®, polyethylene and polypropylene. Thus, there is a special need in the art for hydrophilic coatings for these and similarly difficult to coat substrates.

Adherence of previously known coatings to such surfaces is difficult because the coatings do not form covalent bonds with the silicone. As a result, the coatings have poor adherence, reduced durability, and poor resistance to wet abrasion.

Various polymers have been employed as coatings for medical devices. These include polyethylene oxide (PEO), polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), and polyurethane (PU). PEO and PEG are friction-reducing, blood-compatible polymers that are commercially available in a variety of molecular weights. Both have been used in combination with various other materials to produce lubricious coatings for medical devices. For example, coatings incorporating PEO and isocyanates are known in the art (U.S. Patents 5,459,317, 4,487,808, and 4,585,666 to Lambert; and U.S. Patent 5,558,900 to Fan *et al.*). In addition, polyols may be incorporated into such PEO/isocyanate coatings to produce a crosslinked polyurethane (PU) network entrapping the PEO (U.S. Patents 5,077,352 and 5,179,174 to Elton). PEO has also been combined with structural plastic having a high molecular weight to produce a coating with reduced friction (U.S. Patent 5,041,100 to Rowland).

None of these coatings are acceptable for coating silicone rubber and other difficult to coat substrates. Because these coatings do not form covalent linkages with the silicone surface of the substrate, they have poor adherence and durability and are easily washed from the surface when the substrate is wetted.

5 Another polymer used to coat medical devices is polyvinyl pyrrolidone (PVP). PVP may be used as a coating alone or in combination with other polymers. For example, polyvinyl pyrrolidone may be bonded to a substrate by thermally activated free radical initiators, UV light activated free-radical initiators, or E-beam radiation (WO 89/09246). One disadvantage of using such coatings is
10 that E-beam radiation can be deleterious to some of the materials used in medical devices.

PVP may be used in conjunction with other polymers. One such coating is made from PVP and glycidyl acrylate. This coating requires the presence of amino groups on the surface of the substrate to react with the epoxy groups of
15 the glycidyl acrylate to covalently bond the PVP-containing copolymer to the substrate (Nagoacha *et al.*, *Biomaterials*, 419 (1990)). Silicone rubber does not contain any free amino groups, and thus this type of coating cannot form covalent bonds with the surface of the silicone substrate, resulting in poor adhesion.

Other coatings are composed of a mixture of PVP and polyurethane.
20 These coatings provide low friction surfaces when wet. One such coating is a polyvinyl pyrrolidone-polyurethane interpolymers (U.S. Patents 4,100,309 and 4,119,094 to Micklus *et al.*). Another such coating is composed of hydrophilic blends of polyvinyl pyrrolidone (PVP) and linear preformed polyurethanes (U.S. Patent 4,642,267 to Cresy). In addition, PVP may be incorporated into a PU
25 network by combining a polyisocyanate and a polyol with a PVP solution (U.S. Patents 5,160,790 and 5,290,585 to Elton). Still another such coating is composed of two layers: a primer and a top coat. The primer coat is a polyurethane prepolymer containing free isocyanate groups, while the top coat is a hydrophilic copolymer of PVP and a polymer having active hydrogen groups, such as acrylamide (U.S.
30 Patent 4,373,009 to Winn).

None of these PVP based coatings are acceptable for coating silicone rubber and other difficult to coat substrates. Because these coatings do not form covalent linkages with the silicone surface of the substrate, they have poor adherence and durability and are easily washed from the surface when the substrate is wetted.

35 Hydrophilic polyurethanes have also been used in formulations other than with PVP as coatings for medical devices. For example, the prior art discloses

coatings composed of polyurethane hydrogels containing a random mixture of polyisocyanates and a polyether dispersed in an aqueous liquid phase (U.S. Patent 4,118,354 to Harada *et al.*). Polyurethanes have also been used as coatings in compositions containing chain-extended hydrophilic thermoplastic polyurethane
5 polymers with a variety of hydrophilic high molecular weight non-urethane polymers (U.S. Patent 4,990,357 to Karkelle *et al.*). It is also known to mix urethane with a silicone or siloxane emulsion. The carboxylic acid groups of the substrate and coating may then be linked with a cross-linking agent, such as a polyfunctional aziridine (U.S. Patent 5,026,607 to Kiezulas).

10 Because the urethane and non-urethane polymers cannot react with one another or the surface to be coated, the resulting coatings have poor adhesion, especially to silicone surfaces. Also, since silicone surfaces do not contain free carboxylic acid groups, a crosslinker such as a polyfunctional aziridine will not covalently bond known coatings to the surface of a silicone substrate.

15 Thus there is a critical need in the art for an improved coating which is not slippery when dry but becomes slippery when contacted with aqueous fluids and which will adhere to medical devices made from silicone and other difficult to coat materials.

20 There is also a need in the art for a coating having improved durability and uniformity which retains its lubricity and will adhere to medical devices made from silicone and other difficult to coat materials.

 There is a further need in the art for a process of preparing lubricious coatings for medical devices made from silicone and other difficult to coat materials which is simple and efficient and results in uniformity between batches.

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SUMMARY OF THE INVENTION

An aspect of the present invention provides a process for preparing the manufactured article, wherein the preparation of the silane copolymer with a reduced coefficient of friction when wet has at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group (polyols) reacting with one or more organo-functional silanes having at least two functional groups, which may be the same or different, and that are reactive with an isocyanate functional group, and at least one functional group is reactive with a silicone rubber substrate.

Stated generally, the present invention comprises biocompatible, hydrophilic silane copolymers, their manufacture, and their use as coatings for polydimethylsiloxane rubber and other difficult to coat substrates. The coatings of the invention provide advantageous properties, such as improved durability, uniformity, and adhesion to silicone and other surfaces which are difficult to coat, such as polyethylene and polypropylene. The coatings of the present invention are beneficial because they retain lubricity and do not leach excessively over time.

Stated somewhat more specifically, the invention in a first aspect comprises a method for preparing a silane copolymer from one or more polyisocyanates, from one or more lubricious polymers having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group, and from one or more organo-functional silanes having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group and at least one functional group reactive with a silicone rubber substrate. The invention also comprises the silane copolymers made from the process described above.

In another aspect, the present invention comprises using the silane copolymers described herein to coat polysiloxane rubber and other difficult to coat substrates. The coatings may comprise either a single layer or multiple layers. In one preferred embodiment, the copolymers of the invention are employed as a primer coat over which a top coat is applied. In another preferred embodiment, the coating is applied as the sole coating to the catheter. In yet another preferred embodiment, the copolymer coating incorporates additional components, including other hydrophilic polymers. Also included in the invention are the coatings formed from the silane copolymers and the articles containing such coatings.

Thus, it is an aspect of the present invention to provide an improved coating for silicone and other difficult to coat substrates which is not slippery when dry but becomes slippery when contacted with aqueous fluids.

It is another aspect of the invention to provide a coating with improved durability and uniformity which retains its lubricity.

Further, it is an aspect of the present invention to provide a coating with improved adhesion to silicone and other surfaces that are difficult to coat.

Additionally, it is an aspect of the invention to provide a coating which does not leach over time.

It is an aspect of the invention to provide coatings which are biocompatible and abrasion resistant, having a low coefficient of friction.

It is another aspect of the present invention to provide a single layer, lubricious coating.

It is yet another aspect of the invention to provide a multi-layer coating which comprises a primer coating layer and a lubricious top coat.

It is an aspect of the invention to provide a polyurethane-silane copolymer.

It is another aspect of the present invention to provide a polyurethane-urea-silane copolymer.

It is a further aspect of the present invention to provide a process of preparing lubricious coatings which is simple and efficient and results in uniformity between batches.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It should be understood to those well versed in the art of polymer and polyurethane synthesis that the copolymer coatings of the present invention may take many different forms and may be made by many different methods, and that the disclosure of the preferred embodiments herein do not limit the scope of the invention.

Preparing the Silane Copolymers of the Invention

Generally the present invention comprises a process for preparing silane copolymers. Stated somewhat more specifically, the invention in a first aspect comprises a method for preparing a silane copolymer from one or more polyisocyanates, from one or more lubricious polymers having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group, and from one or more organo-functional silanes having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group and at least one functional group reactive with a silicone rubber substrate.

The process of the invention may be performed in many variations. For example, the silane copolymers of the present invention can be prepared by first forming a prepolymer from the polyisocyanate(s) and lubricious polymer(s) followed by reaction with the organo-functional silane(s). Alternatively, the silane copolymers of the invention can be prepared by first forming a prepolymer from the polyisocyanate(s) and silane(s) followed by reaction with the lubricious polymer(s). Additionally, the silane copolymers of the invention can be prepared by simultaneously adding the polyisocyanate(s), lubricious polymer(s), and silane(s) and allowing them to react with one another to form the copolymer of the invention.

While any monomers satisfying the definition above may be employed in the invention, for convenience, the process of invention will be described further in terms of the production of polyurethane-urea-silane

copolymers. However, it should be understood that these specific copolymers are only preferred embodiments and in no way limit the scope of the invention.

5 In one disclosed embodiment, one or more polyols are reacted with an excess of one or more polyisocyanates in the presence of a catalyst, such as a tin catalyst. The polyurethane product of this first step is then reacted with one or more amino-functional alkoxysilanes to form a polyurethane-urea-silane copolymer having pendant alkoxy groups. This polyurethane-urea-silane copolymer is then optionally stabilized in solution by the addition of an alcohol, preferably the alcohol formed by the reaction of the alkoxy group with water.

10 In a preferred form of the embodiment, one or more polyols are reacted with an excess of a diisocyanate in a first step to form an isocyanate-capped polyurethane prepolymer. The formation of this prepolymer can be facilitated by employing an excess of polyisocyanate. In other words, the number of isocyanate functional groups present in the reaction mixture is greater than the number of alcohol function groups present in the reaction mixture. Preferably, the ratio of isocyanate functional groups to alcohol or other isocyanate reactive functional groups is from 1.1:1 to 2:1. More preferably, the ratio of isocyanate functional groups to alcohol functional groups is from 1.5:1 to 2:1, most preferably 1.6 to 1.8.

20 The reaction between the polyol and polyisocyanate can also be facilitated by employing a catalyst. Nonlimiting examples of suitable catalysts are tertiary amines, such as N,N-dimethylaminoethanol, N,N-dimethyl-cyclohexamine-bis(2-dimethyl aminoethyl) ether, N-ethylmorpholine, N,N,N',N',N''-pentamethyl-diethylene-triamine, and 1-2(hydroxypropyl) imidazole, and metallic catalysts, such as tin, stannous octoate, dibutyl tin dilaurate, dioctyl tin dilaurate, dibutyl tin mercaptide, ferric acetylacetonate, lead octoate, and dibutyl tin diricinoleate. The preferred catalyst is tin. The most preferred catalyst is dioctyl tin dilaurate.

25 In a second step, the isocyanate-capped polyurethane prepolymer is reacted with an organo-functional silane to form a polyurethane-urea-silane copolymer having pendant alkoxy groups. Any organo-functional silane having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group, and at least one functional group reactive with a silicone surface may be used in the process of the present invention. The reaction can be facilitated by performing the polymerization in a dry organic solvent. If the silicone reactive group of the silane is alkoxy, an optional third step comprises stabilization of the alkoxy groups of the polyurethane-urea-silane

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copolymer by the addition an alcohol of the alcohol corresponding to the reaction product of the alkoxy group with water.

5 In a second disclosed embodiment, one or more amino-functional alkoxysilanes are reacted with an excess of one or more polyisocyanates, preferably a diisocyanate. The polyurea product of this first step is then combined with one or more polyols, optionally in the presence of a catalyst, such as a tin catalyst. If a catalyst is used, a polyurethane-urea-silane copolymer having pendant alkoxy groups. This polyurethane-urea-silane copolymer is then optionally stabilized in solution by addition of the alcohol corresponding to the alcohol formed by the reaction of the alkoxy group with water.

10 In a third disclosed embodiment of the process, one or more amino-functional alkoxysilanes are reacted with one or more polyisocyanates, preferably a diisocyanate, and one or more polyols, optionally in the presence of a catalyst, such as a tin catalyst, to form a polyurethane-urea-silane copolymer having pendant alkoxy groups. This polyurethane-urea-silane copolymer is then optionally stabilized in solution by addition of the alcohol corresponding to the alcohol formed by the reaction of the alkoxy group with water.

15 When alkoxysilanes are used in the present invention, the resulting polyurethane-urea-silane copolymers contain numerous free alkoxy groups which react with the silicone surface but can also react with any water present in the reaction system. The reaction of the alkoxy groups with water cleaves alcohol from the copolymer and leaves silanol groups in place of the alkoxy groups. These silanols may react with the silicone substrate or with each other, the latter producing crosslinks in the copolymer which can affect coating properties.

20 Addition to the copolymer solution of the alcohol formed by the reaction of the alkoxy group contained in the copolymer and water helps to stabilize the copolymer by inhibiting the reaction of alkoxy groups with water. Examples of such alcohols include, but are not limited to, methanol, ethanol, 1-propanol, 2-propanol, butanol, hexanol and octanol. The particular alcohol used will depend upon the alkyl portion of the alkoxy group. For example, methanol is used to stabilize a copolymer containing methoxy groups. The alcohol is generally added at the end of polymerization in an amount from 5 to 50% of the total solvent composition, preferably from 10 to 30%.

25 Any polyol may be used in the process of the invention and is preferably dried to less than 1000 ppm water before reaction. Examples of such polyols include, but are not limited to, polyethylene glycols, polyester polyols,

polyether polyols, castor oil polyols, and polyacrylate polyols, including Desmophen™ A450, Desmophen A365, and Desmophen A160 (Mobay Corporation, Pittsburgh, PA).

5 The process advantageously employs a diol as the polyol. Suitable diols include, but are not limited to, poly(ethylene adipates), poly(diethyleneglycol adipates), polycaprolactone diols, polycaprolactone-polyadipate copolymer diols, poly(ethylene-terephthalate)diols, polycarbonate diols, polytetramethylene ether glycol, polyethylene glycol, ethylene oxide adducts of polyoxypropylene diols, ethylene oxide adducts of polyoxypropylene triols. The preferred polyol is the diol
10 polyethylene glycol. The most preferred polyethylene glycol is Carbowax™ 1450 (available from Union Carbide).

Instead of polyols, amine functional polymers may be used in the process of the invention to produce isocyanate-functionalized polyureas for reaction with an amino-functional alkoxysilane. Additionally, amine functional chain
15 extenders common to the art of polyurethane synthesis and water which also produces polyureas by reaction with isocyanates to produce amines, may also be employed. Monomers containing such chain extenders also produce polyureas. Replacement of polyols with other polymers having functional groups reactive with isocyanates, as well as the use of other common polyurethane/polyurea synthetic
20 techniques known to the art are anticipated by the process of the present invention.

Any polyisocyanate may be used in the process of the present invention. The polyisocyanate may be aromatic, aliphatic or cycloaliphatic. Nonlimiting examples of such polyisocyanates are 4,4'-diphenylmethane diisocyanate and position isomers thereof, 2,4- and 2,6- toluene diisocyanate (TDI)
25 and position isomers thereof, 3,4-dichlorophenyl diisocyanate, dicyclohexylmethane-4,4'-diisocyanate (HMDI), 4,4'-diphenylmethane diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI) and position isomers thereof, isophorone diisocyanate (IPDI), and adducts of diisocyanates, such as the adduct of trimethylolpropane and diphenylmethane diisocyanate or toluene
30 diisocyanate. The preferred polyisocyanate is the diisocyanate dicyclohexylmethane-4,4'-diisocyanate (HMDI).

Any organo-functional silanes having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group and at least one functional group reactive with a silicone surface may be used
35 in the process of the present invention. Nonlimiting examples of organo-functional silanes are N-beta-(aminoethyl)-gamma-aminopropyl-trimethoxy silane and N-(2-

aminoethyl)-3-aminopropylmethyl-dimethoxy silane. The preferred organo-functional silane is a diamino-alkoxysilane, such as N-(2-aminoethyl)-3-aminopropylmethyldimethoxy silane.

5 In general, it is beneficial to add a catalyst to the isocyanate reaction mixtures. Although any catalyst known to be useful in isocyanate reactions may be employed, the preferred catalyst for the present invention is any tertiary amine or metallic catalyst. Nonlimiting examples of suitable catalysts include tertiary amines, such as N,N-dimethylaminoethanol, N,N-dimethyl-cyclohexamine-bis(2-dimethyl
10 aminoethyl) ether, N-ethylmorpholine, N,N,N',N',N''-pentamethyl-diethylene-triamine, and 1-2(hydroxypropyl) imidazole, and metallic catalysts, such as tin, stannous octoate, dibutyl tin dilaurate, dioctyl tin dilaurate, dibutyl tin mercaptide, ferric acetylacetonate, lead octoate, and dibutyl tin diricinoleate. The preferred catalyst is tin with the most preferred being dioctyl tin dilaurate.

15 A solvent is advantageously added to the prepolymer or monomer mixture to reduce viscosity. The level of viscosity is important during the synthesis of the copolymers of the present invention. During polymerization, if the copolymer solution attains too high a viscosity, the solution can form a gel from which good quality coatings cannot be made. Once the polymerization is complete, if the copolymer solution has too high a viscosity, the coating formed will be too thick to
20 produce a uniform thin coating on the substrate. Such a coating may also have low durability due to cracking. On the other hand, if copolymer solution has too low a viscosity, the coating formed will exhibit poor and uneven adhesion.

Viscosity is a function of molecular weight of the copolymer and the solids content of the solution and is controlled by addition of solvent to the solution.
25 The preferred copolymer solution for dip coating has a kinematic viscosity in a range of about 1.5 to 20 cS (centistokes), preferably 2.0 to 10 cS, and most preferably 2.5 to 5 cS. The preferred copolymer solution has a solids content in a range of about 0.4 to 5%, most preferably from 0.6 to 1.5%.

It is preferred but not essential that the solvent be dry to prevent
30 water contamination of the prepolymer because water may react with alkoxy groups of the silane. The solvent preferably contains less than 200 ppm water. Solvents which are useful in the present invention include, but are not limited to, tetrahydrofuran, acetonitrile, ethyl acetate, methylene chloride, dibromomethane, chloroform, dichloroethane, and dichloroethylene, with tetrahydrofuran being
35 preferred.

The Silane Copolymers of the Invention

In a second aspect, the present invention comprises the silane copolymers made by the processes described above. These copolymers are preferably polyurethane-urea-silane copolymers. Particularly preferred copolymers are polyurethane-urea-silane copolymers having from 7 to 12% by weight silane based upon the weight of the entire copolymer. The most preferred copolymers of the invention are those comprised of dicyclohexylmethane-4,4'-diisocyanate, N-(2-aminoethyl)-3-aminopropylmethyl-dimethoxy silane, and Carbowax 1450.

The silane copolymers can contain additional components. For example, they may contain viscosity and flow control agents, antioxidants, conventional pigments, air release agents or defoamers, and other hydrophilic polymers.

Antioxidants are not necessary, but may be used to improve the oxidative stability of the coatings. Nonlimiting examples of useful antioxidants are vitamin E, tris(3,5-di-t-butyl-4-hydroxy benzyl)isocyanurate, 2,2'-methylenebis(4-methyl-6-t-butyl phenol), 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxy benzyl) benzene, butyl-hydroxytoluene, octadecyl-3,5-di-t-butyl-4-hydroxy hydrocinnamate, 4,4'-methylenebis(2,6-di-t-butylphenol), p,p'-dioctyl-diphenylamine, and 1,1,3-tris-(2-methyl-4-hydroxy-5-t-butylphenyl)butane.

Conventional dyes and pigments can be added to impart color or radiopacity or to enhance the aesthetic appearance of the coatings produced from the copolymers.

The Use of the Copolymers as Lubricious Coatings

In a third aspect, the present invention comprises a method for using the silane copolymers described above to form a lubricious coating on difficult to coat substrates. Although the preferred substrate is a polysiloxane rubber, the copolymer is also useful for coating other difficult to coat substrates, such as polyethylene and polypropylene, as well as other polymers, glass, metal, and ceramics. Many medical devices, such as guide wires; catheters, including Foley, angioplasty, diagnostic, and balloon catheters; implant devices; contact lenses; IUDs; peristaltic pump chambers; endotracheal tubes; gastroenteric feed tubes; arteriovenous shunts; condoms; and oxygenator and kidney membranes, are made from silicone rubber and these other substrates.

The silane copolymers of the invention may be applied to the substrate by conventional methods known in the art. In general, the substrate is

dipped into a solution of the copolymer of the present invention. Preferably, the substrate is dipped into the copolymer solution at a rate of about 15-80 inches per minute (ipm), preferably about 40 ipm. The substrate is preferably allowed to remain in the coating solution for 0-30 seconds, preferably about 5-15 seconds, and then is withdrawn at a rate of about 10-80 ipm, preferably 15-30 ipm. Once the substrate has been coated with the copolymer of the invention, it is allowed to air dry for at least 1 hour. The substrate may optionally be dried with a hot air stream or in an oven at a temperature of approximately 50 to 100°C for about 5-60 minutes to remove residual solvent.

The silane copolymers of the present invention can be used to form a variety of unique coatings by varying the exact components incorporated into the copolymer. Some of the copolymers are both very lubricious and adhesive to the substrate. These copolymers can be used as the sole coating on the substrate. Other of the copolymers of the invention are less lubricious but have superior adhesion. These copolymers can be used as a primer coat over which a lubricious top coat may be attached.

In a first disclosed embodiment, the silane copolymer of the invention may be applied to the substrate as a primer coat over which a second lubricious top coat is then applied. In this embodiment, the silane copolymer acts as a primer, facilitating adhesion of the second top coat to the substrate. The top coat may be applied by any method, but is advantageously applied by dipping the primed substrate into a solution of the top coat in a manner similar to that by which the primer is applied.

As mentioned above, the preferred polyol used in the preparation of the silane copolymer is polyethylene glycol (PEG). PEG is a polymeric diol which is available in a variety of molecular weights. The use of PEG having different molecular weights affects the molecular weight and lubricity of the coatings formed. When the silane copolymer is used as a primer coat, a PEG having a lower molecular weight, such as Carbowax 1450, is used. The use of Carbowax 1450 provides a prepolymer having a molecular weight that is generally between about 1,900 and 25,000 as measure by gel permeation chromatography (GPC). A copolymer made from such a prepolymer provides improved adhesion of the primer coat to the substrate.

The lubricious top coat may be any coating which enhances the lubricity of the substrate. One preferred top coat is the combination of a higher molecular weight polyethylene oxide, such as Hydroslide™ 121 (C.R. Bard, Inc.,

Murray Hill, N.J.) or a polyvinyl pyrrolidone and a reactive mixture of polyfunctional isocyanate and polyol. Examples of such top coats include the coatings disclosed in U.S. Patents No. 5,077,352; 5,179,174; 5,160,790; and 5,209,585, which may be referred to for further details.

5 Alternatively, the lubricious top coat that is applied over the primer coat is the silane copolymer of the present invention made with a higher molecular weight PEG, such as Carbowax 8000. Copolymers made from a higher molecular weight PEG, such as Carbowax 8000, exhibit an increased lubricity over copolymers made with a lower molecular weight PEG such as that used in the primer coat.

10 In a second disclosed embodiment, the silane copolymers of the invention may be applied to the substrate as a single coating when a sufficiently lubricious polyol, such as Carbowax 8000, is incorporated into the copolymer. The copolymers of the invention may be used alone as the single coating, or may incorporate additional hydrophilic polymers into the copolymer to add desirable
15 properties to the coating. The preferred copolymers of this embodiment contain at least one additional hydrophilic polymer, such as polyethylene glycol (PEG), polyethylene oxide (PEO), or polyvinyl pyrrolidone (PVP).

Hydrophilic polymers that may be added to the copolymer solution include, but are not limited to, polyethylene oxide (PEO), polyethylene glycol
20 (PEG), polysaccharides, hyaluronic acid and its salts and derivatives, sodium alginate, chondroitin sulfate, celluloses, chitin, chitosan, agarose, xanthans, dermatan sulfate, keratin sulfate, emulsan, gellan, curdlan, amylose, carrageenans, amylopectin, dextrans, glycogen, starch, heparin sulfate, and limit dextrans and fragments thereof; synthetic hydrophilic polymers, poly(vinyl alcohol), and poly(N-vinyl) pyrrolidone
25 (PVP). The preferred hydrophilic polymer for use in the present invention is polyethylene glycol.

Properties of Lubricious Coatings of the Invention

The lubricious coatings made by this process have a number of
30 advantageous properties. These properties include a reduced coefficient of friction when wet, providing a very slippery surface, increased coating adhesion to silicone and other difficult to coat substrates, and increased coating durability on such substrates.

Coefficient of friction (COF) is a measure of how slippery the
35 coating is when contacted with another surface, such as body tissue. The lower the COF, the more slippery is the coating. Medical devices whose surfaces become

slippery when wet decrease patient discomfort and decrease trauma to the patient's tissue. It is, therefore, desirable to produce a coating having as low of a COF as possible when wet. The coatings of the present invention have a COF when wet of between 0.01 and 0.2, preferably between 0.01 and 0.12, and more preferably between 0.01 and 0.06. In contrast, uncoated surfaces of most medical devices typically have wet COFs greater than 0.35. Thus, coatings of the present invention are excellent for use on the surface of medical devices, especially those made of silicone and other difficult to coat surfaces because they reduce the COF of the surfaces.

Coating adhesion and durability are both affected by the copolymer's molecular weight. The molecular weight in turn is dependent upon a number of factors: (1) the amount of water initially present in the polyol, (2) the final prepolymer molecular weight, (3) the prepolymer isocyanate functionality, (4) how close the ratio of prepolymer isocyanate groups to amine groups in the organo-functional silane approaches a 1:1 stoichiometric ratio, (5) purity of the silane monomer, (6) the water content of the solvents used, and (7) the degree of viscosity the copolymer is allowed to attain before the final dilution.

An important factor which contributes to both the copolymer molecular weight and the reproducibility of the copolymer synthesis is water contamination. Water can affect the copolymer molecular weight and the reproducibility of the copolymer synthesis in several ways. First, because water reacts with isocyanate groups to form primary amines, it can affect the stoichiometry of the polymerization. Second, water can react with the methoxy groups of DAS to form crosslinks within the copolymer, which dramatically increase the molecular weight of the copolymer. Therefore, it is desirable to limit the amount of water present during manufacture of the coating. Some of the ways to limit water contamination are the use of molecular sieves, vacuum drying, anhydrous reactants and a dry, inert atmosphere. If polyethylene glycol or other hygroscopic starting material is used in the copolymer synthesis, it is preferred that it be adequately dried to a consistent moisture level before use. Hygroscopic materials such as polyethylene glycol can absorb significant quantities of water from the air in a short period of time.

The ratio of isocyanate groups on the prepolymer to amine groups on the organo-functional silane also affects the molecular weight of the copolymer. A 1:1 ratio produces a copolymer approaching infinite molecular weight. The number of free isocyanate groups present in the prepolymer limits the number of

sites available for reaction with the amine groups on the organo-functional silane. Similarly, the purity of the silane affects the number of amine groups available for reaction.

This invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope of the invention.

EXPERIMENTAL DATA

Example 1

10 Preparation of polyethylene glycol

To a glass jar was added 200 g of polyethylene glycol (PEG) 1450 (Union Carbide) followed by the addition of 50 g molecular sieves. The jar was then placed in a vacuum oven at 68°C for 72 hours under full vacuum. The water content of the PEG was then analyzed by Karl Fischer titration and determined to be 15 454 ppm.

Example 2

Preparation of urethane prepolymer

A three neck 300 ml round bottom flask was equipped with an overhead stirrer, a nitrogen inlet, and a nitrogen bubbler. The flask was placed in a 20 70°C oil bath. The nitrogen bubbler was removed and 11.60 g dried, molten PEG 1450 was injected into the flask with a syringe. To the molten PEG was added 4.03 g of Desmodur™ W (Bayer, Inc. Germany) by syringe. The flask was then flushed with nitrogen, and a nitrogen blanket was maintained over the reaction mixture 25 throughout the procedure.

The reaction mixture was stirred until homogenous. Next, 0.015 g of dioctyl tin dilaurate was added to the reaction mixture with a syringe. The mixture was then stirred for 1.2 hours at 68°C to form the urethane prepolymer.

Example 3

30 Synthesis of polurethane-urea-silane copolymer primer

A three-neck, 500 ml, round bottom flask was set up with an overhead stirrer, addition funnel with nitrogen inlet, and septum seal with nitrogen bubbler (outlet). The system was flushed with nitrogen. 111.5 g of dry (less than 35 100 ppm water) tetrahydrofuran (THF) was added to the urethane prepolymer prepared in Example 2, and the mixture was stirred until homogenous.

Next, 1.53 g of N-(2-aminoethyl)-3-aminopropyl-methyldimethoxy silane (DAS) (Gelest, Inc.) was dissolved in 38.63 g THF and added continuously to the prepolymer solution via the addition funnel over a period of approximately five minutes to begin the polymerization. The solids concentration of the solution was approximately 10% at this point.

The viscosity of the mixture was monitored, and when it increased to 70.9 centipoise (cP), 48.3 g of anhydrous THF was added. The viscosity fell and then began building again. When it reached 70.0 cP again, 49.33 g of anhydrous THF was added. This process was repeated, adding another 48.62 g of anhydrous THF when 67.6 cP was reached. When the viscosity reached the fourth target of 66.0 cP, 30.16g of THF was added to produce a 5% solids solution. When the viscosity reached a final viscosity of 67.1 cP, the solution was transferred into a 2 L vessel containing 690 g of THF and stirred until homogeneous. 354.3 g of methanol was then added to stabilize the silane copolymer, producing a final solution concentration of 1.2% solids. The amount of methanol in the solvent mixture was sufficient to produce a final methanol concentration of 25% of the total solvent. The copolymer solution was then diluted to 0.81% solids with a solution of 75% THF and 25% methanol to produce a final viscosity of 4.02 cS.

Example 4

Preparation of Hydroslide 121 polyurethane hydrogel

3.42 g of PolyoxTMN750 (Union Carbide) was dissolved in 580.6 g dichloromethane. 1.09 g PolycinTM12 (Caschem, Inc.) was then added to the Polyox solution and stirred until homogenous. Then, 0.96 g Desmodur CB60N (Bayer, Inc., Germany) was added to the solution and mixed until homogenous.

Example 5

Thirty catheters were dipped into the primer copolymer solution of Example 3 at a rate of about 41.2 ipm. The catheters were allowed to remain in the coating solution for 10 seconds and then withdrawn at a rate of about 14.9 ipm. The catheters were air dried by passing a gentle stream of air through the drainage lumen of the catheters for about 5 minutes, followed by air drying for one hour.

Example 6

The thirty catheters from Example 5 were then dipped into a solution of the Hydroslide 121 coating prepared in Example 4 at a rate of 41.1 ipm and

5 withdrawn at a rate of 15.2 ipm. The catheters were then air dried by passing a gentle stream of air through the drainage lumen for about 5 minutes, air drying them for an additional 30 minutes, and then placing them into an oven at 80 °C for 15 minutes. The catheters were allowed to cool and then packaged and sterilized with ethylene oxide (ETO). After sterilization, the coefficient of friction of 10 pairs of the silicone copolymer coated catheters was evaluated over a 21 day period in which the catheters were incubated in water at 37°C. When compared with the coefficient of friction of uncoated silicone catheters, the results confirmed a highly lubricious, durable hydrophilic coating on the silicone catheters.

10

Coated?	1 Day	7 Day	14 Day	21 Day
YES	0.023	0.026	0.032	0.048
NO	0.216	0.237	0.160	0.183

15 Finally, it will be understood that the preferred embodiments have been disclosed by way of example, and that other modifications may occur to those skilled in the art without separating from the scope and spirit of the appended claims.

WHAT IS CLAIMED IS:

1. An article of manufacture comprising a polysiloxane rubber substrate and a silane copolymer coating with a reduced coefficient of friction when wet, wherein the copolymer coating forms a layer covering the surface of the rubber substrate.
2. The article of Claim 1 wherein the substrate is a medical device.
3. The article of Claim 2 wherein the medical device is a catheter.
4. The article of Claim 1 wherein the silane copolymer coating is the reaction product of one or more polyisocyanates with one or more polymers having at least two functional groups, which may be the same or different, that are reactive with isocyanate, and with one or more organo-functional silanes having at least two functional groups, which may be the same or different, that are reactive with isocyanate, and at least one functional group reactive with a silicone rubber substrate.
5. A process for preparing the manufactured article of claim 1, wherein the preparation of the silane copolymer with a reduced coefficient of friction when wet, having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group (polyols) reacting with one or more organo-functional silanes having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group, and at least one functional group reactive with a silicone rubber substrate.
6. The process of Claim 5 further comprising the addition of a solvent.
7. The process of Claim 5 further comprising the addition of a catalyst.

8. The process of Claim 7 wherein the catalyst is selected from the group consisting of N,N-dimethylaminoethanol, N,N-dimethyl-cyclohexamine-bis(2-dimethyl aminoethyl) ether, N-ethylmorpholine, N,N,N',N',N''-pentamethyl-diethylene-triamine, 1-2(hydroxypropyl) imidazole, stannous octoate, dibutyl tin dilaurate, dioctyltin dilaurate, dibutyl tin mercaptide, ferric acetylacetonate, lead octoate, and dibutyl tin diricinoleate.

9. The process of Claim 5 wherein the polyol is a diol.

10. The process of Claim 9 wherein the diol is selected from the group consisting of poly(ethylene adipates), poly(diethyleneglycol adipates), polycaprolactone diols, polycaprolactone-polyadipate copolymer diols, poly(ethylene-terephthalate)diols, polycarbonate diols, polytetramethylene ether glycol, polyethylene glycol, ethylene oxide adducts of polyoxypropylene diols, and ethylene oxide adducts of polyoxypropylene triols.

11. The process of Claim 10 wherein the polyethylene glycol is a low molecular weight polyethylene glycol.

12. The process of Claim 11 wherein the low molecular weight polyethylene glycol is Carbowax 1450.

13. The process of Claim 10 wherein the polyethylene glycol is a higher molecular weight polyethylene glycol.

14. The process of Claim 5 wherein the polyisocyanate is a diisocyanate.

15. The process of Claim 14 wherein the diisocyanate is selected from the group consisting of 4,4'-diphenylmethane diisocyanate and position isomers thereof, 2,4- and 2,6-toluene diisocyanate (TDI) and position isomers thereof, 3,4-dichlorophenyl diisocyanate, dicyclohexylmethane-4,4'-diisocyanate (HMDI), 4,4'-diphenylmethane diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI) and position isomers thereof, isophorone diisocyanate (IPDI), and adducts of diisocyanates.

16. The process of Claim 15 wherein the diisocyanate is dicyclohexylmethane-4,4'-diisocyanate (HMDI).

5 17. The process of Claim 5 wherein the organo-functional silane is an amino-functional alkoxysilane.

18. The process of Claim 17 wherein the amino-functional alkoxysilane is N-(2-aminoethyl)-3-aminopropyl-methyldimethoxy silane.

10 19. The process of Claim 5 wherein the polyisocyanate is dicyclohexylmethane-4,4'-diisocyanate (HMDI), the amino-functional alkoxysilane is N-(2-aminoethyl)-3-aminopropyl-methyldimethoxy silane, and the polyol is Carbowax 1450.

15 20. The process of Claim 5 comprising the steps of
(a) reacting one or more polyols with an excess of polyisocyanate in the presence of a catalyst to form a polyurethane-urea prepolymer having terminal isocyanate groups;
(b) reacting the prepolymer formed in step (a) with one or more organo-
20 functional silanes having at least two functional groups, which may be the same or different, that are reactive with the isocyanate groups on the polyurethane-urea prepolymer and at least one functional group reactive with a silicone rubber substrate to form a silane copolymer; and
(c) optionally stabilizing the copolymer formed in step (b) by treating the
25 copolymer with an alcohol.

21. The process of Claim 20 wherein step (a) further comprises the addition of a solvent.

30 22. The process of Claim 20 wherein the catalyst is selected from the group consisting of N,N-dimethylaminoethanol, N,N-dimethyl-cyclohexamine-bis(2-dimethyl aminoethyl) ether, N-ethylmorpholine, N,N,N',N',N''-pentamethyl-diethylene-triamine, 1-2(hydroxypropyl) imidazole, stannous octoate, dibutyl tin dilaurate, dioctyltin dilaurate, dibutyl tin mercaptide, ferric acetylacetonate, lead
35 octoate, and dibutyl tin diricinoleate.

23. The process of Claim 20 wherein the polyol is a diol.

24. The process of Claim 23 wherein the diol is selected from the group consisting of, poly(ethylene adipates), poly(diethyleneglycol adipates), polycaprolactone diols, polycaprolactone-polyadipate copolymer diols, poly(ethylene-terephthalate)diols, polycarbonate diols, polytetramethylene ether glycol, polyethylene glycol, ethylene oxide adducts of polyoxypropylene diols, and ethylene oxide adducts of polyoxypropylene triols.

25. The process of Claim 24 wherein the polyethylene glycol is a low molecular weight polyethylene glycol.

26. The process of Claim 25 wherein the low molecular weight polyethylene glycol is Carbowax 1450.

27. The process of Claim 24 wherein the polyethylene glycol is a higher molecular weight polyethylene glycol.

28. The process of Claim 20 wherein the polyisocyanate is a diisocyanate.

29. The process of Claim 28 wherein the diisocyanate is selected from the group consisting of 4,4'-diphenylmethane diisocyanate and position isomers thereof, 2,4- and 2,6-toluene diisocyanate (TDI) and position isomers thereof, 3,4-dichlorophenyl diisocyanate, dicyclohexylmethane-4,4'-diisocyanate (HMDI), 4,4'-diphenylmethane diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI) and position isomers thereof, isophorone diisocyanate (IPDI), and adducts of diisocyanates.

30. The process of Claim 29 wherein the diisocyanate is dicyclohexylmethane-4,4'-diisocyanate (HMDI).

31. The process of Claim 20 wherein the organo-functional silane is an amino-functional alkoxysilane.

32. The process of Claim 31 wherein the amino-functional alkoxysilane is N-(2-aminoethyl)-3-aminopropyl-methyldimethoxy silane.

33. The process of claim 5 comprising the steps of

5 (a) reacting one or more organo-functional silanes having at least two functional groups, which may be the same or different, that are reactive with an isocyanate functional group and at least one functional group reactive with a silicone rubber substrate with an excess of polyisocyanate to form a polyurea prepolymer having terminal isocyanate groups;

10 (b) reacting the polyurea prepolymer formed in step (a) with one or more polyols in the presence of a catalyst to form a silane copolymer; and

(c) optionally stabilizing the copolymer formed in step (b) by treating the copolymer with an alcohol.

15 34. The process of Claim 33 wherein step (a) further comprises the addition of a solvent.

20 35. The process of Claim 33 wherein the catalyst is selected from the group consisting of N,N-dimethylaminoethanol, N,N-dimethyl-cyclohexamine-bis(2-dimethyl aminoethyl) ether, N-ethylmorpholine, N,N,N',N',N''-pentamethyl-diethylene-triamine, 1-2(hydroxypropyl) imidazole, stannous octoate, dibutyl tin dilaurate, dioctyl tin laurate, dibutyl tin mercaptide, ferric acetylacetonate, lead octoate, and dibutyl tin diricinoleate.

25 36. The process of Claim 33 wherein the polyol is a diol.

30 37. The process of Claim 36 wherein the diol is selected from the group consisting of, poly(ethylene adipates), poly(diethyleneglycol adipates), polycaprolactone diols, polycaprolactone-polyadipate copolymer diols, poly(ethylene-terephthalate)diols, polycarbonate diols, polytetramethylene ether glycol, polyethylene glycol, ethylene oxide adducts of polyoxypropylene diols, and ethylene oxide adducts of polyoxypropylene triols.

35 38. The process of Claim 37 wherein the polyethylene glycol is a low molecular weight polyethylene glycol.

39. The process of Claim 38 wherein the low molecular weight polyethylene glycol is Carbowax 1450.

40. The process of Claim 37 wherein the polyethylene glycol is a higher molecular weight polyethylene glycol.

41. The process of Claim 33 herein the polyisocyanate is a diisocyanate.

42. The process of Claim 41 wherein the diisocyanate is selected from the group consisting of 4,4'-diphenylmethane diisocyanate and position isomers thereof, 2,4- and 2,6-toluene diisocyanate (TDI) and position isomers thereof, 3,4-dichlorophenyl diisocyanate, dicyclohexylmethane-4,4'-diisocyanate (HMDI), 4,4'-diphenylmethane diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI) and position isomers thereof, isophorone diisocyanate (IPDI), and adducts of diisocyanates.

43. The process of Claim 42 wherein the polyisocyanate is dicyclohexylmethane-4,4'-diisocyanate (HMDI).

44. The process of Claim 33 wherein the organo-functional silane is an amino-functional alkoxysilane.

45. The process of Claim 44 wherein the amino-functional alkoxysilane is N-(2-aminoethyl)-3-aminopropyl-methyldimethoxy silane.

46. A coating with a reduced coefficient of friction when wet comprising a silane copolymer.

47. The coating of Claim 46 wherein the silane copolymer is a polyurethane-urea-silane copolymer.
48. The coating of Claim 46 wherein the coating further comprises a hydrophilic polymer.
49. The coating of Claim 48 wherein the hydrophilic polymer is selected from the group consisting of polyethylene oxide (PEO), polyethylene glycol (PEG), polysaccharides, hyaluronic acid and its salts and derivatives, sodium alginate, chondroitin sulfate, celluloses, chitin, chitosan, agarose, xanthans, dermatan sulfate, keratin sulfate, emulsan, gellan, curdlan, amylose, carrageenans, amylopectin, dextrans, glycogen, starch, heparin sulfate, and limit dextrans and fragments thereof; synthetic hydrophilic polymers, poly(vinyl alcohol), and poly(N-vinyl) pyrrolidone (PVP).
50. A coating with a reduced coefficient of friction when wet comprising a primer coat containing a silane copolymer and top coat.
51. The coating of Claim 50 wherein the primer coat is the reaction product of one or more polyisocyanates, one or more organo-functional silanes having at least two functional groups, which may be the same or different, that are reactive with isocyanate and at least one functional group reactive with a silicone rubber substrate, and a low molecular weight polyethylene glycol.
52. The coating of Claim 51 wherein the low molecular weight polyethylene glycol is Carbowax 1450.
53. The coating of Claim 50 wherein the top coat is the combination of a high molecular weight polyethylene oxide and a reactive mixture of polyfunctional isocyanate and polyol.

54. The coating of Claim 50 wherein the top coat is the combination of a polyvinyl pyrrolidone and a reactive mixture of polyfunctional isocyanate and polyol.

55. The coating of Claim 50 wherein the top coat is the reaction product of one or more polyisocyanates, one or more organo-functional silanes having at least two functional groups, which may be the same or different, that are reactive with isocyanate and at least one functional group reactive with a silicone rubber substrate, and a higher molecular weight polyethylene glycol.

56. The coating of Claim 55 wherein the higher molecular weight polyethylene glycol is Carbowax 8000.