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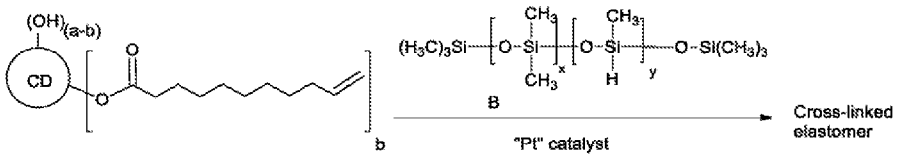

FIG. 1

(57) Abstract: Silicone rubbers exhibiting hydrophilic properties are prepared from crosslinkable components which include organic or inorganic compounds having at least two radicals with aliphatic carbon-carbon multiple bonds, organosilicon compounds with at least two Si-bonded hydrogen atoms, and covalently bonded cyclodextrin groups.

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CYCLODEXTRIN MODIFIED SILICONE COMPOSITION

FIELD OF THE INVENTION

[0001] The present invention relates to a modified silicone composition, and to the silicone rubber produced therefrom by curing. More particularly, the present invention relates to a silicone composition having cyclodextrin or their derivatives covalently bonded to the silicone to create a crosslinked hydrophilic silicone rubber.

BACKGROUND

[0002] Traditionally, cured silicone rubber compositions exhibit hydrophobic properties. The hydrophobic nature of these compositions makes traditional silicone rubber compositions advantageous in many applications. However, many applications exist where hydrophilic properties are desired. The moisture management capabilities provided by hydrophilic compositions is desired in skin contact and medical applications (e.g., wound care applications) to keep and draw moisture, sweat and exudates away from the body. Hydrophilic materials also exhibit a low coefficient of friction useful in applications such as catheters. The resistance to protein adhesion provided by hydrophilic materials is beneficial in body implants and other types of medical devices. Hydrophilic materials are also advantageous in anti-static articles.

[0003] To take advantage of the properties of silicone rubber compositions treatments have been developed to impart hydrophilic properties. A common method for making silicone rubber hydrophilic is plasma treating the surface of the silicone rubber. While this treatment provides hydrophilic properties to the surface of the silicone rubber, the treatment is not permanent and is only effective on the surface of the silicone rubber. Another method is to provide a hydrophilic coating on the silicone rubber, but this treatment is ineffective as well due to delamination issues.

[0004] Additionally, US 2002/160139 disclosed a surface modified polymer and a surface covalently bonded to the surface modifying compound. Formation of the covalent bond between the polymer and the surface modifying compound is achieved by reacting an intrinsic functional group that is present in the polymer and the functional group of the surface modifying compound. By using a polymer having an intrinsic functional group, a separate surface activation step is avoided. Thus, the material has a hydrophilic surface while the bulk

of the material remains hydrophobic. Accordingly, this material does not allow for the uptake of moisture through the material and moisture can thus not be removed effectively.

[0005] Other examples for making these types of materials use incorporation of polyethers to the silicone rubbers. For example, Brook et al. reported the synthesis and characterization of protein rejecting PDMS-based rubbers that were prepared by incorporating asymmetric PEO (bearing a methyl group on one end and a functional triethoxysilyl group on the other) into PDMS during rubber formation using classic room temperature vulcanization (RTV) chemistry and further described their potential for use as biomaterials. (Chen, H., Brook, M.A., Sheardown, H., Biomaterials, 2004, 25(12), 2273-82.) It has been shown that the incorporation of poly(ethylene oxide) into the silicone rubber was able to reduce the protein adsorption. However, incorporation of poly(alkylene oxides) results in possible harmful impurities, and may result in skin irritation. As a result, many industries avoid the use of polyoxyalkylenes, either as units covalently bonded to a polymer, or separately, as non-ionic surfactants.

[0006] Cyclodextrins ("CD") have been used as an additive or a carrier in rubber curing formulations. U.S. Publication No. 2005/260905 discloses the use of cyclodextrin as carriers for different additives in polymeric matrix for use in textile finishing material. Although, the cyclodextrin may be part of a crosslinked network, the formulation does not produce a hydrophilic rubber.

[0007] CN106349705 discloses a high temperature resistant and high flame-retardant silicone rubber cable sheathing material formed by using beta cyclodextrin as one of the components. While the cyclodextrin may be crosslinked, the product does not exhibit hydrophilic properties.

[0008] Cyclodextrins ("CD") have been used in rubber curing formulations to provide hydrophilic properties to silicone rubbers. US 5,391,592 discloses a contact lens made by reacting CD modified with alkenyl groups with SiH containing silicones to produce a lipophilic CD-silicone polymer. The modified CD disclosed no longer contain exclusively free hydroxy groups; rather, some or all of the groups are etherified. Thus, these materials are expected to provide little or no hydrophilicity. In addition, the lipophilic materials obtained are also not expected to exhibit reduced protein adsorbing properties limiting their application.

[0009] Thus, based on the disadvantages still present in the prior art, there is still a need for a crosslinked silicone rubber with hydrophilic properties throughout the bulk of the material, for manufacturing products with moisture control properties, with a low coefficient of friction with respect to polar or wet surfaces (e.g., skin), and biocompatibility. There is also a need in the art for conveniently producing a crosslinked silicone rubber with hydrophilic properties while avoiding potentially harmful impurities.

SUMMARY OF THE INVENTION

[0010] It has now been surprisingly and unexpectedly discovered that silicone rubbers prepared by cross-linking one or more modified cyclodextrin derivatives in a hydrosilylation reaction with one or more organopolysiloxane materials in the presence of a noble metal (e.g., platinum) catalyst, form stable, cured hydrophilic silicone rubbers. The cyclodextrin cavity remains useful for "guest/host" complexes, despite being a constituent of a three-dimensional polymer matrix. Other components such as fillers, plasticizers, pigments, and other additives can be added as required. The inventive hydrophilic rubber can be useful for encapsulation and release of cosmetic or pharmaceutical actives, medical devices, transdermal drug delivery patches/device, wound care materials, low friction materials, body implants, wet seals, water absorbing foams and other applications requiring a biocompatible hydrophilic rubber.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIGURE 1 illustrates schematically one embodiment of the hydrophilic crosslinked silicone rubber of the present invention;

[0012] FIGURE 2 illustrates schematically the formation of undecenoyl modified cyclodextrin for use in the hydrophilic crosslinked silicone rubber of the present invention;

[0013] FIGURE 3 illustrates schematically one embodiment of the hydrophilic crosslinked silicone rubber of the present invention; and

[0014] FIGURE 4 illustrates schematically one embodiment of the hydrophilic crosslinked silicone rubber of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] The inventive hydrophilic crosslinked silicone rubbers (X) are produced in a hydrosilylation reaction between one or more reactants including aliphatic unsaturation such as ethylenic or ethylynic unsaturation, and one or more reactants including Si-H functionality ("silicone-bonded hydrogen"). The reaction is catalyzed by a hydrosilylation catalyst, which may be, for example, a platinum compound or complex. At least one reactant must contain a covalently bonded cyclodextrin moiety, for example a cyclodextrin derivative containing ethylenic or ethylynic unsaturation; a silicone (organopolysiloxane) reactant containing hydrosilylation-reaction functionality, to which one or more cyclodextrin groups are covalently bonded; or a silane or silicone bearing silicon bonded hydrogen to which a cyclodextrin moiety is covalently bonded.

[0016] Embodiments of the inventive hydrophilic crosslinked silicone rubber (X) comprising, besides component (E):

[0017] at least one each of compound (A), (B), and (D), or

[0018] at least one each of compound (A), (B), (C), and (D), or

[0019] at least one (C) and (D)

[0020] where

[0021] (A) is an organic compound or an organosilicon compound, containing at least two radicals with aliphatic carbon-carbon multiple bonds,

[0022] (B) is an organosilicon compound, containing at least two Si-bonded hydrogen atoms,

[0023] (C) is an organosilicon compound, containing SiC-bonded radicals with aliphatic carbon-carbon multiple bonds and Si-bonded hydrogen atoms,

[0024] (D) is a hydrosilylation catalyst, and

[0025] (E) is a cyclodextrin (which may be a mixture of cyclodextrins) modified to include at least one aliphatically unsaturated group such as one containing ethylenic or ethylynic unsaturation, or at least one SiH group, or a combination of at least one aliphatically unsaturated group such as one containing ethylenic or ethylynic unsaturation and at least one SiH group.

[0026] The addition-crosslinking silicone compositions according to the invention may be single-component silicone compositions or else two- or multi-component silicone compositions.

[0027] In two-component compositions, the individual components of the compositions according to the invention can contain all of the constituents in any desired combination, generally with the proviso that one component does not simultaneously comprise siloxanes with an aliphatic multiple bond, siloxanes with Si-bonded hydrogen and catalyst, i.e. essentially not simultaneously the constituents (A), (B) and (D) or (C) and (D). However, the compositions according to the invention are preferably single-component compositions.

[0028] As is known, the compounds (A) and (B) or (C) used in the compositions according to the invention are selected such that a crosslinking is possible. Thus, for example, compound (A) has at least two aliphatically unsaturated radicals and (B) has at least three Si-bonded hydrogen atoms, or compound (A) has at least three aliphatically unsaturated radicals and siloxane (B) has at least two Si-bonded hydrogen atoms, or else instead of compound (A) and (B), siloxane (C) is used which has aliphatically unsaturated radicals and Si-bonded hydrogen atoms in the aforementioned ratios.

[0029] The compound (A) used according to the invention can be a silicon-free organic compound with preferably at least two aliphatically unsaturated groups and can be an organosilicon compound with preferably at least two aliphatically unsaturated groups, or else mixtures thereof.

[0030] Examples of silicon-free organic compounds (A) are 1,3,5-trivinylcyclohexane, 2,3-dimethyl-1,3-butadiene, 7-methyl-3-methylene-1,6-octadiene, 2-methyl-1,3-butadiene, 1,5-hexadiene, 1,7-octadiene, 4,7-methylene-4,7,8,9-tetrahydroindene, methylcyclopentadiene, 5-vinyl-2-norbornene, bicyclo[2.2.1]hepta-2,5-diene, 1,3-diisopropenylbenzene, vinyl-group-containing polybutadiene, 1,4-divinylcyclohexane, 1,3,5-triallylbenzene, 1,3,5-trivinylbenzene, 1,2,4-trivinyl-cyclohexane, 1,3,5-triisopropenylbenzene, 1,4-divinylbenzene, 3-methyl-heptadiene-(1,5), 3-phenyl-hexadiene-(1,5), 3-vinyl-hexadiene-(1,5) and 4,5-dimethyl-4,5-diethyloctadiene-(1,7), N,N′-methylene-bisacrylamide, 1,1,1-tris(hydroxymethyl)propane triacrylate, 1,1,1-tris(hydroxymethyl)propane trimethacrylate, tripropylene glycol diacrylate, diallyl ether, diallylamine, diallyl carbonate, N,N′-diallylurea, triallylamine, tris(2-methylallyl)amine, 2,4,6-triallyloxy-1,3,5-triazine, triallyl-s-triazine-2,4,6(1H,3H,5H)-trione, diallyl malonate,

polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, poly(propylene glycol) dimethacrylate.

[0031] In addition-crosslinking crosslinked silicone rubber (X), constituent (A) may include at least one aliphatically unsaturated organosilicon compound, in which case all aliphatically unsaturated organosilicon compounds used to date in addition-crosslinking compositions may be employed, such as, for example, silicone polymers, copolymers and resins with vinyl functionality, silicone block copolymers with urea segments, silicone block copolymers with amide segments and/or imide segments and/or ester/amide segments and/or polystyrene segments and/or silarylene segments and/or carborane segments and silicone graft copolymers with ether groups.

[0032] The organosilicon compounds (A) that have SiC-bonded radicals with aliphatic carbon-carbon-multiple bonds used are preferably linear or branched organopolysiloxanes of units of the general formula (I)

$$R^4_aR^5_bSiO_{(4-a-b)/2} \quad (I)$$

[0033] where

[0034] R^4, independently of one another, are an organic or inorganic radical free from aliphatic carbon-carbon-multiple bonds,

[0035] R^5, independently of one another, are a monovalent, substituted or unsubstituted, SiC-bonded hydrocarbon radical with at least one aliphatic carbon-carbon-multiple bond,

[0036] a is 0, 1, 2 or 3, and

[0037] b is 0, 1 or 2,

[0038] with the proviso that the sum a+b is less than or equal to 3 and at least 2 radicals R^5 are present per molecule.

[0039] Radicals R^4 may be mono- or polyvalent radicals, with the polyvalent radicals, such as, for example, bivalent, trivalent and tetravalent radicals, then joining together several, for example two, three or four, siloxy units of the formula (I).

[0040] Further examples of R^4 are the monovalent radicals —F, —Cl, —Br, OR^6, —CN, —SCN, —NCO and SiC-bonded, substituted or unsubstituted hydrocarbon radicals which may be interrupted with oxygen atoms or the group —C(O)—, and also bivalent radicals Si-bonded on both sides according to formula (II). If radicals R^4 are SiC-bonded substituted hydrocarbon radicals, preferred substituents are halogen atoms, phosphorus-containing radicals, cyano radicals, —OR^6, —NR^6—, —NR^6_2, —NR^6—C(O)—NR^6_2, —C(O)—NR^6_2, —C(O)R^6, —C(O)OR^6, —SO_2-Ph and —C_6F_5. Here, R^6 are, independently of one another, hydrogen or a monovalent hydrocarbon radical having 1 to 20 carbon atoms, and Ph is the phenyl radical.

[0041] Examples of radicals R^4 are alkyl radicals such as the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, neopentyl, and tert-pentyl radicals, hexyl radicals such as the n-hexyl radical, heptyl radicals such as the n-heptyl radical, octyl radicals such as the n-octyl radical and isooctyl radicals such as the 2,2,4-trimethylpentyl radical, nonyl radicals such as the n-nonyl radical, decyl radicals such as the n-decyl radical, dodecyl radicals such as the n-dodecyl radical, and octadecyl radicals such as the n-octadecyl radical, cycloalkyl radicals such as the cyclopentyl, cyclohexyl, cycloheptyl and methylcyclohexyl radicals, aryl radicals such as the phenyl, naphthyl, anthryl and phenanthryl radicals, alkaryl radicals such as the o-, m-, and p-tolyl radicals, xylyl radicals and ethylphenyl radicals, and aralkyl radicals such as the benzyl radical, and the α- and the β-phenylethyl radicals.

[0042] Examples of substituted radicals R^4 are haloalkyl radicals, such as the 3,3,3-trifluoro-n-propyl radical, the 2,2,2,2′,2′,2′-hexafluoroisopropyl radical, the heptafluoroisopropyl radical, haloaryl radicals, such as the o-, m- and p-chlorophenyl radical, —(CH_2)—$N(R^6)C(O)NR^6_2$, —$(CH_2)_o$—$C(O)NR^6_2$, —$(CH_2)_o$—$C(O)R^6$, —$(CH_2)_o$—$C(O)OR^6$, —$(CH_2)_o$—$C(O)NR^6_2$, —(CH_2)—C(O)—$(CH_2)_pC(O)CH_3$, —(CH_2)—O—CO—R^6, —(CH_2)—NR^6—$(CH_2)_p$—NR^6_2, —$(CH_2)_o$—O—$(CH_2)_pCH(OH)CH_2OH$, —$(CH_2)_o(OCH_2CH_2)_pOR^6$, —$(CH_2)_o$—$SO_2$-Ph and —$(CH_2)_o$—O—$C_6F_5$, where R^6 and Ph corresponds to the meaning given for them above and o and p are identical or different integers between 0 and 10.

[0043] Examples of R^4 being divalent radicals Si-bonded on both sides according to formula (I) are those which are derived from the monovalent examples specified above for radical R^4 by virtue of the fact that an additional bonding takes place by substitution of a hydrogen atom. Examples of such radicals are —(CH_2)—, —$CH(CH_3)$—, —$C(CH_3)_2$—, —

$CH(CH_3)—CH_2—$, $—C_6H_4—$, $—CH(Ph)—CH_2—$, $—C(CF_3)_2—$, $—(CH_2)_o—C_6H_4—(CH_2)_o—$, $—(CH_2)_o—C_6H_4—C_6H_4—(CH_2)_o—$, $—(CH_2O)_p$, $(CH_2CH_2O)_o$, $—(CH_2)_o—O_x—C_6H_4—SO_2—C_6H_4—O_x—(CH_2)_o—$, where x is 0 or 1, and Ph, o and p have the meaning specified above.

[0044] Preferably, radical R^4 is a monovalent SiC-bonded, optionally substituted hydrocarbon radical having 1 to 18 carbon atoms free from aliphatic carbon-carbon-multiple bonds, more preferably a monovalent SiC-bonded hydrocarbon radical having 1 to 6 carbon atoms free from aliphatic carbon-carbon-multiple bonds, and in particular the methyl or phenyl radical.

[0045] Radical R^5 may be any desired groups accessible to an addition reaction (hydrosilylation) with an SiH-functional compound.

[0046] If radicals R^6 are SiC-bonded, substituted hydrocarbon radicals, the substituents are preferably halogen atoms, cyano radicals and $—OR^6$, where R^6 has the aforementioned meaning.

[0047] Preferably, radicals R^5 are alkenyl and alkynyl groups having 2 to 16 carbon atoms, such as vinyl, allyl, methallyl, 1-propenyl, 5-hexenyl, ethynyl, butadienyl, hexadienyl, cyclopentenyl, cyclopentadienyl, cyclohexenyl, vinylcyclohexylethyl, divinylcyclohexylethyl, norbornenyl, vinylphenyl and styryl radicals, with vinyl, allyl and hexenyl radicals being most preferably used.

[0048] The molecular weight of the constituent (A) can vary within wide limits, for example between 10^2 and 10^6 g/mol. Thus, the constituent (A) can be, for example, a relatively low molecular weight alkenyl-functional oligosiloxane, such as 1,2-divinyltetramethyldisiloxane, but also a highly polymeric polydimethylsiloxane which has chain-positioned or terminal Si-bonded vinyl groups, e.g. with a molecular weight of 10^5 g/mol (number-average determined by means of NMR). The structure of the molecules forming the constituent (A) is also not fixed; in particular, the structure of a more highly molecular, i.e. oligomeric or polymeric siloxane, may be linear, cyclic, branched or else resin-like, network-like. Linear and cyclic polysiloxanes are preferably composed of units of the formulae $R^4_3SiO_{1/2}$, $R^5R^4_2SiO_{1/2}$, $R^5R^4SiO_{1/2}$ and $R^4_2SiO_{2/2}$, where R^4 and R^5 have the meanings given above. Branched and network-like polysiloxanes additionally contain trifunctional and/or tetrafunctional units, with those of the formulae $R^4SiO_{3/2}$, $R^5SiO_{3/2}$ and $SiO_{4/2}$ being preferred.

Mixtures of different siloxanes satisfying the criteria of constituent (A) can of course also be used.

[0049] As component (A), particular preference is given to the use of vinyl-functional, essentially linear polydiorganosiloxanes with a viscosity of 0.01 to 500,000 Pa·s, more preferably from 0.1 to 100,000 Pa·s, in each case at 25° C.

[0050] As organosilicon compound(s) (B), it is possible to use all hydrogen-functional organosilicon compounds which have also hitherto been used in addition-crosslinkable compositions.

[0051] The organopolysiloxanes (B) that have Si-bonded hydrogen atoms are preferably linear, cyclic or branched organopolysiloxanes of units of the general formula (II).

$$R^4_cH_dSiO_{(4-c-d)/2} \quad (II)$$

[0052] where

[0053] R^4 has the aforementioned meaning,

[0054] c is 0, 1, 2 or 3 and

[0055] d is 0, 1 or 2,

[0056] with the proviso that the sum of c+d is less than or equal to 3 and at least two Si-bonded hydrogen atoms are present per molecule.

[0057] Preferably, the organopolysiloxane (B) used according to the invention comprise Si-bonded hydrogen in the range from 0.04 to 1.7 percent by weight, based on the total weight of the organopolysiloxane (B).

[0058] The molecular weight of the constituent (B) can likewise vary within wide limits, for example between 10^2 and 10^6 g/mol. Thus, the constituent (B) can for example be a relatively low molecular weight SiH-functional oligosiloxane, such as tetramethyldisiloxane, but also a highly polymeric polydimethylsiloxane that has chain-positioned or terminal SiH-groups, or a silicone resin that has SiH-groups.

[0059] The structure of the molecules forming the constituent (B) is also not fixed; in particular, the structure of a more highly molecular, i.e. oligomeric or polymeric SiH-

containing siloxane may be linear, cyclic, branched or else resin-like, network-like. Linear and cyclic polysiloxanes (B) are preferably composed of units of the formulae $R^4_3SiO_{1/2}$, $HR^4_2SiO_{1/2}$, $HR^4SiO_{2/2}$ and $R^4_2SiO_{2/2}$, where R^4 has the meaning given above. Branched and network-like polysiloxanes additionally comprise trifunctional and/or tetrafunctional units, preference being given to those of the formulae $R^4SiO_{3/2}$, $HSiO_{3/2}$ and $SiO_{4/2}$, where R^4 has the meaning given above.

[0060] It is of course also possible to use mixtures of different siloxanes meeting the criteria of constituent (B). In particular, the molecules forming the constituent (B) can optionally additionally also contain aliphatically unsaturated groups in addition to the obligatory SiH-groups. Particular preference is given to the use of low molecular weight SiH-functional compounds such as tetrakis(dimethylsiloxy)silane and tetramethylcyclotetrasiloxane, as well as more highly molecular, SiH-containing siloxanes, such as poly(hydrogenmethyl)siloxanes and poly(dimethylhydrogenmethyl)siloxanes with a viscosity at 25° C. of from 10 to 10,000 mPa·s, or analogous SiH-containing compounds in which some of the methyl groups are replaced by 3,3,3-trifluoropropyl or phenyl groups.

[0061] Constituent (B) is preferably present in the crosslinkable silicone compositions according to the invention in an amount such that the molar ratio of SiH-groups to aliphatically unsaturated groups from (A) is 0.1 to 20, more preferably between 1.0 and 5.0.

[0062] The components (A) and (B) used according to the invention are standard commercial products and/or can be prepared by processes customary in chemistry.

[0063] Instead of component (A) and (B), the silicone compositions according to the invention can comprise organopolysiloxanes (C) which simultaneously have aliphatic carbon-carbon-multiple bonds and Si-bonded hydrogen atoms. The silicone compositions according to the invention can also comprise all three components (A), (B) and (C).

[0064] If siloxanes (C) are used, these are preferably those of units of the general formulae (III), (IV) and (V)

$$R^4_fSiO_{4/2} \quad (III)$$

$$R^4_gR^5SiO_{3-g/2} \quad (IV)$$

$$R^4_hHSiO_{3-h/2} \quad (V)$$

[0065] where

[0066] R^4 and R^5 have the meaning given for them above,

[0067] f is 0, 1, 2 or 3,

[0068] g is 0, 1 or 2 and

[0069] h is 0, 1 or 2,

[0070] with the proviso that at least 2 radicals R^5 and at least 2 Si-bonded hydrogen atoms are present per molecule.

[0071] Examples of organopolysiloxanes (C) are those made from $SO_{4/2}$, $R^4_3SiO_{1/2}$, $R^4_2R^5SiO_{1/2}$ and $R^4_2HSiO_{1/2}$ units, so-called MQ resins, where these resins can additionally contain $R^4SiO_{3/2}$ and R^4_2SiO units, as well as linear organopolysiloxanes essentially consisting of $R^4_2R^5SiO_{1/2}$, R^4_2SiO and R^4HSiO units where R^4 and R^5 have the aforementioned meaning.

[0072] The organopolysiloxanes (C) preferably have an average viscosity of from 0.01 to 500,000 Pa·s, more preferably 0.1 to 100,000 Pa·s, in each case at 25° C. Organopolysiloxanes (C) can be prepared by methods customary in chemistry.

[0073] As hydrosilylation catalyst (D), it is possible to use all catalysts known to the prior art. Component (D) may be a platinum group metal, for example platinum, rhodium, ruthenium, palladium, osmium or iridium, an organometallic compound or a combination thereof. Examples of component (D) are compounds such as hexachloroplatinic(IV) acid, platinum dichloride, platinum acetylacetonate and complexes of these compounds which are encapsulated in a matrix or a core/shell-like structure.

[0074] Platinum complexes with low molecular weight organopolysiloxanes include 1,3-diethenyl-1,1,3,3-tetramethyldisiloxane complexes with platinum. Further examples are platinum phosphite complexes, platinum phosphine complexes or alkylplatinum complexes. These compounds may be encapsulated in a resin matrix.

[0075] Component (E) is a cyclodextrin (which may be a mixture of cyclodextrins) modified to include at least one aliphatically unsaturated group such as one containing ethylenic or ethylynic unsaturation. The cyclodextrin may also include an SiH functional group or SiH functionality and at least one aliphatically unsaturated group. Cyclodextrins are cyclic oligosaccharides constructed of w units of α-(1,4)-linked anhydroglucose units, where w is

generally from 6-10. The common cyclodextrins contain 6, 7, or 8 anhydroglucose units, and are referred to, respectively, as α-cyclodextrin, β-cyclodextrin, and γ-cyclodextrin, often abbreviated as α-CD, β-CD, and γ-CD. Such cyclodextrins and others where w ≠ 6, 7, or 8, are produced by the enzymatic conversion ("digestion") of starch and are readily commercially available.

[0076] Due to their structure, CDs have a hydrophobic interior. Numerous molecules can enter this cavity and form stable complexes, often in stoichiometric ratios, but not always 1:1 ratios. Whether a particular molecule can be a guest molecule in such host/guest complexes is not always predictable, but depends upon the molecular structure of the guest molecule, its physical size, presence or absence of polar groups, *etc.* The cavity size of CDs increases from α to γ, and larger molecules are generally more easily complexed by the CDs with larger cavities and vice versa. The complexes formed are reversible, in that the guest molecules may often be "liberated" quite easily, and it has been found that some molecules which are notoriously thermally or oxidatively sensitive, curcumin and fish oils being examples, are rendered much more stable by being incorporated into cyclodextrin complexes. In addition, the liberated molecules may be released at a controlled rate to increase effectiveness in various applications. The guest molecules may include natural oils, pharmaceutical products, cosmetic or personal care actives, biocides, insecticides, fungicides, herbicides, pheromones, fragrances, flavorings, pigments, drugs, pharmaceutical active compounds, antigens, active compounds for antistatic finishing or flame-retardant finishing, stabilizers (UV), dyestuffs, etc.

[0077] The solubility of cyclodextrins in water is limited, and with respect to the most common cyclodextrins, α-CD, β-CD, and γ-CD, ranges from 18 mg/ml for β-CD to 232 mg/ml for γ-CD. Thus, CDs are much less soluble in water and polar solvents than other saccharides and oligosaccharides.

[0078] The hydrophilic crosslinked silicone rubber (X) of the present invention are prepared by incorporating cyclodextrin moieties into the rubber through a hydrosilylation reaction. There are various methods of accomplishing this. In one method, a cyclodextrin (which may be a mixture of cyclodextrins) is modified to contain at least one aliphatically unsaturated group such as one containing ethylenic or ethylynic unsaturation (A). On average, the cyclodextrin can contain from 1 to 24 carbon-carbon multiple bonds, preferably 1 to 16 carbon-carbon multiple bonds, more preferably 1 to 8 carbon-carbon multiple bonds, even more preferably 1 to 3 carbon-carbon multiple bonds, still more preferably 1 to 2 carbon-carbon

multiple bonds, yet more preferably from 1 to 2 or less than 2 multiple bonds, and most preferably, 1 carbon-carbon multiple bond.

[0079] The organic groups which contain the carbon-carbon multiple bonds may be, and preferably are, simple alkenyl groups linked to the CDs by an ether linkage, may be a (meth)acrylate group, a maleate or fumarate group, or the like. Such groups may be covalently bound to one of the CD hydroxyl oxygens through any suitable linking group, such as but not limited to, ether, ester, urethane, and urea groups. An example of unsaturation could also be a vinyl silyl group connected to the CD directly or through a linker. The remaining unreacted CD hydroxyl groups may remain as free hydroxyl groups, or may have been derivatized or may be previously or subsequently derivatized with other groups not containing ethylenic or ethylynic unsaturation, such as methyl groups, acetate groups, etc. Derivatized CDs containing such modifying groups and other modifying groups are widely available and can be used as starting materials to form the CDs containing carbon-carbon multiple bonds.

[0080] In the context of the present invention, a "cyclodextrin derivative" is a cyclodextrin which has been derivatized by groups which are not reactive in a hydrosilylation reaction. Such groups include, but are not limited to, groups such as those previously mentioned, e.g. hydrocarbon and hydrocarbonoxy groups containing no aliphatic unsaturation. By a "modified cyclodextrin" herein is meant a cyclodextrin or cyclodextrin derivative which has been modified (functionalized) to contain a group having aliphatic unsaturation which can participate in a hydrosilylation reaction, or to contain a silyl or polyorganosiloxyl group containing silicon-bonded hydrogen.

[0081] Methods for introducing groups containing carbon-carbon multiple bonds onto CDs are known or easily formulated by a chemist. For example, the methods disclosed in M. Yin et al., CHROMATOGRAPHIA (2003), Vol. 58, p. 301, may be used. Other methods include esterification of CD hydroxyl groups by means of an unsaturated carboxylic acid chloride, esterification by reacting with an unsaturated carboxylic acid such as (meth)acrylic acid; by esterification by reaction with an unsaturated anhydride such as maleic anhydride or acrylic anhydride; by urethanization by reaction with an unsaturated isocyanate such as vinyl isocyanate, allyl isocyanate, or isocyanatoethyl(meth)acrylate or isocyanatopropyl(meth)acrylate; by reaction with an unsaturated epoxy compound, and by other reactions known to the art. The number of carbon-carbon multiple bond-containing groups of the unsaturated CD (E) is limited by the number of free hydroxyl groups in principle but may also be limited in practice by steric effects. Of course, the higher the number of

aliphatically unsaturated groups, the more derivatizing reagent must be used, resulting in higher cost.

[0082] A further method of incorporating CD groups by hydrosilylation is to prepare an organopolysiloxane which is reactive in a hydrosilylation reaction by virtue of the presence of aliphatic unsaturation and/or Si-H functionality as an intermediate product, and which contains one or more covalently bonded CD groups on average. For example, an organopolysiloxane containing Si-vinyl groups or Si-H groups and also containing a species reactive with a CD or with a CD derivative may be reacted with the CD to covalently bond the CD to the organopolysiloxane. For non-derivatized CDs or CDs which have been partially derivatized with non-interfering groups such as alkyl groups or acetyl groups, suitable reactive groups on the organopolysiloxanes include anhydride groups such as those derived from maleic anhydride, succinic anhydride, terephthalic anhydride, and phthalic anhydride groups, and other groups reactive with hydroxyl groups, such as isocyanate or epoxy groups.

[0083] If the CD has been derivatized with a group which is reactive in hydrosilylation, *e.g.* an aliphatically unsaturated group or a group bearing or containing an Si-H group, then an organopolysiloxane bearing complementarily reactive groups in stoichiometric excess can be used. For example, a derivatized CD bearing an aliphatically unsaturated group can be reacted with an organopolysiloxane bearing, for example, four Si-H groups, in a 1:1 mol ratio. The hydrosilylated product will contain, on average, one CD moiety per molecule, and will, on average, contain three unreacted Si-H groups to be subsequently reacted to form the rubber.

[0084] Preferably, the CDs which will participate in the reaction to form a rubber will be CDs which have been derivatized to contain, on average, one or more aliphatically unsaturated groups, or the CD will have been covalently bonded to an organopolysiloxane bearing aliphatically unsaturated groups.

[0085] If the CD-containing component is an organopolysiloxane bearing Si-H groups or ethylenically unsaturated groups, then the amount of CD moieties in the final hydrophilic crosslinked silicone rubber (X) product may be limited due to selection of the proper portions of organopolysiloxanes necessary to result in rubber formation. With "free" CDs modified to contain an aliphatically unsaturated group, the reaction is simpler, more economical, and the CD content may be varied over an extremely wide range.

[0086] To catalyze the hydrosilylation reaction of the components (A), (B), and (E) the concentration of component (D) is sufficient to reach acceptable cure for the application. The amount of component (D) can be between 0.1 and 1000 parts per million (ppm), 0.5 and 100 ppm or 1 and 25 ppm of the platinum group metal, depending on the total weight of the component. The curing rate may be low if the constituent of the platinum group metal is below 1 ppm. The use of more than 100 ppm of the platinum group metal is uneconomical or can reduce the stability of the adhesive formulation.

[0087] The inventive hydrophilic crosslinked silicone rubber (X) may optionally include additives such as strengthening fillers as component (F). Component (F) may include fumed or precipitated silicas with BET surface areas of at least 50 m^2/g, as well as carbon blacks and activated carbons such as furnace black and acetylene black, with preference being given to fumed and precipitated silicas with BET surface areas of at least 50 m^2/g. The specified silica fillers can have a hydrophilic character or be hydrophobized by known processes. The content of actively strengthening filler (F) in the crosslinkable composition according to the invention is in the range from 0 to 70% by weight, preferably 0 to 50% by weight.

[0088] Preferably, the crosslinkable silicone compositions according to the invention are characterized in that the filler (F) has been surface-treated. The surface treatment is achieved by processes known in the prior art for the hydrophobization of finely divided fillers. The hydrophobization can take place, for example, either prior to the incorporation into the polyorganosiloxane or else in the presence of a polyorganosiloxane according to the in-situ process. Both processes can be carried out either in the batch process or else continuously. Hydrophobizing agents preferably used are organosilicon compounds which are able to react with the filler surface to form covalent bonds or are permanently physically absorbed onto the filler surface. Examples of hydrophobizing agents are alkylchlorosilanes such as methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, octyltrichlorosilane, octadecyltrichlorosilane, octylmethyldichlorosilane, octadecylmethyldichlorosilane, octyldimethylchlorosilane, octadecyldimethylchlorosilane and tert-butyldimethylchlorosilane; alkylalkoxysilanes such as dimethyldimethoxysilane, dimethyldiethoxysilane, trimethylmethoxysilane and trimethylethoxysilane; trimethylsilanol; cyclic diorgano(poly)siloxanes such as octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane; linear diorganopolysiloxanes such as dimethylpolysiloxanes with trimethylsiloxy end groups, and dimethylpolysiloxanes with silanol or alkoxy end groups; disilazanes such as hexaalkyldisilazanes, in particular hexamethyldisilazane,

divinyltetramethyldisilazane, bis(trifluoropropyl)tetramethyldisilazane; cyclic dimethylsilazanes, such as hexamethylcyclotrisilazane. It is also possible to use mixtures of the hydrophobizing agents specified above. In order to increase the rate of the hydrophobization, catalytically active additives, such as, for example, amines, metal hydroxides and water, can also optionally be added.

[0089] The hydrophobization can take place, for example, in one step using one hydrophobizing agent or a mixture of several hydrophobizing agents, but also using one or more hydrophobizing agents in several steps.

[0090] As a consequence of a surface treatment, preferred fillers (F) have a carbon content of at least 0.01 to at most 20% by weight, preferably between 0.1 and 10% by weight, and more preferably between 0.5 to 5% by weight. Particular preference is given to crosslinkable silicone compositions which are characterized in that the filler (F) is a surface-treated silica having 0.01 to 2% by weight of Si-bonded, aliphatically unsaturated groups. For example, these may be Si-bonded vinyl groups. In the silicone composition according to the invention, the constituent (F) is used preferably as an individual filler or likewise preferably as a mixture of several finely divided fillers.

[0091] The silicone compositions according to the invention can, if desired, may include further additives (G) in a fraction of up to 70% by weight, preferably 0.0001 to 40% by weight. These additives (G) may be e.g. inactive fillers, resin-like polyorganosiloxanes which are different from the siloxanes (A), (B), and (C) and may include fungicides, fragrances, rheological additives, inhibitors and stabilizers for the targeted adjustment of processing time, onset temperature and crosslinking rate, corrosion inhibitors, oxidation inhibitors, light protection agents, flame retardants and agents for influencing the electrical properties, dispersion auxiliaries, solvents, adhesion promoters, pigments, dyes, plasticizers, organic polymers, heat stabilizers etc. These include additives such as quartz flour, diatomaceous earth, clays, chalk, lithopone, graphite, metal oxides, metal carbonates, metal sulfates, metal salts of carboxylic acids, metal dusts, fibers, such as glass fibers, plastic fibers, plastic powders, metal dusts, dyes, pigments, etc.

[0092] Moreover, these fillers may be heat-conducting or electrically conducting. Examples of heat-conducting fillers are aluminum nitride; aluminum oxide; barium titanate; beryllium oxide; boron nitride; diamond; graphite; magnesium oxide; particulate metals such as, copper, gold, nickel or silver; silicon carbide; tungsten carbide; zinc oxide, and

combinations thereof. Heat-conducting fillers are known in the prior art and are commercially available. For example, CB-A20S and Al-43-Me are aluminum oxide fillers in different particle sizes which are commercially available from Showa-Denko, and AA-04, AA-2 and AA18 are aluminum oxide fillers which are commercially available from Sumitomo Chemical Company. Silver fillers are commercially available from Metalor Technologies U.S.A. Corp. of Attleboro, Mass., U.S.A. Boron nitride fillers are commercially available from Advanced Ceramics Corporation, Cleveland, Ohio, U.S.A. It is also possible to use a combination of fillers with different particle sizes and different particle size distribution.

[0093] The silicone composition can additionally optionally comprise a solvent (H). However, it should be ensured that the solvent (H) has no disadvantageous effects on the overall system, and that the solvent (H) has no disadvantages with respect to skin contact and curing. Suitable solvents (H) are known in the prior art and are commercially available. The solvent (H) can be, for example, an organic solvent having 3 to 20 carbon atoms. Non-limiting examples of solvents (H) include aliphatic hydrocarbons such as nonane, decalin and dodecane; aromatic hydrocarbons such as mesitylene, xylene and toluene; esters such as ethyl acetate and butyrolactone; ethers such as n-butyl ether and polyethylene glycol monomethyl ether; ketones such as methyl isobutyl ketone and methyl pentyl ketone; silicone fluids such as linear, branched and cyclic polydimethylsiloxanes, and combinations of these solvents. The optimum concentration of a specific solvent (H) in the silicone composition can be determined easily by means of routine experiments. Depending on the weight of the compound, the amount of solvent (H) can be between 0 and 95% or between 1 and 95%. In some embodiments, it is desired to a volatile solvent such that after initial curing, the resulting hydrophilic silicone rubber may include from about 0 to about 5 weight percent based on the total weight of all components of the silicone rubber, and preferably from 0% to 1%, and more preferably from 0% to about .1%.

[0094] The hydrophilic crosslinked silicone rubber (X) may optionally include hydrosilyation inhibitors and stabilizers (I). Inhibitors and stabilizers (I) serve for the targeted adjustment of the processing time, onset temperature and crosslinking rate of the silicone compositions according to the invention. These inhibitors and stabilizers have been known for a long time in the prior art. Examples of customary inhibitors are acetylenic alcohols, such as 1-ethynyl-1-cyclohexanol, 2-methyl-3-butyn-2-ol and 3,5-dimethyl-1-hexyn-3-ol, 3-methyl-1-dodecyn-3-ol, polymethylvinylcyclosiloxanes such as 1,3,5, 7-tetravinyltetramethyltetracyclosiloxane, low molecular weight silicone oils with methylvinyl-

$SiO_{1/2}$ groups and/or $R_2vinylSiO_{1/2}$ end groups, such as divinyltetramethyldisiloxane, tetravinyldimethyldisiloxane, trialkyl cyanurates, alkyl maleates, such as diallyl maleates, dimethyl maleate and diethyl maleate, alkyl fumarates, such as diallyl fumarate and diethylfumarate, organic hydroperoxides such as cumene hydroperoxide, tert-butyl hydroperoxide and pinane hydroperoxide, organic peroxides, organic sulfoxides, organic amines, diamines and amides, phosphates and phosphites, nitriles, triazoles, diaziridines and oximes. The effect of these inhibitor additives depends on their chemical structure, meaning that the concentration has to be determined individually. Inhibitors and inhibitor mixtures are preferably added in a quantitative fraction of from 0.00001% to 5%, based on the total weight of the mixture, preferably 0.00005 to 2% and more preferably 0.0001 to 1%.

[0095] The reaction temperature of the inventive hydrophilic silicone rubber (X) is preferably from room temperature to about 220°C, more preferably 50 – 200°C, and most preferably from 50 – 190°C. The particular temperature used may reflect thermal sensitivities of ingredients used. In general, lower temperatures require longer reaction times and/or greater amounts of catalyst, and vice versa. At temperatures in the range of 70 – 90°C, the reaction generally takes several minutes to several hours. At temperatures in the range of 160 -190°C, the reaction generally takes seconds.

[0096] The amounts of reactants (A), (B), and (E), and optionally (C) can be varied with respect to each other, as long as a cured rubber is produced. For example, greater amounts of the cyclodextrin-containing component (E) confer greater hydrophilicity and water absorption properties. The amounts of aliphatically unsaturated components, e.g. components (E) (when component (E) is aliphatically unsaturated) and (A) relative to the amount of crosslinker (B) are dependent upon the molecular weight and functionality of the respective components. In general, to achieve crosslinking as opposed to only chain extension, the sum of the average functionality of the aliphatically unsaturated components and the average functionality of the Si-H functional components should be ≥ 4, preferably ≥ 5. With the exception of the cyclodextrin component (E), it is desirable that the average functionality of the other reactive components each be greater than 2. If the total average functionality is not high enough, or if the average functionality of components (A) and/or (B) is/are not high enough, then a cured rubber cannot be formed due to inadequate crosslinking. The relative amounts are able to be determined by one of ordinary skill in the art. Further guidance may be found in U.S. patents, 5,391,592, 5,811,487, 6,365,670, 6,423,322, and 6,881,416, which are incorporated herein by reference. It should be noted that if the CD component (E) contains

more than one aliphatically unsaturated group, then this component may also contribute to crosslinking, and thus the functionalities of components (A) and/or (B) may be reduced.

[0097] The inventive hydrophilic crosslinked silicone rubber (X) is useful in a variety of applications where hydrophilic properties are desired. The water uptake of the inventive silicone rubber can be adjusted depending on the application need. In some embodiments, the water uptake of the inventive silicone rubber may be between 3% and about 1000%, more preferably between 20% and 500%, and in other embodiments preferably between 50% and about 350%.

[0098] The inventive silicone rubbers having hydrophilic properties are useful for a variety of applications that require moisture control, low coefficients of friction and resistance to protein adhesion. These properties are useful in wound care, catheters, body implants and other medical devices, as well as other products that desire the advantages of silicone rubber and hydrophilic properties. The use of silicone rubber also allows for a variety of manufacturing methods to be employed, such as molding, injection molding, thin film, coating, and 3D printing processes.

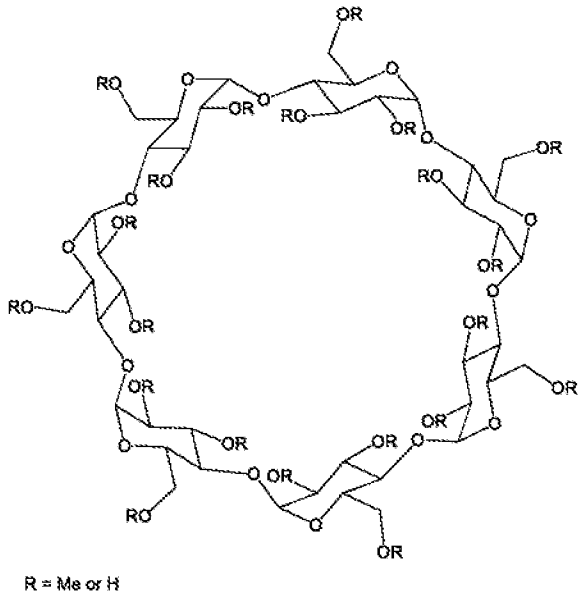
[0099] In applications, such as drug delivery the present application may utilize the cavity present in the CD. The CD can form stable complexes, where a guest molecule is hosted in the cavity in the CD. The complexes that are formed are reversible such that the guest molecule may be released from the CD in a controlled manner. Accordingly, the inventive hydrophilic silicone rubber composition disclosed herein can be used to host a drug for delivery and release this drug in a controlled manner for effective delivery.

[0100] However, many applications exist where hydrophilic properties are desired. The moisture management capabilities provided by the inventive hydrophilic compositions is desired in skin contact and medical applications (e.g., wound care applications) to keep and draw moisture, sweat and exudates away from the body. The inventive ydrophilic materials also exhibit a low coefficient of friction useful in applications such as catheters. The resistance to protein adhesion provided by hydrophilic materials is beneficial in body implants and other types of medical devices. Hydrophilic materials are also advantageous in anti-static articles.

[0101] In one embodiment, the inventive hydrophilic crosslinked silicone rubber is made by reacting an Si-H containing silicone with undecenoyl modified cyclodextrin to provide a cross-linked structure; a simplified scheme is shown in Figure 1.

[0102] The undecenoyl modified cyclodextrin can be made by reacting some of the OH groups of a cyclodextrin with undecanoyl chloride as shown in Figure 2.

[0103] The starting cyclodextrin can be a modified or unmodified α, β, γ cyclodextrin. An example of unmodified β cyclodextrin is CAVAMAX® W7 from Wacker Chemie AG. An example of modified β cyclodextrin is CAVASOL® W7 M from Wacker Chemie AG, which is a methyl modified β cyclodextrin (1.6-1.9 OH groups per glycosidic unit are modified with methyl groups); structure is shown below:



[0104] An example of SiH containing silicone is poly(dimethylsiloxane-*co*-methylhydrosiloxane) having the formula $MD_xD^H_yM$, where x +y = approx.140; x:y = approx. 2:1.

[0105] In another exemplary embodiment of the hydrophilic crosslinked silicone rubber, a cyclodextrin is first modified by reacting with a vinyl silicone containing anhydride functionality. This process results in a CD derivative where the CD unit is connected to the vinyl silicone unit through an ester bond. This modified cyclodextrin is used in a crosslinking composition, also containing an SiH functional silicone, to form a cured rubber as shown in Figure 3.

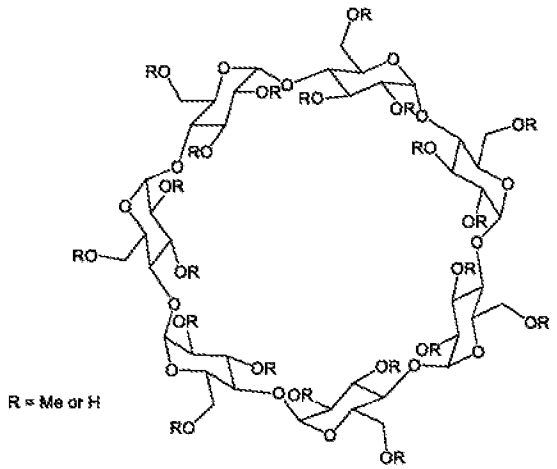
[0106] In still another exemplary embodiment, an alkene modified cyclodextrin (e.g., the undecenoyl modified cyclodextrin discussed above) is first reacted with excess amount of a hydrido functionalized silicone to produce a cyclodextrin derivative that has

pendant SiH groups. This modified cyclodextrin is used in hydrosilylation reaction with a vinyl silicone to produce crosslinked rubber as shown in Figure 4.

[0107] The crosslinked silicone rubber (X) made according to the invention are hydrophilic as demonstrated by absorption of water during the water uptake test as well as lower values of contact angles. Similar compositions that do not include cyclodextrin do not exhibit hydrophilicity or have much lower hydrophilicity and water uptake. Also, compositions that do not use reactive cyclodextrin components experience separation of cyclodextrin from the composition matrix when immersed in water.

[0108] Synthesis Examples:

[0109] For Examples 1, 2 and 3 undecenoyl modified methyl β-cyclodextrin CH-18 was used, which was prepared by modifying methyl β-cyclodextrin CAVASOL® W7 M obtained from Wacker Chemie AG.

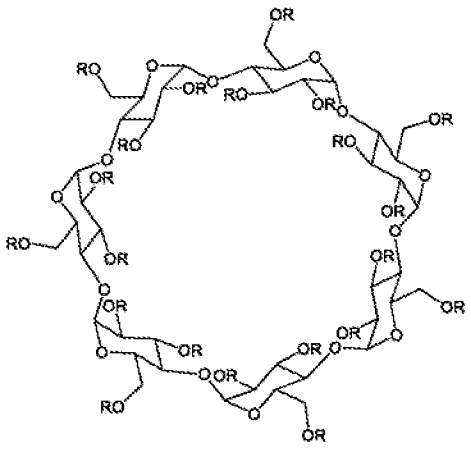


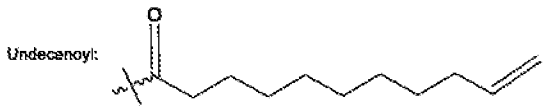
[0110] CAVASOL® W7 M (1.6-1.9 methyl groups on average per glycoside unit)

[0111] Undecenoyl modified methyl β-cyclodextrin CH-18 was prepared as follows:

[0112] Pyridine (253.6 g) was added into a 500 mL round-bottomed flask, stirred with a magnetic stirrer, and heated to 65 ° C. Methyl β-cyclodextrin CAVASOL® W7 M (54.8 g, 41.8 mmol, dried in a desiccator prior to use) was added to the flask over 10 min with continuous stirring. A slightly turbid mixture was formed. The mixture was heated to 65 ° C, and undecenoyl chloride (31.0 g, 151 mmol) was added drop-wise over 1 h at 65 ° C. After the addition was complete, the reaction mixture was left stirring under heating at 65 ° C for 3 hours. After 3 hours, the reaction mixture was cooled down to room temperature, poured into 1 L

water, stirred and allowed to settle. The aqueous layer was decanted off from the top, and the dark brown bottom layer was further washed repeatedly with 1.5 L water to get a viscous liquid. The viscous material was thoroughly dried under reduced pressure to obtain a glassy material, which was ground to obtain 50.7 g of off-white powder. The ^{1}H HMR analysis confirmed the product to be undecenoyl modified methyl β-CD. The approximate structure (0.38 undecenoyl group on average per glycoside unit, Iodine number: 48.5 g iodine/100 g sample) is shown below:





[0113] Measurement of water uptake for cured rubber:

[0114] A weighted sample of cured rubber was placed in deionized water and container was covered to prevent evaporation or contamination. After at least twenty-four (24) hours, the sample was removed from the water, gently patted dry with a paper towel to remove excess droplets on the surface and weighed to determine the change in mass. The water uptake results are reported as the change in mass divided by the original sample mass, in weight percent.

[0115] Contact angle measurement:

[0116] Contact angles for water droplets were measured with a Data Physics OCA 50 measuring device. The values represent the average of three measurements with the standard deviation indicated in the parentheses.

[0117] TABLE I: Examples of the inventive hydrophilic crosslinked silicone rubber and comparative example.

TABLE 1

Example	1	2	3	Comp. Ex. C4
SiH functional silicone/ amount (g)	$MD_xD^H_yM$. x:y ~2:1, x+ y ~140/1.50	$MD_xD^H_yM$. x:y ~2:1, x+ y ~140/2.00	$MD_xD^H_yM$. x:y ~0.3:1. x+ y ~45/ 0.70	$MD_xD^H_yM$. x:y ~2:1, x+ y ~140/0.20
CD or modified CD component/ amount (g)	CH18[1]/5.60	CH18[2]/6.55	CH18[3]/ 6.10	none
Vinyl siloxane component/ amount (g)	none	none	none	$M^{Vi}DxM^{Vi}$ [4]/ 10.0
SiH:Vi mole ratios	0.7:1	0.7:1	0.7:1	0.8:1
Platinum Catalyst[5] (mg)	7.11	8.55	6.80	10.20
Cure conditions	Vacuum oven, 80 °C, 8 h	Vacuum oven, 80 °C, 16 h	Vacuum oven, 80 °C, 16 h	80 °C, 8h
Product appearance	Colorless, transparent, cured	Colorless, transparent, cured	Colorless, transparent, cured	Off-white, transparent, cured, flexible
Water uptake / measurement time	3%/ 3 d	4%/ 4 d	7%/ 4 d	None/ 4 d
Contact angle (°)	100.3±8.6	103.9±3.1	99.9±5.8	107.1±4.8

[0118] [1] pre-dissolved in 5.60 g ethyl acetate to make 50% w/w solution.

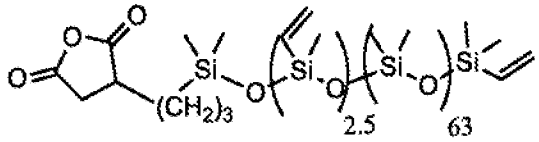
[0119] [2] pre-dissolved in 2.81 g ethyl acetate to make 70% w/w solution.

[0120] [3] pre-dissolved in 2.60 g ethyl acetate to make 70% w/w solution.

[0121] [4] vinyl terminated polydimethylsiloxane with average viscosity of 980 mPa.s and average vinyl content of 0.90 mol%.

[0122] [5] divinyl tetramethyl disiloxane platinum complex diluted in vinyl terminated polysiloxane (1% w/w Pt content)

[0123] For inventive example 5, a vinyl silicone functionalized cyclodextrin SB125 was used, which was synthesized by reacting CAVASOL® W7 M and an anhydride functional vinyl silicone (PY2920) having the following approximate structure:



[0124] Synthesis of vinyl silicone linked cyclodextrin derivative SB125:

[0125] CAVASOL® W7 M 10.0 g (7.63 mmol), dimethyl aminopyridine (DMAP, 0.19 g, 1.53 mmol) and anhydride functional vinyl silicone PY2920 (128.5 g) were dissolved in dichloromethane (300 mL) and mixed for 48 h. Water (100 mL) was added to the mixture, and the mixture was extracted three times with 10% NaHSO4 solution (150 mL each time). The combined dichloromethane layer was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure to obtain a pale yellow opaque viscous liquid (Yield: 76.9 g). The product was characterized by ^{1}H NMR and IR. Iodine number: 7.7 g iodine/100 g material.

[0126] TABLE II: Examples of the inventive hydrophilic crosslinked silicone rubber and comparative example.

TABLE II

Example	5	Comp. Ex. C6
SiH functional silicone/ amount (g)	$MD_xD^H_yM$. x:y ~9:1, x+ y ~60/1.00	$MD_xD^H_yM$. x:y ~9:1, x+ y ~60/ 1.00
CD or modified CD component/ amount (g)	SB125/6.27	CAVASOL® W7 M/ 1.00
Vinyl siloxane component/ amount (g)	none	PY2920/ 6.40
SiH:Vi mole ratios	0.7:1	0.7: 1
Platinum Catalyst[1] (mg)	7.27	8.40
Cure conditions	Oven, 50°C, 4 h	Oven, 50°C, 4 h
Product appearance	Off-white, opaque, cured, flexible	Off-white, turbid, cured, inhomogeneous
Water uptake / measurement time	323%/ 14 d	Cyclodextrin separates out
Contact angle (°)	73.7±18.0	133.6±1.0

[0127] [1] divinyl tetramethyl disiloxane platinum complex diluted in vinyl terminated polysiloxane (1% w/w Pt content)

[0128] For example 7, a silicone hydride functionalized cyclodextrin CH23-2 was used, which was synthesized by reacting undecenoyl modified methyl β-cyclodextrin CH-18 and a hydride terminated silicone (XL27) having the following approximate structure: H-$(SiMe_2O)_xSiMe_2$-H (x ~50); 0.053 weight % Si-bound H.

[0129] Synthesis of Si-H functionalized cyclodextrin derivative CH23-2:

[0130] Undecenoyl methyl β-cyclodextrin CH-18 (10.0 g, 19.7 mmol vinyl groups), prepared according to the previously mentioned method, and toluene (230 mL) were mixed with a magnetic stirrer until the CD dissolved. The mixture was heated to 60 °C and Platinum Catalyst (0.2831 g), at 1% w/wPt content was added. XL27 (75.6 g, 39.4 mmol silicon bound hydrogen) was added with stirring, and the mixture was heated at 80 °C for 2.5 h. The golden solution was cooled to room temperature and the solvent was removed under reduced pressure with a rotary evaporator to get the product as a light brown viscous fluid (44.9 g). The ^{1}H NMR indicated complete reaction of the vinyl groups. Because of the stoichiometric excess of SiH used during the reaction, the modified CD derivative contains residual SiH functionality on the silicone chain. This intermediate was used for example 7.

[0131] TABLE III: Examples of the inventive hydrophilic crosslinked silicone rubber and comparative example.

TABLE III

Example	7	Comp. Ex. C8
SiH functional silicone/ amount (g)	None	XL27/1.08
CD or modified CD component/ amount (g)	CH23-2[1]/2.51	CAVASOL® W7 M/0.28
Vinyl siloxane component/ amount (g)	EL VIPO 300[2]/2.84	EL VIPO 300/2.85
SiH:Vi mole ratios	1:1	1:1
Platinum Catalyst[3] (mg)	13.3	9.90
Cure conditions	80 °C, 1 h	80 °C, 1 h

Product appearance	Colorless, transparent, cured, flexible	Brownish, opaque, partially cured, gummy paste
Water uptake / measurement time	7%/ 5 d	Not measured
Contact angle (°)	101.2±3.2	119.8±1.3

[0132] [1] a small amount of toluene was used to dilute the CD derivative CH 23-2.

[0133] [2] vinyl terminated polydimethylsiloxane with average viscosity of 325 mPa.s and average vinyl content of 1.45 mol%.

[0134] [3] divinyl tetramethyl disiloxane platinum complex diluted in vinyl terminated polysiloxane (1% w/w Pt content)

[0135] The modified cyclodextrin derivatives were mixed with various siloxanes having terminal or pendant SiH groups or siloxanes containing vinyl groups under different conditions, and the resulting mixtures were cured by using a platinum containing catalyst. The cyclodextrin derivative was dissolved in a volatile solvent in some cases; the solvent got removed at elevated temperature during the curing process. Different mixing and curing conditions are shown in Table 1. The mixing was usually done in a Speedmixer™ or a Dispermat™, and the curing was done by pouring the mixture in an aluminum Petri dish and placing in an oven or a vacuum oven.

[0136] It can be seen from the above tables that inventive Examples 1, 2, 3, 5, and 7 provided cured material with hydrophilicity as shown by water uptake. Comparative Example 4, which was without any cyclodextrin incorporation, showed no hydrophilicity. Comparative Example 8 that used unmodified CAVASOL® W7 M did not produce a cured material, and water uptake was not measured. Comparative Example 6 that used unmodified CAVASOL® W7 M produced a cured but inhomogeneous material, however, the cyclodextrin started to separate out after immersion in water because it was not chemically bound to the rubber matrix. Also, in general, the inventive examples show lower water contact angles relative to the comparative examples, which is indicative of their hydrophilic properties.

[0137] As required, detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention that may be embodied in various and alternative forms. The figures are not necessarily to scale; some features may be exaggerated or minimized to show details of

particular components. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a representative basis for teaching one skilled in the art to variously employ the present invention.

[0138] While exemplary embodiments are described above, it is not intended that these embodiments describe all possible forms of the invention. Rather, the words used in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention. Additionally, the features of various implementing embodiments may be combined to form further embodiments of the invention.

WHAT IS CLAIMED IS:

1. A hydrophilic silicone rubber composition (X) comprising:

a crosslinked silicone rubber including at least one covalently bonded cyclodextrin moiety, prepared by hydrosilylative crosslinking of reactants (A), (B), (C), (D) and (E)

(A) optionally, is an organic compound or an organosilicon compound including at least two radicals with aliphatic carbon-carbon multiple bonds;

(B) optionally, is an organosilicon compound comprising at least two Si-bonded hydrogen atoms;

(C) optionally, is an organosilicon compound, containing SiC-bonded radicals with aliphatic carbon-carbon multiple bonds and Si-bonded hydrogen atoms

(D) is a hydrosilylation catalyst; and

(E) is a cyclodextrin reactant comprising a cyclodextrin or cyclodextrin derivative which has been modified to contain an organic group containing aliphatic unsaturation or an organic group containing silicon-bonded hydrogen,

wherein component (C) is not optional when component (A) or component (B) is not present.

2. The hydrophilic silicone rubber composition of claim 1, wherein the hydrosilylative crosslinking is conducted in the presence of a solvent (H).

3. The hydrophilic silicone rubber composition of claim 1 or 2, wherein cyclodextrin reactant (E) comprises cyclodextrin modified to contain at least one aliphatically unsaturated group.

4. The hydrophilic silicone composition of claim 1, 2, or 3, wherein the cyclodextrin reactant (E) contains at least one ether-linked or ester-linked aliphatically unsaturated group.

5. The hydrophilic silicone composition of claim 1, wherein the cyclodextrin reactant (E) comprises the reaction product of a cyclodextrin or an optionally derivatized cyclodextrin with an organopolysiloxane containing an ester-forming group and at least one aliphatically unsaturated group or with an organopolysiloxane containing an ester-forming group and at least one silicon-bonded hydrogen atom.

6. The hydrophilic silicone composition of claims 1-5, further comprising one or more guest molecules complexed by cyclodextrin groups.

7. The hydrophilic silicone composition of claims 1-5, further comprising one or more guest molecules incorporated in the hydrophilic silicone composition inside or outside of cyclodextrin cavity, which can be released at a controlled rate.

8. The hydrophilic silicone composition of claims 6 and 7, wherein at least one guest molecule is selected from natural oils, pharmaceutical products, cosmetic or personal care actives, biocides, insecticides, fungicides, herbicides, pheromones, fragrances, flavorings, pigments, drugs, pharmaceutical active compounds, antigens, active compounds for antistatic finishing or flame-retardant finishing, stabilizers (UV), dyestuffs.

9. The hydrophilic silicone composition of claims 1-8, wherein said hydrophilic silicone composition has a water uptake from 2% to about 1000%.

10. A process for preparing a hydrophilic silicone rubber composition of claim 1, comprising mixing (A), (B), (C), (D), and (E), optionally in the presence of a solvent (H), and crosslinking to form the hydrophilic silicone rubber.

11. The use of the hydrophilic silicone rubber composition of any of claim 1-9, or prepared by the process of claim 10, in medical devices, transdermal drug delivery devices, wound care materials, low friction materials, body implants, wet seals, water absorbing foams, flame retardant materials, high temperature retardant materials, antistatic materials, filtration membranes, or textile materials.

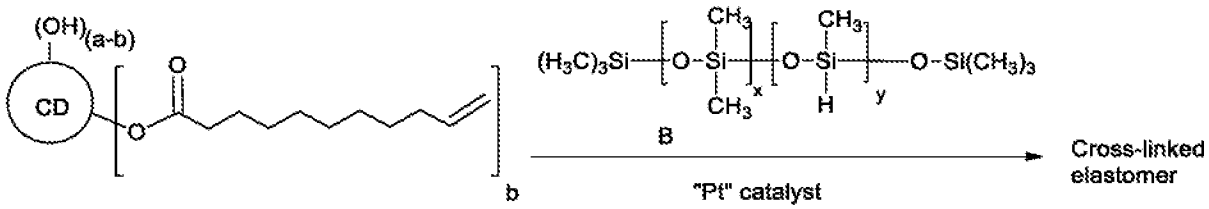

(OH)(a-b)
CD
O
O
b
(H3C)3Si
O
Si
CH3
CH3
x
O
Si
CH3
H
y
O
Si(CH3)3
B
"Pt" catalyst
Cross-linked
elastomer

FIG. 1

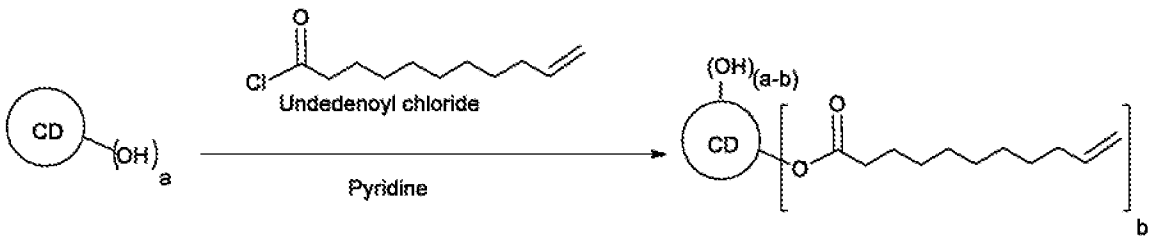

O
Cl
Undedenoyl chloride
CD
(OH)
a
Pyridine
(OH)(a-b)
CD
O
O
b

FIG. 2

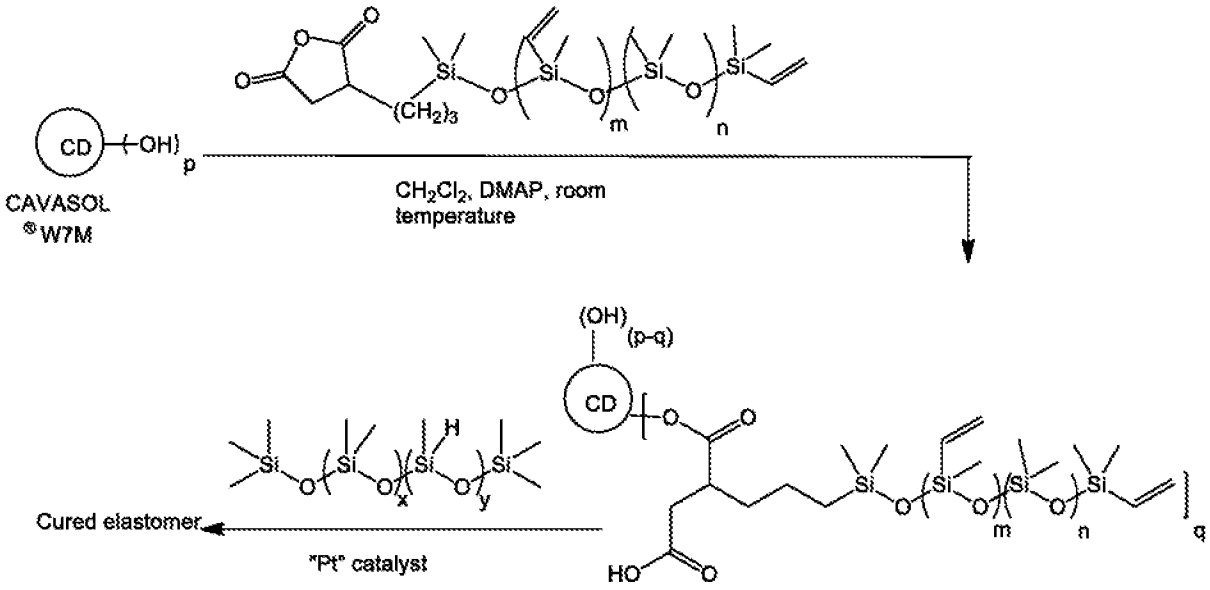

CD
(OH)p
CAVASOL
®W7M
CH2Cl2, DMAP, room temperature
(OH)(p-q)
Cured elastomer
"Pt" catalyst
HO

FIG. 3

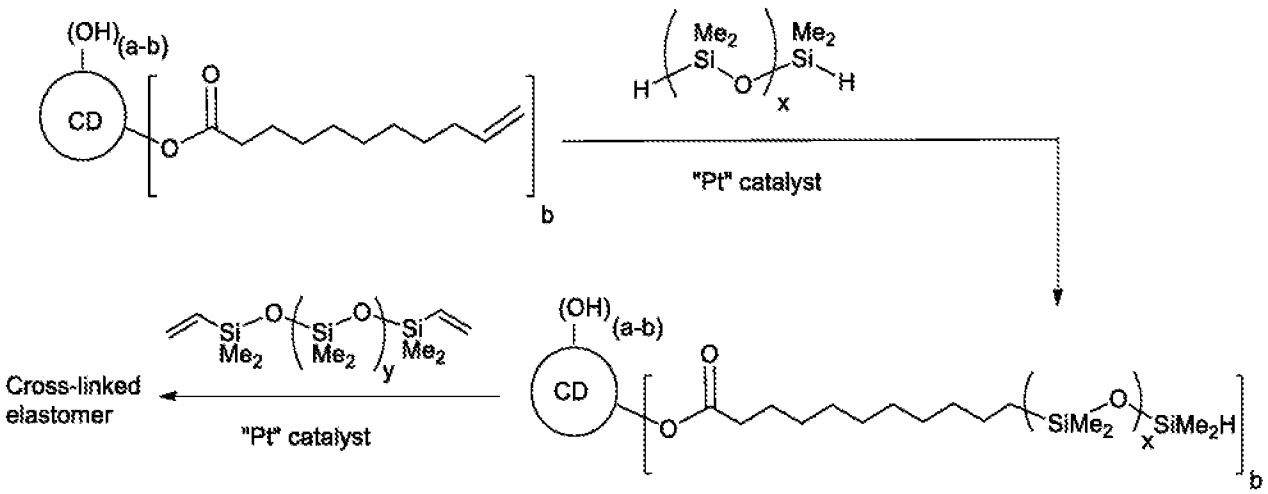

(OH)(a-b)
CD
"Pt" catalyst
Cross-linked elastomer
"Pt" catalyst
SiMe2H

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/068079

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/73 A61K8/89 C08G77/12 C08G77/20 C08G77/38
C08L83/04 C08L83/06 C08G77/42 C08B37/16
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61Q A61K C08G C08L C08B C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 391 592 A (HERBRECHTSMEIER PETER [DE] ET AL) 21 February 1995 (1995-02-21)	1-3,9,10
A	column 1, line 38 - column 2, paragraph 41 column 4, lines 41-57 column 11, lines 1-6 example 2 and 3	11

X	US 5 403 898 A (BRADSHAW JERALD S [US] ET AL) 4 April 1995 (1995-04-04)	1-4,9,10
Y	column 1, lines 27-36	5-8
A	column 4, lines 17-59 column 5, lines 32-68 column 6, lines 10-17 examples 36,37,45,46	11

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 August 2019	20/08/2019

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/068079

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 98/22795 A1 (UNIV CALIFORNIA [US]; YANG XIAOGUANG [US]; SWANSON BASIL I [US]) 28 May 1998 (1998-05-28)	1-3,6,7, 9,10
A	page 5, lines 23-26 example 6 and 7	11

Y	US 2006/009592 A1 (OCHS CHRISTIAN [DE] ET AL) 12 January 2006 (2006-01-12)	5-8
A	page 1, paragraph 8 - page 2, paragraph 23 page 13; example XXIV page 17, paragraph 45-48 page 23, paragraph 146 page 25, paragraph 186-189 page 26, paragraph 192	11

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Information on patent family members

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