Title: RUBBER ARTICLE WITH ELASTOMERIC SILICONE COATING

Abstract: A catheter of organic rubber, such as latex, is coated with surface layer of elastomeric silicone. The catheter may be coated with the silicone on one or both of the inside and outside surfaces thereof. The silicone may contain a bioactive ingredient for preventing and/or treating acquired infections. The elastomeric silicone is prepared by curing a silicone composition via condensation reaction. The silicone composition is tin free. The coated catheter may cause less irritation and/or allergic reaction than an uncoated organic rubber catheter.
RUBBER ARTICLE WITH ELASTOMERIC SILICONE COATING

FIELD OF THE INVENTION

[0001] A rubber article useful in the medical field, such as a catheter (e.g., a Foley catheter) of organic rubber is coated with an elastomeric silicone. The silicone may be on all or a portion of a surface of the rubber article, for example, the silicone may be on an inside surface of the catheter, an outside surface of the catheter, or both. The silicone may optionally contain a bioactive ingredient for preventing and/or treating an acquired infection and/or other medical condition.

BACKGROUND OF THE INVENTION

[0002] Catheters are widely used in the medical field for draining fluid(s) from a user's body, thereby permitting access to the interior of the body. Catheters can be made of organic rubber, e.g., natural rubber such as latex; thermoplastic resins; or metal. For example, a Foley catheter, commonly made from silicone rubber or natural rubber (e.g., latex) is a flexible tube having two separated lumens running down its length. One lumen is open at both ends and allows urine to drain into a collection bag. The other lumen has a valve on the outside end and connects to a balloon at the tip. The balloon may be inflated with sterile water or other suitable fluid (e.g., saline) when it lies inside the bladder to stop the catheter from slipping out.

[0003] Figure 1 shows one example of a Foley catheter 10. The Foley catheter 10 comprises a tube 50 with a balloon 20 on one end. The tube 50 has two separate lumens (not shown) running down its length. One lumen is open at both ends with a cap at the exit 40. The other lumen has a valve 30 on the outside end and connects to the balloon 20.

[0004] When a rubber article such as a catheter contacts living tissue, there is potential for irritation, sensitization (e.g., allergic reaction), and/or infection to occur. Body residues, such as clotted blood and/or lymph in the case of catheters placed in incisions, tend to adhere to some catheters, as can mineralized encrustation (in a severe form, bladder stones) in the case of urinary tract catheters. Frequent replacement of such catheters is typically done to address these problems. Furthermore, latex articles, such as surgical gloves, can cause allergic reactions in sensitive individuals.

BRIEF SUMMARY OF THE INVENTION

[0005] According to one process of the present invention, a method of making a fluid silicone composition includes combining (A) a catalytic quantity of at least one catalytically active condensation reaction catalyst including a metal-ligand complex. The complex comprises a reaction product of (i) a metal precursor having the general formula: M-A_n, where M is a metal selected from Fe, Ti, and Zr, each A is an independently displaceable group, and
subscript \( a \) is an integer representing the valence of the metal selected for \( M \), and (ii) a ligand of formula \( A^2O\overline{A}A^1 \), where \( A^1 \) is selected from an alkyl group, an aryl group, and an alkoxy group, and each \( A^2 \) is selected from an alkyl group and an aryl group. The method further includes combining (B) 100 parts of at least one polyorganosiloxane having an average per molecule of two or more hydrolyzable substituents, a silicone resin, or a combination thereof, (C) an amount of an acetoxy silicone crosslinker sufficient to crosslink ingredient (B), (D) optionally, a filler, (E) optionally, a vehicle, (F) optionally, a bioactive agent, (G) optionally, a filler treatment, (H) optionally, an excipient, and (I) optionally, other additives.

According to one embodiment of the present invention, a fluid silicone composition includes (A) 100 parts of at least one polyorganosiloxane having an average per molecule of two or more hydrolyzable substituents, a silicone resin, or a combination thereof, (B) an amount of an acetoxy silicone crosslinker sufficient to crosslink ingredient (A), (C) optionally, a filler, (D) optionally, a vehicle, and (E) optionally, a bioactive agent. The composition is prepared using a catalytic quantity of at least one catalytically active condensation reaction catalyst comprising a metal-ligand complex. The complex comprises a reaction product of (i) a metal precursor having the general formula: \( M-A_n \), where \( M \) is a metal selected from Fe, Ti, and Zr, each \( A \) is independently a monovalent organic group, and subscript \( a \) is an integer with a value ranging from 2 to 3, and (ii) a ligand of formula \( A^2O\overline{A}A^1 \), where \( A^1 \) is selected from an alkyl group, an aryl group, and an alkoxy group, and each \( A^2 \) is selected from an alkyl group and an aryl group.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The foregoing and other advantages of the invention will become apparent upon reading the following detailed description and upon reference to the drawings.

Figure 1 is a top view of a Foley catheter.

Figure 2 is a schematic representation of a cross section of a tube of the catheter of Figure 1.

While the invention is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and will be described in detail herein. It should be understood, however, that the invention is not intended to be limited to the particular forms disclosed. Rather, the invention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention.
DETAILED DESCRIPTION OF THE INVENTION

[0011] All amounts, ratios, and percentages are by weight unless otherwise indicated. The articles 'a', 'an', and 'the' each refer to one or more, unless otherwise indicated by the context of specification. The disclosure of ranges includes the range itself and also anything subsumed therein, as well as endpoints. Similarly, the disclosure of Markush groups includes the entire group and also any individual members and subgroups subsumed therein. For example, the Markush group including a hydrogen atom, an alkyl group, an aryl group, or an aralkyl group includes the member alkyl individually; the subgroup alkyl and aryl; and any other individual member and subgroup subsumed therein.

[0012] The fluid silicone composition comprises: (A) a catalytic quantity of a catalytically active condensation reaction catalyst comprising a metal-ligand complex, (B) 100 parts of at least one polyorganosiloxane having an average per molecule of two or more hydrolyzable substituents, and (C) an amount of crosslinker sufficient to crosslink ingredient (B). The fluid silicone composition may optionally further comprise one or more additional ingredients, which may include (D) a filler, (E) a vehicle (such as a solvent(s) or diluent(s)), e.g., hexamethyldisiloxane, 0.65 cSt or other trimethylsiloxy-terminated polydimethylsiloxanes, which are available as DOW CORNING® 200 Fluids from Dow Corning Corp., Midland, MI), (F) a bioactive agent, (G) a filler treatment, (H) an excipient, (I) other additives, or (J) any combination thereof.

Ingredient (A) - Catalyst

[0013] Ingredient (A) comprises a catalytically effective amount of a condensation reaction catalyst. The condensation reaction catalyst may comprise a metal-ligand complex. The metal-ligand complex can be prepared by reacting a metal precursor and a ligand. The metal precursor is distinct from a reaction product of the metal precursor and the ligand. The metal precursor has general formula (i):

\[ \text{M-A}_a \]

where M is a metal atom selected from the group consisting of Fe, Ti, and Zr; each A is independently a displaceable group; and subscript a is an integer representing the valence of the metal atom selected for M. For example, when M is iron, then subscript a has a value ranging from 2 to 3. Examples of monovalent organic groups for A include monovalent hydrocarbon groups, amino groups, silazane groups, carboxylic ester groups, hydrocarbonoxy groups, alkyl groups, or any combination thereof.

[0014] Examples of monovalent hydrocarbon groups for A include, but are not limited to, alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, ethylhexyl, octyl, decyl, dodecyl, undecyl, and octadecyl; alkenyl such as vinyl, allyl, propenyl, and hexenyl; carbocyclic groups exemplified by saturated carbocyclic groups, e.g., cycloalkyl such as cyclopentyl and cyclohexyl, or unsaturated carbocyclic groups such as cyclopentadienyl or
cyclooctadieny1; aryl such as phenyl, tolyl, xylyl, mesityl, and naphthyl; and aralkyl such as benzyl or 2-phenylethyl.

[0015] Examples of amino groups for A have formula -NA'\textsubscript{2}, where each A is independently a hydrogen atom or a monovalent hydrocarbon group. Exemplary monovalent hydrocarbon groups for A' include, but are not limited to, alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, ethylhexyl, octyl, decyl, dodecyl, undecyl, and octadecyl; alkenyl such as vinyl, allyl, propenyl, and hexenyl; carboxyclic groups exemplified by saturated carboxyclic groups, e.g., cycloalkyl such as cyclopentyl and cyclohexyl, or unsaturated carboxyclic groups such as cyclopentadienyl or cyclooctadienyl; aryl such as phenyl, tolyl, xylyl, mesityl, and naphthyl; and aralkyl such as benzyl or 2-phenylethyl. Alternatively, each A may be a hydrogen atom or an alkyl group of 1 to 4 carbon atoms, such as methyl or ethyl.

[0016] Alternatively, each A in general formula (i) may be a silazane group.

[0017] Alternatively, each A in general formula (i) may be a carboxylic ester group. Examples of suitable carboxylic ester groups for A include, but are not limited to, ethylhexanoate (such as 2-ethylhexanoate), neodecanoate, octanoate, and stearate.

[0018] Examples of monovalent hydrocarbonoxy groups for A may have formula -O-A', where A' is a monovalent hydrocarbon group. Examples of monovalent hydrocarbon groups for A' include, but are not limited to, alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, ethylhexyl, octyl, decyl, dodecyl, undecyl, and octadecyl; alkenyl such as vinyl, allyl, propenyl, and hexenyl; cycloalkyl such as cyclopentyl and cyclohexyl; aryl such as phenyl, tolyl, xylyl, and naphthyl; aralkyl such as benzyl or 2-phenylethyl. Alternatively, each A' may be an alkyl group, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, or t-butyl. Alternatively, each A' may be an alkyl group, and alternatively each A' may be ethyl, propyl (e.g., iso-propyl or n-propyl), or butyl.

[0019] Alternatively, each A in general formula (i) may be an alkyl group, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, or t-butyl. Alternatively, each A may be selected from the group consisting of ethyl, benzyl, mesityl, phenyl, -NEt\textsubscript{2}, cyclooctadiene, ethoxide, iso-propoxide, butoxide, 2-ethylhexanoate, neodecanoate, octanoate, and stearate. Alternatively, each A may be an alkoxy group such as ethoxy or isopropoxy. Alternatively, each A may be a carboxylic ester group, such as 2-ethylhexanoate, 2,4-pentanedionate, or stearate. Alternatively, each A may be an acrylate group. Alternatively, each A may be an acetyl group.

[0020] Organic compounds of Fe suitable for use as precursors are generally available. For example, Fe(2,2,6,6-tetramethyl-3,5-heptanedionato)\textsubscript{3}, Fe(0-Et)\textsubscript{3}, Iron(II) acetate, Iron(III) acetyl acetonate, Iron (II) stearate, and Fe(trifluoroacetacetonate)\textsubscript{3} are each available from Strem Chemicals, Inc., Newburyport, MA. Fe(2-ethylhexanoate)\textsubscript{3} and Fe(0-iPr)\textsubscript{3} are each available from Alfa Aesar, Ward Hill, MA.
Organic compounds of Ti suitable for use as precursors are generally available. For example, Titanium(IV) ethoxide and Titanium(IV) isopropoxide are available from Strem Chemicals Inc. of Newburyport, Massachusetts. Titanium(IV) n-butoxide and Titanium(IV) t-butoxide are available from Sigma-Aldrich, St. Louis, MO. Amino compounds of titanium, such as Ti(NMe$_2$)$_4$ and Ti(NEt$_2$)$_4$, are also available from Strem Chemicals, Inc. Tetrabenzyl titanium is available from MCAT GmbH, Konstanz, Germany.

Alternatively, the precursor may comprise a Zirconium alkoxide, such as Zirconium (IV) ethoxide, Zirconium (IV) n-butoxide, or Zirconium (IV) propoxide, all of which are available from Strem Chemicals, Inc. Alternatively, the precursor used to prepare ingredient (A) may comprise Tetrabenzylzirconium, also from Strem Chemicals, Inc. Alternatively, the precursor used to prepare ingredient (A) may comprise Zirconium (IV) t-butoxide, which is available from Sigma-Aldrich. Alternatively, the precursor used to prepare ingredient (A) may comprise Zr(NMe$_2$)$_4$, which is available from Strem Chemicals, Inc. or Gelest, Inc., Morrisville, PA.

The ligand is an organic compound that coordinates with Fe. The organic compound includes neutral and conjugate base forms. The neutral forms of suitable ligands of formula (I) are shown below in Table 1.

Table 1 - Ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td><img src="image" alt="MeO Structure" /></td>
</tr>
<tr>
<td>F$_3$C</td>
<td><img src="image" alt="F$_3$C Structure" /></td>
</tr>
<tr>
<td>NC</td>
<td><img src="image" alt="NC Structure" /></td>
</tr>
<tr>
<td>Cl</td>
<td><img src="image" alt="Cl Structure" /></td>
</tr>
</tbody>
</table>

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**Ingredient (B) - Polyorganosiloxane**

[0024] Ingredient (B) is a polyorganosiloxane having an average, per molecule, of 2 or more hydrolyzable substituents covalently bonded thereto. Alternatively, the 2 or more hydrolyzable substituents are hydrolyzable silyl substituents. The polyorganosiloxane for
ingredient (B) may comprise a polydiorganosiloxane. The hydrolyzable substituents may be exemplified by: halogen atoms; amido groups such as acetamido groups, benzamido groups, or methylacetamido groups; acyloxy groups such as acetoxy groups; hydrocarbonoxy groups such as alkoxy groups or alkenyloxy groups; amino groups; aminoxo groups; hydroxyl groups; mercapto groups; oximo groups; ketoximo groups; alkoxyisilylhydrocarbylene groups; or and combination thereof. The hydrolyzable substituent in ingredient (B) may be located at terminal, pendant, or both terminal and pendant positions on the polyorganosiloxane backbone. Alternatively, the hydrolyzable substituent in ingredient (B) may be located at one or more terminal positions on the polyorganosiloxane backbone. Ingredient (B) may comprise a linear structure, branched structure, cyclic structure, resinous structure, or a combination thereof. Ingredient (B) may comprise a homopolymer or a copolymer or a combination thereof.

[0025] Ingredient (B) may have the hydrolyzable substituents contained in groups of the formula (ii):

$$
-D\left[ \begin{array}{c}
R_{2-a} \\
\text{Si} \\
X_{a}
\end{array} \right]_{b} \left[ \begin{array}{c}
R_{3-c} \\
\text{Si} \\
X_{c}
\end{array} \right]
$$

where each D independently represents an oxygen atom, a divalent organic group, a divalent silicone organic group, or a combination of a divalent hydrocarbon group and a divalent siloxane group; each X independently represents a hydrolyzable substituent; each R independently represents a monovalent hydrocarbon group; subscript c represents 0, 1, 2, or 3; subscript a represents 0, 1, or 2; and subscript b has a value of 0 or greater, with the proviso that the sum of (a + c) is at least 1, such that, on average, at least one X is present in the formula. In one embodiment, subscript b may have a value ranging from 0 to 18.

[0026] Alternatively, each D may be independently selected from an oxygen atom and a divalent hydrocarbon group. Alternatively, each D may be an oxygen atom. Alternatively, each D may be a divalent hydrocarbon group exemplified by an alkylene group such as ethylene, propylene, butylene, or hexylene; an arylene group such as phenylene, or an alkylarylene group such as:

$$
\begin{align*}
&\text{H}_2 \text{C} \text{C} \text{C} \text{C} \text{C} \text{H}_2 \\
&\text{H}_2 \text{H}_2 \text{H}_2 \text{H}_2
\end{align*}
$$

or

$$
\begin{align*}
&\text{H}_2 \text{C} \text{C} \text{C} \text{C} \text{H}_2 \\
&\text{H}_2 \text{H}_2 \text{H}_2 \text{H}_2
\end{align*}
$$

Alternatively, an instance of D may be an oxygen atom while a different instance of D is a divalent hydrocarbon group.
[0027] Alternatively, each X may be a hydrolyzable substituent independently selected from: an alkoxy group; an alkenyloxy group; an amido group, such as an acetamido, a methylacetamido group, or benzamido group; an acyloxy group such as acetoxy; an amino group; an aminooxy group; a hydroxyl group; a mercapto group; an oximo group; a ketoximo group; and a halogen atom. Alternatively, each X may be independently selected from an alkoxy group, an amido group, an acyloxy group, an amino group, a hydroxyl group, and an oximo group.

[0028] Alternatively, each R in formula (ii) above may be independently selected from alkyl groups of 1 to 20 carbon atoms, aryl groups of 6 to 20 carbon atoms, and aralkyl groups of 7 to 20 carbon atoms.

[0029] Alternatively, subscript b may be 0.

[0030] Ingredient (B) may comprise the groups described by formula (ii) above in an amount of the base polymer ranging from about 0.2 mol % to about 10 mol %, alternatively about 0.5 mol % to about 5.0 mol %, alternatively 0.5 mol % to about 2.0 mol %, alternatively about 0.5 mol % to about 1.5 mol %, and alternatively about 0.6 mol % to about 1.2 mol %.

[0031] Ingredient (B) may have a polyorganosiloxane backbone with a linear structure, i.e., a polydiorganosiloxane backbone. When ingredient (B) has a polydiorganosiloxane backbone, ingredient (B) may comprise an alkoxy-endblocked polydiorganosiloxane, an alkoxyorganosilylhydrocarbylene-endblocked polydiorganosiloxane, a hydroxyl-endblocked polydiorganosiloxane, or a combination thereof.

[0032] Ingredient (B) may comprise a polydiorganosiloxane of formula (I):

\[
R^1_d-Si-R^3_e, \quad (Si-O)_{R^2} \quad Si-R^3-e, \quad (Si-O)_{R^2} \quad Si-R^3_d, \quad (3-d)
\]

where each \( R^1 \) is independently a hydrolyzable substituent, each \( R^2 \) is independently a monovalent organic group, each \( R^3 \) is independently an oxygen atom or a divalent hydrocarbon group, each subscript \( d \) is independently 1, 2, or 3, and subscript \( e \) is an integer having a value sufficient to provide the polydiorganosiloxane with a viscosity of at least 100 mPa-s at 25 °C and/or a DP of at least 87. DP may be measured by GPC using polystyrene calibration. Alternatively, subscript \( e \) may have a value ranging from 1 to about 200,000.

[0033] Suitable hydrolyzable substituents for \( R^1 \) include, but are not limited to, the hydrolyzable substituents described above for group X. Alternatively, the hydrolyzable substituents for \( R^1 \) may be selected from a halogen atom, an acetamido group, an acyloxy group such as acetoxy, an alkoxy group, an amido group, an amino group, an aminooxy group, a hydroxyl group, an oximo group, a ketoximo group, and a methylacetamido group.
Suitable organic groups for \( R^2 \) include, but are not limited to, monovalent organic groups such as hydrocarbon groups and halogenated hydrocarbon groups. Examples of monovalent hydrocarbon groups for \( R^2 \) include, but are not limited to, alkyl such as methyl, ethyl, propyl, pentyl, octyl, decyl, dodecyl, undecyl, and octadecyl; cycloalkyl such as cyclopentyl and cyclohexyl; aryl such as phenyl, tolyl, xylol, and benzyl; and aralkyl such as 2-phenylethyl. Examples of monovalent halogenated hydrocarbon groups for \( R^2 \) include, but are not limited to: chlorinated alkyl groups such as chloromethyl and chloropropyl groups; fluorinated alkyl groups such as fluoromethyl, 2-fluoropropyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl, 4,4,4,3,3-pentafluorobutyl, 5,5,5,4,4,3,3-heptafluoropentyl, 6,6,6,5,4,4,3,3-nonfluorohexyl, and 8,8,8,7,7-pentafluorooctyl; chlorinated cycloalkyl groups such as 2,2-dichlorocyclopropyl, 2,3-dichlorocyclopropyl; fluorinated cycloalkyl groups such as 2,2-difluorocyclopropyl, 2,3-difluorocyclobutyl, 3,4-difluorocyclohexyl, and 3,4-difluoro-5-methylcycloheptyl; and any combination thereof. Examples of other monovalent organic groups for \( R^2 \) include, but are not limited to, hydrocarbon groups substituted with oxygen atoms such as glycidoxyalkyl and hydrocarbon groups substituted with nitrogen atoms such as aminoalkyl and cyano-functional groups such as cyanoethyl and cyanopropyl. Alternatively, each \( R^2 \) may be an alkyl group such as methyl.

Ingredient (B) may comprise an \( \alpha,\omega \)-difunctional-polydiorganosiloxane when, in formula (I) above, each subscript \( d \) is 1 and each \( R^3 \) is an oxygen atom. For example, ingredient (B) may have formula (II): \( R^1R^2SiO-(R^2SiO)_eSiR^2R^1 \), where \( R^1 \) and \( R^2 \) are as described above and subscript \( e' \) is an integer having a value sufficient to give the polydiorganosiloxane of formula (II) the viscosity described above. Alternatively, subscript \( e' \) may have a value ranging from 1 to about 200,000, alternatively about 50 to about 1,000, and alternatively about 200 to about 700.

Alternatively, ingredient (B) may comprise a hydroxyl-functional polydiorganosiloxane of formula (II) described above, in which each \( R^1 \) may be a hydroxyl group, each \( R^2 \) may be an alkyl group such as methyl, and subscript \( e' \) may have a value such that the hydroxyl functional polydiorganosiloxane has a viscosity of at least 100 mPa-s at 25 °C. Alternatively, subscript \( e' \) may have a value ranging from 50 to 700. Exemplary hydroxyl-endblocked polydiorganosiloxanes are hydroxyl-endblocked polydimethylsiloxanes. Hydroxyl-endblocked polydiorganosiloxanes suitable for use as ingredient (B) may be prepared by methods known in the art, such as hydrolysis and condensation of the corresponding organohalosilanes or equilibration of cyclic polydiorganosiloxanes.

Alternatively, ingredient (B) may comprise an alkoxyalkyldiorganosiloxane-endblocked polydiorganosiloxane, for example, when in formula (I) above each \( R^3 \) is divalent a hydrocarbon group or a combination of a divalent hydrocarbon group and a divalent siloxane.
group. Each \( R^3 \) may be an alkylene group such as ethylene, propylene, or hexylene; an arylene group such as phenylene; or an alkylarylene group such as:

\[
\begin{align*}
\text{H}_2 & \quad \text{C} - \text{C} - \text{C} - \text{H}_2 \\
\text{C} & \quad \text{H}_2 \\
\text{H}_2 & \quad \text{C} - \text{C} - \text{H}_2 \\
\end{align*}
\]

or

\[
\begin{align*}
\text{H}_2 & \quad \text{C} - \text{C} - \text{C} - \text{H}_2 \\
\text{C} & \quad \text{H}_2 \\
\text{H}_2 & \quad \text{C} - \text{C} - \text{H}_2 \\
\end{align*}
\]

Alternatively, each \( R^1 \) and each \( R^2 \) may be alkyl, each \( R^3 \) may be alkylene such as ethylene, and each subscript \( d \) may be 3.

[0038] Alkoxysilylhydrocarbylene-endblocked polydiorganosiloxanes may be prepared by reacting a vinyl-terminated, polydimethylsiloxane with (alkoxysilylhydrocarbyl)tetrasmethyldisiloxane.

[0039] Alternatively, ingredient (B) may comprise a silicone resin, in addition to or instead of one of the polyorganosiloxanes described above for ingredient (B). Suitable silicone resins are exemplified by an MQ resin, which comprises siloxane units of the formulae: \( R^{29}_w R^{30}_o \), \( \text{SiO}_2 \), where \( R^{29} \) and \( R^{30} \) are monovalent organic groups, such as monovalent hydrocarbon groups exemplified by alkyl such as methyl, ethyl, propyl, pentyl, octyl, decyl, dodecyl, undecyl, and octadecyl; cycloalkyl such as cyclopentyl and cyclohexy; aryl such as phenyl, tolyl, xyl, and benzyl; alkoxy such as 2-phenylethyl; halogenated hydrocarbon group exemplified by chlorinated alkyl groups such as chloromethyl and chloropropyl groups; fluorinated alkyl groups such as fluoromethyl, 2-fluoropropyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl, 4,4,4,3-pentafluorobutyl, 5,5,5,4,4,3,3-heptafluoropentyl, 6,6,6,5,4,4,3,3,nonafluorohexyl, and 8,8,8,7,7-pentafluoroctyl; chlorinated cycloalkyl groups such as 2,2-dichlorocyclopropyl, 2,3-dichlorocyclopentyl; fluorinated cycloalkyl groups such as 2,2-difluorocyclopropyl, 2,3-difluorocyclobutyl, 3,4-difluorocyclohexyl, and 3,4-difluoro-5-methylcycloheptyl; and other monovalent organic groups such as hydrocarbon groups substituted with oxygen atoms such as glycidoxyalkyl, and hydrocarbon groups substituted with nitrogen atoms such as aminooalkyl and cyano-functional groups such as cyanoethyl and cyanopropyl; and each instance of subscript \( w \) is 0, 1, or 2. Alternatively, each \( R^{29} \) and each \( R^{30} \) may be an alkyl group. The MQ resin may have a molar ratio of M units to Q units (M:Q) ranging from 0.5:1 to 1.5:1. These mole ratios are conveniently measured by \( \text{Si}^{29} \) NMR spectroscopy. This technique is capable of quantitatively determining the concentration of \( R^3_3 \) \( \text{SiO} \) units derived from the silicone resin and from the neopentamer, \( \text{SiO}_4 \), present in the initial silicone resin, in addition to the total hydroxyl content of the silicone resin.

[0040] The MQ silicone resin is soluble in solvents such as liquid hydrocarbons exemplified by benzene, toluene, xylene, and heptane, or in liquid organosilicon compounds such as a low viscosity cyclic and linear polydiorganosiloxanes.
The MQ silicone resin may contain about 2.0% or less, alternatively about 0.7% or less, alternatively about 0.3% or less, of terminal units represented by the formula $X^{n}SiO_{3/2}$, where $X^{n}$ represents hydroxyl or a hydrolyzable group such as alkoxy such as methoxy and ethoxy; alkenyloxy such as isopropenyloxy; ketoximo such as methyethylketoximo; carboxy such as acetoxy; amidoxy such as acetamidoxy; and aminoxo such as N,N-dimethylaminoxy. The concentration of silanol groups present in the silicone resin can be determined using FTIR.

The Mn desired to achieve the desired flow characteristics of the MQ silicone resin can depend at least in part on the Mn of the silicone resin and the type of organic group, represented by $R^{n}$, that are present in this ingredient. The Mn of the MQ silicone resin is typically greater than about 3,000, more typically from about 4,500 to about 7,500.

Various suitable MQ resins are available from sources such as Dow Corning Corporation, Momentive Performance Materials, Albany, NY, and Bluestar Silicones USA Corp., East Brunswick, NJ. For example, DOW CORNING® MQ-1600 Solid Resin, DOW CORNING® MQ-1601 Solid Resin, DOW CORNING® 1250 Surfactant, and DOW CORNING® 7466 Resin, all of which are available from Dow Corning Corporation, are suitable for use in the methods described herein. Other suitable MQ resins may also be used including, but not limited to, those disclosed in U.S. Patent No. 5,082,706 (e.g.,
methylhydrogencyclopolysiloxanes having the unit formula \( \text{MeHSiO}_2 \); linear methylhydrogenpolysiloxanes having the formulae \( \text{Me}_3\text{SiO(MeHSiO)}_j(\text{Me}_2\text{SiO})_i\text{SiMe}_3 \) and \( \text{HMe}_2\text{SiO(MeHSiO)}_j(\text{Me}_2\text{SiO})_i \); \( \text{SiMe}_2\text{H} \) where \( i \) and \( j \) have values of zero or more; and branched siloxanes such as \( (\text{HMe}_2\text{SiO})_4\text{Si}) \). Alternatively, a resin containing \( M, T, \) and \( Q \) units may be used, such as DOW CORNING® MQ-1 640 Flake Resin, which is also available from Dow Corning Corporation. Such resins may be supplied in organic solvent.

Alternatively, the silicone resin may comprise a silsesquioxane resin, i.e., a resin containing \( T \) units of formula \((\text{R}^3\text{SiO}_{1.5})\). Each \( \text{R}^1 \) may be independently selected from a hydrogen atom and a monovalent organic group, such as a monovalent hydrocarbon group exemplified by an alkyl, such as methyl, ethyl, propyl, pentyl, octyl, decyl, dodecyl, undecyl, and octadecyl; cycloalkyl, such as cyclopentyl and cyclohexyl; aryly, such as phenyl, tolyl, xylyl, and benzyl; aralkyl, such as 2-phenylethyl; halogenated hydrocarbon group, exemplified by chlorinated alkyl groups such as chloromethyl and chloropropyl groups; a fluorinated alkyl group, such as fluoromethyl, 2-fluoropropyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl, 4,4,4,3,3-pentafluorobutyl, 5,5,5,4,4,3,3-heptafluoropentyl, 6,6,6,5,4,4,3,3-nonahexoheptyl, and 8,8,8,7,7-pentafluoroctyl; chlorinated cycloalkyl groups, such as 2,2-dichlorocyclopropyl, 2,3-dichlorocyclopentyl; fluorinated cycloalkyl groups, such as 2,2-difluorocyclopropyl, 2,3-difluorocyclopentyl; and 3,4-difluorocyclohexyl, and 3,4-difluoro-5-methylcycloheptyl; another monovalent organic group such as a hydrocarbon group substituted with oxygen atoms such as glycidoxyalkyl; a hydrocarbon group substituted with a nitrogen atom such as aminoalkyl and cyano-functional groups such as cyanoethyl and cyanopropyl; and any combination thereof. Silsesquioxane resins suitable for use herein are known in the art and are generally available. For example, a methylmethoxysiloxane methylsilsesquioxane resin having a DP of about 15 and an average molecular weight (MW) of about 1200 g/mol is available as DOW CORNING® US-CF 2403 Resin from Dow Corning Corporation. Alternatively, the silsesquioxane resin may have phenylsilsesquioxane units, methylsilsesquioxane units, or a combination thereof. Such resins are known in the art and are available as, e.g., XIAMETER® Flake resins such as product numbers RSM-021 7, RSN-0220, RSN-0233, RSN-0249, RSN-0255, also available from Dow Corning Corporation. Alternatively, the silicone resin may comprise \( D \) units of formulae \((\text{R}^3\text{SiO}_{1.5})\) and/or \((\text{R}^4\text{R}^*\text{SiO}^*)\) and \( T \) units of formulae \((\text{R}^3\text{SiO}_{1.5})\) and/or \((\text{R}^3\text{SiO}_{1.5})\), i.e., a DT resin, where \( \text{R}^1 \) is as described above and \( \text{R}^3 \) is a hydrolyzable group such as group X described above.

DT resins are known in the art and are available as, for example, methoxy functional DT resins including XIAMETER® RSN-3074 and XIAMETER® RSN-3037 resins; and silanol functional resins including XIAMETER® RSN-0804, RSN-0805, RSN-0806, RSN-0808, and RSN-0840 resins, which are also available from Dow Corning Corporation. Other suitable resins include DT resins containing methyl and phenyl groups.
[0048] The amount of silicone resin added to the composition can vary depending on the end use of the composition. For example, when the reaction product of the composition is a gel, little or no silicone resin may be added. However, the amount of silicone resin in the composition may range from about 0% to about 90%, alternatively about 0.1% to about 50%, based on the weight of all ingredients in the composition.

[0049] The amount of ingredient (B) can depend on various factors including the end use of the reaction product of the composition, the type of base polymer selected for ingredient (B), and the type(s) and amount(s) of any additional ingredient(s) present, if any. However, the amount of ingredient (B) may range from about 0.01% to about 99%, alternatively about 10% to about 95%, alternatively about 10% to about 65% of the composition.

[0050] Ingredient (B) can be one single polyorganosiloxane or a combination comprising two or more polyorganosiloxanes that differ in at least one of the following properties: average molecular weight, hydrolyzable substituents, siloxane units, sequence, and viscosity.

Ingredient (C) - Crosslinker

[0051] Ingredient (C) is a crosslinker. Generally, ingredient (C) is selected with functionality that can vary depending on the degree of crosslinking desired in the reaction product of the composition and such that the reaction product does not exhibit too much weight loss from by-products of the condensation reaction. Generally, the selection of ingredient (C) is made such that the composition remains sufficiently reactable to be useful during storage for several months in a moisture impermeable package. The exact amount of ingredient (C) can vary depending on factors including the type of polyorganosiloxane selected for ingredient (B) and crosslinker selected for ingredient (C), the reactivity of the hydrolyzable substituents on the ingredients (B) and (C), and the desired crosslink density of the reaction product. However, the amount of crosslinker may range from about 0.5 to about 100 parts based on 100 parts by weight of ingredient (B).

[0052] Ingredient (C) may comprise a silane crosslinker having hydrolyzable groups or partial or full hydrolysis products thereof. Ingredient (C) has an average, per molecule, of greater than two substituents reactive with the hydrolyzable substituents on ingredient (B). Examples of suitable silane crosslinkers for ingredient (C) may have the general formula (III) \( R^8_kSi(R^9)^{d-k} \), where each \( R^8 \) is independently a monovalent hydrocarbon group such as an alkyl group; each \( R^9 \) is a hydrolyzable substituent, which may be the same as \( X \) described above for ingredient (B). Alternatively, each \( R^9 \) may be, for example, a halogen atom, an acetamido group, an acyloxy group such as acetoxy, an alkoxy group, an amido group, an amino group, an aminoxyl group, a hydroxyl group, an oximino group, a ketoxy group, or a methylacetamido group; and each instance of subscript \( k \) may be 0, 1, 2, or 3. For ingredient (C), subscript \( k \) has an average value greater than 2. Alternatively, subscript \( k \) may have a value ranging from 3 to 4. Alternatively, each \( R^9 \) may be independently selected
from hydroxyl, alkoxy, acetoxy, amide, or oxime. Alternatively, ingredient (C) may be selected from an acyloxysilane, an alkoxy silane, a ketoximosilane, and an oximosilane.

Ingredient (C) may comprise an alkoxy silane exemplified by a dialkylalkoxysilane, such as a dialkylalkoxy silane; a trialkoxysilane, such as an alkyltrialkoxy silane; a tetraalkoxy silane; or partial or full hydrolysis products thereof, or another combination thereof. Examples of suitable trialkoxysilanes include methyltrimethoxysilane, methy triethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, isobutyltrimethoxysilane, isobutyltriethoxysilane, and a combination thereof, and alternatively methyltrimethoxysilane. Examples of suitable tetraalkoxysilanes include tetraethoxysilane. The amount of the alkoxy silane that is used in the curable silicone composition may range from about 0.5 to about 15, parts by weight per 100 parts by weight of ingredient (B).

Ingredient (C) may comprise an acyloxysilane, such as an acetoxy silane. Acetoxysilanes include a tetraacetoxy silane, an organotriacetoxy silane, a diorganodiacetoxy silane, or a combination thereof. The acetoxy silane may contain alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, and tertiary butyl; alkenyl groups such as vinyl, allyl, or hexenyl; aryl groups such as phenyl, tolyl, or xylyl; aralkyl groups such as benzyl or 2-phenylethyl; and fluorinated alkyl groups such as 3,3,3-trifluoropropyl. Exemplary acetoxy silanes may include, but are not limited to, tetraacetoxy silane, methyltriacetoxy silane, ethyltriacetoxy silane, vinyltriacetoxy silane, propyltriacetoxy silane, butyltriacetoxy silane, phenyltriacetoxy silane, octyltriacetoxy silane, dimethyl diacetoxy silane, phenylmethyl diacetoxy silane, vinylmethyl diacetoxy silane, diphenyl diacetoxy silane, tetraacetoxy silane, and combinations thereof. Alternatively, ingredient (C) may comprise organotriacetoxy silanes, for example mixtures comprising methyltriacetoxy silane and ethyltriacetoxy silane. The amount of the acetoxy silane that is used in the curable silicone composition may range from about 0.5 to about 15 parts by weight per 100 parts by weight of ingredient (B); alternatively about 3 to about 10 parts by weight of acetoxy silane per 100 parts by weight of ingredient (B).

Examples of silanes suitable for ingredient (C) containing both alkoxy and acetoxy groups that may be used in the composition include methyl diacetoxy methoxysilane, methylacetoxy dimethoxysilane, vinyl diacetoxy methoxysilane, vinyl acetox y dimethoxysilane, methyl diacetoxy ethoxysilane, methylacetoxy diethoxysilane, and any combination(s) thereof.

Aminofunctional alkoxysilanes suitable for ingredient (C) are exemplified by

\[
\begin{align*}
H_2N(CH_2)_2Si(OCH_3)_3, & \quad H_2N(CH_2)_2Si(OCH_2CH_3)_3, & \quad H_2N(CH_2)_2Si(OCH_3)_3, \\
H_2N(CH_2)_3Si(OCH_2CH_3)_3, & \quad CH_3NH(CH_2)_3Si(OCH_3)_3, & \quad CH_3NH(CH_2)_3Si(OCH_2CH_3)_3, \\
CH_3NH(CH_2)_2Si(OCH_3)_3, & \quad CH_3NH(CH_2)_5Si(OCH_2CH_3)_3, & \quad H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3, \\
H_2N(CH_2)_2NH(CH_2)_3Si(OCH_2CH_3)_3, & \quad CH_3NH(CH_2)_2NH(CH_2)_3Si(OCH_3)_3, & \quad CH_3NH(CH_2)_2NH(CH_2)_3Si(OCH_2CH_3)_3, \\
CH_3NH(CH_2)_2NH(CH_2)_3Si(OCH_2CH_3)_3, & \quad C_4H_9NH(CH_2)_2NH(CH_2)_3Si(OCH_3)_3.
\end{align*}
\]
Suitable oximosilanes for ingredient (C) include alkyltrioximosilanes such as methyltrioximosilane, ethyltrioximosilane, propyltrioximosilane, and butyltrioximosilane; alkoxytrioximosilanes such as methoxytrioximosilane, ethoxytrioximosilane, and propoxytrioximosilane; or alkenyltrioximosilanes such as propenyltrioximosilane or butenyltrioximosilane; alkenylalkyldioximosilanes such as vinyl methyl dioxisolane, vinyl ethyldioxisolane, vinyl methyldioxisolane, or vinyldioxisolane; or any combination thereof.

Suitable ketoximosilanes for ingredient (C) include methyl tris(dimethylketoximo)silane, methyl tris(methylethylketoximo)silane, methyl tris(methylpropylketoximo)silane, methyl tris(methylisobutylketoximo)silane, ethyl tris(dimethylketoximo)silane, ethyl tris(methylethylketoximo)silane, ethyl tris(methylpropylketoximo)silane, ethyl tris(methylisobutylketoximo)silane, vinyl tris(dimethylketoximo)silane, vinyl tris(methylethylketoximo)silane, vinyl tris(methylpropylketoximo)silane, vinyl tris(methylisobutylketoximo)silane, tetrakis(dimethylketoximo)silane, tetrakis(methylethylketoximo)silane, tetrakis(methylpropylketoximo)silane, tetrakis(methylisobutylketoximo)silane, methylbis(dimethylketoximo)silane, methylbis(cyclohexylketoximo)silane, triethoxy(ethylethylketoxime)silane, diethoxydi(ethylethylketoxime)silane, ethoxytrithi(ethylethylketoxime)silane, methylvinylbis(methylisobutylketoximo)silane, or a combination thereof.

Alternatively, ingredient (C) may be polymeric. For example, ingredient (C) may comprise a disilane such as bis(triethoxysilyl)hexane, 1,4-bis[trimethoxysilyl(ethyl)]benzene, and bis[3-(triethoxysilyl)propyl]tetrasulfide.

Ingredient (C) can be one single crosslinker or a combination of two or more crosslinkers that differ in at least one of the following properties: hydrolyzable substituents and other organic groups bonded to silicon, and when a polymeric crosslinker is used, siloxane units, structure, molecular weight, and sequence.

Ingredient (D) - Filler

Optional ingredient (D) is a filler. The filler may be added in an amount ranging from about 0% to about 50%, based on the weight of the composition. The exact amount of
ingredient (D) may depend on various factors including the form of the reaction product of the composition and whether any other fillers are added. Examples of fillers include amorphous silica, fume silica, silica aerogel, silica xerogel, precipitated silica, crushed quartz, aluminum oxide, magnesium oxide, calcium carbonate such as precipitated calcium carbonate, zinc oxide, talc, diatomaceous earth, iron oxide, clays, mica, chalk, titanium dioxide, zirconia, sand, carbon black, graphite, or a combination thereof. Various fillers are known in the art and are generally available. For example, fumed silicas are sold under the name CAB-O-SIL® (Cabot Corporation, Boston, MA). Ground silica is sold under the name MIN-U-SIL® (U.S. Silica, Berkeley Springs, WV). Precipitated calcium carbonates included WINNOFIL® SPM (Solvay, Ixelles, Brussels) and ULTRAPFLEX™ and ULTRAPFLEX™ 100 (SMI, New York, NY).

Ingredient (E) - Vehicle

[0062] A vehicle (e.g., a solvent and/or diluent) may optionally be used in the compositions of the embodiments of the present invention. The vehicle may facilitate flow of the composition, application to the rubber substrate, and/or introduction of certain ingredients, such as silicone resin and/or certain bioactive ingredients. Vehicles used herein are those that help fluidize the ingredients of the composition but essentially do not react with any of these ingredients. Vehicle may be selected based on solubility the ingredients in the composition and volatility. The solubility refers to the vehicle being sufficient to dissolve and/or disperse ingredients of the composition. Volatility refers to vapor pressure of the vehicle. If the vehicle is too volatile (having too high vapor pressure) bubbles may form in the composition at the application temperature, and the bubbles may cause cracks or otherwise weaken or detrimentally affect properties of the cured product. However, if the vehicle is not volatile enough (e.g., if the vapor pressure is too low) the vehicle may remain as a plasticizer in the reaction product of the composition, or the amount of time for the reaction product to develop physical properties may be longer than desired.

[0063] Suitable vehicles include polyorganosiloxanes with suitable vapor pressures, such as hexamethyldisiloxane, octamethyltrisiloxane, hexamethylycyclotrisiloxane, and other low molecular weight polyorganosiloxanes, such as 0.5 to 1.5 centiStoke (cSt) DOW CORNING® 200 Fluids, which are available from Dow Corning Corporation.

[0064] Alternatively, the vehicle may be an organic solvent. The organic solvent may be an alcohol such as methanol, ethanol, isopropanol, butanol, or n-propanol; a ketone such as acetone, methylethyl ketone, or methyl isobutyl ketone; an aromatic hydrocarbon such as benzene, toluene, or xylene; an aliphatic hydrocarbon such as heptane, hexane, octane, or isododecane; a glycol ether such as propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, or ethylene glycol n-butyl ether, a halogenated hydrocarbon such as dichloromethane, 1,1,1-trichloroethane or
methylene chloride; chloroform; dimethyl sulfoxide; dimethyl formamide; acetonitrile; tetrahydrofuran; white spirits; mineral spirits; naphtha; n-methyl pyrrolidone; or any combination thereof.

[0065] The amount of vehicle can depend on various factors including the type of vehicle selected and the amount and type of other ingredients selected for the composition. However, the amount of vehicle may range from about 1% to about 99%, alternatively about 2% to about 50%, based on the weight of the composition.

Ingredient (F) - Bioactive Agent

[0066] Optional ingredient (F) is a bioactive agent. The amount of ingredient (F) may vary depending on factors including the type of bioactive agent selected and the benefit desired. However, the amount of ingredient (F) may range from greater than about 0% to about 25% based on the weight of all ingredients in the composition. Ingredient (F) is exemplified by (f1) a fungicide, (f2) an herbicide, (f3) a pesticide, (f4) an antimicrobial, (f5) other bioactive agents, or any combination thereof.

[0067] Ingredient (f1) is a fungicide, which may include N-substituted benzimidazole carbamate, benzimidazolyl carbamate such as methyl 2-benzimidazolylcarbamate, ethyl 2-benzimidazolylcarbamate, isopropyl 2-benzimidazolylcarbamate, methyl N-[2-[N,N-dimethylcarbamoyl]benzimidazolyl]carbamate, methyl N-[2-[1-(N,N-dimethylcarbamoyl)-6-methylbenzimidazolyl]]carbamate, methyl N-[2-[1-(N,N-dimethylcarbamoyl)-5-methylbenzimidazolyl]]carbamate, methyl N-[2-[1-(N-methylcarbamoyl)-6-methylbenzimidazolyl]]carbamate, methyl N-[2-[1-(N-methylcarbamoyl)-5-methylbenzimidazolyl]]carbamate, methyl N-[1-(N,N-dimethylcarbamoyl)benzimidazolyl]carbamate, methyl N-[2-[1-(N,N-dimethylcarbamoyl)-6-methylbenzimidazolyl]]carbamate, ethyl N-[2-[1-(N,N-dimethylcarbamoyl)benzimidazolyl]]carbamate, ethyl N-[2-[1-(N,N-dimethylcarbamoyl)-5-methylbenzimidazolyl]]carbamate, ethyl N-[2-[1-(N,N-dimethylcarbamoyl)-6-methylbenzimidazolyl]]carbamate, ethyl N-[2-[1-(N,N-dimethylcarbamoyl)-6-methylbenzimidazolyl]]carbamate, isopropyl N-[2-[1-(N,N-dimethylcarbamoyl)-6-methylbenzimidazolyl]]carbamate, isopropyl N-[2-[1-(N,N-dimethylcarbamoyl)-5-methylbenzimidazolyl]]carbamate, isopropyl N-[2-[1-(N,N-dimethylcarbamoyl)-6-methylbenzimidazolyl]]carbamate, isopropyl N-[2-[1-(N,N-dimethylcarbamoyl)-5-methylbenzimidazolyl]]carbamate, methyl N-[2-[1-(N,N-propylcarbamoyl)-benzimidazolyl]]carbamate, methyl N-[2-[1-(N,N-butylcarbamoyl)benzimidazolyl]]carbamate, methoxyethyl N-[2-[1-(N,N-propylcarbamoyl)benzimidazolyl]]carbamate, methoxyethyl N-[2-[1-(N,N-butylcarbamoyl)benzimidazolyl]]carbamate, ethoxyethyl N-[2-[1-(N,N-propylcarbamoyl)benzimidazolyl]]carbamate, ethoxyethyl N-[2-[1-(N,N-butylcarbamoyl)benzimidazolyl]]carbamate, methyl N-[1-(N,N-dimethylcarbamoyloxy)benzimidazolyl]carbamate, methyl N-[2-[1-(N,N-methylcarbamoyloxy)benzimidazolyl]]carbamate, methyl N-[2-[1-(N,N-butylcarbamoyloxy)benzimidazolyl]carbamate, ethoxyethyl N-[2-[1-(N-N-
propylcarbamoyl)benzimidazolyl]carbamate, ethoxyethyl N-[2-[1-(N-
butylcarbamoyloxy)benzimidazolyl]carbamate, methyl N-[2-[1-(N,N-dimethylcarbamoyl)-6-
chlorobenzimidazolyl]carbamate, and methyl N-[2-[1-(N,N-dimethylcarbamoyl)-6-
nitrobenzimidazolyl]carbamate; 10, 10'-oxybisphenoxarsine (trade name: VINYZEN®
OBPA, Rohm and Haas Chemicals, Philadelphia, PA), diiodomethyl-para-tolysulfone,
benzothiophene-2-cyclohexylcarboxamide-S,S-dioxide, N-
(fluordichloridemethylthio)phthalimide (trade names: FLUOR-FOLPER™, PREVENTOL®
A3, Lanxess, Leverkusen, Germany); di-iodomethyl-para-tolylsulfone,
benzothiophene-2-cyclohexylcarboxamide-S,S-dioxide, N-
-(fluordichloridemethylthio)phthalimide (trade names: FLUOR-FOLPER™, PREVENTOL®
A3, Lanxess, Leverkusen, Germany); methyl-benzimideazol-2-ylcarbamate (trade
names: Carbendazim, PREVENTOL® BCM, Lanxess, Leverkusen, Germany),
Zinc-bis(2-pyridylthio-1-oxide) (zinc pyrithion) 2-(4-thiazolyl)-benzimidazol, N-phenyl-iodpropargylcarbamate, N-
octyl-4-isothiazolin-3-on, 4,5-dichloride-2-n-octyl-4-isothiazolin-3-on, N-butyl-1,2-
benzisothiazolin-3-on and/or Triazolyl-compounds, such as tebuconazol in combination
with zeolites containing silver; any combination thereof, or the like.

[0068] Ingredient (f2) is an herbicide, including, for example, amide herbicides such as
allidochlor /V.,V-diallyl-2-chloroacetamide; CDEA 2-chloro-/V.,V-diethylacetamide; etnipromid
(RS)-2-[5-(2,4-dichlorophenoxy)-2-nitrophenoxy] /V-ethylpropionamide; anilide herbicides such as
cisaniilide c/s,2,5-dimethylpyrrrolidine-1-carboxanilide; flufenacet 4'-fluoro-/V-
isopropyl-2-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yloxy]acatanilide; naproanilide (RS)-a-2-
naphthoxypropionanilide; arylalanine herbicides such as benzoylprop /V-benzoyl-/V-(3,4-
dichlorophenyl)-DL-alanine; flamprop-M /V-benzoyl-/V-(3-chloro-4-fluorophenyl)-D-alanine;
chloroacetanilide herbicides such as butachlor /V-butoxymethyl-2-chloro-2',6'-
diethylacetanilide; metazachlor 2-chloro-/V-(pyrazol-1 -ylmethyl)acet-2',6'-xylidide; prynachlor
(RS)-2-chloro-/V-(1-methylprop-2-ynyl)acetanilide; sulphonanilide herbicides such as
cloransulam 3-chloro-2-(5-ethoxy-7-fluoro[1 ,2,4]triazolo[1 ,5-c]pyrimidin-2-
ylsulphonamido)benzoic acid; metosulam 2',6'-dichloro-5,7-dimethoxy-3'-
methyl[1,2,4]triazolo[1,5-a]pyrimidine-2-sulphonanilide; antibiotic herbicides such as
bilanafos 4-[hydroxy(methyl)phosphinoyl]-L-homoalanyl-L-alanyl-L-alanine; benzoic acid
herbicides such as chloramben 3-amino-2,5-dichlorobenzoic acid; 2,3,6-TBA 2,3,6-
trichlorobenzoic acid; pyrimidinylloxybenzoic acid herbicides such as bispyribac 2,6-bis(4,6-
dimethoxy)pyrimidin-2-yloxy)benzoic acid; pyrimidinylthiobenzoic acid herbicides such as
pyrithiobac 2-chloro-6-(4,6-dimethoxy)pyrimidin-2-thiol)benzoic acid; phthalic acid herbicides
such as chlorthal tetrachloroterephthalic acid; picolinic acid herbicides such as
aminopyralid 4-amino-3,6-dichloropyridine-2-carboxylic acid; quinolinecarboxylic acid
herbicides such as quinclorac 3,7-dichloroquinoline-8-carboxylic acid; arsenical herbicides
such as CMA calcium bis(hydrogen methylarsonate); MAMA ammonium hydrogen
methylarsonate; sodium arsenite; benzoylcyclohexanidine herbicides such as mesotrione
2-(4-mesyI-2-nitrobenzoyl)cyclohexane-1,3-dione; benzfuranyl alkylsulphonate herbicides
such as benfuresate 2,3-dihydro-3,3-dimethylbenzofuran-5-yl ethanesulphonate; carbamate herbicides such as carboxazole methyl 5-fe/t-butyl-1,2-oxazol-3-ylcarbamate; fenazulam methyl 4-[2-(4-chloro-o-tolyloxy)acetamido]phenylsulphonylcarbamate; carbanilate herbicides such as BCPC (RS)-sec-butyl 3-chlorocarbanilate; desmedipham ethyl 3-phenylcarbamoyloxyphenylcarbamate; swep methyl 3,4-dichlorocarbanilate; cyclohexene oxime herbicides such as butroxydim (RS)-(£Z)-5-(3-butyl-2,4,6-trimethylphenyl)-2-{1-ethoxyiminopropyl}-3-hydroxy cyclohex-2-en-1-one; tepraloxydim (RS)-(£Z)-2-{1-[(2£)-3-chloroallyloxyimino]propyl}-3-hydroxy-5-perhydropyran-4-yl cyclohex-2-en-1-one; cyclopropylisoxazole herbicides such as isoxachlortole 4-chloro-2-mesitylphenyl 5-cyclopropyl-1,2-oxazol-4-yl ketone; dicarboximide herbicides such as flumezin 2-methyl-4-(a,a,a-trifluoro-m-tolyl)-1,2,4-oxadiazinane-3,5-dione; dinitroaniline herbicides such as ethalfluralin /V-ethyl-a,a,a-trifluoro-/V-(2-methylallyl)-2,6-dinitro-p-toluidine; prodiamine 5-dipropylylamino-a,a,a-trifluoro-4,6-dinitro-o-toluidine; dinitrophenol herbicides such as dinoprop 4,6-dinitro-o-cymen-3-ol; etinofen a-ethoxy-4,6-dinitro-o-cresol; diphenyl ether herbicides such as ethoxyfen 0-[2-chloro-5-(2-chloro-a,a,a-trifluoro-p-tolyloxy)benzoyl]-L-lactic acid; nitrophenyl ether herbicides such as aclonifen 2-chloro-6-nitro-o-cresol; dithiocarbamate herbicides such as dazomet 3,5-dimethyl-1,3,5-thiadiazinane-2-thione; halogenated aliphatic herbicides such as dalapon 2,2-dichloropropionic acid; chloroacetic acid; imidazolinone herbicides such as imazapyr (RS)-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid; inorganic herbicides such as disodium tetraborate decahydrate; sodium azide; nitrile herbicides such as chloroxynil 3,5-dichloro-4-hydroxybenzonitrile; ioxynil 4-hydroxy-3,5-diiodobenzonitrile; organophosphorus herbicides such as anilofos S-4-chloro-/V-isopropylcarbaniloylmethyl 0,0-dimethyl phosphorodithioate; glufosinate 4-[hydroxy(methyl)phosphinoyl]-DL-homoalanine; phenoxy herbicides such as clomoxyn (RS)-2-(2,4-dichloro-m-tolyloxy)propionanilide; fenteracol 2-(2,4,5-trichlorophenoxy)ethanol; phenoxyacetic herbicides such as MCPA 4-(4-chloro-2-methylphenoxy)acetic acid; phenoxybutyric herbicides such as MCPB 4-(4-chloro-o-tolyloxy)butyric acid; phenoxypropionic herbicides such as fenoprop (RS)-2-(2,4,5-trichlorophenoxy)propionic acid; arylxyloxypropionic herbicides such as isoxapryrifop (RS)-2-[2-(4-(3,5-dichloro-2-pyridyl)oxy)phenoxy]propionyl]isoxazolidine; phenylenediamine herbicides such as dinitramine N,N-diethyl-2,6-dinitro-4-trifluoromethyl-m-phenylenediamine, pyrazolylphenoxyacetophenone herbicides such as pyrazoxyfen 2-[2-(2,4-dichlorobenzoyl)-1,3-dimethylpyrazol-5-yl]acetophenone; pyrazolylphenyl herbicides such as pyraflufen 2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenoxyacetic acid; pyridazine herbicides such as pyridafol 6-chloro-3-phenylpyridazin-4-ol; pyridazinone herbicides such as chloridazon 5-amino-4-chloro-2-phenylpyridazin-3(2/-/)-one; oxapyrazon
5-bromo-1,6-dihydro-6-oxo-1-phenylpyridazin-4-yloxamic acid; pyridine herbicides such as fluroxypyr, 4-amino-3,5-dichloro-6-fluoro-2-pyridyloxyacetic acid; thiazopyr methyl 2-difluoromethyl-5-(4,5-dihydro-1,3-thiazol-2-yl)-4-isobutyl-6-trifluoromethyl nicotinate; pyrimidinediamine herbicides such as ipyrimidam e-chloro-A^-isopropylpyrimidine^\textsuperscript{4}^-diamine; quaternary ammonium herbicides such as diethamquat 1,1\textsuperscript{1^-bis(diethylcarbamoylmethyl)-4,4\textsuperscript{4^-bipyrirdinium; paraquat 1,1\textsuperscript{1^-dimethyl-4,4\textsuperscript{1^-bipyrirdinium; thiocarbamate herbicides such as cycloate S-ethyl cyclohexyl(ethyl)thiocarbamate; tiocarbazil S-benzyl di-sec-butylthioiocarbamate; thiocarbonate herbicides such as EXD 0,0-diethyl dithiobis(thioformate); thiourea herbicides such as methiuron 1,1-dimethyl-3-m-tolyl-2-thioure; triazine herbicides such as triaziflam (RS)-N-[2-(3,5-dimethylphenox)-1-methylethyl]-6-(1-fluoro-1-methylethyl)-1,3,5-triazine-2,4-diamine; chlorotriazine herbicides such as cyprazine e-chloro-A^-cyclopropyl-A^-isopropyl-A^-isopropyl-l,3,5-triazine-2,4-diamine; propazine e-chloro^-/N^-diisopropyl-l.S.S-triazine^^^^diamine; methoxytriazine herbicides such as prometon /V^-A^-diisopropyl e-methoxy-l,3,5-triazine-2,4-diamine; methylthiotriazine herbicides such as cyanatryn 2-(4-ethylamino-6-methylthio-1,3,5-triazin-2-ylamino)-2-methylpropionitrile; triazinone herbicides such as hexazinone 3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4(1/-/-1^-/-^-1^-/-^-2^-/-^-/-^-)/^-^-dione; triazole herbicides such as eprazon /V-ethyl/V-propyl-3-propylsulphonyl-1^-/-^-1^-/^/-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^-^,
Ingredient (f3) is a pesticide. Suitable pesticides are exemplified by atrazine, diazinon, and chlorpyrifos. For purposes of this application, pesticide includes insect repellents, such as N,N-diethyl-meta-toluamide, and pyrethroids, such as pyrethrin.

Ingredient (f4) is an antimicrobial agent. Suitable antimicrobials are generally available, such as DOW CORNING® 5700 and DOW CORNING® 5772, which are available from Dow Corning Corporation.

Alternatively or additionally, ingredient (F) may comprise a boron-containing material, e.g., boric anhydride, borax, or disodium octaborate tetrahydrate, which may function as a pesticide, fungicide, and/or flame retardant.

The bioactive ingredient (F) may include any component that is intended to furnish pharmacological activity (such as active ingredients) or other direct effect in the diagnosis, cure, mitigation, treatment, or prevention of disease, or to affect the structure or any function of the body of a human or other animal. This can include those components that may undergo a chemical change in the manufacture of drug products and be present in drug products in a modified form intended to furnish the specified activity or effect.

Some representative examples of active ingredients include drugs, vitamins, minerals, hormones, topical antimicrobial agents such as antibiotic active ingredients, and antifungal active ingredients.

Other types of active ingredients include vitamins and derivatives thereof, including "pro-vitamins." Non-limiting examples of vitamins that may be used herein include, but are not limited to, Vitamin A-1, retinol, C10-C-18 esters of retinol, vitamin E, tocopherol, esters of Vitamin E, and combinations thereof. Retinol may include trans-retinol, 1, 3-cis-retinol, 11-cis-retinol, 9-cis-retinol, and 3,4-didehydro-retinol, Vitamin C and its derivatives, Vitamin B-1, Vitamin B2, Pro Vitamin B5, panthenol, Vitamin Bg, Vitamin B-2, niacin, folic acid, biotin, and pantothenic acid. Other suitable vitamins and the INCI names for the vitamins included herein include ascorbyl dipalmitate, ascorbyl methylsilanol pectinate, ascorbyl palmitate, ascorbyl stearate, ascorbyl glucocide, sodium ascorbyl phosphate, sodium ascorbate, disodium ascorbyl sulfate, potassium (ascorbyl/tocopheryl) phosphate.

Retinol, it should be noted, is an International Nomenclature Cosmetic Ingredient Name (INCI) designated by The Cosmetic, Toiletry, and Fragrance Association (CTFA, Washington D.C.) for Vitamin A. Other suitable vitamins and the INCI names for the vitamins included herein include retinyl acetate, retinyl palminate, retinyl propionate, α-tocopherol, tocophersolan, tocopheryl acetate, tocopheryl linoleate, tocopheryl nicotinate, and tocopheryl succinate.

Some examples of products suitable for use herein include Vitamin A Acetate and Vitamin C, both products of Fluka Chemie AG, Buchs, Switzerland; COVI-OX® T-50 and
COV-OX® T-70, both Vitamin E products of Henkel Corporation, La Grange, IL; and Vitamin E Acetate, a product of Roche Vitamins & Fine Chemicals, Nutley, NJ.

[0077] The active ingredient can be an active drug ingredient. Representative examples of suitable active drug ingredients that may be used are hydrocortisone, ketoprofen, timolol, pilocarpine, adriamycin, mitomycin C, morphine, hydromorphone, diltiazem, theophylline, doxorubicin, daunorubicin, heparin, penicillin G, carbenicillin, cephalothin, cefoxitin, cefotaxime, 5-fluorouracil, cytarabine, 6-azauridine, 6-thioguanine, vinblastine, vincristine, bleomycin sulfate, aurothioglucose, suramin, mebendazole, clonidine, scopolamine, propranolol, phenylpropanolamine hydrochloride, ouabain, atropine, haloperidol, isosorbide, nitroglycerin, ibuprofen, ubiquinones, indomethacin, prostaglandins, naproxen, salbutamol, guanabenz, labetalol, pheniramine, metrifonate, steroids, any combination thereof, or the like.

[0078] Considered to be included herein as active drug ingredients for purposes of the present invention are antibacterial agents such as chlorohexadiene gluconate; antifungal agents such as miconazole nitrate; anti-inflammatory agents; corticosteroidal drugs; non-steroidal anti-inflammatory agents such as diclofenac; anesthetic agents such as lidocaine; antipruritic agents; antidermatitis agents; and agents generally considered barrier films.

[0079] The bioactive ingredient (F) of the present invention may be a protein, such as an enzyme. Enzymes include, but are not limited to, commercially available types, improved types, recombinant types, wild types, variants not found in nature, mixtures thereof, and the like. For example, suitable enzymes may include hydrolases, cutinases, oxidases, transferases, reductases, hemicellulases, esterases, isomerases, pectinases, lactases, peroxidases, laccases, catalases, and mixtures thereof. Hydrolases include, but are not limited to, proteases (bacterial, fungal, acid, neutral or alkaline), amylases (alpha or beta), lipases, mannanases, cellulases, collagenases, l isozymes, superoxide dismutase, catalase, and mixtures thereof. Said proteases include, but are not limited to, trypsin, chymotrypsin, pepsin, pancreatin and other mammalian enzymes; papain, bromelain and other botanical enzymes; subtilisin, epidermin, nisin, naringinase(L-rhamnosidase) urokinase and other bacterial enzymes. Said lipases include, but are not limited to, triacyl-glycerol lipases, monoacyl-glycerol lipases, lipoprotein lipases, e.g., steapsin, erepsin, pepsin, other mammalian, botanical, bacterial lipases and purified ones. Further, stimulating hormones, e.g., insulin, can also be used with the enzyme(s).

[0080] Ingredient (F) may also include one or more plant extract. Examples of these components are as follows: Ashitaba extract, avocado extract, hydrangea extract, Althea extract, Arnica extract, aloe extract, apricot extract, apricot kernel extract, Ginkgo Biloba extract, fennel extract, turmeric[Curcuma] extract, oolong tea extract, rose fruit extract, Echinacea extract, Scutellaria root extract, Phellodendoro bark extract, Japanese Coptis
extract, Barley extract, Hyperium extract, White Nettle extract, Watercress extract, Orange extract, Dehydrated saltwater, seaweed extract, hydrolyzed elastin, hydrolyzed wheat powder, hydrolyzed silk, Chamomile extract, Carrot extract, Artemisia extract, Glycyrrhiza extract, hibiscustea extract, Pyracantha Fortuneeana Fruit extract, Kiwi extract, Cinchona extract, cucumber extract, guanocine, Gardenia extract, Sasa Albo-marginata extract, Sophora root extract, Walnut extract, Grapefruit extract, Clematis extract, Chlorella extract, mulberry extract, Gentiana extract, black tea extract, yeast extract, burdock extract, rice bran ferment extract, rice germ oil, comfrey extract, collagen, cowberry extract, Gardenia extract, Asiasarum Root extract, Family of Bupleurum extract, umbilical cord extract, Salvia extract, Saponaria extract, Bamboo extract, Crataegus fruit extract, Zanthoxylum fruit extract, shiitake extract, Rehmannia root extract, gromwell extract, Perilla extract, linden extract, Filipendula extract, peony extract, Calamus Root extract, white birch extract, Horsetail extract, Hedera Helix(Ivy) extract, hawthorn extract, Sambucus nigra extract, Achillea millefolium extract, Mentha piperita extract, sage extract, mallow extract, Cnidium officinale Root extract, Japanese green gentian extract, soybean extract, jujube extract, thyme extract, tea extract, clove extract, Gramineae imperata cyrillo extract, Citrus unshiu peel extract, Japanese Angelica Root extract, Calendula extract, Peach Kernel extract, Bitter orange peel extract, Houttuyna cordata extract, tomato extract, natto extract, Ginseng extract, Green tea extract (camelliae sinesis), garlic extract, wild rose extract, hibiscus extract, Ophiopogon tuber extract, Nelumbo nucifera extract, parsley extract, honey, hamamelis extract, Parietaria extract, Isodonis herba extract, bisabolol extract, Loquat extract, coltsfoot extract, butterbur extract, Porid cocos wolf extract, extract of butcher's broom, grape extract, propolis extract, luffa extract, safflower extract, peppermintextract, linden tree extract, Paonia extract, hop extract, pine tree extract, horse chestnut extract, Mizu-bashou [Lysichiton camtschatcesejectract, Mukuroiss peel extract, Melissa extract, peach extract, cornflower extract, eucalyptus extract, saxifrage extract, citron extract, coix extract, mugwort extract, lavender extract, apple extract, lettuce extract, lemon extract, Chinese milk vetch extract, rose extract, rosemary extract, Roman Chamomile extract, royal jelly extract, any combination thereof, and the like.

[0081] The amount of Ingredient (F) present in the silicone composition may vary, but typically ranges from about 0.0005 wt % to about 50 wt %, alternatively about 1 wt % to about 25 wt %, or alternatively about 1 wt % to about 10 wt %, based on the total weight of the fluid silicone composition.

Ingredient (G) - Treating Agent

[0082] The composition may, optionally, further comprise ingredient (G), a filler treating agent. The amount of ingredient (G) can vary depending on factors such as the type of treating agent selected and the type and amount of particulates to be treated, and whether
the particulates are treated before being added to the composition, or whether the particulates are treated in situ. Ingredient (G) may be used in an amount ranging from about 0.01% to about 20%, alternatively about 0.1% to about 15%, and alternatively about 0.5% to about 5%, based on the weight of the composition. Particulates, such as the filler, the physical drying agent, certain flame retardants, certain pigments, and/or certain water release agents, when present, may optionally be surface treated with ingredient (G). Particulates may be treated with ingredient (G) before being added to the composition, or in situ. Ingredient (G) may comprise an alkoxy silane, an alkoxy-functional oligosiloxane, a cyclic polyorganosiloxane, a hydroxyl-functional oligosiloxane such as a dimethyl siloxane or methyl phenyl siloxane, or a fatty acid. Examples of fatty acids include stearates such as calcium stearate.

[0083] Some representative organosilicon filler treating agents that may be used as ingredient (G) include compositions normally used to treat silica fillers such as organochlorosilanes, organosiloxanes, organosilanes such as hexaalkyl disilazanes, and organoalkoxysilanes such as C₆H₄₃Si(OCH₃)₃, C₈H₁₇Si(OCC₂H₅)₃, C₉H₁₈Si(OCH₃)₃, C₁₂H₂₅Si(OCH₃)₃, C₁₄H₂₉Si(OCC₂H₅)₃, and C₆H₅CH₂CH₂Si(OCH₃)₃. Other treating agents that may be used include alkylthiols, fatty acids, titanates, titanate coupling agents, zirconate coupling agents, any combination thereof, or the like.

[0084] Alternatively, ingredient (G) may comprise an alkoxy silane having the formula: \( R^{13}_0 Si(OR^p)(4-p) \), where subscript p may have a value ranging from about 1 to about 3. In one embodiment, the value of subscript p is 3. Each \( R^{13} \) is independently a monovalent organic group, such as a monovalent hydrocarbon group of about 1 to about 50 carbon atoms, alternatively about 8 to about 30 carbon atoms, alternatively about 8 to about 18 carbon atoms. \( R^{13} \) is exemplified by alkyl groups such as hexyl, octyl, dodecyl, tetradecyl, hexadecyl, and octadecyl; and aromatic groups such as benzyl and phenylethyl. \( R^{13} \) may be saturated or unsaturated and branched or unbranched. In one embodiment, \( R^{13} \) may be saturated and unbranched.

[0085] Each \( R^{14} \) independently a saturated hydrocarbon group of about 1 to about 4 carbon atoms, alternatively about 1 to about 2 carbon atoms. Ingredient (G) is exemplified by hexyltrimethoxysilane, octyltriethoxysilane, decyltrimethoxysilane, dodecyldimethoxysilane, tetradecyltrimethoxysilane, phenylethyltrimethoxysilane, octadecyltrimethoxysilane, and combinations thereof.

[0086] Alkoxy-functional oligosiloxanes may also be used as treating agents. For example, suitable alkoxy-functional oligosiloxanes include those of the formula \( (R^{15}_0)q Si(OSiR^{16}2R^{17})4(q) \). In this formula, subscript q is 1, 2 or 3, alternatively subscript
q is 3. Each $R^{15}_m$ may be an alkyl group. Each $R^{16}_a$ may be an unsaturated monovalent hydrocarbon group of about 1 to about 10 carbon atoms. Each $R^{17}_b$ may be an unsaturated monovalent hydrocarbon group having at least 10 carbon atoms.

[0087] Certain particulates, such as metal fillers may be treated with alkylthiols such as octadecyl mercaptan; fatty acids such as oleic acid and stearic acid; and any combination thereof.

[0088] Other treating agents include alkenyl functional polyorganosiloxanes. Suitable alkenyl functional polyorganosiloxanes include, but are not limited to:

$$\text{CH}_3 \text{CH}_3 \text{CH}_3$$

$$\text{CH}_2=\text{CH-Si-(OSi)}_r\text{-OSi-CH}_3$$

$$\text{CH}_3 \text{CH}_3 \text{CH}_3$$

where subscript $r$ has a value up to about 1,500.

[0089] Alternatively, a polyorganosiloxane capable of hydrogen bonding may be used as a treating agent. This strategy to treating a surface of a filler takes advantage of multiple hydrogen bonds, either clustered, dispersed, or both, as a means to tether the compatibilization moiety to the filler surface. The polyorganosiloxane capable of hydrogen bonding has an average, per molecule, of at least one silicon-bonded group capable of hydrogen bonding. The group may be selected from: an organic group having multiple hydroxyl functionalities or an organic group having at least one amino functional group. The polyorganosiloxane capable of hydrogen bonding means that hydrogen bonding is the primary mode of attachment of the polyorganosiloxane to a filler. The polyorganosiloxane may be incapable of forming covalent bonds with the filler. The polyorganosiloxane may be free of condensable silyl groups, e.g., silicon bonded alkoxy groups, silazanes, and silanols. The polyorganosiloxane capable of hydrogen bonding may be selected from the group consisting of a saccharide-siloxane polymer, an amino-functional polyorganosiloxane, and a combination thereof. Alternatively, the polyorganosiloxane capable of hydrogen bonding may be a saccharide-siloxane polymer.

Ingredient (H) - Excipients

[0090] The compositions of the embodiments of the present invention may also include pharmaceutical excipients - inactive ingredients that may be present in a formulation to aid in active loading, stabilization and/or release. The US Food and Drug Administration maintains a list of excipients, called for the moment the "Inactive Ingredients Database." Those materials and others that may in the future be added to the database are intended to be included herein.
Ingredient (I) - Other additives

[0091] The compositions of the embodiments of the present invention may also include other suitable components. For example, the composition may include one or more antioxidants, processing aids, pigments, additives to enable or limit heat and/or electrical conductivity, any combination thereof, or the like.

Exemplary Method of Making the Composition

[0092] According to one non-limiting process, the composition described above may be prepared as a one-part composition, e.g., by combining all ingredients by any convenient means, such as mixing. For example, a one-part composition may be made by optionally combining ingredient (B) (the polyorganosiloxane) with all or part of optional ingredient (D) (the filler), and mixing this with a pre-mix comprising ingredient (C) (the crosslinker) and ingredient (A) (the catalyst). Other additives such as ingredient (E) (the vehicle) and the ingredient (F) (the bioactive agent) may be added to the mixture at any desired stage. A final mixing step may be performed under substantially anhydrous conditions, and the resulting fluid silicone compositions are generally stored under substantially anhydrous conditions, for example in sealed containers, until ready for use.

[0093] Alternatively, the composition may be prepared as a multiple part (e.g., 2 or 3 part) composition. In this instance, the catalyst (A) and crosslinker (C) are stored in separate parts, and the parts are combined shortly before use of the composition. For example, a two part curable composition may be prepared by combining ingredients (A) and (B) to form a first (curing agent) part by any convenient means such as mixing. A second (base) part may be prepared by combining ingredients (B), (C), and optionally (D) by any convenient means such as mixing. Optionally, a third (vehicle) part may include a vehicle (E). The ingredients may be combined at ambient or elevated temperature and under ambient or anhydrous conditions, depending on various factors including whether a one part or multiple part composition is selected. The base part and curing agent part may be combined by any convenient means, such as mixing, shortly before use. The base part and curing agent part may be combined in relative amounts of base:curing agent ranging from about 1:1 to about 10:1. Alternatively, when a 3 part composition is prepared, the parts may be combined in amounts of about 40:0.25:59.75 to about 51:2:47 (curing agent part:base part:vehicle part), alternatively this ratio may be about 49:1:50.

[0094] The equipment used for mixing the ingredients is not specifically restricted. Examples of suitable mixing equipment may be selected depending on the type and amount of each ingredient selected. For example, agitated batch kettles may be used for relatively low viscosity compositions. Alternatively, continuous compounding equipment, e.g., extruders such as twin screw extruders, may be used for more viscous compositions and compositions containing relatively high amounts of filler.
[0095] It is contemplated that any suitable method can be used to prepare the compositions described herein. Exemplary methods that can be used to prepare the compositions described herein include those disclosed in, for example, U.S. Patent Application Publication Nos. 2009/0291238 and 2008/0300358. For example, the process may be either a batch compounding process or a continuous compounding process. Moreover, the compositions of the embodiments of the present invention may be formulated as one-part compositions or multiple-part compositions, such as a two-part composition. A one-part composition may be prepared by a process comprising mixing the ingredients under shear. The ingredients may be mixed under vacuum or a dry inert gas, or both. The ingredients may be mixed under ambient or elevated temperature, or a combination thereof. An exemplary two-part composition comprises a wet (water containing) part and a dry part. Another suitable method includes mixing the ingredients and heating the ingredients at a temperature above the boiling point of the solvent as the ingredients pass through a reaction zone of a continuous mixing apparatus for a residence time sufficient to produce a pressure-sensitive adhesive (PSA) containing volatile species comprising water, volatile siloxane, and the solvent, and removing essentially all volatile species from the PSA. One skilled in the art would recognize that these steps may be performed concurrently.

[0096] These compositions made as described above may be stable when the stored in containers that protect the compositions from exposure to moisture, but these compositions may react via condensation reaction when exposed to atmospheric moisture. Alternatively, when a low permeability composition is formulated, the composition may cure to form a cured product when moisture is released from a water release agent.

Method of Using the Composition

[0097] The fluid silicone composition described above is curable to form an elastomeric silicone. The fluid silicone composition, and elastomeric silicone prepared therefrom, can be used to coat rubber products useful in the medical field, such as catheters and/or gloves.

[0098] A coated rubber article comprises: (i) a rubber substrate and (ii) an elastomeric silicone coated on at least one surface of the tube. The rubber substrate may be, for example, a catheter, or a portion thereof or a glove such as a latex glove. When the rubber substrate is a catheter such as a Foley catheter, or a portion thereof, the silicone may be coated on the inside of the lumen, on the outside of the tube, or both. The silicone on the inside of the lumen may be the same as the silicone on the outside of the tube. Alternatively, the silicone on the inside of the lumen may differ from the silicone on the outside of the tube.

[0099] Figure 2 shows a cross section of a Foley catheter tube, e.g., tube 50 of Figure 1, according to one embodiment. The tube 50 has a natural rubber core 51, with a layer of primer 60 on the outside surface 70 of the core 51. A layer of elastomeric silicone 80 is
attached to the outside surface 70 via the primer 60. Inside the tube 50 is a first lumen 100 for draining fluid from the body and a second lumen 200 for inflating the balloon 20 (see Figure 1). Each lumen 100, 200 has an inside surface 171, a layer of primer 160 coating the inside surface 171, and a layer of elastomeric silicone 180 adhered to the inside surface 171 by the primer 160.

[00100] The silicone may be adhered to the rubber substrate by a method comprising: i) applying the fluid silicone rubber composition described above to the at least one surface and ii) curing the composition to form the elastomeric silicone. The method may optionally further comprise iii) removing all or a portion of the vehicle, if one is present in the composition after step ii). The method may optionally further comprise washing the substrate before step i), e.g., to remove surface contaminates, improve wetting of the surface, and/or improve adhesion of the elastomeric silicone to the substrate. Washing may be performed by any convenient means, such as spraying the rubber substrate with, or immersing the rubber substrate in, a vehicle as described above; and allowing the substrate to dry.

[00101] Adhesion of the silicone to the substrate may optionally be improved by treating the at least one surface before applying the fluid silicone composition thereto. Treating may be performed by any convenient means, such as exposure to radiation (e.g., plasma) to form reaction sites on the surface and/or application of a primer to increase adhesion between the rubber article and the silicone. Suitable primers for bonding silicones to organic rubbers include epoxy-functional alkoxysilanes and oligomers thereof, aminofunctional alkoxysilanes, and mixtures thereof, alternatively, mercaptosilanes. Other suitable primers include, for example, those disclosed in U.S. Patent No. 3,434,869, (e.g., primers made of the reaction products of aminoorganosilicon compounds and epoxy resins).

[00102] The primer can be applied to the at least one surface of the rubber article by any convenient means such as dipping or spraying. The primer may be allowed to dry, at ambient temperature or with heating to a temperature that does not degrade the rubber. If the rubber article is a catheter or portion thereof, any solvent used in the primer should be selected so as not to cause significant swelling of the rubber or thermoplastic of the catheter.

[00103] The fluid silicone composition may then be applied to all, or a portion, of the at least one surface of the rubber substrate. The fluid silicone composition may be applied by any convenient means, such as dipping, spraying, or drawing the rubber article through a solution or dispersion of the fluid silicone composition at a rate sufficiently slow to allow uniform coating of the composition on the rubber substrate. Optionally, the vehicle may be removed, if a vehicle is present in the composition, for example by allowing the vehicle to evaporate under ambient conditions or with heating. The fluid silicone composition may then be cured by exposure to moisture to form the elastomeric silicone. Curing may be
performed by any convenient means, such as exposure to atmospheric moisture or submersion in water, with or without heating, thereby curing the composition to form the elastomeric silicone. The steps of applying the fluid silicone composition to the rubber substrate, optionally removing the vehicle, and curing the composition to form an elastomeric silicone may each independently be repeated one or more times, for example, if a thicker coating is desired.

EXAMPLES

[00104] The examples provided below are intended to illustrate some embodiments of the invention and should not be interpreted as limiting the scope of the invention set forth in the claims. Reference examples should not be deemed to be prior art unless so indicated.

Reference Example 1

[00105] Multiple part composition samples were prepared as follows. A base part was prepared by combining about 0.09 weight part dimethylvinyl-siloxy terminated poly(dimethyl/methylvinyl)siloxane, about 1 weight part amorphous silica, about 9 weight parts hydroxyl-terminated polydimethylsiloxane, and about 89 weight parts hexamethyldisiloxane. A cure package, or catalyst part (which generally includes a crosslinker and a catalyst), was prepared by mixing about 44 weight parts methyltriacetoxysilane, about 49 weight parts ethyltriacetoxysilane, and about 1 weight part of a catalyst. This catalyst part was used in the examples below. Also in the examples below, the catalyst was a metal-ligand complex, as shown in the table below. Dibutyl tin diacetate was used in the comparative examples.

Example 1

[00106] A Ti-ligand complex was prepared by mixing a solution of about 0.16 g of titanium (IV) isopropoxide (about 0.56 mmole) in about 10 ml toluene with about 0.074 g (about 0.56 mmole) of a ligand of formula: \[ \text{O} - \text{O} \]. The final solution was heated at about 75° C for about 2 hours. The solution was evacuated with a mechanical pump to remove volatiles.

Example 2

[00107] A Ti-ligand complex was prepared by mixing a solution of about 0.16 g of titanium (IV) isopropoxide (about 0.56 mmole) in about 10 ml toluene with about 0.150 g (about 1.15 mmole) of a ligand of formula: \[ \text{O} - \text{O} \]. The final solution was heated at 75° C for about 2 hours. The solution was evacuated with a mechanical pump to remove volatiles.
Example 3

[00108] A Fe-ligand complex was prepared by mixing about 100 ml of about 0.05 M Fe(2-ethylhexanoate)₃, which was made from about 4.848 g of about 50 wt % Fe(2-ethylhexanoate)₃ in mineral spirit (purchased from Alfa Aeras, Ward Hill, MA) (about 5 mmole) and about 95 ml toluene, with about 1.282 gm (about 10 mmole) of a ligand of

The final solution was heated at about 75°C for about 2 hour with agitation. The solution was evacuated with a mechanical pump to remove toluene.

Example 4

[00109] The complex of Example 1 was used in the formulation of Reference Example 1. The base part and the curing agent part were mixed at an about 50:1 ratio (weight basis). The resulting mixture was coated on a substrate by dip coating. The resulting mixture was cured by drying in ambient conditions.

Example 5

[00110] The complex of Example 2 was used in the formulation of Reference Example 1. The base part and the curing agent part were mixed at an about 50:1 ratio (weight basis). The resulting mixture was coated on a substrate by dip coating. The resulting mixture was cured by drying in ambient conditions.

Comparative Example 6

[00111] Dibutyl tin diacetate was used in the formulation of Reference Example 1. The base part and the curing agent part were mixed at an about 50:1 ratio (weight basis). The resulting mixture was coated on a substrate by dip coating. The resulting mixture was cured by drying in ambient conditions.

Industrial Applicability

[00112] Without wishing to be bound by theory, it is thought that a rubber article, such as the catheter, of this invention may cause less tissue irritation and/or allergic reaction than an uncoated catheter or a catheter coated with a different coating than the silicone described herein. The silicone may provide the benefits of not easily delaminating from the catheter and/or migrating into the body.

[00113] While the invention is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the examples and described in detail herein. It should be understood, however, that the invention is not intended to be limited to the particular forms disclosed. Rather, the invention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.
Claims:

1. A method of making a fluid silicone composition comprising combining:
   (A) a catalytic quantity of at least one catalytically active condensation reaction catalyst including a metal-ligand complex, wherein the complex comprises a reaction product of
      (i) a metal precursor having the general formula: M-Aₐ, where M is a metal selected from Fe, Ti, and Zr, each A is an independently displaceable group, and subscript a is an integer representing the valence of the metal selected for M, and
      (ii) a ligand of formula \( A^2 \), where \( A^1 \) is selected from an alkyl group, an aryl group, and an alkoxy group, and each \( A^2 \) is selected from an alkyl group and an aryl group;
   (B) 100 parts of at least one polyorganosiloxane having an average per molecule of two or more hydrolyzable substituents, a silicone resin, or a combination thereof;
   (C) an amount of an acetoxysilane crosslinker sufficient to crosslink ingredient (B);
   (D) optionally, a filler;
   (E) optionally, a vehicle;
   (F) optionally, a bioactive agent;
   (G) optionally, a filler treatment;
   (H) optionally, an excipient; and
   (I) optionally, other additives.

2. The method of claim 1, wherein the ligand is selected from

   \[
   \begin{align*}
   &\text{and } \quad \text{and }
   \end{align*}
   \]

3. The method of any one of claims 1 to 2, wherein each A is independently selected from a monovalent organic group including a monovalent hydrocarbon group, an amino group, a silazane group, a carboxylic ester group, a hydrocarbonoxy group, an alkyl group, or any combination thereof.

4. The method of any one of claims 1 to 3, wherein the hydrolyzable substituents of ingredient (B) are included in groups of the following formula:
wherein each D independently represents an oxygen atom, a divalent organic group, a
divalent silicone organic group, or a combination of a divalent hydrocarbon group and a
divalent siloxane group, each X independently represents a hydrolyzable substituent, each R
independently represents a monovalent hydrocarbon group or an alkyl group, each subscript
c is independently 0, 1, 2, or 3, each subscript a is independently 0, 1, or 2, subscript b has a
value of 0 or greater, and wherein the sum of (a + c) is at least 1.

5. The method of any one of claims 1 to 4, wherein ingredient (B) includes a
polydiorganosiloxane of the formula

\[
\begin{align*}
&D = \left[ \begin{array}{ccc}
R_{2-a}^2 & R_{3-c}^2 & X_a^b \\
\text{Si} & \text{O} & \text{Si} & \text{X}_c \\
\end{array} \right] \\
\end{align*}
\]

wherein each R independently is a hydrolyzable substituent, each R is independently a
monovalent organic group, each R is independently an oxygen atom or a divalent
hydrocarbon group, each subscript d is independently 1, 2, or 3, and subscript e has a value ranging from 1 to 200,000.

6. The method of any one of claims 1 to 4, wherein ingredient (B) includes a silicone
resin comprising siloxane units of the formula

\[
R^{29}wR^{3}(3-w)SiO_{v/2} \text{ and } SiO_{4/2},
\]

where R and R are monovalent organic groups, and each subscript w is independently 0, 1, or 2.

7. The method of any one of claims 1 to 4, wherein ingredient (B) includes a silicone
resin comprising a silsesquioxane resin.

8. The method of any one of claims 1 to 7, wherein ingredient (D) includes amorphous
silica, fume silica, silica aerogel, silica xerogel, precipitated silica, crushed quartz, aluminum
oxide, magnesium oxide, calcium carbonate, zinc oxide, talc, diatomaceous earth, iron
oxide, clays, mica, chalk, titanium dioxide, zirconia, sand, carbon black, graphite, or any combination thereof.

9. The method of any one of claims 1 to 8, wherein ingredient (E) includes a solvent, a diluent, a polyorganosiloxane, a trimethylsiloxy-terminated polydimethylsiloxane, or any combination thereof.

10. The method of any one of claims 1 to 9, further comprising:
   (i) applying the composition of claim 1 to a surface of a rubber article, and
   (ii) curing the composition to form an elastomeric silicone.

11. A rubber article comprising:
   (i) a rubber substrate having a surface, and
   (ii) an elastomeric silicone on at least a portion of the surface of the rubber substrate, where the elastomeric silicone is prepared by the method of claim 10.

12. A Foley catheter comprising:
   a tube having an outer surface, a first end, and an opposing second end, the tube including a first and second lumen running through its length, each of the first and second lumens having an inner surface, the first lumen being open at the first and second ends of the tube, the second lumen having a valve at the first end; and
   a balloon positioned near the second end of the tube,
   wherein at least one of the outer surface of the tube, the inner surface of the first lumen, and the inner surface of the second lumen is at least partially coated with the elastomeric silicone prepared by the method of any one of claims 10 to 11.

13. A fluid silicone composition produced by the method of any one of claims 1 to 9.

14. A fluid silicone composition comprising:
   (A) 100 parts of at least one polyorganosiloxane having an average per molecule of two or more hydrolyzable substituents, a silicone resin, or a combination thereof;
   (B) an amount of an acetoxyisilane crosslinker sufficient to crosslink ingredient (A);
   (C) optionally, a filler;
   (D) optionally, a vehicle; and
   (E) optionally, a bioactive agent,
wherein the composition is prepared using a catalytic quantity of at least one catalytically active condensation reaction catalyst comprising a metal-ligand complex, wherein the complex comprises a reaction product of:

(i) a metal precursor having the general formula: M-A\textsubscript{a}, where M is a metal selected from Fe, Ti, and Zr, each A is independently a monovalent organic group, and subscript a is an integer with a value ranging from 2 to 3, and

(ii) a ligand of formula \[
\begin{array}{c}
\text{A}^2 \\
\text{A}^1 \\
\end{array}
\], where A\textsubscript{1} is selected from an alkyl group, an aryl group, and an alkoxy group, and each A\textsubscript{2} is selected from an alkyl group and an aryl group.

15. A rubber article comprising:

(i) a rubber substrate having a surface, and

(ii) a coating on at least a portion of the surface of the rubber substrate, where the coating includes the composition of claim 14.
### INTERNATIONAL SEARCH REPORT

**International application No**

PCT/US2013/029058

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A. **CLASSIFICATION OF SUBJECT MATTER**

**INV. C08G77/18 C08L83/04**

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

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B. **FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C08G C08L

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

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C. **DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>A</td>
<td>page 16, line 35 - line 37; claims; examples 5, 6 &amp; US 2013/102720 AI (IRELAND TANIA [FR]) 25 April 2013 (2013-04-25)</td>
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X See patent family annex.

**Further documents are listed in the continuation of Box C.**

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Date of the actual completion of the international search

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Name and mailing address of the ISA:

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Kolitz, Roderich

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