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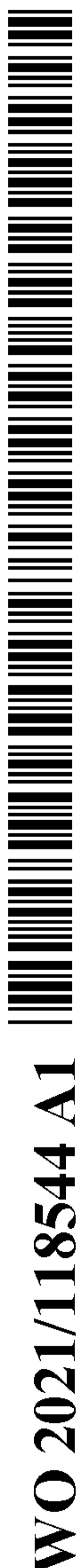
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(54) Title: ALKOXY GROUP-CONTAINING SILICONES WITH REACTIVE FUNCTIONAL GROUPS OF DEFINED REACTIVITY

(57) Abstract: Organopolysiloxanes with reactive functional groups which dominate reactivity of the organopolysiloxane are prepared by a cohydrolysis involving alkoxy-functional silanes or siloxanes and hydroxyl-functional reagents, such that the resulting polymers contain less than 10 weight percent of unreacted alkoxy groups, and a ratio of non-reactive groups to silicon of greater than 1:1.



**ALKOXY GROUP-CONTAINING SILICONES WITH REACTIVE FUNCTIONAL
GROUPS OF DEFINED REACTIVITY**

5 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention pertains to reactive organopolysiloxanes (silicones) bearing alkoxy
10 groups, and reactive functional groups which dominate the overall reactivity of the reactive
silicone. The reactive silicones are prepared through hydrolytic condensation of hydrolyzable
precursors. The invention further pertains to curable compositions containing the reactive
organopolysiloxanes, and to their use, particularly in coatings and encapsulants.

15 2. Description of the Related Art

Silicones having reactive organic functional groups such as hydroxyalkyl, aminoalkyl,
isocyanatoalkyl and the like are known. Such reactive silicones may be prepared, for example,
by hydrosilylating an ethylenically unsaturated compound also bearing a desired reactive group,
20 for example allylamine or isocyanatoethylmethacrylate with a silane or polysiloxane bearing
silicon-bonded hydrogen ($\equiv\text{Si-H}$). A desirable characteristic of these reactive silicones is that
they react exclusively through the reactive organic functionality to form macromolecules having
the desired properties. However, a disadvantage is that more expensive Si-H functional
organosilicon compounds must be used to prepare them, and that ethylenically unsaturated
25 compounds bearing the desired reactive group may not be available, may not have the desired
stability, or are available at only relatively high cost.

A further disadvantage is that hydrosilylation generally employs a noble metal
hydrosilylation catalyst, generally a platinum-based catalyst, which adds to the expense. If the
30 hydrosilylation reaction is not complete, unreacted ethylenically unsaturated reactants must be
removed, *e.g.* by subjecting the product mixture to stripping or vacuum, which is not always
effective unless the temperature is raised. For some reactive groups, however, raising the

temperature is contraindicated, as the reactive functional groups may react or condense. Furthermore, if the final product contains unreacted Si-H groups, these may give rise to storage problems, especially if water is present. Reaction with water can liberate explosive hydrogen gas.

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In U.S. Patent 5,814,703, highly branched silicones having aminoalkyl, epoxyalkyl, or ethylenically unsaturated groups are prepared, not by hydrosilylation, but by hydrolytic condensation of a functional dialkoxysilane or trialkoxysilane with a non-functional dialkoxysilane or trialkoxysilane, optionally together with tetra-alkoxysilanes. These highly branched reactive silicones contain minimally 10 mol percent of "T-units," $\text{RSiO}_{3/2}$, which form branching sites. Moreover, they contain a limited amount of non-functional hydrocarbon groups relative to the number of silicon atoms. Due to these requirements and preparation method, the desired reactive functional group is accompanied by a large quantity of non-hydrolyzed alkoxy groups. These reactive silicones may be used to form hard coatings when admixed with a non-functional polymer resin, or preferably, a reactive, crosslinkable polymer resin.

It has been found, however, that reactive silicones such as those disclosed in U.S. 5,814,703, have numerous drawbacks. First, the relatively high proportion of alkoxy groups allows the silicone, once the organic reactive groups have reacted, to further crosslink in the presence of moisture, which is unavoidable in coatings and articles intended for normal use. Thus, the chemical bonds formed are only partially the result of reaction of the intended organic functional groups. "Designed reactivity" under such conditions is impossible to achieve. Moreover, under conditions of high humidity, the alkoxy groups may react even prior to reaction of the organic functional groups, decreasing mobility of the growing polymer chains to the extent that a proportion of the functional groups may remain unreacted. Furthermore, the products, particularly when used in sections thicker than thin films, show evidence of cracking, shrinkage, and voids (from outgassing of condensation reaction alcohol) which may occur even as early as during initial cure. Such compositions are completely unsuitable as encapsulants for electronic devices, for example. Finally, these reactive silicones display poor compatibility with many polymers, as a result of which a homogeneous coating composition is difficult or even impossible to obtain, or which may be subject to phase-out into silicone-rich and silicone-poor regions in the cured product.

It would be desirable to provide reactive silicone polymers by a method which avoids hydrosilylation and its disadvantages, yet provides a greater degree of defined reactivity. It would be further desirable to provide reactive silicone resins which are flexible and exhibit little tendency to crack or develop voids during cure or thereafter, and which exhibit greater compatibility with organic polymers.

SUMMARY OF THE INVENTION

It has now been surprisingly and unexpectedly discovered that if the number of non-reactive silicon-bonded organic groups in a reactive silicone is increased beyond a ratio of 1 per silicon atom, and the residual alkoxy group content is kept below 10 weight percent, that a greater degree of defined reactivity, lesser tendency to crack during or after cure, and greater compatibility with organic polymers can be simultaneously obtained. This is achieved by synthesis of the reactive silicone by careful selection of the hydrolyzable precursor reactants such that the ratio of non-functional groups to silicon in the reactive silicone polymer is greater than 1:1, and the alkoxy content is less than 10 weight percent, while having a reactive functionality greater than 2 on average per molecule, this functionality selected from among epoxy, amino, carboxylic acid, and (meth)acrylic functionalities.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The first embodiment of the present invention is a reactive organopolysiloxane prepared by hydrolytic condensation, comprising on average

- a) at least two reactive functional groups per molecule, selected from the group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof, the functional groups bonded to silicon atoms in the reactive organopolysiloxanes, and
- b) alkoxy groups, in a concentration of less than 10 weight percent based on the total weight of the reactive organopolysiloxanes calculated on the basis of methoxy groups, and
- c) non-reactive optionally substituted hydrocarbon groups Si-C bonded to silicon atoms of the reactive organopolysiloxane, the non-reactive optionally substituted hydrocarbon groups present in a ratio of >1 hydrocarbon group per atom of Si in the reactive organopolysiloxane, and

wherein the at least two reactive functional groups are introduced into the reactive organopolysiloxane by one of the following two condensation processes i) or ii)

i) condensing

5 a plurality of alkoxysilanes or their partial hydrolysates, with at least one organic compound comprising a hydroxyl group and a reactive functional group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof, and with at least one second alkoxysilane or second partial hydrolysate bearing 1, 2, or 3
10 non-reactive, optionally substituted hydrocarbon groups, or

ii) condensing

a silanol-stopped or alkoxysilyl-stopped organopolysiloxane or their partial hydrolysates, with at least one organic compound comprising a hydroxyl group and a reactive functional group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and
15 mixtures thereof, and optionally with an alkoxysilane bearing 1, 2, or 3 non-reactive, optionally substituted hydrocarbon groups.

Preferably the at least two reactive functional groups per molecule are selected from the
20 group consisting of amino, carboxy, and (meth)acrylate groups, more preferably from acrylate and methacrylate groups. Preferably, the reactive functional groups are the same or of the same type of functional groups.

The second embodiment of the present invention is a curable composition, comprising

25 A) at least one of the above mentioned reactive organopolysiloxanes, and a catalyst effective to cause polymerization of the respective reactive functional groups,

or

30 B) at least one of the above mentioned reactive organopolysiloxanes, and at least one curing agent bearing complementary reactive functional groups reactive with the reactive functional groups of the above mentioned reactive organopolysiloxanes,

- and optionally a catalyst effective to catalyze the reaction of the reactive functional groups with the complementary reactive functional groups; or
- C) at least a first of the above mentioned reactive organopolysiloxanes, and at least a second at least one of the above mentioned reactive organopolysiloxanes bearing complementarily reactive functional groups reactive with the reactive functional groups of the first reactive organopolysiloxane, and optionally a catalyst effective to catalyze the reaction of the reactive functional groups of the first reactive organopolysiloxanes with the second reactive organopolysiloxane.

In a preferred embodiment the curable composition comprising at least one reactive organopolysiloxane with acrylate and/or methacrylate groups and

- i) further comprising a free radical initiator effective to polymerize the (meth)acrylate groups,
- or
- ii) further comprising an Si-H functional crosslinker and an effective amount of a hydrosilylation catalyst.

The third embodiment of the present invention is the process for the preparation of the above mentioned reactive organopolysiloxane comprising on average

a) at least two reactive functional groups per molecule, selected from the group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof, the functional groups bonded to silicon atoms in the reactive organopolysiloxanes, and

b) alkoxy groups, in a concentration of less than 10 weight percent based on the total weight of the reactive organopolysiloxanes calculated on the basis of methoxy groups, and

c) non-reactive optionally substituted hydrocarbon groups Si-C bonded to silicon atoms of the reactive organopolysiloxane, the non-reactive optionally substituted hydrocarbon groups present in a ratio of >1 hydrocarbon group per atom of Si in the reactive organopolysiloxane, and

wherein the at least two reactive functional groups are introduced into the

reactive organopolysiloxane by one of the following two condensation processes i) or ii)

i) condensing

a plurality of alkoxy silanes or their partial hydrolysates,

with at least one organic compound comprising a hydroxyl group and a reactive functional group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof,

and with at least one second alkoxy silane or second partial hydrolysate bearing 1, 2, or 3 non-reactive, optionally substituted hydrocarbon groups,

or

ii) condensing

a silanol-stopped or alkoxy silyl-stopped organopolysiloxane or their partial hydrolysates,

with at least one organic compound comprising a hydroxyl group and a reactive functional group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof,

and optionally with an alkoxy silane bearing 1, 2, or 3 non-reactive, optionally substituted hydrocarbon groups.

The reactive silicones of the present invention are prepared by the cohydrolytic condensation of hydroxy bearing reagents bearing reactive epoxy, amino, carboxylic acid, or (meth)acrylic groups with silanol or alkoxy functional polysiloxanes and silanes bearing non-functional groups. The usage of hydroxy terminated reagents facilitates a low alkoxy content, less than 10 weight percent calculated as methoxy groups based on the total weight of the reactive silicone, preferably less than 9 weight percent, and preferably also in the range of 1 to 8 weight percent, more preferably 2 to 8 weight percent, and also 2 to 7 weight percent, and more than 1 non-functional group per silicon atom, on average, in the reactive silicone, more preferably on average 1.1 to 1.5 non-functional groups per silicon atom. If other than methoxy groups are present, the appropriate weight percent are calculated as if the alkoxy groups present were methoxy groups.

Another advantage of the use of hydroxy bearing reagents is that it allows the direct condensation of the functional group containing reagent to the siloxane. Prior art using alkoxy silanes and alkoxy siloxanes requires an intermediate hydrolysis step of some of these alkoxy groups for the condensation reaction to proceed. This hydrolysis step can be unpredictable and lead to the undesirable self-condensation of some of the reaction components.

Most preferably, the reactive functional groups are supplied by hydrolytic condensation of a hydroxy bearing reagents bearing the desired functional group, for example 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 4-hydroxybutyl acrylate, when, for example an acrylate group is the desired functionality. Hydroxy bearing epoxy, amino, carboxylic acid, methacrylate, ethylacrylate, and other alkylacrylate reagents may be used in analogous fashion to prepare the respective functional silicones. Also, preferably, an alkoxysilane or alkoxypolysiloxane bearing non-functional groups, most preferably an alkoxypolysiloxane, optionally together with an alkoxysilane, is used to provide the non-functional groups.

15

By "non-functional" group is meant an organic group R with little or no reactivity under expected preparation conditions, and subsequently under curing conditions. Such groups include, but are not limited to, Si-C bonded, optionally substituted hydrocarbon groups, examples of which are alkyl groups, alkenyl groups (when the reactive group is other than a (meth)acrylic group), aryl groups, aralkyl groups, and alkaryl groups, where the alkyl groups may be linear or branched or cyclic. "Non-functional" groups do not include Si-O bonded alkoxy groups, Si-N bonded nitrogen-containing groups, and silicon-bonded halogen.

20

Suitable R groups are, for example, linear alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, octadecyl, *etc.*, branched alkyl groups such as 2-butyl, and ethylhexyl; cycloalkyl groups such as cyclopentyl, cyclohexyl, methylcyclohexyl, and cyclohexylmethyl; alkenyl groups such as vinyl, ω -hexene, and allyl, preferably vinyl; aryl groups such as phenyl and naphthyl; alkaryl groups such as tolyl and xylyl; and arylalkyl groups such as benzyl, and the α - and β - phenylethyl groups. This list is non-limiting.

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Examples of substituted non-reactive groups are halo-substituted hydrocarbon groups such as fluorinated and chlorinated hydrocarbon groups, for example, perfluoropropyl,

chloropropyl, chloroethyl, o-, m-, and p-chlorophenyl, and the like, and hydrocarbon groups substituted with cyano groups, hydroxyl groups or alkoxy groups (including polyoxyalkylene groups).

5 The reactive silicones of the present invention contain M units, D units, optionally T units, and optionally Q units, defined as follows:



10 where a, b, and c are each 0 to 3 and the sum of a+b+c is 3;



where a, b, and c are each 0 to 2 and the sum of a+b+c is 2;

15



where a, b, and c are 0 or 1 and the sum of a+b+c is 1; and

20



In these formulae, R is a non-reactive group as previously defined, R¹ is a reactive functional group which contains an epoxy group, amino group, carboxylic acid group, or (meth)acrylate group in each case Si-O bonded to silicon; and OR² is an Si-O bonded alkoxy group, R² being the same as R.

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The reactive silicones may thus be described as



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where M, D, T, and Q are defined as above, where M is such that all chain ends are terminated with M groups, n is 1 to 10,000, preferably 2 to 1000, and more preferably 2 to 100, o is 0 to

100, preferably 1 to 20, and most preferably 2 to 15; and p is 0 to 10, preferably 0 to 5, and more preferably 0 to 3. Most preferably, the silicones contain no Q units, or only those present as an unavoidable consequence of the hydrolytic condensation. On average, each molecule contains at least two reactive functional groups R¹, and the proportion of alkoxy groups, calculated on the basis of methoxy groups, is less than 10 weight percent. By (meth)acrylic group is meant an acrylate or methacrylate bound to the organopolysiloxane.

The reactive organopolysiloxanes are generally liquids, for example with a viscosity of 50 cps to 10⁶ cps, more preferably 100 cps to 10⁵ cps, and may be described as lightly to moderately branched organopolysiloxanes, but can be described as silicone resins, which are highly branched, network like polymers dominated by T and Q groups, and which are generally solids.

The reactive organopolysiloxanes of the present invention are prepared by condensation of hydroxy bearing reagents containing the desired functional group, with alkoxy-functional reactants, optionally also with Si-OH functional polymers. Any suitable method of preparation may be used, but two methods are preferably used. In the first of these methods, which may be termed an *ab initio* synthesis, the principle reactants are silanes, optionally also using alkoxy-rich partial hydrolysates of these silanes, along with a hydroxyl bearing reagent bearing the desired epoxy, anhydride, amino, carboxylic acid, or (alkyl)acrylate group. Each silane contains at least one condensable group, preferably a lower alkyl alkoxy group, more preferably methoxy, ethoxy, or butoxy groups, or mixtures of these.

Hereafter, the synthesis will be illustrated for acrylate and methacrylate group-containing reactive organosiloxanes, employing acrylate and methacrylate group-containing reactants, *i.e.* those containing A_{(m)a} groups, and more particularly A'_{(m)a}-B-groups as hereafter defined. However the synthetic methods are equally applicable for epoxy group-containing reactive organopolysiloxanes where A_{(m)a} and A'_{(m)a}-B- are replaced by E and E'-B respectively, amino group-containing reactive organopolysiloxanes where A_{(m)a} and A'_{(m)a}-B- are replaced by A and A'-B-, carboxy group-containing reactive organopolysiloxanes where A_{(m)a} and A'_{(m)a}-B- are replaced by Ac and Ac'-B, respectively. It is noted that unless extreme care is taken with respect to reaction conditions, particularly pH, it is generally impossible to prepare reactive

organopolysiloxanes containing more than one type of reactive functionality selected from epoxy, amino, and carboxylic, since these groups are generally inter-reactive.

5 Examples of hydroxyl bearing acrylates as listed previously 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 4-hydroxybutyl acrylate, etc.

Suitable hydroxy bearing alkylacrylates include 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 4-hydroxybutyl methacrylate, and corresponding hydroxyalkylated ethyl, propyl, and butyl acrylates.

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Suitable hydroxyl bearing epoxies include glycidol.

Suitable hydroxyl terminated amino reagents include 3-amino-1-propanol, 4-amino-1-butanol, 5-amino-1-pentanol, 6-amino-1-hexanol, etc.

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Suitable hydroxyl bearing carboxylic acids include, for example, 3-hydroxypropanoic acid, 2-hydroxybutanoic acid, 6-hydroxyhexanoic acid, 8-hydroxyoctanoic acid, 9-hydroxynonanoic acid, 10-hydroxydecanoic acid, 11-hydroxyundecanoic acid, and others.

20

In addition to the functional silanes bearing E, A, Ac or A_{(m)n} groups, non-functional silanes are also used. These are preferably conventional mono-, di-, tri-, and tetra-alkoxysilanes having the formula



25 where R and R² are as previously defined, and e is 0, 1, 2, or 3. Examples include alkyltrimethoxysilanes, dialkyldimethoxysilanes, and trialkylmethoxysilanes, and their ethoxy analogs; phenyltrimethoxysilane, phenylmethyldimethoxysilane, diphenyldimethoxysilane, diphenylmethoxysilane, phenyldimethylmethoxysilane and their ethoxy analogs, and the like. For increased compatibility with relatively non-polar substances, for example in coatings containing relatively non-polar reactive or non-reactive polymers, the alkyl groups in the
30 alkylalkoxysilanes may be long chain alkyl groups or cycloalkyl groups such as C₆-C₂₀ alkyl

groups, preferably C₈₋₁₈ alkyl groups, and C₅₋₂₀ cycloalkyl groups such as cyclohexyl, methylcyclohexyl, cyclohexylmethyl, norbornyl, and the like. Aryl groups such as naphthyl, anthryl, *etc.* may be present, as well as aryl group-containing compounds such as biphenyl, 4-(phenylmethyl)phenyl, and the like.

5

The trialkoxysilanes and tetraalkoxysilanes such as tetraethoxysilanes and tetramethoxysilane may be used to impart branching. As indicated previously, highly branched structures are not preferred, as these are generally of high viscosity or are solids, and as the large number of siloxane bonds may make it impossible to achieve a ratio of non-functional groups to silicon of more than 1:1. However, some of the multi-alkoxy functional compounds may remain in part uncondensed, for example at the polymer termini or along the polymer chain as alkoxy groups.

To increase the ratio of non-functional R groups to silicon, the molar amounts of trialkoxy and tetraalkoxysilanes are reduced, and the amounts of dialkoxysilanes and monoalkoxysilanes are correspondingly increased. The silane mixture is condensed, in one or a plurality of steps, by addition of water, generally with the aid of an acidic or basic condensation catalyst such as an alkali metal hydroxide. Methods and conditions of condensation of silanes are well known in the art. Liberated alcohol is removed, for example as an overhead, and the amount of water collected, *e.g.* in a cooled condenser, may be used to assess the progress of condensation. Adding greater amounts of water will result in a greater degree of condensation, higher molecular weight, and a reduction in residual alkoxy group content, and the reverse is also true.

When plural steps are used in the synthesis, one or more of the silanes may be partially hydrolyzed to produce an alkoxy-rich intermediate product, which can then be further reacted (hydrolyzed) by itself or with addition of the same or other silanes. Such multistep addition can be used to tailor the polymer structure, and to some degree, the location of the reactive functional groups in the final polymer structure.

30

In the second preparation method, which is preferred, a preformed, alkoxy-functional organopolysiloxane is employed. This preformed organopolysiloxane may be, for example, a

partial hydrolysate of one or more starting silanes. The remaining hydroxy bearing reagent, silanes, water, and catalyst, when required, are added, and further condensation takes place onto the preformed organopolysiloxanes. This method has the advantage of employing readily available, partially condensed organopolysiloxanes having a defined structure, thus being able to more accurately synthesize desired product structures. This method is used in the Examples. Rather than an alkoxy-functional polymer, an α,ω -silanol stopped organopolysiloxanes may be used, either directly, or after reaction with an alkoxy silane to produce alkoxy silyl end groups.

The reactive organopolysiloxanes have numerous uses, for example in coatings, as molded resins, impregnants, hydrophobing compositions, encapsulants, etc. In these uses, the reactive organopolysiloxanes are generally used with a hardener, or curative, or with a curing catalyst.

A "hardener" or "curative" or "curing agent" as used herein is a compound, which may be of low molecular weight, or "monomeric," or oligomeric or polymeric, which provides complementary reactive groups with which the reactive groups of the reactive silicone react. The hardener and reactive organopolysiloxanes may each be of low functionality such that predominately linear chain extension takes place, producing a generally flexible product, or one or both of the hardener or reactive silicone may be of higher functionality such that extensive crosslinking takes place, producing a harder and generally less flexible product.

When the reactive functional group of the reactive organopolysiloxanes is the epoxy group, suitable complementary reactive groups of the hardener are, for example, hydroxyalkyl groups, isocyanate groups, anhydride groups, carboxylic acid groups, primary and secondary amino groups, phenol/formaldehyde condensates, melamine/formaldehyde condensates, and similar condensates, and the like. Such complementary reactive groups are well known in the art of epoxy resins. The hardener may be a "monomeric" organic compound of low molecular weight such as bisphenol A, ethylene glycol, methylenedianiline ("MDA"), etc., or may be oligomeric or polymeric, such as polyethyleneimines or addition polymers containing residues of acrylic acid, methacrylic acid, maleic anhydride, or the like. See, e.g. EPOXY RESINS: CHEMISTRY AND TECHNOLOGY, Clayton May, Ed., Marcel Dekker, © 1988, and HANDBOOK OF EPOXY RESINS, Henry Lee, et al., McGraw-Hill, © 1967.

For amino reactive groups, complementary reactive groups include epoxy groups, isocyanate groups, cyanate groups, anhydride groups, *etc.*, and may be of low or high molecular weight, monomeric, oligomeric, or polymeric.

5 For each of these systems, it is also possible to use a complementary reactive organopolysiloxane as the hardener. For example, a curable composition with very high silicone content can be created by using an amino-functional organopolysiloxane with either or both of an isocyanate-functional organopolysiloxane and/or an epoxy-functional organopolysiloxanes. Such systems may also contain other hardeners, and may contain a catalyst as well.

10

Suitable complementary groups for carboxy functionality include isocyanate groups, amino groups, hydroxyl groups, and the like, whereas for (meth)acrylic groups, the complementary groups may be (meth)acrylic groups or other ethylenically unsaturated groups, or Si-H functional silanes and organopolysiloxanes. The (meth)acrylic group-functional organopolysiloxanes may also be cured without a complementary-reactive crosslinker, for
15 example by free radical polymerization using standard free radical initiators such as peroxides, hydroperoxides, azo compounds, or photocatalysts. When Si-H functional crosslinkers or curing agents are used, standard hydrosilylation catalysts, particularly platinum, iridium and rhodium, and their compounds may be used and more particularly platinum and its compounds, for
20 example the Karstedt catalyst.

The term "catalyst" as used herein refers to substances which facilitate reaction but are not complementary reactive, *e.g.* the catalyst is not generally chemically bonded in the cured product, as distinguished by hardeners which do become a substantial part of the product.
25 Epoxy-functional, isocyanate-functional, and (meth)acrylate-functional systems may all be catalyzed. For epoxy systems, suitable catalysts are those known in the art, and include acids, bases, and tertiary amines, as well as a variety of metal compounds, both organic and inorganic. While amino-functional and anhydride-functional organopolysiloxanes generally require a hardener to cure, epoxy- and isocyanate-functional organopolysiloxanes may be cured
30 catalytically without use of a hardener, as may also (meth)acrylate-functional organopolysiloxanes.

The curable compositions may also contain non-reactive polymers, generally film forming polymers, and may produce homogenous cured compositions or interpenetrating polymer network compositions. By the term "non-reactive polymers" is meant polymers which have no complementary reactive groups or such a low concentration of such groups that a solid, cured composition cannot be obtained without the use of either or both of a separate hardener or catalyst. Examples of such polymers are polyvinylacetate, polyvinyl chloride, other polyvinyl ester polymers, polyacrylates, including polyacrylates with a very small proportion of residual unsaturated acrylic acid or methacrylic acid groups, polyvinyl acetals, polycarbonates, polyether sulfones, polyurethanes, polyureas, polyamides, and the like. It is preferred that the non-reactive polymers have a very minor amount of reactive groups so that despite being unable to cure the composition, the polymer becomes covalently bonded within the composition.

Along with traditional curing methods the curable compositions of the invention may also be cured using high-energy radiation from a radiation source. Many types of radiation are suitable for this purpose, for instance electron beams (E-Beam), γ -rays, X-rays, UV light such as that having wavelengths in the range from 200 to 400 nm, and visible light such as that having a wavelength of from 400 to 600 nm, i.e. "halogen light". Ultraviolet light can be generated, for example, in xenon lamps, mercury low-pressure lamps, mercury medium-pressure lamps or mercury high-pressure lamps and excimer lamps. Preferably UV light and electron beams is used.

In the embodiments cured using UV light curing photopolymerization initiators are used. Known photopolymerization initiators that may be used in the present invention, include but are not limited to 2,2-dimethoxy-1-hydroxy - cyclohexyl - phenyl - ketone, 1- [4- (2-hydroxyethoxy) - phenyl] -2-hydroxy-2-methyl-1-propan-1-one, 2-methyl-1- [4- (methylthio) phenyl] -2-morpholinopropan-1-one , 2-benzyl-2-dimethylamino-1- (4-morpholinophenyl) - butanone-1, bis (2,4,6-trimethylbenzoyl) - phenyl phosphine oxide, 2-hydroxy-1- {4- [4- (2-hydroxy-2-methyl - propionyl) - benzyl] - phenyl} -2-methyl - propane, 1,2-octanedione, 1- [4- (phenylene Thio) -, 2- (O-benzoyl oxime)], 2-hydroxy-2-methyl-1-phenyl - propane-1-one, phenylglyoxylate butyric acid methyl ester, 2,4,6-trimethyl benzoyl - diphenyl, or combinations thereof. Also phosphine oxide and the like, as long as it is able to absorb the light generated from the light source used for photocuring.

The above compounds are commercially available, IRGACURE™ 651, 184, 2959, the 907, the 369, the 379, the 819, the 127, the OXE01,02, DAROCUR™ 1173, the MBF, the TPO (manufactured by BASF Japan Co., Ltd.), ESACURE® KIP150, same TZI, same KTO46, the 1001M, the KB1, the KS300, the KL200, the TPO, the ITX, the EDB (manufactured by Japan
5 Siber Hegner Co., Ltd.), and the like.

The content of the photopolymerization initiator in the curable composition of the present invention is preferably from 0.5 to 20% by weight relative to the polymerizable compound, and more preferably from 1% to 10% by weight relative to the polymerizable compound.

10

The inventive composition may also be cured with high energy radiation, such as electron beam radiation or cobalt 60. A variety of procedures for E-beam curing are well-known. The cure depends on the specific equipment used to deliver the electron beam, and those skilled in the art can define a dose calibration model for the equipment used. However, curing of the
15 inventive composition may generally be accomplished in the range of 2 to 20 megarads. Such radiation curing may be done without initiators but accelerators, such as triallycyanurate isocyanurate may be added.

It is also possible to cure the siloxane compositions of the invention exclusively
20 thermally, in which case the addition of free-radical-forming peroxides or azo compounds (CE) is preferred. Examples of components (CE) which may be added are, preferably, lauroyl peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxides, azobisisobutyronitrile, hydroperoxides such as tert-butyl hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, p-menthane hydroperoxide, 2,5-dimethyl-2,5-dihydroperoxyhexane, 2,5-
25 dimethyl-2,5-dihydroperoxy-3-hexyne, and pinene hydroperoxide; dialkyl peroxides such as diisobutyl peroxide, di-tert-butyl peroxide, di-tert-amyl peroxide, tert-butyl cumyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)-3-hexyne, alpha,alpha'-bis(tert-butylperoxy)-di(iso butylperoxy)benzene, 1,1-bis(tertbutylperoxy)-3,3,5-trimethylcyclohexane, n-butyl 4,4'-bis(tertbutylperoxy)valerate, 2,2-
30 bis(4,4-di-tert-butylperoxycyclohexyl)propane, 2,2-bis(tert-butylperoxy)butane, and 1,1-di(tert-butylperoxy)cyclohexane; diacyl peroxides such as decanoyl peroxide, lauroyl peroxide, stearoyl peroxide, succinyl peroxide, benzoyl peroxide, p-chlorobenzoyl peroxide, o-

chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, and octanoyl peroxide; peroxy esters such as tert-butyl peroxyacetate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxy laurate, tert-butyl peroxybenzoate, di-tert-butyl diperoxyphthalate, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, tert-butylperoxymaleic acid, tert-butylperoxyisopropyl carbonate, 5 tert-butylperoxypivalate, and tert-butylperoxy neodecanoate; peroxy dicarbonates such as diisopropyl peroxydicarbonate and di-2-ethylhexyl peroxydicarbonate; and ketone peroxide.

Peroxide curing is preferably carried out at a temperature of from -70°C to 200°C, particularly preferably from -40°C to 150°C, and at the pressure of the surrounding atmosphere, 10 i.e. from 900 hPa to 1100 hPa. The surrounding atmosphere can here be air, nitrogen, xenon or another protective gas. The amount of the organic peroxide added to the inventive composition as a curing agent is usually in the range from 0.1 to 5 parts by weight per 100 parts by weight of the organopolysiloxane.

15 Curable compositions which comprise the reactive organopolysiloxanes may take numerous forms. They may contain a condensation catalyst in an amount effective to polymerize the organopolysiloxanes through a single kind of reactive group. Examples of such compositions include reactive organopolysiloxanes bearing isocyanate groups, epoxy groups, or (meth)acrylic groups.

20

The compositions may also include a reactive organopolysiloxane and a compound which reacts with the reactive functional groups of the reactive organopolysiloxanes, i.e. contains complimentary reactive groups. The compound containing the complimentary reactive groups may be a monomeric, oligomeric, or polymeric organic compound, or may be a 25 complementary reactive organosilane or oligomeric or polymeric organopolysiloxane, including silicone resins. The complimentary reactive organopolysiloxanes themselves may be a reactive organopolysiloxane as disclosed herein, or may be a non-inventive organopolysiloxane, for example one containing more than 20 weight percent alkoxy groups, or containing no alkoxy groups. One example of the latter are the commercially available aminoalkyl-functional 30 organopolysiloxanes where the amino alkyl groups may be terminal, pendant, or both terminal and pendant.

The curable compositions may also contain non-inventive organopolysiloxanes bearing the same type of reactive group as the inventive organopolysiloxane, or monomeric, oligomeric, or polymeric organic compounds bearing the same type of reactive functional group. One example of such a curable system, for example, might include as a first reactive component an inventive epoxy-functional reactive organopolysiloxane and a bisphenol A-type epoxy resin, and as a second component an aminoalkyl-functional organopolysiloxane, a di- or polyamine, or a mixture of these. Such mixtures are made possible by the inventive reactive organopolysiloxanes which have high compatibility with other purely organic or substantially purely organic compounds.

10

When catalysts are used, these are advantageously formulated as a second component. It is possible, for example, to provide the catalyst dissolved or dispersed in a suitable solvent, in an organopolysiloxane, including non-reactive organopolysiloxanes which may serve as an extender or plasticizer, in a paraffinic or naphthenic oil, or the like. In some cases, when the catalyst is activatable only at elevated temperature, or when an inhibitor is present, or in aqueous compositions where reaction takes place only after evaporation of water or after coalescence of the organic (including organosilicon) phase, the catalyst may be included in the composition, resulting in a one component system.

15

20

The curable compositions may be "neat" in the sense that they contain no solvent or are not in the form of a dispersion, e.g. an aqueous dispersion, or may be formulated with a solvent or dispersing liquid. Preferable solvents are those with a low global warming potential such as tertiary butylacetate, but conventional solvents such as alcohols, ethers, esters, paraffinic hydrocarbons, and aromatic solvents such as toluene and xylene may also be used.

25

30

The reactive organopolysiloxanes may be prepared and used as an aqueous dispersion, with or without additional ingredients. In such cases, dispersions may be prepared by using high shear mixers, generally with the aid of a surfactant. For storage stable compositions, a surfactant which does not bear complementarily reactive groups and which does not function as a catalyst is preferably selected. Anionic, cationic, and zwitterionic catalysts may be used, depending upon the nature of the reactive organopolysiloxanes, but non-ionic surfactants such as polyoxyalkylated glycols or alcohols are preferred. The curable compositions are generally two-

component compositions in which each component simultaneously does not include the reactive organopolysiloxanes and hardener or catalyst.

5 The curable compositions may include numerous additives, including antistats, fragrances, biocides, dyes, pigments, fillers, UV and/or thermal stabilizers, coalescing agents, glossing agents, flattening agents, plasticizers, electrically conducting additives such as carbon black, adhesion promoters, hydrophobing agents such as waxes, silicone oils, and fluorine-containing compounds, and other additives generally used.

10 When used as coatings, plural component compositions, particularly two component compositions are preferably employed. One component, for example, may contain the reactive organopolysiloxane and other non-reactive components such as dyes, pigments, non-reactive polymer, *etc.*, dispersed in water, and a second component may contain catalyst and/or hardener, reactive or non-reactive polymer, dyes, pigments, *etc.* The components are mixed prior to use,
15 and applied to a substrate by any suitable method, including brushing, spraying, dipping, roll coating, doctor blade coating, curtain coating, and the like, and are then allowed to dry and cure. Cure, and optionally drying, advantageously take place at elevated temperature, *e.g.* up to 350°C, preferably no more than 250°C, and yet more preferably no more than 200°C.

20 In some preferred compositions, it is desirable to reduce or eliminate the use of epoxy-functional trialkoxysilanes, and to use epoxy-functional dialkoxysilanes. It has been surprisingly and unexpectedly discovered that cured polymers prepared from inventive organopolysiloxane polymers synthesized in this way, although exhibiting reduced hardness, achieve maximum hardness faster than when the functional organopolysiloxane is prepared using trialkoxysilanes.
25 In addition, volatiles are reduced by about 33%. Such compositions are well suited for encapsulation or the preparation of thick moldings. Preferred systems of this nature include an aminoalkyl-functional organopolysiloxane free of alkoxy groups, and an inventive epoxysiloxane.

30 In the examples described below, all parts and percentages are, unless indicated otherwise, by weight. Unless indicated otherwise, the following examples are carried out at the pressure of the surrounding atmosphere, *i.e.* at about 1000 hPa, and at room temperature, *i.e.* at

about 20°C, or at a temperature which is established on combining the reactants at room temperature without additional heating or cooling. In the following, all viscosities relate to the dynamic viscosity at a temperature of 20°C and a shear rate 1 s^{-1} . The following examples illustrate the invention without having a limiting effect.

5

Examples

Examples 1-3:

Alkoxy-functional organopolysiloxane, non-functional silane, and 2-
 10 hydroxyethylacrylate are charged to a 500 ml reaction flask and blanketed with nitrogen gas. To begin hydrolytic condensation, dodecylbenzosulfonic acid was slowly added. The contents were stirred without heating for 15 minutes, following which the temperature was increased to 55°C. The reaction mixture was refluxed at 55°C until the appropriate amount of alcohol was collected in a cooled trap. The charges and product properties are reported in Table 1.

15

Table 1

	Ex. 1	Ex. 2	Ex. 3
Charge to 500 ml reaction flask			
Alkoxy functional siloxane (Wacker SILRES® IC232) ¹	283.56	286.16	
Alkoxy functional siloxane (Wacker SILRES® MSE100) ²			294.72
2-hydroxyethylacrylate	115.24		61.0
2-hydroxyethylmethacrylate		112.64	
n-octanol			43.8
Dodecylbenzosulfonic acid	1.2		0.52
p-Toluenesulfonic acid		1.2	
20% HCl (aq)			
Water			

Heat @ 55°C under partial vacuum until appropriate amount of alcohol has been collected			
-----------------------------------------------------------------------------------------	--	--	--

¹SILRES® IC232 is a methoxy-functional methyl/phenyl organopolysiloxane containing about 20 weight percent alkoxy groups, available from Wacker Chemical Corp., Adrian, Michigan.

²SILRES® MSE100 is a methoxy-functional methyl organopolysiloxane containing about 30 weight percent alkoxy groups, available from Wacker Chemical Corp., Adrian, Michigan.

5

Examples 4-10:

Following the procedure of Examples 1-3, additional reactive silicones were prepared. The starting materials and amounts, in percentage by weight, and the epoxy and alkoxy contents of the final products in weight percent are presented in Table 2.

10

Example	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
Alkoxy functional siloxane I ¹	73.97	72.43		76.74		67.63	41.07
Alkoxy functional siloxane II ²			76.74				
Silanol functional siloxane					60.47		
2-hydroxyethyl acrylate	25.98		12.84	14.59	9.29	32.11	17.83
3-glycidoxypropyltrimethoxy silane				24.07			
Glycidol			10.33				
n-Octanol							
2-hydroxyethyl methacrylate		27.49					
(Methacryloxymethyl)metalydimethoxy silane							
Catalyst	0.05	0.08	.09	.05		0.26	0.03
Toluene					30.24		41.07
Water				2.81			
Theoretical % alkoxy	4.47	4.73	4.08	9.72	0.00	0.98	2.58

Table 2

¹ Alkoxy functional siloxane I is a methoxy-functional methyl/phenyl organopolysiloxane containing 16 weight percent methoxy groups, and available as SILRES® IC232 from Wacker Chemical Corp., Adrian, Michigan.

² Alkoxy-functional siloxane II is a methoxy functional methyl organopolysiloxane having 30 weight percent methoxy groups, available as SILRES® MSE 100 from Wacker Chemical Corp., Adrian, Michigan.

³Silanol functional siloxane III is a 75% solution of a silanol-functional methyl/phenyl organopolysiloxane in xylene containing 4-7 weight percent silanol groups, and available as SILRES® SY409 from Wacker Chemical Corp., Adrian, Michigan.

Examples 11-18

Coatings were prepared from the inventive reactive silicones from Examples 4 and 5 according to Table 3 using 5 wet mil drawdown bar on untreated aluminum panels.

Table 3

		11	12	13	14	15	16	17	18
Example 4		30.0	70.0	30.0	70.0				
Example 5						30.0	70.0	30.0	70.0
HDDA ¹		50.0	10.0			50.0	10.0		
DPGDA ²				50.0	10.0			50.0	10.0
TMPTA ³		20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Speedcure 2022 ⁴		5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
D-Bulb light									
intensity	Age	König Hardness							
740 mJ/cm	Initial	80	44	78	51	84	84	84	49
	Aged 10d	75	44	58	51	86	95	96	60
500 mJ/cm	Initial	83	50	82	48	81	60	76	49
	Aged 10d	95	60	93	61	97	63	71	65
292 mJ/cm	Initial	68	34	70	36	71	57	63	47
	Aged 10d	80	51	74	52	81	53	84	60

¹ HDDA is 1,6-hexanediol diacrylate and is available from BASF.

² DPGDA is dipropylene glycol diacrylate and is available from BASF.

³ TMPTA is trimethylolpropane triacrylate and is available from BASF.

⁴ Speedcure 2022 is liquid formulated blend of photoinitiators available from Lambson.

As can be seen from the Table 3, no appreciable post-hardening was observed except when film received minimal light cure intensities. Observed “softening” is attributed to segmental siloxane bond rotation which is common with polymer matrices based on siloxane chemistry such as in self-healing coatings.

5

All films were clear and glossy, demonstrating the compatibility of these reactive siloxanes with commonly used acrylate monomers.

While embodiments of the invention have been illustrated and described, it is not intended that these embodiments illustrate and describe all possible forms of the invention. Rather, the words in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention.

15

WHAT IS CLAIMED IS:

1. A reactive organopolysiloxane prepared by hydrolytic condensation, comprising on average

5 a) at least two reactive functional groups per molecule, selected from the group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof, the functional groups bonded to silicon atoms in the reactive organopolysiloxanes, and

10 b) alkoxy groups, in a concentration of less than 10 weight percent based on the total weight of the reactive organopolysiloxanes calculated on the basis of methoxy groups, and

15 c) non-reactive optionally substituted hydrocarbon groups Si-C bonded to silicon atoms of the reactive organopolysiloxane, the non-reactive optionally substituted hydrocarbon groups present in a ratio of >1 hydrocarbon group per atom of Si in the reactive organopolysiloxane, and

wherein the at least two reactive functional groups are introduced into the reactive organopolysiloxane by one of the following two condensation processes i) or ii)

i) condensing

20 a plurality of alkoxysilanes or their partial hydrolysates, with at least one organic compound comprising a hydroxyl group and a reactive functional group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof, and with at least one second alkoxysilane or second partial hydrolysate bearing 1, 2, or 3 non-reactive, optionally substituted hydrocarbon groups, or

ii) condensing

25 a silanol-stopped or alkoxysilyl-stopped organopolysiloxane or their partial hydrolysates, with at least one organic compound comprising a hydroxyl group and a reactive functional group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof,

30

and optionally with an alkoxysilane bearing 1, 2, or 3 non-reactive, optionally substituted hydrocarbon groups.

2. The reactive organopolysiloxane of claim 1, wherein the reactive functional groups are selected from the group consisting of epoxy, acrylate and methacrylate groups.

3. The reactive organopolysiloxanes of claim 1, wherein the reactive functional groups are selected from the group consisting of acrylate and methacrylate groups.

4. A curable composition, comprising

A) at least one reactive organopolysiloxanes of claim 1 to 3, and a catalyst effective to cause polymerization of the respective reactive functional groups,

or

B) at least one reactive organopolysiloxane of claim 1 to 3, and at least one curing agent bearing complementary reactive functional groups reactive with the reactive functional groups of the reactive organopolysiloxane of claim 1 to 3, and optionally a catalyst effective to catalyze the reaction of the reactive functional groups with the complementary reactive functional groups; or

C) at least a first reactive organopolysiloxane of claim 1 to 3, and at least a second reactive organopolysiloxane of claim 1 to 3 bearing complementarily reactive functional groups reactive with the reactive functional groups of the first reactive organopolysiloxane, and optionally a catalyst effective to catalyze the reaction of the reactive functional groups of the first reactive organopolysiloxanes with the second reactive organopolysiloxane.

5. The curable composition of claim 4, comprising at least one reactive organopolysiloxane of claim 3 and

5 i) further comprising a free radical initiator effective to polymerize the (meth)acrylate groups,

or

ii) further comprising an Si-H functional crosslinker and an effective amount of a hydrosilylation catalyst.

10

6. A process for the preparation of a reactive organopolysiloxane comprising on average

15 a) at least two reactive functional groups per molecule, selected from the group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof, the functional groups bonded to silicon atoms in the reactive organopolysiloxanes, and

b) alkoxy groups, in a concentration of less than 10 weight percent based on the total weight of the reactive organopolysiloxanes calculated on the basis of methoxy groups, and

20

c) non-reactive optionally substituted hydrocarbon groups Si-C bonded to silicon atoms of the reactive organopolysiloxane, the non-reactive optionally substituted hydrocarbon groups present in a ratio of >1 hydrocarbon group per atom of Si in the reactive organopolysiloxane, and

25

wherein the at least two reactive functional groups are introduced into the reactive organopolysiloxane by one of the following two condensation processes i) or ii)

i) condensing

a plurality of alkoxy silanes or their partial hydrolyses,

with at least one organic compound comprising a hydroxyl group

30

and a reactive functional group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof,

and with at least one second alkoxy silane or second partial hydrolysate bearing 1, 2, or 3 non-reactive, optionally substituted hydrocarbon groups, or

ii) condensing

5 a silanol-stopped or alkoxy silyl-stopped organopolysiloxane or their partial hydrolysates,
with at least one organic compound comprising a hydroxyl group and a reactive functional group consisting of epoxy, amino, carboxy, and (meth)acrylate groups, and mixtures thereof,
10 and optionally with an alkoxy silane bearing 1, 2, or 3 non-reactive, optionally substituted hydrocarbon groups.

7. A coating prepared by

15 -applying a curable composition of claim 4 or 5 to a substrate in a desired thickness,
-curing the curable composition.

8. The coating of claim 7 wherein the curing is initiated via radiation from a radiation source.

20 9. The coating of claim 8 wherein the radiation is selected from UV-light and electron beams.

INTERNATIONAL SEARCH REPORT

International application No PCT/US2019/065586

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C08F283/12	C08G77/14	C08G77/16	C08G77/18	C08G77/20
	C08G77/42	C08G77/00	C08K5/00	C08K5/5415	C08K5/5425
	C08K5/5435	C08K5/544	C08L83/06	C09D183/06	C09D183/08
According to International Patent Classification (IPC) or to both national classification and IPC					

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols) C08K C08L H01L C08G C08F C09D C09J

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2010 248446 A (YOKOHAMA RUBBER CO LTD) 4 November 2010 (2010-11-04) paragraphs [0009], [0010], [0023], [0035] - [0037], [0039], [0040]; example 1	1-9
X	US 2015/267004 A1 (MCCORMACK TIMOTHY [US] ET AL) 24 September 2015 (2015-09-24) page 3, paragraph 30-31 page 4, paragraphs 37,41 examples 10-12; table 2 examples 16,17; table 3 claims 1,8,19	1-9

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search 20 August 2020	Date of mailing of the international search report 28/08/2020
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Denis, Cécile
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/065586

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 945 172 A (YAMAYA MASAOKI [JP] ET AL) 31 August 1999 (1999-08-31) column 5, lines 21-59 column 8, lines 51-57 column 9, lines 5-8 column 10, lines 58-67 examples 3,6; tables 1-1 example 9; table 2 -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

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