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(54) Title: MICROCAPSULES HAVING ENCAPSULATED CATALYSTS

(57) **Abstract:** The present invention provides processes for preparing microcapsules encapsulating a catalyst, the process comprising forming an aqueous emulsion comprising particles having the catalyst, an aqueous continuous phase, and an interface between the particles and the aqueous continuous phase; adding a water reactive silicon compound to the aqueous continuous phase; polymerizing the water reactive silicon compound at the interface of the particles and the continuous phase to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer in an aqueous medium; and removing the aqueous medium to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer and having from 0 to 1 % of water based on the weight of the microcapsules. The present invention also provides processes for curing a composition wherein the processes comprise microcapsules encapsulating catalysts, encapsulated catalyst compositions comprising microcapsules encapsulating catalysts, and one-part compositions for making hydrosilylation product free of cure inhibitors.



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MICROCAPSULES HAVING ENCAPSULTED CATALYSTS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application claims the benefit of United States Provisional Patent Application No. 62/118481 filed February 20, 2015 and European Patent Application No. 15305272.5 filed February 20, 2015.

TECHNICAL FIELD OF THE INVENTION

10 [0002] The present invention relates to encapsulated catalysts, processes for preparing the encapsulated catalysts and for curing a composition comprising the encapsulated catalyst, and one-part compositions comprising the encapsulated catalysts. More particularly, the present invention relates to microcapsules encapsulating catalysts in a shell of a silicon-based network polymer, processes for preparing the microcapsules and for curing a composition comprising the microcapsules, and one-part compositions comprising the microcapsules.

15 BACKGROUND OF THE INVENTION

[0003] Encapsulation techniques based on silicate shell having an organic core are known. International published application WO2003/066209 describes an encapsulation process by ex-situ emulsion polymerization from tetraalkoxysilanes. International published application WO2010/077774 describes microcapsules having a burst aid. In order to use encapsulated catalysts in systems that require catalysts, the microcapsules must be rigid enough to
20 withstand processing and remain stable in order not to leak out or release the catalysts prematurely. The microcapsules must be compatible and miscible in the systems. Furthermore, the microcapsules must be breakable in a controlled manner so that the catalysts can be released at the desirable time. Such release mechanisms are needed for
25 certain applications such as in coatings or adhesives in electronic and health care applications. Therefore, there still remains a need for microcapsules encapsulating catalysts that are stable and rigid and easily made compatible, but at the same time able to release the catalysts in a controlled manner.

SUMMARY OF THE INVENTION

30 [0004] The present invention provides microcapsules encapsulating catalysts in a shell of a silicon-based network polymer, processes for preparing the microcapsules and for curing a composition comprising the microcapsules, and one-part compositions comprising the microcapsules.

[0005] In one embodiment, the present invention provides processes for preparing
35 microcapsules encapsulating a catalyst, the processes comprising:

- A. forming an aqueous emulsion comprising particles having the catalyst, an aqueous continuous phase, and an interface between the particles and the aqueous continuous phase;
- B. adding a water reactive silicon compound to the aqueous continuous phase;
- 5 C. polymerizing the water reactive silicon compound at the interface of the particles and the continuous phase to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer in an aqueous medium; and
- 10 D. removing the aqueous medium to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer and having from 0 to 1% of water based on the weight of the microcapsules.

[0006] In another embodiment, the present invention provides processes for curing a composition, the processes comprising:

- 15 A. preparing microcapsules encapsulating catalysts, wherein the microcapsules comprise a core having a hydrosilylation catalyst surrounded by a shell of a silicon-based network polymer and the microcapsules have from 0 to 1% water based on the weight of the microcapsules;
- B. mixing the microcapsules with alkenyl-functional polyorganosiloxane and SiH-functional polyorganosiloxane to form a mixture;
- 20 C. rupturing the microcapsules to release the hydrosilylation catalyst by shear and/or by heating the mixture at a temperature of from 40 to 140°C; and
- D. reacting the SiH-functional polyorganosiloxane and the alkenyl-functional polyorganosiloxane in the presence of the hydrosilylation catalyst to form a cured composition.

25 **[0007]** In another embodiment, the present invention provides encapsulated catalyst compositions, the compositions comprising microcapsules comprising a core having a catalyst surrounded by a shell of a silicon-based network polymer, wherein the microcapsules have a mean diameter size from 20 nm to 100 µm and the microcapsules are impermeable to the catalyst so that the catalyst does not leak out of the microcapsules but is

30 released upon rupturing of the microcapsules, and the compositions comprise from 0 to 1% water based on the weight of the microcapsules.

[0008] In yet another embodiment, the present invention provides one-part compositions for making a hydrosilylation product, the one-part compositions comprising microcapsules encapsulating catalysts, alkenyl-functional polyorganosiloxane, and SiH-functional

35 polyorganosiloxane, optionally an additive, wherein the one-part compositions are free of cure inhibitors.

DETAILED DESCRIPTION OF THE INVENTION

[0009] All amounts, ratios, and percentages are by weight unless otherwise indicated.

[0010] The articles 'a', 'an', and 'the' each refers to one or more, unless otherwise indicated by the context of the specification.

5 [0011] The disclosure of ranges includes the range itself and also anything subsumed therein, as well as endpoints. For example, disclosure of a range of 2.0 to 4.0 includes not only the range of 2.0 to 4.0, but also 2.1, 2.3, 3.4, 3.5, and 4.0 individually, as well as any other number subsumed in the range. Furthermore, disclosure of a range of, for example, 2.0 to 4.0 includes the subsets of, for example, 2.1 to 3.5, 2.3 to 3.4, 2.6 to 3.7, and 3.8 to
10 4.0, as well as any other subset subsumed in the range.

[0012] Similarly, the disclosure of Markush groups includes the entire group and also any individual members and subgroups subsumed therein. For example, disclosure of the Markush group a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, or an alkaryl group includes the member alkyl individually; the subgroup alkyl and aryl; and any
15 other individual member and subgroup subsumed therein.

[0013] For U.S. practice, all patent application publications and patents referenced herein, or a portion thereof if only the portion is referenced, are hereby incorporated by reference to the extent that incorporated subject matter does not conflict with the present description, which would control in any such conflict.

20 [0014] The term "alternatively" indicates a different and distinct embodiment.

[0015] The term "comprises" and its variants (comprising, comprised of) are open ended.

[0016] The term "consists of" and its variants (consisting of) are closed ended.

[0017] The term "may" confers a choice, not an imperative.

[0001] The term "optionally" means is absent, or alternatively is present.

25 [0002] The term "substituted" as used in relation to another group, for example, a hydrocarbon group, means, unless indicated otherwise, one or more hydrogen atoms in the hydrocarbon group has been replaced with another substituent. Examples of such substituents include, for example, halogen atoms such as chlorine, fluorine, bromine, and iodine; halogen atom containing groups such as chloromethyl, perfluorobutyl, trifluoroethyl, and nonafluorohexyl; oxygen atoms; oxygen atom containing groups such as (meth)acrylic
30 and carboxyl; nitrogen atoms; nitrogen atom containing groups such as amines, amino-functional groups, amido-functional groups, and cyano-functional groups; sulphur atoms; and sulphur atom containing groups such as mercapto groups.

[0018] All viscosity measurements referred to herein were measured at 23°C unless
35 otherwise indicated.

[0019] The phrase “based on the weight of the emulsion” means that a component is present by weight percent relative to the combined weight of the aqueous emulsion and the water reactive silicon compound that is added to the aqueous continuous phase.

[0020] In one embodiment, the present invention provides processes for preparing

5 microcapsules encapsulating a catalyst, the processes comprising:

A. forming an aqueous emulsion comprising particles having the catalyst, an aqueous continuous phase, and an interface between the particles and the aqueous continuous phase;

B. adding a water reactive silicon compound to the aqueous continuous phase;

10 C. polymerizing the water reactive silicon compound at the interface of the particles and the continuous phase to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer; polymer in an aqueous medium; and

15 D. removing the aqueous medium to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer and having from 0 to 1% of water based on the weight of the microcapsules.

[0021] The catalyst in the aqueous emulsion may be one type of catalyst or more than one type of catalyst. The catalyst in the aqueous emulsion may be from 0.001 to 20.0 %, alternatively from 0.001 to 15.0 %, alternatively from 0.001 to 10.0 %, alternatively from
20 0.001 to 8.0 %, alternatively from 0.001 to 5.0 %, alternatively from 0.001 to 3.0 %, or alternatively from 0.001 to 1.0 % based on the weight of the emulsion.

[0022] The catalyst may be emulsified in an aqueous medium in the presence of a surfactant to form the aqueous emulsion. The surfactant may be a cationic surfactant so that the aqueous emulsion has a positive zeta-potential.

25 [0023] The water reactive silicon compound comprises at least one silicon-bonded hydrolyzable group per molecule. Alternatively, the water reactive silicon compound comprises an average of more than 2 silicon-bonded hydrolyzable groups per molecule. In one particular embodiment, the hydrolyzable group on the water reactive silicon compound may be an alkoxy group. In another embodiment, the water reactive silicon compound
30 comprises monoalkoxysilane, dialkoxysilane, alkyltrialkoxysilane wherein the alkyl group is substituted or unsubstituted, tetraalkoxysilane, or any combination thereof. In one particular embodiment, the water reactive silicon compound comprises tetraethyl orthosilicate.

[0024] Polymerizing the water reactive silicon compound at the interface of the particles and the continuous phase produces silicon-based network polymer shell around the
35 microcapsule, enclosing or encapsulating the catalyst. In one embodiment, the silicon-

based network polymer is silica or an organo-modified silica, such as, but not limited to, organo-modified silsesquioxane, alkylsilsesquioxane or aminosilsesquioxane.

[0025] In one embodiment, a catalyst for the polymerization of the water reactive silicon compound is added to the emulsion before, during or after the addition of the water-reactive silicon compound. The catalyst may be an organic tin compound. The aqueous emulsion may be passed through a high shear mixer before addition of the water-reactive silicon compound. A thickener may be added to the aqueous emulsion before addition of the tetraalkoxysilane.

[0026] The microcapsules have a mean diameter size from 20 nm to 100 μm , alternatively 1 μm to 50 μm , alternatively 1 μm to 25 μm , alternatively 1 μm to 10 μm , or alternatively 1 μm to 5 μm , or alternatively 0.5 μm to 50 μm , alternatively 0.5 μm to 25 μm , alternatively 0.5 μm to 10 μm , or alternatively 0.5 μm to 5 μm . The microcapsules may be post-treated with cationic polymer. The microcapsules in the aqueous medium may further be processed by concentrating the microcapsules; mixing the concentrated microcapsules with a solvent; and separating the microcapsules from the solvent to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer and having from 0 to 1% of water based on the weight of the microcapsules. The mixing of the concentrated microcapsules with the solvent, and separating the microcapsules from the solvent may be carried out at least one time or at least two times. The steps of concentrating and separating may be carried out by centrifugation. The solvent is one that is miscible in water and in polyorganosiloxane, such as, dipropylene glycol and glycerol.

[0027] The microcapsules comprising from 0 to 1% by weight of water may be mixed with a polyorganosiloxane, functionalized polyorganosiloxane and/or an additive. The functionalized polyorganosiloxane may be vinyl-functional polyorganosiloxane or SiH-functional polyorganosiloxane. The additive includes, but is not limited to, a filler, such as, silica, silicone resins or calcium carbonate, diluents, preservatives, freeze thaw stabilizers, or inorganic salts to buffer pH.

[0028] The microcapsules may have a payload load capacity from 1 to 99.99% by volume of the microcapsule. The payload capacity may be from 90 to 99%, or alternatively 95 to 98% by volume of the microcapsule.

[0029] The microcapsules are impermeable to the catalyst so that the catalyst does not leak out of the microcapsules. The catalyst can be released upon rupturing of the microcapsules. The catalyst may be a hydrosilylation catalyst, a condensation catalyst or a peroxide catalyst.

[0030] In one embodiment, the hydrosilylation catalyst is selected from the group consisting of platinum, ruthenium, rhodium, palladium, osmium, iridium, complexes thereof, and any combinations thereof.

[0031] In another embodiment, the present invention provides processes for curing

5 compositions, the processes comprising:

- A. preparing microcapsules encapsulating catalysts, wherein the microcapsules comprise a core having a hydrosilylation catalyst surrounded by a shell of a silicon-based network polymer and the microcapsules have from 0 to 1% water based on the weight of the microcapsules;
- 10 B. mixing the microcapsules with alkenyl-functional polyorganosiloxane and SiH-functional polyorganosiloxane to form a mixture;
- C. rupturing the microcapsules to release the hydrosilylation catalyst by shear or/and by heating the mixture at a temperature of from 40 to 140°C; and
- D. reacting the SiH-functional polyorganosiloxane and the alkenyl-functional
15 polyorganosiloxane in the presence of the hydrosilylation catalyst to form a cured composition.

[0032] In another embodiment, the present invention provides encapsulated catalyst compositions, the compositions comprising microcapsules comprising a core having a catalyst surrounded by a shell of a silicon-based network polymer, wherein the

20 microcapsules have a mean diameter size from 20 nm to 100 µm and the microcapsules are impermeable to the catalyst so that the catalyst does not leak out of the microcapsules but is released upon rupturing of the microcapsules, and the composition have from 0 to 1% water based on the weight of the microcapsules.

[0033] In another embodiment, the present invention provides one-part compositions for making a hydrosilylation product, the one-part compositions comprising the microcapsules encapsulating catalysts, alkenyl-functional polyorganosiloxane, and SiH-functional polyorganosiloxane, optionally an additive, wherein the one-part composition is free of a cure inhibitor or comprises a cure inhibitor.

[0034] In one embodiment, the present invention provides processes for preparing

30 microcapsules encapsulating a catalyst, the processes comprising a step of forming an aqueous emulsion comprising particles having the catalyst, an aqueous continuous phase, and an interface between the particles and the aqueous continuous phase; adding a water reactive silicon compound to the aqueous continuous phase; polymerizing the water reactive silicon compound at the interface of the particles and the continuous phase to obtain
35 microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer in an aqueous medium.

[0035] The core of the microcapsules, that is, the material surrounded by the shell comprising a silicon-based network polymer, is also referred to as the "oil phase." The oil phase encompasses the catalyst and any other compound, or mixture of compounds that is hydrophobic. Typically, the oil phase is liquid when forming the oil in water emulsions. The oil phase may contain any organic, silicone, or fluorocarbon based oil, or any combination thereof. The oil phase may also contain any solvent or diluent, which may be added for the purpose of solubilizing a solid hydrophobic compounds and/or the catalyst to create the liquid oil phase during formation of the aqueous emulsion.

[0036] The catalyst in the microcapsules may be released upon rupturing of the microcapsules. Rupturing of the microcapsules may be achieved by any force that breaks the shell of the microcapsule. In one embodiment, a burst aid may be added to the oil phase so that upon formation of the microcapsules the burst aid is trapped in the core. The burst aid encompasses any compound, or mixture of compounds added to the oil phase. The burst aids may be selected from volatile hydrophobic organic or siloxane compounds. The burst aid may be a volatile linear hydrocarbons, including but not limited to, pentane, hexane, heptane, octane, nonane; volatile cyclic hydrocarbons such as cyclopentane, cyclohexane, cycloheptane, cyclooctane; volatile branched hydrocarbons such as isohexane, isoheptane, isooctane, isodecane, isododecane; volatile linear siloxanes, including but not limited to, hexamethyldisiloxane, decamethyltetrasiloxane; and volatile cyclic siloxanes such as octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecylmethylcyclohexasiloxane.

[0037] Upon heating the microcapsule to a trigger temperature, the burst aid volatilizes so that the encapsulated core material is released in a temperature controlled manner. The trigger temperature may be from 40°C to 150°C, alternatively from 40°C to 130°C, alternatively from 40°C to 120°C, alternatively from 40°C to 110°C, alternatively from 40°C to 100°C, alternatively from 40°C to 100°C, alternatively from 40°C to 90°C, alternatively from 40°C to 80°C, alternatively from 40°C to 70°C, alternatively from 40°C to 60°C, alternatively from 40°C to 50°C, alternatively from 50°C to 70°C, alternatively from 55°C to 60°C, alternatively from 60°C to 95°C, alternatively from 60°C to 90°C, alternatively from 70°C to 140°C, alternatively from 75°C to 130°C, or alternatively from 75°C to 100°C.

[0038] Heating causes an increase in the vapor pressure of the burst aid, which subsequently ruptures the silicate shell to release the active material contained in the core. The amount of heat necessary will vary depending on the choice of the burst aid and thickness of the silicate shell, the composition of the core, the level of surfactant and the level of tetraalkoxysilane.

[0039] The amount of burst aid added to the oil phase, present in the microcapsules as a percentage of the oil phase weight prior to encapsulation, is from 0.1 to 50%, alternatively from 0.1 to 40%, alternatively from 0.1 to 30%, alternatively from 0.1 to 20%, alternatively from 0.1 to 10%, alternatively from 0.2 to 40%, alternatively from 0.2 to 30%, alternatively from 0.2 to 20%, or alternatively from 0.2 to 10%.

[0040] In another embodiment, the catalyst in the microcapsules may be released upon rupturing of the microcapsules after exposure to shear, such as, but not limited to, a shear rate of 1000/sec or higher.

[0041] In another embodiment, the core of the microcapsule comprises a hydrosilylation catalyst. The hydrosilylation catalyst may be present together with the burst aid in the core. The hydrosilylation catalyst may be selected from any platinum group metal-containing catalysts. By platinum group it is meant ruthenium, rhodium, palladium, osmium, iridium and platinum and complexes thereof. Platinum group metal-containing catalysts are the platinum complexes prepared as described by Willing et al., U.S. Pat. No. 3,419,593, and Brown et al., U.S. Pat. No. 5,175,325, each of which is hereby incorporated by reference to show such complexes and their preparation. Other examples of useful platinum group metal-containing catalysts can be found in Lee et al., U.S. Pat. No. 3,989,668; Chang et al., U.S. Pat. No. 5,036,117; Ashby et al., U.S. Pat. No. 3,159,601; Lamoreaux et al., U.S. Pat. No. 3,220,972; Chalk et al., U.S. Pat. No. 3,296,291; Modic et al., U.S. Pat. No. 3,516,946; Karstedt et al., U.S. Pat. No. 3,814,730; and Chandra et al., U.S. Pat. No. 3,928,629, all of which are hereby incorporated by reference to show useful platinum group metal-containing catalysts and methods for their preparation. Preferred platinum-containing catalysts include chloroplatinic acid, either in hexahydrate form or anhydrous form, and/or a platinum-containing catalyst which is obtained by a method comprising reacting chloroplatinic acid with an aliphatically unsaturated organosilicon compound such as divinyltetramethyldisiloxane, or alkene-platinum-silyl complexes, such as (COD)Pt(SiMeCl₂)₂, where COD is 1,5-cyclooctadiene and Me is methyl.

[0042] More particularly, the hydrosilylation catalyst is of the following:

pentamethylcyclopentadienyltris(acetonitrile)-ruthenium(II) hexafluorophosphate, chloroplatinic acid hydrate, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst), bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate hydrate, (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer, tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst), benzenedichlororuthenium(II) dimer, dichloro(p-cymene)ruthenium(II) dimer, benzyldienebis(tricyclohexylphosphine)dichloro-ruthenium(II) (Grubb's catalyst), pentamethylcyclopentadienyltris(acetonitrile)-ruthenium(II) hexafluorophosphate, (2,2'-bipyridine)dichloroplatinum(II), cis-bis(acetonitrile)dichloroplatinum(II), cis-

bis(benzonitrile)dichloroplatinum(II), bis(tri-tert-butylphosphine)platinum(0), chloroplatinic acid hexahydrate, chloroplatinic acid (Speier's catalyst), (1,5-cyclooctadiene)dimethylplatinum(II), cis-diamineplatinum(II) dichloride, diamminedinitritoplatinum(II), cis-dichlorobis(diethyl sulfide)platinum(II), dichlorobis(dimethyl sulfide)platinum(II) mixture of cis and trans, cis-dichlorobis(dimethyl sulfoxide)platinum(II), cis-dichlorobis(pyridine)platinum(II), cis-dichlorobis(triethylphosphine)platinum(II), trans-dichlorobis(triethylphosphine)platinum(II), cis-dichlorobis(triphenylphosphine)platinum(II), trans-dichlorobis(triphenylphosphine)platinum(II), dichloro(1,5-cyclooctadiene)platinum(II), dichloro(1,2-diaminocyclohexane)platinum(II), dichloro(dicyclopentadienyl)platinum(II), dDichloro(ethylenediamine)platinum(II), dichloro(norbornadiene)platinum(II), dichloro(1,10-phenanthroline)platinum(II), ethylenebis(triphenylphosphine)platinum(0), (ethylenediamine)iodoplatinum(II) dimer dinitrate, platinum(II) acetylacetonate, platinum(II) bromide, platinum(II) chloride, platinum(IV) chloride, platinum cobalt, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, platinum(II) iodide, platinum(IV) oxide, platinum(IV) oxide monohydrate, platinum-ruthenium alloy, platinum(0)-2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane complex, potassium hexachloroplatinate(IV), potassium trichloro(ethylene)platinate(II) hydrate, sodium hexahydroxyplatinate(IV), tetraammineplatinum(II) chloride, tetraammineplatinum(II) hydroxide hydrate, tetraammineplatinum(II) nitrate, tetrabutylammonium hexachloroplatinate(IV), tetrakis(triphenylphosphine)platinum(0), (N,N,N'-trimethylethylenediamine)platinum(II) chloride, trimethyl(methylcyclopentadienyl)platinum(IV), or any combination thereof.

[0043] In one embodiment, the oil phase is mixed with an aqueous solution of a surfactant. The surfactant may vary, but typically is chosen from those surfactants that enhance the formation of the aqueous emulsion. The surfactant in the aqueous emulsion may be present from 0.01 to 10.0 %, alternatively 0.01 to 8.0 %, alternatively 0.01 to 5.0 %, alternatively 0.01 to 3.0 %, alternatively 0.01 to 1.0 %, alternatively 0.01 to 0.5 %, alternatively 0.1 to 0.5 % by weight of the emulsion.

[0044] In one particular embodiment, a cationic surfactant is used to form the aqueous emulsion, wherein the aqueous emulsion comprises a positive zeta-potential. The cationic surfactant in the aqueous emulsion may be present from 0.01 to 10.0 %, alternatively 0.01 to 8.0 %, alternatively 0.01 to 5.0 %, alternatively 0.01 to 3.0 %, alternatively 0.01 to 1.0 %, alternatively 0.01 to 0.5 %, alternatively 0.1 to 0.5 % by weight of the aqueous emulsion.

[0045] Cationic surfactants useful in the present invention include, but are not limited to, alkylamine salts, quaternary ammonium salts, sulphonium salts, phosphonium salts, quaternary ammonium hydroxides such as octyl trimethyl ammonium hydroxide, dodecyl trimethyl ammonium hydroxide, hexadecyl trimethyl ammonium hydroxide, octyl dimethyl

benzyl ammonium hydroxide, decyl dimethyl benzyl ammonium hydroxide, didodecyl dimethyl ammonium hydroxide, dioctadecyl dimethyl ammonium hydroxide, tallow trimethyl ammonium hydroxide and coco trimethyl ammonium hydroxide as well as corresponding salts of these materials; fatty amines and fatty acid amides and their derivatives; basic
5 pyridinium compounds; quaternary ammonium bases of benzimidazolines; and polypropanolpolyethanol amines. A preferred cationic surfactant is cetyl trimethyl ammonium chloride.

[0046] Further examples of cationic surfactant include, but are not limited to, an amphoteric surfactant such as cocamidopropyl betaine, cocamidopropyl hydroxysulfate, cocobetaine,
10 sodium cocoamidoacetate, cocodimethyl betaine, N-coco-3-aminobutyric acid, imidazolinium carboxyl compounds, imidazoline compounds, alkylaminoacid salts, betaines, N-alkylamidobetaines and derivatives thereof, proteins and derivatives thereof, glycine derivatives, sultaines, alkyl polyaminocarboxylates and alkylamphoacetates, and mixtures thereof.

[0047] The above surfactants may be used individually or in combination. The cationic or amphoteric surfactant is dissolved in water and the resulting aqueous solution used as a component in aqueous or continuous phase of the aqueous emulsion.

[0048] Although not wishing to be bound by any theory, the present inventors believe the use of a cationic or amphoteric surfactant promotes condensation and polymerisation of the
20 tetraalkoxysilane at the interface of the emulsified droplets comprising the catalyst, leading to non-diffusive microcapsules. The tetraalkoxysilane hydrolyzes and condenses upon reacting in the emulsion. The anionically charged hydrolysis product is attracted to the cationic or amphoteric surfactant at the interface where it forms the silicon based polymer shell.

[0049] In one embodiment, the concentration of the cationic surfactant during the formation of the aqueous emulsion may be between 0.1% and 0.3% by weight of the oil phase. The use of cationic or amphoteric surfactant during emulsification of the oil phase to provide a positive charge and/or the hydrolysis reaction of the water reactive silicon compound comprising a alkoxysilane and/or incorporation into the shell leads to microcapsules which
30 are more resistant to diffusion or leaching of the oil phase from the microcapsules.

[0050] The aqueous solution of the cationic or amphoteric surfactant may contain additional and/or optional components, providing they are water soluble. For example a water-miscible organic solvent such as an alcohol or lactam may be added. Such components include, but is not limited to, surfactants, thickeners, preservatives, and antimicrobials.

[0051] Additional surfactants include, but are not limited to, nonionic surfactants. Nonionic surfactants includes, but are not limited to, polyoxyalkylene alkyl ethers such as polyethylene

glycol long chain (12-14 carbon atoms) alkyl ether, polyoxyalkylene sorbitan ethers, polyoxyalkylene alkoxyate esters, polyoxyalkylene alkylphenol ethers, ethylene glycol propylene glycol copolymers, polyvinyl alcohol and alkylpolysaccharides. The

alkylpolysaccharides may have the formula $R^1-O-(R^2O)_m-(G)_n$ wherein R^1 represents a

5 linear or branched alkyl group, a linear or branched alkenyl group or an alkylphenyl group, R^2 represent an alkylene group, G represents a reduced sugar, m denotes 0 or a positive integer and n represent a positive integer. Specific examples of alkylpolysaccharides are described in U.S. Patent No. 5,035,832.

[0052] Further examples of nonionic surfactants include, but are not limited to, condensates

10 of ethylene oxide with long chain fatty alcohols or fatty acids such as a C12-16 alcohol,

condensates of ethylene oxide with an amine or an amide, condensation products of ethylene and propylene oxide, esters of glycerol, sucrose, sorbitol, fatty acid alkylol amides, sucrose esters, fluoro-surfactants, fatty amine oxides, and mixtures thereof. Further

examples of nonionic surfactants include polyoxyethylene fatty alcohols such as

15 polyoxyethylene (23) lauryl ether, polyoxyethylene (4) lauryl ether; ethoxylated alcohols such as ethoxylated trimethylnonanol, C₁₂-C₁₄ secondary alcohol ethoxylates, ethoxylated, C10-

Guerbet alcohol, ethoxylated, iso-C13 alcohol; poly(oxyethylene)-poly(oxypropylene)-

poly(oxyethylene) tri-block copolymer (also referred to as poloxamers); tetrafunctional poly(oxyethylene)-poly(oxypropylene) block copolymer derived from the sequential addition

20 of propylene oxide and ethylene oxide to ethylene diamine (also referred to as poloxamines),

silicone polyethers, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenol ethers, polyoxyethylene lauryl ethers, straight-chain, primary alcohol alkoxyates, straight-chain secondary alcohol alkoxyates, alkyl phenol alkoxyates, olefinic alkoxyates, branched chain alkoxyates, polyoxyethylene sorbitan monoleates, polyoxyethylene alkyl esters,

25 polyoxyethylene sorbitan alkyl esters, polyethylene glycol, polypropylene glycol, diethylene glycol, ethoxylated trimethylnonanols, polyoxyalkylene-substituted silicones (rake or ABn types), silicone alkanolamides, silicone esters, silicone glycosides, dimethicone copolyols,

fatty acid esters of polyols, for instance sorbitol or glyceryl mono-, di-, tri- or sesquioleates or stearates, glyceryl or polyethylene glycol laurates; fatty acid esters of polyethylene glycol

30 (polyethylene glycol monostearate or monolaurate); polyoxyethylenated fatty acid esters

(stearate or oleate) of sorbitol; polyoxyethylenated alkyl (lauryl, cetyl, stearyl or octyl)ethers, and mixtures thereof.

[0053] When mixtures containing nonionic surfactants are used, one nonionic surfactant

may have a low Hydrophile-Lipophile Balance (HLB) and the other nonionic surfactant(s)

may have a high HLB, such that the nonionic surfactants have a combined HLB of 11 -15, alternatively a combined HLB of 12.5-14.5.

[0054] The oil phase and aqueous solution of the cationic or amphoteric surfactant are mixed together to form an aqueous emulsion (and oil-in-water emulsion). Mixing and emulsion formation may occur using any known techniques in the emulsion art. Typically, the oil phase and aqueous solution of the cationic or amphoteric surfactant are combined using simple stirring techniques to form an emulsion. Particle size of the aqueous emulsion may be reduced before addition of the water reactive silicon compound. Useful emulsification devices in this invention include, but are not limited to, homogenizer, sonolator, rotor-stator turbines, colloid mill, microfluidizer, blades, helix and combination thereof. The particle size may be reduced to a range from 0.2 to 100 micrometers, or a range from 0.02 micrometers to 100 micrometers.

[0055] The weight ratio of oil phase to aqueous phase in the emulsion can generally be between 40:1 and 1:50, although the higher proportions of aqueous phase are economically disadvantageous particularly when forming a suspension of microcapsules. Usually the weight ratio of oil phase to aqueous phase is between 2:1 and 1:3. If the oil phase composition is highly viscous, a phase inversion process can be used in which the oil phase is mixed with surfactant and a small amount of water, for example 2.5 to 10% by weight based on the oil phase, forming a water-in-oil emulsion which inverts to an oil-in-water emulsion as it is sheared. Further water can then be added to dilute the emulsion to the required concentration.

[0056] The preparation of microcapsules encapsulating catalysts involves adding a water reactive silicon compound to the aqueous emulsion, and polymerizing the water reactive silicon compound at the oil/water interface of the emulsion to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer.

[0057] Although not wishing to be bound by any theory, the present inventors believe that the third step involves an "ex-situ emulsion polymerization" by which the water reactive silicon compound hydrolyzes and condenses at the oil/water interface via a phase transfer of the water reactive silicon compound precursors leading to the formation of microcapsules having a core surrounded by a shell.

[0058] The water reactive silicon compound comprises at least one silicon-bonded hydrolyzable group per molecule, or an average of more than 2 silicon-bonded hydrolyzable groups per molecule. The hydrolyzable groups on the water reactive silicon compound is any group capable of hydrolyzing and condensing to form a silicon-based network polymer. In one particular embodiment, the hydrolyzable groups comprises alkoxy groups, acyloxy, or

hydroxy groups, or any combination thereof. In another embodiment, the water reactive silicon compound comprises monoalkoxysilane, dialkoxysilane, alkyltrialkoxysilane wherein the alkyl group has from 1 to 12 carbon atoms and is substituted or unsubstituted, tetraalkoxysilane, or any combination thereof. In another embodiment, the water reactive
5 silicon compound comprises tetraethyl orthosilicate (tetraethoxysilane or TEOS).

[0059] The tetraalkoxysilanes, such as tetraethoxysilane, may be used in monomeric form or as a liquid partial condensate. The tetraalkoxysilane can be used in conjunction with one or more other water reactive silicon compound having at least two, preferably at least three, hydrolyzable groups bonded to silicon, for example, silanol Si-OH groups, an
10 alkyltrialkoxysilane such as methyltrimethoxysilane or a liquid condensate of an alkyltrialkoxysilane. The water reactive silicon compound may comprise 75-100% by weight tetraalkoxysilane and 0-25% trialkoxysilane. The alkyl moiety of the alkoxy groups in the tetraalkoxysilanes or other silanes contain 1 to 4 carbon atoms, most preferably 1 or 2 carbon atoms. The tetraalkoxysilane, and other water reactive silicon compound hydrolyzes
15 and condenses to form a network polymer, that is, a three-dimensional network of silicon-based material around the emulsified droplets having the catalyst.

[0060] The water reactive silicon compound preferably consists of at least 10%, and most preferably 90-100% tetraalkoxysilane. The inventors have found that use of tetraalkoxysilane, such as tetraethoxysilane, forms impermeable microcapsules, forming a
20 three-dimensional network consisting of $\text{SiO}_{4/2}$ units.

[0061] The tetraalkoxysilane, and other water reactive silicon compounds, can be added to the aqueous emulsion as an undiluted liquid or as a solution in an organic solvent or in an emulsion form. The tetraalkoxysilane and aqueous emulsion are mixed, and subsequently polymerization of the tetraalkoxysilane forms the silicon-based network polymer shell on the
25 surface of the emulsified droplets, encapsulating the catalyst. Mixing is typically effected with any stirring techniques. Common stirring techniques are typically sufficient to maintain the particle size of the starting aqueous emulsion while allowing the tetraalkoxysilane to polymerize and condense at the oil/water interface in the aqueous emulsion.

[0062] The amount of tetraalkoxysilane added for the polymerization step typically ranges
30 from 6:1 to 1:13, alternatively from 1.2:1 to 1:7.3, alternatively from 1.3 to 1:6.1 based on the weight amount of oil phase present in the aqueous emulsion.

[0063] The polymerization of the tetraalkoxysilane at the oil/water interface typically is a condensation reaction which may be conducted at acidic, neutral or basic pH. The condensation reaction is generally carried out at ambient temperature and pressure, but can
35 be carried out at increased temperature, for example up to 95 °C, and increased or

decreased pressure, for example under vacuum to strip the volatile alcohol produced during the condensation reaction.

[0064] Any catalyst known to promote the polymerization of the water reactive silicon compound may be used to form the shell of the microcapsule. The catalyst may be a polymerization catalyst that promotes polymerization of tetraalkoxysilanes. The polymerization catalyst may alternatively be added to the aqueous emulsion just before the addition of the water reactive silicon compound, or simultaneously with the water reactive silicon compound, or after the addition of the water reactive silicon compound, in which case the catalyst helps to harden and make more impervious the shell of silicon-based network polymer. Encapsulation can however be achieved without a polymerization catalyst.

[0065] The polymerization catalyst includes, but is not limited to, an oil soluble organic metal compound, for example an organic tin compound, particularly an organotin compound such as a diorganotin diester, for example dimethyl tin di(neodecanoate), dibutyl tin dilaurate or dibutyl tin diacetate, or alternatively a tin carboxylate such as stannous octoate, or an organic titanium compound such as tetrabutyl titanate. An organotin catalyst can for example be used at 0.05 to 2% by weight based on the water reactive silicon compound. Alternatively, the polymerization catalyst may typically be present at 1 to 200 parts per million based on the combined weight of the aqueous emulsion. An organotin catalyst has the advantage of promoting catalysis at neutral pH.

[0066] The polymerization catalyst is typically mixed with the oil phase components before emulsification to form the aqueous emulsion, as this promotes condensation of the water reactive silicon compound at the surface of the emulsified oil phase droplets. The polymerization catalyst, when used, may be added undiluted, or as a solution in an organic solvent such as a hydrocarbon, alcohol or ketone, or as a multiphase system such as an emulsion or suspension.

[0067] In some embodiments, the polymerization catalyst may comprise an acid as a hydrolysis catalyst or a base as a condensation catalyst for the polymerization of the water reactive silicon compound.

[0068] In one embodiment, the polymerization of the water reactive silicon compound, such as tetraalkoxysilane, is allowed to proceed so as to form the shell of a microcapsule that is at least 18 nanometers thick, alternatively the shell has a thickness in the range of 18 to 150 nanometers, alternatively from 18 to 100 nanometers.

[0069] Shell thicknesses may be determined from the particle size (PS) of the resulting microcapsules in suspension and the amounts of the oil phase and tetraalkoxysilane used in the process to prepare the microcapsules according to the following formula:

$$\text{Shell Thickness (nm)} = [(PS/2) - ((PS/2) * (\text{Payload}/100)^{1/3})] * 1000$$

where PS is the particle size (Dv 0.5) expressed in micrometers;

payload = volume of the oil phase*100/(volume of the oil phase+volume of the shell);

volume of the oil phase = mass of the oil phase/density of the oil phase; and

volume of the shell = mass of the shell/density of the shell.

- 5 **[0070]** This equation is based on the spherically shaped microcapsules having an average diameter as determined by their average particle size (Dv 0.5). Thus, the shell thickness is the difference between the radius of the microcapsule and the radius of the core material in the microcapsule.

$$\text{Shell thickness} = r_{\text{microcapsule}} - r_{\text{core}}$$

- 10 where $r_{\text{microcapsule}} = (\text{PS})/2$

$$\text{and } r_{\text{core}} = (\text{PS}/2) * (\text{Payload}/100)^{1/3}$$

[0071] Payload represents the percentage of the microcapsule occupied by the core material, as determined by the amount of oil phase present in the aqueous emulsion.

Payload is calculated by the relationship:

- 15 Payload = volume of the oil phase*100/(volume of the oil phase + volume of the shell)

[0072] The volume of the oil phase is the mass of the oil phase divided by the density of the oil phase. The mass of the oil phase is the same as the amount added for making the aqueous emulsion.

- [0073]** The volume of the shell is the mass of the shell divided by the density of silica. The silicon-based network polymer comprising the shell is expected to have an average chemical composition with the empirical formula SiO_2 . The density of the shell is estimated to be 2 g/mL, which approximates the density of silica (SiO_2). The mass of the shell is calculated from the amount of tetraalkoxysilane added. More specifically, the mass of the shell is based on the expected stoichiometric yield of silicon-based network polymer of empirical formula SiO_2 given the type and amount of the tetraalkoxysilane used in the process. In one embodiment, the tetraalkoxysilane is tetraethoxysilane having a density of 0.934 g/mL. In this embodiment, assuming complete hydrolysis and condensation, 1 g of tetraethoxysilane produces 0.288 g of SiO_2 polymer network.

- [0074]** After preparation of microcapsules encapsulating catalysts comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer, the microcapsules are in an aqueous medium. The aqueous medium constitutes the aqueous continuous phase of the aqueous emulsion. The aqueous medium may be removed to produce microcapsules having reduced water content. The water content may be reduced to 1% or less by weight. The microcapsules having reduced water content may be made by spray or freeze drying or any other methods for removing water, including, but not limited to, a solvent exchange

procedure wherein water is replaced with a non-aqueous solvent. The microcapsules having reduced water content, after removal of the aqueous medium, may be suspended in a solvent, for example, in a non-aqueous solvent. Examples of non-aqueous solvents include, but are not limited to, organic solvents or polyorganosiloxanes.

5 **[0075]** In one embodiment, the processes for preparing the microcapsules encapsulating catalysts further comprises concentrating the microcapsules, mixing the concentrated microcapsules with a solvent; and separating the microcapsules from the solvent to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer and having from 0 to 1% of water based on the weight of the
10 microcapsules. The concentrating and separating steps may be carried out by centrifugation or filtration. The solvent is any non-aqueous solvent that is miscible with water and polyorganosiloxanes. The solvent includes, but is not limited to, dipropylene glycol, glycerol, alcohols, polyethylene glycols, or acetones.

[0076] Particle size measurements are made by laser diffraction technique using a
15 "Mastersizer S" from Malvern Instruments Ltd., UK, and further information on the measuring particle sizes can be, for example, found in "Basic principles of particle size analytics", Dr. Alan Rawle, Malvern Instruments Limited, WR14 1XZ, UK and the "Manual of Malvern Mastersizer S particle size analyzer". All particle sizes indicated in the present application are mean average volume particle size according to $D(v, 0.5)$ and are measured with a
20 Malvern Mastersizer S, if nothing else is stated or obvious.

[0077] Suitable laser diffraction techniques are well known in the art. The particle size is obtained from a particle size distribution (PSD). The PSD can be determined on a volume, surface, length basis. The volume particle size is equal to the diameter of the sphere that has the same volume as a given particle. The term D_v , as used herein, represents the
25 average volume particle size of the dispersed particles. D_{v50} is the particle size measured in volume corresponding to 50% of the cumulative particle population. In other words, if $D_{v50} = 10 \mu\text{m}$, 50% of the particle have an average volume particle size below $10 \mu\text{m}$ and 50% of the particle have a volume average particle size above $10 \mu\text{m}$. D_{v90} is the particle size measured in volume corresponding to 90% of the cumulative particle population.

30 **[0078]** The microcapsules according to the present invention are stable and inhibit diffusion or leaching of the catalysts from the microcapsules. The catalyst may be released from the microcapsules in a controlled rate of release. Suspension stabilization is determined by the amount of separation as measured as a percentage of the total suspension height over a six months timeframe. The active triggered release temperature for controlled release of the
35 catalyst is determined by a headspace GC/MS analysis of the suspension tracking the presence of burst aid with increasing temperature.

[0079] The microcapsules encapsulating catalysts prepared by the processes of the present invention exhibit advantages. One advantage is in hydrosilylation applications where a one-pot system can be used. Hydrosilylation applications of the prior art use strong cure inhibitors and curing must be done at high temperatures, for example, 120-140 °C. The ability for curing at lower temperatures or at room temperature is an advantage exhibited by the microcapsules encapsulating catalysts of the present invention. In addition, microcapsules encapsulating catalysts of the present invention can avoid the use of cure inhibitors, or at least allow for using cheaper and weaker cure inhibitors. The microcapsules encapsulating catalysts of the present invention allows for simpler manufacturing processes, easier molding and casting products, improved adhesion, and consuming less energy. The microcapsules encapsulating catalysts of the present invention provide advantages for dual or multiply curing systems because microcapsules encapsulating different catalysts can be used in a curing system. Furthermore, the microcapsules encapsulating catalysts of the present invention are robust and withstand further processing and remain stable in a variety of silicone formulations.

[0080] Having described the invention with reference to certain embodiments, other embodiments will become apparent to one skilled in the art from consideration of the specification. The invention is further defined by reference to the following examples describing the preparation of the emulsions and methods of the invention. It will be apparent to those skilled in the art that many modifications, both to materials and methods, may be practiced without departing from the scope of the invention

Examples

[0081] The following examples are included to illustrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention. All percentages are in weight percent. All measurements were conducted at 23°C unless indicated otherwise.

Example 1: Formulation of a microcapsule suspension.

[0082] The oil phase (core material) was prepared by mixing 150 g of vinylterminated polydimethyl siloxane and 50 g of a composition such that the oil phase contained 0.35% of 1,3-Diethenyl-1,1,3,3 -Tetramethyldisiloxane Complexes (Platinum). In separated beacher, 3.2 g of Arquad® 16-29 from AKZO-Nobel was mixed with 622 g of water until complete

dissolution. The oil phase was added to that Arquad® 16-29 solution under stirring to form a coarse oil-in-water emulsion. The stable coarse emulsion was passed twice through an homogenizer to get a fine emulsion having a mean average particle size Dv0.5 of 3.8 µm and a Dv0.9 of 10.4 µm.

- 5 **[0083]** To 767 g of the fine emulsion, 1.37 g of HCl 1N was added under stirring to obtain a pH of 3.1. Then 80.3 g of tetraethylorthosilica (TEOS) was added under stirring. The final microcapsule suspension had a non-volatile content of 24%. The microcapsule suspension had the following composition.

	water	68.14%
10	cationic surfactant (Arquad 16-29)	0.35%
	Dimethyl siloxane, dimethylvinyl-terminated	16.42%
	Platinum catalyst composition	5.47%
	HCl 1N	0.16%
	TEOS	9.45%

15 **Example 2: Formulation of a microcapsule suspension.**

- [0084]** The oil phase (core material) was prepared by mixing 150 g of vinyterminated polydimethyl siloxane and 50 g of a composition such that the oil phase contained 0.35% of 1,3-Diethenyl-1,1,3,3 -Tetramethyldisiloxane Complexes (Platinum). In separated beacher, 3.2 g of Arquad® 16-29 from AKZO-Nobel was mixed with 622 g of water until complete
 20 dissolution. The oil phase was added to that Arquad® 16-29 solution under stirring to form a coarse oil-in-water emulsion. The stable coarse emulsion was passed twice through an homogenizer to get a fine emulsion having a mean average particle size Dv0.5 of 3.8 µm and a Dv0.9 of 10.4 µm.

- [0085]** To 767 g of the fine emulsion, 1.37 g of HCl 1N was added under stirring to obtain a
 25 pH of 3.1. Then 80.3 g of tetraethylorthosilica (TEOS) and 8 gr of methytriethoxysilane (MTES) was added under stirring. The final microcapsule suspension had a non-volatile content of 24%. Addition of MTES in combination with TEOS produces a shell comprising methylsilsesquioxane. The microcapsule suspension had the following composition:

	Water	67.19%
30	cationic surfactant (Arquad 16-29)	0.35%
	Dimethyl siloxane, dimethylvinyl-terminated	16.42%
	Platinum catalyst composition	5.47%
	HCl 1N	0.16%
	TEOS	9.45%
35	MTES	0.95%

CLAIMS

What is claimed is:

1. A process for preparing microcapsules encapsulating a catalyst, the process comprising:
 - A. forming an aqueous emulsion comprising particles having the catalyst, an aqueous
5 continuous phase, and an interface between the particles and the aqueous continuous phase;
 - B. adding a water reactive silicon compound to the aqueous continuous phase;
 - C. polymerizing the water reactive silicon compound at the interface of the particles and the continuous phase to obtain microcapsules comprising a core having the
10 catalyst surrounded by a shell of a silicon-based network polymer in an aqueous medium; and
 - D. removing the aqueous medium to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer and having from 0 to 1% of water based on the weight of the microcapsules.
- 15 2. The process according to claim 1, wherein the catalyst in the aqueous emulsion is from 0.001 to 5.0 % by weight of the emulsion.
3. The process according to any of the preceding claims, wherein the catalyst is emulsified in an aqueous medium in the presence of a surfactant to form the aqueous emulsion.
4. The process according to claim 3, wherein the surfactant is a cationic surfactant and the
20 aqueous emulsion has a positive zeta-potential.
5. The process according to any of the preceding, wherein the water reactive silicon compound comprises at least one silicon-bonded hydrolyzable group per molecule.
6. The process according to any of the preceding, wherein the water reactive silicon compound comprises an average of more than 2 silicon-bonded hydrolyzable groups per
25 molecule.
7. The process according to any of the preceding, wherein the hydrolyzable group on the water reactive silicon compound is an alkoxy group.
8. The process according to any of the preceding claims, wherein the water reactive silicon compound comprises monoalkoxysilane, dialkoxysilane, alkyltrialkoxysilane wherein the
30 alkyl group is substituted or unsubstituted, tetraalkoxysilane, or any combination thereof.

9. The process according to any of the preceding claims, wherein the water reactive silicon compound comprises tetraethyl orthosilicate.
10. The process of any of the preceding claims, wherein the silicon-based network polymer is silica or an organo-modified silica.
- 5 11. A process according to any of claims 3 to 10, wherein the surfactant in the aqueous emulsion is 0.01 to 5.0 % by weight of the emulsion.
12. A process according to any of the preceding claims, wherein a catalyst for the polymerization of the water reactive silicon compound is added to the emulsion before, during or after the addition of the water-reactive silicon compound.
- 10 13. A process according to claim 12, wherein the catalyst is an organic tin compound.
14. The process according to any of the preceding claims, wherein the aqueous emulsion is passed through a high shear mixer before addition of the water-reactive silicon compound.
- 15 15. The process according to any of one of the preceding claims, wherein a thickener is added to the aqueous emulsion before addition of the tetraalkoxysilane.
16. The process according to any of the preceding claims, wherein the microcapsules have a mean diameter size from 20 nm to 100 μm .
17. The process according to any of the preceding claims, wherein the microcapsules have a mean diameter size from 0.5 μm to 50 μm or 0.5 μm to 25 μm or 0.5 μm to 10 μm or 0.5 μm to 5 μm .
- 20 18. The process according to any of the preceding claims, wherein the microcapsules are post-treated with cationic polymer.
19. The process of any of the preceding claims, further comprising concentrating the microcapsules; mixing the concentrated microcapsules with a solvent; and separating
- 25 the microcapsules from the solvent to obtain microcapsules comprising a core having the catalyst surrounded by a shell of a silicon-based network polymer and having from 0 to 1% of water based on the weight of the microcapsules.

20. The process according to claim 19, wherein mixing the concentrated microcapsules with a solvent, and separating the microcapsules from the solvent is carried out at least one time or at least two times.
21. The process according to claim 19 or 20, wherein the steps of concentrating and
5 separating are carried out by centrifugation.
22. The process according to any of claims 19 to 21, wherein the solvent is soluble in water and polyorganosiloxane.
23. The process according to any of claims 19 to 22, wherein the solvent is dipropylene glycol or glycerol.
- 10 24. The process according to any of the preceding claims, further comprising the steps of mixing the microcapsules substantially free of water with polyorganosiloxane, functionalized polyorganosiloxane and/or an additive.
25. The process according to claim 24, wherein the functionalized polyorganosiloxane is vinyl-functional polyorganosiloxane or SiH-functional polyorganosiloxane.
- 15 26. The process according to claim 24, wherein the additive is a filler.
27. The process according to any of the preceding claims, wherein the microcapsules have a payload load capacity from 1 to 99.99 % by volume of the microcapsule, wherein the payload capacity is the ratio of the volume of the core of the microcapsule to the sum of the volume of the core and the volume of the shell of the microcapsule.
- 20 28. The process according to claim 27, wherein the payload capacity is from 90 to 99 %, or 95 to 98 % by volume of the microcapsule.
29. The process according to any of the preceding claims, wherein the microcapsules are impermeable to the catalyst so that the catalyst does not leak out of the microcapsules and wherein the catalyst is released upon rupturing of the microcapsules.
- 25 30. The process according to any of the preceding claims, wherein the catalyst is a hydrosilylation catalyst, condensation catalyst or peroxide catalyst.
31. The process according to claim 29, wherein the hydrosilylation catalyst is selected from the group consisting of platinum, ruthenium, rhodium, palladium, osmium, iridium, complexes thereof, and any combinations thereof.

32. The process according to claim 29, wherein the hydrosilylation catalyst is pentamethylcyclopentadienyltris(acetonitrile)-ruthenium(II) hexafluorophosphate, chloroplatinic acid hydrate, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst), bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate hydrate, 5 (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer, tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst), benzenedichlororuthenium(II) dimer, dichloro(p-cymene)ruthenium(II) dimer, benzylidenebis(tricyclohexylphosphine)dichloro-ruthenium(II) (Grubb's catalyst), pentamethylcyclopentadienyltris(acetonitrile)-ruthenium(II) hexafluorophosphate, (2,2'- 10 bipyridine)dichloroplatinum(II), cis-bis(acetonitrile)dichloroplatinum(II), cis-bis(benzonitrile)dichloroplatinum(II), bis(tri-tert-butylphosphine)platinum(0), chloroplatinic acid hexahydrate, chloroplatinic acid (Speier's catalyst), (1,5-cyclooctadiene)dimethylplatinum(II), cis-diamineplatinum(II) dichloride, diamminedinitroplatinum(II), cis-dichlorobis(diethyl sulfide)platinum(II), 15 dichlorobis(dimethyl sulfide)platinum(II) mixture of cis and trans, cis-dichlorobis(dimethyl sulfoxide)platinum(II), cis-dichlorobis(pyridine)platinum(II), cis-dichlorobis(triethylphosphine)platinum(II), trans-dichlorobis(triethylphosphine)platinum(II), cis-dichlorobis(triphenylphosphine)platinum(II), trans-dichlorobis(triphenylphosphine)platinum(II), dichloro(1,5-cyclooctadiene)platinum(II), dichloro(1,2-diaminocyclohexane)platinum(II), 20 dichloro(dicyclopentadienyl)platinum(II), dDichloro(ethylenediamine)platinum(II), dichloro(norbornadiene)platinum(II), dichloro(1,10-phenanthroline)platinum(II), ethylenebis(triphenylphosphine)platinum(0), (ethylenediamine)iodoplatinum(II) dimer dinitrate, platinum(II) acetylacetonate, platinum(II) bromide, platinum(II) chloride, 25 platinum(IV) chloride, platinum cobalt, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, platinum(II) iodide, platinum(IV) oxide, platinum(IV) oxide monohydrate, platinum-ruthenium alloy, platinum(0)-2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane complex, potassium hexachloroplatinate(IV), potassium trichloro(ethylene)platinate(II) hydrate, sodium hexahydroxyplatinate(IV), 30 tetraammineplatinum(II) chloride, tetraammineplatinum(II) hydroxide hydrate, tetraammineplatinum(II) nitrate, tetrabutylammonium hexachloroplatinate(IV), tetrakis(triphenylphosphine)platinum(0), (N,N,N'-trimethylethylenediamine)platinum(II) chloride, trimethyl(methylcyclopentadienyl)platinum(IV), or any combination thereof.

33. A process for curing a composition, the process comprising:

- 5 A. preparing microcapsules according to any of the preceding claims, wherein the microcapsules comprise a core having a hydrosilylation catalyst surrounded by a shell of a silicon-based network polymer and the microcapsules have from 0 to 1% water based on the weight of the microcapsules;
- B. mixing the microcapsules with alkenyl-functional polyorganosiloxane and SiH-functional polyorganosiloxane to form a mixture;
- C. rupturing the microcapsules to release the hydrosilylation catalyst by shear and/or by heating the mixture at a temperature of from 40 to 140°C; and
- 10 D. reacting the SiH-functional polyorganosiloxane and the alkenyl-functional polyorganosiloxane in the presence of the hydrosilylation catalyst to form a cured composition.
34. An encapsulated catalyst composition, the composition comprising microcapsules comprising a core having a catalyst surrounded by a shell of a silicon-based network polymer, wherein the microcapsules have a mean diameter size from 20 nm to 100 μm and the microcapsules are impermeable to the catalyst so that the catalyst does not leak out of the microcapsules but is released upon rupturing of the microcapsules, and the composition comprises from 0 to 1% water based on the weight of the microcapsules.
- 15
35. A one-part composition for making a hydrosilylation product, the one-part composition comprising the encapsulated catalyst composition of claim 34, alkenyl-functional polyorganosiloxane, and SiH-functional polyorganosiloxane, optionally an additive, wherein the one-part composition is free of a cure inhibitor or comprises a cure inhibitor.
- 20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/018147**A. CLASSIFICATION OF SUBJECT MATTER****B01J 13/18(2006.01)i, B01J 37/04(2006.01)i, B01J 35/08(2006.01)i**

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)

B01J 13/18; C08L 83/07; C08K 5/3435; A61Q 19/00; A61K 35/00; C08L 83/02; A61K 9/50; B65D 25/00; C01B 33/12; A61K 8/18; B01J 37/04; B01J 35/08

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: microcapsule, silicon, catalyst, shell, hydrosilylation, polyorganosiloxane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0236498 A1 (MARTEAUX, LEON ANDRE et al.) 29 September 2011 See abstract; paragraphs [0013],[0017]; and claim 1.	1-4,34
Y		35
Y	US 2012-0101227 A1 (GALEONE, FABRIZIO et al.) 26 April 2012 See abstract; and claims 1, 10, 13.	35
A	US 2014-0341958 A1 (LES INNOVATIONS MATERIUM INC.) 20 November 2014 See abstract; and claims 25-28.	1-4,34,35
A	US 2013-0210969 A1 (GRIGORIEV, DMITRY O. et al.) 15 August 2013 See abstract; and claim 1.	1-4,34,35
A	US 8110284 B2 (NAIGERTSIK, OLEG et al.) 07 February 2012 See abstract; and claim 1.	1-4,34,35



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

30 May 2016 (30.05.2016)

Date of mailing of the international search report

30 May 2016 (30.05.2016)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2016/018147**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: claims 13, 20, 25, 26, 28, 31, 32
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 13, 20, 25, 26, 28, 31, 32 are unclear since they refer to one of claims which are not searchable due to not being drafted in accordance with third sentences of Rule 6.4(a).
3. ☒ Claims Nos.: claims 5-12, 14-19, 21-24, 27, 29, 30, 33
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/018147

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CN 102227254 B	13/08/2014
		EP 2367619 A2	28/09/2011
		JP 2012-512025 A	31/05/2012
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