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(54) Title: MICROPARTICLES AND CURABLE ORGANOPOLYSILOXANE COMPOSITION CONTAINING THE SAME

(57) Abstract: The present invention relates to microparticles comprising: (i) at least one type of an organic metal compound selected from the group consisting of organic titanium compounds, organic zirconium compounds, organic aluminum compounds, and organic tin compounds, and (ii) a thermoplastic polyolefin resin with a Z-average (Mz) of a weight average molecular weight (Mw) of at least 2500 and Mz/Mw of not more than 2.0, wherein the organic metal compound is dispersed in the thermoplastic polyolefin resin. The microparticles can provide a curable organopolysiloxane composition which forms a cured product having excellent adhesion with various base materials when heated and enables the sufficient suppression of the diminishment of the hardness and adhesiveness of the cured product due to changes over time during the storage of the curable organopolysiloxane composition.

DESCRIPTION

MICROPARTICLES AND CURABLE ORGANOPOLYSILOXANE COMPOSITION CONTAINING THE SAME

Technical Field

[0001] The present invention relates to microparticles containing an organic metal compound and a thermoplastic resin, the organic metal compound being dispersed in the thermoplastic resin, and to a curable organopolysiloxane composition with excellent storage stability containing the microparticles.

[0002] Priority is claimed on Japanese Patent Application No. 2012-167361, filed on July 27, 2012, the content of which is incorporated herein by reference.

Background Art

[0003] A curable organopolysiloxane composition which is cured by a hydrosilylation reaction typically has poor adhesiveness. Therefore, it is known that adhesiveness can be provided by mixing an organic metal compound such as zirconium tetra(acetylacetonate) into the organopolysiloxane composition. Known examples include a composition containing an epoxy compound and an organic aluminum compound (see Japanese Unexamined Patent Application Publication No. S60-101146), a composition containing an organic silicon compound having silicon-bonded unsaturated groups and alkoxy groups and an aluminum compound or a zirconium compound (see Japanese Unexamined Patent Application Publication No. S62-240361), and a composition containing a zirconium (IV) compound and an organic silicon compound selected from the group consisting of bis(trialkoxysilyl)alkanes, disilanes having silicon-bonded alkoxy groups, and epoxy group-containing alkoxysilanes or siloxanes (see Japanese Unexamined Patent Application Publication No. H04-222871).

[0004] However, such curable organopolysiloxane compositions undergo changes over time during storage due to condensation reactions or other reactions between silicon-bonded hydrogen atoms and water or silanol groups caused by the organic metal compound, which leads to the problem that the hardness of the cured product formed by the composition is diminished in comparison to the hardness of the original specifications and that the adhesiveness is also diminished.

[0005] In order to solve this problem, it has been proposed to suppress changes over time during storage by adding thermoplastic resin microparticles containing an organic

metal compound to a hydrosilylation reaction-curable organopolysiloxane composition, thereby suppressing the diminishment of the adhesiveness of a cured product formed by the composition (see Japanese Unexamined Patent Application Publication No. 2006-002093).

[0006] However, the present inventors discovered that the diminishment of the adhesiveness of a cured product caused by changes over time in a hydrosilylation reaction-curable organopolysiloxane composition cannot be sufficiently suppressed with conventional thermoplastic resin microparticles containing an organic metal compound.

[0007] Accordingly, an object of the present invention is to obtain thermoplastic resin microparticles containing an organic metal compound for providing a curable organopolysiloxane composition which forms a cured product having excellent adhesion with various base materials when heated and enables the sufficient suppression of the diminishment of the hardness and adhesiveness of the cured product due to changes over time during the storage of the curable organopolysiloxane composition.

[0008] Another object of the present invention is to obtain a hydrosilylation reaction-curable organopolysiloxane composition containing an encapsulated organic metal compound demonstrating favorable storage stability.

Disclosure of Invention

[0009] The first object of the present invention is achieved by microparticles comprising:

(i) at least one type of an organic metal compound selected from the group consisting of organic titanium compounds, organic zirconium compounds, organic aluminum compounds, and organic tin compounds and

(ii) a thermoplastic polyolefin resin with a Z-average (Mz) of a weight average molecular weight (Mw) of at least 2500 and Mz/Mw of not more than 2.0,

wherein the organic metal compound is dispersed in the thermoplastic polyolefin resin.

[0010] A melting point of the thermoplastic polyolefin resin is preferably from 40 to 200°C.

[0011] The thermoplastic polyolefin resin is preferably a polyolefin wax.

[0012] The polyolefin wax is preferably selected from the group consisting of polyethylene waxes, polypropylene waxes, polybutene waxes, or combinations thereof.

[0013] An average particle diameter of the microparticles is preferably from 0.01 to 500 μm.

[0014] The organic metal compound is preferably a metal chelate compound.

[0015] A content of the organic metal compound is preferably from 1 to 99.9 weight%.

[0016] The second object of the present invention is achieved by a curable organopolysiloxane composition comprising:

(A) an organopolysiloxane represented by the average unit formula:

$R_aSiO_{(4-a)/2}$

wherein, R is a substituted or unsubstituted monovalent hydrocarbon group, and "a" is a number from 1.0 to 2.3, and having at least an average of 1.5 alkenyl groups in a molecule;

(B) an organopolysiloxane having at least an average of 1.5 silicon-bonded hydrogen atoms in a molecule;

(C) a hydrosilylation reaction catalyst; and

(D) the microparticles described above.

[0017] A content of component (B) is preferably in an amount such that a quantity of silicon-bonded hydrogen atoms in component (B) is from 0.05 to 20 mol per 1 mol of alkenyl groups in component (A).

[0018] A content of component (C) is preferably in an amount to promote crosslinking of the composition by a hydrosilylation reaction.

[0019] Component (C) is preferably dispersed in microparticles of a thermoplastic resin. That is, component (C) may be microparticles of a thermoplastic resin containing a hydrosilylation reaction catalyst.

[0020] A melting point of the thermoplastic resin in component (C) is preferably from 40 to 200°C.

[0021] The thermoplastic resin in component (C) is preferably a polyolefin resin, a methyl methacrylate resin, a polycarbonate resin, a polystyrene resin, a silicone resin, or a combination thereof.

[0022] A content of component (D) is preferably from 0.001 to 50 parts by weight per 100 parts by weight of component (A).

[0023] The composition may further comprise (E) an adhesion-imparting agent in an amount of from 0.01 to 30 parts by weight per 100 parts by weight of component (A).

[0024] Component (E) is preferably an organic silicon compound having at least one type of functional group selected from the group consisting of epoxy groups, acryloxy groups, and methacryloxy groups.

[0025] The composition may further comprise (F) a reaction inhibitor in an amount of from 0.001 to 5 parts by weight per 100 parts by weight of component (A).

Effects of Invention

[0026] The microparticles of the present invention containing an organic metal compound and a thermoplastic resin can provide a curable organopolysiloxane composition which forms a cured product having excellent adhesion with various base materials when heated and enables the sufficient suppression of the diminishment of the hardness and adhesiveness of the cured product due to changes over time during the storage of the curable organopolysiloxane composition. That is, the microparticles of the present invention make it possible to obtain a curable organopolysiloxane composition having characteristics such as excellent storage stability. In addition, the hydrosilylation reaction-curable organopolysiloxane composition containing the microparticles of the present invention has the feature that the composition can be cured at a low temperature while demonstrating favorable storage stability, with very little diminishment in the hardness and adhesiveness of the cured product due to changes over time.

Detailed Description of the Invention

[0027] As a result of dedicated research, the present inventors discovered that the storage stability of a hydrosilylation reaction-curable organopolysiloxane composition containing an encapsulated organic metal compound depends on the characteristics related to the molecular weight of the thermoplastic polyolefin resin used in the encapsulation of the organic metal compound. Therefore, in the present invention, an encapsulated organic metal compound providing excellent storage stability is provided by controlling the characteristics related to the molecular weight of the material encapsulating the organic metal compound.

[0028] The present invention uses a thermoplastic polyolefin resin with a Z-average (Mz) of the weight average molecular weight (Mw) of at least 2500 and Mz/Mw of not more than 2.0. The Z-average (Mz) of the weight average molecular weight (Mw) is preferably at least 3000, at least 3100, at least 3200, at least 3300, at least 3400, at least 3500, or at least 3600. In addition, the Z-average (Mz) of the weight average molecular

weight (Mw) is preferably not more than 7300, not more than 7500, not more than 8500, not more than 10,000, or not more than 15,000. Mz/Mw is preferably 2.0, not more than 1.9, not more than 1.8, not more than 1.7, not more than 1.6, not more than 1.5, not more than 1.4, not more than 1.3, or not more than 1.2.

[0029] The molecular weight and molecular weight distribution are measured using gel permeation chromatography (GPC). Gel permeation chromatography (GPC) is a type of liquid chromatography for separating molecules based on differences in molecular size and is a technique for measuring the molecular weight distribution and the average molecular weight distribution of a polymer substance. When a sample solution is injected into a column filled with a pulverized gel having fine pores of approximately the same size as the size of polymer chains in a dilute solution (hydrodynamic volume), molecules with high molecular weights - that is, molecules with large molecular sizes in the solution - move into the column and are eluted more quickly than molecules with low molecular weights (size separation), with little permeation into the fine pores of the gel surface. Based on this separation mechanism, GPC is generally called size exclusion chromatography (SEC). In the present invention, GPC is performed under the following conditions.

[0030] Table 1

Apparatus:	Gel permeation liquid chromatography GPC (PL-220)		(Polymer Laboratories)
Detector:	Differential refractive index detector RI		(Polymer Laboratories)
Column:	Shodex HT806M (2 columns)		(Showa Denko K.K.)
Solvent:	1,2,4-trichlorobenzene (TCB)		(Wako Pure Chemical Industries, Ltd.)
	Containing 0.1% BHT		
Flow rate:	1.0 mL/min		
Column temperature:	140°C		
Sample:	[Dissolution method]	10 mL of a measurement solvent was added to 10 mg of the sample and stirred while heating for 20 minutes at 120°C.	
	[Concentration]	Approximately 0.1%	
	[Solubility]	Good (confirmed visually)	
	[Filtration]	Filtration was performed with a 0.5 μm filter (made by Waters).	
Injection rate:	0.200 mL		
Standard sample:	Standard polystyrene		

[0031] The weight average molecular weight (Mw) determined by GPC was $\sum(Ni \cdot Mi^2)/\sum(Ni \cdot Mi)$. In this formula, Mi is the molecular weight of each elution position of a GPC curve obtained via a molecular weight calibration curve (created by measuring monodispersed polystyrene with a known molecular weight and making a third-order approximation of the relationship with the elution time and the molecular weight), and Ni is the number of molecules.

[0032] The Z-average (Mz) of the weight average molecular weight determined by GPC is $\sum(Ni \cdot Mi^3)/\sum(Ni \cdot Mi^2)$. Mi and Ni are as described above.

[0033] The thermoplastic polyolefin resin used in the present invention is not particularly limited as long as the resin does not inhibit the action of the organic metal compound, but a polyolefin wax is preferable. A preferable wax is selected from the group consisting of polyethylene waxes, polypropylene waxes, polybutene waxes, and combinations thereof. An example of a polyethylene wax is POLYWAX (registered trademark) made by the Baker Hughes Inc. POLYWAX 1000 or POLYWAX 2000 is preferable.

[0034] A melting point of the thermoplastic polyolefin resin used in the present invention is not particularly limited, but the upper limit is preferably 200°C, even more preferably 150°C, and particularly preferably 130°C. On the other hand, the lower limit is preferably 40°C, even more preferably 60°C, and particularly preferably 80°C. This is because if the melting point of the thermoplastic polyolefin resin is less than the lower limit described above, it will be necessary to prepare and store the microparticle composition at a low temperature, whereas if the melting point exceeds the upper limit described above, it will be difficult to provide sufficient adhesiveness to a cured product obtained by curing a curable organopolysiloxane composition containing the thermoplastic polyolefin resin at a relatively low temperature. The melting point may be measured with any known method. For example, the endothermic peak value resulting from melting at the time of measurement under heating conditions of 5°C/minute using a differential scanning calorimeter (DSC) may be used as the melting point.

[0035] Although an average particle diameter of the microparticles of the present invention is not particularly limited, the upper limit is preferably 500 μm, even more preferably 200 μm, and particularly preferably 100 μm, 50 μm, 30 μm, or 20 μm. On the other hand, the lower limit is preferably 0.01 μm, even more preferably 0.05 μm, and particularly preferably 0.1 μm, 0.5 μm, or 1 μm. This is because if the average particle

diameter is less than the lower limit described above, the resulting thermoplastic polyolefin resin particles themselves will become prone to agglomeration, making the microparticles difficult to disperse in the curable organopolysiloxane composition. On the other hand, if the average particle diameter exceeds the upper limit described above, the dispersibility of the organic metal compound will be diminished when the curable organopolysiloxane composition containing the microparticles is heated, which will make it difficult to provide sufficient adhesiveness to the cured product formed by the composition.

[0036] Examples of the organic metal compound used in the present invention include organic titanium compounds, organic zirconium compounds, organic aluminum compounds, organic tin compounds, or combinations thereof. The organic metal compound used in the present invention has the effect of providing adhesiveness to the cured product formed by the composition of the present invention.

[0037] Examples of the organic titanium compounds include organic titanic acid esters such as tetrabutyl titanate or tetraisopropyl titanate; and organic titanium chelate compounds such as diisopropoxy bis(acetylacetate)titanium or diisopropoxy bis(ethylacetoacetate)titanium. Examples of the organic zirconium compounds include organic zirconium esters such as zirconium tetrapropylate or zirconium tetrabutylate; and organic zirconium chelate compounds such as zirconium diacetate, zirconium tetra(acetylacetonate), tributoxyzirconium acetylacetonate, dibutoxyzirconium bis(acetylacetonate), tributoxyzirconium acetoacetate, or dibutoxyzirconium acetylacetonate(ethylacetoacetate). Examples of the organic aluminum compounds include organic aluminum esters such as aluminum triethylate, aluminum triisopropylate, aluminum tri(sec-butylate), or mono(sec-butoxy)aluminum diisopropylate; and organic aluminum chelate compounds such as diisopropxy aluminum (ethylacetoacetate), aluminum tris(ethylacetoacetate), aluminum bis(ethylacetoacetate) monoacetylacetonate, or aluminum tris(acetylacetonate). Examples of the organic tin compounds include organic tin compounds such as dibutyltin dioctoate, dibutyltin dilaurate, or butyltin-2-ethylhexoate; and organic tin carboxylates such as tin naphthenate, tin oleate, or tin butylate. One type or two or more types of these compounds may be used in combination as the organic metal compound. In particular, the organic metal compound is preferably a metal chelate compound.

[0038] Although a content of the organic metal compound contained in the microparticles of the present invention is not particularly limited, the content is preferably

within the range of from 1 to 99.9 weight%, even more preferably within the range of from 2 to 90 weight%, and particularly preferably within the range of from 5 to 90 weight%. This is because if the content of the organic metal compound is less than the lower limit of the range described above, it will be necessary to add a large quantity of microparticles to the curable organopolysiloxane composition in order to achieve sufficient adhesion, which diminishes the mechanical characteristics of the cured product formed by the composition. On the other hand, if the content exceeds the upper limit of the range described above, it will become difficult to include the organic metal compound in the thermoplastic polyolefin resin.

[0039] A production method of the microparticles of the present invention is not particularly limited. For example, it is possible to employ a chemical method such as a conventionally known interfacial polymerization method or an in-situ polymerization method; a physicochemical method such as a coacervation method or a liquid drying method; or a physical/mechanical method such as a spray drying method. The production of the microparticles of the present invention is particularly preferably realized by a spray drying method. The resulting microparticles are preferably washed with a solvent such as isopropyl alcohol or ethanol, for example.

[0040] The curable organopolysiloxane composition of the present invention will be described in detail hereinafter.

[0041] Component (A), which is a base compound of the present composition, is an organopolysiloxane represented by the average unit formula: $R_aSiO_{(4-a)/2}$ and having at least an average of 1.5 alkenyl groups in a molecule. In the formula above, R is a substituted or unsubstituted monovalent hydrocarbon group, and examples of this monovalent hydrocarbon group include alkyl groups such as methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, and hexyl groups; alkenyl groups such as vinyl groups, allyl groups, butenyl groups, pentenyl groups, hexenyl groups, and heptenyl groups; aryl groups such as phenyl groups, tolyl groups, and xylyl groups; aralkyl groups such as benzyl groups and phenethyl groups; and halogenated alkyl groups such as 3-chloropropyl groups and 3,3,3-trifluoropropyl groups. Here, at least an average of 1.5 groups of R in a molecule are alkenyl groups such as those described above. Vinyl groups and hexenyl groups are preferable as the alkenyl groups. Methyl groups and phenyl groups are preferable as silicon-bonded groups other than the alkenyl groups. In the formula above, "a" is a number from 1.0 to 2.3. Examples of molecular structures of

such component (A) include a straight chain structure, a partially branched straight chain structure, a branched chain structure, a reticulated structure, and a dendritic structure. Component (A) may be a mixture of two or more types of organopolysiloxanes having these molecular structures. That is, a may be either $1 \leq a < 2$ or $2 \leq a < 2.3$. A viscosity at 25°C of component (A) is not particularly limited but is preferably within the range of from 50 to 1,000,000 mPa·s and particularly preferably within the range of from 100 to 500,000 mPa·s.

[0042] Examples of the organopolysiloxane for component (A) include dimethylsiloxane-methylvinylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, methylvinylpolysiloxanes capped at both molecular terminals with trimethylsiloxy groups, methylvinylsiloxane-methylphenylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, dimethylsiloxane-methylvinylsiloxane-methylphenylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, dimethylpolysiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, methylvinylpolysiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, methylphenylpolysiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, dimethylsiloxane-methylvinylsiloxane copolymers capped at both molecular terminals with dimethylvinylsiloxy groups, methylvinylsiloxane-methylphenylsiloxane copolymers capped at both molecular terminals with dimethylvinylsiloxy groups, methylvinylsiloxane-diphenylsiloxane copolymers capped at both molecular terminals with dimethylvinylsiloxy groups, methylvinylpolysiloxanes capped at one molecular terminal with a trimethylsiloxy group and the other molecular terminal with a dimethylvinylsiloxy group, dimethylsiloxane-methylvinylsiloxane copolymers capped at one molecular terminal with a trimethylsiloxy group and the other molecular terminal with a dimethylvinylsiloxy group, organopolysiloxanes comprising a unit represented by the formula: $R_3SiO_{1/2}$ and a unit represented by the formula: $SiO_{4/2}$, organopolysiloxanes comprising a unit represented by the formula: $RSiO_{3/2}$, organopolysiloxanes comprising a unit represented by the formula: $R_2SiO_{2/2}$ and a unit represented by the formula: $RSiO_{3/2}$, organopolysiloxanes comprising a unit represented by the formula: $R_2SiO_{2/2}$, a unit represented by the formula: $RSiO_{3/2}$, and a unit represented by the formula: $SiO_{4/2}$, and mixtures of two or more types of these organopolysiloxanes. R in the formulas above is a substituted or unsubstituted monovalent hydrocarbon group as described above.

[0043] As the organopolysiloxane for component (A), it is also possible to use an organopolysiloxane mixture with an average number of 1.5 alkenyl groups in a molecule by mixing an organopolysiloxane listed above having at least 2 alkenyl groups in a molecule and an organopolysiloxane listed below having no alkenyl groups or having less than 2 alkenyl groups in a molecule. Examples of such an organopolysiloxane having no alkenyl groups or having less than 2 alkenyl groups in a molecule include dimethylpolysiloxanes capped at one molecular terminal with a dimethylvinylsiloxy group and the other molecular terminal with a trimethylsiloxy group, methylphenylpolysiloxanes capped at one molecular terminal with a dimethylvinylsiloxy group and the other molecular terminal with a trimethylsiloxy group, dimethylsiloxane-methylvinylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups and having 1 vinyl group on the molecular side chains, dimethylpolysiloxanes capped at both molecular terminals with trimethylsiloxy groups, and methylphenylpolysiloxanes capped at both molecular terminals with trimethylsiloxy groups.

[0044] Component (B) is a crosslinking agent of the present composition and is an organopolysiloxane having at least an average of 1.5 silicon-bonded hydrogen atoms in a molecule. It is particularly preferable for there to be at least an average of 2 silicon-bonded hydrogen atoms in a molecule. The bonding sites of the silicon-bonded hydrogen atoms are not particularly limited and may be molecular terminals, molecular side chains, or molecular terminals and molecular side chains, for example. Examples of silicon-bonded groups other than hydrogen atoms include substituted or unsubstituted monovalent hydrocarbon groups excluding alkenyl groups such as alkyl groups such as methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, and hexyl groups; allyl groups such as phenyl groups, tolyl groups, and xylyl groups; aralkyl groups such as benzyl groups and phenethyl groups; and halogenated alkyl groups such as 3-chloropropyl groups and 3,3,3-trifluoropropyl groups. Examples of molecular structures of such component (B) include a straight chain structure, a partially branched straight chain structure, a branched chain structure, a reticulated structure, and a dendritic structure. Component (B) may be a mixture of two or more types of organopolysiloxanes having these molecular structures. A viscosity at 25°C of component (B) is not particularly limited but is preferably within the range of from 1 to 500,000 mPa·s and particularly preferably within the range of from 1 to 1,000 mPa·s.

[0045] Examples of the organopolysiloxane for component (B) include methylhydrogenpolysiloxanes capped at both molecular terminals with trimethylsiloxy groups, dimethylsiloxane-methylhydrogensiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, methylhydrogensiloxane-methylphenylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, dimethylsiloxane-methylhydrogensiloxane-methylphenylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, dimethylpolysiloxanes capped at both molecular terminals with dimethylhydrogensiloxy groups, methylhydrogenpolysiloxanes capped at both molecular terminals with dimethylhydrogensiloxy groups, dimethylsiloxane-methylhydrogensiloxane copolymers capped at both molecular terminals with dimethylhydrogensiloxy groups, dimethylsiloxane-methylphenylsiloxane copolymers capped at both molecular terminals with dimethylhydrogensiloxy groups, dimethylsiloxane-methylhydrogensiloxane-methylphenylsiloxane copolymers capped at both molecular terminals with dimethylhydrogensiloxy groups, organopolysiloxanes comprising a unit represented by the formula: $R'_3SiO_{1/2}$ and a unit represented by the formula: $SiO_{4/2}$, organopolysiloxanes comprising a unit represented by the formula: $R'SiO_{3/2}$, organopolysiloxanes comprising a unit represented by the formula: $R'_2SiO_{2/2}$ and a unit represented by the formula: $R'SiO_{3/2}$, organopolysiloxanes comprising a unit represented by the formula: $R'_2SiO_{2/2}$, a unit represented by the formula: $R'SiO_{3/2}$, and a unit represented by the formula: $SiO_{4/2}$, and mixtures of two or more types of these organopolysiloxanes. R' in the formulas above is a substituted or unsubstituted monovalent hydrocarbon group excluding alkenyl groups or a hydrogen atom, and examples of this monovalent hydrocarbon group include the alkyl groups, aryl groups, aralkyl groups, or halogenated alkyl groups described above. In particular, component (B) is preferably a mixture of an organopolysiloxane having silicon-bonded hydrogen atoms only at both molecular terminals and an organopolysiloxane having at least 3 silicon-bonded hydrogen atoms in a molecule due to the excellent mechanical characteristics - the elongation, in particular - of the cured product formed by the present composition.

[0046] A content of component (B) is preferably in an amount such that a quantity of silicon-bonded hydrogen atoms in component (B) is within the range of from 0.05 to 20 mol per 1 mol of alkenyl groups in component (A), preferably within the range of from 0.1 to 20 mol, and particularly preferably within the range of from 0.1 to 10 mol. If the

content of component (B) is less than the lower limit of the range described above, the composition will tend not to be cured sufficiently, whereas if the content exceeds the upper limit of the range described above, the composition will tend to foam during curing, which diminishes the mechanical characteristics of the cured product formed by the composition.

[0047] Component (C) is a catalyst for promoting the crosslinking of the present composition by a hydrosilylation reaction between the alkenyl groups in component (A) and the silicon-bonded hydrogen atoms in component (B). Examples of such component (C) include hydrosilylation reaction catalysts such as platinum-based catalysts such as platinum black, platinum-supported alumina powders, platinum-supported silica powders, platinum-supported carbon powders, chloroplatinic acids, alcohol solutions of chloroplatinic acids, olefin complexes of platinum, and alkenyl siloxane complexes of platinum; palladium-based catalysts such as tetrakis(triphenylphosphine)palladium; and rhodium-based catalysts as well as microparticles containing these hydrosilylation reaction catalysts and a thermoplastic resin, wherein the hydrosilylation reaction catalyst is dispersed in the thermoplastic resin. This thermoplastic resin is not particularly limited as long as the thermoplastic resin does not inhibit the action of the hydrosilylation reaction catalyst, and preferable examples include polyolefin resins, methylmethacrylate resins, polycarbonate resins, polystyrene resins, silicone resins, or combinations thereof. It is particularly preferable to encapsulate the hydrosilylation reaction catalyst using a thermoplastic resin described above as a resin that may be used to encapsulate the organic metal compound. A melting point of this thermoplastic resin is not particularly limited but is preferably within the range of from 40 to 200°C, even more preferably within the range of from 60 to 150°C, and particularly preferably within the range of from 80 to 130°C. This is because if the melting point of the thermoplastic resin is less than the lower limit described above, it will be necessary to prepare and store the composition at a low temperature, whereas if the melting point exceeds the upper limit described above, it will be difficult to cure at a relatively low temperature. The production method of a hydrosilylation reaction catalyst comprising these thermoplastic resin particles is publicly known due to Japanese Unexamined Patent Application Publication No. S64-45468 (specification of U.S. Patent No. 4,766,176), for example.

[0048] A content of component (C) is not particularly limited but is preferably in an amount to promote crosslinking the present composition by a hydrosilylation reaction. Specifically, it is preferable for the content to be in an amount such that the catalyst metal

in component (C) is within the range of from 0.1 to 10,000 ppm in weight units per the total amount of components (A) and (B). This is because if the content of component (C) is less than the lower limit of the range described above, the composition will tend not to cure sufficiently, whereas if the content exceeds the upper limit described above, the curing of the composition will not be promoted substantially.

[0049] Component (D) comprises the microparticles of the present invention containing an organic metal compound.

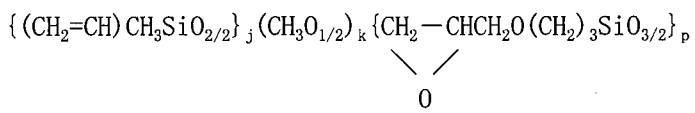
[0050] A content of component (D) is within the range of from 0.001 to 50 parts by weight per 100 parts by weight of component (A), for example, and is preferably within the range of from 0.01 to 50 parts by weight, even more preferably within the range of from 0.01 to 20 parts by weight, and particularly preferably within the range of from 0.1 to 20 parts by weight. This is because if the content of component (D) is less than the lower limit of the range described above, the adhesiveness of the composition will be diminished, whereas if the content exceeds the upper limit of the range described above, the mechanical characteristics of the cured product formed by the composition will be diminished.

[0051] The present composition comprises components (A) to (D), but the composition may also further comprise (E) an adhesion-imparting agent as an additional optional component. As component (E), a well-known agent other than the organic metal compound in component (D) may be used as the adhesion-imparting agent of the hydrosilylation reaction-curable organopolysiloxane composition. Such component (E) is preferably an organic silicon compound having a functional group such as an epoxy group, an acryloxy group, or a methacryloxy group and further having a silicon-bonded alkoxy group. Examples of the epoxy group in component (E) include glycidoxyalkyl groups such as 3-glycidoxypropyl groups or 4-glycidoxybutyl groups; epoxycylohexylalkyl groups such as 2-(3,4-epoxycyclohexyl)ethyl groups or 3-(3,4-epoxycyclohexyl)propyl groups; and oxiranylalkyl groups such as 4-oxiranylbutyl groups or 8-oxiranyloctyl groups. An example of the acryloxy group in component (E) is a 3-acryloxypropyl group. An example of the methacryloxy group in component (E) is a 3-methacryloxypropyl group. Examples of the alkoxy group in component (E) include methoxy groups, ethoxy groups, propoxy groups, butoxy groups, and methoxyethoxy groups, and methoxy groups are particularly preferable. Component (E) preferably contains an epoxy group and a silicon-bonded alkoxy group. Examples of other silicon-bonded organic groups in component

(E) include substituted or unsubstituted monovalent hydrocarbon groups such as alkyl groups such as methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, and hexyl groups; alkenyl groups such as vinyl groups, allyl groups, butenyl groups, pentenyl groups, hexenyl groups, and heptenyl groups; aryl groups such as phenyl groups, tolyl groups, and xylyl groups; aralkyl groups such as benzyl groups and phenethyl groups, and halogenated alkyl groups such as 3-chloropropyl groups and 3,3,3-trifluoropropyl groups as well as acryloxyalkyl groups such as 3-methacryloxypropyl groups.

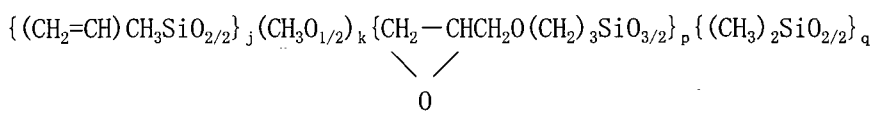
[0052] Examples of the organic silicon compound for component (E) include organosilane compounds, organosiloxane oligomers, and alkyl silicates. A molecular structure of the organosiloxane oligomer or alkyl silicate is exemplified by a straight chain structure, partially branched straight chain structure, branched chain structure, cyclic structure, and reticulated structure. A straight chain structure, branched chain structure, and reticulated structure are particularly preferred. Examples of such an organic silicon compound include silane compounds such as 3-glycidoxypropyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and 3-methacryloxy propyltrimethoxysilane; mixtures of a siloxane compound having at least 1 silicon-bonded alkenyl group and 1 silicon-bonded alkoxy group in a molecule, a silane compound or a siloxane compound having at least 1 silicon-bonded alkoxy group, and a siloxane group having at least 1 silicon-bonded hydroxy group and 1 silicon-bonded alkenyl group in a molecule, siloxane compounds expressed by the formula:

Formula 1



(where "j", "k", and "p" are positive numbers), siloxane compounds expressed by the formula:

Formula 2



(where "j", "k", "p", and "q" are positive numbers),

methyl polysilicate, ethyl polysilicate, and epoxy-group containing ethyl polysilicate.

Component (E) is preferably a low-viscosity liquid, and a viscosity at 25°C of component (E) is not particularly limited but is preferably within the range of from 1 to 500 mPa·s.

[0053] A content of component (E) is preferably within the range of from 0.01 to 30 parts by weight, even more preferably within the range of from 0.1 to 30 parts by weight, and particularly preferably within the range of from 0.1 to 20 parts by weight per 100 parts by weight of component (A). This is because if the content of component (E) is less than the lower limit of the range described above, substantial improvements in adhesiveness will not be observed, whereas if the content exceeds the upper limit of the range described above, the mechanical characteristics of the resulting cured product will be diminished.

[0054] The present composition comprises components (A) to (D), but the composition may further comprise (F) a reaction inhibitor as an additional optional component. Examples of component (F) include acetylene alcohols such as 1-ethynyl-1-cyclohexanol, 2-methyl-3-butyn-2-ol, 2-phenyl-3-butyn-2-ol, 2-ethynylisopropanol, 2-ethynylbutan-2-ol, and 3,5-dimethyl-1-hexyn-3-ol; silylated acetylene alcohols such as trimethyl(3,5-dimethyl-1-hexyn-3-oxy)silane, methylvinylbis(3-methyl-1-butyn-3-oxy)silane, and ((1,1-dimethyl-2-propynyl)oxy)trimethylsilane; unsaturated carboxylic acid esters such as diallyl malate, dimethyl malate, diethylfumarate, diallyl fumarate, and bis(methoxyisopropyl)malate; conjugated ene-yne compounds such as 2-isobutyl-1-buten-3-yne, 3,5-dimethyl-3-hexen-1-yne, 3-methyl-3-penten-1-yne, 3-methyl-3-hexen-1-yne, 1-ethynylcyclohexene, 3-ethyl-3-buten-1-yne, and 3-phenyl-3-buten-1-yne; and alkenyl group-containing cyclic siloxanes such as 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane. A content of component (F) is not particularly limited but is preferably within the range of from 0.001 to 5 parts by weight per 100 parts by weight of component (A).

[0055] The present composition may also comprise (G) an inorganic filler to improve the mechanical strength of the cured product formed by the present composition as an additional optional component. Examples of component (G) include fumed silica, precipitated silica, titanium dioxide, carbon black, alumina, quartz powder, and inorganic fillers prepared by surface-treating these inorganic fillers with organic silicon compounds such as organoalkoxysilanes, organochlorosilanes, or organosilazanes. In the present composition, a content of component (G) is not particularly limited but is preferably less than 100 parts by weight and particularly preferably within the range of from 0.1 to 20 parts by weight per 100 parts by weight of component (A).

[0056] The curing of the present composition progresses as a result of heating, but the composition is preferably heated at a temperature greater than or equal to the melting point

of the thermoplastic polyolefin resin in component (D) so that the composition can favorably adhere to various base materials. The form of the cured product formed by the curing of the present composition is preferably an elastomer and particularly preferably a gel or a rubber.

Examples

[0057] The microparticles containing a thermoplastic polyolefin resin and an organic metal compound and the curable organopolysiloxane composition according to the present invention will be described in detail hereinafter using practical examples. An adhesive strength of the cured product formed by the curable organopolysiloxane composition was measured in accordance with the tensile shear adhesive strength test method stipulated in JIS K 6850.

[0058]

[Reference Example 1]

A platinum catalyst (chloroplatinic acid aqueous solution (platinum content = 33 weight%)) was mixed and dispersed in a polyethylene wax (POLYWAX (registered trademark) 1000 made by the Baker Hughes Inc.) with an Mz of 3600 and Mz/Mw of 1.17, which was melted by heating at 150°C, so that the content was 0.5 weight%. This dispersed product was continuously sprayed into a spray dryer tank (made by the Ashizawa Niro Atomizer Ltd.) with a hot air flow consisting of a nitrogen gas using a two-fluid nozzle. Here, the hot air flow temperature of the nitrogen gas was 95°C at the inlet of the spray dryer and 45°C at the outlet of the spray dryer, and the hot air flow rate was 1.3 m^3/min. After running for one hour, platinum catalyst-containing polyethylene wax microparticles were collected with a bag filter. The amount of the platinum catalyst was converted based on the atomic weight of platinum.

[0059]

[Reference Example 2]

Zirconium tetra(acetylacetonate) ($Zr(acac)_4$) with an average particle diameter of 1 μm was mixed and dispersed in a polyethylene wax (POLYWAX (registered trademark) 1000 produced by the Baker Hughes Inc.) with an Mz of 3600 and Mz/Mw of 1.17, which was melted by heating at 150°C, so that the content was 10 weight%. This dispersed product was continuously sprayed into a spray dryer tank (produced by the Ashizawa Niro Atomizer, Ltd.) with a hot air flow consisting of a nitrogen gas using a two-fluid nozzle. Here, the hot air flow temperature of the nitrogen gas was 95°C at the inlet of the spray

dryer and 45°C at the outlet of the spray dryer, and the hot air flow rate was 1.3 m^3/min.After running for one hour, microparticles were collected with a bag filter. The average particle diameter was 19 μm. The average particle diameter was measured with the method stipulated in JIS K 8825-1. An IA500 laser diffraction/scattering-type particle size analyzer manufactured by Horiba, Ltd. was used for measurements. After 10 g of the resulting microparticles were placed in 40 g of ethanol and stirred, the ethanol was removed by centrifugation. The microparticles were then dried by leaving the microparticles to stand for one week in an environment with a temperature of 25°C and 50% relative humidity (RH) to obtain microparticles 1. Microparticles 2 were also obtained in the same manner as described above with the exception of using isopropyl alcohol (IPA) instead of ethanol. The particles prior to washing with a solvent were used as microparticles 3.

[0060]

[Reference Example 3]

Microparticles 4 were obtained in the same manner as in the case of microparticles 1 with the exception of adding $Zr(acac)_4$ to a polyethylene wax (HW100P produced by Mitsui Chemicals Inc.) with an Mz of 5920 and Mz/Mw of 2.17 so that the content was 10 weight%. The average particle diameter was 25 μm.

[0061]

[Reference Example 4]

Microparticles 5 were obtained in the same manner as in the case of microparticles 1 with the exception of adding $Zr(acac)_4$ to a polyethylene wax (POLYWAX (registered trademark) 655 produced by Baker Hughes Inc.) with an Mz of 2270 and Mz/Mw of 1.16 so that the content was 10 weight%. The average particle diameter was 17 μm.

[0062] The microparticles 1 to 5 obtained as described above are shown in Table 2.

[0063] Table 2

		Microparticles				
		1	2	3	4	5
$Zr(acac)_4$-containing polyethylene wax microparticles	Melting point (°C)	113	113	113	119	99
	Mz	3600	3600	3600	5920	2270
	Mz/Mw	1.17	1.17	1.17	2.17	1.16
	Concentration (weight%) of $Zr(acac)_4$ in the microparticles	10	10	10	10	10
	Average particle diameter (μm)	19	19	19	25	17
	Washing solvent	Ethanol	IPA	None	Ethanol	Ethanol

[0064] The curable organopolysiloxane compositions of Practical Examples 1 to 6 and Comparative Examples 1 to 4 were prepared as described below.

[0065] The components described below were mixed at the compounded amounts shown in Table 3 and lightly stirred. The content was in an amount such that, in the curable organopolysiloxane compositions, the quantity of silicon-bonded hydrogen atoms in component (B) was 1.5 mol per a total of 1 mol of vinyl groups in component (A-1), and components (C-1) and (C-2) and components (D-1) to (D-6) were added last and stirred well.

Component (A-1): Organopolysiloxane with a viscosity at 25°C of 33,000 mPa·s (vinyl group content = 0.7 weight%), comprising 67 weight% of a dimethylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups with a viscosity at 25°C of 35,000 mPa·s and 33 weight% of an organopolysiloxane represented by the average unit formula:

$[(CH_3(CH_2=CH)SiO_{1/2}]_{0.6}(SiO_{4/2})_1$

Component (B): A dimethylsiloxane-methylhydrogensiloxane copolymer capped at both molecular terminals with trimethylsiloxy groups with a viscosity at 25°C of 5 mPa·s (silicon-bonded hydrogen atom content = 0.7 weight%)

Component (C-1): 1,3-Divinyltetramethyldisiloxane solution of a 1,3-divinyltetramethylsiloxane platinum complex (platinum content = 4.8 weight%)

Component (C-2): Platinum catalyst-containing polyethylene wax microparticles prepared in Reference Example 1

Component (D-1): Microparticles 1 prepared in Reference Example 2

Component (D-2): Microparticles 2 prepared in Reference Example 2

Component (D-3): Microparticles 3 prepared in Reference Example 2

Component (D-4): Microparticles 4 prepared in Reference Example 3

Component (D-5): Microparticles 5 prepared in Reference Example 4

Component (D-6): Zirconium tetra(acetylacetonate) ($Zr(acac)_4$) with an average particle diameter of 1 μm

Component (E): 3-Glycidoxypropyl trimethoxysilane

Component (F): 2-Phenyl-3-butyn-2-ol

Component (G): Pulverized silica fine powder with an average particle diameter of 2 μm

[0066] Immediately after preparation, these compositions were sandwiched between two test pieces made of polybutylene terephthalate (hereinafter, referred to as PBT), polyphenylene sulfide (hereinafter, referred to as PPS), or polycarbonate (hereinafter, referred to as PC) so that the thickness was 1 mm. The compositions were then cured by heating for one hour in an oven at 110°C to prepare test samples in which two test pieces were formed integrally via a rubber-like cured product. Next, each test sample was placed in a tensile tester, and the percentage (%) of cohesive failure (CF) was observed. A CF level of 0% indicates adhesive failure (AF). Further, after the curable organopolysiloxane compositions of Practical Examples 1 to 6 and Comparative Examples 1 to 4 were stored for 4 and 6 months at 5°C, the compositions were cured under the same conditions as those described above, and cohesive failure was observed in the same manner. These results are shown in Table 3.

[0067]

Table 3

Composition (parts by weight)	Practical Examples						Comparative Examples			
	1	2	3	4	5	6	1	2	3	4
Component (A-1)	60	60	60	60	60	60	60	60	60	60
Component (B)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Component (C-1)	-	-	-	-	-	0.023	-	-	-	-
Component (C-2)	0.22	0.22	0.22	0.22	0.22	-	0.22	0.22	0.22	0.22
Component (D-1)	1	3	-	-	-	1	-	-	-	-
Component (D-2)	-	-	1	3	-	-	-	-	-	-
Component (D-3)	-	-	-	-	1	-	-	-	-	-
Component (D-4)	-	-	-	-	-	-	1	-	-	-
Component (D-5)	-	-	-	-	-	-	-	1	-	-
Component (D-6)	-	-	-	-	-	-	-	-	0.1	-
Component (E)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Component (F)	200 ppm	200 ppm	200 ppm	200 ppm	200 ppm	200 ppm	200 ppm	200 ppm	200 ppm	200 ppm
Component (G)	34	34	34	34	34	34	34	34	34	34
Initial adhesion										
PBT	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	AF
PPS	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	AF
PC	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	AF
Adhesion after storage (4 months at 5°C)										
PBT	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	50%CF	AF	AF
PPS	100%CF	100%CF	100%CF	100%CF	90%CF	100%CF	AF	AF	AF	AF
PC	100%CF	100%CF	100%CF	100%CF	100%CF	100%CF	AF	AF	AF	AF
Adhesion after storage (6 months at 5°C)										
PBT	100%CF	100%CF	100%CF	100%CF	100%CF	Impossible to measure	100%CF	AF	AF	AF
PPS	100%CF	100%CF	100%CF	100%CF	30%CF		AF	AF	AF	AF
PC	100%CF	100%CF	100%CF	100%CF	100%CF		AF	AF	AF	AF

Industrial Applicability

[0068] The microparticles of the present invention are able to prevent or reduce the diminishment of adhesiveness and hardness over time in a cured product of a hydrosilylation reaction-curable organopolysiloxane composition and can therefore be suitably used as an adhesion promoter for the composition. The curable organopolysiloxane composition of the present invention can be stored for long periods of time and can be cured at relatively low temperatures, so the composition is easy to handle. Moreover, the curable organopolysiloxane composition of the present invention has excellent adhesiveness with respect to various base materials and is therefore suitable as a sealant for a case of an electronic product in automotive applications, an adhesive for electrical/electronic use, a potting agent, a protective coating, or an underfill agent.

CLAIMS

1. Microparticles comprising:
at least one type of an organic metal compound selected from the group consisting of organic titanium compounds, organic zirconium compounds, organic aluminum compounds, and organic tin compounds; and
a thermoplastic polyolefin resin with a Z-average (Mz) of a weight average molecular weight (Mw) of at least 2500 and Mz/Mw of not more than 2.0,
the organic metal compound being dispersed in the thermoplastic polyolefin resin.

2. The microparticles according to Claim 1, wherein a melting point of the thermoplastic polyolefin resin is from 40 to 200°C.

3. The microparticles according to Claim 1, wherein the thermoplastic polyolefin resin is a polyolefin wax.

4. The microparticles according to Claim 3, wherein the polyolefin wax is selected from the group consisting of polyethylene waxes, polypropylene waxes, polybutene waxes, and combinations thereof.

5. The microparticles according to any one of Claims 1 to 4, wherein an average particle diameter is from 0.01 to 500 μm.

6. The microparticles according to any one of Claims 1 to 5, wherein the organic metal compound is a metal chelate compound.

7. The microparticles according to any one of Claims 1 to 6, wherein a content of the organic metal compound is from 1 to 99.9 weight%.

8. A curable organopolysiloxane composition comprising:
(A) an organopolysiloxane represented by the average unit formula:

$$R_aSiO_{(4-a)/2}$$

wherein, R is a substituted or unsubstituted monovalent hydrocarbon group, and "a" is a number from 1.0 to 2.3, and having at least an average of 1.5 alkenyl groups in a molecule;
(B) an organopolysiloxane having at least an average of 1.5 silicon-bonded hydrogen atoms in a molecule;
(C) a hydrosilylation reaction catalyst; and

(D) the microparticles described in any one of Claims 1 to 7.

9. The curable organopolysiloxane composition according to Claim 8, wherein a content of component (B) is in an amount such that a quantity of silicon-bonded hydrogen atoms in component (B) is from 0.05 to 20 mol per 1 mol of alkenyl groups in component (A).

10. The curable organopolysiloxane composition according to Claim 8 or 9, wherein a content of component (C) is in an amount to promote crosslinking of the composition by a hydrosilylation reaction.

11. The curable organopolysiloxane composition according to any one of Claims 8 to 10, wherein component (C) is dispersed in thermoplastic resin microparticles.

12. The curable organopolysiloxane composition according to Claim 11, wherein a melting point of the thermoplastic resin in Component (C) is from 40 to 200°C.

13. The curable organopolysiloxane composition according to Claim 11 or 12, wherein the thermoplastic resin in component (C) is a polyolefin resin, a methylmethacrylate resin, a polycarbonate resin, a polystyrene resin, a silicone resin, or a combination thereof.

14. The curable organopolysiloxane composition according to any one of Claims 8 to 13, wherein a content of component (D) is from 0.001 to 50 parts by weight per 100 parts by weight of component (A).

15. The curable organopolysiloxane composition according to any one of Claims 8 to 14, further comprising (E) an adhesion-imparting agent in an amount of from 0.01 to 30 parts by weight of per 100 parts by weight of component (A).

16. The curable organopolysiloxane composition according to Claim 15, wherein component (E) is an organic silicon compound having at least one type of functional group selected from the group consisting of epoxy groups, acryloxy groups, and methacryloxy groups.

17. The curable organopolysiloxane composition according to any one of Claims 8 to 16, further comprising (F) a reaction inhibitor in an amount of from 0.001 to 5 parts by weight per 100 parts by weight of component (A).

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2013/070954

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/56 C08L23/00 C08K3/00 C08K5/57 C08K13/00
C08L83/04 C08K9/10
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08K C08L

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2005/123839 A1 (DOW CORNING TORAY CO LTD [JP]; NAKATA TOSHIKI [JP]; ONISHI MASAYUKI [J) 29 December 2005 (2005-12-29) cited in the application abstract; claims 1-11 paragraphs [0009], [0013], [0015], [0017] - [0020]	1-17
A	EP 0 586 151 A1 (DOW CORNING [US]) 9 March 1994 (1994-03-09) abstract; claims 1,2 page 3, lines 56-57 page 4, lines 12-14,24-26,38-39	1-17

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

☒ See patent family annex.

* Special categories of cited documents :

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 October 2013	21/10/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schütte, Maya

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2013/070954

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