

MICROPARTICLE CATALYSTS FOR HYDROSILYLATION REACTIONS AND THERMOSETTING SILICONE COMPOSITIONS CONTAINING SAID CATALYST

This invention relates to microparticle catalysts for hydrosilylation reactions and thermosetting silicone compositions containing said catalyst. Our microparticle catalysts have high catalytic activity and provide thermosetting silicone compositions of superior storage stability which can be maintained in an unhardened state for long periods.

Thermoplastic resin catalysts that contain metallic catalysts for hydrosilylation reactions and thermosetting silicone compositions that contain such catalysts are generally known. For example, catalysts having softening points or melting points on the order of 40 to 200°C have been proposed in JP-As 49-134786, 58-37053, 2-4833, and 2-9448. Microparticle catalysts comprised of metallic catalysts and organic resins have also been proposed in JP-As 58-37053, 64-45468, 64-47442, 64-51140, 3-68659, and 7-41678. However, the metallic catalysts of these microparticle catalysts are easily decomposed by heating operations during manufacture, with decreased catalytic activity. Even when the decomposition is very slight and sufficient catalytic activity is obtained, discoloration due to the decomposition products cannot be avoided. Moreover, when these microparticle catalysts are used as a curing catalyst in an organosiloxane composition, there is the problem that composition hardening proceeds during storage and that an unhardened state is not be maintained for a long period.

As a result of intensive studies, we arrived at this invention by finding that the aforementioned problems are solved when a metallic catalyst for

hydrosilylation reactions and specified disiloxanes are present together in our claimed microparticle catalysts for hydrosilylation reactions.

The objective of this invention is to provide a microparticle catalyst for hydrosilylation reactions of superior catalytic activity and to provide a thermosetting silicone composition of superior storage stability that is stored in an unhardened state for long periods.

This invention is a microparticle catalyst, having an average particle diameter of 0.1 to 20 μm , for hydrosilylation reactions comprising:

- (i) a metallic catalyst for hydrosilylation reactions having 0.01 to 5 wt % of metal atoms;
- (ii) 0.1 to 5 wt % of a disiloxane having the general formula



where R^1 is an alkenyl group, R^2 is a monovalent hydrocarbon group and Ar is an aryl group; and (iii) a resin having a glass transition temperature of 40 to 200°C.

This invention also to a thermosetting silicone composition comprising:

- (A) 100 parts by weight of organopolysiloxane that contains an average of at least two silicon-bonded alkenyl groups per molecule;
- (B) an organohydrogenpolysiloxane that contains an average of at least two silicon-bonded hydrogen atoms per molecule, in an amount sufficient to provide a amount such that the ratio of the number of moles of silicon-bonded hydrogen atoms in this component and of the number of moles of silicon-bonded alkenyl groups in component (A) is in the range of 0.5/1 to 10/1; and
- (C) 0.005 to 100 parts by weight of a microparticle catalyst for hydrosilylation reactions comprising
 - (i) a metallic catalyst for hydrosilylation reactions having 0.01 to 5 wt % of metal atoms;

(ii) 0.01 to 5 wt % of a disiloxane having the general formula



where R^1 is an alkenyl group, R^2 is a monovalent hydrocarbon group and Ar is an aryl group; and

(iii) a resin having a glass transition temperature of 40 to 200°; wherein said microparticle catalyst has an average particle diameter of 0.1 to 20 μ m.

The metallic catalyst of this invention is a metallic catalyst having catalytic activity for hydrosilylation reactions. Examples include, but are not limited to, platinum catalysts, such as chloroplatinic acid, or alcohol modified chloroplatinic acid; complexes of platinum and olefins; complexes of platinum or chloroplatinic acid and diketones; complexes of platinum or chloroplatinic acid and divinyl disiloxane; platinum carried on alumina, silica and carbon black; palladium catalysts such as tetrakis (triphenylphosphine) palladium; and metallic catalysts such as rhodium, nickel and cobalt. Of these, platinum catalysts are preferred, and complexes of platinum and divinyl disiloxane are particularly preferred from the standpoint of catalytic activity. These catalysts can be used individually or as mixture of two or more. A catalyst that has been dissolved in a liquid may also be used. When a complex of platinum and divinyl disiloxane is used, it may be dissolved in an alcohol, a hydrocarbon solvent or a liquid polysiloxane at normal temperature. The quantity of said metallic catalyst in the microparticle of this invention is 0.01 to 5 wt %, and, preferably, 0.05 to 2 wt%, as metal atoms. When the content is less than 0.01 wt %, the quantity of the composition of this invention is excessive, and the inherent properties of said composition are lost. When it exceeds 5 wt %, it is difficult to maintain the metallic catalyst in the microparticle of this invention.

The microparticle catalysts of the present invention are characterized by the presence of a disiloxane having the general formula



The disiloxane acts to stabilize the metallic catalyst of our microparticle catalyst. When added to a composition that cures via a hydrosilylation reaction, our composition can be maintained in an uncured state for a long period. In the above formula, R^1 is an alkenyl group, preferably a vinyl group or an allyl group. Of these, vinyl groups are particularly preferred. R^2 is a monovalent hydrocarbon group. R^2 is exemplified by, but not limited to, alkyl groups, such as a methyl group or an ethyl group; alkenyl groups, such as a vinyl group or an allyl group; and aryl groups, such as a phenyl group or a naphthyl group. Ar of the formula is an aryl group and preferably, a phenyl group or a naphthyl group. Of these, phenyl groups are preferable. Examples of disiloxanes that are used in the present invention include, but are not limited to, syn-divinyldimethyldiphenyldisiloxane, syn-divinyltetraphenyldisiloxane and syn-tetravinyldiphenyldisiloxane. The amount of disiloxane present in the microparticle catalyst of the present invention is 0.1 to 5 wt %. When the amount of disiloxane is less than 0.1 wt %, the effect of the disiloxane cannot be manifested. When the amount of disiloxane present in the microparticle catalyst exceeds 5 wt %, compositions containing the microparticle catalyst tend to harden during storage.

The resin that is used in our microparticle catalyst should not be a substance that poisons the metallic catalyst for hydrosilylation reactions. Examples of usable resins include, but are not limited to, silicone resins, polysilane resins, polycarbonate resins, acrylic resins such as polymethyl acrylate and copolymers of methyl methacrylate and butyl methacrylate, polyester resins, polyethylene, polystyrene, polyvinyl chloride, polyvinylidene chloride, copolymers of polyvinyl chloride and polyvinylidene chloride, polyamides,

cellulose esters such as cellulose acetate and cellulose acetate butyrate. Suitable silicone resins include, for example, resins comprised of monophenylsiloxane units, diphenylsiloxane units and dimethylsiloxane units; resins comprised of monophenylsiloxane units and dimethylsiloxane units; and resins comprised of monophenylsiloxane units and methylvinylsiloxane units. Polysilane resins can include, for example, resins comprised of methylphenylsilane units and dimethylsilane units. It is necessary that the glass transition point of these resins be in the range of 40 to 200°C. When the glass transition point of the resin is less than 40°C, the manufacture of the microparticle catalysts of this invention is difficult, and the compositions that contain this microparticle catalyst cannot be stored for long periods in an unhardened state. When the glass transition point exceeds 200°C, the cure rate of the composition containing the microparticle catalyst is not sufficient. The aforementioned resins are all known as thermoplastic resins. Resins that are generally classified as thermosetting resins can also be used. Thermosetting resins that are useful in the present invention must also have glass transition points within the range of 40 to 200°C. The glass transition point is determined using a DSC (differential scanning calorimeter).

The microparticle catalyst of the present invention has an average particle diameter of 0.1 to 20 μm . When the average particle diameter is less than 0.1 μm , the storage stability of compositions containing the microparticle catalyst is not sufficient. When the average particle diameter exceeds 20 μm , the cure of compositions containing the microparticle catalyst is not uniform. There are no particular limitations on the shape of our microparticle catalyst. However, a spherical form is desirable for obtaining good reproducibility of stable catalytic activity inhibition and manifestation of catalytic activity.

Methods of manufacturing the microparticle catalyst of this invention include, for example, a method in which the metallic catalyst, the disiloxane and the resin are dissolved in a solvent such as toluene, after which a resin containing

the metallic catalyst and the disiloxane is manufactured by drying away the solvent (see JP-A 58-37053); a method in which the metallic catalyst, the disiloxane and the resin are dissolved in a solvent having a low boiling point such as methylene chloride, chloroform, tetrahydrofuran or diethyl ether, then the product solution is added dropwise to an aqueous solution of a surfactant to make an oil and water type emulsion, therefore solid microparticles are obtained by gradually removing the solvent (see JP-A 2-4833); and a method in which the metallic catalyst, the disiloxane and the resin are dissolved in a solvent such as toluene or dicyclomethane, said solution is next sprayed into a hot air stream, with the solvent being volatilized and with the resin containing the metallic catalyst and the disiloxane in the spray state being solidified (see JP-A 4-29748). The microparticle catalyst of this invention, obtained in this way, may be used in this unaltered form, or the metallic catalyst which is present on the surface of the particles may be removed by washing using a solvent such as methyl alcohol, ethyl alcohol, hexamethyl disiloxane and octamethylcyclotetrasiloxane that removes the metallic catalyst without dissolving the resin.

Component (A), which is an organopolysiloxane, is the component which forms the principal agent of the silicone composition of this invention, it has an average of at least two silicon-bonded alkenyl groups per molecule. Examples of the alkenyl groups include vinyl, allyl and hexenyl. Examples of organic groups that are bonded with the silicon atom in addition to the alkenyl group in this organopolysiloxane include alkyl, such as methyl, ethyl, propyl, butyl, hexyl and octyl; aryl, such as phenyl; and monovalent hydrocarbon groups as exemplified by substituted hydrocarbons such as 3,3,3-trifluoropropyl groups. The number of organic groups that are bonded to the silicon atom should average 1.0 to 2.3. This organopolysiloxane is generally a straight chain but may also have some branched chains. The viscosity of this organopolysiloxane at 25°C is in the range of 10 to 1,000,000 mm²/s (centipoise). Examples of

organopolysiloxanes that constitute this component include dimethylpolysiloxane blocked at both terminals by dimethylvinylsiloxane groups, dimethylsiloxane-methylvinylsiloxane copolymers blocked at both terminals by trimethylsiloxane groups, dimethylsiloxane-methylhexenylsiloxane copolymers blocked at both terminals by dimethylhexenylsiloxane groups and methyltrifluoropropylpolysiloxanes blocked at both terminals by dimethylvinylsiloxane groups. Single polymers, copolymers or mixtures of two or more polymers can be used.

Component (B), an organohydrogenpolysiloxane, is the crosslinking agent for component (A). Component (B) has an average of at least two silicon-bonded hydrogen atoms per molecule. Organic groups that are bonded with the silicon atoms in this component in addition to hydrogen atoms include alkyl groups, such as methyl, ethyl, propyl, butyl, hexyl and octyl; aryl groups, such as phenyl; and monovalent hydrocarbon groups, as exemplified by substituted hydrocarbons such as 3,3,3-trifluoropropyl groups. The molecular structure of this organohydrogenpolysiloxane may be straight chain, network or three-dimensional. Single polymers, copolymers or mixtures of two or more polymers can be used. The viscosity of this organohydrogenpolysiloxane at 25°C is in the range of 0.5 to 50,000 mm²/s (centipoise), and, preferably, in the range of 1 to 10,000 mm²/s (centipoise). The quantity of this component compounded is a quantity such that the ratio of the moles of silicon-bonded hydrogen atoms in this component to the number of moles of silicon-bonded alkenyl groups in component (A) is in the range of 0.5/1 to 10/1. The organohydrogenpolysiloxane can be a dimethylsiloxane-methylhydrogensiloxane copolymer blocked at both terminals by trimethylsiloxane groups, a dimethylsiloxane-methylhydrogensiloxane copolymer blocked at both terminals by dimethylhydrogensiloxane groups or a methylhydrogencyclosiloxane having three or more silicon atoms.

Component (C) is a microparticle catalyst for hydrosilylation reactions that is described above. Component (C) is the catalyst for effecting crosslinking of component (A), the alkenyl groups bonded with the silicon atoms, and component (B), the hydrogen atoms bonded with the silicon atoms, via a hydrosilylation reaction. The microparticle catalyst of this invention has an average particle diameter of 0.1 to 20 μm , and it contains the aforementioned metallic catalyst in an amount of 0.01 to 5 wt % as metal atoms with 0.1 to 5 wt % of the aforementioned disiloxane. The quantity of this component that is compounded is in the range of 0.005 to 100 parts of component (C) per 100 parts by weight of component (A) and, preferably, in the range of 0.1 to 100 ppm, calculated as metal atoms, in the organosiloxane composition.

The composition of this invention is comprised of the aforementioned components (A) through (C). In addition, various additives may be compounded as long as the objectives of the invention are not impaired. Additives which can be compounded into the compositions of the present invention include, but are not limited to, powdered silicas, such as foamed silica and wet silica; powdered silica that has been subjected to surface hydrophobic treatment; crepe hardening inhibitors; polymers other than silicone; organic solvents; iron oxide; heat resistant agents, such as rare earth compounds; flame retardants, such as manganese carbonate and aerosol titanium oxide; compounds containing phosphorus such as triphenylphosphine; compounds containing nitrogen such as tributylamine, tetramethylethylenediamine and benzotriazole; compounds containing sulfur; acetylene compounds; compounds containing two or more alkenyl groups; hydroperoxy compounds; hydrosilylation reaction inhibiting compounds such as maleic acid derivatives; diatomaceous earth; calcium carbonate; glass fibers; and carbon black.

The composition of this invention is easily obtained by mixing the aforementioned components (A) through (C) uniformly. For example, component

(C) may be added to a small quantity of component (A) and uniformly dispersed in it, after which this mixture may be added to a mixture of component (A) and component (B). It is desirable that the temperature does not exceed the glass transition temperature of the resin that constitutes component (C) by more than 50°C.

Our microparticle catalyst for the hydrosilylation reaction is of high catalytic activity, and the discoloration due to decomposition products is not seen. Because of this, the claimed microparticle catalyst invention is suitable for use as catalyst for elastomers and resin compositions in which an organopolysiloxane is used as the base polymer. Further, the thermosetting silicone composition of this invention, which contains our microparticle catalyst, has the characteristics of remaining in an unhardened state at room temperature for long periods, and after storage rapidly curing by heat. Consequently, the silicone composition of this invention is extremely useful as a single solution thermosetting silicone composition.

Next, a detailed description of this invention is demonstrated by means of examples. In the examples, Ph indicates a phenyl group, Me indicates a methyl group, Vi indicates a vinyl group and g is grams. Viscosity is the value determined at 25°C and cp is centipoise.

COMPARATIVE EXAMPLE 1

6 g of aqueous solution of chloroplatinic acid (platinum metal content of 33 wt %) and 16 g of 1,3-divinyltetramethyldisiloxane were dissolved in 35 g of isopropyl alcohol. 10 g of sodium bicarbonate were added to this solution and a reaction was carried out in a state of suspension for 30 minutes at 70 to 80°C as the solution was stirred. After cooling, the solid component was removed by filtration and a 4.2 wt % isopropyl alcohol solution of platinum vinyl siloxane component containing platinum metal was prepared.

EXAMPLE 1

819 g of thermoplastic silicone resin, having a glass transition point of 66.5°C as indicated by the average unit formula $(\text{PhSiO}_{3/2})_{0.78} (\text{Me}_2\text{SiO})_{0.22}$, and having a glass transition point of 66.5°C 72 g of thermoplastic silicone resin, having a glass transition point of 65.2°C as indicated by the average unit formula $(\text{PhSiO}_{3/2})_{0.78} (\text{MeViSiO})_{0.22}$ and; having a glass transition point of 65.2°C and 9.0 g of syn-dimethyldiphenyldivinylsiloxane were introduced into a mixed solvent of 500 g of toluene and 4,600 g of dichloromethane in a container equipped with a stirrer and were stirred to a uniform state. Next, 88.8 g of the isopropyl alcohol solution of the platinum vinyl siloxane complex obtained in Comparative Example 1 was introduced into this mixture and a uniform solution was obtained by mixing. This solution was sprayed continuously into a spray dryer tank (manufactured by Ashizawa Nitro Atomizers Ltd. in which nitrogen gas was present as a hot gas flow using a two-fluid nozzle. The temperature of the hot flow of nitrogen gas was 95°C at the inlet of the spray dryer, and was 45°C at the outlet of the spray dryer with the hot gas flow rate at 1.3 m³/minute. The operation was carried out for 1 hour under the aforementioned conditions, and 415 g of the white microparticle catalyst for hydrosilylation reaction that was produced was collected by means of a back filter. The average particle diameter of the microparticle catalyst obtained was 1.5 μm and the platinum content was 0.40 wt % as metal atoms.

COMPARATIVE EXAMPLE 2

408 g of microparticle catalyst for the hydrosilylation reaction was manufactured in the same way as in Example 1 except that the syn-dimethyldiphenyldivinylsiloxane was not added, and the quantity of thermoplastic silicone resin compounded was changed to 828 g. The obtained

microparticle catalyst was grayish-white; its average particle diameter was 1.6 μm ; and its platinum content was 0.40 wt %.

EXAMPLE 2

20 g of fumed silica, the surface of which had been subjected to hydrophobic treatment with hexamethyldisilazane, with a specific surface area 150 m^2/g , was added to and thoroughly mixed with a mixture of 100 g of dimethylvinylsiloxane-terminated dimethylpolysiloxane of a viscosity of 12,000 mm^2/s (cp) and 100 g of dimethylvinylsiloxane-terminated dimethyl polysiloxane of a viscosity of 1,500 mm^2/s (cp), after which 2.8 g of a diorganosiloxane as indicated by the average molecular formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_3(\text{MeHSiO})_5\text{SiMe}_3$ and 0.04 g of phenylbutynol were added, and then mixed to a uniform state. Next, the microparticle catalyst of Example 1 was added to this mixture in a quantity such that the platinum metal content of the mixture was 5 ppm, after which the materials were thoroughly mixed, with a thermosetting silicone composition being prepared. The thermosetting characteristics of the thermosetting silicone composition obtained were determined at 130°C and 150°C with a model 5 Curastometer TM (manufactured by the Orientech Company). The thermosetting characteristics were determined taking the time until torque reached a maximum of 10% as the hardening initiation time (T_{10}), and the time until torque reached a maximum of 90% as hardening completion time (T_{90}). The product thermosetting silicone composition was introduced into a sealed container and was aged at 50°C. The number of days required to hardening was determined, and the finding was reported as storage stability. The results are shown in Table 1. On the basis of these results, it was ascertained that the hardening rate during heating increased, and that the unhardened state at room temperature could be maintained for long periods by adding syn-dimethyldiphenyldivinylsiloxane.

COMPARATIVE EXAMPLE 3

The thermosetting silicone composition of Example 2 was prepared in the same way except that the microparticle catalyst for hydrosilylation reactions obtained in Comparative Example 2 was added instead of the microparticle catalyst of Example 1. The thermosetting properties and storage stability of the obtained thermosetting silicone composition were determined as in Example 2. The results are also shown in Table 1.

Table 1

	Example 2	Comparative Example 3
Thermosetting characteristics		
130°C T ₁₀ (seconds)	72.6	78.0
T ₉₀ (seconds)	84.6	91.2
150°C T ₁₀ (seconds)	23.4	23.4
T ₉₀ (seconds)	29.4	30.0
Storage stability (days)	41	29

EXAMPLE 3

500 g of polycarbonate resin having a glass transition point of approximately 140°C (Inpilon H-3000 manufactured by Mitsubishi Gas Chemical Company, Ltd. of Tokyo, Japan) was dissolved in 8.5 kg of dichloromethane and 5.0 g of syn-dimethyldiphenyldivinylsiloxane and 1.0 kg of toluene were added and mixed. Next, 23.8 g of the isopropyl alcohol solution of the platinum vinylsiloxane complex obtained in Comparative Example 1 was introduced into and mixed with this solution, until a uniform solution was

obtained. This solution was sprayed continuously into the spray dryer tank of Example 1. The temperature of the hot flow of nitrogen gas was 100°C at the inlet of the spray dryer, and was 70°C at the outlet of the spray dryer with the hot gas flow rate at 1.3 m³/minute. The operation was carried out for 5 hours under the aforementioned conditions and 380 g of the white microparticle catalyst for hydrosilylation reaction that was produced was collected by means of a back filter. The average particle diameter of the microparticle catalyst obtained was 1.47 µm and the platinum content was 0.2 wt %.

COMPARATIVE EXAMPLE 4

408 g of microparticle catalyst for hydrosilylation reaction was manufactured in the same way as except that the syn-dimethyldiphenyldivinylsiloxane in Example 3 was not added. The microparticle catalyst that was obtained was gray, its average particle diameter was 1.44 µm and its platinum content was 0.2 wt %.

EXAMPLE 4

20 g of fumed silica, with a specific surface area of 150 m²/g, the surface of which had been subjected to hydrophobic treatment with hexamethyldisilazane, was added to and thoroughly mixed with a mixture of 100 g of dimethylvinylsiloxane-terminated dimethyl polysiloxane of a viscosity of 12,000 mm²/s (cp) and 100 g of dimethylvinylsiloxane-terminated dimethyl polysiloxane of a viscosity of 1,500 mm²/s (cp), after which 2.8 g of a diorganosiloxane as indicated by the average molecular formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_3(\text{MeHSiO})_5\text{SiMe}_3$ and 0.04 g of phenylbutynol were added, and then mixed to a uniform state. Next, the microparticle catalyst of Example 3 was added to this mixture in a quantity such that the platinum metal content of the mixture was 2.5 ppm, after which the materials were thoroughly mixed, with a thermosetting silicone

composition being prepared. The thermosetting characteristics of the thermosetting silicone composition that was obtained were determined at 150°C and 170°C with a model 5 Curastometer Tm like used in Example 2. The thermosetting characteristics were determined (T_{10}) and (T_{90}) as in Example 2. The product thermosetting silicone composition was introduced into a sealed container and was aged at 50°C. The number of days for hardening was determined and the finding was taken as storage stability. The results are shown in Table 2. On the basis of these results, it was ascertained that the hardening rate during heating increased, and that the unhardened state at room temperature could be maintained for long periods by adding syn-dimethyldiphenyldivinylsiloxane.

COMPARATIVE EXAMPLE 5

The thermosetting silicone composition of Example 4 was prepared in the same way except that the microparticle catalyst for hydrosilylation reactions obtained in Comparative Example 4 was added instead of the microparticle catalyst Example 3. The thermosetting properties and storage stability of the thermosetting silicone composition that was obtained were determined as in Example 4. The results are shown in Table 2.

Table 2

	Example 4	Comparative Example 5
Thermosetting characteristics		
150°C T_{10} (seconds)	130.8	167.4
T_{90} (seconds)	162.0	205.2
170°C T_{10} (seconds)	26.4	30.6
T_{90} (seconds)	39.6	48.6
Storage stability (days)	247	217

EXAMPLE 5

500 g of a copolymer of methyl methacrylate and butyl methacrylate having a glass transition point of approximately 80°C (ELVACITE TM 2013; a registered trademark of E.I. Du Pont De Nemours & Co. of Wilmington, DE.) was dissolved in 8.5 kg of dichloromethane and 5.0 g of syn-dimethyldiphenyldivinyldisiloxane. 1.0 kg of toluene was then added and mixed. Next, 44.4 g of the isopropyl alcohol solution of the platinum vinylsiloxane complex obtained in Comparative Example 1 was introduced into and mixed with this solution, until a uniform solution was obtained. This solution was sprayed continuously into the spray dryer tank of example 1. The temperature of the hot flow of nitrogen gas was 95°C at the inlet of the spray dryer and was 50°C at the outlet of the spray dryer with the hot gas flow rate at 1.3 m³/minute. The operation was carried out for 5 hours under the aforementioned conditions and 365 g of the white microparticle catalyst for the hydrosilylation reaction that was produced was collected by means of a back filter. The average particle diameter of the obtained microparticle catalyst was 1.78 μm, and the platinum content was 0.4 wt %.

EXAMPLE 6

20 g of fumed silica, with a specific surface area 150 m²/g the surface of which had been subjected to hydrophobic treatment with hexamethyldisilazane, was added to and thoroughly mixed with a mixture of 100 g of dimethylvinylsiloxane-terminated dimethylpolysiloxane of a viscosity of 12,000 mm²/s (cp) and 100 g of dimethylvinylsiloxane-terminated dimethylpolysiloxane of a viscosity of 1,500 mm²/s (cp), after which 2.8 g of a diorganosiloxane as

indicated by the average molecular formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_3(\text{MeHSiO})_5\text{SiMe}_3$ and 0.04 g of phenylbutynol were added, and then mixed to a uniform state. Next, the microparticle catalyst of Example 5 was added to this mixture in a quantity such that the platinum metal content of the mixture was 5 ppm, after which the materials were thoroughly mixed, with a thermosetting silicone composition being prepared. The thermosetting characteristics of the thermosetting silicone composition obtained were determined at 130°C and 150°C with a model 5 Curastometer TM as used in Example 2. The thermosetting characteristics were determined for (T_{10}) and (T_{90}) as in Example 2. At 130°C, the T_{10} value of the obtained silicone composition was 85.6 seconds, and the T_{90} value was 98.2 seconds. At 150°C the T_{10} value was 32.6 seconds, and the T_{90} value was 46.2 seconds. When this thermosetting silicone composition was aged at 50°C, an unhardened state was maintained for 87 days.

EXAMPLE 7

500 g of resin with glass transition point of approximately 140°C (IUPILON TM H-3000 a registered trademark of Mitsubishi Gas Chemical Company, LTD was dissolved in 8.5 kg of dichloromethane and 5.0 g of syn-tetraphenyldivinylsiloxane. Then, 1.0 kg of toluene was added and mixed. Next, 23.8 g of the isopropyl alcohol solution of the platinum vinylsiloxane complex obtained in Comparative Example 1 was introduced into and mixed with this solution, until a uniform solution was obtained. This solution was sprayed continuously into the spray dryer tank of Example 1. The temperature of the hot flow of nitrogen gas was 100°C at the inlet of the spray dryer, and was 70°C at the outlet of the spray dryer with the hot gas flow rate at 1.3 m³/minute. The operation was carried out for 5 hours under the aforementioned conditions, and 385 g of the white microparticle catalyst for hydrosilylation reaction that was

produced was collected by means of a back filter. The average particle diameter of the microparticle catalyst obtained was 1.52 μm , and the platinum content was 0.2 wt %.

EXAMPLE 8

20 g of fumed silica, with a specific surface area of 150 m^2/g , the surface of which had been subjected to hydrophobic treatment with hexamethyldisilazane, was added to and thoroughly mixed with a mixture of 100 g of dimethylvinylsiloxane-terminated dimethylpolysiloxane of a viscosity of 12,000 mm^2/s (cp) and 100 g of dimethylvinylsiloxane-terminated dimethylpolysiloxane of a viscosity of 1,500 mm^2/s (cp), after which 2.8 g of a diorganosiloxane as indicated by the average molecular formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_3(\text{MeHSiO})_5\text{SiMe}_3$ and 0.04 g of phenylbutynol were added, and then mixed to a uniform state. Next, the microparticle catalyst of Example 7 was added to this mixture in a quantity such that the platinum metal content of the mixture was 2.5 ppm, after which the materials were thoroughly mixed, with a thermosetting silicone composition being prepared. The thermosetting characteristics of the obtained thermosetting silicone composition were determined at 150°C and 170°C with a model 5 Curastometer TM as in Example 2. The thermosetting characteristics for (T_{10}) and (T_{90}) were determined like in Example 2. At 150°C, the T_{10} value of the thermosetting silicone composition was 122.1 seconds, and the T_{90} value was 157.1 seconds. At 170°C, the T_{10} value was 26.0 seconds, and the T_{90} value was 38.1 seconds. When this thermosetting silicone composition was aged at 50°C, an unhardened state was maintained for 268 days.

Thus, the microparticle catalyst for hydrosilylation reactions of this invention is comprised of a metal catalyst for hydrosilylation reactions, specified disiloxanes and a resin having a glass transition point of 40 to 200°C, and has a high catalytic activity. In addition, the thermosetting silicone composition that

contains this microparticle catalyst of this invention has superior storage stability and an unhardened state that can be maintained for a long period.

**Claims:****1. A microparticle catalyst comprising:**

- (i) a metallic catalyst comprising 0.01 to 5 wt % metal atoms;
- (ii) 0.1 to 5 wt % of a disiloxane having the general formula



wherein R^1 is an alkenyl group, R^2 is a monovalent hydrocarbon group and Ar is an aryl group; and

- (iii) a resin having a glass transition temperature of 40 to 200 °C;

wherein said microparticle catalyst has an average particle diameter of 0.1 to 20 μm .

2.. An organosiloxane composition comprising:

(A) 100 parts by weight of an organopolysiloxane having an average of at least two silicon-bonded alkenyl groups per molecule;

(B) an organohydrogenpolysiloxane having an average of at least two silicon-bonded hydrogen atoms per molecule, in an amount sufficient to provide a ratio of the number of moles of silicon-bonded hydrogen atoms bonded in component (B) to the number of moles of silicon bonded alkenyl groups in component (A) is in the range of 0.5/1 to 10/1; and

(C) 0.005 to 100 parts by weight of the microparticle catalyst of claim 1.

**MICROPARTICLE CATALYSTS FOR HYDROSILYLATION REACTIONS AND
THERMOSETTING SILICONE COMPOSITIONS CONTAINING SAID CATALYST**

ABSTRACT

A microparticle catalyst is described for use in hydrosilylation reactions. Said catalyst consists of microparticles of an average particle diameter of 0.1 to 20 μm comprised of a metallic catalyst for hydrosilylation reactions; a disiloxane having the general formula $(\text{R}^1\text{R}^2\text{ArSi})_2\text{O}$, wherein, R^1 is an alkenyl group, R^2 is a monovalent hydrocarbon group and Ar is an aryl group and a resin having a glass transition temperature of 40 to 200°C. A thermosetting silicone composition in combination with said microparticle catalyst is also disclosed.

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