

PATENT APPLICATION
FOR
LIQUID SILICONE RUBBER COMPOSITION AND METHOD FOR
MANUFACTURE AND METHOD FOR MANUFACTURING
FOAMED SILICONE RUBBER

BACKGROUND OF INVENTION

The present invention relates to a liquid silicone rubber composition, to a method for manufacturing this composition, and to a method for manufacturing a foamed silicone rubber. More particularly, it relates to a liquid silicone rubber composition that is easy to work with in mixing and that upon curing becomes a foamed silicone rubber with a low specific gravity and low thermal conductivity, to a method for manufacturing this composition, and to a method for manufacturing a foamed silicone rubber with a low specific gravity and low thermal conductivity.

There is a known method in which a thermoplastic resin hollow-particle powder that expands when heated is compounded with a silicone rubber composition, the silicone rubber composition is heated and cured during which time the thermoplastic resin hollow-particle powder expands and a foamed silicone rubber is obtained (see Japanese Laid-Open Patent Application H5-209080). There has also been proposed a method for obtaining a silicone rubber composition with low specific gravity by compounding a pre-expanded thermoplastic resin hollow-particle powder into a silicone rubber composition. With the former method, however, it is difficult to control the curing rate of the silicone rubber composition and the expansion rate of the thermoplastic resin hollow-particle powder, so a problem is that the cells are not uniform in size and the resulting foamed silicone rubber varies considerably in its specific gravity. With the latter method it is extremely difficult to blend a pre-expanded thermoplastic resin hollow-particle powder into a silicone rubber composition and even if this compounding is successful a problem is the extremely high viscosity of the silicone rubber composition after compounding.

Another problem is that a pre-expanded thermoplastic resin hollow-particle powder is extremely high in bulk and therefore tends to scatter when handled and is otherwise generally difficult to work with. To solve these problems, paints and plastics have been proposed which contain plastic fines treated with a liquid substance such as water, an organic solvent, or silicone oil (see Japanese Laid-Open Patent Application H4-071664). Air spraying is complicated, however, and there is also the danger that the liquid substance used in the treatment will become admixed in the silicone rubber and adversely affect its characteristics.

It is an object of the present invention to provide a liquid silicone rubber composition that is easy to work with in mixing and that upon curing becomes a foamed silicone rubber with a low specific gravity and low thermal conductivity, a method for manufacturing this composition, and method for manufacturing a foamed silicone rubber.

SUMMARY OF INVENTION

The present invention relates to a liquid silicone rubber composition comprising a liquid silicone rubber base compound produced by mixing (A) a liquid diorganopolysiloxane containing an optional inorganic filler with (B) a thermoplastic resin hollow-particle powder that expands when heated and performing a heat treatment at a temperature sufficient to cause expansion of component (B) and (C) a curing agent in an amount sufficient to cure the liquid diorganopolysiloxane; to a method for manufacturing this composition; and to a method for manufacturing a foamed silicone rubber characterized in that the above-mentioned liquid silicone rubber composition is heated and cured.

DESCRIPTION OF INVENTION

The present invention is a liquid silicone rubber composition comprising a liquid silicone rubber base compound produced by mixing (A) a liquid diorganopolysiloxane containing an optional inorganic filler with (B) a thermoplastic resin hollow-particle powder that expands when heated and performing a heat treatment at a temperature

sufficient to cause expansion of component (B) and (C) a curing agent in an amount sufficient to cure the liquid diorganopolysiloxane; a method for manufacturing this composition; and a method for manufacturing a foamed silicone rubber characterized in that the above-mentioned liquid silicone rubber composition is heated and cured.

Component (A) is the main agent in the present composition and can be diorganopolysiloxane described by average unit formula $R_a(OH)_bSiO_{(4-a-b)/2}$, where R is a monovalent hydrocarbon group or a halogenated alkyl group. Examples of monovalent hydrocarbon groups include alkyl groups such as the methyl, ethyl, and propyl; alkenyl groups such as the vinyl and allyl; cycloalkyl groups such as cyclohexyl; aralkyl groups such as the β -phenylethyl; and aryl groups such as phenyl. Examples of halogenated alkyl groups include chloromethyl, 3-chloropropyl, and 3,3,3-trichloropropyl. In the formula a is a number from 1.9 to 2.1 and b is a number from 0 to 0.1. A diorganopolysiloxane such as this usually has a viscosity (at 25°C) between 100 and 1,000,000 mPa · s.

The molecular structure of this component (A) is substantially linear, but part of the molecular chain may be slightly branched. Specific examples of this diorganopolysiloxane include dimethylpolysiloxane capped with dimethylvinylsiloxyl groups, a copolymer of methylvinylsiloxane and dimethylsiloxane capped with dimethylvinylsiloxyl groups, a copolymer of methylvinylsiloxane and dimethylsiloxane capped with silanol groups, a copolymer of methylphenylsiloxane and dimethylsiloxane capped with dimethylvinylsiloxyl groups, a copolymer of methylphenylsiloxane, methylvinylsiloxane, and dimethylsiloxane capped with dimethylvinylsiloxyl groups, a copolymer of diphenylsiloxane and dimethylsiloxane capped with dimethylvinylsiloxyl groups, a copolymer of diphenylsiloxane, methylvinylsiloxane, and dimethylsiloxane capped with dimethylvinylsiloxyl groups, a copolymer of methyl(3,3,3-trifluoropropyl)siloxane and dimethylsiloxane capped with dimethylvinylsiloxyl groups, and a copolymer of methyl(3,3,3-trifluoropropyl)siloxane, methylvinylsiloxane, and dimethylsiloxane capped with dimethylvinylsiloxyl groups.

Component (A) may contain an optional inorganic filler that serves to impart mechanical strength to the silicone rubber. The inorganic filler can be any that is known as a reinforcing filler or semi-reinforcing filler of silicone rubber. Examples of reinforcing fillers include dry process silica, wet process silica, hydrophobic silica where the surface of one of these types of silica has been treated with an organochlorosilicon, organoalkoxysilane, organopolysiloxane, organosilazane, or the like; carbon black; and colloidal calcium carbonate. Of these, particulate silica with a specific surface area of at least $100 \text{ m}^2/\text{g}$ are preferable. Examples of non-reinforcing fillers include diatomaceous earth, quartz powder, mica, aluminum oxide, and titanium oxide.

Component (B) is a thermoplastic resin hollow-particle powder that expands when heated and comprises a volatile substance enclosed in spherical shells composed of a thermoplastic resin. Examples of the thermoplastic resin that forms the shell of this component include polyethylene, polystyrene, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polyacrylonitrile, polymethyl methacrylate, polybutadiene, polychloroprene, and other vinyl polymers and copolymers; nylon 6, nylon 66, and other polyamides; and polyethylene terephthalate, polyacetal, and blends of these. Examples of the volatile substance enclosed in the thermoplastic resin hollow-particle powder include butane, isobutane, propane, and other hydrocarbons; methanol, ethanol, and other alcohols; dichloroethane, trichloroethane, trichloroethylene, and other halogenated hydrocarbons; and diethyl ether, isopropyl ether, and other ethers. It is preferable for the particle diameter of component (B) to be 1 to $50 \text{ }\mu\text{m}$ prior to expansion and 5 to $200 \text{ }\mu\text{m}$ after expansion. This is because thermal conductivity will not be low if this particle diameter is less than $1 \text{ }\mu\text{m}$, but if $50 \text{ }\mu\text{m}$ is exceeded, the strength of the thermoplastic resin hollow-particle powder will decrease to the point that the particles will break up during compounding into the liquid silicone rubber base composition. The amount in which component (B) is compounded is usually 0.1 to 15 wt% in the present composition. This is because thermal conductivity will not be low if the amount is less than this, but if the amount is larger than this the viscosity of the liquid silicone rubber

base composition will be too high for processing or the thermal conductivity will be too low and heat treatment will take a long time.

The liquid silicone rubber compound used in the present invention is obtained by mixing the above-mentioned component (B) into component (A) then expanding component (B) by performing a heat treatment at a temperature over the thermal expansion commencement temperature of this component (B). The temperature at which the mixture of components (A) and (B) is heat treated is usually between 80 and 180°C. How much component (B) is expanded will vary with the type of component (B) being used and other factors, but component (B) can be expanded up to, but not including, the size at which the shell breaks.

The curing agent of component (C) can be an organic peroxide, or a platinum-based catalyst can be used together with an organopolysiloxane containing hydrogen atoms bonded to silicon atoms. Examples of the organic peroxide include benzoyl peroxide, t-butyl benzoate, o-methylbenzoyl peroxide, p-methylbenzoyl peroxide, m-methylbenzoyl peroxide, dicumyl peroxide, and 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane. The amount at which this component is compounded is between 0.1 and 10 weight parts per 100 weight parts component (A).

As to the latter use of a platinum-based catalyst together with an organopolysiloxane containing hydrogen atoms bonded to silicon atoms, examples of the platinum-based catalyst include platinum fines, platinum black, chloroplatinic acid, alcohol-modified chloroplatinic acid, an olefin complex of chloroplatinic acid, and a complex compound of chloroplatinic acid and an alkenylsiloxane. The organopolysiloxane containing hydrogen atoms bonded to silicon atoms serves as a crosslinking agent to cure the composition of the present invention through reaction with the above-mentioned component (A) in the presence of a platinum-based catalyst. Examples of such an organopolysiloxane containing hydrogen atoms bonded to silicon atoms include methylhydrogenpolysiloxane capped at both ends with trimethylsiloxy groups, a copolymer of methylhydrogensiloxane and dimethylsiloxane capped at both ends with trimethylsiloxy groups, a copolymer of methylhydrogensiloxane and

dimethylhydrogensiloxane capped at both ends with dimethylhydrogensiloxy groups, and tetramethyltetrahydrogencyclotetrasiloxane. In this case, a known compound such as 1-ethynyl-cyclohexanol, 3-methyl-1-penten-3-ol, 3,5-dimethyl-1-hexyn-3-ol, or benzotriazole can be added as an inhibitor of catalytic activity of the platinum-based catalyst.

The present composition is a liquid silicone rubber base compound composed of the above-mentioned component (A), component (B), and component (C), but as long as the object of the present invention is not compromised, various additives known to be added to silicone rubber compositions may also be used in addition to the above components. Such additional components include carbon black, iron oxide red, and other pigments; rare earth oxides; rare earth hydroxides; cerium silanolate, cerium fatty acid salts, and other heat resistance agents; fumed titanium dioxide, carbon black, zinc carbonate, and various other flame retardants; and internal release agents.

The composition of the present invention is manufactured by compounding the above-mentioned component (C) with the liquid silicone rubber base compound composed of component (A) and component (B). Any of various mixers used in the manufacture of silicone rubber compositions can be used for the manufacturing apparatus here, examples of which include a kneader mixer, pressurized kneader mixer, Ross mixer, continuous kneader extruder, and other such mixers.

When heated and cured, the present composition becomes a foamed silicone rubber. The heating temperature here is usually at least 100°C, and a range of 100 to 180°C is preferable. The foamed silicone rubber thus obtained usually has a thermal conductivity between 0.05 and 0.17 W/(m · K).

The composition of the present invention as described above is easy to work with in mixing and upon curing becomes a foamed silicone rubber with a low thermal conductivity. Therefore, this composition can be used to advantage in applications that demand these characteristics, such as thermal insulating gaskets, thermal insulating sealants, thermal insulating adhesives, coatings for copier rolls, and so forth.

The present invention will now be described through examples. In these examples, "parts" indicates "weight parts," and viscosity is the value measured at 25°C. The hardness of the foamed silicone rubber was measured according to JIS K 6249. Thermal conductivity was measured according to JIS R 2618.

Example 1. 100 Parts of a dimethylpolysiloxane that was capped at both ends of the molecular chain with dimethylvinylsiloxy groups and that had a viscosity of 2000 mPa · s and 10 parts of fumed silica that had been treated with hexamethyldisilazane and had a BET specific surface area of 130 m²/g were put into a Ross mixer and mixed until uniform to prepare a compound that had fluidity. Next, 5 weight parts of a thermoplastic resin hollow-particle powder enclosing isobutane on the inside (this hollow-particle powder had a particle diameter between 10 and 16 μm, and its expansion commencement temperature was between 120 and 128°C; this powder is commercially available under the brand name "Expancell 091DU" from Expancell) was added and mixed until uniform. This mixture was heated treated at a temperature of 170°C to prepare a liquid silicone rubber base compound that had fluidity. To this liquid silicone rubber base compound were then added 2 parts of a copolymer of dimethylsiloxane and methylhydrogensiloxane capped at both ends with trimethylsiloxy groups and composed of 4 mol of dimethylsiloxane units and 6 mol of methylhydrogensiloxane units, 0.15 part (0.4 wt% platinum content) of a complex of chloroplatinic acid and divinyltetramethyldisiloxane, and 0.05 part 3,5-dimethyl-1-hexyn-3-ol (used as a curing inhibitor), and these components were mixed until uniform to prepare a liquid silicone rubber composition. The viscosity of this composition was 600 Pa · s. This composition was then press cured at 120°C to obtain a foamed silicone rubber with a thickness of 6 mm. This foamed silicone rubber was sliced and the cut surface thereof was observed under a microscope, which revealed that the size of the cells included in this foam was between 30 and 50 μm, and the cells were uniform in size. The specific gravity of this foamed silicone rubber was 0.60, the hardness was 30, and the thermal conductivity was 0.13 W/(m · K). These results are given in Table 1 below.

Comparative Example 1. 100 Parts of a dimethylpolysiloxane that was capped at both ends of the molecular chain with dimethylvinylsiloxy groups and that had a viscosity of 2000 mPa · s and 10 parts of fumed silica that had been treated with hexamethyldisilazane and had a BET specific surface area of 130 m²/g were put into a Ross mixer and mixed until uniform to prepare a compound that had fluidity. Next, 5 weight parts of a thermoplastic resin hollow-particle powder enclosing isobutane on the inside (this hollow-particle powder had a particle diameter between 10 and 16 μm, and its expansion commencement temperature was between 120 and 128°C; this powder is commercially available under the brand name "Expancell 091DU" from Expancell) was added and mixed until uniform to prepare a liquid silicone rubber base compound that had fluidity. To this liquid silicone rubber base compound were then added 2 parts of a copolymer of dimethylsiloxane and methylhydrogensiloxane capped at both ends with trimethylsiloxy groups and composed of 4 mol of dimethylsiloxane units and 6 mol of methylhydrogensiloxane units, 0.15 part (0.4 wt% platinum content) of a complex of chloroplatinic acid and divinyltetramethyldisiloxane, and 0.05 part 3,5-dimethyl-1-hexyn-3-ol (used as a curing inhibitor), and these components were mixed until uniform to prepare a liquid silicone rubber composition. The viscosity of this composition was 90 Pa · s. This composition was then press cured at 120°C to obtain a foamed silicone rubber with a thickness of 6 mm. This foamed silicone rubber was sliced and the cut surface thereof was observed under a microscope, which revealed that the size of the cells included in this foam was between 10 and 20 μm, and the cells had hardly expanded at all. The specific gravity of this foamed silicone rubber was 1.02, the hardness was 30, and the thermal conductivity was 0.19 W/(m · K). These results are given in Table 1 below.

Comparative Example 2. 100 Parts of a dimethylpolysiloxane that was capped at both ends of the molecular chain with dimethylvinylsiloxy groups and that had a viscosity of 2000 mPa · s and 10 parts of fumed silica that had been treated with hexamethyldisilazane and had a BET specific surface area of 130 m²/g were put into a Ross mixer and mixed until uniform to prepare a compound that had fluidity. Next, 5

weight parts of a hollow-particle powder that had already been expanded by heating a thermoplastic resin hollow-particle powder enclosing isobutane on the inside (this hollow-particle powder had a particle diameter between 35 and 55 μm , and is commercially available under the brand name "Expancell 091DE" from Expancell) was added and mixed until uniform to prepare a liquid silicone rubber base composition that had fluidity. This previously heated and expanded hollow-particle powder was extremely prone to scattering, and furthermore was high in bulk, which made it tremendously difficult to work with in mixing. To this liquid silicone rubber base composition were then added 2 parts of a copolymer of dimethylsiloxane and methylhydrogensiloxane capped at both ends with trimethylsiloxy groups and composed of 4 mol of dimethylsiloxane units and 6 mol of methylhydrogensiloxane units, 0.15 part (0.4 wt% platinum content) of a complex of chloroplatinic acid and divinyltetramethyldisiloxane, and 0.05 part 3,5-dimethyl-1-hexyn-3-ol (used as a curing inhibitor), and these components were mixed until uniform to prepare a liquid silicone rubber composition. The viscosity of this composition was 900 Pa $\cdot$ s. This composition was then press cured at 120°C to obtain a foamed silicone rubber with a thickness of 6 mm. This foamed silicone rubber was sliced and the cut surface thereof was observed under a microscope, which revealed that the size of the cells included in this foam was between 30 and 50 μm , and the cells were uniform in size. The specific gravity of this foamed silicone rubber was 0.62, the hardness was 32 (JIS type A), and the thermal conductivity was 0.14 W/(m $\cdot$ K). These results are given in Table 1 below.

Comparative Example 3. 100 Parts of a dimethylpolysiloxane that was capped at both ends of the molecular chain with dimethylvinylsiloxy groups and that had a viscosity of 2000 mPa $\cdot$ s and 10 parts of fumed silica that had been treated with hexamethyldisilazane and had a BET specific surface area of 130 m²/g were put into a Ross mixer and mixed until uniform to prepare a compound that had fluidity. Next, 5 weight parts of a hollow-particle powder that had undergone an anti-scattering treatment, in which a hollow-particle powder that had already been expanded by heating a thermoplastic resin hollow-particle powder enclosing isobutane on the inside (this

hollow-particle powder had a particle diameter between 35 and 55 μm , and is commercially available under the brand name "Expancell 091DE" from Expancell) was treated by air spraying with 5 parts of a dimethylpolysiloxane having a viscosity of 10 $\text{mPa} \cdot \text{s}$, was added and mixed until uniform to prepare a liquid silicone rubber base compound that had fluidity. This hollow-particle powder that had undergone the anti-scattering treatment posed no problem in mixing. To this liquid silicone rubber base composition were then added 2 parts of a copolymer of dimethylsiloxane and methylhydrogensiloxane capped at both ends with trimethylsiloxy groups and composed of 4 mol of dimethylsiloxane units and 6 mol of methylhydrogensiloxane units, 0.15 part (0.4 wt% platinum content) of a complex of chloroplatinic acid and divinyltetramethyldisiloxane, and 0.05 part 3,5-dimethyl-1-hexyn-3-ol (used as a curing inhibitor), and these components were mixed until uniform to prepare a liquid silicone rubber composition. The viscosity of this composition was 500 $\text{Pa} \cdot \text{s}$. This composition was then press cured at 120°C to obtain a foamed silicone rubber with a thickness of 6 mm. This foamed silicone rubber was sliced and the cut surface thereof was observed under a microscope, which revealed that the size of the cells included in this foam was between 30 and 50 μm , and the cells were uniform in size. The specific gravity of this foamed silicone rubber was 0.60, the hardness was 28 (JIS type A), and the thermal conductivity was 0.14 $\text{W}/(\text{m} \cdot \text{K})$. These results are given in Table 1 below.

Table 1

	Example	Comparative Example		
	Example 1	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
Type of thermoplastic resin hollow-particle powder	unexpanded hollow-particle powder	unexpanded hollow-particle powder	pre-expanded hollow-particle powder	pre-expanded hollow-particle powder treated with oil
Ease of work during mixing	good	good	good	good
Viscosity (Pa · s)	600	90	900	500
Curing temp. (°C)	120	120	120	120
Hardness (type A)	30	30	32	28
Specific gravity	0.60	1.02	0.62	0.60
Thermal conductivity (W/(m · K))	0.13	0.19	0.14	0.14
Oil seepage	no	no	no	yes

I claim:



1. A liquid silicone rubber composition comprising a liquid silicone rubber base compound produced by mixing (A) a liquid diorganopolysiloxane and optionally an inorganic filler with (B) a thermoplastic resin hollow-particle powder that expands when heated and performing a heat treatment at a temperature sufficient to cause expansion of component (B) and (C) a curing agent in an amount sufficient to cure the liquid diorganopolysiloxane.
2. A foamed silicone rubber prepared from the composition of claim 1 having a thermal conductivity of 0.05 to 0.17 W/(m · K).
3. A method for making a liquid silicone rubber composition comprising the steps of
 - (I) mixing a (A) liquid diorganopolysiloxane and optionally an inorganic filler with (B) a thermoplastic resin hollow-particle powder that expands when heated ,
 - (II) performing a heat treatment at a temperature sufficient to cause expansion of component (B), and
 - (III) (C) adding a curing agent in an amount sufficient to cure the liquid diorganopolysiloxane.
4. A liquid silicone rubber composition according to Claim 1, where the diorganopolysiloxane is described by average formula $R_a(OH)_bSiO_{(4-a-b)/2}$, R is a monovalent hydrocarbon group or a halogenated alkyl group, a is a number from 1.9 to 2.1, and b is a number from 0 to 0.1.
5. A liquid silicone rubber composition according to Claim 1, where the diorganopolysiloxane has a viscosity between 100 and 1,000,000 mPa·s at 25°C.



6. A liquid silicone rubber composition according to Claim 1, where the thermoplastic resin hollow-particle powder has an particle diameter of 1 to 50 μ m prior to expansion.
7. A liquid silicone rubber composition according to Claim 1, where component (B) comprises 0.1 to 15 weight percent of the silicone rubber base compound.
8. A liquid silicone rubber composition according to Claim 1, where the curing agent is an organic peroxide.
9. A liquid silicone rubber composition according to Claim 1, where the curing agent comprises a platinum-based catalyst and an organopolysiloxane containing hydrogen atoms bonded to silicon atoms.
10. A method for making a liquid silicone rubber composition according to Claim 3, where the diorganopolysiloxane is described by average formula $R_a(OH)_bSiO_{(4-a-b)/2}$, R is a monovalent hydrocarbon group or a halogenated alkyl group, a is a number from 1.9 to 2.1, and b is a number from 0 to 0.1.
11. A method for making a liquid silicone rubber composition according to Claim 3, where the diorganopolysiloxane has a viscosity between 100 and 1,000,000 mPa·s at 25°C.



12. A method for making a liquid silicone rubber composition according to Claim 3, where the thermoplastic resin hollow-particle powder has an particle diameter of 1 to 50 μ m prior to expansion.
13. A method for making a liquid silicone rubber composition according to Claim 3, where component (B) comprises 0.1 to 15 weight percent of the silicone rubber base compound.
14. A method for making a liquid silicone rubber composition according to Claim 3, where the curing agent is an organic peroxide.
15. A method for making a liquid silicone rubber composition according to Claim 3, where the curing agent comprises a platinum-based catalyst and an organopolysiloxane containing hydrogen atoms bonded to silicon atoms.