

**CURABLE ORGANOPOLYSILOXANE COMPOSITION  
AND CURED ARTICLES THEREFROM,**

This invention relates to curable organopolysiloxane compositions and to the cured articles therefrom. More particularly, this invention relates to a curable organopolysiloxane composition that have excellent pre-cure handling characteristics and that cures into highly heat-resistant cured articles. The invention also relates to the highly heat-resistant cured articles afforded by the cure of the subject composition.

Curable organopolysiloxane compositions that cure into highly heat-resistant products are known. For example, Japanese Patent Application (Kokai) 58-21893(1983) provides a curable organopolysiloxane composition comprising an organopolysiloxane having at least 2 silicon-bonded lower alkenyl groups in each molecule, an organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule, silica filler, iron oxide and/or carbon black, and a platinum catalyst. Japanese Patent Application (Kokai) 60-173051(1985) provides a curable organopolysiloxane composition comprising an organopolysiloxane having at least 2 silicon-bonded lower alkenyl groups in each molecule, an organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule, silica filler, iron sesquioxide, and a platinum catalyst.

Finally, Japanese Patent Application (Kokai) 7-292256(1995) discloses a curable organopolysiloxane composition comprising an organopolysiloxane having at least 2 silicon-bonded lower alkenyl groups in each molecule, an organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule, very finely divided iron oxide yellow, and a platinum catalyst.

However, the curable organopolysiloxane compositions disclosed in the preceding 3 references suffer from various problems. Thus, these compositions require the addition of large amounts of a heat stabilizer in order to achieve excellent heat resistance in their cured articles, but such additions cause these compositions to have poor handling characteristics and prevent the fabrication of relatively articles having a relatively low hardness.

Furthermore, the cured articles obtained from such compositions do not manifest a satisfactory heat resistance because the heat stabilizer is not uniformly dispersed therein, and these articles are also limited in color selection to reddish-brown and black.

The inventors achieved the present invention as a result of extensive research on the problems described above.

In specific terms, an object of the present invention is to provide a curable organopolysiloxane composition that has excellent pre-cure handling

characteristics and that cures into highly heat-resistant cured articles. An additional object of the invention is to provide highly heat-resistant cured articles.

The curable organopolysiloxane composition of the present invention comprises

- (A) 100 parts by weight of an alkenyl-containing organopolysiloxane having at least 2 silicon-bonded lower alkenyl groups in each molecule,
  - (B) an organohydrogenpolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity that provides from 0.1 to 20 moles of silicon-bonded hydrogen atoms in component (B) per 1 mole of silicon-bonded lower alkenyl groups in component (A),
  - (C) 0.0001 to 20 parts by weight of ferrocene or a derivative thereof,
- and
- (D) a hydrosilylation reaction catalyst in sufficient quantity to cure said composition.

Cured articles according to the present invention are characteristically afforded by the cure of the above-described organopolysiloxane composition.

The curable organopolysiloxane composition according to the present invention will be explained in detail below.

Component (A), which is the base ingredient of the subject composition, is an alkenyl-containing organopolysiloxane having at least 2 silicon-bonded lower alkenyl groups in each molecule. The silicon-bonded lower alkenyl groups in component (A) are preferably selected from the group consisting of vinyl, allyl, butenyl, pentenyl, hexenyl, and heptenyl; with vinyl being more preferred. The lower alkenyl groups in component (A) can be bonded in component (A) in pendant or terminal position on the molecular chain. The silicon-bonded groups in component (A) other than the lower alkenyl are selected from the group consisting of alkyl groups, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, and the like; cycloalkyl groups such as cyclopentyl, cyclohexyl, and the like; aryl groups such as phenyl, tolyl, xylyl, naphthyl, and the like; aralkyl groups such as benzyl, phenethyl, phenylpropyl, and the like; and perfluoroalkyl groups such as 3,3,3-trifluoropropyl, 3,3,4,4,4-pentafluorobutyl, 3,3,4,4,5,5,5-heptafluoropentyl, 3,3,4,4,5,5,6,6,6-nonafluorohexyl, and the like. Alkyl, aryl, and perfluoroalkyl groups are preferred.

In a preferred embodiment, perfluoroalkyl makes up at least 5 mole% of the silicon-bonded groups. While curable organopolysiloxane compositions in which

at least 1 silicon-bonded group in component (A) is perfluoroalkyl cure, as a general rule, into poorly heat-resistant products. Such compositions are nevertheless endowed with an excellent heat resistance through the use of the component (C) heat stabilizer in the composition according to the present invention. The molecular structure of component (A) is exemplified by straight-chain, partially branched straight-chain, branched-chain, cyclic, and network structures, and straight-chain and partially branched straight-chain structures are particularly preferred. The viscosity of component (A) at 25°C is preferably from 20 to 1,000,000 centipoise (20 to 1,000,000 mPa.s) and more preferably from 100 to 500,000 centipoise (100 to 500,000 mPa.s).

Component (A) is exemplified by  
trimethylsiloxy-endblocked methylvinylpolysiloxanes;  
trimethylsiloxy-endblocked dimethylsiloxane-  
methylvinylsiloxane copolymers;  
trimethylsiloxy-endblocked dimethylsiloxane-  
methylvinylsiloxane-methylphenylsiloxane  
copolymers;  
trimethylsiloxy-endblocked methylvinylsiloxane-  
methyl(3,3,3-trifluoropropyl)siloxane copolymers;  
trimethylsiloxy-endblocked dimethylsiloxane-  
methylvinylsiloxane-methyl(3,3,3-  
trifluoropropyl)siloxane copolymers;

trimethylsiloxyl-endblocked methylvinylsiloxane-  
 methyl (3,3,4,4,4-pentafluorobutyl) siloxane  
 copolymers;

trimethylsiloxyl-endblocked dimethylsiloxane-  
 methylvinylsiloxane-methyl (3,3,4,4,4-  
 pentafluorobutyl) siloxane copolymers;

dimethylvinylsiloxyl-endblocked dimethylpolysiloxanes;

dimethylvinylsiloxyl-endblocked  
 methylvinylpolysiloxanes;

dimethylvinylsiloxyl-endblocked dimethylsiloxane-  
 methylvinylsiloxane copolymers;

dimethylvinylsiloxyl-endblocked dimethylsiloxane-  
 methylvinylsiloxane-methylphenylsiloxane  
 copolymers;

dimethylvinylsiloxyl-endblocked methyl (3,3,3-  
 trifluoropropyl) polysiloxanes;

dimethylvinylsiloxyl-endblocked dimethylsiloxane-  
 methyl (3,3,3-trifluoropropyl) siloxane copolymers;

organopolysiloxanes comprising  $R^1_3SiO_{1/2}$ ,  $R^1_2R^2SiO_{1/2}$ ,  
 and  $SiO_{4/2}$  siloxane units;

organopolysiloxanes comprising  $R^1_2R^2SiO_{1/2}$  and  $SiO_{4/2}$   
 siloxane units;

organopolysiloxanes comprising  $R^1R^2SiO_{2/2}$  and  $R^1SiO_{3/2}$   
 or  $R^2SiO_{3/2}$  siloxane units; and

mixtures of two or more selections from the preceding  
 organopolysiloxanes.  $R^1$  in the preceding formulas

denotes monovalent hydrocarbon groups other than lower alkenyl groups.

$R^1$  is preferably selected from the group selected from alkyl groups, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, and the like; cycloalkyl groups such as cyclopentyl, cyclohexyl, and the like; aryl groups such as phenyl, tolyl, xylyl, naphthyl, and the like; aralkyl groups such as benzyl, phenethyl, phenylpropyl, and the like; and perfluoroalkyl groups such as 3,3,3-trifluoropropyl, 3,3,4,4,4-pentafluorobutyl, 3,3,4,4,5,5,5-heptafluoropentyl, 3,3,4,4,5,5,6,6,6-nonafluorohexyl, and the like.

Alkyl, aryl, and perfluoroalkyl are more preferred for  $R^1$ .  $R^2$  in the preceding formulas is a lower alkenyl groups.  $R^2$  is preferably selected from the group consisting of vinyl, allyl, butenyl, pentenyl, hexenyl, and heptenyl, with vinyl being more preferred.

Component (B), which is the curing agent for the subject composition, is an organohydrogenpolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule. This silicon-bonded hydrogen atom can be bonded in pendant or terminal position on the molecular chain. The non-hydrogen silicon-bonded groups in component (B) are preferably selected from the group consisting of alkyl groups, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, and the like; cycloalkyl groups

such as cyclopentyl, cyclohexyl, and the like; aryl groups such as phenyl, tolyl, xylyl, naphthyl, and the like; aralkyl groups such as benzyl, phenethyl, phenylpropyl, and the like; and perfluoroalkyl groups such as 3,3,3-trifluoropropyl, 3,3,4,4,4-pentafluorobutyl, 3,3,4,4,5,5,5-heptafluoropentyl, 3,3,4,4,5,5,6,6,6-nonafluorohexyl, and the like. Alkyl, aryl, and perfluoroalkyl are more preferred. The molecular structure of component (B) is exemplified by straight-chain, partially branched straight-chain, branched-chain, cyclic, and network structures, with straight-chain structures being particularly preferred. The viscosity of component (B) at 25°C is preferably from 1 to 1,000,000 centipoise (1 to 1,000,000 mPa.s) and more preferably from 10 to 500,000 centipoise (10 to 500,000 mPa.s).

Component (B) is exemplified by  
 trimethylsiloxy-endblocked methylhydrogenpolysiloxanes;  
 trimethylsiloxy-endblocked dimethylsiloxane-  
     methylhydrogensiloxane copolymers;  
 trimethylsiloxy-endblocked dimethylsiloxane-  
     methylhydrogensiloxane-methylphenylsiloxane  
     copolymers;  
 trimethylsiloxy-endblocked methylhydrogensiloxane-  
     methyl(3,3,3-trifluoropropyl)siloxane copolymers;  
 trimethylsiloxy-endblocked dimethylsiloxane-  
     methylhydrogensiloxane-methyl(3,3,3-  
     trifluoropropyl)siloxane copolymers;

trimethylsiloxy-endblocked methylhydrogensiloxane-  
methyl(3,3,4,4,4-pentafluorobutyl)siloxane  
copolymers;

trimethylsiloxy-endblocked dimethylsiloxane-  
methylhydrogensiloxane-methyl(3,3,4,4,4-  
pentafluorobutyl)siloxane copolymers;

dimethylhydrogensiloxy-endblocked  
dimethylpolysiloxanes;

dimethylhydrogensiloxy-endblocked  
methylhydrogenpolysiloxanes;

dimethylhydrogensiloxy-endblocked dimethylsiloxane-  
methylhydrogensiloxane copolymers;

dimethylhydrogensiloxy-endblocked dimethylsiloxane-  
methylhydrogensiloxane-methylphenylsiloxane  
copolymers;

dimethylhydrogensiloxy-endblocked methyl(3,3,3-  
trifluoropropyl)polysiloxanes;

dimethylhydrogensiloxy-endblocked dimethylsiloxane-  
methyl(3,3,3-trifluoropropyl)siloxane copolymers;

trimethylsiloxy-endblocked  
dimethylhydrogensiloxy(3,3,3-  
trifluoropropyl)polysiloxanes;

trimethylsiloxy-endblocked dimethylsiloxane-  
dimethylhydrogensiloxy(3,3,3-  
trifluoropropyl)siloxane copolymers;

dimethylhydrogensiloxy-endblocked  
dimethylhydrogensiloxy(3,3,3-  
trifluoropropyl)polysiloxanes;

dimethylhydrogensiloxy-endblocked dimethylsiloxane-dimethylhydrogensiloxy(3,3,3-trifluoropropyl)siloxane copolymers;  
 organopolysiloxanes comprising  $R^1_3SiO_{1/2}$ ,  $R^1_2HSiO_{1/2}$ , and  $SiO_{4/2}$  siloxane units;  
 organopolysiloxanes comprising  $R^1_2HSiO_{1/2}$  and  $SiO_{4/2}$  siloxane units;  
 organopolysiloxanes comprising  $R^1HSiO_{2/2}$  and  $R^1SiO_{3/2}$  or  $HSiO_{3/2}$  siloxane units; and  
 mixtures of two or more selections of the preceding organopolysiloxanes.  $R^1$  in the preceding formulas denotes monovalent hydrocarbon group free of ethylenic unsaturation.  $R^1$  is preferably selected from the group consisting of alkyl groups, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, and the like; cycloalkyl groups such as cyclopentyl, cyclohexyl, and the like; aryl groups such as phenyl, tolyl, xylyl, naphthyl, and the like; aralkyl groups, such as benzyl, phenethyl, phenylpropyl, and the like; and perfluoroalkyl groups, such as 3,3,3-trifluoropropyl, 3,3,4,4,4-pentafluorobutyl, 3,3,4,4,5,5,5-heptafluoropentyl, 3,3,4,4,5,5,6,6,6-nonafluorohexyl, and the like. Alkyl, aryl, and perfluoroalkyl are more preferred.

Component (B) is added in a quantity that provides from 0.1 to 20 moles, preferably from 0.1 to

10 moles, and particularly preferably from 0.1 to 5 moles of silicon-bonded hydrogen atom in component (B) per 1 mole silicon-bonded lower alkenyl groups in component (A). A thorough cure is not obtained when the curable organopolysiloxane composition contains less than 0.1 mole of silicon-bonded hydrogen in component (B) per 1 mole silicon-bonded lower alkenyl in component (A). When the curable organopolysiloxane composition contains more than 20 moles of silicon-bonded hydrogen in component (B) per 1 mole silicon-bonded lower alkenyl in component (A), the resulting cured article will suffer from such problems as cracking, swelling, and a reduced heat resistance.

Component (C), which is ferrocene or a derivative thereof, functions to impart a high level of heat resistance to the cured article without causing a decline in the handling characteristics of the composition. Component (C) is preferably selected from ferrocene, acetylferrocene, vinylferrocene, ethynylferrocene, ferrocenylmethanol, bis( $\eta$ -cyclopentadienyl)iron(III) tetrachloroferrate(III), tetracarbonylbis( $\eta$ -cyclopentadienyl)diiron(I), 1,1'-bis(trimethylsilyl)ferrocene, 1,1'-(dimethylphenoxysilyl)ferrocene, and 1,1'-bis(dimethylethoxysilyl)ferrocene. Ferrocene and acetylferrocene are particularly preferred. Component (C) is well-suited for use in the present composition to fabricate a cured article having a relatively low

hardness. This is because only a relatively small amounts of component (C) must be mixed into the subject composition in order to obtain highly heat-resistant cured articles. Moreover, component (C) induces a substantial improvement in the heat resistance of the otherwise poorly heat-resistant cured articles afforded by curable organopolysiloxane compositions in which at least 1 silicon-bonded group in component (A) is perfluoroalkyl.

Component (C) is added from 0.0001 to 20 weight parts, preferably from 0.001 to 10 weight parts, and more preferably from 0.005 to 5 weight parts, in each case per 100 weight parts component (A). When the curable organopolysiloxane composition contains less than 0.0001 weight part component (C) per 100 weight parts component (A), the cured article afforded therefrom will have a poor heat resistance. The curable organopolysiloxane composition containing more than 20 weight parts has a poor storage stability. Component (C) is preferably mixed into the subject composition by dissolving component (C) in component (A) prior to the composition mixing step. An organic solvent can be used in the dissolution of component (C) in component (A). The particular organic solvent used here is not critical as long as it does not adversely affect the hydrosilylation reaction. Examples of organic solvents which may be used include toluene, xylene, hexane, and heptane. The organic solvent is

preferably removed after component (C) has been dissolved in component (A). As stated above, the presence of even relatively small amounts of component (C) in the curable organopolysiloxane composition results in a substantial improvement in the heat resistance of the cured product, which makes this component particularly well-suited for application in curable organopolysiloxane compositions intended for use in the fabrication of low-hardness cured gel. The hardness of said cured gel is preferably from 10 to 300 as measured by the 1/4-consistency test specified in JIS K 2220. In addition, since the subject component (C) has a relatively low hiding power, it supports the preparation of cured articles in any color as may be generated by pigments and dyes.

The hydrosilylation reaction catalyst (D) accelerates the cure of the present composition. Component (D) is preferably a platinum catalysts, such as finely divided platinum, platinum black, platinum-on-active carbon, platinum-on-silica, chloroplatinic acid, platinum tetrachloride, alcohol solutions of chloroplatinic acid, platinum-olefin complexes, platinum/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complexes, and the like; palladium catalysts, such as tetrakis(triphenylphosphine)palladium; rhodium catalysts; and resin powders comprising a catalyst as listed above dispersed or encapsulated in a thermoplastic resin such as polystyrene resin,

polycarbonate resin, acrylic resin, methacrylic resin, or silicone resin. Platinum catalysts are particularly preferred.

Component (D) is added in sufficient quantity to cure the subject composition. From a practical standpoint, component (D) is added in a quantity that provides preferably from 0.1 to 1,000 weight-ppm metal and more preferably from 0.5 to 500 weight-ppm metal in component (D) based on component (A). When component (D) provides less than 0.1 weight-ppm metal with reference to component (A), the curable organopolysiloxane composition will have a very slow reaction rate and becomes very vulnerable to cure inhibition. Additions to the curable organopolysiloxane composition in excess of 1,000 ppm provide almost no improvement in cure rate and thus are uneconomical.

The curable organopolysiloxane composition according to the present invention may contain other components on an optional basis insofar as the objects of the present invention are not impaired. These optional components are exemplified by inorganic filler such as dry-process silica, wet-process silica, powdered quartz, calcium carbonate, fumed titanium dioxide, diatomaceous earth, aluminum hydroxide, aluminum oxide, magnesium carbonate, magnesium oxide, zinc oxide, zinc carbonate, microparticulated mica, and the like; the preceding inorganic fillers after surface

hydrophobicization by treatment with organosilazane, organocyclosiloxane, organochlorosilane, organoalkoxysilane, low-molecular-weight straight-chain siloxane, and the like; addition reaction inhibitors such as acetylenic compounds (e.g., 3-methyl-1-butyne-3-ol, 3,5-dimethyl-1-hexyne-3-ol, 3-phenyl-1-butyne-3-ol, etc.), ene-yne compounds (e.g., 3-methyl-3-penten-1-yne, 3,5-dimethyl-3-hexen-1-yne, etc.), alkenyl-functional siloxanes (e.g., 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetrahexenylcyclotetrasiloxane, etc.), and triazoles such as benzotriazole; other heat stabilizers such as iron oxide black, carbon black, and the like; organic solvents such as toluene, xylene, hexane, heptane, and the like; antimolds; flame retardants; plasticizers; thixotropy donors; adhesion promoters; cure accelerators; pigments; and dyes.

The curable organopolysiloxane composition according to the present invention cures to give highly heat-resistant cured articles. The nature of the cured article is not critical and it may be, for example, a gel, rubber, or resin. Since the curable organopolysiloxane composition according to the present invention provides very heat-resistant cured products — even when cured to give a gel with a 1/4-consistency according to JIS K 2220 of from 10 to 300, it is, as a result, well-suited as a sealant, coating, or potting

agent for electrical and electronic devices and instruments and the like.

Cured articles according to the present invention will now be considered in detail.

Cured articles according to the present invention are characteristically afforded by the cure of the curable organopolysiloxane composition described hereinabove. The nature of the cured article is not critical and it may be, for example, a gel, rubber, or resin. However, the cured article is preferably a gel with a 1/4-consistency of 10 to 300 according to JIS K 2220.

The curable organopolysiloxane composition according to the present invention evidences excellent pre-cure handling characteristics and cures to give highly heat-resistant cured articles. It can therefore be used as a sealant, coating, or potting agent for electrical and electronic devices and instruments and the like. Moreover, the curable organopolysiloxane composition according to the present invention can form heat-resistant cured articles of any color.

#### EXAMPLES

The curable organopolysiloxane composition according to the present invention and cured articles therefrom will be considered in greater detail below through working examples. The viscosity values reported in the examples were measured at 25°C. The

handling characteristics of the curable organopolysiloxane compositions and the cured article heat resistance were measured as follows.

Handling of the curable organopolysiloxane compositions

The viscosity of the particular curable organopolysiloxane composition was measured at 25°C and the handling of the curable organopolysiloxane composition was evaluated based on this viscosity value.

Heat resistance of the cured article

About 40 g of the particular curable organopolysiloxane composition was poured into a 50-mL glass beaker, defoamed, and then cured in a forced convection oven at 150°C for 1 hour. The 1/4-consistency of the resulting cured material was measured according to JIS K 2220. This cured material was subsequently held in the forced convection oven at 150°C for the specified period of time, cooled to room temperature, and then again submitted to measurement of the 1/4-consistency. The heat resistance of the cured material was evaluated based on the change in the 1/4-consistency values.

Example 1

A curable organopolysiloxane composition was prepared by mixing the following to homogeneity: 100

weight parts dimethylvinylsiloxyl-endblocked methyl(3,3,3-trifluoropropyl)polysiloxane with a viscosity of 1,000 centipoise and a silicon-bonded vinyl content of 1.0 weight%; 3.5 weight parts dimethylhydrogensiloxyl-endblocked dimethylhydrogensiloxyl(3,3,3-trifluoropropyl)polysiloxane with a viscosity of 10 centipoise (10 mPa.s) and a silicon-bonded hydrogen content of 0.5 weight%; 0.01 weight part ferrocene; and sufficient platinum/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex to provide 5 weight-ppm platinum metal in this complex relative to the dimethylvinylsiloxyl-endblocked methyl(3,3,3-trifluoropropyl)polysiloxane.

Table 1 reports the results for the evaluation of the handling characteristics of this curable organopolysiloxane composition and the heat resistance of the cured gel afforded by the cure of this composition.

#### Example 2

A curable organopolysiloxane composition was prepared by mixing the following to homogeneity: 100 weight parts dimethylvinylsiloxyl-endblocked methyl(3,3,3-trifluoropropyl)polysiloxane with a viscosity of 1,000 centipoise (1,000 mPa.s) and a silicon-bonded vinyl content of 1.0 weight%; 3.5 weight parts dimethylhydrogensiloxyl-endblocked

dimethylhydrogensiloxy(3,3,3-trifluoropropyl)polysiloxane with a viscosity of 10 centipoise (10 mPa.s) and a silicon-bonded hydrogen content of 0.5 weight%; 0.01 weight part acetylferrocene; and sufficient platinum/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex to provide 5 weight-ppm platinum metal in this complex relative to the dimethylvinylsiloxy-endblocked methyl(3,3,3-trifluoropropyl)polysiloxane.

Table 1 reports the results for the evaluation of the handling characteristics of this curable organopolysiloxane composition and the heat resistance of the cured gel afforded by the cure of this composition.

#### Comparative Example 1

A curable organopolysiloxane composition was prepared by mixing the following to homogeneity: 100 weight parts dimethylvinylsiloxy-endblocked methyl(3,3,3-trifluoropropyl)polysiloxane with a viscosity of 1,000 centipoise (1,000 mPa.s) and a silicon-bonded vinyl content of 1.0 weight%; 3.5 weight parts dimethylhydrogensiloxy-endblocked dimethylhydrogensiloxy(3,3,3-trifluoropropyl)polysiloxane with a viscosity of 10 centipoise (10 mPa.s) and a silicon-bonded hydrogen content of 0.5 weight%; and sufficient platinum/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex to

provide 5 weight-ppm platinum metal in this complex relative to the dimethylvinylsiloxyl-endblocked methyl(3,3,3-trifluoropropyl)polysiloxane.

Table 1 reports the results for the evaluation of the handling characteristics of this curable organopolysiloxane composition and the heat resistance of the cured gel afforded by the cure of this composition.

#### Comparative Example 2

A curable organopolysiloxane composition was prepared by mixing the following to homogeneity: 100 weight parts dimethylvinylsiloxyl-endblocked methyl(3,3,3-trifluoropropyl)polysiloxane with a viscosity of 1,000 centipoise (1,000 mPa.s) and a silicon-bonded vinyl content of 1.0 weight%; 3.5 weight parts dimethylhydrogensiloxyl-endblocked dimethylhydrogensiloxyl(3,3,3-trifluoropropyl)polysiloxane with a viscosity of 10 centipoise (10 mPa.s) and a silicon-bonded hydrogen content of 0.5 weight%; 10 weight parts iron oxide yellow micropowder (NYB-40 from Nippon Bengara Kogyo Kabushiki Kaisha); 10 weight parts iron oxide red micropowder (Tensho Bengara from Nippon Bengara Kogyo Kabushiki Kaisha); and sufficient platinum/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex to provide 5 weight-ppm platinum metal in this complex relative to

the dimethylvinylsiloxyl-endblocked methyl(3,3,3-trifluoropropyl)polysiloxane.

Table 1 reports the results for the evaluation of the handling characteristics of this curable organopolysiloxane composition and the heat resistance of the cured gel afforded by the cure of this composition.

### Comparative Example 3

A curable organopolysiloxane composition was prepared by mixing the following to homogeneity: 100 weight parts dimethylvinylsiloxyl-endblocked methyl(3,3,3-trifluoropropyl)polysiloxane with a viscosity of 1,000 centipoise (1,000 mPa.s) and a silicon-bonded vinyl content of 1.0 weight%; 3.5 weight parts dimethylhydrogensiloxyl-endblocked dimethylhydrogensiloxyl(3,3,3-trifluoropropyl)polysiloxane with a viscosity of 10 centipoise (10 mPa.s) and a silicon-bonded hydrogen content of 0.5 weight%; 1 weight part iron oxide yellow micropowder (NYB-40 from Nippon Bengara Kogyo Kabushiki Kaisha); 1 weight part iron oxide red micropowder (Tensho Bengara from Nippon Bengara Kogyo Kabushiki Kaisha); and sufficient platinum/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex to provide 5 weight-ppm platinum metal in this complex relative to the dimethylvinylsiloxyl-endblocked methyl(3,3,3-trifluoropropyl)polysiloxane.

Table 1 reports the results for the evaluation of the handling characteristics of this curable organopolysiloxane composition and the heat resistance of the cured gel afforded by the cure of this composition.

Table 1

|                                                                                                                                                                                              | Present Invention                     |                                       | Comparative Examples                     |                                         |                                         |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|---------------------------------------|------------------------------------------|-----------------------------------------|-----------------------------------------|
|                                                                                                                                                                                              | Example 1                             | Example 2                             | Comparative Example 1                    | Comparative Example 2                   | Comparative Example 3                   |
| <ul style="list-style-type: none"> <li>the curable organopolysiloxane composition</li> <li>handling</li> <li>viscosity (mPa.s)</li> </ul>                                                    | excellent<br>800                      | excellent<br>800                      | excellent<br>800                         | poor<br>76,000                          | poor<br>2,000                           |
| <ul style="list-style-type: none"> <li>the cured material appearance</li> <li>heat resistance (1/4-consistency)</li> <li>initial</li> <li>after 68 hours</li> <li>after 184 hours</li> </ul> | yellow, transparent<br>64<br>62<br>62 | yellow, transparent<br>64<br>61<br>61 | colorless, transparent<br>68<br>50<br>23 | reddish-brown, opaque<br>42<br>32<br>20 | reddish-brown, opaque<br>62<br>52<br>25 |

### Example 3

A curable organopolysiloxane composition was prepared by mixing the following to homogeneity: 100 weight parts dimethylvinylsiloxyl-terminated dimethylpolysiloxane with a viscosity of 400 centipoise (400 mPa.s) and a silicon-bonded vinyl content of 0.4 weight%; 0.5 weight part trimethylsiloxyl-terminated methylhydrogenpolysiloxane with a viscosity of 20 centipoise and a silicon-bonded hydrogen content of 1.6 weight%; 0.01 weight part ferrocene; and sufficient platinum/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex to provide 5 weight-ppm platinum metal in this complex relative to the dimethylvinylsiloxyl-terminated dimethylpolysiloxane.

Table 2 reports the results for the evaluation of the handling characteristics of this curable organopolysiloxane composition and the heat resistance of the cured gel afforded by the cure of this composition.

### Example 4

A curable organopolysiloxane composition was prepared by mixing the following to homogeneity: 100 weight parts dimethylvinylsiloxyl-terminated dimethylpolysiloxane with a viscosity of 400 centipoise (400 mPa.s) and a silicon-bonded vinyl content of 0.4 weight%; 0.5 weight part trimethylsiloxyl-terminated methylhydrogenpolysiloxane with a viscosity of 20

centipoise (20 mPa.s) and a silicon-bonded hydrogen content of 1.6 weight%; 0.1 weight part acetylferrocene; and sufficient platinum/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex to provide 5 weight-ppm platinum metal in this complex relative to the dimethylvinylsiloxyl-endblocked dimethylpolysiloxane.

Table 2 reports the results for the evaluation of the handling characteristics of this curable organopolysiloxane composition and the heat resistance of the cured gel afforded by the cure of this composition.

#### Comparative Example 4

A curable organopolysiloxane composition was prepared by mixing the following to homogeneity: 100 weight parts dimethylvinylsiloxyl-endblocked dimethylpolysiloxane with a viscosity of 400 centipoise (400 mPa.s) and a silicon-bonded vinyl content of 0.4 weight%; 0.5 weight part trimethylsiloxyl-endblocked methylhydrogenpolysiloxane with a viscosity of 20 centipoise (mPa.s) and a silicon-bonded hydrogen content of 1.6 weight%; and sufficient platinum/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex to provide 5 weight-ppm platinum metal in the complex relative to the dimethylvinylsiloxyl-endblocked dimethylpolysiloxane.

Table 2 reports the results for the evaluation of the handling characteristics of this curable organopolysiloxane composition and the heat resistance of the cured gel afforded by the cure of this composition.

#### Comparative Example 5

A curable organopolysiloxane composition was prepared by mixing the following to homogeneity: 100 weight parts dimethylvinylsiloxyl-terminated dimethylpolysiloxane with a viscosity of 400 centipoise (400 mPa.s) and a silicon-bonded vinyl content of 0.4 weight%; 0.5 weight part trimethylsiloxyl-terminated methylhydrogenpolysiloxane with a viscosity of 20 centipoise (20 mPa.s) and a silicon-bonded hydrogen content of 1.6 weight%; 10 weight parts iron oxide yellow micropowder (NYB-40 from Nippon Bengara Kogyo Kabushiki Kaisha); 10 weight parts iron oxide red micropowder (Tensho Bengara from Nippon Bengara Kogyo Kabushiki Kaisha); and sufficient platinum/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex to provide 5 weight-ppm platinum metal in this complex relative to the dimethylvinylsiloxyl-terminated dimethylpolysiloxane.

Table 2 reports the results for the evaluation of the handling characteristics of this curable organopolysiloxane composition and the heat

resistance of the cured gel afforded by the cure of this composition.

Table 2

|                                                                                               | Present Invention      |                        | Comparative Examples      |                              |
|-----------------------------------------------------------------------------------------------|------------------------|------------------------|---------------------------|------------------------------|
|                                                                                               | Example 3              | Example 4              | Comp.<br>Example 4        | Comp.<br>Example 5           |
| <ul style="list-style-type: none"> <li>the curable organopoly-siloxane composition</li> </ul> |                        |                        |                           |                              |
| handling                                                                                      | excellent              | excellent              | excellent                 | poor                         |
| viscosity (mPa.s)                                                                             | 380                    | 390                    | 380                       | 66,000                       |
| <ul style="list-style-type: none"> <li>the cured material</li> </ul>                          |                        |                        |                           |                              |
| appearance                                                                                    | yellow,<br>transparent | yellow,<br>transparent | colorless,<br>transparent | reddish-<br>brown,<br>opaque |
| heat resistance<br>(1/4-consistency)                                                          |                        |                        |                           |                              |
| initial                                                                                       | 55                     | 55                     | 55                        | 50                           |
| after 90 hours                                                                                | 56                     | 52                     | 48                        | 45                           |
| after 300 hours                                                                               | 54                     | 52                     | 35                        | 42                           |

The curable organopolysiloxane composition according to the present invention, because it comprises components (A) to (D) and in particular because it contains ferrocene or a derivative thereof as component (C), is characterized by excellent pre-cure handling characteristics and by the ability to cure into highly heat-resistant cured articles. Moreover, cured articles according to the present invention, because they are generated by the cure of the subject curable organopolysiloxane composition, are characterized by an excellent heat resistance.



Claims:

1. A curable organopolysiloxane composition comprising

- (A) 100 parts by weight of an alkenyl-containing organopolysiloxane having at least 2 silicon-bonded lower alkenyl groups in each molecule;
  - (B) an organohydrogenpolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity that provides from 0.1 to 20 moles of silicon-bonded hydrogen in component (B) per mole of silicon-bonded alkenyl in component (A);
  - (C) 0.0001 to 20 parts by weight of ferrocene or a derivative thereof;
- and
- (D) a hydrosilylation reaction catalyst in sufficient quantity to cure said composition.

2. The curable organopolysiloxane composition of claim 1, wherein component (A) has an average of at least one silicon-bonded perfluoroalkyl group per molecule.



3. The curable organopolysiloxane composition of claims 1 or 2 wherein said composition yields, upon cure, a gel having a 1/4 consistency of from 10 to 300, when measured according to JIS K 2200.

**CURABLE ORGANOPOLYSILOXANE COMPOSITION AND CURED  
ARTICLES THEREFROM,**

**ABSTRACT**

A curable organopolysiloxane composition is claimed herein comprising

- (A) 100 weight parts organopolysiloxane having at least 2 silicon-bonded alkenyl groups in each molecule,
  - (B) organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity that provides from 0.1 to 20 moles silicon-bonded hydrogen in component (B) per 1 mole silicon-bonded lower alkenyl in component (A),
  - (C) 0.0001 to 20 weight parts ferrocene or derivative thereof,
- and
- (D) hydrosilylation reaction catalyst in sufficient quantity to cure the subject composition.

Also, cured articles afforded by the cure of the subject composition.

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