



(43) International Publication Date
19 September 2013 (19.09.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/137472 A1

(51) International Patent Classification:

A61M 25/00 (2006.01) *C08L 83/04* (2006.01)
C08G 77/50 (2006.01) *C08L 83/07* (2006.01)

(21) International Application Number:

PCT/JP2013/057579

(22) International Filing Date:

12 March 2013 (12.03.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2012-056760 14 March 2012 (14.03.2012) JP

(71) Applicant: **DOW CORNING TORAY CO., LTD.**
[JP/JP]; 5-1, Otemachi 1-chome, Chiyoda-ku, Tokyo,
1000004 (JP).

(72) Inventors: **YAMAMOTO, Shinichi**; c/o Dow Corning
Toray Co., Ltd., 2-2, Chigusaigaigan, Ichihara-shi, Chiba,
2990108 (JP). **HASEGAWA, Chiichiro**; c/o Dow Corning
Toray Co., Ltd., 2-2, Chigusaigaigan, Ichihara-shi, Chiba,
2990108 (JP).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: SILICONE ELASTOMER COMPOSITION, ELASTIC MATERIAL FOR MEDICAL DEVICE, AND MEDICAL BALLOON

(57) Abstract: A silicone elastomer composition which contains: (A) 100 parts by weight of an organopolysiloxane including components (A1) and (A2) at a weight ratio of from 5/95 to 90/10 and exhibiting a raw rubber state, (A1) an organopolysiloxane having: an average degree of polymerization of 2,000 or greater, and alkenyl groups at only the molecular terminals of the organopolysiloxane (A1), (A2) an organopolysiloxane having: an average degree of polymerization of 2,000 or greater, which has alkenyl groups at molecular terminals and in side chains, and an alkenyl group content of less than 0.10 wt.%; (B) from 0.2 to 20 parts by weight of an organohydrogenpolysiloxane; (C) an inorganic filler; and (D) an addition reaction catalyst, and which provides a cured product having: a hardness of from 20 to 40 and a permanent elongation of less than 10% after holding a material at an elongation of up to 700%.



WO 2013/137472 A1

DESCRIPTION**TITLE OF INVENTION****SILICONE ELASTOMER COMPOSITION, ELASTIC MATERIAL FOR MEDICAL DEVICE, AND
MEDICAL BALLOON**

5

TECHNICAL FIELD

[0001] Priority is claimed on Japanese Patent Application No. 2012-056760 filed on March 14, 2012, the content of which are incorporated herein by reference.

[0002] The present invention relates to a novel addition-curable silicone elastomer composition able
10 to provide a cured product which has appropriate hardness and physical strength for a medical
balloon in particular and which has a permanent elongation of less than 10% after holding a
material at an elongation of up to 700% for 10 minutes. In addition, the present invention relates
to a molded cured product of said silicone elastomer composition, an elastic material for a medical
device, and especially a medical balloon, comprising the same, and a balloon catheter obtained by
15 using the same. More specifically, the present invention relates to an addition-curable silicone
elastomer composition which can form a silicone elastomer that is highly stretchable when formed
into a balloon-like shape and can avoid the risk of breakage for a long period of time due to
exhibiting high tearing strength and tensile strength so that a cured product of the composition has
appropriate softness, no surface tackiness, high rebound resilience and a high degree of elongation,
20 and which is useful for forming a medical balloon in particular.

BACKGROUND ART

[0003] Silicone elastomers exhibit excellent heat resistance, cold resistance, hardness, physical
strength, durability and safety, and are therefore used in a wide variety of applications, including
medical materials (for example, see Patent Documents 1 to 4). In particular, medical balloons are
25 examples of elastic materials for medical devices that exhibit these properties. Balloon catheters
using medical balloons comprising silicone elastomers are used in a variety of medical applications,
and can be used to enlarge a site where a tubular organ in the body (such as a digestive organ or a
blood vessel) is obstructed. In addition, in the case of balloon catheters for blood transmission,
which are used in aortic aneurysm operations and the like, because that part of the aorta having the
30 aneurysm is replaced by an artificial blood vessel, the heart is stopped temporarily and a balloon
catheter for blood transmission is connected to an artificial pump oxygenator and used to circulate
blood to blood vessels that branch off from the aorta. The balloon catheter for blood transmission
enlarges a balloon in the blood vessel, thereby holding the balloon at the correct position in the
blood vessel. In addition, balloon catheters are also widely used for continuous drug solution
35 injection in order to carry out treatment by injecting a drug solution into the enlarged balloon,

holding the balloon at this location and administering a certain quantity of the drug solution to the affected part, such as administering an anaesthetic or analgesic for post-operative pain or administering anti-cancer drugs. (For example, see patent document 5.)

[0004] An addition reaction-curable silicone elastomer composition does not generate by-products caused by degradation of organic peroxides, as is the case with organic peroxide curing type products, and can therefore be advantageously used as a silicone elastomer for this type of medical balloon in the above-mentioned applications from the perspective of safety in particular. However, a publicly known addition reaction-curable silicone elastomer composition (for example, see Patent Document 6) exhibits appropriate hardness and physical strength for a medical balloon and, when used to enlarge a balloon in a blood vessel for a long period of time, the permanent elongation thereof tends to be extremely high, which leads to the risk of problems when handling the balloon catheter during or after an operation, and this publicly known addition reaction-curable silicone elastomer composition cannot therefore be advantageously used.

[0005] Meanwhile, by using an organopolysiloxane resin comprising $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units, and especially an alkenyl group-containing organopolysiloxane having a high degree of polymerization (for example, see Patent Document 3 or Patent Document 7) in order to improve permanent elongation characteristics, the hardness of a cured product is increased beyond that required for a medical balloon or stickiness and tackiness occurs in a cured product, meaning that handlability deteriorates and the composition cannot be advantageously used as an elastic material for a medical device such as a medical balloon.

[0006] In addition, in order to improve the physical properties of an addition reaction-curable silicone elastomer composition, it is possible to carry out secondary vulcanization (post-curing) following primary vulcanization, but by doing so, the cycle time required for production tends to increase. Therefore, there is a pressing need for an addition-curable silicone elastomer composition which has satisfactory physical properties for a medical balloon (especially hardness and permanent elongation characteristics) by carrying out primary vulcanization only and which provides a cured product having excellent safety.

PRIOR ART DOCUMENTS

Patent Documents

[0007] Patent Document 1: Japanese Unexamined Patent Application Publication No. S-60-126163
Patent Document 2: Japanese Unexamined Patent Application Publication No. S-61-255664
Patent Document 3: Japanese Unexamined Patent Application Publication No. H-08-323857
Patent Document 4: Japanese Unexamined Patent Application Publication No. 2010-201007A
Patent Document 5: Japanese Unexamined Patent Application Publication No. 2001-029461A
Patent Document 6: Japanese Unexamined Patent Application Publication No. 2007-217713A

Patent Document 7: Japanese Unexamined Patent Application Publication No. H-07-331079

DISCLOSURE OF THE INVENTION

Technical Problem

[0008] An objective of the present invention is to provide a silicone elastomer composition which has an appropriate hardness for a medical balloon (a hardness as measured in accordance with JIS K 6253 using a type A durometer hardness tester (hereinafter referred to as "JIS-A hardness" or "hardness") of 20 to 40), while having no surface tackiness and excellent handlability, high rebound resilience and a high degree of elongation, thereby enabling the formation of a silicone elastomer which is highly stretchable when formed into a balloon-like shape and can avoid the risk of breakage for a long period of time due to exhibiting high tearing strength and tensile strength, which has a permanent elongation of less than 10% after holding a material at an elongation of up to 700% for 10 minutes, and which exhibits good permanent elongation characteristics.

[0009] Furthermore, another objective of the invention of the present application is to provide a molded cured product of said silicone elastomer composition, and an elastic material for a medical device obtained by using the same. In particular, an objective of the invention of the present application is to provide a medical balloon which is excellent in terms of a variety of characteristics, such as appropriate formability, safety, durability and degree of elongation for a medical balloon, in which the above-mentioned hardness is from 20 to 40, and which exhibits excellent permanent elongation characteristics, and a balloon catheter obtained by using the same.

Solution To Problem

[0010] As a result of diligent research, the inventors of the present invention found that it was possible to solve the above-mentioned problems by using an addition-curable silicone elastomer composition that contains an organopolysiloxane which exhibits a raw rubber state at room temperature, contains silicon-bonded alkenyl groups, and is a mixture of organopolysiloxanes having a low content of silicon-bonded alkenyl groups and different alkenyl group bonding sites (component (A1), which has terminal alkenyl functional groups, and component (A2), which has terminal and side chain alkenyl functional groups), and an inorganic filler, and a molded cured product thereof, and thereby completed the present invention.

[0011] Specifically, the inventors of the present invention found that it was possible to solve the above-mentioned problems by means of a silicone elastomer composition which contains:

(A) 100 parts by weight of an organopolysiloxane having silicon-bonded alkenyl groups and exhibiting a raw rubber state at room temperature, the organopolysiloxane (A) including components (A1) and (A2) at a weight ratio of from 5/95 to 90/10,

(A1) an organopolysiloxane having: a number-average degree of polymerization of 2,000 or greater based on the number-average molecular weight in terms of polystyrene equivalent as measured by

gel permeation chromatography (GPC), and an average of two or more silicon-bonded alkenyl groups at only the molecular terminals of the organopolysiloxane (A1),

(A2) an organopolysiloxane having: a number-average degree of polymerization of 2,000 or greater based on the number-average molecular weight in terms of polystyrene equivalent as measured by

gel permeation chromatography (GPC), an average of three or more alkenyl groups at the molecular terminals and in side chains, and an alkenyl group content of less than 0.10 wt.%;

(B) from 0.3 to 20 parts by weight of an organopolysiloxane having an average of two or more silicon-bonded hydrogen atoms in the molecule;

(C) from 5 to 50 parts by weight of an inorganic filler; and

(D) a catalytic quantity of an addition reaction catalyst,

wherein after press curing at 120°C for 10 minutes,

the silicone elastomer composition provides a cured product having: a hardness of from 20 to 40, as measured in accordance with JIS K 6253 using a type A durometer hardness tester and

a permanent elongation of less than 10% after holding a material at an elongation of up to 700% for

10 minutes in accordance with JIS K 6301, and thereby completed the present invention. In

particular, the inventors of the present invention found that it was possible to better solve the

above-mentioned problems if the aforementioned inorganic filler of component (C) is an inorganic filler in which fumed silica having a BET specific surface area in the range of from 50 to 250 m²/g

accounts for 50 wt.% or more of the total quantity of component (C), and thereby completed the

present invention.

[0012] Furthermore, the inventors of the present invention found that it was possible to better solve the above-mentioned problems by means of a silicone elastomer composition which optionally contains, in addition to the above-mentioned components (A) to (D),

(E) from 0.1 to 50 parts by weight of a dimethylpolysiloxane having silanol groups at molecular

terminals and a number-average degree of polymerization of 100 or less based on the number-average molecular weight in terms of polystyrene equivalent as measured by gel

permeation chromatography (GPC),

(G) from 5 to 100 parts by weight of an organopolysiloxane having a number-average degree of polymerization of from 250 to a degree of polymerization whereby the composition exhibits a raw

rubber state at room temperature based on the number-average molecular weight in terms of polystyrene equivalent as measured by gel permeation chromatography (GPC), the

organopolysiloxane being free of silicon-bonded alkenyl groups and having at least one silanol group in the molecule,

and in which the total content of: (X1) an organopolysiloxane capped at both molecular terminals

with trialkylsilyl groups (excluding compounds corresponding to the component (B)),

(X2) an organopolysiloxane resin essentially comprising $R^1_3SiO_{1/2}$ units (wherein, R^1 are each independently hydroxyl groups, alkoxy groups having from 1 to 6 carbons or substituted or unsubstituted monovalent hydrocarbon groups having from 1 to 10 carbons) and $SiO_{4/2}$ units, and (X3) an organopolysiloxane having an alkenyl group content of 0.10 wt.% or more

is less than 1 wt.% of the overall composition, and thereby completed the present invention.

[0013] In addition, the inventors of the present invention found that it was possible to better solve the above-mentioned problems by means of a molded cured product of said silicone elastomer composition, and an elastic material for a medical device (and especially a medical balloon) or balloon catheter obtained by using the same.

ADVANTAGEOUS EFFECTS OF INVENTION

[0014] According to the present invention, it is possible to provide a silicone elastomer composition which has an appropriate hardness for a medical balloon (a JIS-A hardness of 20 to 40), which has no surface tackiness, excellent handlability, high rebound resilience and a high degree of elongation, thereby enabling the formation of a silicone elastomer which is highly stretchable when formed into a balloon-like shape, which can avoid the risk of breakage for a long period of time due to exhibiting high tearing strength and tensile strength, which has a permanent elongation of less than 10% after holding a material at an elongation of up to 700% for 10 minutes, and which exhibits good permanent elongation characteristics.

[0015] In addition, according to the present invention, it is possible to provide a molded cured product of said silicone elastomer composition, and an elastic material for a medical device (and especially a medical balloon) or balloon catheter obtained by using the same.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The silicone elastomer composition of the present invention will now be explained in detail.

[0017] Component (A) is the main component in the silicone elastomer composition according to the present invention, and is a characterizing component that realizes the physical properties of the composition. Specifically, component (A) is an organopolysiloxane which exhibits a raw rubber state at room temperature, contains silicon-bonded alkenyl groups, has a low content of silicon-bonded alkenyl groups, and contains component (A1) and component (A2), which have different alkenyl group bonding sites, at a weight ratio of from 5/95 to 90/10.

[0018] Component (A) is an organopolysiloxane which has a number-average degree of polymerization of 2,000 or greater based on the number-average molecular weight in terms of standard polystyrene equivalent as measured by gel permeation chromatography (GPC) (hereinafter referred to as "number-average degree of polymerization"), and which exhibits a raw rubber state at room temperature, and which is represented by the average composition formula below, and contains component (A1) and component (A2), which have different alkenyl group

bonding sites. Moreover, it is possible and preferable to remove low molecular weight siloxanes having degrees of polymerization of 10 or less from these components (A) to a content of 1,000 ppm or less in advance by using a publicly known means such as stripping.



(wherein R may be the same or different and are substituted or unsubstituted monovalent hydrocarbon groups having from 1 to 10 carbons, and preferably from 1 to 8 carbons, and "a" is a positive number from 1.8 to 2.5, and preferably from 1.9 to 2.1.)

[0019] Here, examples of the substituted or unsubstituted monovalent hydrocarbon groups bonded to silicon atoms represented by R above include alkyl groups such as methyl groups, ethyl groups, propyl groups, isopropyl groups, butyl groups, isobutyl groups, tert-butyl groups, pentyl groups, neopentyl groups, hexyl groups, cyclohexyl groups, octyl groups, nonyl groups and decyl groups; aryl groups such as phenyl groups, tolyl groups, xylyl groups and naphthyl groups; aralkyl groups such as benzyl groups, phenylethyl groups and phenylpropyl groups; alkenyl groups such as vinyl groups, allyl groups, propenyl groups, isopropenyl groups, butenyl groups, hexenyl groups, cyclohexenyl groups and octenyl groups; groups obtained by substituting some or all of the hydrogen atoms in the aforementioned groups with halogen atoms such as fluorine atoms, bromine atoms and chlorine atoms, cyano groups and the like, such as chloromethyl groups, chloropropyl groups, bromoethyl groups, trifluoropropyl groups and cyanoethyl groups, but it is preferable for 90% or more of the R groups to be methyl groups.

[0020] Component (A1) is an organopolysiloxane which has a number-average degree of polymerization of 2,000 or greater, has an average of two or more silicon-bonded alkenyl groups at only the molecular terminals of the component (A1), and exhibits a raw rubber state at room temperature. In terms of the structure of this component, the content of silicon-bonded alkenyl groups is determined according to the degree of polymerization and the presence/absence of branches on the main chain, but component (A1) is preferably a straight chain or partially branched organopolysiloxane in which the alkenyl group content is from 0.001 to 0.050 wt.%, and more preferably a straight chain organopolysiloxane having an average of two or more silicon-bonded alkenyl groups at both molecular terminals.

[0021] The structure of component (A1) is such that the molecular terminals are capped by triorganosiloxy groups having silicon-bonded alkenyl groups and the main chain has a straight chain structure comprising repeating diorganosiloxane units, but may be a partially branched chain structure. The molecular weight of component (A1) is such that the number-average degree of polymerization is 2,000 or greater (from 2,000 to 100,000) and component (A1) exhibits in a raw rubber state, and the number-average degree of polymerization is preferably 3,000 or greater (from 3,000 to 8,000). If the number-average degree of polymerization is less than the aforementioned

lower limit, it is not possible to obtain a satisfactory rubbery feeling, the surface may become sticky or tacky and it is not possible to achieve the objective of the present invention even when used in combination with component (A2).

[0022] Component (A2) is an organopolysiloxane which has a number-average degree of polymerization of 2,000 or greater, has an average of three or more alkenyl groups at molecular terminals and in side chains, has an alkenyl group content of less than 0.10 wt.%, and exhibits a raw rubber state at room temperature. Component (A2) has silicon-bonded alkenyl groups at molecular terminals and in side chains, but the alkenyl group content must be less than 0.10 wt.% and is preferably less than 0.095 wt.%, and more preferably from 0.001 to 0.090 wt.%. It is most preferable for the alkenyl group content in component (A2) to be from 0.010 to 0.080 wt.%.

[0023] The structure of component (A2) is such that the molecular terminals are capped by triorganosiloxy groups having silicon-bonded alkenyl groups, the main chain has a straight chain structure comprising repeating diorganosiloxane units, and a part of the main chain contains one or more alkenyl group-containing diorganosiloxane units. In addition, component (A2) may be a straight chain organopolysiloxane in which one molecular terminal is capped by a triorganosiloxy group having silicon-bonded alkenyl groups and a part of the main chain contains two or more alkenyl group-containing diorganosiloxane units. In addition, component (A2) may be a partially branched chain structure. The molecular weight of component (A2) is such that the number-average degree of polymerization is 2,000 or greater (from 2,000 to 100,000) and component (A2) exhibits a raw rubber state, and the number-average degree of polymerization is preferably 3,000 or greater (from 3,000 to 8,000). If the number-average degree of polymerization is less than the aforementioned lower limit, it is not possible to obtain a satisfactory rubbery feeling, the surface may become sticky or tacky and it is not possible to achieve the objective of the invention of the present application even when used in combination with component (A1).

[0024] Component (A) in the present invention contains the above-mentioned components (A1) and (A2) at a weight ratio of from 5/95 to 90/10, and it is more preferable for the content of component (A1) to be higher than that of component (A2). Specifically, a weight ratio of component (A1) / component (A2) is preferably from 30/70 to 90/10, more preferably from 50/50 to 85/15, and particularly preferably from 60/40 to 80/20. Meanwhile, if the proportion of component (A1) or component (A2) falls outside the aforementioned lower limit or upper limit, even if these components are used in combination, physical properties such as hardness and degree of elongation may deteriorate, the surface may become sticky or tacky and it is not possible to satisfactorily achieve the objective of the invention of the present application. Moreover, these components may be mixed in advance when forming the composition, but may also be mixed separately with other components, and this preparation process has no adverse effect on the

properties of the composition.

[0025] The organopolysiloxane of component (B) is a crosslinking agent for the present composition, and is an organopolysiloxane having an average of two or more silicon-bonded hydrogen atoms in the molecule. The bonding sites of the silicon-bonded hydrogen atoms in component (B) are not particularly limited, and may be molecular terminals, side molecular chains or molecular terminals and side molecular chains. In addition, examples of silicon-bonded groups other than hydrogen atoms in component (B) include monovalent hydrocarbon groups having no unsaturated aliphatic bonds, for example, alkyl groups such as methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups and hexyl groups; cycloalkyl groups such as cyclopentyl groups and cyclohexyl groups; aryl groups such as phenyl groups, tolyl groups and xylyl groups; aralkyl groups such as benzyl groups and phenethyl groups; halogenated alkyl groups such as 3,3,3-trifluoropropyl groups and 3-chloropropyl groups, with alkyl groups and aryl groups being preferred and methyl groups and phenyl groups being particularly preferred.

[0026] The molecular structure of component (B) is not limited, and may be, for example, straight chain, branched chain, straight chain having some branches, cyclic or dendritic (dendrimer-like). Component (B) may be a homopolymer having these molecular structures, a copolymer comprising these molecular structures or a mixture thereof.

[0027] The viscosity of component (B) is not limited, but the viscosity at 25°C (as measured using a rotational viscometer and the like) is preferably from 1 to 100,000 mPa·s, more preferably from 1 to 10,000 mPa·s, and particularly preferably from 1 to 5,000 mPa·s.

[0028] Examples of this type of component (B) include methylhydrogenpolysiloxanes capped at both molecular terminals with trimethylsiloxy groups, copolymers of dimethylsiloxane and methyl hydrogen siloxane capped at both molecular terminals with trimethylsiloxy groups, dimethylpolysiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups, methylhydrogenpolysiloxanes capped at both molecular terminals with dimethylhydrogensiloxy groups, copolymers of dimethylsiloxane and methyl hydrogen siloxane capped at both molecular terminals with dimethylhydrogensiloxy groups, cyclic methylhydrogenpolysiloxanes, organosiloxanes comprising siloxane units represented by the formula $(\text{CH}_3)_3\text{SiO}_{1/2}$, siloxane units represented by the formula $(\text{CH}_3)_2\text{HSiO}_{1/2}$ and siloxane units represented by the formula $\text{SiO}_{4/2}$, tetra(dimethylhydrogensiloxy)silanes and methyltri(dimethylhydrogensiloxy)silanes.

[0029] In the present composition, the content of component (B) is from 0.3 to 20 parts by weight per 100 parts by weight of component (A), and is preferably such that the amount of silicon-bonded hydrogen atoms in component (B) is from 1.0 to 20 moles, more preferably from 1.0 to 10 moles, and particularly preferably from 1.0 to 6 moles, per 1 mole of silicon-bonded alkenyl groups in component (A). This is because if the content of component (B) is less than the lower limit of the

above-mentioned range, crosslinking is inadequate, the hardness of the obtained cured silicone elastomer product is insufficient, the surface may become sticky or tacky and it is not possible to satisfactorily achieve the objective of the invention of the present application. Meanwhile, if the content of component (B) exceeds the upper limit of the above-mentioned range, hydrogen gas is generated from the obtained cured silicone elastomer product, foaming occurs in a molded product, and it may be difficult to release a molded product from a mold. A preferred compounded amount of component (B) is from 0.4 to 10 parts weight, and especially from 0.5 to 5 parts by weight, per 100 parts by weight of component (A).

[0030] Component (C) is an inorganic filler, is essential in order to impart the silicone elastomer with satisfactory strength and is not particularly limited as long as the inorganic filler imparts the silicone elastomer with hardness and permanent elongation, as described below. It is possible to use one or more types of inorganic filler, and component (C) can be a reinforcing filler such as a silica fine powder or fumed titanium oxide; a non-reinforcing filler such as diatomaceous earth, an aluminosilicate, iron oxide, zinc oxide or calcium carbonate; or a thermally conductive filler such as aluminum oxide; fused silica or silver powder. A silica fine powder can be a dry type silica such as fumed silica or a synthetic silica such as a wet type silica, and preferably has a specific surface area, as measured using the BET method, of $50 \text{ m}^2/\text{g}$ or more, and more preferably from 50 to $300 \text{ m}^2/\text{g}$. Moreover, the surface of the silica fine powder may be treated with a silicon compound such as an organoalkoxysilane, an organohalosilane or an organosilazane, or a cyclic diorganosiloxane oligomer such as octamethyltetrasiloxane or decamethylpentasiloxane.

[0031] From the perspective of improvement of permanent elongation characteristics in particular, the inorganic filler of component (C) is preferably an inorganic filler in which fumed silica having a BET specific surface area of from 50 to $250 \text{ m}^2/\text{g}$ accounts for 50 wt.% or more of the total quantity of component (C), and particularly preferably an inorganic filler in which fumed silica having a BET specific surface area of from 50 to $250 \text{ m}^2/\text{g}$ accounts for 90 to 100 wt.% of the total quantity of component (C). In addition, the BET specific surface area of the fumed silica is preferably from 75 to $250 \text{ m}^2/\text{g}$, and more preferably from 100 to $225 \text{ m}^2/\text{g}$, and it is most preferable for the center value of the BET specific surface area to be $200 \text{ m}^2/\text{g}$. If the BET specific surface area of the fumed silica in the inorganic filler is less than the aforementioned lower limit, satisfactory strength cannot be achieved and the transparency of a molded product may deteriorate. In addition, in cases where a large quantity of a silica fine powder (and especially untreated fumed silica and the like) having a BET specific surface area greater than $300 \text{ m}^2/\text{g}$ is compounded in the composition, the permanent elongation characteristics may deteriorate, the characteristics required of a medical balloon are not satisfied, the silica fine powder may be difficult to compound, and discoloration may occur.

[0032] The inorganic filler of component (C) (for example, fumed silica) may be used without further modification, but is preferably treated in advance with a surface hydrophobization treatment agent or treated by adding a surface treatment agent when kneading with a silicone oil. These surface treatment agents may be one type of publicly known surface treatment agent, such as an

5 alkylalkoxysilane, an alkylchlorosilane, an alkylsilazane, a silane coupling agent, a titanate-based treatment agent or a fatty acid ester, but it is also possible to use two or more of these surface treatment agents either simultaneously or at different times.

[0033] In addition, the compounded amount of the inorganic filler of component (C) is preferably from 5 to 50 parts by weight, and especially from 15 to 35 parts by weight, per 100 parts by weight

10 of component (A). If the compounded amount is less than the aforementioned lower limit, it is not possible to achieve satisfactory hardness and physical strength, and if the compounded amount exceeds the aforementioned upper limit, the hardness increases and the composition may not be suitable for use as a medical balloon.

[0034] The addition reaction catalyst of component (D) is a catalyst used to facilitate curing of the

15 present composition, and may be a platinum-based catalyst, a palladium-based catalyst, a rhodium-based catalyst and the like. A platinum metal-type catalyst is particularly preferred. Examples of component (D) include platinum-based catalysts, for example, platinum fine powders, platinum black, chloroplatinic acid, platinum tetrachloride, alcohol-modified chloroplatinic acid, olefin complexes of platinum, alkenylsiloxane complexes of platinum, carbonyl complexes of platinum,

20 powdered thermoplastic organic resins, such as methyl methacrylate resins, polycarbonate resins, polystyrene resins and silicone resins, containing these platinum-based catalysts; rhodium-based catalysts represented by the formulae $[\text{Rh}(\text{O}_2\text{CCH}_3)_2]_2$, $\text{Rh}(\text{O}_2\text{CCH}_3)_3$, $\text{Rh}_2(\text{C}_8\text{H}_{15}\text{O}_2)_4$, $\text{Rh}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{Rh}(\text{C}_5\text{H}_7\text{O}_2)(\text{CO})_2$, $\text{Rh}(\text{CO})[\text{Ph}_3\text{P}](\text{C}_5\text{H}_7\text{O}_2)$, $\text{RhX}_3[(\text{R})_2\text{S}]_3$, $(\text{R}^1\text{P})_2\text{Rh}(\text{CO})\text{X}$, $(\text{R}^2\text{P})_2\text{Rh}(\text{CO})\text{H}$, $\text{Rh}_2\text{X}_2\text{Y}_4$, $\text{H}_f\text{Rh}_g(\text{En})_h\text{Cl}_i$ and $\text{Rh}[\text{O}(\text{CO})\text{R}]_{3-j}(\text{OH})_j$ (wherein, X is a hydrogen atom, a chlorine atom, a

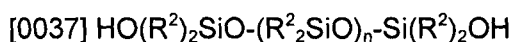
25 bromine atom or an iodine atom, Y is an alkyl group such as a methyl group or an ethyl group, CO, C_8H_{14} or $0.5\text{C}_8\text{H}_{12}$, R is an alkyl group such as a methyl group, an ethyl group or a propyl group; a cycloalkyl group such as a cycloheptyl group or a cyclohexyl group; or an aryl group such as a phenyl group or xylyl group, R¹ is an alkyl group such as a methyl group, an ethyl group or a propyl group; an aryl group such as a phenyl group, a tolyl group or a xylyl group; an alkoxy group such

30 as a methoxy group or an ethoxy group; or an aryloxy group such as a phenoxy group, En is an olefin such as ethylene, propylene, butene or hexene, f is 0 or 1, g is 1 or 2, h is an integer from 1 to 4, i is 2, 3 or 4, and j is 0 or 1); and iridium-based catalysts represented by the formulae $\text{Ir}(\text{OOCCH}_3)_3$, $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)_3$, $[\text{Ir}(\text{Z})(\text{En})_2]_2$ or $[\text{Ir}(\text{Z})(\text{Dien})]_2$ (wherein Z is a chlorine atom, a bromine atom, an iodine atom or an alkoxy group such as a methoxy group or an ethoxy group, En is an

35 olefin such as ethylene, propylene, butene or hexene, and Dien is cyclooctadiene).

[0035] The content of component (D) in the present composition is a catalytic quantity, but is more specifically an amount where the quantity of a platinum group metal in component (D) is from 0.01 to 1,000 ppm by weight, and preferably from 0.1 to 500 ppm by weight, relative to the total quantity of component (A) and component (B). This is because the obtained silicone elastomer composition is not sufficiently cured if the content of component (D) is less than the lower limit of the above-mentioned range and the curing speed of the obtained silicone elastomer composition is not significantly improved even if the content of component (D) is greater than the upper limit of the above-mentioned range.

[0036] The silicone elastomer composition according to the present invention must contain the above-mentioned components (A) to (D), but preferably also contains (E) a dimethylpolysiloxane which has silicon-bonded hydroxyl groups (silanol groups) at molecular terminals and which has a number-average degree of polymerization of 100 or less. Component (E) does not have an addition reaction functional group (that is, a functional group which may take part in a hydrosilylation addition reaction and which comprises an alkenyl group such as a vinyl group and a silicon-bonded hydrogen atom (SiH group), is a dimethylpolysiloxane having a number-average degree of polymerization of 100 or less, and is represented by the average molecular formula below.



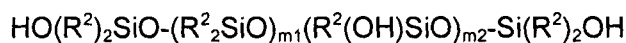
(Wherein, R^2 is a monovalent hydrocarbon group having from 1 to 6 carbons and not having an unsaturated aliphatic bond, and it is preferable for 90% or more of the R^2 groups to be methyl groups or phenyl groups. n is a number in a range of 0 to 98.)

[0038] It is particularly preferable for component (E) to be used to treat the surface of the fumed silica of the aforementioned component (C). Component (E) is an optional component that may be compounded if necessary, and the compounded amount thereof is from 0.1 to 50 parts by weight, and preferably from 1 to 20 parts by weight, per 100 parts by weight of component (A). If this compounded amount exceeds 50 parts by weight, there are concerns that the rubbery properties of a cured product will significantly deteriorate.

[0039] It is preferable for the silicone elastomer composition according to the present invention to contain from 5 to 100 parts by weight, and preferably from 10 to 75 parts by weight, of (G) an organopolysiloxane which has a number-average degree of polymerization of from 250 or more to a degree of polymerization whereby the composition exhibits a raw rubber state at room temperature based on the number-average molecular weight in terms of polystyrene equivalent as measured by gel permeation chromatography (GPC), the organopolysiloxane being free of silicon-bonded alkenyl groups, and having at least one silanol group in the molecule. Because this component (G) is an organopolysiloxane which has a silanol group and has a fixed chain length, when component (G) is

used in combination with the above-mentioned components (A) to (D), it is possible to suppress an increase in the hardness of an obtained cured product and the permanent elongation will be less than 10%, and may be further improved, after holding a material at an elongation of up to 700% for 10 minutes in accordance with JIS K 6301.

[0040] The structure of component (G) is such that component (G) is free of silicon-bonded alkenyl groups in the molecule, the molecular terminals are capped by silanol groups or triorganosiloxy groups, and the main chain has a straight chain structure comprising repeating diorganosiloxane units or repeating silanol organosiloxane units, but may be a partially branched chain structure. With regard to the degree of polymerization, the number-average degree of polymerization may be from 250 or more to a degree of polymerization whereby the composition exhibits a raw rubber state at room temperature, and the number-average degree of polymerization is from 250 to 100,000, and preferably from 1,000 to 8,000. It is particularly preferable for component (G) to have a straight chain and to have a silanol group at both molecular terminals, and in such cases, component (G) is represented by the average molecular formula below. Moreover, it is possible and preferable to remove low molecular weight siloxanes having degrees of polymerization of 10 or less from component (G) to a content of 1,000 ppm or less in advance by using a publicly known means such as stripping.



(Wherein, R^2 is a monovalent hydrocarbon group having from 1 to 6 carbons and not having an unsaturated aliphatic bond, and it is preferable for 90% or more of the R^2 groups to be methyl groups or phenyl groups. The value of $m1 + m2$ is 248 or more, $m1$ is a positive number, and $m2$ is 0 or a positive number.)

[0041] It is particularly preferable for component (G) to be an organopolysiloxane which has a number-average degree of polymerization of 2,000 or greater based on the number-average molecular weight in terms of standard polystyrene equivalent, exhibits a raw rubber state at room temperature, is free of silicon-bonded alkenyl groups in the molecule, and has a silanol group at both molecular terminals. By using this type of organopolysiloxane which has silanol terminals and which exhibits a raw rubber state, it is possible to further improve permanent elongation characteristics and obtain a silicone elastomer that better satisfies the characteristics required for a medical balloon.

[0042] In order for the addition-curable silicone elastomer composition according to the present invention to exhibit improved moisture resistance, it is possible to further compound at least one type of magnesium compound selected from the group consisting of magnesium oxide (MgO), magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and magnesium carbonate salts. Examples of magnesium carbonate salts include magnesium carbonate (MgCO_3) and basic magnesium carbonates

($m\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, such as $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$). These magnesium compounds may be hydrates or anhydrides. In addition, two or more magnesium compounds may be used in combination. Because such magnesium compounds have been approved for use by the FDA, the silicone elastomer composition of the present invention may be advantageously used in food/drink applications in addition to medical applications. In addition, even if silicone elastomers that contain these magnesium compounds are in contact for long periods of time with aqueous media that contain chloride ions (including balloon-enlarging solutions that are non-toxic to humans, such as tap water, physiological saline, mixtures of angiographic agents and physiological saline, glucose solutions, bodily fluids such as blood and gastric acid and drug solutions for treatment), it is possible to prevent or reduce degradation or the occurrence of appearance defects such as whitening, and the silicone elastomer composition of the present invention can be advantageously used in medical components that come into contact with blood, gastric acid, physiological saline, acidic cleaning solutions and the like (for example, stomach catheters, balloons, catheter balloons, artificial dialysis machines, blood dialysis machines and implant components).

[0043] The lower limit of the compounded amount of the aforementioned magnesium compounds is not particularly limited as long as the above-mentioned effect can be achieved, but this compounded amount is preferably from 0.01 to 3 wt.%, and more preferably from 0.1 to 0.5 wt.%, relative to the total weight (mass) of the curability silicone elastomer composition.

[0044] The form of the aforementioned magnesium compounds is not particularly limited, and can be, for example, bulk-like or particulate (including a regular spherical shape or an approximately spherical shape), but is preferably particulate. The average particle diameter of a particulate magnesium compound is generally from 0.1 to 10 μm , and particularly preferably from 0.5 to 5 μm . In addition, it is possible, and preferable, to treat the surface of such magnesium compounds with a surface treatment agent such as an aluminum compound, a zinc compound, a silicon compound or a higher fatty acid.

[0045] The addition-curable silicone elastomer composition according to the present invention may contain a curing retarder in order to adjust the curing speed or pot life. Examples of curing retarders include alcohol derivatives having carbon-carbon triple bonds, such as 3-methyl-1-butyne-3-ol, 3,5-dimethyl-1-hexyne-3-ol, phenylbutynol and 1-ethynyl-1-cyclohexanol; ene-yne compounds such as 3-methyl-3-penten-1-yne and 3,5-dimethyl-3-hexen-1-yne; alkenyl group-containing low molecular weight siloxanes such as tetramethyltetravinylcyclotetrasiloxane and tetramethyltetrahexenylcyclotetrasiloxane; and alkyne-containing silanes such as methyl-tris(3-methyl-1-butyne-3-oxy)silane and vinyl-tris(3-methyl-1-butyne-3-oxy)silane.

[0046] The compounded amount of the curing retarder may be selected as appropriate according to the usage method, molding method and the like of the addition-curable silicone elastomer

composition. A commonly used compounded amount is from 0.001 to 5 wt.% (mass%) relative to the total weight (mass) of the composition.

[0047] The addition-curable silicone elastomer composition according to the present invention may contain carbon black such as acetylene black, furnace black or channel black as long as the objective of the present invention is not impaired. In addition, the addition-curable silicone elastomer composition according to the present invention may, if necessary, contain additives such as pigments (coloring agents such as red iron oxide and organic pigments, titanium dioxide and the like), heat-resistant agents, flame retardants, internal release agents, plasticizers, non-functional silicone oils and the like. Moreover, examples of internal release agents include higher fatty acid salts such as calcium stearate. Moreover, it is particularly preferable to use additives such as heat-resistant agents and flame retardants when the addition-curable silicone elastomer composition according to the present invention is used as a medical balloon in an environment that is exposed to high temperatures, such as in heat sterilization or in a thermocouple.

[0048] However, it is preferable for the addition-curable silicone elastomer composition according to the present invention to contain essentially no (X1) an organopolysiloxane capped at both molecular terminals with trialkylsilyl groups (excluding compounds corresponding to the component (B)), (X2) an organopolysiloxane resin essentially comprising $R^1_3SiO_{1/2}$ units (wherein, R^1 are each independently hydroxyl groups, alkoxy groups having from 1 to 6 carbons or substituted or unsubstituted monovalent hydrocarbon groups having from 1 to 10 carbons) and $SiO_{4/2}$ units or (X3) an organopolysiloxane having an alkenyl group content of 0.10 wt.% or more. Specifically, the total content of these components is preferably less than 5 wt.% of the overall composition, more preferably less than 1 wt.%, and most preferably a quantity that has essentially no effect on the properties of the cured product, that is, not contained in the composition (less than 0.1 wt.%).

[0049] If the addition-curable silicone elastomer composition according to the present invention contains a substantial quantity of the above-mentioned organopolysiloxane capped at both molecular terminals with trialkylsilyl groups of component (X1), the organopolysiloxane resin of component (X2) or the organopolysiloxane having an alkenyl group content of 0.10 wt.% or more of component (X3), the hardness of the obtained cured product is increased beyond that required for a medical balloon and stickiness and tackiness occurs in a cured product, meaning that handlability deteriorates and such a composition may not be suitable for use as an elastic material for a medical device such as a medical balloon. In particular, if the content of the organopolysiloxane capped at both molecular terminals with trialkylsilyl groups of component (X1) exceeds 5 wt.% of the overall composition, stickiness and tackiness occurs in a cured product, and even if the composition is useful in terms of hardness or permanent elongation characteristics, there may be an adverse effect on handlability (such as roll applicability) or formability (such as mold release properties).

[0050] The curable silicone rubber composition of the present invention can be easily produced by homogeneously mixing a composition that contains the above-mentioned components and, if necessary, a variety of additives using a publicly known kneading means such as a Ross mixer, a two roll mill or a kneader mixer.

5 [0051] The method for molding or curing the addition-curable silicone elastomer composition according to the present invention may be a commonly used method, but the molding method is preferably an injection molding method, a compression molding method or an extrusion molding method (including hot air vulcanization). In addition, curing conditions such as the curing
10 temperature and the curing time are not particularly limited, and good curing is generally carried out at a temperature from room temperature to 220°C. From the perspective of industrial production of an elastic material for a medical device such as a medical balloon, it is possible to use heat curing conditions of from 80 to 230°C for a period of from 3 seconds to 60 minutes, and preferably from 100 to 200°C for a period of from 5 seconds to 30 minutes. In addition, by press curing (compression molding) the addition-curable silicone elastomer composition according to the
15 present invention at 120°C for 10 minutes, as described below, an elastic material for a medical device can exhibit appropriate hardness and permanent elongation characteristics, but it is also possible to cure the composition by means of a stepwise vulcanization (step curing) process, such as carrying out primary vulcanization and then carrying out secondary vulcanization. In such cases, however, the cycle time required for production may be increased and productivity may
20 decrease.

[0052] Specifically, the addition-curable silicone elastomer composition according to the present invention may be cured in a single step at the above-mentioned temperatures. Furthermore, characteristics such as permanent elongation may be further improved by step curing in which the composition is first heated to a temperature from room temperature to 150°C, and preferably from
25 60 to 150°C, and then heated to from 80 to 200°C, and preferably from 100 to 180°C. In addition, in order to remove small quantities or trace quantities of volatile components and further improve characteristics such as permanent elongation, it is preferable to carry out secondary vulcanization (heat aging) at from 150 to 250°C for a period of from 10 minutes to 2 hours following completion of the curing.

30 [0053] By having the constitution described above, the addition-curable silicone elastomer composition according to the present invention is characterized by giving a cured product having a JIS-A hardness of from 20 to 40 following press curing at 120°C for 10 minutes. The JIS-A hardness is preferably from 20 to 35, and more preferably from 22 to 33. If the hardness falls outside the aforementioned range when using the above-mentioned curing conditions, the strength
35 and flexibility of the cured product may be insufficient and the cured product may not be suitable for

use as a medical balloon.

[0054] By having the constitution described above, the addition-curable silicone elastomer composition according to the present invention is further characterized by giving a cured product having a permanent elongation of less than 10% after holding a material at an elongation of up to 700% for 10 minutes in accordance with JIS K 6301 following press curing at 120°C for 10 minutes. Under similar conditions, the permanent elongation of the cured product is preferably less than 9.5%, and more preferably less than 8.5%. If the permanent elongation is 10% or more following curing under the above-mentioned conditions, the cured product may not be suitable for use as a medical balloon in particular.

[0055] The above-mentioned hardness and permanent elongation characteristics are physical properties that are realized as a direct result of the constitution of the addition-curable silicone elastomer composition according to the present invention. Furthermore, from the perspective of use as an elastic material for a medical device such as a medical balloon, the addition-curable silicone elastomer composition according to the present invention has a 100% modulus (M100), as measured in accordance with JIS K 6251, of 0.75 MPa or less, and particularly preferably 0.5 MPa or less, following press curing at 120°C for 10 minutes.

[0056] Similarly, from the perspectives of handlability during molding and strength as an elastic material for a medical device, the addition-curable silicone elastomer composition according to the present invention has a tensile strength, as specified in JIS K 6251, of 5 MPa or more, more preferably from 5.5 to 15 MPa, and particularly preferably from 6 to 12 MPa. Furthermore, the addition-curable silicone elastomer composition according to the present invention has a breaking elongation of 800% or more, and preferably from 850 to 1200%.

[0057] Similarly, from the perspectives of strength and service life as an elastic material for a medical device, the addition-curable silicone elastomer composition according to the present invention preferably has a tearing strength, as measured in accordance with JIS K 6252 using a crescent mold, of 10 kN/m or more, and especially from 12.5 to 50 kN/m.

[0058] A cured product comprising the silicone elastomer composition according to the present invention can be used in a variety of applications, such as electrical equipment, vehicles, construction, medical care and foods. For example, a cured product comprising the silicone elastomer composition according to the present invention can be used in rubber contacts for remote controllers, typewriters, word processors, computer terminals, musical instruments and the like; gaskets for construction; rollers such as copier rollers, developing rollers, transfer rollers, charging rollers and paper feed rollers; rubber vibration insulators for motorcycles and the like; packing for compact disks used in computers and the like; water distribution components such as valves, hoses, tubes, packing, seals and joints; children's toys, tableware, cookware (including

silicone steamers), toothbrushes, teats for baby bottles, infants' pacifiers, artificial teats, sporting goods, underwater eyeglasses for diving, goggles for diving, vehicle components, scale models and artificial skin components for robots.

[0059] In particular, a cured product comprising the silicone elastomer composition according to the present invention exhibits excellent safety and durability and exhibits appropriate hardness, permanent elongation and other physical properties, and can therefore be used in elastic medical materials used to treat humans or animals. For example, a cured product comprising the silicone elastomer composition according to the present invention is also suitable for use in a variety of medical tubes, stomach catheters, medical balloons, catheter balloons, artificial dialysis machines, blood dialysis machines, implant components, chemical stoppers and O-rings. Moreover, a cured product comprising the silicone elastomer composition according to the present invention exhibits excellent heat resistance, acid resistance, radiation resistance and the like and does not suffer from a deterioration in physical properties, and can therefore be easily sterilized. In addition, by using the aforementioned fumed silica, which is a preferred inorganic filler, it is possible to obtain a cured product having a transparent appearance and excellent scratch resistance, and a cured product comprising the silicone elastomer composition according to the present invention therefore enables excellent visibility of the contents of a balloon or the flow of a liquid in a catheter.

[0060] The silicone elastomer according to the present invention is most preferably used as a medical catheter or expansion member (medical balloon), and can be used, for example, to enlarge a site where a tubular organ in the body is obstructed (for example, a digestive organ such as the gastrointestinal tract, a circulatory organ such as a blood vessel, a urinary organ such as the urethra, the uterus or the fallopian tubes) or as a tool for continuously administering a drug solution. In addition, a medical balloon comprising the silicone elastomer composition according to the present invention can be used for blood transmission in a variety of blood vessel formation operations, stent grafts, blood clot blocking, embolism prevention, and aortic aneurysm operations. Similarly, the medical balloon according to the present invention can be advantageously used in treatment by injecting a drug solution into the enlarged balloon, holding the balloon at a certain location and administering a certain quantity of the drug solution to the affected part. Specifically, the medical balloon according to the present invention can be advantageously used to continuously administer a drug solution, such as administering an anaesthetic or analgesic for post-operative pain or administering anti-cancer drugs. A balloon in a balloon catheter must move smoothly and without resistance into a body cavity and reach a site of stenosis, that is, the obstructed site where the balloon is to be enlarged, but the silicone elastomer according to the present invention has an appropriate hardness, and therefore retains flexibility inside the body and can reach the site of stenosis without placing a burden on the body. In addition, after reaching the site of stenosis, the

balloon is sufficiently enlarged by pumping and because the balloon has a low permanent elongation, removal of the balloon from the affected part following use is easy. Moreover, the balloon can be enlarged using a publicly known means, but this can be achieved by using a balloon-enlarging liquid that is non-toxic humans, such as mixtures of angiographic agents and physiological saline, physiological saline and glucose solutions. Moreover, the silicone elastomer according to the present invention can be easily molded, and the shape, internal structure, size and film thickness of the balloon are such that an appropriate publicly known shape and the like can be selected according to the intended use or the organ in which the balloon is to be used. In addition, in cases where the silicone elastomer according to the present invention is used in a tool for continuously injecting a drug solution, a preferred mode of use is one in which the tool is provided with a drug solution injection port, a balloon and a drug solution outlet port, the drug solution is charged inside the balloon, the balloon is enlarged and deformed, and the contractile force of the balloon acts as the driving force for supplying the solution. In particular, the silicone elastomer of the present invention has a low permanent elongation, and therefore has a low permanent deformation caused by contraction following injection of the drug solution, leaves little drug solution remaining in the balloon and can realize effective drug solution injection.

[0061] A balloon catheter that uses a medical balloon comprising the silicone elastomer according to the present invention generally has a constitution that contains a flexible tube connected to said medical balloon, a joint, a branch tube and a connector for enlarging and contracting the balloon, but may, if necessary, be provided with a second branch tube, a connector for measuring the pressure of a fluid, such as blood pressure, an oscillating part or an observational component for monitoring the affected part.

EXAMPLES

[0062] Hereinafter, the present invention is described in detail with reference to Practical Examples and Comparative Examples, but it should be understood that the present invention is not limited to these Practical Examples. The viscosity (dynamic viscosity) values are measured at 25°C. In addition, "parts" means parts by weight and "%" means wt. % in the tables.

[0063] [Measurement of number-average molecular weight and average degree of polymerization] In the Practical Examples and the like, the average degree of polymerization of an organopolysiloxane is the number-average degree of polymerization, based on the number-average molecular weight in terms of polystyrene equivalent as measured by gel permeation chromatography (GPC) using an analytical apparatus described below, and was measured under the following conditions.

Measurement temperature: 40°C (column oven temperature)

Sample: 1 wt. % toluene solution of organopolysiloxane

Detector: RI detector

Polymer for calibration curve: Standard polystyrene

[0064] [Sample preparation and curing conditions]

The components shown in Table 1 (Practical Examples and Comparative Examples) were

5 homogeneously mixed in a two roll mill and then press vulcanized at 120°C for 10 minutes to obtain samples having thicknesses of 2 mm.

[0065] Practical Examples 1 to 3 and Comparative Examples 1 to 4

The components shown in Table 1 and Table 2 below were homogeneously mixed to obtain the addition-curable liquid silicone elastomer compositions of Practical Examples 1 to 3 and

10 Comparative Examples 1 to 4.

[0066] The following physical properties of the compositions of Practical Examples 1 to 3 and Comparative Examples 1 to 4 were measured. The results are shown in Table 1.

[0067] [Initial physical properties]

(1) JIS-A hardness: The hardness of a cured silicone rubber sample was measured in
15 accordance with JIS K 6251 (tensile testing methods for vulcanized rubber) (JIS-A hardness, measured using a JIS type A durometer).

(2) Tensile strength, 100% modulus: Measured in accordance with JIS K 6251 using an "Autograph SES-1000" manufactured by Shimadzu Corporation. Moreover, the tensile stress at 100% elongation was recorded as the 100% modulus.

20 (3) Tearing strength: A crescent shaped sample as described in JIS K 6252 (tear test methods for vulcanized rubbers) was cut out from the above-mentioned sample and used as a sample. Using this sample, the tearing strength was measured in accordance with JIS K 6252 using an "Autograph SES-1000" manufactured by Shimadzu Corporation.

(4) Breaking elongation: This was measured in accordance with JIS K 6251 using an "Autograph
25 SES-1000" manufactured by Shimadzu Corporation, and the elongation at the point where the sample broke was expressed as a proportion (%) relative to the initial value.

[0068] [Permanent elongation]

In accordance with JIS K-6301, a pressed sample obtained having a thickness of 2 mm, which was obtained by press curing a silicone elastomer composition at 120°C for 10 minutes, was cut into the
30 shape of a no. 1 type dumbbell (JIS K-6301), reference lines marked 2 cm apart on the sample were elongated to 700%, the sample was held for 10 minutes in this elongated state and then released, and 10 minutes after release, the distance between the reference lines (l1) was measured, and the residual permanent strain was measured. The permanent strain was expressed as a proportion (%) relative to the original length of elongation 2cm, L0).

35 Permanent elongation (PS) = $(l1 - L0) / L0 \times 100 (\%)$

Moreover, samples having breaking elongations of less than 700% were evaluated as "not measurable".

[0069] [Roll processability]

Formability and processability were evaluated using a roll adhesion test.

- 5 Specifically, 300 g of a sample (unvulcanized rubber) was placed in a two-roll mill (6 inch rolls) having a front roll rotation speed of 35 rpm and a back roll rotation speed of 25 rpm, that is, a rotational ratio of 1.4 (front roll) to 1.0 (back roll). The roll interval was 2 mm, and the sample was wound onto the front roll and then discharged, peeled by hand from the surface of a drawing roll and evaluated according to the following criteria.

10 <Evaluation>

Smooth peeling off was evaluated as suitable adhesion (○, good processability).

If peeling was not possible, this was evaluated as unsuitable adhesion occurred (×, poor processability).

[0070] Table 1

Component (parts)	Practical Example			Comparative Example			
	1	2	3	1	2	3	4
(a1) Organopolysiloxane 1 (gum-like state) (Vi at both terminals)	49.30	56.90	49.30		72.79	72.0	49.30
(a2) Organopolysiloxane 2 (gum-like state) (terminal/side chain Vi content: 0.061%)	18.90	18.90	18.90	75.80		3.80	18.90
(g) Organopolysiloxane 3 (gum-like state)	7.60						7.60
(x1) Organopolysiloxane 4			7.60				
(a') Organopolysiloxane 5 (gum-like state) (Side chain Vi content: 1.420%)					3.01		
(c) Fumed silica	19.7	19.7	19.7	19.7	19.7	19.7	19.7
(e) Organopolysiloxane 6 (Silanol groups at both terminals)	4.5	4.5	4.5	4.5	4.5	4.5	4.5
(b) Organohydrogen- polysiloxane	0.83	0.83	0.83	0.83	0.83	0.83	0.12
(d) Addition reaction catalyst	An amount whereby the quantity of platinum metal is 4 ppm in terms of mass units relative to the silicone elastomer composition						
(f) Curing retarder	0.025	0.025	0.025	0.025	0.025	0.025	0.025
SiH/Vi weight ratio	6.4	6.1	6.4	3.3	3.0	8.0	0.96
<Physical properties of cured product >							
Density	1.10	1.10	1.10	1.10	1.09	1.09	1.10
JIS-A hardness	25	31	26	38	29	27	15
Permanent elongation (%)	7.4	8.9	8.3	Not measurable	40.0	16.0	27.8
Roll processability	○	○	×	○	○	○	○
Tensile strength (MPa)	10.3	9.4	7.7	6.0	5.9	11.9	8.3
100% modulus (MPa)	0.37	0.44	0.39	0.47	0.44	0.45	0.24
Breaking elongation (%)	1090	1060	990	520	1650	1220	1650
Tearing strength (kN/m)	15	15	14	6	17	23	15

[0071] In Table 1, the components used in the Practical Examples and Comparative Examples were as follows.

(a1) Organopolysiloxane 1 (gum-like state)

Dimethylsiloxane capped at both molecular terminals with vinyltrimethylsilyl groups (average
5 degree of polymerization: 4473)

(a2) Organopolysiloxane 2 (gum-like state)

Copolymer of dimethylsiloxane and methylvinylsiloxane capped at both molecular terminals with
vinyltrimethylsilyl groups (average degree of polymerization: 4340, vinyl group content: 0.061 wt.%)

(g) Organopolysiloxane 3 (gum-like state)

10 Dimethylsiloxane capped at both molecular terminals with hydroxydimethylsilyl groups (average
degree of polymerization: 3764)

(x1) Organopolysiloxane 4

Dimethylsiloxane capped at both molecular terminals with trimethylsilyl groups (viscosity: 350 mPa·
s, average degree of polymerization: approximately 120)

15 (a') Organopolysiloxane 5 (gum-like state)

Copolymer of dimethylsiloxane and methylvinylsiloxane capped at both molecular terminals with
trimethylsilyl groups (number-average degree of polymerization: 3764, vinyl group content: 1.420
wt.%)

(c): Fumed silica

20 Fumed silica having a BET specific surface area of 200 m²/g (product name "Aerosil 200",
manufactured by Nippon Aerosil)

(e) Organopolysiloxane 6

Dimethylsiloxane capped at both molecular terminals with hydroxydimethylsilyl groups (viscosity: 30
mPa·s, average degree of polymerization: approximately 11)

25 (b) Organohydrogenpolysiloxane

Copolymer of dimethylsiloxane and methyl hydrogen siloxane capped at both molecular terminals
with trimethylsilyl groups (viscosity: 15 mPa·s, Si-H content: 0.83 wt.%)

(d) Addition reaction catalyst

Platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex

30 (In this complex, platinum metal was added at 4 ppm in terms of mass units relative to the silicone
elastomer composition)

(f) Curing retarder : 1-ethynyl-1-cyclohexanol

[0072] As shown in Table 1, each of the compositions of Practical Examples 1 to 3 was press cured

at 120°C for 10 minutes to provide a silicone elastomer which had an appropriate hardness for an elastic medical material (especially a medical balloon) and which had a low permanent elongation. Furthermore, these silicone elastomers had superior breaking elongation to the other silicone elastomers. Moreover, although not as good as Comparative Example 3, these silicone elastomers exhibited good tensile strength and tearing strength. Practical Example 1 in particular exhibited the lowest permanent elongation by using a methylsiloxane gum having silanol terminals. However, Practical Example 3 contained 5 wt.% or more of a dimethylsiloxane capped at both molecular terminals with trimethylsilyl groups (viscosity: 350 mPa·s) as component (X1), but the silicone elastomer was sticky and exhibited poor roll processability. It can be understood from this that a component such as component (X1) is preferably not added to the composition in cases where handlability and formability are to be improved in addition to achieving hardness and permanent elongation that are suitable for an elastic medical material (especially a medical balloon).

[0073] In addition, in Comparative Example 1, it was not possible to elongate to 700%, meaning that it was not possible to measure the permanent elongation and the breaking elongation was also inadequate.

Furthermore, in Comparative Examples 2 to 4, a permanent elongation of 10% or more occurred when elongated to 700%, and it was not possible to obtain a silicone elastomer having a low permanent elongation.

[0074] Therefore, by using the silicone elastomer compositions of Practical Examples 1 to 3 according to the invention of the present application, it was possible to obtain a cured product having physical properties such as appropriate hardness and permanent elongation for an elastic medical material (especially a medical balloon). In particular, the cured products of Practical Examples 1 to 2 exhibit excellent processability with no stickiness, and can therefore be molded as desired using a publicly known means and can be used as a component such as a balloon catheter by molding into a medical balloon.

CLAIMS

1. A silicone elastomer composition comprising:

(A) 100 parts by weight of an organopolysiloxane having silicon-bonded alkenyl groups and exhibiting a raw rubber state at room temperature, the organopolysiloxane (A) including

components (A1) and (A2) at a weight ratio of from 5/95 to 90/10,

(A1) an organopolysiloxane having: a number-average degree of polymerization of 2,000 or greater based on the number-average molecular weight in terms of polystyrene equivalent as measured by gel permeation chromatography (GPC), and an average of two or more silicon-bonded alkenyl groups at only the molecular terminals,

(A2) an organopolysiloxane having: a number-average degree of polymerization of 2,000 or greater based on the number-average molecular weight in terms of polystyrene equivalent as measured by gel permeation chromatography (GPC), an average of three or more alkenyl groups at the molecular terminals and the side chains, and an alkenyl group content of less than 0.10 wt.%;

(B) from 0.3 to 20 parts by weight of an organopolysiloxane having an average of two or more silicon-bonded hydrogen atoms in the molecule;

(C) from 5 to 50 parts by weight of an inorganic filler; and

(D) a catalytic quantity of an addition reaction catalyst;

wherein

after press curing at 120°C for 10 minutes,

the silicone elastomer composition provides a cured product having: a hardness of from 20 to 40, as measured in accordance with JIS K 6253 using a type A durometer hardness tester and a permanent elongation of less than 10% after holding a material at an elongation of up to 700% for 10 minutes in accordance with JIS K 6301.

2. The silicone elastomer composition according to claim 1, further comprising: (E) from 0.1 to 50 parts by weight of a dimethylpolysiloxane having silanol groups at molecular terminals and a number-average degree of polymerization of 100 or less based on the number-average molecular weight in terms of polystyrene equivalent as measured by gel permeation chromatography (GPC).

3. The silicone elastomer composition according to claim 1 or 2, further comprising: (G) from 5 to 100 parts by weight of an organopolysiloxane having a number-average degree of polymerization of from 250 to a degree of polymerization whereby the composition exhibits a raw rubber state at room temperature based on the number-average molecular weight in terms of polystyrene equivalent as measured by gel permeation chromatography (GPC), the organopolysiloxane being

free of silicon-bonded alkenyl groups and having at least one silanol group in the molecule.

4. The silicone elastomer composition according to any one of claims 1 to 3, wherein the total content of: (X1) an organopolysiloxane capped at both molecular terminals with trialkylsilyl groups (excluding compounds corresponding to the component (B)),

(X2) an organopolysiloxane resin essentially comprising $R^1_3SiO_{1/2}$ units (wherein R^1 are each independently hydroxyl groups, alkoxy groups having from 1 to 6 carbons or substituted or unsubstituted monovalent hydrocarbon groups having from 1 to 10 carbons) and $SiO_{4/2}$ units, and (X3) an organopolysiloxane having an alkenyl group content of 0.10 wt.% or more

is less than 1 wt.% of the total composition.

5. The silicone elastomer composition according to any one of claims 1 to 4, wherein the component (C) is an inorganic filler in which fumed silica having a BET specific surface area in a range of 50 to 250 m^2/g accounts for 50 wt.% or more of the total quantity of the component (C).

6. The silicone elastomer composition according to any one of claims 3 to 5, wherein the component (G) is: (G1) an organopolysiloxane which has a number-average degree of polymerization of 2,000 or greater based on the number-average molecular weight in terms of polystyrene equivalent as measured by gel permeation chromatography (GPC), exhibits a raw rubber state at room temperature, is free of silicon-bonded alkenyl groups, and has silanol groups at the molecular terminals.

7. A molded cured product of the silicone elastomer composition according to any one of claims 1 to 6.

8. An elastic material for a medical device comprising a molded cured product of the silicone elastomer composition described in any one of claims 1 to 6.

9. A medical balloon comprising a molded cured product of the silicone elastomer composition according to any one of claims 1 to 6.

10. A balloon catheter comprising a molded cured product of the silicone elastomer composition according to any one of claims 1 to 6 in at least a part of the constitution of the balloon catheter.

INTERNATIONAL SEARCH REPORT

International application No

PCT/JP2013/057579

A. CLASSIFICATION OF SUBJECT MATTER

INV. A61M25/00 C08G77/50 C08L83/04 C08L83/07
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A61M C08G C08L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 908 878 A (BAITY JUDITH DIANE FAIRCLOUGH [US] ET AL) 1 June 1999 (1999-06-01) column 1, lines 6-13 column 3, lines 35-47 claims 1,20; example 1; table 1 -----	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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

"&" document member of the same patent family

Date of the actual completion of the international search

6 May 2013

Date of mailing of the international search report

17/05/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

Bergmeier, Martin

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2013/057579

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5908878	A	01-06-1999	
		DE 69822057 D1	08-04-2004
		DE 69822057 T2	24-02-2005
		EP 0903379 A2	24-03-1999
		JP 4405608 B2	27-01-2010
		JP H11147957 A	02-06-1999
		US 5908878 A	01-06-1999
