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(54) FIBERS TO WHICH SILICONE HAS BEEN FIXED, AND PRODUCTION METHOD THEREOF

(57) In one embodiment, the present invention relates to silicone-fixed fibers including fibers and silicone fixed to the fibers. The silicone includes an acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule. A rate of decrease in the amount of Si after the silicone-fixed fibers are washed 10 times is less than 50%. The present invention relates to a method for producing silicone-fixed fibers. The method includes coating or impregnating the fibers with a fiber treatment agent containing silicone, and irradiating the fibers coated or impregnated with the fiber treatment agent with an electron beam so that the silicone is fixed to the fibers. The silicone includes an acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule. Thus, the present invention provides silicone-fixed fibers that include fibers to which silicone is fixed by electron beam irradiation and have a good texture even after washing, and a method for producing the silicone-fixed fibers.

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Description

Technical Field

[0001] The present invention relates to fibers to which silicone is fixed and a method for producing the fibers. Specifically, the present invention relates to fibers to which silicone is fixed by electron beam irradiation and a method for producing the fibers.

Background Art

[0002] A wide variety of organopolysiloxanes such as a dimethylpolysiloxane, an epoxy group containing organopolysiloxane, and an amino group containing organopolysiloxane have been used as a fiber treatment agent for imparting softness, smoothness, etc. to various fibers and fiber products. In particular, the amino group containing organopolysiloxane provides good softness and is used in a larger amount than any other organopolysiloxane. The fiber treatment agent is generally in the form of an emulsion containing water as a dispersion medium. In the most common method for the treatment of fibers, the fibers are coated or impregnated with the emulsion, and then dried by heating. The fibers treated with silicone have an excellent texture immediately after the treatment. However, the effective component (silicone) of the treatment agent is washed away from the fibers after washing several times, and thus the texture will be reduced. The reason for this may be that the above silicone treatment agent is unable to react with the fibers, and the silicone is not fixed to the fiber surface, but is present on the fiber surface due to a weak adsorption effect of the amino group on the fibers.

[0003] Therefore, e.g., further studies have been made to incorporate silicone oil into synthetic resins to form synthetic fibers such as polyester fibers, nylon fibers, and acrylic fibers. However, since the compatibility between the silicone and these synthetic resins is low, it is very difficult to form uniform fibers in which the synthetic resins and the silicone are mixed together. Accordingly, the use of silicone having a functional group that may react with a functional group present on the fiber surface, such as an epoxy group or an alkoxy group, has also been considered. However, if the silicone having such a functional group is in the form of an emulsion, the emulsion has poor stability over time, so that the treatment agent cannot be used because it becomes thickened before use.

[0004] To deal with the issue, there is a method for forming a silicone rubber film on the surface. The rubber film is composed of a curable silicone emulsion composition, which is conventionally known to have various compositions. For example, Patent Document 1 proposes a silicone emulsion composition that includes an anionically stabilized hydroxylated diorganopolysiloxane, colloidal silica, and an organotin compound or an organic amine compound and has a pH of 9 to 11.5. Patent Document 2 discloses a silicone latex composition that includes a siloxane block copolymer having dimethylsiloxane units and monophenylsiloxane units, water, a cationic surfactant, a filler, and an aminosilane. Patent Document 3 proposes a silicone emulsion composition that includes a hydroxyl group containing organopolysiloxane, a Si-H group containing organopolysiloxane, colloidal silica, an amide group and carboxyl group containing silane, an epoxy group containing silane, and a curing catalyst. Patent Document 4 proposes a silicone emulsion composition that includes an alkenyl group containing organopolysiloxane, a Si-H group containing organopolysiloxane, colloidal silica, a reaction product of an aminosilane and an acid anhydride, an epoxysilane, and an addition reaction catalyst. Patent Document 5 proposes a silicone emulsion composition that includes a hydrogen siloxane in which the molecular terminal is blocked with a hydroxyl group, an emulsifier, water, and a curing catalyst. Patent Documents 6 to 8 propose a silicone emulsion composition that includes a colloidal silica-silicone core-shell body, a curing catalyst, an emulsifier, and water. Patent Document 9 proposes a silicone emulsion composition that includes a hydroxyl group containing organopolysiloxane, colloidal silica, an amide group and carboxyl group containing silane, an epoxy group containing silane, a curing catalyst, and a photocatalytic oxide. Patent Document 10 proposes a silicone emulsion composition that includes a hydroxyl group containing organopolysiloxane, colloidal silica, an amide group and carboxyl group containing silane, and an epoxy group containing silane.

Prior Art Documents

Patent Documents

[0005]

Patent Document 1: JP S56(1981)-16553 A
Patent Document 2: US 3,817,894
Patent Document 3: JP H8(1996)-85760 A
Patent Document 4: JP H9(1997)-208826 A

Patent Document 5: JP H9(1997)-208900 A
Patent Document 6: JP H9(1997)-208901 A
Patent Document 7: JP H9(1997)-208902 A
Patent Document 8: JP H9(1997)-208903 A
Patent Document 9: JP 2002-363494 A
Patent Document 10: JP 2008-231276 A

Disclosure of Invention

Problem to be Solved by the Invention

[0006] In Patent Documents 1 to 10, organotin compounds are typically used as a curing catalyst. However, the use of organotin compounds is being restricted or regulated in applications, fields, and countries because of its toxicity. Therefore, the replacement of dibutyltin compounds by octyltin compounds, and further the replacement of octyltin compounds by inorganic tin compounds or other metal compounds have been proposed, but no effective catalyst system has been found yet. Thus, it is still required that the effect of the silicone treatment agent can be maintained even after washing without using, e.g., toxic metal catalysts.

[0007] In order to solve the above problems, the present invention provides silicone-fixed fibers that include fibers to which silicone is fixed and have a good texture even after washing, and a method for producing the silicone-fixed fibers.

Means for Solving Problem

[0008] In one embodiment, the present invention relates to silicone-fixed fibers including fibers and silicone fixed to the fibers. The silicone includes an acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule. A rate of decrease in the amount of Si after the silicone-fixed fibers are washed 10 times is less than 50%.

[0009] In one embodiment, the present invention relates to a method for producing silicone-fixed fibers including fibers and silicone fixed to the fibers. The method includes the following: coating or impregnating the fibers with a fiber treatment agent containing silicone; and irradiating the fibers coated or impregnated with the fiber treatment agent with an electron beam so that the silicone is fixed to the fibers. The silicone includes an acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule.

Effects of the Invention

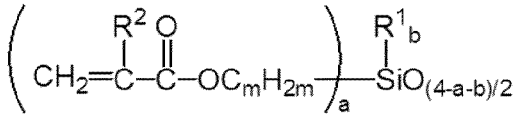
[0010] The present invention can provide silicone-fixed fibers that include fibers to which silicone is firmly fixed and that have a good texture even after washing. The production method of the present invention can provide silicone-fixed fibers that include fibers to which silicone is firmly fixed by electron beam irradiation and that have a good texture even after washing.

Description of the Invention

[0011] The present inventors conducted many studies to fix silicone to fibers so as to give them a good texture even after washing. Consequently, the present inventors found that when fibers were coated or impregnated with a fiber treatment agent containing an acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule, and then the treated fibers were irradiated with an electron beam, silicone was firmly fixed to the fibers and the fibers could have a soft texture of silicone even after washing. Based on these findings, the present inventors have reached the present invention. In this specification, the term "silicone" means a compound in which the main skeleton is composed of a siloxane bond of silicon and oxygen, and an organic group is attached to the silicon. Since the acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule is used as the silicone, radicals are generated by electron beam irradiation and a crosslinking reaction of the silicones proceeds.

[0012] The acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule is not particularly limited and may be, e.g., an acrylic-modified organopolysiloxane that has two or more acrylic groups per molecule and contains a unit represented by the following general formula (1) in the molecule.

[Chemical Formula 1]



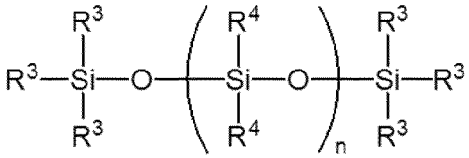
(1)

[0013] In the general formula (1), R^1 represents the same or different substituted or unsubstituted monovalent hydrocarbon group having 1 to 18 carbon atoms, R^2 represents a hydrogen atom, m is an integer of 1 to 8, and a and b are positive numbers and satisfy $a + b \leq 3$. The substituted or unsubstituted monovalent hydrocarbon group having 1 to 18 carbon atoms is not particularly limited. Examples of the substituted or unsubstituted monovalent hydrocarbon group having 1 to 18 carbon atoms include the following: alkyl groups such as methyl, ethyl, propyl, and butyl groups; alkenyl groups such as vinyl and allyl groups; aryl groups such as phenyl and tolyl groups; and substituted forms of these groups in which some or all hydrogen atoms bonded to carbon atoms are substituted by halogen atoms or cyano groups, including, e.g., chloromethyl group, trifluoropropyl group, and cyanoethyl group. In the general formula (1), R^1 is more preferably a methyl group.

[0014] The viscosity of the acrylic-modified organopolysiloxane (A) is preferably 50 to 5000 mPa·s at 25°C. If the viscosity is less than 50 mPa·s, the acrylic-modified organopolysiloxane (A) is not likely to adhere to the fibers. If the viscosity is more than 5000 mPa·s, the composition will have a higher viscosity and thus the treatment of the fibers tends to be difficult. The viscosity of the acrylic-modified organopolysiloxane (A) is more preferably 100 to 1000 mPa·s at 25°C. The acrylic-modified organopolysiloxane (A) may be either a single acrylic-modified organopolysiloxane or a mixture of a plurality of acrylic-modified organopolysiloxanes which differ in the degree of polymerization and the amount of functional groups.

[0015] In one embodiment of the present invention, from the viewpoint of improving the softness of the fibers, it is preferable that the silicone further includes an amino-modified organopolysiloxane (B) having one or more amino groups per molecule, as represented by the following general formula (2).

[Chemical Formula 2]



(2)

[0016] In the general formula (2), a plurality of R^3s represent the same or different substituted or unsubstituted monovalent hydrocarbon group having 1 to 18 carbon atoms, a hydroxyl group, an alkoxy group, or an amino group. A plurality of R^4s represent the same or different substituted or unsubstituted monovalent hydrocarbon group having 1 to 18 carbon atoms or an amino group. At least one of R^3s and R^4s is an amino group. Moreover, n is a positive number. Examples of the substituted or unsubstituted monovalent hydrocarbon group having 1 to 18 carbon atoms may be the same as those described above. In the general formula (2), the amino group represented by R^3 or R^4 is not particularly limited and may be, e.g., an amino group represented by the following general formula (3).

[Chemical Formula 3] $-R^5(NR^6CH_2CH_2)cNR^7R^8$ (3)

[0017] In the general formula (3), R^5 represents a substituted or unsubstituted divalent hydrocarbon group having 1 to 8 carbon atoms, R^6, R^7, and R^8 each represent a hydrogen atom, a substituted or unsubstituted monovalent hydrocarbon group having 1 to 4 carbon atoms, or $-CH_2CH(OH)CH_2OH$, and c is an integer of 0 to 4. Examples of the divalent hydrocarbon group having 1 to 8 carbon atoms include the following: alkylene groups such as ethylene, trimethylene, tetramethylene, hexamethylene, and isobutylene groups; methylene-phenylene group; and methylene-phenylene-methylene group. Among them, the trimethylene group is preferred. Examples of the substituted or unsubstituted monovalent hydrocarbon group having 1 to 4 carbon atoms include the following: alkyl groups such as methyl, ethyl, propyl, and butyl groups; alkenyl groups such as vinyl and allyl groups; and substituted forms of these groups in which some of hydrogen atoms bonded to carbon atoms are substituted by halogen atoms. Among them, the methyl group is particularly

preferred in terms of water repellency, smoothness and softness.

[0018] The viscosity of the amino-modified organopolysiloxane (B) is preferably 50 to 5000 mPa·s at 25°C. If the viscosity is less than 50 mPa·s, the amino-modified organopolysiloxane (B) is not likely to adhere to the fibers. If the viscosity is more than 5000 mPa·s, the composition will have a higher viscosity, and thus the treatment of the fibers tends to be difficult. The viscosity of the amino-modified organopolysiloxane (B) is more preferably 100 to 1000 mPa·s at 25°C.

[0019] In one embodiment of the present invention, from the viewpoint of improving the fixing properties of the silicone to the fibers and the texture of the fibers, when the total mass of the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B) is 100% by mass, the blending amount of the acrylic-modified organopolysiloxane (A) is preferably, but not limited to, 10 to 95% by mass, and more preferably 30 to 90% by mass and the blending amount of the amino-modified organopolysiloxane (B) is preferably, but not limited to, 5 to 90% by mass, and more preferably 10 to 70% by mass.

[0020] In the present invention, a rate of decrease in the amount of Si after the fibers to which silicone is fixed (i.e., the silicone-fixed fibers) are washed 10 times is less than 50%, preferably 35% or less, more preferably 15% or less, and further preferably 10% or less. With this configuration, the silicone-fixed fibers can have a good texture even after washing. In the silicone-fixed fibers of the present invention, as will be described later, the fibers are coated or impregnated with a fiber treatment agent containing the acrylic-modified organopolysiloxane (A) or a fiber treatment agent containing the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B), and then the treated fibers are irradiated with an electron beam, so that silicone can be fixed to the fibers. In one embodiment of the present invention, the amount of Si in the fibers may be measured in the following manner.

[0021] The fibers are not particularly limited and may be either natural fibers or synthetic fibers. The natural fibers are not particularly limited and may be, e.g., cotton, silk, hemp, wool, angora, or mohair. The synthetic fibers are not particularly limited and may be, e.g., polyester fibers, nylon fibers, acrylic fibers, or spandex. From the viewpoint of improving the fixing properties of the silicone to the fibers, the fibers preferably include one or more natural fibers selected from the group consisting of cotton, silk, hemp, wool, angora, and mohair.

[0022] The form of the fibers is not particularly limited. The fibers may be in any form such as staple, filament, tow, yarn, woven fabric, knitted fabric, wadding, nonwoven fabric, paper, sheet, or film.

[0023] The silicone-fixed fibers may be produced, e.g., by coating or impregnating the fibers with a fiber treatment agent containing silicone, and irradiating the fibers coated or impregnated with the fiber treatment agent with an electron beam so that the silicone is fixed to the fibers. As described above, the silicone includes the acrylic-modified organopolysiloxane (A) or a mixture of the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B).

[0024] The silicone, i.e., the acrylic-modified organopolysiloxane (A) or the mixture of the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B) (also referred to simply as a "silicone component" in the following) may be directly used as the fiber treatment agent.

[0025] In one embodiment of the present invention, from the viewpoint of handleability, the silicone (silicone component) may be diluted with an organic solvent to form a solution, and this solution may be used as a fiber treatment agent. Any organic solvent that can dissolve the silicone may be used. Examples of the organic solvent include the following: aromatic hydrocarbon solvents such as toluene and xylene; aliphatic hydrocarbon solvents such as hexane, octane, and isoparaffin; ether solvents such as diisopropyl ether and 1,4-dioxane; and a mixed solvent thereof. The aromatic hydrocarbon solvents such as toluene and xylene and the aliphatic hydrocarbon solvents such as hexane, octane, and isoparaffin are particularly preferred. The dilute concentration of the silicone component is not particularly limited. For example, the concentration of the acrylic-modified organopolysiloxane (A) or the total concentration of the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B) may be 1 to 60% by mass, and more preferably 1 to 20% by mass.

[0026] In one embodiment of the present invention, the silicone component may be dispersed in water as a dispersion medium to form an emulsion, and this emulsion may be used as a fiber treatment agent for electron beam fixing. The emulsification may use, e.g., a nonionic surfactant, an anionic surfactant, a cationic surfactant, or an amphoteric surfactant. The nonionic surfactant is not particularly limited and may be, e.g., polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, sorbitan alkylate, or polyoxyethylene sorbitan alkylate. The anionic surfactant is not particularly limited and may be, e.g., alkylbenzene sulfonate or alkyl phosphate. The cationic surfactant is not particularly limited and may be, e.g., quaternary ammonium salts or alkylamine salts. The amphoteric surfactant is not particularly limited and may be, e.g., alkyl betaine or alkyl imidazoline. These surfactants may be used individually or in combinations of two or more. There is no particular limitation to the surfactants. However, from the viewpoint of ease of emulsification of the silicone, the HLB (hydrophilic-lipophilic balance) of the surfactants is preferably 11 to 18, and more preferably 13 to 16.

[0027] The amount of the surfactant used is preferably 5 to 50 parts by mass, and more preferably 10 to 30 parts by mass with respect to 100 parts by mass of the silicone component, i.e., the acrylic-modified organopolysiloxane (A) or the mixture of the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B). Any suitable

amount of water may be used for emulsification. However, water may be used in an amount such that the concentration of the acrylic-modified organopolysiloxane (A) or the total concentration of the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B) is generally 1 to 60% by mass, and preferably 1 to 20% by mass. The emulsification may be performed by mixing the acrylic-modified organopolysiloxane (A) or the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B) with the surfactant, and emulsifying the mixture with an emulsifier such as a homomixer, a homogenizer, a colloid mill, or a line mixer.

[0028] In one embodiment of the present invention, when both the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B) are used as the silicone component, these components may be mixed in advance to form a solution or an emulsion. Alternatively, these components may be separately formed in advance into solutions or emulsions, and then the respective solutions or emulsions may be mixed together.

[0029] In one embodiment of the present invention, other agents for fibers such as an anticrease agent, a flame retardant, an antistatic agent, and a heat resistant agent may be added to the fiber treatment agent as long as the properties of the fiber treatment agent are not impaired.

[0030] First, the fibers are coated or impregnated with the fiber treatment agent containing the silicone. The fibers that serve as a base material are not particularly limited and may be the same as those described above.

[0031] In this case, any known method such as roll coating, gravure coating, wire doctor coating, air knife coating, or dipping may be used to coat or impregnate the fibers with the fiber treatment agent. The coating or impregnation amount is preferably 0.01 to 20.0 g/m^2, and more preferably 0.01 to 5 g/m^2. When the coating or impregnation amount is within the above range, the adhesion of the silicone to the fibers can be improved.

[0032] In one embodiment of the present invention, when the fiber treatment agent is a solution obtained by diluting the silicone with an organic solvent, or an emulsion obtained by dispersing the silicone in water, the fibers coated or impregnated with the fiber treatment agent may be dried to vaporize the organic solvent or the water (the dispersion medium of the emulsion). The drying may be performed, e.g., by blowing hot air on the fibers or using a heating furnace. The drying temperature and the drying time may be determined as desired so as not to affect the fibers. For example, the drying temperature may be 100 to 150°C and the drying time may be 10 sec to 5 min.

[0033] Next, the fibers coated or impregnated with the fiber treatment agent are irradiated with an electron beam so that the silicone is fixed to the fibers. The electron beam irradiation apparatus is not particularly limited and may be, e.g., a curtain system, a scanning system, or a double scanning system. The acceleration voltage of the electron beam by the electron beam irradiation is not particularly limited and may be, e.g., 100 to 1000 kV. If the acceleration voltage is less than 100 kV, there may be a lack of energy transmission. If the acceleration voltage is more than 1000 kV, economic efficiency may be reduced. Moreover, the irradiation amount of the electron beam is not particularly limited and may be, e.g., 5 to 100 kGy. If the irradiation amount is less than 5 kGy, curing failure may occur. If the irradiation amount is 100 kGy or more, the fibers may be degraded. When the fiber treatment agent is a solution obtained by diluting the silicone with an organic solvent, the fibers may be immersed (washed) in the organic solvent that has been used for dilution of the silicone, after the electron beam irradiation, thereby removing unreacted silicone. On the other hand, when the fiber treatment agent is an emulsion obtained by dispersing the silicone in water, the fibers may be washed with water after the electron beam irradiation, thereby removing unreacted silicone.

Examples

[0034] Next, embodiments of the present invention will be described in detail based on examples. However, the present invention is not limited to the following examples. In the following examples and comparative examples, the term "part" indicates "part by mass" and the physical property values indicate measured values by the following test methods.

(Measurement of initial amount of Si)

[0035] Using an X-ray fluorescence analyzer ZSX100e manufactured by Rigaku Corporation, the mass of all elements (W0t) and the mass of Si atoms (W0s) contained in each sample before washing were measured by the EZ-scan method, and the initial amount of Si was calculated by the following formula.

$$\text{Initial amount of Si (\% by mass)} = (W0s) / (W0t) \times 100$$

(Measurement of amount of Si after washing)

[0036] The samples were washed 10 times or 50 times in accordance with the JIS L 0217 103 method (detergent: JAFET) and dried. Then, using the X-ray fluorescence analyzer ZSX100e manufactured by Rigaku Corporation, the

mass of all elements (W10t or W50t) and the mass of Si atoms (W10s or W50s) contained in the individual samples after 10 times washing or 50 times washing were measured by the EZ-scan method, and the amount of Si after 10 times washing and the amount of Si after 50 times washing were calculated by the following formulas.

$$\text{Amount of Si after 10 times washing (\% by mass)} = (W10s) / (W10t) \times 100$$

$$\text{Amount of Si after 50 times washing (\% by mass)} = (W50s) / (W50t) \times 100$$

(Rate of decrease in amount of Si after 10 times washing)

$$\text{Rate of decrease in amount of Si after 10 times washing (\%)} = (W0s\% - W10s\%) / W0s\% \times 100$$

[0037] In the formula, W0s% indicates the initial amount of Si and W10s% indicates the amount of Si after 10 times washing.

(Initial texture)

[0038] Three panelists touched the samples by hand to check the softness of the samples and evaluated them based on the following criteria.

A: very good
B: good
C: poor

(Texture after washing)

[0039] The samples were washed 10 times or 50 times in accordance with the JIS L 0217 103 (detergent: JAFET). Subsequently, three panelists touched the samples by hand to check the softness of the samples after washing and evaluated them based on the following criteria.

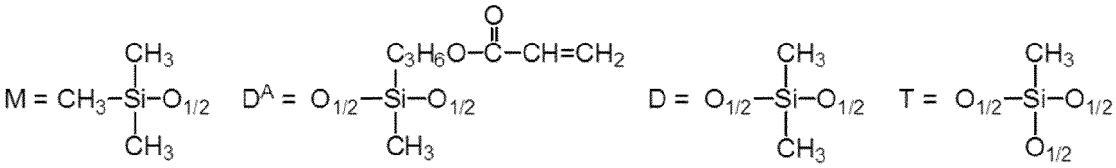
A: very good
B: good
C: poor

(Example 1)

[0040] First, an acrylic-modified organopolysiloxane (A1) represented by the following average molecular formula (4) was diluted with toluene to prepare a fiber treatment agent (a) in which the concentration of the acrylic-modified organopolysiloxane (A1) was 10% by mass. Next, a broadcloth made of 100% by mass of cotton (manufactured by KURABO) was immersed in the fiber treatment agent (a), squeezed by a mangle roller at a squeeze rate of 100%, and dried at 110°C for 90 seconds. Then, the broadcloth was irradiated with an electron beam of 40 kGy at an acceleration voltage of 200 kV in a nitrogen atmosphere using an area beam type electron beam irradiation apparatus EC250/15/180L (manufactured by IWASAKI ELECTRIC CO., LTD.). The fibers (i.e., the broadcloth made of 100% by mass of cotton) thus treated with the electron beam were immersed in toluene for 1 minute and then squeezed by a mangle roller at a squeeze rate of 60%. Further, the fibers were again immersed in fresh toluene for 1 minute, squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds. Thus, silicone-fixed fibers were produced.

[Chemical Formula 4]

$$M_3D^A_6D_{114}T \quad (4)$$

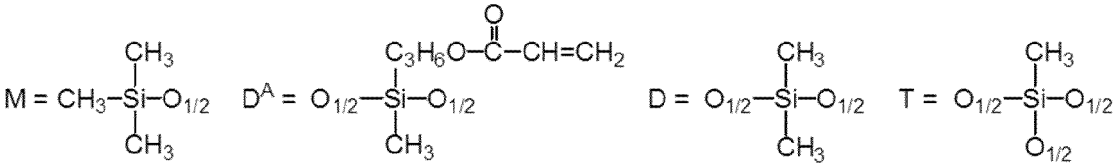


(Example 2)

[0041] An acrylic-modified organopolysiloxane (A2) represented by the following average molecular formula (5) was diluted with toluene to prepare a fiber treatment agent (b) in which the concentration of the acrylic-modified organopolysiloxane (A2) was 10% by mass. A broadcloth made of 100% by mass of cotton (manufactured by KURABO) was immersed in the fiber treatment agent (b), squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds. Then, the broadcloth was irradiated with an electron beam of 40 kGy at an acceleration voltage of 200 kV in a nitrogen atmosphere using an area beam type electron beam irradiation apparatus EC250/30/90L (manufactured by IWASAKI ELECTRIC CO., LTD.). The fibers (i.e., the broadcloth made of 100% by mass of cotton) thus treated with the electron beam were immersed in toluene for 1 minute and then squeezed by a mangle roller at a squeeze rate of 60%. Further, the fibers were again immersed in fresh toluene for 1 minute, squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds. Thus, silicone-fixed fibers were produced.

[Chemical Formula 5]

$$M_3D^A_{18}D_{180}T \qquad (5)$$



(Example 3)

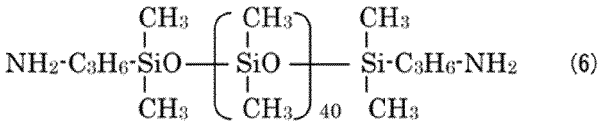
[0042] First, 300 g of the acrylic-modified organopolysiloxane (A2) used in Example 2, 7.8 g of polyoxyethylene (4) lauryl ether (product name "EMULGEN 104P" manufactured by Kao Corporation, nonionic surfactant, HLB value: 9.6), and 22.2 g of polyoxyethylene (23) lauryl ether (product name "EMULGEN 123P" manufactured by Kao Corporation, nonionic surfactant, HLB value: 16.9) were charged in a 2 L polyethylene jug and sufficiently mixed at a high speed with a homomixer. Then, 18 g of phase-inverted water (ion-exchanged water) was added to the mixture and kneaded. Subsequently, 280g of ion-exchanged water was added to the mixture and mixed at 2500 rpm for 20 minutes with a homomixer. Thus, an oil-in-water emulsion (I) in which the concentration of the acrylic-modified organopolysiloxane (A2) was 50% by mass was obtained. The oil-in-water emulsion (I) was further diluted with ion-exchanged water to prepare a fiber treatment agent (c) in which the concentration of the acrylic-modified organopolysiloxane (A2) was 10% by mass. Abroadcloth made of 100% by mass of cotton (manufactured by KURABO) was immersed in the fiber treatment agent (c), squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds. Then, the broadcloth was irradiated with an electron beam of 40 kGy at an acceleration voltage of 200 kV in a nitrogen atmosphere using an area beam type electron beam irradiation apparatus EC250/30/90L (manufactured by IWASAKI ELECTRIC CO., LTD.). The fibers (i.e., the broadcloth made of 100% by mass of cotton) thus treated with the electron beam were washed with water, squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds. Thus, silicone-fixed fibers were produced.

(Example 4)

[0043] First, 300 g of an amino-modified organopolysiloxane (B1) represented by the following average molecular formula (6), 1.8 g of polyoxyethylene (4) lauryl ether (product name "EMULGEN 104P" manufactured by Kao Corporation, nonionic surfactant, HLB value: 9.6), and 4.2 g of polyoxyethylene (23) lauryl ether (product name "EMULGEN 123P" manufactured by Kao Corporation, nonionic surfactant, HLB value: 16.9) were charged in a 2 L polyethylene jug and sufficiently mixed at a high speed with a homomixer. Then, 18 g of phase-inverted water (ion-exchanged water) was added to the mixture and kneaded. Subsequently, 280g of ion-exchanged water was added to the mixture and mixed

at 2500 rpm for 20 minutes with a homomixer. Thus, an oil-in-water emulsion (II) in which the concentration of the amino-modified organopolysiloxane (B1) was 50% by mass was obtained. The oil-in-water emulsion (II) was mixed with the oil-in-water emulsion (I) prepared in the same manner as Example 3 at a ratio of the oil-in-water emulsion (I) to the oil-in-water emulsion (II) of 50 parts by mass / 50 parts by mass to form an oil-in-water emulsion (III). The oil-in-water emulsion (III) was diluted with ion-exchanged water to prepare a fiber treatment agent (d) in which the concentration of the organopolysiloxane (i.e., the total concentration of the acrylic-modified organopolysiloxane (A2) and the amino-modified organopolysiloxane (B1)) was 10% by mass. A broadcloth made of 100% by mass of cotton (manufactured by KURABO) was immersed in the fiber treatment agent (d), squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds. Then, the broadcloth was irradiated with an electron beam of 40 kGy at an acceleration voltage of 200 kV in a nitrogen atmosphere using an area beam type electron beam irradiation apparatus EC250/30/90L (manufactured by IWASAKI ELECTRIC CO., LTD.). The fibers (i.e., the broadcloth made of 100% by mass of cotton) thus treated with the electron beam were washed with water, squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds. Thus, silicone-fixed fibers were produced.

[Chemical Formula 6]



(6)

(Comparative Example 1)

[0044] First, a dimethylpolysiloxane having no organic group other than a methyl group and having a viscosity of 1000 mm^2/s was diluted with toluene to prepare a fiber treatment agent (Z) in which the concentration of the dimethylpolysiloxane was 10% by mass. Abroadcloth made of 100% cotton (manufactured by KURABO) was immersed in the fiber treatment agent (Z), squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds. Then, the broadcloth was irradiated with an electron beam of 40 kGy at an acceleration voltage of 200 kV in a nitrogen atmosphere using an area beam type electron beam irradiation apparatus EC250/30/90L (manufactured by IWASAKI ELECTRIC CO., LTD.). The fibers (i.e., the broadcloth made of 100% cotton) thus treated with the electron beam were immersed in a toluene solution for 1 minute and then squeezed by a mangle roller at a squeeze rate of 60%. Further, the fibers were again immersed in a fresh toluene solution for 1 minute, squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds.

(Comparative Example 2)

[0045] A fiber treatment agent (c) was prepared in the same manner as Example 3. A broadcloth made of 100% cotton (manufactured by KURABO) was immersed in the fiber treatment agent (c), squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds. Then, the fibers (i.e., the broadcloth made of 100% cotton) thus treated with the fiber treatment agent (c) were washed with water, squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds.

(Comparative Example 3)

[0046] An oil-in-water emulsion (II) in which the concentration of an amino-modified organopolysiloxane (B1) was 50% by mass was prepared in the same manner as Example 4. The oil-in-water emulsion (II) was diluted with ion-exchanged water to prepare a fiber treatment agent (Y) in which the concentration of the amino-modified organopolysiloxane (B1) was 10% by mass. A broadcloth made of 100% cotton (manufactured by KURABO) was immersed in the fiber treatment agent (Y), squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds. Then, the fibers (i.e., the broadcloth made of 100% cotton) thus treated with the fiber treatment agent (Y) were washed with water, squeezed by a mangle roller at a squeeze rate of 60%, and dried at 110°C for 90 seconds.

[0047] The initial amount of Si (the amount of Si before washing), the amount of Si after 10 times washing, the amount of Si after 50 times washing, the initial texture, and the texture after washing of the respective fibers (i.e., the broadcloths made of 100% cotton) obtained in Examples 1 to 4 and Comparative Examples 1 to 3 were measured in the above manner. Table 1 shows the results.

[TABLE 1]

	Amount of Si (% by mass)			Rate of decrease in amount of Si after 10 times washing (%)	Texture		
	Before washing (initial)	After 10 times washing	After 50 times washing		Before washing	After 10 times washing	After 50 times washing
Ex. 1	0.520	0.343	0.140	34.0	B	B	C
Ex. 2	0.541	0.548	0.441	0	B	B	B
Ex. 3	0.880	0.788	-	10.5	B	B	B
Ex. 4	1.250	1.130	0.738	9.6	A	A	A
Comp. Ex. 1	0.037	0.015	0.006	59.5	B	C	C
Comp. Ex. 2	0.056	0.025	-	55.4	B	C	C
Comp. Ex. 3	0.520	0.190	-	63.5	A	C	C

[0048] In Examples 1 and 2, the fibers had been impregnated with the fiber treatment agent, in which the acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule was dissolved in the organic solvent, and then irradiated with the electron beam. Consequently, these fibers had good softness, and the acrylic-modified organopolysiloxane (A) was fixed to the fibers even after washing. Specifically, a considerable amount of the acrylic-modified organopolysiloxane was fixed to the fibers after they were washed 10 times. In particular, in Example 2, a certain amount of the acrylic-modified organopolysiloxane was fixed to the fibers even after they were washed 50 times. The fixing properties of the acrylic-modified organopolysiloxane (A) to the fibers were higher in Example 2 than in Example 1, since the acrylic-modified organopolysiloxane (A) used in Example 2 had a large number of acrylic groups as compared to the acrylic-modified organopolysiloxane (A) used in Example 1.

[0049] In Example 3, the fibers had been treated with the fiber treatment agent, in which the acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule was emulsified. Consequently, the fibers also had good softness. Comparing Example 3 and Example 4 shows that when the acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule was used in combination with the amino-modified organopolysiloxane (B) having one or more amino groups per molecule, the initial amount of silicone fixed to the fibers was increased, the softness of the fibers was very good, and the organopolysiloxane was sufficiently fixed to the fibers even after they were washed 10 times.

[0050] On the other hand, in Comparative Example 1, the fibers had been treated with the dimethylpolysiloxane having no acrylic group. Consequently, the initial amount of dimethylpolysiloxane adhering to the fibers was small, and almost no dimethylpolysiloxane was left after the fibers were washed 10 times or 50 times. In Comparative Example 2, the fibers had been treated with the fiber treatment agent in which the acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule was emulsified, but had not been subjected to electron beam irradiation. Consequently, the amount of the acrylic-modified organopolysiloxane (A) adhering to the fibers was small, and the softness of the fibers was poor. In Comparative Example 3, the fibers had been treated with the fiber treatment agent, in which the amino-modified organopolysiloxane (B) having one or more amino groups per molecule was emulsified. Consequently, although a considerable amount of the amino-modified organopolysiloxane (B) adhered to the fibers at the initial stage (washing), the amount of the amino-modified organopolysiloxane (B) was significantly reduced after washing, and the softness of the fibers became poor.

[0051] In the Examples, it was found that the acrylic-modified organopolysiloxane (A) was graft-polymerized onto the fibers, and crosslinking between the silicone components also proceeded, so that the silicone was firmly fixed to the fibers, and thus the fibers had good softness even after washing. On the other hand, in the Comparative Examples, it was found that the silicone was not fixed to the fibers.

Claims

1. Silicone-fixed fibers comprising fibers and silicone fixed to the fibers,

wherein the silicone comprises an acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule, and
a rate of decrease in an amount of Si after the silicone-fixed fibers are washed 10 times is less than 50%.

2. The silicone-fixed fibers according to claim 1, wherein the silicone further comprises an amino-modified organopolysiloxane (B) having one or more amino groups per molecule.

3. The silicone-fixed fibers according to claim 1 or 2, wherein the fibers comprise one or more natural fibers selected from the group consisting of cotton, silk, hemp, wool, angora, and mohair.

4. The silicone-fixed fibers according to any one of claims 1 to 3, wherein the fibers are in at least one form selected from the group consisting of staple, filament, tow, yarn, woven fabric, knitted fabric, wadding, and nonwoven fabric.

5. A method for producing silicone-fixed fibers comprising fibers and silicone fixed to the fibers,
the method comprising:

coating or impregnating the fibers with a fiber treatment agent comprising silicone; and
irradiating the fibers coated or impregnated with the fiber treatment agent with an electron beam so that the silicone is fixed to the fibers,
wherein the silicone comprises an acrylic-modified organopolysiloxane (A) having two or more acrylic groups per molecule.

6. The method according to claim 5, wherein the silicone further comprises an amino-modified organopolysiloxane (B) having one or more amino groups per molecule.

7. The method according to claim 5 or 6, wherein the fiber treatment agent is a solution in which the silicone is diluted with an organic solvent, or an emulsion in which the silicone is dispersed in water as a dispersion medium.

8. The method according to claim 7, comprising a drying process before irradiating the fibers coated or impregnated with the fiber treatment agent with the electron beam.

9. The method according to any one of claims 6 to 8, wherein the fiber treatment agent is a solution obtained by diluting the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B) simultaneously with an organic solvent, or an emulsion obtained by dispersing the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B) simultaneously in water as a dispersion medium.

10. The method according to any one of claims 6 to 8, wherein the fiber treatment agent is prepared by diluting the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B) separately with an organic solvent to form solutions and then mixing the solutions together, or by dispersing the acrylic-modified organopolysiloxane (A) and the amino-modified organopolysiloxane (B) separately in water as a dispersion medium to form emulsions and then mixing the emulsions together.

11. The method according to any one of claims 5 to 10, wherein the fibers comprise one or more natural fibers selected from the group consisting of cotton, silk, hemp, wool, angora, and mohair.

12. The method according to any one of claims 5 to 11, wherein the fibers are in at least one form selected from the group consisting of staple, filament, tow, yarn, woven fabric, knitted fabric, wadding, and nonwoven fabric.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/010486

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. D06M15/643(2006.01)i, D06M14/20(2006.01)i

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)
Int.Cl. D06M15/643, D06M14/20

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2018
Registered utility model specifications of Japan 1996-2018
Published registered utility model applications of Japan 1994-2018

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 63-128074 A (DOW CORNING CORPORATION) 31 May 1988, claim 1, page 10, lower right column, line 17 to page 11, upper left column, line 6, examples & US 4698406 A, claim 1, column 12, lines 36-46, examples & EP 267004 A2 & CA 1296449 A	1-4 5-12
X A	JP 52-132171 A (JOHNSON & JOHNSON K.K.) 05 November 1977, claim 1, page 4, upper right column, lines 1-7, examples (Family: none)	1, 4-5, 7-8, 12 2-3, 6, 9-11

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 April 2018 (17.04.2018)	01 May 2018 (01.05.2018)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/010486

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2007-177232 A (LION CORP.) 12 July 2007, claim 1, paragraph [0057] (Family: none)	1-12
A	JP 2016-199712 A (NICCA CHEMICAL CO., LTD.) 01 December 2016, claim 1, paragraph [0052] (Family: none)	1-12

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REFERENCES CITED IN THE DESCRIPTION

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- JP H8199685760 A **[0005]**
- JP H91997208826 A **[0005]**
- JP H91997208900 A **[0005]**
- JP H91997208901 A **[0005]**
- JP H91997208902 A **[0005]**
- JP H91997208903 A **[0005]**
- JP 2002363494 A **[0005]**
- JP 2008231276 A **[0005]**