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(54) MODIFIED REGENERATED COLLAGEN FIBERS, PRODUCTION METHOD THEREFOR, AND HEADDRESS PRODUCT INCLUDING SAME

(57) The present invention relates to modified regenerated collagen fibers which have improved water resistance and heat resistance problematic in regenerated collagen fibers, impart heat shape memory ability, are excellent in stretchability (tenacity) and the feel of the surfaces, and have no coloring. The modified regenerated collagen fibers of the present invention contain the following component (A) or a polymerized product containing the component (A) as a constituent monomer in regenerated collagen fibers: (A) vinylbenzoic acid or a salt thereof.

Description

Field of the Invention

[0001] The present invention relates to regenerated collagen fibers to which water resistance, heat resistance, and heat shape memory ability are imparted, and preferably relates to regenerated collagen fibers used in fiber products such as headdress products such as wigs and extensions.

Background of the Invention

[0002] Unlike synthetic fibers, regenerated collagen fibers generally have natural texture and appearance originating from a natural material. The present regenerated collagen fibers are obtained by solubilizing acid-soluble collagen or by solubilizing insoluble collagen with an alkali or an enzyme to obtain a spinning stock solution, and discharging the spinning stock solution into a coagulation bath through a spinning nozzle to form fibers.

[0003] However, regenerated collagen fibers generally have higher hydrophilicity and hence higher water absorption as compared to synthetic fibers, and the regenerated collagen fibers have extremely low mechanical strength when they contain a large amount of water. This leads to deterioration of suitability as a fiber product such as headdress products such that during washing, mechanical strength significantly decreases because of the higher water absorption, and during subsequent drying, rupture occurs.

[0004] Regenerated collagen fibers also have the problem of low heat resistance, so that, for example, if a heat set using a hair iron or the like is performed at a temperature as high as that for human hair, shrinkage or crimping occurs, resulting in impairment of visual quality.

[0005] Further, in plastic synthetic fibers, the shape in a heat set with an iron or the like is continuously memorized even after subsequent washing (there is heat shape memory ability), whereas in regenerated collagen fibers, the shape in a heat set with an iron or the like is lost through subsequent one time washing (there is no heat shape memory ability). Therefore, regenerated collagen fibers may be inferior to conventional plastic synthetic fibers in terms of degree of freedom of shape set.

[0006] The above points are a factor in limiting popularization of regenerated collagen fibers for fiber products. In particular, water resistance, that is, a decrease in mechanical strength when it is wet has a significant impact.

[0007] On the other hand, in the field of human hair fibers, a method is known in which to human hair fibers having essentially no heat shape memory ability, a specific aldehyde derivative and phenolic compound are applied for newly imparting heat shape memory ability (Patent Literature 1).

[0008] Patent Literature 1: JP-A-2019-143281

Summary of the Invention

[0009] The present invention provides modified regenerated collagen fibers comprising the following component (A) or a polymerized product containing the component (A) as a constituent monomer in regenerated collagen fibers:

(A) vinylbenzoic acid or a salt thereof.

[0010] Further, the present invention provides a method for treating regenerated collagen fibers comprising the following (i):

(i) immersing regenerated collagen fibers in a fiber-treating agent which is a one-part type fiber-treating agent formed of a single composition or a multiple-part type fiber-treating agent formed of a plurality of compositions, and which comprises the following component (A) and component (B) in a total composition:

(A): vinylbenzoic acid or a salt thereof; and
(B): an azo polymerization initiator.

[0011] Further, the present invention provides a method for producing modified regenerated collagen fibers, comprising treating regenerated collagen fibers by the above-described method for treating regenerated collagen fibers.

[0012] Further, the present invention provides a method for producing a headdress product, comprising treating regenerated collagen fibers by the above-described method for treating regenerated collagen fibers.

[0013] Further, the present invention provides a headdress product comprising the above-described modified regenerated collagen fibers as a constituent element.

Detailed Description of the Invention

[0014] In some situations of production of fiber products, fibers are intensively extended, and in the technique disclosed in Patent Literature 1, there are cases where the stretchability (tenacity) of treated fibers is not sufficient. For this reason, it is required to enhance the stretchability of treated fibers for preventing rupture during extension. In the technique disclosed in Patent Literature 1, there are also cases where coloring of fibers is caused.

[0015] Therefore, the present invention relates to modified regenerated collagen fibers which have improved water resistance and heat resistance problematic in regenerated collagen fibers, impart heat shape memory ability, are excellent in stretchability (tenacity) and the feel of the surfaces, and have no coloring.

[0016] The present inventors conducted intensive studies and as a result, found that, in modified regenerated collagen fibers containing vinylbenzoic acid or a salt thereof, not only the vinylbenzoic acid and the like are polymerized, but also its carboxyl group is strongly coordinated with a metal (mainly polyvalent metal) in regenerated collagen fibers, so that the strength in water and heat resistance of the fibers are improved, and the leakage of vinylbenzoic acid, a salt thereof, or a polymerized product thereof from the fibers is prevented. As a result, the present inventors found that not only water resistance, and heat resistance in both dry state and wet state of the modified regenerated collagen fibers are improved, and the shape can be imparted by a heat set, but also surprisingly, the stretchability (tenacity) is improved as compared to that before treatment and can be enhanced to a level close to that of human hair, and further, no coloring accompanied with modification treatment is caused, leading to completion of the present invention.

[0017] According to the present invention, it is possible to provide modified regenerated collagen fibers which have improved water resistance and heat resistance problematic in regenerated collagen fibers, impart heat shape memory ability, have improved stretchability (tenacity) and the feel of the surfaces, and have no coloring.

[Fibers to be treated in the present invention]

[0018] Fibers to be treated with the fiber treatment of the present invention are artificially produced fibers using a polymer or oligomer derived from collagen as a raw material, that is, regenerated collagen fibers using collagen as a raw material.

[0019] Regenerated collagen fibers can be produced by a known technique, are not required to have a composition of collagen 100%, and may contain a natural or synthetic polymer and additives for improvement of quality. Further, regenerated collagen may be post-processed. Regenerated collagen fibers are preferably in the form of filaments. Filaments are generally taken from fibers wound around a bobbin or packed in a box. It is also possible to directly use filaments coming out from a drying step in a production process of regenerated collagen fibers.

[0020] As the raw material of collagen used for producing regenerated collagen fibers, a split portion is preferably used. Splits are obtained from fresh splits obtained by sacrificing livestock animals such as cattle and from salt cured hides. A large part of these splits and the like is composed of insoluble collagen fibers, and they are generally used after removing flesh portions adhered in a mesh form, and then removing salts which are used to prevent decomposition and change in quality.

[0021] In the insoluble collagen fibers, there are impurities such as lipids such as glycerides, phosphatides, and free fatty acid; glycoproteins; proteins other than collagen, such as albumin. These impurities have a great influence on spinning stability, qualities such as brilliance and strength and elongation, odor, and the like upon forming fibers. Thus, these impurities are preferably removed in advance, for example, by liming insoluble collagen fibers to hydrolyze the fat content therein, disentangling collagen fibers, and then subjecting the fibers to conventionally and generally performed hide and leather treatment such as acid/alkaline treatment, enzyme treatment, or solvent treatment.

[0022] The insoluble collagen subjected to treatment as described above is subjected to solubilization treatment to cut the cross-linked peptide moiety. As the method for such solubilization treatment, a generally employed known alkaline solubilization method, enzyme solubilization method, or the like can be applied. Further, the above-described alkaline solubilization method and enzyme solubilization method may be used in combination.

[0023] When the alkaline solubilization method is applied, neutralization is preferable with an acid such as hydrochloric acid. As an improved method of the conventionally known alkaline solubilization method, a method described in JP-B-S46-15033 may be used.

[0024] The enzyme solubilization method has such an advantage that soluble collagen having a uniform molecular weight can be obtained, and is thus a method preferably employed in the present invention. As such an enzyme solubilization method, for example, methods described in JP-B-S43-25829, JP-B-S43-27513, and the like can be employed.

[0025] When collagen subjected to solubilization treatment as described above is further subjected to an operation such as pH adjustment, salting-out, washing with water, or solvent treatment, regenerated collagen fibers excellent in quality can be obtained. Thus, collagen is preferably subjected to the above-described treatment.

[0026] The obtained soluble collagen is, for example, dissolved with an acid such as hydrochloric acid, acetic acid, or lactic acid, and adjusted so as to obtain an aqueous collagen solution having a pH of from 2 to 4.5 and a collagen concentration of 1 mass% or more, preferably 2 mass% or more, and 15 mass% or less, preferably 10 mass% or less. The aqueous collagen solution may be defoamed by stirring under reduced pressure and filtered to remove fine wastes which are water-insoluble contents, as necessary. For example, to improve mechanical strength, water resistance and heat resistance, brilliance, and spinnability, and prevent coloring, corrosion, and the like, an appropriate amount of additive such as a stabilizer or a water-soluble polymer compound may be further formulated in the aqueous collagen solution, as necessary.

[0027] The aqueous collagen solution is discharged through, for example, a spinning nozzle or a slit, and immersed in an aqueous inorganic salt solution, thereby forming regenerated collagen fibers. As the aqueous inorganic salt solution, for example, an aqueous solution of a water-soluble inorganic salt such as sodium sulfate, sodium chloride, or ammonium sulfate is used. The concentration of the inorganic salt in the aqueous inorganic salt solution is generally adjusted to from 10 to 40 mass%. The pH of the aqueous inorganic salt solution is preferably 2 or more, more preferably 4 or more, and preferably 13 or less, more preferably 12 or less. In the adjustment of pH, for example, a metal salt such as sodium borate or sodium acetate, hydrochloric acid, boric acid, acetic acid, or sodium hydroxide may be used. When the pH of the aqueous inorganic salt solution is in the above-described range, the peptide bond of collagen is unlikely hydrolyzed and the intended fibers are easily obtained. The temperature of the aqueous inorganic salt solution is not particularly limited, and desirably, usually 35°C or lower since soluble collagen is not denatured, the strength of spun fibers is not reduced, and stable production of fibers is easy. The lower limit of the temperature of the aqueous inorganic salt solution is not particularly limited, and is generally, appropriately adjusted depending on the solubility of the inorganic salt.

[0028] The regenerated collagen fibers may be subjected to pretreatment (cross-linking treatment) by immersing the regenerated collagen fibers in an epoxy compound or a solution thereof. The amount of the epoxy compound is preferably 0.1 equivalents or more, more preferably 0.5 equivalents or more, further more preferably 1 equivalent or more, and preferably 500 equivalents or less, more preferably 100 equivalents or less, further more preferably 50 equivalents or less with respect to the amount of the amino group capable of reacting with the epoxy compound in the regenerated collagen fibers measured by an amino acid analysis. When the amount of the epoxy compound is in the range, not only the effect of insolubilizing regenerated collagen fibers in water can be sufficiently imparted, but also it is preferable in terms of industrial handleability and environment.

[0029] The epoxy compound is used as it is or by being dissolved in various solvents. Examples of the solvent include water; alcohols such as methyl alcohol, ethyl alcohol, and isopropanol; ethers such as tetrahydrofuran and dioxane; halogen organic solvents such as dichloromethane, chloroform, and carbon tetrachloride; and neutral organic solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO). These solvents may be used alone, or two or more solvents may be used as a mixture. When water is used as the solvent, an aqueous solution of an inorganic salt such as sodium sulfate, sodium chloride, or ammonium sulfate may be used, as necessary. The concentration of the inorganic salt in the aqueous solution of the inorganic salt is generally adjusted to from 10 to 40 mass%. The pH of the aqueous solution may be adjusted by, for example, a metal salt such as sodium borate and sodium acetate; hydrochloric acid, boric acid, acetic acid, or sodium hydroxide. In this case, the pH of the aqueous solution is preferably 6 or more, more preferably 8 or more, from the viewpoint of preventing the reaction between the epoxy group of the epoxy compound and the amino group of collagen from becoming slow and achieving sufficient insolubilization in water. Since the pH of the aqueous solution of the inorganic salt tends to be reduced with time, a buffer may be used, as necessary.

[0030] The treatment temperature of the regenerated collagen fibers by the epoxy compound is preferably 50°C or lower, from the viewpoint of preventing regenerated collagen fibers from being denatured, preventing the strength of the fibers to be obtained from being reduced, and making stable production of fibers easy.

[0031] Then, the regenerated collagen fibers may be subjected to washing with water, oiling, or drying. Washing with water can be performed by, for example, washing the fibers for from 10 minutes to 4 hours with running water. As the oil agent used in oiling, for example, an oil agent composed of an emulsion such as amino modified silicone, epoxy modified silicone, or polyether modified silicone, and a pluronic polyether antistatic agent can be used. The drying temperature is preferably 100°C or lower, more preferably 75°C or lower.

[0032] The regenerated collagen fibers to be treated preferably contain a polyvalent metal, or a salt or complex thereof from the viewpoint of improving water resistance. Examples of the polyvalent metal include calcium, magnesium, strontium, barium, zinc, chromium, aluminum, titanium, zirconium, tin, lead, antimony, iron, and copper. From the viewpoint of improving water resistance, reducing coloring of fibers, reducing effects on the environment, and improving economic efficiency, aluminum, zirconium, or titanium is preferably used, and aluminum is more preferably used. The content of the polyvalent metal, or the salt or complex thereof in the regenerated collagen fibers is, as the amount of the metal element, preferably 1.0 mass% or more, more preferably 2.0 mass% or more, further more preferably 3.0 mass% or more, even more preferably 5.0 mass% or more, from the viewpoint of improving water resistance, and preferably 40 mass% or less, more preferably 30 mass% or less, further more preferably 20 mass% or less, even more preferably 10 mass% or less, from the viewpoint of improving the feel of the fiber surfaces.

[0033] That is, the content of the polyvalent metal, or the salt or complex thereof in the regenerated collagen fibers to be treated is, as the amount of the metal element, preferably from 1.0 to 40 mass%, more preferably from 2.0 to 30 mass%, further more preferably from 3.0 to 20 mass%, even more preferably from 5.0 to 10 mass%, from the above viewpoint.

[Method for treating fibers]

(One-step treatment and multistep treatment)

[0034] The method for treating fibers of the present invention includes any form of one-step treatment using a one-part type fiber-treating agent formed of a single composition, and multistep treatment in which a multiple-part type fiber-treating agent formed of a plurality of compositions, such as a two-part type fiber-treating agent, is used and regenerated collagen fibers are sequentially immersed in the plurality of compositions. The one-part type fiber-treating agent includes one used as a single composition by mixing a plurality of compositions upon use.

[0035] In the present invention, the content in the fiber-treating agent refers to, in the case of the one-step treatment, the content in a single composition that forms the one-part type fiber-treating agent, and in the case of the multistep treatment, the content in each treating agent to be used in each step.

(Basic treatment)

[0036] The method for treating fibers of the present invention comprises the following step (i), and therefore, it is possible to provide modified regenerated collagen fibers which have improved water resistance and heat resistance problematic in regenerated collagen fibers, impart heat shape memory ability, have improved stretchability (tenacity) and the feel of the surfaces, and have no coloring.

[0037] step (i) immersing regenerated collagen fibers in a fiber-treating agent which is a one-part type fiber-treating agent formed of a single composition or a multiple-part type fiber-treating agent formed of a plurality of compositions, and which comprises the following component (A) and component (B) in a total composition:

(A): vinylbenzoic acid or a salt thereof; and
(B): an azo polymerization initiator.

[0038] Examples of the multiple-part type fiber-treating agent include a two-part type fiber-treating agent composed of a first part containing the component (A) and a second part containing the component (B). When such a multiple-part type fiber-treating agent is used, the step (i) is multistep treatment in which regenerated collagen fibers are sequentially immersed in each agent. For example, when the two-part type fiber-treating agent is used, the step (i) is two-step treatment in which regenerated collagen fibers are immersed in the first part containing the component (A), and the regenerated collagen fibers treated with the first part are then immersed in the second part containing the component (B), or two-step treatment in which regenerated collagen fibers are immersed in the second part containing the component (B), and the regenerated collagen fibers treated with the second part are then immersed in the first part containing the component (A).

[0039] The component (A) is vinylbenzoic acid or a salt thereof. Examples of vinylbenzoic acid include 2-vinylbenzoic acid, 3-vinylbenzoic acid, 4-vinylbenzoic acid, and a mixture of two or three selected from the group consisting of them, and a mixture of three is preferable from the viewpoint of easy availability and good feel quality of the surface of fibers after treatment. On the other hand, 4-vinylbenzoic acid is preferable from the viewpoint of imparting water resistance. When the component (A) is a salt, examples of the salt include alkaline metal salts such as sodium salts and potassium salts.

[0040] The content of the component (A) in the fiber-treating agent is different depending on the pH range of the fiber-treating agent, and the following range is preferable. When the fiber-treating agent is a multiple-part type fiber-treating agent, "the content of the component (A)" here refers to the content in the composition containing the component (A), and "the pH of the fiber-treating agent" here refers to the pH of the treating agent containing the component (A). When there is a plurality of treating agents containing the component (A), the preferred range of the content is determined depending on the pH of each treating agent. As described above, the fiber-treating agent used as a single composition by mixing a plurality of compositions upon use is included in the one-part type fiber-treating agent, and "the pH of the fiber-treating agent" refers to pH after mixing.

[0041] When the pH of the fiber-treating agent is 2.0 or more and less than 6.5, the content of the component (A) in the fiber-treating agent is, on a vinylbenzoic acid monomer basis, preferably 0.1 mass% or more, more preferably 0.2 mass% or more, further more preferably 0.5 mass% or more, even more preferably 1.0 mass% or more, from the viewpoint of imparting higher shape sustainability, water resistance, stretchability (tenacity, that is, high breaking elongation during fiber tensioning), and heat resistance to the treated modified regenerated collagen fibers, and preferably 30 mass% or less, more preferably 25 mass% or less, further more preferably 20 mass% or less, even more preferably 15 mass% or less, from the viewpoint of improving the feel of the fiber surfaces.

[0042] That is, when the pH of the fiber-treating agent is 2.0 or more and less than 6.5, the content of the component (A) in the fiber-treating agent is, on a vinylbenzoic acid monomer basis, preferably from 0.1 to 30 mass%, more preferably from

0.2 to 25 mass%, further more preferably from 0.5 to 20 mass%, even more preferably from 1.0 to 15 mass%, from the above viewpoint.

[0043] When the pH of the fiber-treating agent is 6.5 or more and 11.0 or less, the content of the component (A) in the fiber-treating agent is, on a vinylbenzoic acid monomer basis, preferably 1.0 mass% or more, more preferably 2.0 mass% or more, further more preferably 5.0 mass% or more, even more preferably 10 mass% or more, from the viewpoint of imparting higher shape sustainability, water resistance, stretchability (tenacity, that is, high breaking elongation during fiber tensioning), and heat resistance to the treated modified regenerated collagen fibers, and preferably 90 mass% or less, more preferably 80 mass% or less, further more preferably 70 mass% or less, even more preferably 60 mass% or less, from the viewpoint of improving the feel of the fiber surfaces.

[0044] That is, when the pH of the fiber-treating agent is 6.5 or more and 11.0 or less, the content of the component (A) in the fiber-treating agent is, on a vinylbenzoic acid monomer basis, preferably from 1.0 to 90 mass%, more preferably from 2.0 to 80 mass%, further more preferably from 5.0 to 70 mass%, even more preferably from 10 to 60 mass%, from the above viewpoint.

[0045] The component (B) is an azo polymerization initiator for polymerizing the component (A). The component (B) may be contained in the composition containing the component (A), but when the fiber-treating agent to be used is made into a multiple-part type, for example, a two-part type agent, the component (B) may be contained in a composition (the second part) different from the composition containing the component (A) (the first part).

[0046] Examples of the azo polymerization initiator include 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 1,1'-azobis(cyclohexane-1-carbonitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile), dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis(2-hydroxymethylpropionitrile), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis[2-(2-imidazolin-2-yl)propane], 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine], 2,2'-azobis(2-methylpropionamidine) dihydrochloride, and 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride.

[0047] The fiber-treating agent for hydrophilic regenerated collagen fibers is preferably an aqueous solution from the viewpoint of promoting penetration of the compound in the solution into fibers, and therefore, also as the azo polymerization initiator to be formulated in the fiber-treating agent, a water-soluble azo polymerization initiator is preferable. As the water-soluble azo polymerization initiator, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis[2-(2-imidazolin-2-yl)propane], 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine], 2,2'-azobis(2-methylpropionamidine) dihydrochloride, 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride, or the like is preferable.

[0048] Here, the water-soluble azo polymerization initiator refers to, in the following terms showing the degree of solubility which is defined by the volume (mL) of water required to dissolve 1 g of azo polymerization initiator powder within 30 minutes when the powder is put in water and vigorously shaken for 30 seconds every 5 minutes at 20°C±5°C in accordance with JIS K8001 general rules for test methods of reagents, an azo polymerization initiator preferably corresponding to "slightly soluble" to "very soluble", more preferably "sparingly soluble" to "very soluble", further more preferably "soluble" to "very soluble", even more preferably "freely soluble" to "very soluble", even more preferably "very soluble".

<Amount of water required to dissolve 1 g of azo polymerization initiator>

[0049]

Very soluble: less than 1 mL
Freely soluble: 1 mL or more and less than 10 mL
Soluble: 10 mL or more and less than 30 mL
Sparingly soluble: 30 mL or more and less than 100 mL
Slightly soluble: 100 mL or more and less than 1 000 mL
Very slightly soluble: 1 000 mL or more and less than 10 000 mL
Practically insoluble: 10 000 mL or more

[0050] Further, as the treating agent for regenerated collagen fibers having a low heat resistance, an azo polymerization initiator having a low 10-hour half-life temperature such that it is efficiently cleaved even at a low treatment temperature and functions as a radical initiator is more preferably used. Among them, 2,2'-azobis[2-(2-imidazolin-2-yl)propane] (10-hour half-life temperature: 61°C), 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine] (10-hour half-life temperature: 57°C), 2,2'-azobis(2-methylpropionamidine) dihydrochloride (10-hour half-life temperature: 56°C), or 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (10-hour half-life temperature: 44°C) is preferable.

[0051] Here, the 10-hour half-life temperature of the azo polymerization initiator refers to a temperature at which 50% of the azo polymerization initiator is decomposed after 10 hours. The 10-hour half-life temperature of the azo polymerization initiator is preferably 80°C or lower, more preferably 70°C or lower, further more preferably 60°C or lower, even more preferably 50°C or lower, from the viewpoint of efficiently progressing the reaction at a low temperature without damaging regenerated collagen fibers susceptible to high temperatures, and is preferably 0°C or higher, more preferably 10°C or higher, further more preferably 20°C or higher, from the viewpoint of exhibiting no excess reactivity during storage at ambient temperature and being advantageous in storage and transport.

[0052] One component (B) may be used alone, or two or more components (B) may be used in combination. The content of the component (B) in the fiber-treating agent is, on an undissociated form basis in the case of a salt or a complex, preferably 0.001 mass% or more, more preferably 0.01 mass% or more, further more preferably 0.1 mass% or more, even more preferably 0.5 mass% or more, from the viewpoint of efficiently progressing the reaction and imparting higher shape sustainability, water resistance, stretchability (tenacity, that is, high breaking elongation during fiber tensioning), and heat resistance to the treated modified regenerated collagen fibers, and is preferably 80 mass% or less, more preferably 60 mass% or less, further more preferably 40 mass% or less, even more preferably 20 mass% or less from the viewpoint of preventing the molecular weight of the polymerized product produced by excess concentration from being too low. When the fiber-treating agent is a multiple-part type fiber-treating agent, "the content of the component (B)" here refers to the content in the composition containing the component (B).

[0053] The mass ratio of the component (B) to the component (A), (B)/(A) in the fiber-treating agent is preferably 0.001 or more, more preferably 0.01 or more, and preferably 200 or less, more preferably 50 or less, from the viewpoint of efficiently progressing the reaction and imparting higher shape sustainability, water resistance, stretchability (tenacity, that is, high breaking elongation during fiber tensioning), and heat resistance to the treated modified regenerated collagen fibers. In the case of the multiple-part type fiber-treating agent in which the component (A) and the component (B) are contained in different treating agents, the mass ratio (B)/(A) in a mixed solution obtained by virtually mixing both agents is preferably within the range.

[0054] The fiber-treating agent used in the step (i) has water as a medium. The content of water in the fiber-treating agent is preferably 10 mass% or more, more preferably 20 mass% or more, further more preferably 30 mass% or more, even more preferably 40 mass% or more, and preferably 95 mass% or less, more preferably 90 mass% or less, even more preferably 85 mass% or less.

[0055] That is, the content of water in the fiber-treating agent is preferably from 10 to 95 mass%, more preferably from 20 to 90 mass%, further more preferably from 30 to 85 mass%, even more preferably from 40 to 85 mass%.

[0056] The pH of the fiber-treating agent used in the step (i) is preferably 2.0 or more, more preferably 3.0 or more, further more preferably 3.5 or more, even more preferably 4.0 or more, and preferably 11.0 or less, more preferably 10.0 or less, further more preferably 9.0 or less, from the viewpoint of suppressing damage to and improving durability of regenerated collagen fibers. The pH in the present invention is a value at 25°C.

[0057] That is, the pH of the fiber-treating agent is preferably from 2.0 to 11.0, more preferably from 3.0 to 10.0, further more preferably from 3.5 to 9.0, even more preferably from 4.0 to 9.0, from the viewpoint of suppressing damage to and improving durability of regenerated collagen fibers.

[0058] In the case of the multiple-part type fiber-treating agent, the above conditions are applied to the pH of each agent. However, the pH of each agent is preferably close to each other, and specifically, the difference in pH between the agent having the highest pH and the agent having the lowest pH is preferably 3.0 or less, more preferably 2.0 or less, further more preferably 1.0 or less, even more preferably 0.5 or less. As described above, the fiber-treating agent used as a single composition by mixing a plurality of compositions upon use is included in the one-part type fiber-treating agent, and "the pH of the fiber-treating agent" refers to pH after mixing.

[0059] In the step (i), the regenerated collagen fibers to be subjected to fiber treatment may be dry or wet. For example, the regenerated collagen fibers may be directly treated in a state before drying upon production of the regenerated collagen fibers. The amount of the fiber-treating agent in which the regenerated collagen fibers are immersed is preferably 2.0 or more, more preferably 3.0 or more, further more preferably 5.0 or more, even more preferably 10 or more, even more preferably 20 or more, and preferably 500 or less, more preferably 250 or less, further more preferably 100 or less, in terms of bath ratio to the mass of the regenerated collagen fibers (mass of fiber-treating agent/mass of regenerated collagen fibers).

[0060] That is, the bath ratio is preferably from 2.0 to 500, more preferably from 3.0 to 250, further more preferably from 5.0 to 100, even more preferably from 10 to 100, even more preferably from 20 to 100.

[0061] In the step (i), the regenerated collagen fibers are fixed with a curler or the like in advance, followed by being subjected to the fiber treatment of the present invention under heating. This enables a desired shape to be imparted to the regenerated collagen fibers together with heat shape memory ability and high durability.

[0062] It is preferable that the immersion of the regenerated collagen fibers in the fiber-treating agent in the step (i) be performed under heating, and this heating is performed by heating the fiber-treating agent. This heating may be performed by immersing the regenerated collagen fibers in the fiber-treating agent being heated, or by immersing the regenerated collagen fibers in the fiber-treating agent at a low temperature, and then performing heating. The temperature of the fiber-treating agent is preferably 20°C or higher, more preferably 35°C or higher, further more preferably 45°C or higher to obtain the effect of the present invention by increasing the interaction between the component (A) or a polymerized product containing the component (A) as a constituent monomer and fiber-forming molecules in the regenerated collagen fibers, for example, protein molecules, and preferably less than 100°C, more preferably 80°C or lower, further more preferably 70°C or lower, further more preferably 60°C or lower to prevent the regenerated collagen fibers from being modified by heat and deteriorating.

[0063] The immersion time in the step (i) is appropriately adjusted depending on the heating temperature, and is, for example, preferably 15 minutes or more, more preferably 30 minutes or more, further more preferably 1 hour or more, from the viewpoint of exhibiting a stretchability improving effect on regenerated collagen fibers, and is preferably 48 hours or less, more preferably 24 hours or less, further more preferably 12 hours or less, for suppressing damage to regenerated collagen fibers.

[0064] It is preferable to carry out the step (i) in an environment where evaporation of moisture is suppressed. Examples of the specific means for suppressing evaporation of moisture include a method in which a container of the fiber-treating agent in which regenerated collagen fibers are immersed is covered with a film-shaped material, a cap, a lid or the like made of a material impermeable to water vapor.

[0065] In the case of multistep treatment using a multiple-part type fiber-treating agent, the bath ratio, temperature, immersion time, and other conditions are applied to each step. In the case of multistep treatment, rinsing, drying, or the like may be performed between each step.

[0066] After the step (i), the regenerated collagen fibers may be rinsed or may not be rinsed, but are preferably rinsed from the viewpoint of preventing deterioration of the feel of the surfaces of regenerated collagen fibers by an excess component (A) or an excess polymerized product containing a component (A) as a constituent monomer.

[0067] The treatment of the step (i) may allow the components (A) and (B) to penetrate into the regenerated collagen fibers, to be polymerized using the component (A) as the constituent monomer, and to be strongly coordinated with metals in the fibers, for example, polyvalent metals, thereby producing various effects. That is, it is possible to produce modified regenerated collagen fibers containing the component (A) in the fibers by the method for treating regenerated collagen fibers comprising the step (i), and the obtained modified regenerated collagen fibers are fibers which can impart the shape by a heat set, are excellent in water resistance, heat resistance, and tensile elastic modulus, and have highly improved stretchability (tenacity) of the regenerated collagen fibers.

[Modified regenerated collagen fibers]

[0068] Hereinafter, the modified regenerated collagen fibers of the present invention obtained by the above-described method will be described.

(Component (A): vinylbenzoic acid or salt thereof)

[0069] The modified regenerated collagen fibers of the present invention contain the component (A) vinylbenzoic acid or a salt thereof, or a polymerized product containing the component (A) as a constituent monomer. Examples of vinylbenzoic acid include 2-vinylbenzoic acid, 3-vinylbenzoic acid, 4-vinylbenzoic acid, and a mixture of two or three selected from the group consisting of them, and a mixture of three is preferable from the viewpoint of easy availability and good feel quality of the surface of fibers after treatment. On the other hand, 4-vinylbenzoic acid is preferable from the viewpoint of water resistance. When the component (A) is a salt, examples of the salt include alkaline metal salts such as sodium salts and potassium salts.

[0070] The content of the component (A) and the polymerized product containing the component (A) as a constituent monomer in the modified regenerated collagen fibers of the present invention is, on a vinylbenzoic acid monomer basis, preferably 1.0 mass% or more, more preferably 5.0 mass% or more, further more preferably 10 mass% or more, even more preferably 15 mass% or more, even more preferably 20 mass% or more, from the viewpoint of having higher shape sustainability, water resistance, and heat resistance, and preferably 70 mass% or less, more preferably 60 mass% or less, further more preferably 50 mass% or less, even more preferably 40 mass% or less, from the viewpoint of improving the feel of the fiber surfaces.

[0071] That is, the content of the component (A) and the polymerized product containing the component (A) as a constituent monomer in the modified regenerated collagen fibers of the present invention is, on a vinylbenzoic acid monomer basis, preferably from 1.0 to 70 mass%, more preferably from 5.0 to 60 mass%, further more preferably from 10 to 50 mass%, even more preferably from 15 to 40 mass%, even more preferably from 20 to 40 mass%, from the above viewpoint.

(Component (C): polyvalent metal, or salt or complex thereof)

[0072] The modified regenerated collagen fibers of the present invention preferably contain (C) a polyvalent metal, or a salt or complex thereof, from the viewpoint of improving water resistance. Examples of the polyvalent metal include calcium, magnesium, strontium, barium, zinc, chromium, aluminum, titanium, zirconium, tin, lead, antimony, iron, and copper. From the viewpoint of improving water resistance, reducing coloring of fibers, reducing effects on the environment, and improving economic efficiency, aluminum, zirconium, or titanium is preferably used, and aluminum is more preferably used. These polyvalent metals may be used either alone or in combination of two or more.

[0073] The content of the component (C) in the modified regenerated collagen fibers of the present invention is, as the amount of the metal element, preferably 0.1 mass% or more, more preferably 0.5 mass% or more, further more preferably 1.0 mass% or more, even more preferably 2.0 mass% or more, from the viewpoint of improving water resistance, and preferably 40 mass% or less, more preferably 30 mass% or less, further more preferably 20 mass% or less, even more preferably 10 mass% or less, from the viewpoint of improving the feel of the fiber surfaces.

[0074] That is, the content of the component (C) in the modified regenerated collagen fibers of the present invention is, as the amount of the metal element, preferably from 0.1 to 40 mass%, more preferably from 0.5 to 30 mass%, further more preferably from 1.0 to 20 mass%, even more preferably from 2.0 to 10 mass%, from the above viewpoint.

[0075] The modified regenerated collagen fibers of the present invention are fibers which can impart the shape by a heat set, are excellent in water resistance, heat resistance, and tensile elastic modulus, and have highly improved stretchability (tenacity) of the regenerated collagen fibers. Therefore, the modified regenerated collagen fibers of the present invention can be preferably used as the fibers for headdress products, and various headdress products can be produced using the fibers.

[0076] In the present invention, examples of suitable headdress products include hair wigs, wigs, weavings, hair extensions, blade hairs, hair accessories, and doll hairs.

[0077] The modified regenerated collagen fibers of the present invention may be used as the headdress products alone, or may be mixed with other fibers to produce headdress products. Other fibers may be fibers which can be used in headdress products and are not particularly limited. Examples of other fibers include polyester fibers, human hair, animal hair, polyvinyl chloride fibers, modacrylic fibers, polyamide fibers, and polyolefin fibers. Among them, polyester fibers are preferable, and flame-retardant polyester fibers are more preferable, from the viewpoint of being excellent in heat resistance, flame retardancy, and curl retention properties.

[0078] The flame-retardant polyester fibers are not particularly limited, and it is preferable to contain from 5 to 40 parts by mass of a brominated epoxy flame retardant with respect to 100 parts by mass of one or more polyester resins selected from the group consisting of polyalkylene terephthalate and copolymerized polyester mainly composed of polyalkylene terephthalate, from the viewpoint of flame retardancy. In the present invention, "mainly composed of" means containing 50 mol% or more, and "copolymerized polyester mainly composed of polyalkylene terephthalate" refers to copolymerized polyester containing 50 mol% or more of polyalkylene terephthalate. Preferably, "copolymerized polyester mainly composed of polyalkylene terephthalate" contains 60 mol% or more, more preferably 70 mol% or more, further more preferably 80 mol% or more of polyalkylene terephthalate. It is preferable that the flame-retardant polyester fibers further contain from 0 to 5 parts by mass of an antimony compound with respect to 100 parts by mass of the polyester resin. By containing the antimony compound, flame retardancy of polyester fibers improves.

[0079] Concerning the embodiments described above, preferred aspects of the present invention will be further disclosed below.

<1> Modified regenerated collagen fibers comprising the following component (A) or a polymerized product containing the component (A) as a constituent monomer in regenerated collagen fibers:

(A) vinylbenzoic acid or a salt thereof.

<2> The modified regenerated collagen fibers according to <1>, wherein a content of the component (A) is, on a vinylbenzoic acid monomer basis, preferably 1.0 mass% or more, more preferably 5.0 mass% or more, further more preferably 10 mass% or more, even more preferably 15 mass% or more, even more preferably 20 mass% or more, and preferably 70 mass% or less, more preferably 60 mass% or less, further more preferably 50 mass% or less, even more preferably 40 mass% or less.

<3> The modified regenerated collagen fibers according to <1> or <2>, preferably, further comprising the following component (C):

(C) a polyvalent metal, or a salt or complex thereof.

<4> The modified regenerated collagen fibers according to <3>, wherein the component (C) is preferably one or more polyvalent metals selected from the group consisting of calcium, magnesium, strontium, barium, zinc, chromium, aluminum, titanium, zirconium, tin, lead, antimony, iron, and copper, or a salt or complex thereof, more preferably one or more polyvalent metals selected from the group consisting of aluminum, zirconium, and titanium, or a salt or complex thereof, further more preferably aluminum, or a salt or complex thereof.

<5> The modified regenerated collagen fibers according to <3> or <4>, wherein a content of the component (C) is, as

the amount of the metal element, preferably 0.1 mass% or more, more preferably 0.5 mass% or more, further more preferably 1.0 mass% or more, even more preferably 2.0 mass% or more, and preferably 40 mass% or less, more preferably 30 mass% or less, further more preferably 20 mass% or less, even more preferably 10 mass% or less.
<6> A method for treating regenerated collagen fibers comprising the following step (i):
step (i) immersing regenerated collagen fibers in a fiber-treating agent which is a one-part type fiber-treating agent formed of a single composition or a multiple-part type fiber-treating agent formed of a plurality of compositions, and which comprises the following component (A) and component (B) in a total composition:

(A): vinylbenzoic acid or a salt thereof; and
(B): an azo polymerization initiator.

<7> The method for treating regenerated collagen fibers according to <6>, wherein the fiber-treating agent in the step (i) is a multiple-part type fiber-treating agent comprising a first part containing the component (A) and a second part containing the component (B); and
the step (i) comprises immersing the regenerated collagen fibers in the first part, and then immersing the regenerated collagen fibers treated with the first part in the second part, or immersing the regenerated collagen fibers in the second part, and then immersing the regenerated collagen fibers treated with the second part in the first part.
<8> The method for treating regenerated collagen fibers according to <6> or <7>, comprising a regenerated collagen fiber production step of subjecting insoluble collagen fibers using a split of a livestock animal as a raw material to solubilization treatment, discharging the obtained aqueous soluble collagen solution through a spinning nozzle or a slit, and immersing the aqueous soluble collagen solution in an aqueous inorganic salt solution, before the step (i).
<9> The method for treating regenerated collagen fibers according to <8>, preferably comprising a cross-linking treatment step of immersing the regenerated collagen fibers in an epoxy compound or a solution thereof, after the regenerated collagen fiber production step.
<10> The method for treating regenerated collagen fibers according to any one of <6> to <9>, wherein the component (B) is preferably a water-soluble azo polymerization initiator, more preferably one or more selected from the group consisting of 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis [2-(2-imidazolin-2-yl)propane], 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine], 2,2'-azobis(2-methylpropionamidine) dihydrochloride, and 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride.
<11> The method for treating regenerated collagen fibers according to any one of <6> to <10>, wherein a content of the component (B) in the fiber-treating agent (in the case of the multiple-part type fiber-treating agent, a content of the component (B) in a composition containing the component (B)) is, on an undissociated form basis, preferably 0.001 mass% or more, more preferably 0.01 mass% or more, further more preferably 0.1 mass% or more, even more preferably 0.5 mass% or more, and preferably 80 mass% or less, more preferably 60 mass% or less, further more preferably 40 mass% or less, even more preferably 20 mass% or less.
<12> The method for treating regenerated collagen fibers according to any one of <6> to <11>, wherein the regenerated collagen fibers comprise the following component (C):
(C) a polyvalent metal, or a salt or complex thereof.
<13> The method for treating regenerated collagen fibers according to <12>, wherein the component (C) is preferably one or more polyvalent metals selected from the group consisting of calcium, magnesium, strontium, barium, zinc, chromium, aluminum, titanium, zirconium, tin, lead, antimony, iron, and copper, or a salt or complex thereof, more preferably one or more polyvalent metals selected from the group consisting of aluminum, zirconium, and titanium, or a salt or complex thereof, further more preferably aluminum, or a salt or complex thereof.
<14> The method for treating regenerated collagen fibers according to any one of <6> to <13>, wherein a pH of the fiber-treating agent used in the step (i) at 25°C is preferably 2.0 or more, more preferably 3.0 or more, further more preferably 3.5 or more, even more preferably 4.0 or more, and preferably 11.0 or less, more preferably 10.0 or less, further more preferably 9.0 or less.
<15> The method for treating regenerated collagen fibers according to any one of <6> to <14>, wherein a pH of the treating agent containing the component (A) used in the step (i) is 2.0 or more and less than 6.5, and a content of the component (A) in the treating agent is, on a vinylbenzoic acid monomer basis, preferably 0.1 mass% or more, more preferably 0.2 mass% or more, further more preferably 0.5 mass% or more, even more preferably 1.0 mass% or more, and preferably 30 mass% or less, more preferably 25 mass% or less, further more preferably 20 mass% or less, even more preferably 15 mass% or less.
<16> The method for treating regenerated collagen fibers according to any one of <6> to <14>, wherein a pH of the treating agent containing the component (A) used in the step (i) is 6.5 or more and 11.0 or less, and a content of the component (A) in the treating agent is, on a vinylbenzoic acid monomer basis, preferably 1.0 mass% or more, more preferably 2.0 mass% or more, further more preferably 5.0 mass% or more, even more preferably 10 mass% or more, and preferably 90 mass% or less, more preferably 80 mass% or less, further more preferably 70 mass% or less, even

more preferably 60 mass% or less.

<17> The method for treating regenerated collagen fibers according to any one of <6> to <16>, wherein a mass ratio of the component (B) to the component (A), (B)/(A) in the fiber-treating agent (in the case of a multiple-part type fiber-treating agent in which the component (A) and the component (B) are contained in different treating agents, in a mixed solution obtained by virtually mixing both agents) is preferably 0.001 or more, more preferably 0.01 or more, and preferably 200 or less, more preferably 50 or less.

<18> The method for treating regenerated collagen fibers according to any one of <6> to <17>, wherein the fiber-treating agent used in the step (i) has water as a medium, and a content of water in the fiber-treating agent is preferably 10 mass% or more, more preferably 20 mass% or more, further more preferably 30 mass% or more, even more preferably 40 mass% or more, and preferably 95 mass% or less, more preferably 90 mass% or less, further more preferably 85 mass% or less.

<19> The method for treating regenerated collagen fibers according to any one of <6> to <18>, wherein an amount of the fiber-treating agent in which the regenerated collagen fibers are immersed in the step (i) is preferably 2.0 or more, more preferably 3.0 or more, further more preferably 5.0 or more, even more preferably 10 or more, even more preferably 20 or more, and preferably 500 or less, more preferably 250 or less, further more preferably 100 or less, in terms of bath ratio to a mass of the regenerated collagen fibers (mass of fiber-treating agent/mass of regenerated collagen fibers).

<20> The method for treating regenerated collagen fibers according to any one of <6> to <19>, wherein a temperature of the fiber-treating agent in which the regenerated collagen fibers are immersed in the step (i) is preferably 20°C or higher, more preferably 35°C or higher, further more preferably 45°C or higher, and preferably less than 100°C, more preferably 80°C or lower, further more preferably 70°C or lower, further more preferably 60°C or lower.

<21> The method for treating regenerated collagen fibers according to any one of <6> to <20>, wherein an immersion time in the step (i) is preferably 15 minutes or more, more preferably 30 minutes or more, further more preferably 1 hour or more, and preferably 48 hours or less, more preferably 24 hours or less, further more preferably 12 hours or less.

<22> The method for treating regenerated collagen fibers according to any one of <6> to <21>, wherein it is preferable to carry out the step (i) in an environment where evaporation of moisture is suppressed.

<23> A method for producing modified regenerated collagen fibers, comprising treating regenerated collagen fibers by the method for treating regenerated collagen fibers according to any one of <6> to <22>.

<24> A method for producing a headdress product, comprising treating regenerated collagen fibers by the method for treating regenerated collagen fibers according to any one of <6> to <22>.

<25> A headdress product comprising the modified regenerated collagen fibers according to any one of <1> to <5> as a constituent element.

<26> The headdress product according to <25>, wherein the headdress product is selected from the group consisting of hair wigs, wigs, weavings, hair extensions, blade hairs, hair accessories, and doll hairs.

Examples

Example 1 and Comparative Examples 1 to 3

[0080] Using compositions whose formulations are shown in Table 1, regenerated collagen fibers were treated by the following method, and various properties were evaluated. The pH of each composition was measured with the prepared composition directly applied to a pH meter (F-52 manufactured by HORIBA, Ltd.) at room temperature (25°C).

<Treatment method>

[0081] 1. A 22 cm-long tress with 0.50 g of regenerated collagen fibers (*) was immersed in a container containing the fiber-treating agent in such an amount that the bath ratio as shown in the table is achieved, the opening of the container was closed, the container was immersed together with its contents in a water bath (manufacturer: TOYO SEISAKUSHO, Ltd./Model: TBS221FA) at the temperature as shown in the table, and heating was performed for the time as shown in the table.

[0082] *: Regenerated collagen fibers manufactured by Kaneka Corporation were purchased in the form of a commercially available extension product, and cut, and the cut fibers were segmented into tresses, and used for evaluation. In this evaluation, extension products having a notation of the use of Ultima 100% as a fiber species, and being white with a color number of 30, and straight in shape, were used.

[0083] These regenerated collagen fibers manufactured by Kaneka Corporation contained aluminum, and each aluminum content measured by the following analysis was 6.8 mass%.

[0084] The regenerated collagen fibers were dried with a desiccator, 0.1 g of these fibers were then placed in a mixed solution of 5 mL of nitric acid and 15 mL of hydrochloric acid, and heated and dissolved. After cooling, this solution was diluted with water to 50 times, and the aluminum content in the diluted aqueous solution was measured using an atomic absorption spectrophotometer (Z-5300) manufactured by Hitachi, Ltd.

[0085] 2. The container containing the tress was taken out from the water bath, and brought back to room temperature.

[0086] 3. The tress was taken out from the container, then rinsed with running tap water at 30°C for 30 seconds, lathered with evaluating shampoo for 60 seconds, rinsed with running tap water at 30°C for 30 seconds, and lightly drained with a towel, and the tress was dried by a hot air dryer (Nobby White NB 3 000 manufactured by TESCOM Company) while being combed.

<Formulation of evaluating shampoo>

[0087]

Component	(mass%)
sodium laureth sulfate	15.5
lauramide DEA	1.5
EDTA-2Na	0.3
phosphoric acid	amount required to adjust pH to 7
ion-exchange water	balance
total	100

<Increase in average breaking elongation during fiber tensioning>

[0088] As an index of water resistance and stretchability (tenacity) during fiber tensioning, an average breaking elongation, that is, an average value in evaluation on a plurality of fibers (ten fibers) for the percentage by which the fiber was stretched by tensioning with respect to the original fiber length when rupture occurred was used. The evaluation was performed in the following procedure using a tress immediately after treatment performed as described in <Treatment method> above.

1. Ten fibers were cut from the root of the tress. A 3 cm fiber fragment was taken from near the center between the root and the hair tip of each fiber, so that a total of ten 3 cm hair fragments were obtained.
2. The fiber fragment was set in "MTT690 Miniature Tensile Tester" manufactured by DIA-STRON Limited. After the fiber was allowed to stand for 30 minutes while being immersed in water, automatic measurement was started, and an average breaking elongation was determined in a state where the fiber was immersed in water. A large numerical value indicates that the fiber has high stretchability, and is excellent in tenacity and excellent in durability.

[0089] The degree of increase (C%) in average breaking elongation of the treated tress (B%) with respect to an untreated state when the average breaking elongation during fiber tensioning in an intact state (untreated; Comparative Example 1) at the time of being cut from the commercially available product (A%) is used as a reference is determined from the following expression, and shown as "ratio of increase in average breaking elongation during fiber tensioning [%]" in the table.

$$C\ (\%) = B\ (\%) - A\ (\%)$$

<Increase in average breaking load during fiber tensioning>

[0090] As an index of water resistance during fiber tensioning, an average breaking load during fiber tensioning was used. Evaluation was performed using a tress immediately after treatment performed as described in <Treatment method> above. As a numerical value, an average value in evaluation on a plurality of fibers (ten fibers) was used. The evaluation was performed in the following procedure.

1. Ten fibers were cut from the root of the tress. A 3 cm fiber fragment was taken from near the center between the root and the hair tip of each fiber, so that a total of ten 3 cm hair fragments were obtained.
2. The fiber fragment was set in "MTT690 Miniature Tensile Tester" manufactured by DIA-STRON Limited. After the fiber was allowed to stand for 30 minutes while being immersed in water, automatic measurement was started, and a breaking load was determined when the fiber stretched while being immersed in water. A large numerical value indicates that the fiber has suppleness and resilience, and is insusceptible to stretching by an external force, and

excellent in durability.

[0091] The degree of increase (Y (gf)) in average breaking load of the treated tress (W_1 (gf)) with respect to an untreated state when the average breaking load during fiber tensioning in an intact state (untreated; Comparative Example 1) at the time of being cut from the commercially available product (W_0 (gf)) is used as a reference is determined from the following expression, and shown as "amount of increase in average breaking load during fiber tensioning [gf]" in the table.

$$Y\ (gf) = W_1\ (gf) - W_0\ (gf)$$

<Shrinkage ratio during set with iron at high temperature>

[0092] As an index of heat resistance, a shrinkage ratio during a set with an iron at a high temperature was used. The evaluation was performed using a tress immediately after treatment performed as described in <Treatment method> above. As a numerical value, an average value in evaluation on a plurality of fibers (five fibers) was used. The evaluation was performed in the following procedure.

1. Five fibers were cut from the root of the tress immediately after treatment performed as described in <Treatment method> above, and marked. The lengths of these five fibers after treatment were measured, and an average value was recorded (length L_1). Then, these marked five fibers after treatment were bundled together with separately prepared two untreated tresses with 0.5 g of regenerated collagen fibers (1 g in total) so as to be sandwiched therebetween to thereby produce a new tress (hereinafter, large tress), and a flat iron (manufactured by Miki Denki Sangyo K.K./Model: AHI-938) set at 180°C was applied throughout the large tress ten times at a rate of 5 cm/sec.
2. After the iron operation, marked five fibers after treatment were taken out from the large tress, and the lengths of these marked five fibers after treatment were measured again, and an average value was recorded (length L_2).
3. The shrinkage ratio during a set with an iron at a high temperature was defined as $S_{dry} = \{1 - (L_2/L_1)\} \times 100$ [%]. When S_{dry} is close to 0%, the fiber is unlikely to shrink by dry heat and thus excellent in heat resistance.

<Shrinkage ratio during hot-water heating>

[0093] As an index of water resistance and heat resistance, a shrinkage ratio during hot-water heating was used. The evaluation was performed using a tress immediately after treatment performed as described in <Treatment method> above. As a numerical value, an average value in evaluation on a plurality of fibers (five fibers) was used. The evaluation was performed in the following procedure.

1. Five fibers were cut from the root of the tress, an average value of the lengths of the fibers was recorded (length L_1), and the fibers were immersed in a water bath (manufacturer: TOYO SEISAKUSHO, Ltd./Model: TBS221FA) at 90°C and heated for 1 minute.
2. After the heating operation, five fibers were taken out, lightly drained with a towel, and dried at ambient temperature and ambient humidity for 30 minutes, and then an average value of the lengths of the fibers was recorded again (length L_2).
3. The shrinkage ratio during hot-water heating was defined as $S_{wet} = \{1-(L_2/L_1)\} \times 100$[%]. When S_{wet} is close to 0%, the fiber is unlikely to shrink by wet heat and thus excellent in heat resistance.

<Heat shape memory ability>

[0094] Evaluation of heat shape memory ability was performed using a tress immediately after treatment performed as described in <Treatment method> above. When the value of the result of "I: shaping (curl)" was 5% or less, it was determined that there was no effect, and subsequent treatment and evaluation were not performed.

- I: Shaping (curl)

[0095]

1. A 22 cm-long tress with 0.5 g of regenerated collagen fibers was wetted with tap water at 30°C for 30 seconds, and the wet tress was then wound around a plastic rod having a diameter of 14 mm, and fixed with a clip.
2. The tress wound around the rod was immersed in a water bath (manufacturer: TOYO SEISAKUSHO, Ltd./Model: TBS221FA) at 60°C, and heated for 1 minute.

3. The tress was taken out from the water bath, immersed in water at 25°C for 1 minute, and taken out from water to be brought back to room temperature.
4. The tress was removed from the rod, combed three times, and then, hung and photographed right from the side 3 minutes after being taken out from water.

(Evaluation criteria)

[0096] The curling-up ratio = ratio of decrease in tress length (I) (%) determined from the following expression, where L_0 is an untreated tress length (22 cm) and L is a treated tress length, was defined as curling strength.

$$I = [(L_0 - L)/L_0] \times 100$$

- II: Reshaping (straight)

[0097]

1. The tress evaluated in I was combed to eliminate entanglement, and a flat iron (manufactured by Miki Denki Sangyo K.K./Model: AHI-938) set at 180°C was then slid over the tress six times at a rate of 5 cm/sec.
2. The tress was rinsed with running tap water at 30°C for 30 seconds, lathered with evaluating shampoo for 60 seconds, then rinsed with running tap water at 30°C for 30 seconds, and dried with a towel.
3. The tress was hung and naturally dried at 20°C and 65%RH for 12 hours, combed, and then visually observed right from the side while being hung.

(Evaluation criteria)

[0098] The straightening ratio (ST) (%) determined from the following expression, where L_0 is an untreated tress length (22 cm) and L is a treated tress length, was defined as a degree of attainment straightening. The tress is completely straightened when ST is 100%.

$$ST = [1 - (L_0 - L)/L_0] \times 100$$

- III: Re-reshaping (Curl)

[0099]

1. The tress evaluated in II was wetted with tap water at 30°C for 30 seconds, and the wet tress was then wound around a plastic rod having a diameter of 14 mm, and fixed with a clip.
2. The tress wound around the rod was immersed in a water bath (manufacturer: TOYO SEISAKUSHO, Ltd./Model: TBS221FA) at 60°C, and heated for 1 minute.
3. The tress was taken out from the water bath, immersed in water at 25°C for 1 minute, and taken out from water to be brought back to room temperature.
4. The tress was removed from the rod, combed three times, and then, hung and photographed right from the side 3 minutes after being taken out from water.

(Evaluation criteria)

[0100] The curling-up ratio = ratio of decrease in tress length (I) (%) determined from the following expression, where L_0 is an untreated tress length (22 cm) and L is a treated tress length, was defined as curling strength.

$$I = [(L_0 - L)/L_0] \times 100$$

<Surface feel quality>

[0101] For evaluation of the feel of the surfaces, five skilled panelists performed evaluation on the basis of the following criteria for feel smoothness when the tress immediately after treatment performed as described in <Treatment method> was touched by hand, and a total value for the five panelists was taken as an evaluation result.

(Evaluation criteria)

[0102]

5: Much smoother hand feel over untreated fibers (Comparative Example 1).
4: Smoother hand feel over untreated fibers (Comparative Example 1).
3: Slightly smoother hand feel over untreated fibers (Comparative Example 1).
2: Comparable in hand feel to untreated fibers (Comparative Example 1).
1: Rougher, more frictional and poorer in hand feel than untreated fibers (Comparative Example 1).

<Suppression of coloring on fibers>

[0103]

1. For each of the front and the back of the tress, the color in each of the vicinity of the root, the vicinity of the center and the vicinity of the hair tip was measured with a colorimeter (Colorimeter CR-400 manufactured by KONICA MINOLTA, INC.), and an average value for a total of six points was taken as a colorimetric value (L, a, b).
2. The degree of coloring was evaluated by ΔE*ab using an untreated white tress with a color number of 30 (*) (Comparative Example 1) as a reference. The color was measured on the day when the treatment was performed.

(*) Untreated white tress with a color number of 30

[0104] Regenerated collagen fibers manufactured by Kaneka Corporation were purchased in the form of a commercially available extension product, and cut, and the cut fibers were segmented into tresses, and used for evaluation. In this evaluation, extension products having a notation of the use of Ultima 100% as a fiber species, and being white with a color number of 30, and straight in shape, were used.

[0105] These regenerated collagen fibers manufactured by Kaneka Corporation contained aluminum, and each aluminum content measured by the above-described analysis was 6.8 mass%.

[0106] ΔE*ab was defined as $[(L_1 - L_0)^2 + (a_1 - a_0)^2 + (b_1 - b_0)^2]^{1/2}$, where (L_0, a_0, b_0) is a measured value for the untreated white tress with a color number of 30 and (L_1, a_1, b_1) is a measured value for the treated tress, and a coloring suppressing effect was determined on the basis of the following criteria.

5:

$$\Delta E^*ab \leq 5.0$$

4:

$$5.0 < \Delta E^*ab \leq 10.0$$

3:

$$10.0 < \Delta E^*ab \leq 15.0$$

2:

$$15.0 < \Delta E^*ab \leq 20.0$$

1:

$$20.0 < \Delta E^*ab$$

[Table 1]

			Example	Comparative Example		
			1	1	2	3
Treating agent (mass%)	(A)	4-Vinylbenzoic acid	5.0	-	5.0	-
	(B)	2,2'-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (in parenthesis, amount as undissociated compound)	5.0 (3.9)	-	-	5.0 (3.9)
		Water	Balance	-	Balance	Balance
	pH adjuster	Hydrochloric acid or sodium hydroxide	*	-	*	*
	Total		100	-	100	100
	pH(25°C)		5.5	-	5.5	5.5
Treatment	Bath ratio		40	-	40	40
	Heating condition		50°C 3h	-	40°C 1h	50°C 3h
Effect	Durability improvement	Ratio of increase in average breaking elongation during fiber tensioning [%]	4.6	Reference	0.1	0.2
		Amount of increase in average breaking load during fiber tensioning [gf]	30.1	Reference	10.8	4.0
	Heat resistance improvement	Shrinkage ratio during set with iron at high temperature [%]	10.7	14.7	14.0	14.0
		Shrinkage ratio during hot-water heating [%]	16.0	76.0	28.0	40.0
	Heat shape memory	I: Shaping (curl)	34	1	24	9
		II: Reshaping (straight)	99	90	95	100
		III: Re-reshaping (curl)	39	6	27	12
	Surface feel quality		15	Reference	10	10
	Suppression of coloring on fibers		5	Reference	5	5

*: Amount of pH adjustment

Examples 2 to 6

[0107] Using the first parts and the second parts whose formulations are shown in Table 2, the regenerated collagen fibers were treated by the following method, and various properties were evaluated. The pH of each composition was measured with the prepared composition directly applied to a pH meter (F-52 manufactured by HORIBA, Ltd.) at room temperature (25°C) .

[0108] The concentration of each component shown in the table is the concentration in the first part or the second part.

<Treatment method>

[0109]

1. A 22 cm-long tress with 0.5 g of regenerated collagen fibers (*) was immersed in a container containing the first part in such an amount that the bath ratio as shown in the table is achieved, the opening of the container was closed, the container was immersed together with its contents in a water bath (manufacturer: TOYO SEISAKUSHO, Ltd./Model: TBS221FA) at the temperature as shown in the table, and heating was performed for the time as shown in the table.

[0110] *: Regenerated collagen fibers manufactured by Kaneka Corporation were purchased in the form of a commercially available extension product, and cut, and the cut fibers were segmented into tresses, and used for evaluation. In this evaluation, extension products having a notation of the use of Ultima 100% as a fiber species, and being white with a color number of 30, and straight in shape, were used.

[0111] These regenerated collagen fibers manufactured by Kaneka Corporation contained aluminum, and each aluminum content measured by the above-described analysis was 6.8 mass%.

[0112] 2. The container containing the tress was taken out from the water bath, and brought back to room temperature.

[0113] 3. The tress was taken out from the container, rinsed with running tap water at 30°C for 30 seconds, lathered with evaluating shampoo for 60 seconds, rinsed with running tap water at 30°C for 30 seconds, and lightly drained with a towel, and the tress was then dried by a hot air dryer (Nobby White NB 3 000 manufactured by TESCOM Company) while being combed.

[0114] 4. The tress was immersed in a container containing the second part in such an amount that the bath ratio as shown in the table is achieved, the opening of the container was closed, the container was immersed together with its contents in a water bath (manufacturer: TOYO SEISAKUSHO, Ltd./Model: TBS221FA) at the temperature as shown in the table, and heating was performed for the time as shown in the table.

[0115] 5. The container containing the tress was taken out from the water bath, and brought back to room temperature.

[0116] 6. The tress was taken out from the container, then rinsed with running tap water at 30°C for 30 seconds, lathered with evaluating shampoo for 60 seconds, rinsed with running tap water at 30°C for 30 seconds, and lightly drained with a towel, and the tress was then dried by a hot air dryer (Nobby White NB 3 000 manufactured by TESCOM Company) while being combed. At this time, the tress remained straight.

[Table 2]

			Example				
			2	3	4	5	6
First part (mass%)	(A)	4-Vinylbenzoic acid	5.0	20.	1.0	5.0	5.0
		Water	Balance	Balance	Balance	Balance	Balance
	pH adjuster	Hydrochloric acid or sodium hydroxide	*	*	*	*	*
	Total		100	100	100	100	100
	pH(25°C)		5.5	5.5	5.5	5.5	5.5
First part Treatment	Bath ratio		40	40	40	40	40
	Heating condition		40°C 1h	40°C 1h	40°C 1h	40°C 1h	40°C 1h
Second part (mass%)	(B)	2,2'-Azobis[2-(2-imidazolin-2-yl) propane] dihydrochloride (in parenthesis, amount as undissociated compound)	5.0 (3.9)	5.0 (3.9)	5.0 (3.9)	20.0 (15.5)	1.0 (0.77)
		Water	Balance	Balance	Balance	Balance	Balance
	pH adjuster	Hydrochloric acid or sodium hydroxide	*	*	*	*	*
	Total		100	100	100	100	100
	pH(25°C)		5.5	5.5	5.5	5.5	5.5
Second part Treatment	Bath ratio		40	40	40	40	40
	Heating condition		50°C 3h	50°C 3h	50°C 3h	50°C 3h	50°C 3h

(continued)

			Example				
			2	3	4	5	6
Effect	Durability improvement	Ratio of increase in average breaking elongation during fiber tensioning [%]	1.5	3.1	1.1	2.0	1.4
		Amount of increase in average breaking load during fiber tensioning [gf]	17.9	29.3	15.6	23.1	17.5
	Heat resistance improvement	Shrinkage ratio during set with iron at high temperature [%]	12.0	12.7	13.3	11.3	11.3
		Shrinkage ratio during hot-water heating [%]	37.0	37.0	47.0	9.0	29.0
	Heat shape memory	I: Shaping (curl)	37	41	32	40	41
		II: Reshaping (straight)	97	97	98	97	95
		III: Re-reshaping (curl)	39	38	36	38	44
	Surface feel quality		20	20	20	20	20
	Suppression of coloring on fibers		5	5	5	5	5
*: Amount of pH adjustment							

Comparative Example 4

[0117] Using the following formulation, regenerated collagen fibers were treated by <Treatment method> in Example 1 and Comparative Examples 1 to 3. The degree of coloring of the treated tress was evaluated in the same manner as above, and as a result, brownish coloring was found (evaluation 1).

Raw material name	Amount formulated [mass%]
Formaldehyde	10.0
Resorcin	15.0
Water	Balance
pH adjuster (hydrochloric acid or sodium hydroxide)	(Amount of pH adjustment)
Total	100.0
pH (25°C): 5.5 Bath ratio: 40 Heating condition: 50°C 3 h	

[0118] The tresses treated in Examples above can all be used directly as extensions by attachment to head hair with pins or the like, and can exhibit sufficient performance on the human head.

Claims

1. Modified regenerated collagen fibers comprising the following component (A) or a polymerized product containing the component (A) as a constituent monomer in regenerated collagen fibers:

(A) vinylbenzoic acid or a salt thereof.

2. The modified regenerated collagen fibers according to claim 1, further comprising the following component (C):
(C) a polyvalent metal, or a salt or complex thereof.

3. The modified regenerated collagen fibers according to claim 2, wherein the component (C) is aluminum, or a salt or complex thereof.

4. A method for treating regenerated collagen fibers comprising the following step (i):
step (i) immersing regenerated collagen fibers in a fiber-treating agent which is a one-part type fiber-treating agent formed of a single composition or a multiple-part type fiber-treating agent formed of a plurality of compositions, and which comprises the following component (A) and component (B) in a total composition:

(A): vinylbenzoic acid or a salt thereof; and
(B): an azo polymerization initiator.

5. The method for treating regenerated collagen fibers according to claim 4, wherein the fiber-treating agent in the step (i) is a multiple-part type fiber-treating agent comprising a first part containing the component (A) and a second part containing the component (B); and
the step (i) comprises immersing the regenerated collagen fibers in the first part, and then immersing the regenerated collagen fibers treated with the first part in the second part, or immersing the regenerated collagen fibers in the second part, and then immersing the regenerated collagen fibers treated with the second part in the first part.

6. The method for treating regenerated collagen fibers according to claim 4 or 5, wherein the regenerated collagen fibers contain the following component (C):
(C) a polyvalent metal, or a salt or complex thereof.

7. The method for treating regenerated collagen fibers according to claim 6, wherein the component (C) is aluminum, or a salt or complex thereof.

8. A method for producing modified regenerated collagen fibers, comprising treating regenerated collagen fibers by the method for treating regenerated collagen fibers according to any one of claims 4 to 7.

9. A method for producing a headdress product, comprising treating regenerated collagen fibers by the method for treating regenerated collagen fibers according to any one of claims 4 to 7.

10. A headdress product comprising the modified regenerated collagen fibers according to any one of claims 1 to 3 as a constituent element.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/018108

A. CLASSIFICATION OF SUBJECT MATTER

D06M 15/263(2006.01)i; ***D01F 4/00***(2006.01)i; *D06M 101/14*(2006.01)n
FI: D06M15/263; D01F4/00 A; D06M101:14

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)

D06M13/00-15/715; D01F4/00; D06M101/14

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 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

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.
A	WO 01/06045 A1 (KANEGAFUCHI CHEMICAL INDUSTRY CO., LTD.) 25 January 2001 (2001-01-25) claims	1-10
A	JP 2647950 B2 (KAO CORP.) 27 August 1997 (1997-08-27) claims, example 1	1-10
A	JP 11-12936 A (LION CORP.) 19 January 1999 (1999-01-19) claims, example 1, paragraph [0005]	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
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"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 **10 July 2023**	Date of mailing of the international search report **18 July 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/018108

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 01/06045 A1	25 January 2001	EP 1229156 A1 claims JP 4578749 B2 US 6713537 B1 HK 1056000 A KR 10-2002-0036833 A CN 1420949 A	
JP 2647950 B2	27 August 1997	JP 2-221463 A	
JP 11-12936 A	19 January 1999	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

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- JP 2019143281 A **[0008]**
- JP S4615033 B **[0023]**
- JP S4325829 B **[0024]**
- JP S4327513 B **[0024]**