(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 528 021 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
26.03.2025 Bulletin 2025/13

(21) Application number: **23807604.6**

(22) Date of filing: **15.05.2023**

(51) International Patent Classification (IPC):
D06M 13/188 $^{(2006.01)}$ ***D01F 4/00*** $^{(2006.01)}$
D06M 101/14 $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
D01F 4/00; D06M 13/188

(86) International application number:
PCT/JP2023/018109

(87) International publication number:
WO 2023/224002 (23.11.2023 Gazette 2023/47)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **18.05.2022 JP 2022081670**

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(54) FIBER-TREATING AGENT

(57) The present invention relates to a fiber-treating agent which improves water resistance and heat resistance problematic in naturally derived fibers, imparts heat shape memory ability, improves stretchability (tenacity) and the feel of the surfaces, and causes no coloring of naturally derived fibers. The fiber-treating agent of the present invention contains the following components (A) and (B): (A): a compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 $MPa^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring; and (B): water.

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Description

Field of the Invention

[0001] The present invention relates to a fiber-treating agent for imparting water resistance, heat resistance and heat shape memory ability to naturally derived fibers, and preferably relates to a fiber-treating agent for naturally derived fibers used in fiber products such as headdress products such as wigs and extensions.

Background of the Invention

[0002] Unlike synthetic fibers, naturally derived fibers generally have natural texture and appearance originating from a natural material. Among naturally derived fibers, regenerated protein fibers, for example, regenerated collagen fibers, are obtained by solubilizing acid-soluble collagen or by solubilizing acid-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, naturally derived fibers generally have higher hydrophilicity and hence higher water absorption as compared to synthetic fibers, and the fibers have generally low mechanical strength when they contain a large amount of water, and in particular, regenerated protein fibers have extremely low mechanical strength. This leads to deterioration of suitability as a fiber product such that during washing, mechanical strength significantly deteriorates because of the higher water absorption, and during subsequent drying, rupture occurs.

[0004] Among naturally derived fibers, regenerated protein fibers also have a 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 naturally derived 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, naturally derived fibers may be inferior to conventional plastic synthetic fibers in terms of degree of freedom of shape set.

[0006] The above points were supposed to be factors in limiting popularization of naturally derived fibers, in particular regenerated protein fibers for fiber products such as headdress 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 which are naturally derived 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).

Citation List

Patent Literature

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

Summary of the Invention

[0009] The present invention provides a fiber-treating agent comprising the following components (A) and (B):

(A): a compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 $MPa^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring; and
(B): water.

Detailed Description of the Invention

[0010] In some situations of production of fiber products such as headdress 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.

[0011] Therefore, the present invention relates to a fiber-treating agent which improves water resistance and heat resistance problematic in naturally derived fibers, imparts heat shape memory ability, improves stretchability (tenacity) and the feel of the surfaces, and causes no coloring of naturally derived fibers.

[0012] The present inventors have conducted intensive studies and as a result, found that by treating naturally derived fibers with a composition containing a compound having a carboxy group and a hydrogen bond term in Hansen solubility parameter of a certain value or less, the carboxy group of the compound penetrated into the fibers is strongly coordinated with a metal (mainly polyvalent metal) in the naturally derived fibers, so that the inside of the fibers is hydrophobized and the leakage of the compound 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 in the naturally derived fibers are improved, so that the shape can be imparted by a heat set, but also surprisingly, the stretchability (tenacity) of the naturally derived fibers 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 is caused, leading to completion of the present invention.

[0013] According to the present invention, it is possible to provide a fiber-treating agent which improves water resistance and heat resistance problematic in naturally derived fibers, can impart heat shape memory ability, improves stretchability (tenacity) and the feel of the surfaces, and further, causes no coloring of naturally derived fibers.

[Fibers to be treated in the present invention]

[0014] Fibers to be treated with the fiber-treating agent of the present invention are preferably metal-containing fibers, preferably naturally derived metal-containing fibers or synthetic metal-containing fibers, and among them, naturally derived metal-containing fibers are preferable. The naturally derived fiber refers to fibers which are taken from a natural animal or plant, or artificially produced fibers using a polymer or an oligomer, such as protein derived from keratin, collagen, casein, soybeans, peanuts, corn, silk flocks, silk protein (for example, silk fibroin) or the like or a polysaccharide, as a raw material. Among them, artificially produced fibers using a polymer or an oligomer, such as protein derived from keratin, collagen, casein, soybeans, peanuts, corn, silk flocks, silk protein (for example, silk fibroin) or the like or a polysaccharide, as a raw material are preferable, regenerated protein fibers using protein derived from keratin, collagen, casein, soybean protein, peanut protein, corn protein, silk protein (for example, silk fibroin) or the like as a raw material are more preferable, regenerated protein fibers such as regenerated collagen fibers made from collagen as a raw material or regenerated silk fibers made from silk fibroin as a raw material are more preferable, and regenerated collagen fibers are further more preferable.

[0015] 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. 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.

[0016] Synthetic metal-containing fibers may be metal-treated synthetic fibers. Naturally derived metal-containing fibers include those originally containing a metal such as fibers taken from a natural animal or plant. In this case, those originally containing a metal are not required to contain additional metal, but may be treated with a metal salt, as fibers treated with an aluminum salt to achieve water resistance as described in, for example, JP-A-2003-027318, and the like.

[Component (A): compound having hydrogen bond term δH in Hansen solubility parameter of 18.3 MPa$^{1/2}$ or less, at least one of carboxy group or salt thereof, and no fused ring]

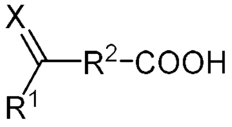
[0017] The component (A) is a compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 MPa$^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring. In the present invention, the hydrogen bond term in Hansen solubility parameter refers to δH (MPa$^{1/2}$) (the energy term by the hydrogen bond between molecules) calculated at 25°C in the DIY program using Software Package HSPiP 4th Edition 4.1.07 based on Hansen Solubility Parameters: A User's Handbook, CRC Press, Boca Raton FL, 2007. When the component (A) is a salt, examples of the salt include alkaline metal salts such as sodium salts and potassium salts.

[0018] Examples of the compound of the component (A) include the following (A1) and (A2):

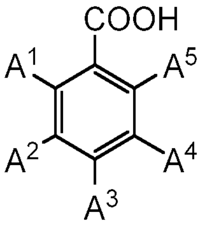
(A1) an aromatic compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 MPa$^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring; and

(A2) a compound having a hydrogen bond term δH in Hansen solubility parameter of 11.0 MPa$^{1/2}$ or more and 18.3 MPa$^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring (excluding aromatic compounds).

[0019] Examples of the aromatic compound of the component (A1) include a compound of the following formula (1) or formula (2), or a salt thereof:

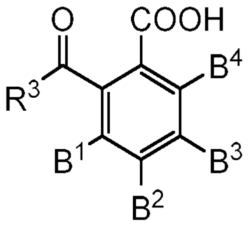

(1)

wherein =X represents a methylidene group or an oxo group, R^1 represents a hydrogen atom, a hydroxy group, or an optionally substituted alkyl group, aryl group, alkoxy group, aryloxy group, or aralkyloxy group, and R^2 is an o-phenylene group, an m-phenylene group, a p-phenylene group, a benzylidene group, or an optionally substituted alkylene group, provided that when R^2 has no aryl group, R^1 is an aryl group, an aryloxy group, or an aralkyloxy group; and

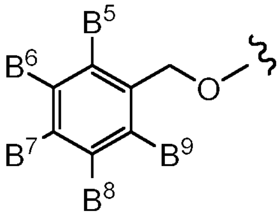

(2)

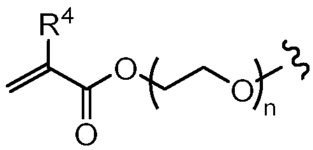
wherein A^1 to A^5 each independently represent a hydrogen atom, an acetyl group, a halogen atom, or a linear or branched alkyl group, alkenyl group, alkoxy group, or alkenyloxy group having 1 to 6 carbon atoms.

[0020] In the component (A1), examples of the aromatic compound of formula (1) include a compound of the following formula (1A), (1B), or (1C):

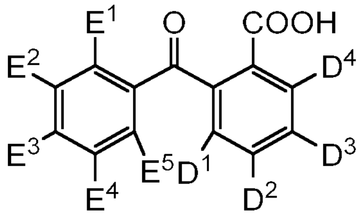

(1A)

wherein B^1 to B^4 each independently represent a hydrogen atom, an acetyl group, a halogen atom, or a linear or branched alkyl group, alkenyl group, alkoxy group, or alkenyloxy group having 1 to 6 carbon atoms, and R^3 represents a hydroxy group or a group of the following formula (1A)-a or (1A)-b:


(1A)-a

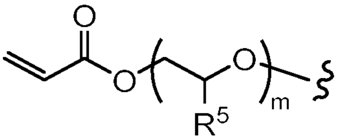

(1A)-b

wherein B^5 to B^9 represent the same meaning as the B^1 to B^4, R^4 represents a hydrogen atom or a methyl group, and n represents an integer of 0 to 2;



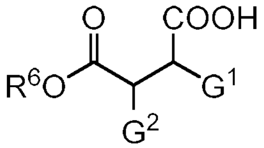
(1B)

wherein D^1 to D^4 each independently represent a hydrogen atom, an acetyl group, a halogen atom, or a linear or branched alkyl group, alkenyl group, alkoxy group, or alkenyloxy group having 1 to 6 carbon atoms, and E^1 to E^5 each independently represent the same group as D^1 to D^4 or a group of formula (1B)-a:



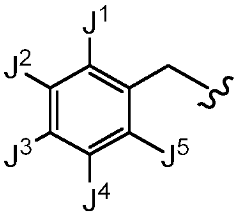
(1B)-a

wherein m represents an integer of 0 to 4; and



(1C)

wherein R^6 represents a hydrogen atom or a group of formula (1C)-a, G^1 and G^2 each independently represent a hydrogen atom, an acetyl group, a halogen atom, an optionally substituted aryl group, an aralkyl group or arylalkenyl group having 7 to 12 carbon atoms, or a linear or branched alkyl group, alkenyl group, alkoxy group, alkenyloxy group, or aroyloxy group having 1 to 6 carbon atoms, provided that when R^6 is a hydrogen atom, at least one of G^1 and G^2 is an optionally substituted aryl group, or an aralkyl group, arylalkenyl group, or aroyloxy group having 7 to 12 carbon atoms:



(1C)-a

wherein J^1 to J^5 each independently represent a hydrogen atom, an acetyl group, a halogen atom, or a linear or branched alkyl group, alkenyl group, alkoxy group, or alkenyloxy group having 1 to 6 carbon atoms.

[0021] In the compound of formula (1A), examples of the compound in which R^3 is a hydroxy group include 2-carboxy benzoic acid (phthalic acid) (hydrogen bond term δH in Hansen solubility parameter: 13.4 $MPa^{1/2}$) (hereinafter, a numerical value in parenthesis described after each compound name indicates the hydrogen bond term δH calculated by the above method) .

[0022] In the compound of formula (1A), examples of the compound in which R^3 is a group of formula (1A)-a include 2-(((4-vinylbenzyl)oxy)carbonyl)benzoic acid (7.0 $MPa^{1/2}$).

[0023] In the compound of formula (1A), examples of the compound in which R^3 is a group of formula (1A)-b include 2-((2-(acryloyloxy)ethoxy)carbonyl)benzoic acid (9.1 $MPa^{1/2}$) and 2-((2-(methacryloyloxy)ethoxy)carbonyl)benzoic acid (8.4 $MPa^{1/2}$).

[0024] Examples of the compound of formula (1B) include 2-benzoylbenzoic acid (7.5 $MPa^{1/2}$), 2-(2-methylbenzoyl) benzoic acid (6.9 $MPa^{1/2}$), 2-(3-methylbenzoyl)benzoic acid (6.6 $MPa^{1/2}$), 2-(4-methylbenzoyl)benzoic acid (7.2 $MPa^{1/2}$), 2-(2-chlorobenzoyl)benzoic acid (7.1 $MPa^{1/2}$), 2-(3-chlorobenzoyl)benzoic acid (6.9 $MPa^{1/2}$), 2-(4-chlorobenzoyl)benzoic acid (7.5 $MPa^{1/2}$), and 2-(4-(2-(2-(acryloyloxy)ethoxy)ethoxy)benzoyl)benzoic acid (8.7 $Mpa^{1/2}$).

[0025] In the compound of formula (1C), examples of the compound in which R^6 is a hydrogen atom include phenylsuccinic acid (15.8 $MPa^{1/2}$), 2,3-diphenylsuccinic acid (11.9 $MPa^{1/2}$), and (+)-di-p-toluoyl-D-tartaric acid (10.2 $MPa^{1/2}$).

[0026] In the compound of formula (1C), examples of the compound in which R^6 is a group of formula (1C)-a include 4-

oxo-4-((4-vinylbenzyl)oxy)butanoic acid (10.1 $MPa^{1/2}$).

[0027] In addition, examples of the compound which is included in formula (1) but is not included in any of formula (1A), (1B), and (1C) include 3-carboxybenzoic acid (isophthalic acid) (12.9 $MPa^{1/2}$), 4-carboxybenzoic acid (terephthalic acid) (13.7 $MPa^{1/2}$), 3-benzoylbenzoic acid (7.2 $MPa^{1/2}$), and 4-benzoylbenzoic acid (7.9 $MPa^{1/2}$). The numerical value in parenthesis described after each compound name is the hydrogen bond term δH calculated by the above method.

[0028] In the component (A1), specific examples of the aromatic compound of formula (2) include benzoic acid (9.5 $MPa^{1/2}$), 2-methylbenzoic acid (8.4 $MPa^{1/2}$), 3-methylbenzoic acid (8.0 $MPa^{1/2}$), 4-methylbenzoic acid (8.8 $MPa^{1/2}$), 2-ethylbenzoic acid (7.7 $MPa^{1/2}$), 3-ethylbenzoic acid (7.4 $MPa^{1/2}$), 4-ethylbenzoic acid (8.1 $MPa^{1/2}$), 2-propylbenzoic acid (7.0 $MPa^{1/2}$), 3-propylbenzoic acid (6.7 $MPa^{1/2}$), 4-propylbenzoic acid (7.4 $MPa^{1/2}$), 2-isopropylbenzoic acid (6.7 $MPa^{1/2}$), 3-isopropylbenzoic acid (6.5 $MPa^{1/2}$), 4-isopropylbenzoic acid (7.1 $MPa^{1/2}$), 2-n-butylbenzoic acid (6.8 $MPa^{1/2}$), 3-n-butylbenzoic acid (6.5 $MPa^{1/2}$), 4-n-butylbenzoic acid (7.2 $MPa^{1/2}$), 2-tert-butylbenzoic acid (6.1 $MPa^{1/2}$), 3-tert-butylbenzoic acid (5.9 $MPa^{1/2}$), 4-tert-butylbenzoic acid (6.5 $MPa^{1/2}$), 2-vinylbenzoic acid (8.0 $MPa^{1/2}$), 3-vinylbenzoic acid (7.7 $MPa^{1/2}$), 4-vinylbenzoic acid (8.5 $MPa^{1/2}$), 2-acetylbenzoic acid (8.6 $MPa^{1/2}$), 3-acetylbenzoic acid (8.2 $MPa^{1/2}$), 4-acetylbenzoic acid (8.9 $MPa^{1/2}$), 2-methoxybenzoic acid (9.7 $MPa^{1/2}$), 3-methoxybenzoic acid (9.3 $MPa^{1/2}$), 4-methoxybenzoic acid (10.1 $MPa^{1/2}$), 2-chlorobenzoic acid (8.7 $MPa^{1/2}$), 3-chlorobenzoic acid (8.4 $MPa^{1/2}$), 4-chlorobenzoic acid (9.2 $MPa^{1/2}$), 2-bromobenzoic acid (9.1 $MPa^{1/2}$), 3-bromobenzoic acid (8.8 $MPa^{1/2}$), and 4-bromobenzoic acid (10.1 $MPa^{1/2}$). Among them, 4-ethylbenzoic acid, 4-vinylbenzoic acid, and benzoic acid are preferable.

[0029] In the component (A1), examples of the compound other than the compounds of formulas (1) and (2) include phenylbutanoic acid.

[0030] Examples of the compound of the component (A2) include potassium 2,4-hexadienoate (12.5 $MPa^{1/2}$).

[0031] The hydrogen bond term δH of the aromatic compound of the component (A1) is preferably 16.0 $MPa^{1/2}$ or less, more preferably 13.5 $MPa^{1/2}$ or less, further more preferably 12.0 $MPa^{1/2}$ or less, further more preferably 10.0 $MPa^{1/2}$ or less, and preferably 3.0 $MPa^{1/2}$ or more, more preferably 4.0 $MPa^{1/2}$ or more, further more preferably 5.0 $MPa^{1/2}$ or more, from the viewpoint of moderately hydrophobizing the inside of fibers.

[0032] The hydrogen bond term δH of the compound of the component (A2) is preferably 16.0 $MPa^{1/2}$ or less, more preferably 15.0 $MPa^{1/2}$ or less, further more preferably 14.0 $MPa^{1/2}$ or less, further more preferably 13.0 $MPa^{1/2}$ or less, and preferably 11.0 $MPa^{1/2}$ or more, more preferably 11.5 $MPa^{1/2}$ or more, further more preferably 12.0 $MPa^{1/2}$ or more, from the viewpoint of moderately hydrophobizing the inside of fibers.

[0033] Hereinafter, the preferred content of the component (A) is described in accordance with the kind of the component (A). Here, in the present invention, in the case where the component (A) is a salt, the content of the component (A) refers to the content of the corresponding acid form. The content of the component (A) varies different depending on the pH range of the fiber-treating agent, and the following range is preferable.

[0034] Particularly with respect to benzoic acid or a salt thereof (hereinafter, sometimes referred to as "the component (A1-1)") which is the component (A1) in the component (A), when a pH of the fiber-treating agent is 2.0 or more and less than 6.5, the content of the component (A1-1) in the fiber-treating agent is, as benzoic acid (acid form), preferably 0.8 mass% or more, more preferably 3.0 mass% or more, further more preferably 5.0 mass% or more, even more preferably 10 mass% or more, even more preferably 15 mass% or more, even more preferably 20 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 treated naturally derived fibers, and preferably 90 mass% or less, more preferably 80 mass% or less, further more preferably 70 mass% or less, even more preferably 50 mass% or less, further more preferably 40 mass% or less, even more preferably 35 mass% or less, from the viewpoint of improving the feel of the fiber surfaces.

[0035] That is, when the component (A) is (A1-1) benzoic acid or a salt thereof and the pH of the fiber-treating agent is 2.0 or more and less than 6.5, the content of the component (A1-1) in the fiber-treating agent of the present invention is, as benzoic acid (acid form), preferably from 0.8 to 90 mass%, more preferably from 3.0 to 80 mass%, further more preferably from 5.0 to 70 mass%, even more preferably from 10 to 50 mass%, even more preferably from 15 to 40 mass%, even more preferably from 20 to 35 mass%, from the above viewpoint.

[0036] When the component (A) is (A1-1) benzoic acid or a salt thereof and the pH of the fiber-treating agent is 6.5 or more and 11.0 or less, the content of the component (A1-1) in the fiber-treating agent is, as benzoic acid (acid form), preferably 0.8 mass% or more, more preferably 3.0 mass% or more, further more preferably 5.0 mass% or more, even more preferably 10 mass% or more, even more preferably 15 mass% or more, even more preferably 20 mass% or more, even more preferably 25 mass% or more, even more preferably 26 mass% or more, even more preferably 28 mass% or more, even more preferably 30 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 treated naturally derived fibers, and preferably 90 mass% or less, more preferably 80 mass% or less, further more preferably 70 mass% or less, even more preferably 50 mass% or less, even more preferably 45 mass% or less, even more preferably 40 mass% or less, from the viewpoint of improving the feel of the fiber surfaces.

[0037] That is, when the component (A) is (A1-1) benzoic acid or a salt thereof and the pH of the fiber-treating agent is 6.5

or more and 11.0 or less, the content of the component (A1-1) in the fiber-treating agent of the present invention is, as benzoic acid (acid form), preferably from 0.8 to 90 mass%, more preferably from 3.0 to 80 mass%, further more preferably from 5.0 to 70 mass%, even more preferably from 10 to 70 mass%, even more preferably from 15 to 50 mass%, even more preferably from 20 to 50 mass%, even more preferably from 25 to 45 mass%, even more preferably from 26 to 45 mass%, even more preferably from 28 to 40 mass%, even more preferably from 30 to 40 mass%, from the above viewpoint.

[0038] With respect to a component (A1) other than benzoic acid or a salt thereof (hereinafter, sometimes referred to as "the component (A1-2)") in the component (A), when the pH of the fiber-treating agent is 2.0 or more and less than 6.5, the content of the component (A1-2) in the fiber-treating agent is 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 treated naturally derived fibers, and preferably 70 mass% or less, more preferably 60 mass% or less, further more preferably 50 mass% or less, even more preferably 45 mass% or less, from the viewpoint of improving the feel of the fiber surfaces.

[0039] That is, when the component (A) is (A1-2) (the component (A1) other than benzoic acid or a salt thereof) and the pH of the fiber-treating agent is 2.0 or more and less than 6.5, the content of the component (A1-2) in the fiber-treating agent of the present invention is preferably from 0.1 to 70 mass%, more preferably from 0.2 to 60 mass%, further more preferably from 0.5 to 50 mass%, even more preferably from 1.0 to 45 mass%, from the above viewpoint.

[0040] When the component (A) is (A1-2) (the component (A1) other than benzoic acid or a salt thereof) and the pH of the fiber-treating agent is 6.5 or more and 11.0 or less, the content of the component (A1-2) in the fiber-treating agent is 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 treated naturally derived fibers, 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.

[0041] That is, when the component (A) is (A1-2) (the component (A1) other than benzoic acid or a salt thereof) and the pH of the fiber-treating agent is 6.5 or more and 11.0 or less, the content of the component (A1-2) in the fiber-treating agent of the present invention is preferably from 1.0 to 70 mass%, more preferably from 2.0 to 60 mass%, further more preferably from 5.0 to 50 mass%, even more preferably from 10 to 40 mass%, from the above viewpoint.

[0042] When the component (A) is the component (A2) and the pH of the fiber-treating agent is 2.0 or more and less than 6.5, the content of the component (A2) in the fiber-treating agent is 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 treated naturally derived fibers, and preferably 60 mass% or less, more preferably 50 mass% or less, further more preferably 40 mass% or less, even more preferably 30 mass% or less, from the viewpoint of improving the feel of the fiber surfaces.

[0043] That is, when the component (A) is the component (A2) and the pH of the fiber-treating agent is 2.0 or more and less than 6.5, the content of the component (A2) in the fiber-treating agent of the present invention is preferably from 0.1 to 60 mass%, more preferably from 0.2 to 50 mass%, further more preferably from 0.5 to 40 mass%, even more preferably from 1.0 to 30 mass%, from the above viewpoint.

[0044] When the component (A) is the component (A2) and the pH of the fiber-treating agent is 6.5 or more and 11.0 or less, the content of the component (A2) in the fiber-treating agent is 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 treated naturally derived fibers, 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.

[0045] That is, when the component (A) is the component (A2) and the pH of the fiber-treating agent is 6.5 or more and 11.0 or less, the content of the component (A2) in the fiber-treating agent is preferably from 1.0 to 70 mass%, more preferably from 2.0 to 60 mass%, further more preferably from 5.0 to 50 mass%, even more preferably from 10 to 40 mass%, from the above viewpoint.

[0046] When two or more compounds are contained as the component (A) in the fiber-treating agent, the solubility of the entire component (A) tends to be increased. Thus, the fiber-treating agent preferably contains two or more compounds as the component (A), from the viewpoint of improving the solubility of the entire component (A) to reduce the turbidity of the fiber-treating agent, allowing fibers to be uniformly treated, and thereby improving the feel of fiber surfaces after treatment. When the fiber-treating agent contains two or more compounds as the component (A), at least one compound is preferably an aromatic compound of formula (2), and more preferably benzoic acid or a salt thereof. When the aromatic compound of formula (2) is contained in the component (A), the content of the above compound is preferably the highest among the components (A), and when benzoic acid or a salt thereof is contained, the content of the above compound is more preferably the highest among the components (A).

[0047] When the pH of the fiber-treating agent is 2.0 or more and less than 6.5 and the fiber-treating agent contains two or more compounds as the component (A), the content of the component (A) left after excluding a compound present at the highest concentration in the entire component (A) in the fiber-treating agent is preferably 0.1 mass% or more, more preferably 0.5 mass% or more, further more preferably 1.0 mass% or more, and preferably 20 mass% or less, more preferably 10 mass% or less, further more preferably 5.0 mass% or less, from the viewpoint of improving the solubility of the entire component (A) to reduce the turbidity of the fiber-treating agent, allowing fibers to be uniformly treated, and thereby improving the feel of fiber surfaces after treatment.

[0048] When the pH of the fiber-treating agent is 6.5 or more and 11.0 or less and the fiber-treating agent contains two or more compounds as the component (A), the content of the component (A) left after excluding a compound present at the highest concentration in the entire component (A) in the fiber-treating agent is preferably 0.5 mass% or more, more preferably 1.0 mass% or more, further more preferably 2.0 mass% or more, and preferably 30 mass% or less, more preferably 20 mass% or less, further more preferably 10 mass% or less, from the viewpoint of improving the solubility of the entire component (A) to reduce the turbidity of the fiber-treating agent, allowing fibers to be uniformly treated, and thereby improving the feel of fiber surfaces after treatment.

[0049] In whichever case of the pH of the fiber-treating agent, when the fiber-treating agent contains two or more compounds as the component (A), a mass ratio of the component (A) left after excluding a compound present at the highest concentration in the entire component (A) to the compound in the fiber-treating agent (a mass of the component (A) left after excluding a compound present at the highest concentration in the entire component (A))/(a mass of the compound present at the highest concentration in the component (A)) is preferably 0.01 or more, more preferably 0.05 or more, further more preferably 0.10 or more, and preferably 1.0 or less, more preferably 0.5 or less, further more preferably 0.25 or less, from the viewpoint of improving the solubility of the entire component (A) to reduce the turbidity of the fiber-treating agent, allowing fibers to be uniformly treated, and thereby improving the feel of fiber surfaces after treatment.

[Component (B): water]

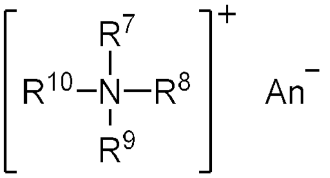
[0050] The fiber-treating agent of the present invention contains water as a medium. The content of the component (B) in the fiber-treating agent of the present invention is preferably 10 mass% or more, more preferably 20 mass% or more, further more preferably 30 mass% or more, even more preferably 40 mass% or more, and preferably 99 mass% or less, more preferably 95 mass% or less, further more preferably 90 mass% or less, even more preferably 85 mass% or less.

[0051] That is, the content of the component (B) in the fiber-treating agent of the present invention is preferably from 10 to 99 mass%, more preferably from 20 to 95 mass%, further more preferably from 30 to 90 mass%, even more preferably from 40 to 85 mass%.

[Cationic surfactant]

[0052] The fiber-treating agent of the present invention may contain a cationic surfactant as long as the effects of the present invention are not impaired. The cationic surfactant is preferably a long chain monoalkyl quaternary ammonium salt having one alkyl group having 8 to 24 carbon atoms and three alkyl groups having 1 to 4 carbon atoms.

[0053] Preferably, at least one long chain monoalkyl quaternary ammonium surfactant is selected from the group consisting of compounds of the following formula (3):



$$\left[R^{10}-\overset{\displaystyle R^{7}}{\underset{\displaystyle R^{9}}{N}}-R^{8} \right]^{+} An^{-} \qquad (3)$$

wherein R^7 is a saturated or unsaturated linear or branched alkyl group having 8 to 22 carbon atoms, R^{11}-CO-NH-$(CH_2)_m$- or R^{11}-CO-O-$(CH_2)_m$- (R^{11} represents a saturated or unsaturated linear or branched alkyl chain having 7 to 21 carbon atoms, and p represents an integer of 1 to 4), R^8, R^9 and R^{10} independently represent an alkyl group having 1 to 4 carbon atoms, or a hydroxyalkyl group having 1 to 4 carbon atoms, and An^- represents a chloride ion, a bromide ion, a methosulfate ion or an ethosulfate ion.

[0054] Examples of the suitable cationic surfactant include long chain quaternary ammonium compounds such as cetyltrimethylammonium chloride, myristyltrimethylammonium chloride, behentrimonium chloride, cetyltrimethylammonium bromide and stearamidopropyltrimonium chloride. One of them may be used alone, or a mixture thereof may be used.

[0055] The content of the cationic surfactant in the fiber-treating agent of the present invention is preferably 0.05 mass%

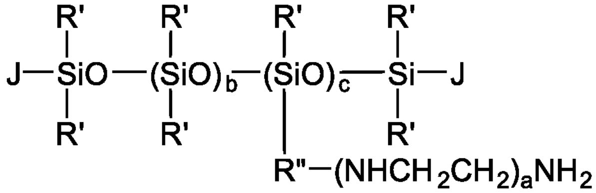
or more, more preferably 0.10 mass% or more, and preferably 10 mass% or less, more preferably 5.0 mass% or less, from the viewpoint of improving the feel of the surfaces of naturally derived fibers after treatment, and further improving the effects of the present invention.

[Silicone]

[0056] The fiber-treating agent of the present invention may contain silicone from the viewpoint of improving the feel of the surfaces of naturally derived fibers after treatment, and improving styling ease. The silicone is preferably one or more selected from the group consisting of dimethylpolysiloxane and amino-modified silicone.

[0057] As the dimethylpolysiloxane, any of cyclic or acyclic dimethylsiloxane polymers can be used, and examples thereof include SH200 Series, BY22-019, BY22-020, BY11-026, B22-029, BY22-034, BY22-050A, BY22-055, BY22-060, BY22-083 and FZ-4188 (each manufactured by Dow Corning Toray), and KF-9088, KM-900 Series, MK-15H and MK-88 (each manufactured by Shin-Etsu Chemical Co., Ltd.).

[0058] As the amino-modified silicone, any silicone having an amino group or an ammonium group can be used, and examples thereof include amino-modified silicone oil which is terminal-blocked at all or a part of terminal hydroxyl groups with a methyl group or the like, and amodimethicone which is not terminal-blocked. Examples of the amino-modified silicone preferable from the viewpoint of improving the feel of the surfaces of naturally derived fibers after treatment and improving styling ease include compounds of the following formula:



$$J-\overset{R'}{\underset{R'}{\mathrm{Si}}}O-(\overset{R'}{\underset{R'}{\mathrm{Si}}}O)_b-(\overset{R'}{\underset{R''-(NHCH_2CH_2)_aNH_2}{\mathrm{Si}}}O)_c-\overset{R'}{\underset{R'}{\mathrm{Si}}}-J$$

wherein R' represents a hydrogen atom, a hydroxy group or R^X, where R^X represents a substituted or unsubstituted monovalent hydrocarbon group having 1 to 20 carbon atoms, J represents R^X, $R''-(NHCH_2CH_2)aNH_2$, OR^X or a hydroxy group, R" represents a divalent hydrocarbon group having 1 to 8 carbon atoms, a represents a number of 0 to 3, and b and c represent numbers whose sum is 10 or more and less than 20 000, preferably 20 or more and less than 3 000, more preferably 30 or more and less than 1 000, further more preferably 40 or more and less than 800, in terms of number average.

[0059] Specific examples of the suitable commercially available product of amino-modified silicone include amino-modified silicone oils such as SF8452C and SS3551 (each manufactured by Dow Corning Toray) and KF-8004, KF-867S and KF-8015 (each manufactured by Shin-Etsu Chemical Co., Ltd.), and amodimethicone emulsions such as SM8704C, SM8904, BY22-079, FZ-4671 and FZ4672 (each manufactured by Dow Corning Toray).

[0060] The content of silicone in the fiber-treating agent of the present invention is preferably 0.1 mass% or more, more preferably 0.2 mass% or more, further more preferably 0.5 mass% or more, and preferably 20 mass% or less, more preferably 10 mass% or less, further more preferably 5.0 mass% or less, from the viewpoint of improving the feel of the surfaces of naturally derived fibers after treatment, and further improving the effects of the present invention.

[Cationic polymer]

[0061] The fiber-treating agent of the present invention may contain a cationic polymer from the viewpoint of improving the feel of the surfaces of naturally derived fibers after treatment.

[0062] The cationic polymer refers to a polymer having a cationic group, or a group capable of being ionized into a cationic group, and also includes an amphoteric polymer which is cationic as a whole. That is, examples of the cationic polymer include those in the form of an aqueous solution, which contain an amino group or an ammonium group on the side chain of the polymer chain or contain a diallyl quaternary ammonium salt as a constituent unit, for example, cationized cellulose derivatives, cationic starch, cationized guar gum derivatives, polymers or copolymers of a diallyl quaternary ammonium salt, and quaternized polyvinylpyrrolidone derivatives. Among them, one or more selected from the group consisting of a polymer containing a diallyl quaternary ammonium salt as a constituent unit, a quaternized polyvinylpyrrolidone derivative and a cationized cellulose derivative are preferable, and one or more selected from the group consisting of a polymer or copolymer of a diallyl quaternary ammonium salt and a cationized cellulose derivative are more preferable, from the viewpoint of improving the effects of softness in the feel, smoothness and finger-combability during rinsing and shampooing and ease of styling and moisture retainability during drying, and the stability of the agent.

[0063] Specific examples of the suitable polymer or copolymer of a diallyl quaternary ammonium salt include dimethyldiallylammonium chloride polymers (polyquaternium-6, for example, MERQUAT 100; Lubrizol Advanced Materials, Inc.), dimethyldiallylammonium chloride/acrylic acid copolymers (polyquaternium-22, for example, MERQUATs 280 and 295; Lubrizol Advanced Materials, Inc.), and dimethyldiallylammonium chloride/acrylamide copolymers (polyquaternium-7, for example, MERQUAT 550; Lubrizol Advanced Materials, Inc.).

[0064] Specific examples of the suitable quaternized polyvinylpyrrolidone derivative include polymers obtained by polymerizing a vinylpyrrolidone copolymer and dimethylaminoethyl methacrylate (polyquaternium 11, for example, GAFQUAT 734, GAFQUAT 755 and GAFQUAT 755N (Ashland Inc.)).

[0065] Specific examples of the suitable cationized cellulose include polymers obtained by adding glycidyltrimethylammonium chloride to hydroxycellulose (polyquaternium 10, for example, LEOGARDs G and GP (Lion Corporation) and POLYMERs JR-125, JR-400, JR-30M, LR-400 and LR-30M (Amerchol Corporation)), and hydroxyethylcellulose dimethyldiallylammonium chloride (polyquaternium-4, for example, CELQUATs H-100 and L-200 (Akzo Nobel N.V.)).

[0066] The content of the cationic polymer in the fiber-treating agent of the present invention is preferably 0.001 mass% or more, more preferably 0.01 mass% or more, further more preferably 0.05 mass% or more, and preferably 20 mass% or less, more preferably 10 mass% or less, from the viewpoint of improving the feel of the surfaces of naturally derived fibers after treatment.

[0067] Further, the fiber-treating agent of the present invention may contain an antioxidant such as ascorbic acid, and a pH adjuster such as sodium hydroxide, potassium hydroxide, phosphoric acid or hydrochloric acid.

[pH]

[0068] The pH of the fiber-treating agent of the present invention 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 naturally derived fibers. The pH in the present invention is a value at 25°C.

[0069] That is, the pH of the fiber-treating agent of the present invention 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 naturally derived fibers.

[Method for storing fiber-treating agent]

[0070] When the fiber-treating agent produced as described above is transported and stored before being applied to fibers, or a raw material before preparation of the fiber-treating agent is transported and stored, the storage temperature can be set to a cool temperature or a high temperature or gap portions in a storage container can be filled with nitrogen for the purpose of preventing progress of an unintentional reaction or recrystallization of the component (A) during transportation .

[0071] The storage temperature of the fiber-treating agent is preferably 1°C or higher, more preferably 2°C or higher, further more preferably 5°C or higher, from the viewpoint of preventing occurrence of freezing and recrystallization, and preferably 25°C or lower, more preferably 20°C or lower, further more preferably 15°C or lower, from the viewpoint of preventing coloring by oxidation and progress of an unintentional reaction.

[0072] The storage temperature of the fiber-treating agent is preferably 20°C or higher, more preferably 30°C or higher, further more preferably 40°C or higher, from the viewpoint of preventing recrystallization of a highly concentrated solution, and preferably 80°C or lower, more preferably 70°C or lower, further more preferably 60°C or lower, from the viewpoint of preventing coloring by oxidation and progress of an unintentional reaction.

[Method for treating fibers]

(Basic treatment)

[0073] By using the fiber-treating agent of the present invention and treating naturally derived fibers with a method comprising the following step (i), it is possible to improve water resistance and heat resistance which are problems of naturally derived fibers, impart heat shape memory ability, and improve stretchability (tenacity) and the feel of the surfaces.

[0074] Step (i) Immersing naturally derived fibers in the fiber-treating agent of the present invention.

[0075] In the step (i), the naturally derived fibers immersed in the fiber-treating agent may be dry or wet. The amount of the fiber-treating agent in which the naturally derived fibers are immersed is preferably 2 or more, more preferably 3 or more, further more preferably 5 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 naturally derived fibers (mass of fiber-treating agent/mass of naturally derived fibers).

[0076] That is, the bath ratio is preferably from 2 to 500, more preferably from 3 to 250, further more preferably from 5 to 100, even more preferably from 10 to 100, even more preferably from 20 to 100.

[0077] In the step (i), the naturally derived fibers may be fixed with a curler or the like, followed by immersion in the fiber-treating agent of the present invention under heating. This enables a desired shape to be imparted to the naturally derived fibers together with heat shape memory ability and high durability.

[0078] It is preferable that the immersion of the naturally derived 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 naturally derived fibers in the fiber-treating agent being heated, or by immersing the naturally derived 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 for increasing interaction of the component (A) with fiber constituent molecules, for example protein molecules, in the naturally derived fibers to obtain the effects of the present invention, and preferably lower than 100°C, more preferably 80°C or lower, further more preferably 70°C or lower, further more preferably 60°C or lower for preventing the naturally derived fibers from being degenerated by heat and thus degraded.

[0079] 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 naturally derived 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 naturally derived fibers.

[0080] 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 naturally derived 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.

[0081] After the step (i), naturally derived 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 naturally derived fibers by an excess component (A).

[0082] These treatments may allow the component (A) to penetrate into the naturally derived fibers, and to be strongly coordinated with metals in the fibers, for example, polyvalent metals, thereby producing various effects.

[Optionally added treatment]

[0083] One or more treatments selected from the group consisting of bleaching, dyeing, surface finish for imparting hydrophobicity and reducing friction, and heating treatment for further improving fiber stretchability (tenacity) may be performed in addition to the step (i).

[0084] Here, the treatments of bleaching and dyeing may be performed before or after the step (i). A plurality of steps may be combined and added, and when both bleaching and dyeing are added, any of the treatments may be performed first except that it is necessary to perform bleaching before dyeing. It is also possible to perform another treatment between bleaching and dyeing.

[0085] On the other hand, surface finish for imparting hydrophobicity and reducing friction and heating treatment for further improving fiber stretchability (tenacity) need to be performed after the step (i), but their treatment order relation with bleaching and dyeing is not particularly limited. One of surface finish for imparting hydrophobicity and reducing friction and heating treatment for further improving fiber stretchability (tenacity) may be performed before or after the other.

(Bleaching)

[0086] The bleaching is performed by immersing naturally derived fibers in a bleach composition containing an alkali agent, an oxidizing agent and water. The bleach composition is typically composed of two-part formulation. The first part contains an alkali agent and water, and the second part contains an oxidizing agent and water. These two parts are typically stored separately, and mixed before immersion of naturally derived fibers.

[0087] Examples of the suitable alkali agent include, but are not limited to, ammonia and salts thereof; alkanolamines (monoethanolamine, isopropanolamine, 2-amino-2-methylpropanol, 2-aminobutanol and the like) and salts thereof; alkanediamines (1,3-propanediamine and the like) and salts thereof; carbonates (guanidine carbonate, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate and the like); and mixtures thereof.

[0088] The content of the alkali agent in the bleach composition (mixture of first part and second part for two-part type) is preferably 0.1 mass% or more, more preferably 0.5 mass% or more, further more preferably 1.0 mass% or more, and preferably 15 mass% or less, more preferably 10 mass% or less, further more preferably 7.5 mass% or less.

[0089] Examples of the suitable oxidizing agent include, but are not limited to, hydrogen peroxide, urea peroxide, melamine peroxide and sodium bromate. Among these oxidizing agents, hydrogen peroxide is preferable.

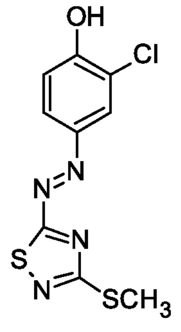
[0090] The content of the oxidizing agent in the bleach composition is preferably 1 mass% or more, more preferably 2 mass% or more, and preferably 15 mass% or less, more preferably 12 mass% or less, further more preferably 9 mass% or less.

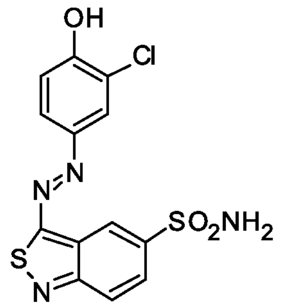
[0091] When the first part and the second part are stored separately, the pH of the second part at 25°C is preferably 2.0 or more, more preferably 2.5 or more, and preferably 6.0 or less, more preferably 4.0 or less. The pH can be adjusted by a suitable buffering agent. The pH of the bleach composition at 25°C is preferably 6 or more, more preferably 6.5 or more, further more preferably 6.8 or more, and preferably 11.0 or less, more preferably 10.5 or less, further more preferably 10.0 or less.

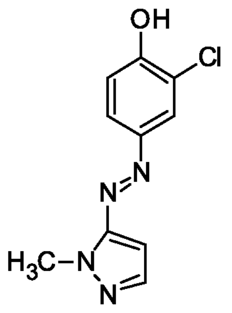
(Dyeing)

[0092] The dyeing is performed by immersing naturally derived fibers in a hair dye composition. The hair dye composition contains a dye, and optionally contains an alkali agent or an acid, an oxidizing agent or the like. Examples of the dye include direct dyes, oxidative dyes, and combinations thereof.

[0093] The type of the direct dye is not particularly limited, and any direct dye suitable for dyeing can be used. Examples of the direct dye include anionic dyes, nitro dyes, disperse dyes, cationic dyes, and dyes having an azo-phenol structure selected from the group consisting of the following HC Red 18, HC Blue 18 and HC Yellow 16, salts thereof, and mixtures thereof.


HC Red 18


HC Blue 18


HC Yellow 16

[0094] Examples of the cationic dye include, but are not limited to, Basic Blue 6, Basic Blue 7, Basic Blue 9, Basic Blue 26, Basic Blue 41, Basic Blue 99, Basic Brown 4, Basic Brown 16, Basic Brown 17, Natural Brown 7, Basic Green 1, Basic Orange 31, Basic Red 2, Basic Red 12, Basic Red 22, Basic Red 51, Basic Red 76, Basic Violet 1, Basic Violet 2, Basic Violet 3, Basic Violet 10, Basic Violet 14, Basic yellow 57, Basic Yellow 87, and mixtures thereof. Basic Red 51, Basic Orange 31, Basin Yellow 87 and Mixtures thereof are particularly preferable.

[0095] Examples of the anionic dye include, but are not limited to, Acid Black 1, Acid Blue 1, Acid Blue 3, Food Blue 5, Acid Blue 7, Acid Blue 9, Acid Blue 74, Acid Orange 3, Acid Orange 4, Acid Orange 6, Acid Orange 7, Acid Orange 10, Acid Red 1, Acid Red 14, Acid Red 18, Acid Red 27, Acid Red 33, Acid Red 50, Acid Red 52, Acid Red 73, Acid Red 87, Acid Red 88, Acid Red 92, Acid Red 155, Acid Red 180, Acid Violet 2, Acid Violet 9, Acid Violet 43, Acid Violet 49, Acid Yellow 1, Acid Yellow 10, Acid Yellow 23, Acid Yellow 3, Food Yellow No. 8, D&C Brown No. 1, D&C Green No. 5, D&C Green No. 8, D&C Orange No. 4, D&C Orange No. 10, D&C Orange No. 11, D&C Red No. 21, D&C Red No. 27, D&C Red No. 33, D&C Violet 2, D&C Yellow No. 7, D&C Yellow No. 8, D&C Yellow No. 10, FD&C Red 2, FD&C Red 40, FD&C Red No. 4, FD&C Yellow No. 6, FD&C Blue 1, Food Black 1, Food Black 2, alkali metal salts (sodium salts, potassium salts and the like) thereof, and mixtures thereof.

[0096] Among them, preferred anionic dyes are Acid Black 1, Acid Red 52, Acid Violet 2, Acid Violet 43, Acid Red 33, Acid Orange 4, Acid Orange 7, Acid Red 27, Acid Yellow 3, Acid Yellow 10, and salts thereof. More preferred anionic dyes are Acid Red 52, Acid Violet 2, Acid red 33, Acid Orange 4, Acid Yellow 10, and salts and mixtures thereof.

[0097] Examples of the nitro dye include, but are not limited to, HC Blue No. 2, HC Blue No. 4, HC Blue No. 5, HC Blue No. 6, HC Blue No. 7, HC Blue No. 8, HC Blue No. 9, HC Blue No. 10, HC Blue No. 11, HC Blue No. 12, HC Blue No. 13, HC Brown No. 1, HC Brown No. 2, HC Green No. 1, HC Orange No. 1, HC Orange No. 2, HC Orange No. 3, HC Orange No. 5, HC Red BN, HC Red No. 1, HC Red No. 3, HC Red No. 7, HC Red No. 8, HC Red No. 9, HC Red No. 10, HC Red No. 11, HC Red No. 13, HC Red No. 54, HC Red No. 14, HC Violet BS, HC Violet No. 1, HC Violet No. 2, HC Yellow No. 2, HC Yellow No. 4, HC Yellow No. 5, HC Yellow No. 6, HC Yellow No. 7, HC Yellow No. 8, HC Yellow No. 9, HC Yellow No. 10, HC Yellow No. 11, HC Yellow No. 12, HC Yellow No. 13, HC Yellow No. 14, HC Yellow No. 15, 2-amino-6-chloro-4-nitrophenol, picramic acid, 1,2-diamino-4-nitrobenzole, 1,4-diamino-2-nitrobenzole, 3-nitro-4-aminophenol, 1-hydroxy-2-amino-3-nitrobenzole, 2-hydroxyethylpicramic acid, and mixtures thereof.

[0098] Examples of the disperse dye include, but are not limited to, Disperse Blue 1, Disperse Black 9, Disperse Violet 1, and mixtures thereof.

[0099] One of these direct dyes may be used alone, or two or more thereof may be used in combination. Direct dyes different in ionicity may be used in combination.

[0100] The content of the direct dye in the hair dye composition is preferably 0.001 mass% or more, more preferably 0.01 mass% or more, further more preferably 0.05 the mass% or more, from the viewpoint of obtaining sufficient dyeability, and preferably 10 mass% or less, more preferably 7.5 mass% or less, further more preferably 5.0 mass% or less, further more preferably 3.0 mass% or less, from the viewpoint of compatibility.

[0101] When the hair dye composition contains only direct dyes, an oxidizing agent is not necessary for dyeing naturally derived fibers. When it is desirable that the color of naturally derived fibers be lighter, the composition may contain an oxidizing agent.

[0102] When the hair dye composition contains an oxidative dye, the composition is typically of two-part type. The first part contains an oxidative dye intermediate (precursor and coupler) and an alkali agent, and the second part contains an oxidizing agent such as hydrogen peroxide. These two parts are typically stored separately, and mixed before immersion of naturally derived fibers.

[0103] The oxidative dye intermediate is not particularly limited, and it is possible to suitably use any known of precursors and couplers which are commonly used for dyed products.

[0104] Examples of the precursor include, but are not limited to, paraphenylenediamine, toluene-2,5-diamine, 2-chloroparaphenylenediamine, N-methoxyethyl-para-phenylenediamine, N-phenylparaphenylenediamine, N,N-bis(2-hydroxyethyl)-paraphenylenediamine, 2-(2-hydroxyethyl)-paraphenylenediamine, 2,6-dimethyl-paraphenylenediamine, 4,4'-diaminodiphenylamine, 1,3-bis(N-(2-hydroxyethyl)-N-(4-aminophenyl)amino)-2-propanol, PEG-3,3,2'-paraphenylenediamine, paraaminophenol, paramethylaminophenol, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 2-(2-hydroxyethylaminoethyl)-4-aminophenol, ortho-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-acetamidephenol, 3,4-diaminobenzoic acid, 5-aminosalicylic acid, 2,4,5,6-tetraaminopyrimidine, 2,5,6-triamino-4-hydroxypyrimidine, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1-hydroxyethylpyrazole, salts of these substances, and mixture thereof.

[0105] Examples of the coupler include, but are not limited to, metaphenylenediamine, 2,4-diaminophenoxyethanol, 2-amino-4-(2-hydroxyethylamino)anisole, 2,4-diamino-5-methylphenetole, 2,4-diamino-5-(2-hydroxyethoxy)toluene, 2,4-dimethoxy-1,3-diaminobenzene, 2,6-bis(2-hydroxyethylamino) toluene, 2,4-diamino-5-fluorotoluene, 1,3-bis(2,4-diaminophenoxy)propane, metaaminophenol, 2-methyl-5-aminophenol, 2-methyl-5-(2-hydroxyethylamino)phenol, 2,4-dichloro-3-aminophenol, 2-chloro-3-amino-6-methylphenol, 2-methyl-4-chloro-5-aminophenol, N-cyclopentyl-metaaminophenol, 2-methyl-4-methoxy-5-(2-hydroxyethylamino)phenol, 2-methyl-4-fluoro-5-aminophenol, paraaminoorthocresol, resorcin, 2-methylresorcin, 4-chlororesorcin, 1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2-isopropyl-5-methylphenol, 4-hydroxyindole, 5-hydroxyindole, 6-hydroxyindole, 7-hydroxyindole, 6-hydroxybenzomorpholine, 3,4-methylenedioxyphenol, 2-bromo-4,5-methylenedioxyphenol, 3,4-methylenedioxyaniline, 1-(2-hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dimethoxy-3,5-diaminopyridine, 2,3-diamino-6-methoxypyridine, 2-methylamino-3-amino-6-methoxypyridine, 2-amino-3-hydroxypyridine, 2,6-diaminopyridine, salts of these substances, and mixtures thereof.

[0106] The content of each of the precursor and the coupler in the hair dye composition is preferably 0.01 mass% or more, more preferably 0.1 mass% or more, and preferably 10 mass% or less, more preferably 7.5 mass% or less, further more preferably 5.0 mass% or less.

[0107] When the hair dye composition contains an oxidative dye, the hair dye composition further contains an alkali agent. Examples of the suitable alkali agent include, but are not limited to, ammonia and salts thereof; alkanolamines (monoethanolamine, isopropanolamine, 2-amino-2-methylpropanol, 2-aminobutanol and the like) and salts thereof; alkanediamines (1,3-propanediamine and the like) and salts thereof; carbonates (guanidine carbonate, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate and the like); and mixtures thereof.

[0108] The content of the alkali agent in the hair dye composition is preferably 0.1 mass% or more, more preferably 0.5 mass% or more, further more preferably 1.0 mass% or more, and preferably 15 mass% or less, more preferably 10 mass% or less, further more preferably 7.5 mass% or less.

[0109] The composition containing an oxidizing agent (second part) when the hair dye composition contains an oxidative dye is stored separately from the composition containing an oxidative dye (first part), and mixed before naturally derived fibers are immersed. Examples of the suitable oxidizing agent include, but are not limited to, hydrogen peroxide, urea peroxide, melamine peroxide and sodium brominate. Among these oxidizing agents, hydrogen peroxide is preferable.

[0110] The content of the oxidizing agent in the hair dye composition is preferably 1 mass% or more, more preferably 2 mass% or more, and preferably 15 mass% or less, more preferably 12 mass% or less, further more preferably 9 mass% or less.

[0111] When the first part and the second part are stored separately, the pH of the second part at 25°C is preferably 2 or more, more preferably 2.5 or more, and preferably 6 or less, more preferably 4 or less. The pH can be adjusted by a suitable buffering agent. The pH of the hair dye composition at 25°C obtained by mixing the first part and the second part is preferably 6 or more, more preferably 6.5 or more, further more preferably 6.8 or more, and preferably 11 or less, more preferably 10.5 or less, further more preferably 10 or less.

[0112] When the hair dye composition contains an oxidative dye, the hair dye composition may further contain any of the direct dyes exemplified above.

[0113] Preferably, the hair dye composition may further contain the following surfactant, conditioning component and the like. Preferably, the hair dye composition can be in the form of solution, emulsion, cream, paste and mousse.

[0114] The temperature of the hair dye composition is preferably 0°C or higher, more preferably 10°C or higher, further more preferably 20°C or higher, and preferably 90°C or lower, more preferably 80°C or lower, from the viewpoint of efficiently having the hair dye composition penetrated and diffused into naturally derived fibers to enhance the effect of dyeing.

(Post-heating: heating treatment for further improving fiber stretchability (tenacity))

[0115] Further, from the viewpoint of more effectively improving the stretchability of naturally derived fibers, naturally derived fibers can be heated while being stretched by applying tension to the fibers. When the naturally derived fibers are small in amount, it is preferable to use a hair iron for the heating, and when the naturally derived fibers are large in amount, an equivalent result can be obtained by, for example, performing hot air heating while tension is applied by a rewinder.

[0116] The fiber elongation percentage during heating is preferably 0.1% or more, more preferably 0.2% or more, further more preferably 0.5% or more, from the viewpoint of more effectively improving the stretchability of the fibers, and preferably 10% or less, more preferably 5.0% or less, further more preferably 2.0% or less, from the viewpoint of suppressing damage to the fibers.

[0117] The heating temperature is preferably 120°C or higher, more preferably 140°C or higher, further more preferably 160°C or higher, from the viewpoint of more effectively improving the stretchability of the fibers, and preferably 240°C or lower, more preferably 220°C or lower, further more preferably 200°C or lower, from the viewpoint of suppressing damage to the fibers.

[0118] The heating time is preferably 1 second or more, more preferably 3 seconds or more, further more preferably 5 seconds or more, from the viewpoint of more effectively improving the stretchability of the fibers, and preferably 60 seconds or less, more preferably 30 seconds or less, further more preferably 20 seconds or less, from the viewpoint of suppressing damage to the fibers.

[0119] After heating, from the viewpoint of more effectively improving the stretchability of the fibers, naturally derived fibers can be left to stand in water while being stretched by applying tension to the fibers.

[0120] The elongation percentage here is preferably 0.1% or more, more preferably 0.2% or more, further more preferably 0.5% or more, from the viewpoint of more effectively improving the stretchability of the fibers, and preferably 10% or less, more preferably 5.0% or less, further more preferably 2.0% or less, from the viewpoint of suppressing damage to the fibers.

[0121] The water temperature is preferably 5°C or higher, more preferably 20°C or higher, further more preferably 30°C, from the viewpoint of more effectively improving the stretchability of the fibers, and preferably 80°C or lower, more preferably 60°C or lower, further more preferably 50°C or lower, from the viewpoint of suppressing damage to the fibers.

[0122] The time for leaving the fibers to stand in water is preferably 1 minute or more, more preferably 5 minutes or more, further more preferably 30 minutes or more, from the viewpoint of more effectively improving the stretchability of the fibers, and preferably 48 hours or less, more preferably 24 hours or less, further more preferably 3 hours or less, from the viewpoint of suppressing damage to the fibers.

[0123] Depending on conditions for treatment in the step (i), stretchability of the fibers at dry state can achieve the equivalent to that of human hair.

[0124] The feel of the above fibers subjected to various treatments can be improved by subsequent commonly used after-treatment for fibers, such as treatment with a fiber-treating agent such as softening agent or treatment with a hair care agent such as conditioner or hair treatment.

[0125] When naturally derived fibers are treated by the above method for treating fibers, the fibers contain the component (A), so that it is possible to produce fibers, preferably fibers for headdress products and the like, in which the shape of the fiber is possible to be imparted by a heat set, the fibers are excellent in water resistance, heat resistance, and tensile elastic modulus, and the stretchability (tenacity) of the naturally derived fibers is highly improved, and to produce various fiber products using the fibers, preferably headdress products and the like.

[0126] In the present invention, examples of suitable headdress products include hair wigs, wigs, weavings, hair extensions, blade hairs, hair accessories, and doll hairs.

[0127] Concerning the embodiments described above, preferred aspects of the present invention will be further disclosed below.

[0128]

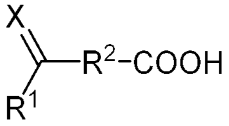
<1> A fiber-treating agent comprising the following components (A) and (B) :

(A): a compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 $MPa^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring; and
(B): water.

<2> The fiber-treating agent according to <1>, wherein the component (A) is preferably one or more compounds selected from the group consisting of the following components (A1) and (A2):

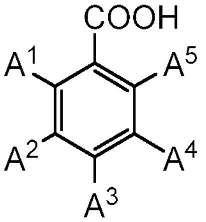
(A1) an aromatic compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 $MPa^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring; and
(A2) a compound having a hydrogen bond term δH in Hansen solubility parameter of 11.0 $MPa^{1/2}$ or more and 18.3 $MPa^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring (excluding aromatic compounds).

<3> The fiber-treating agent according to <2>, wherein the component (A1) is a compound of the following formula (1) or formula (2) or a salt thereof, or phenylbutanoic acid:



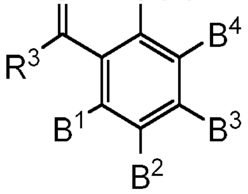
(1)

wherein =X represents a methylidene group or an oxo group, R^1 represents a hydrogen atom, a hydroxy group, or an optionally substituted alkyl group, aryl group, alkoxy group, aryloxy group, or aralkyloxy group, and R^2 is an o-phenylene group, an m-phenylene group, a p-phenylene group, a benzylidene group, or an optionally substituted alkylene group, provided that when R^2 has no aryl group, R^1 is an aryl group, an aryloxy group, or an aralkyloxy group; and



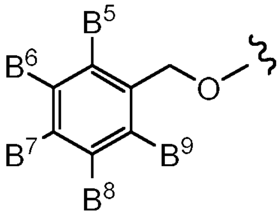
(2)

wherein A^1 to A^5 each independently represent a hydrogen atom, an acetyl group, a halogen atom, or a linear or branched alkyl group, alkenyl group, alkoxy group, or alkenyloxy group having 1 to 6 carbon atoms.
<4> The fiber-treating agent according to <3>, wherein the compound of formula (1) is a compound of the following formula (1A), (1B), or (1C), 3-carboxybenzoic acid (isophthalic acid), 4-carboxybenzoic acid (terephthalic acid), 3-benzoylbenzoic acid, or 4-benzoylbenzoic acid:

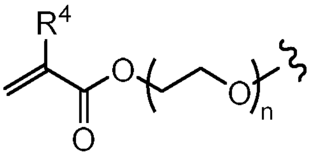


(1A)

wherein B^1 to B^4 each independently represent a hydrogen atom, an acetyl group, a halogen atom, or a linear or branched alkyl group, alkenyl group, alkoxy group, or alkenyloxy group having 1 to 6 carbon atoms, and R^3 represents a hydroxy group, or a group of the following formula (1A)-a or (1A)-b:

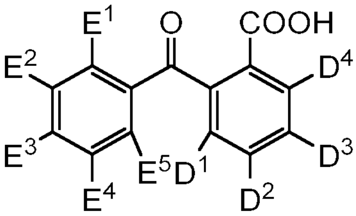


(1A)-a



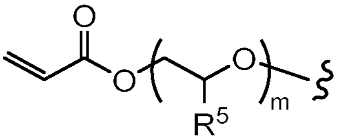
(1A)-b

wherein B^5 to B^9 represent the same meaning as the B^1 to B^4, R^4 represents a hydrogen atom or a methyl group, and n represents an integer of 0 to 2;



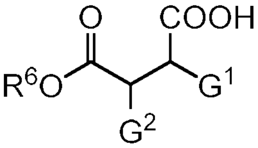
(1B)

wherein D^1 to D^4 each independently represent a hydrogen atom, an acetyl group, a halogen atom, or a linear or branched alkyl group, alkenyl group, alkoxy group, or alkenyloxy group having 1 to 6 carbon atoms, and E^1 to E^5 each independently represent the same group as D^1 to D^4 or a group of formula (1B)-a:



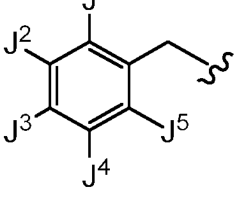
(1B)-a

wherein m represents an integer of 0 to 4; and



(1C)

wherein R^6 represents a hydrogen atom or a group of formula (1C)-a, G^1 and G^2 each independently represent a hydrogen atom, an acetyl group, a halogen atom, an optionally substituted aryl group, an aralkyl group or arylalkenyl group having 7 to 12 carbon atoms, or a linear or branched alkyl group, alkenyl group, alkoxy group, alkenyloxy group, or aroyloxy group having 1 to 6 carbon atoms, provided that when R^6 is a hydrogen atom, at least one of G^1 and G^2 is an optionally substituted aryl group, or an aralkyl group, arylalkenyl group, or aroyloxy group having 7 to 12 carbon atoms:



(1C)-a

wherein J^1 to J^5 each independently represent a hydrogen atom, an acetyl group, a halogen atom, or a linear or branched alkyl group, alkenyl group, alkoxy group, or alkenyloxy group having 1 to 6 carbon atoms.

<5> The fiber-treating agent according to <4>, wherein the compound of formula (1A) is preferably 2-carboxy benzoic acid (phthalic acid), 2-(((4-vinylbenzyl)oxy)carbonyl)benzoic acid, 2-((2-(acryloyloxy)ethoxy)carbonyl)benzoic acid, or 2-((2-(methacryloyloxy)ethoxy)carbonyl)benzoic acid.

<6> The fiber-treating agent according to <4>, wherein the compound of formula (1B) is preferably 2-benzoylbenzoic acid, 2-(2-methylbenzoyl)benzoic acid, 2-(3-methylbenzoyl)benzoic acid, 2-(4-methylbenzoyl)benzoic acid, 2-(2-chlorobenzoyl)benzoic acid, 2-(3-chlorobenzoyl)benzoic acid, 2-(4-chlorobenzoyl)benzoic acid, or 2-(4-(2-(2-(acryloyloxy)ethoxy)ethoxy)benzoyl)benzoic acid.

<7> The fiber-treating agent according to <4>, wherein the compound of formula (1C) is preferably phenylsuccinic acid, 2,3-diphenylsuccinic acid, (+)-di-p-toluoyl-D-tartaric acid, or 4-oxo-4-((4-vinylbenzyl)oxy)butanoic acid.

<8> The fiber-treating agent according to <3>, wherein the compound of formula (2) is benzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 4-methylbenzoic acid, 2-ethylbenzoic acid, 3-ethylbenzoic acid, 4-ethylbenzoic acid, 2-propylbenzoic acid, 3-propylbenzoic acid, 4-propylbenzoic acid, 2-isopropylbenzoic acid, 3-isopropylbenzoic acid, 4-isopropylbenzoic acid, 2-n-butylbenzoic acid, 3-n-butylbenzoic acid, 4-n-butylbenzoic acid, 2-tert-butylbenzoic acid, 3-tert-butylbenzoic acid, 4-tert-butylbenzoic acid, 2-vinylbenzoic acid, 3-vinylbenzoic acid, 4-vinylbenzoic acid, 2-acetylbenzoic acid, 3-acetylbenzoic acid, 4-acetylbenzoic acid, 2-methoxybenzoic acid, 3-methoxybenzoic acid, 4-methoxybenzoic acid, 2-chlorobenzoic acid, 3-chlorobenzoic acid, 4-chlorobenzoic acid, 2-bromobenzoic acid, 3-bromobenzoic acid, or 4-bromobenzoic acid, more preferably 4-ethylbenzoic acid, 4-vinylbenzoic acid, or benzoic acid.

<9> The fiber-treating agent according to any one of <2> to <8>, wherein the hydrogen bond term δH of the aromatic compound of the component (A1) is preferably 16.0 MPa$^{1/2}$ or less, more preferably 13.5 MPa$^{1/2}$ or less, further more preferably 12.0 MPa$^{1/2}$ or less, further more preferably 10.0 MPa$^{1/2}$ or less, and preferably 3.0 MPa$^{1/2}$ or more, more preferably 4.0 MPa$^{1/2}$ or more, further more preferably 5.0 MPa$^{1/2}$ or more.

<10> The fiber-treating agent according to <2>, wherein the component (A2) is potassium 2,4-hexadienoate.

<11> The fiber-treating agent according to <2> or <10>, wherein the hydrogen bond term δH of the compound of the component (A2) is preferably 16.0 MPa$^{1/2}$ or less, more preferably 15.0 MPa$^{1/2}$ or less, further more preferably 14.0 MPa$^{1/2}$ or less, further more preferably 13.0 MPa$^{1/2}$ or less, and preferably 11.0 MPa$^{1/2}$ or more, more preferably 11.5 MPa$^{1/2}$ or more, further more preferably 12.0 MPa$^{1/2}$ or more.

<12> The fiber-treating agent according to any one of <1> to <11>, wherein a content of the component (B) 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 99 mass% or less, more preferably 95 mass% or less, further more preferably 90 mass% or less, even more preferably 85 mass% or less.

<13> The fiber-treating agent according to any one of <1> to <12>, wherein a pH 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.

<14> The fiber-treating agent according to any one of <1> to <13>, wherein the component (A) contains (A1-1) benzoic acid or a salt thereof.

<15> The fiber-treating agent according to <14>, wherein a pH of the fiber-treating agent is 2.0 or more and less than 6.5, and a content of the component (A1-1) in the fiber-treating agent is, as benzoic acid (acid form), preferably 0.8 mass% or more, more preferably 3.0 mass% or more, further more preferably 5.0 mass% or more, even more preferably 10 mass% or more, even more preferably 15 mass% or more, even more preferably 20 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 50 mass% or less, further more preferably 40 mass% or less, even more preferably 35 mass% or less.

<16> The fiber-treating agent according to <14>, wherein a pH of the fiber-treating agent is 6.5 or more and 11.0 or less, and a content of the component (A1-1) in the fiber-treating agent is, as benzoic acid (acid form), preferably 0.8 mass% or more, more preferably 3.0 mass% or more, further more preferably 5.0 mass% or more, even more preferably 10 mass% or more, even more preferably 15 mass% or more, even more preferably 20 mass% or more, even more preferably 25 mass% or more, even more preferably 26 mass% or more, even more preferably 28 mass% or more, even more preferably 30 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 50 mass% or less, even more preferably 45 mass% or less, even more preferably 40 mass% or less.

<17> The fiber-treating agent according to any one of <1> to <13>, wherein the component (A) contains (A1-2) a component (A1) other than benzoic acid or a salt thereof.

<18> The fiber-treating agent according to <17>, wherein the pH of the fiber-treating agent is 2.0 or more and less than 6.5, and a content of the component (A1-2) in the fiber-treating agent is 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 70 mass% or less, more preferably 60 mass% or less, further more preferably 50 mass% or less, even more preferably 45 mass% or less.

<19> The fiber-treating agent according to <17>, wherein the pH of the fiber-treating agent is 6.5 or more and 11.0 or less, and a content of the component (A1-2) in the fiber-treating agent is 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 70 mass% or less, more preferably 60 mass% or less, further more preferably 50 mass% or less, even more preferably 40 mass% or less.

<20> The fiber-treating agent according to any one of <1> to <13>, wherein the component (A) contains the component (A2).

<21> The fiber-treating agent according to <20>, wherein a pH of the fiber-treating agent is 2.0 or more and less than 6.5, and a content of the component (A2) in the fiber-treating agent is 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 60 mass% or less, more preferably 50 mass% or less, further more preferably 40 mass% or less, even more preferably 30 mass% or less.

<22> The fiber-treating agent according to <20>, wherein a pH of the fiber-treating agent is 6.5 or more and 11.0 or less, and a content of the component (A2) in the fiber-treating agent is 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 70 mass% or less, more preferably 60 mass% or less, further more preferably 50 mass% or less, even more preferably 40 mass% or less.

<23> The fiber-treating agent according to any one of <1> to <22>, wherein the fiber-treating agent contains two or more compounds as the component (A).

<24> The fiber-treating agent according to <23>, wherein at least one component (A) is preferably an aromatic compound of formula (2), more preferably benzoic acid or a salt thereof.

<25> The fiber-treating agent according to <24>, wherein a content of the aromatic compound of formula (2) is preferably the highest in the component (A), and a content of benzoic acid or a salt thereof is more preferably the highest in the component (A).

<26> The fiber-treating agent according to any one of <23> to <25>, wherein the pH of the fiber-treating agent is 2.0 or more and less than 6.5, and a content of the component (A) left after excluding a compound present at the highest concentration in the entire component (A) in the fiber-treating agent is preferably 0.1 mass% or more, more preferably 0.5 mass% or more, further more preferably 1.0 mass% or more, and preferably 20 mass% or less, more preferably 10 mass% or less, further more preferably 5.0 mass% or less.

<27> The fiber-treating agent according to any one of <23> to <25>, wherein the pH of the fiber-treating agent is 6.5 or more and 11.0 or less, and a content of the component (A) left after excluding a compound present at the highest concentration in the entire component (A) in the fiber-treating agent is preferably 0.5 mass% or more, more preferably 1.0 mass% or more, further more preferably 2.0 mass% or more, and preferably 30 mass% or less, more preferably 20 mass% or less, further more preferably 10 mass% or less.

<28> The fiber-treating agent according to any one of <23> to <27>, wherein a mass ratio of the component (A) left after excluding a compound present at the highest concentration in the entire component (A) to the compound in the fiber-treating agent (a mass of the component (A) left after excluding a compound present at the highest concentration in the entire component (A))/(a mass of the compound present at the highest concentration in the component (A)) is preferably 0.01 or more, more preferably 0.05 or more, further more preferably 0.10 or more, and preferably 1.0 or less, more preferably 0.5 or less, further more preferably 0.25 or less.

<29> A method for treating fibers, comprising the following step (i):
step (i) immersing naturally derived fibers in a composition containing the following components (A) and (B):

> (A): a compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 $MPa^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring; and
> (B): water.

<30> A method for treating fibers, comprising the following step (i):
step (i) immersing naturally derived fibers in a composition containing the following components (A1-2) and (B):

> (A1-2): a compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 $MPa^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring (excluding benzoic acid and a salt thereof); and
> (B): water.

<31> Use of a composition containing the following components (A) and (B) as a fiber-treating agent:

> (A): a compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 $MPa^{1/2}$ or less, and

having at least one of a carboxy group or a salt thereof, and no fused ring; and
(B): water.

<32> Use of a composition containing the following components (A1-2) and (B) as a fiber-treating agent:

(A1-2): a compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 $\mathrm{MPa}^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring (excluding benzoic acid and a salt thereof); and
(B): water.

Examples

Examples 1 to 22 and Comparative Examples 1 to 3

[0129] By using compositions whose formulations are shown in Tables 1 and 2, 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>

[0130]

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.

   *: 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.

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

[0131]

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>

[0132] As an index of water resistance and stretchability (tenacity), an average breaking elongation during fiber tensioning, 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.

[0133] 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>

[0134] As an index of water resistance, 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.

[0135] 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>

[0136] 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 three times at a rate of 5 cm/sec.
2. After the ironing 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 shrunk by dry heat and thus excellent in heat resistance.

<Shrinkage ratio during hot-water heating>

[0137] 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 Swet = $\{1-(L_2/L_1)\} \times 100[\%]$. When Swet is close to 0%, the fiber is unlikely to shrunk by wet heat and thus excellent in heat resistance.

<Heat shape memory ability>

[0138] 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)

  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)

[0139] 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.

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

[0140]

- II: Reshaping (straight)

  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)

[0141] 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%.

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

[0142]

- III: Re-reshaping (Curl)

  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)

[0143] 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>

[0144] 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)

[0145]

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>

[0146]

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 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 the evaluation this time, 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.

[0147] 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]

			Examples											Comparative Examples		
			1	2	3	4	5	6	7	8	9	10	11	1	2	3
Treating agent (mass%)	(A)	Sodium benzoate (in parenthesis, amount as acid form)	39.0 (33.0)	37.5 (31.8)	35.0 (29.7)	30.0 (25.4)	30.0 (25.4)	20.0 (16.9)	15.0 (12.7)	5.0 (4.2)	1.0 (0.8)	5.0 (4.2)	5.0 (4.2)	-	-	
	(A')	2,3-Naphthalenedicarboxylic acid	-	-	-	-	-	-	-	-	-	-	-	-	5.0	-
		Gallic acid	-	-	-	-	-	-	-	-	-	-	-	-	-	5.0
	(B)	Water	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	-	Balance	Balance
	pH adjuster	Hydrochloric acid or sodium hydroxide	*	*	*	*	*	*	*	*	*	*	*	-	*	*
	Total		100	100	100	100	100	100	100	100	100	100	100	-	100	100
	pH(25°C)		7.0	7.0	7.0	7.0	5.5	5.5	5.5	5.5	5.5	4.0	9.0	-	9.0	9.0
Treatment	Bath ratio		40	40	40	40	40	40	40	40	40	40	40	-	40	40
	Heating condition		50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	-	50°C 1h	50°C 1h
Effect	Durability improvement	Ratio of increase in average breaking elongation during fiber tensioning [%]	78.8	63.2	37.9	24.9	16.2	12.8	9.4	4.1	1.1	3.7	3.7	Reference	0.6	-1.9
		Amount of increase in average breaking load during fiber tensioning [gf]	0.3	2.1	6.8	7.1	20.9	25.8	6.7	16.8	7.6	26.6	13.4	Reference	5.3	-25.8
	Heat resistance improvement	Shrinkage ratio during set with iron at high temperature [%]	5.0	6.0	8.0	9.0	6.0	6.7	10.7	12.7	14.0	8.0	12.0	14.0	13.3	33.3
		Shrinkage ratio during hot-water heating [%]	23.0	23.0	21.6	31.0	27.0	19.0	34.0	40.0	57.0	21.0	56.0	76.0	60.0	43.0
	Heat-shape memory ability	I: Shaping (curl)	29	35	36	36	39	38	33	33	26	35	28	1	20	1
		II: Reshaping (straight)	98	97	100	97	98	98	96	100	96	98	97	90	97	85
		III: Re-reshaping (curl)	30	31	30	34	43	38	33	35	25	33	29	6	25	8
	Surface feel quality		20	20	20	20	20	20	18	16	12	16	16	10	8	8
	Suppression of coloring on fibers		5	5	5	5	5	5	5	5	5	5	5	Reference	3	1

*: **Amount of pH adjustment**

[Table 2]

			Examples										
			12	13	14	15	16	17	18	19	20	21	22
Treating agent (mass%)	(A)	Potassium 2,4-hexadienoate (in parenthesis, amount as acid form)	5.0 (3.7)	-	-	-	-	-	-	-	-	-	-
		4-Ethylbenzoic acid	-	5.0	-	-	-	-	-	-	-	-	-
		4-Vinylbenzoic acid	-	-	5.0	-	-	-	-	-	-	-	-
		2-(((4-Vinylbenzyl)oxy)carbonyl)benzoic acid	-	-	-	5.0	-	-	-	-	-	-	-
		2-((2-(Methacryloyloxy) ethoxy)carbonyl)benzoic acid	-	-	-	-	5.0	-	-	-	-	-	-
		2-Benzoylbenzoic acid	-	-	-	-	-	5.0	-	-	-	-	-
		2-(4-Methylbenzoyl)benzoic acid	-	-	-	-	-	-	5.0	-	-	-	-
		2-(4-Chlorobenzoyl)benzoic acid	-	-	-	-	-	-	-	5.0	-	-	-
		2-(4-(2-(2-(Acryloyloxy) ethoxy)ethoxy)benzoyl) benzoic acid	-	-	-	-	-	-	-	-	5.0	-	-
		Phenylsuccinic acid	-	-	-	-	-	-	-	-	-	5.0	-
		4-Oxo-4-((4-vinylbenzyl) oxy)butanoic acid	-	-	-	-	-	-	-	-	-	-	5.0
	(B)	Water	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
	pH adjuster)	Hydrochloric acid or sodium hydroxide	*	*	*	*	*	*	*	*	*	*	*
	Total		100	100	100	100	100	100	100	100	100	100	100
	pH(25°C)		5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5
Treatment	Bath ratio		40	40	40	40	40	40	40	40	40	40	40
	Heating condition		50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h	50°C 1h

(continued)

			Examples										
			12	13	14	15	16	17	18	19	20	21	22
Effect	Durability improvement	Ratio of increase in average breaking elongation during fiber tensioning [%]	2.4	3.9	2.2	4.6	2.4	3.4	2.6	2.6	5.1	2.6	1.0
		Amount of increase in average breaking load during fiber tensioning [gf]	21.7	31.5	27.1	27.9	6.4	20.3	31.1	23.8	10.1	17.8	1.9
	Heat resistance improvement	Shrinkage ratio during set with iron at high temperature [%]	12.7	10.7	12.7	12.7	12.7	10.7	12.7	12.0	12.7	11.3	12.0
		Shrinkage ratio during hot-water heating [%]	52.0	18.0	39.0	72.0	57.0	25.0	22.0	40.0	69.0	40.0	50.0
	Heat-shape memory ability	I: Shaping (curl)	33	43	42	43	26	43	35	31	33	34	9
		II: Reshaping (straight)	92	94	92	88	95	95	96	94	96	95	90
		III: Re-reshaping (curl)	33	40	32	39	31	38	35	27	28	37	14
	Surface feel quality		16	16	16	16	16	16	16	16	16	16	16
	Suppression of coloring on fibers		2	5	5	5	5	5	5	5	2	4	5

*: Amount of pH adjustment

Claims

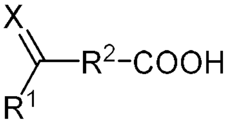
1. A fiber-treating agent comprising the following components (A) and (B) :

   (A): a compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 $MPa^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring; and
   (B): water.

2. The fiber-treating agent according to claim 1, wherein the component (A) is one or more compounds selected from the group consisting of the following components (A1) and (A2):

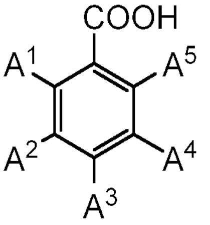
   (A1) an aromatic compound having a hydrogen bond term δH in Hansen solubility parameter of 18.3 $MPa^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring; and
   (A2) a compound having a hydrogen bond term δH in Hansen solubility parameter of 11.0 $MPa^{1/2}$ or more and 18.3 $MPa^{1/2}$ or less, and having at least one of a carboxy group or a salt thereof, and no fused ring (excluding aromatic compounds).

3. The fiber-treating agent according to claim 2, wherein the component (A1) is a compound of the following formula (1) or a salt thereof, or a compound of the following formula (2) or a salt thereof:



(1)

   wherein =X represents a methylidene group or an oxo group, R^1 represents a hydrogen atom, a hydroxy group, or an optionally substituted alkyl group, aryl group, alkoxy group, aryloxy group, or aralkyloxy group, and R^2 is an o-phenylene group, an m-phenylene group, a p-phenylene group, a benzylidene group, or an optionally substituted alkylene group, provided that when R^2 has no aryl group, R^1 is an aryl group, an aryloxy group, or an aralkyloxy group; and



(2)

   wherein A^1 to A^5 each independently represent a hydrogen atom, an acetyl group, a halogen atom, or a linear or branched alkyl group, alkenyl group, alkoxy group, or alkenyloxy group having 1 to 6 carbon atoms.

4. The fiber-treating agent according to any one of claims 1 to 3, wherein the component (A) contains a component (A1-1) benzoic acid or a salt thereof.

5. The fiber-treating agent according to claim 4, wherein a pH of the fiber-treating agent is 2.0 or more and less than 6.5, and a content of the component (A1-1) benzoic acid or a salt thereof in the fiber-treating agent is, as benzoic acid (acid form), 0.8 mass% or more and 40 mass% or less.

6. The fiber-treating agent according to claim 4, wherein a pH of the fiber-treating agent is 2.0 or more and less than 6.5, and a content of the component (A1-1) benzoic acid or a salt thereof in the fiber-treating agent is, as benzoic acid (acid form), 5.0 mass% or more and 40 mass% or less.

7. The fiber-treating agent according to claim 4, wherein a pH of the fiber-treating agent is 6.5 or more and 11.0 or less, and a content of the component (A1-1) benzoic acid or a salt thereof in the fiber-treating agent is, as benzoic acid (acid form), 0.8 mass% or more and 40 mass% or less.

8. The fiber-treating agent according to claim 4, wherein a pH of the fiber-treating agent is 6.5 or more and 11.0 or less, and a content of the component (A1-1) benzoic acid or a salt thereof in the fiber-treating agent is, as benzoic acid (acid form), 5.0 mass% or more and 40 mass% or less.

9. The fiber-treating agent according to any one of claims 1 to 8, comprising two or more compounds as the component (A).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/018109

A. CLASSIFICATION OF SUBJECT MATTER

D06M 13/188(2006.01)i; ***D01F 4/00***(2006.01)i; *D06M 101/14*(2006.01)n
FI: D06M13/188; 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.
X	JP 2525035 B2 (KURARAY CO LTD) 14 August 1996 (1996-08-14) column 6, lines 13-25, example 1	1-9
X	JP 2009-526897 A (GRIEM, John) 23 July 2009 (2009-07-23) claims, paragraphs [0001], [0016]	1-8
A		9
A	WO 2016/158702 A1 (KANEKA CORPORATION) 06 October 2016 (2016-10-06) claims	1-9

☐ 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
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"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.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/018109

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2525035 B2	14 August 1996	JP 1-292170 A	
JP 2009-526897 A	23 July 2009	WO 2007/094800 A1 claims, paragraphs [0001], [0016] US 2007/0187657 A1 EP 1984437 A1 CA 2642594 A CN 101374898 A RU 2008131542 A HK 1122586 A AU 2006338246 A MX 2008010433 A KR 10-2009-0003204 A	
WO 2016/158702 A1	06 October 2016	US 2018/0016709 A1 claims	

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2019143281 A **[0008]**
- JP 2003027318 A **[0016]**

Non-patent literature cited in the description

- Hansen Solubility Parameters: A User's Handbook. CRC Press, 2007 **[0017]**