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

(11) EP 4 509 653 A1

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

(43) Date of publication:
19.02.2025 Bulletin 2025/08

(21) Application number: **23788295.6**

(22) Date of filing: **10.04.2023**

(51) International Patent Classification (IPC):
D06M 13/224 $^{(2006.01)}$ ***D06M 13/17*** $^{(2006.01)}$
D06M 15/53 $^{(2006.01)}$ ***D06M 101/28*** $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
D06M 13/17; D06M 13/224; D06M 13/256;
D06M 13/262; D06M 15/53

(86) International application number:
PCT/JP2023/014487

(87) International publication number:
WO 2023/199877 (19.10.2023 Gazette 2023/42)

(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: **15.04.2022 JP 2022067616**

(71) Applicant: **TAKEMOTO OIL & FAT CO., LTD.**
Aichi 443-8611 (JP)

(72) Inventors:
- **MATSUNAGA Takuya**
  Gamagori-shi, Aichi 443-8611 (JP)
- **OSHIMA Keiichiro**
  Gamagori-shi, Aichi 443-8611 (JP)

(74) Representative: **Daub, Thomas**
Patent- und Rechtsanwaltskanzlei Daub
Bahnhofstrasse 5
88662 Überlingen (DE)

(54) TREATMENT AGENT FOR CARBON FIBER PRECURSOR, AND CARBON FIBER PRECURSOR

(57) The present invention addresses the problem of providing: a treatment agent for a carbon fiber precursor, which is capable of reducing fluff in flame-resistant fibers; and a carbon fiber precursor. The treatment agent for a carbon fiber precursor according to the present invention is characterized by containing: a smoothing agent (A) containing an ester compound (A1) of glycerin and a fatty acid containing a fatty acid (X); and a (poly)oxyalkylene derivative (B), wherein the ratio of the total mass of fatty acids having 16 to 24 carbon atoms derived from the ester compound (A1) to the total mass of fatty acids derived from the ester compound (A1) in the treatment agent for a carbon fiber precursor is at least 50 mass%. The fatty acid (X) is a fatty acid having 16 to 24 carbon atoms.

Processed by Luminess, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a carbon fiber precursor treatment agent capable of reducing fluff in flameproofed fibers, and to a carbon fiber precursor obtained by using the treatment agent.

BACKGROUND ART

[0002] In general, carbon fibers are widely used in various fields, such as construction materials and transportation equipment, for example, as carbon fiber composite materials or flame-retardant and flameproof materials in combination with matrix resins. For instance, carbon fibers are produced through processes such as spinning acrylic fibers, which serve as carbon fiber precursors, followed by fiber drawing, flameproofing, and carbonization. During the spinning process of the carbon fiber precursor, a carbon fiber precursor treatment agent may be used to impart bundling properties to the fibers.

[0003] A carbon fiber precursor treatment agent known in the related art is disclosed in Patent Document 1. Patent Document 1 discloses an acrylic synthetic fiber treatment agent comprising: a polyoxyalkylene block copolymer obtained by the addition polymerization of an alkylene oxide to an aliphatic hydroxy compound having a hydroxyl group; an oil or fat primarily composed of glyceride having a fatty acid residue with 12 to 22 carbon atoms; and a specific polyoxyethylene glycol alkenyl ether in a predetermined ratio.

CITATIONS LIST

PATENT LITERATURE

[0004] Patent Document 1: Japanese Laid-Open Patent Publication No. 2002-88654

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0005] However, the known carbon fiber precursor treatment agent has a problem in that its effect of reducing fluff in flameproofed fibers, which are obtained after flameproofing a carbon fiber precursor treated with the carbon fiber precursor treatment agent, is insufficient.

SOLUTION TO PROBLEM

[0006] As a result of research to solve the aforementioned problems, the inventors of the present application have found that a carbon fiber precursor treatment agent containing a specific ester compound and a (poly)oxyalkylene derivative is particularly suitable.

[0007] To solve the above problems and in accordance with one aspect of the present invention, the carbon fiber precursor treatment agent contains a smoothing agent (A), which contains an ester compound (A1) of glycerin and a fatty acid containing fatty acid (X), and a (poly)oxyalkylene derivative (B). The proportion of the fatty acid (X), determined by the following mathematical equation 1, is 50% by mass or more.

[0008] The fatty acid (X) is a fatty acid with 16 to 24 carbon atoms.

Proportion of fatty acid (X) = (Total mass of fatty acid with 16 to 24 carbon atoms derived from ester compound (A1) in the carbon fiber precursor treatment agent / Total mass of fatty acid derived from ester compound (A1) in the carbon fiber precursor treatment agent) × 100. [Mathematical Equation 1]

[0009] In the carbon fiber precursor treatment agent, the proportion of the fatty acid (X) determined by the mathematical equation 1 described above may be 70% by mass or more.

[0010] In the carbon fiber precursor treatment agent, the (poly)oxyalkylene derivative (B) may contain a compound obtained by adding an alkylene oxide with 2 to 4 carbon atoms to an ester compound of a monohydric to trihydric alcohol and a monovalent fatty acid with 16 to 24 carbon atoms.

[0011] When the sum of the contents of the smoothing agent (A) and the (poly)oxyalkylene derivative (B) in the carbon fiber precursor treatment agent is taken as 100% by mass, the carbon fiber precursor treatment agent may contain the smoothing agent (A) in an amount of 10% by mass or more and 90% by mass or less and the (poly)oxyalkylene derivative (B) in an amount of 10% by mass or more and 90% by mass or less.

[0012] The carbon fiber precursor treatment agent may further contain a condensed hydroxy fatty acid (C).

[0013] When the sum of the contents of the smoothing agent (A), the (poly)oxyalkylene derivative (B), and the condensed hydroxy fatty acid (C) in the carbon fiber precursor treatment agent is taken as 100% by mass, the carbon fiber precursor treatment agent may contain the smoothing agent (A) in an amount of 9.9% by mass or more and 89.9% by mass or less, the (poly)oxyalkylene derivative (B) in an amount of 10% by mass or more and 90% by mass or less, and the condensed hydroxy fatty acid (C) in an amount of 0.1% by mass or more and 50% by mass or less.

[0014] The carbon fiber precursor treatment agent may further contain an ionic component (D).

[0015] The carbon fiber precursor treatment agent may further contain a condensed hydroxy fatty acid (C) and an ionic component (D).

[0016] When the sum of the contents of the smoothing agent (A), the (poly)oxyalkylene derivative (B), the condensed hydroxy fatty acid (C), and the ionic component (D) in the carbon fiber precursor treatment agent is taken as 100% by mass, the carbon fiber precursor treatment agent may contain the smoothing agent (A) in an amount of 9.9% by mass or more and 89.9% by mass or less, the (poly)oxyalkylene derivative (B) in an amount of 9.9% by mass or more and 89.9% by mass or less, the condensed hydroxy fatty acid (C) in an amount of 0.1% by mass or more and 50% by mass or less, and the ionic component in an amount of 0.1% by mass or more and 10% by mass or less.

[0017] To solve the above problems and in accordance with another aspect of the present invention, the carbon fiber precursor has the carbon fiber precursor treatment agent adhered thereto.

ADVANTAGEOUS EFFECTS OF INVENTION

[0018] According to the present invention, it is possible to reduce fluff in flameproofed fibers obtained after flameproofing a carbon fiber precursor treated with a carbon fiber precursor treatment agent.

DESCRIPTION OF EMBODIMENTS

<First embodiment>

[0019] Hereinafter, a first embodiment of the carbon fiber precursor treatment agent (hereinafter sometimes simply referred to as the "treatment agent") according to the present invention will be described. In this embodiment, the treatment agent contains a smoothing agent (A), which contains an ester compound (A1), and a (poly)oxyalkylene derivative (B).

(Smoothing agent (A))

[0020] The smoothing agent (A) used in the present embodiment contains an ester compound (A1) of glycerin and a fatty acid containing the following fatty acid (X). The fatty acid (X) is a fatty acid with 16 to 24 carbon atoms. Any known fatty acid can be appropriately used as the fatty acid forming the ester compound (A1), and either a saturated fatty acid or an unsaturated fatty acid may be used. Furthermore, the fatty acid may have either a linear structure or a branched structure. The fatty acid may be a monocarboxylic acid or a polycarboxylic acid. Alternatively, the fatty acid may also be an oxycarboxylic acid having a hydroxyl group.

[0021] Specific examples of the saturated fatty acid include hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), eicosanoic acid (arachidic acid), docosanoic acid (behenic acid), and tetracosanoic acid. Specific examples of the unsaturated fatty acid include palmitoleic acid, oleic acid, vaccenic acid, eicosenoic acid, linoleic acid, α-linolenic acid, γ-linolenic acid, and arachidonic acid. Specific examples of the oxycarboxylic acid include ricinoleic acid.

[0022] In the ester compound (A1), the proportion of the fatty acid (X), as determined by the following mathematical equation, is 50% by mass or more, and preferably 70% by mass or more. By defining the proportion within these numerical ranges, the effects of the present invention can be further enhanced.

Proportion of fatty acid (X) = (Total mass of fatty acid with 16 to 24 carbon atoms derived from ester compound (A1) in the carbon fiber precursor treatment agent / Total mass of fatty acid derived from ester compound (A1) in the carbon fiber precursor treatment agent) × 100 [Mathematical Equation 2]

[0023] Specific examples of the ester compound (A1) include castor oil (with the value of the mathematical equation being 100% by mass), rapeseed oil (with the value of the mathematical equation being 100% by mass), sesame oil (with the value of the mathematical equation being 100% by mass), palm oil (with the value of the mathematical equation being

99% by mass), linseed oil (with the value of the mathematical equation being 100% by mass), sunflower oil (with the value of the mathematical equation being 100% by mass), an ester compound of glycerin, ricinoleic acid, and another fatty acid (with the value of the mathematical equation being 50% by mass or more), an ester compound of glycerin, palmitic acid, and another fatty acid (with the value of the mathematical equation being 50% by mass or more), and an ester compound of glycerin, oleic acid, and a different fatty acid (with the value of the mathematical equation being 50% by mass or more).

[0024] One type of these ester compounds (A1) may be used alone, or two or more types may be used in combination.

[0025] The lower limit of the content of the ester compound (A1) in the treatment agent is set as appropriate, and is preferably 5% by mass or more, and more preferably 10% by mass or more. When the content is 5% by mass or more, it is possible to further reduce the fluff in flameproofed fibers obtained after flameproofing the carbon fiber precursor treated with the treatment agent. The upper limit of the content of the ester compound (A1) is set as appropriate, and is preferably 90% by mass or less, and more preferably 85% by mass or less. When the content is 90% by mass or less, the stability of the treatment agent can be improved. A range can also be defined by any combination of these upper and lower limits.

[0026] The smoothing agent (A) may contain an additional smoothing component other than the ester compound (A1), as long as it does not impair the effects of the present invention. The additional smoothing component is not particularly limited, and any known smoothing agent used in treatment agents can be employed. Examples of such known smoothing agents include silicone oils, mineral oils, polyolefins, and ester compounds other than those mentioned above. The use of silicone oil may cause contamination in the baking furnace. Therefore, the content of silicone oil in the treatment agent is preferably 5% by mass or less, more preferably 1% by mass or less, and most preferably, the treatment agent contains no silicone oil. The content of the ester compound (A1) in the smoothing agent (A) is set as appropriate, as long as it does not impair the effects of the present invention, and is, for example, 50% by mass or more and 100% by mass or less, or 80% by mass or more and 100% by mass or less. A range can also be defined by any combination of these upper and lower limits.

[0027] One type of these smoothing agents (A) may be used alone, or two or more types may be used in combination.

(Poly)oxyalkylene derivative (B)

[0028] The (poly)oxyalkylene derivative (B) used in the present embodiment serves as a surfactant, enhancing the stability of the treatment agent and thereby improving its overall functionality.

[0029] Examples of the (poly)oxyalkylene derivative (B) include a compound with a (poly)oxyalkylene structure in which an alkylene oxide is added to an alcohol or a carboxylic acid; an ether-ester compound with a (poly)oxyalkylene structure in which an alkylene oxide is added to an ester compound of a carboxylic acid and a polyhydric alcohol; a compound with a (poly)oxyalkylene structure in which an alkylene oxide is added to an aliphatic amine as an amine compound; a compound with a (poly)oxyalkylene structure in which an alkylene oxide is added to a fatty acid amide; and a block copolymer composed of a polyoxyethylene and polyoxypropylene chains.

[0030] Specific examples of the alcohol used as a raw material for the (poly)oxyalkylene derivative (B) include (1) linear alkyl alcohols, such as methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, eicosanol, heneicosanol, docosanol, tricosanol, tetracosanol, pentacosanol, hexacosanol, heptacosanol, octacosanol, nonacosanol, and triacontanol; (2) branched alkyl alcohols, such as isopropanol, isobutanol, isohexanol, 2-ethylhexanol, isononanol, isodecanol, isododecanol, isotridecanol, isotetradecanol, isotriacontanol, isohexadecanol, isoheptadecanol, isooctadecanol, isononadecanol, isoeicosanol, isoheneicosanol, isodocosanol, isotricosanol, isotetracosanol, isopentacosanol, isohexacosanol, isoheptacosanol, isooctacosanol, isononacosanol, and isopentadecanol; (3) linear alkenyl alcohols, such as tetradecenol, hexadecenol, heptadecenol, octadecenol, and nonadecenol; (4) branched alkenyl alcohols, such as isohexadecenol and isooctadecenol; (5) cyclic alkyl alcohols, such as cyclopentanol and cyclohexanol; and (6) aromatic alcohols, such as phenol, nonylphenol, benzyl alcohol, monostyrenated phenol, distyrenated phenol, and tristyrenated phenol.

[0031] Specific examples of the carboxylic acid used as a raw material for the (poly)oxyalkylene derivative (B) include (1) linear alkyl carboxylic acids, such as octylic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, eicosanoic acid, heneicosanoic acid, and docosanoic acid; (2) branched alkyl carboxylic acids, such as 2-ethylhexanoic acid, isododecanoic acid, isotridecanoic acid, isotetradecanoic acid, isohexadecanoic acid, and isooctadecanoic acid; (3) linear alkenyl carboxylic acids, such as octadecenoic acid, octadecadienoic acid, and octadecatrienoic acid; (4) aromatic carboxylic acids, such as benzoic acid; and (5) hydroxycarboxylic acids, such as ricinoleic acid.

[0032] The alkylene oxide used as a raw material for forming the (poly)oxyalkylene structure of the (poly)oxyalkylene derivative (B) is preferably an alkylene oxide with 2 or more and 4 or less carbon atoms. Specific examples of the alkylene oxide include ethylene oxide, propylene oxide, and butylene oxide. The number of moles of alkylene oxide to be added is set as appropriate, and is preferably 0.1 moles or more and 250 moles or less, more preferably 1 mole or more and 200 moles or less, and still more preferably 2 moles or more and 150 moles or less. A range can also be defined by any combination of these upper and lower limits. The number of moles of alkylene oxide refers to the moles of alkylene oxide added per mole of the compound being used in the raw material mixture. One type of alkylene oxide may be used alone, or two or more types of alkylene oxides may be used in combination as appropriate. When two or more types of alkylene oxides are used, the addition may be performed through block addition, random addition, or a combination of both, with no particular limitation.

[0033] Specific examples of the polyhydric alcohol used as a raw material for the (poly)oxyalkylene derivative (B) include ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2-methyl-1,2-propanediol, 1,5-pentanediol, 1,6-hexanediol, 2,5-hexanediol, 2-methyl-2,4-pentanediol, 2,3-dimethyl-2,3-butanediol, glycerin, 2-methyl-2-hydroxymethyl-1,3-propanediol, trimethylolpropane, sorbitan, pentaerythritol, and sorbitol.

[0034] Specific examples of the aliphatic amine used as a raw material for the (poly)oxyalkylene derivative (B) include methylamine, ethylamine, butylamine, octylamine, laurylamine, octadecylamine, octadecenylamine, and cocoamine.

[0035] Specific examples of the fatty acid amide used as a raw material for the (poly)oxyalkylene derivative (B) include octylic acid amide, lauric acid amide, palmitic acid amide, stearic acid amide, oleic acid amide, behenic acid amide, and lignoceric acid amide.

[0036] The block copolymer composed of polyoxyethylene and polyoxypropylene chains is not particularly limited, as long as it includes a polyoxypropylene chain with low hydrophilicity and a polyoxyethylene chain with high hydrophilicity, and exhibits surfactant properties. The number of polyoxyethylene and polyoxypropylene chains in the molecule is also not particularly limited. For example, the block copolymer may consist of one polyoxypropylene chain and one polyoxyethylene chain, or it may be a poloxamer surfactant consisting of a polyoxypropylene chain and two polyoxyethylene chains sandwiching the polyoxypropylene chain. The number of moles of ethylene oxide added to form the polyoxyethylene chain is not particularly limited and can be, for example, 5 moles or more and 200 moles or less. The number of moles of propylene oxide added to form the polyoxypropylene chain is not particularly limited and can be, for example, 5 moles or more and 100 moles or less.

[0037] Among these, a compound obtained by adding an alkylene oxide with 2 to 4 carbon atoms to an ester compound of a monohydric alcohol or a polyhydric alcohol with three or fewer hydroxyl groups, and a monovalent fatty acid with 16 to 24 carbon atoms, is preferable. The use of such a compound can further improve the stability of the treatment agent.

[0038] Specific examples of the (poly)oxyalkylene derivative (B) include ω-hydroxy (polyoxyethylene) (n=7, indicating the number of moles of ethylene oxide added, the same applies hereinafter) castor oil; ω-hydroxy (polyoxyethylene) (n=20) hydrogenated castor oil; hydroxy (polyoxypropylene polyoxyethylene) (m=13, indicating the number of moles of propylene oxide added, the same applies hereinafter, n=10) castor oil; hydroxy (polyoxypropylene polyoxyethylene) (m=12, n=12) hydrogenated castor oil; an oil-and-fat ethylene oxide adduct prepared by the addition polymerization of ethylene oxide at 200 moles per mole of castor oil; α-dodecyl-ω-hydroxy (polyoxyethylene) (n=7); a polyoxyalkylene block copolymer with a number average molecular weight of 5000, prepared by the block addition polymerization of ethylene oxide and propylene oxide to ethylene glycol, in which the polyoxyalkylene group consists of oxyethylene units/oxypropylene units in a 30/70 molar ratio; a polyoxyalkylene block copolymer with a number average molecular weight of 10,000, prepared by the block addition polymerization of ethylene oxide and propylene oxide to ethylene glycol, in which the polyoxyalkylene group consists of oxyethylene units/oxypropylene units in a 70/30 molar ratio; and a polyoxyethylene glycol octadecenyl ether with a repeat number of 20 oxyethylene units.

[0039] One type of these (poly)oxyalkylene derivatives (B) may be used alone, or two or more types may be used in combination as appropriate.

[0040] The lower limit of the content of the (poly)oxyalkylene derivative (B) in the treatment agent is set as appropriate, and is preferably 5% by mass or more, and more preferably 10% by mass or more. When the content is 5% by mass or more, the stability of the treatment agent can be further improved. The upper limit of the content of the (poly)oxyalkylene derivative (B) is set as appropriate, and is preferably 95% by mass or less, and more preferably 90% by mass or less. When the content is 95% by mass or less, it is possible to further reduce the fluff in flameproofed fibers obtained after flameproofing the carbon fiber precursor treated with the treatment agent. A range can also be defined by any combination of these upper and lower limits.

[0041] When the sum of the contents of the smoothing agent (A) and the (poly)oxyalkylene derivative (B) in the treatment agent is taken as 100% by mass, it is preferable for the treatment agent to contain the smoothing agent (A) in an amount of 10% by mass or more and 90% by mass or less, and the (poly)oxyalkylene derivative (B) in an amount of 10% by mass or more and 90% by mass or less. Defining the contents within these ranges allows for further improvement in the effects of the present invention.

(Condensed hydroxy fatty acid (C))

[0042] The treatment agent may further contain a condensed hydroxy fatty acid (C). The condensed hydroxy fatty acid (C) used in the present embodiment can improve the bundling properties of flameproofed fibers obtained after flameproofing the carbon fiber precursor treated with the treatment agent.

[0043] The condensed hydroxy fatty acid (C) is prepared, for example, by subjecting one type of hydroxy fatty acid or a mixture of two or more types of hydroxy fatty acids, to a dehydration condensation reaction at 100°C to 200°C for 30 minutes to 12 hours under a stream of an inert gas, such as nitrogen gas. Specific examples of the hydroxy fatty acid include 12-hydroxy-9-octadecenoic acid (ricinoleic acid), 12-hydroxystearic acid, 16-hydroxyhexadecanoic acid (juniperic acid), 18-hydroxyoctadecanoic acid, 9-hydroxystearic acid, 10-hydroxystearic acid, 12-hydroxydecanoic acid (sabinic acid), 9,10-dihydroxyoctadecanoic acid, castor oil fatty acid, and hydrogenated castor oil fatty acid. The degree of condensation of the condensed hydroxy fatty acid is set as appropriate, and is preferably a dimer or higher and a hexamer or lower.

[0044] Specific examples of the condensed hydroxy fatty acid (C) include a condensed 12-hydroxystearic acid hexamer, a condensed castor oil fatty acid dimer, a condensed castor oil fatty acid trimer, a condensed castor oil fatty acid tetramer, a condensed castor oil fatty acid pentamer, and a condensed castor oil fatty acid hexamer.

[0045] One type of these condensed hydroxy fatty acids (C) may be used alone, or two or more types may be used in combination as appropriate.

[0046] The lower limit of the content of the condensed hydroxy fatty acid (C) in the treatment agent is set as appropriate, and is preferably 0.1% by mass or more, and more preferably 0.3% by mass or more. When the content is 0.1% by mass or more, it is possible to further improve the bundling properties of flameproofed fibers obtained after flameproofing the carbon fiber precursor treated with the treatment agent. The upper limit of the content of the condensed hydroxy fatty acid (C) is set as appropriate, and is preferably 60% by mass or less, and more preferably 50% by mass or less. When the content is 60% by mass or less, the stability of the treatment agent can be improved. A range can also be defined by any combination of these upper and lower limits.

[0047] When the sum of the contents of the smoothing agent (A), the (poly)oxyalkylene derivative (B), and the condensed hydroxy fatty acid (C) in the treatment agent is taken as 100% by mass, it is preferable for the treatment agent to contain the smoothing agent (A) in an amount of 9.9% by mass or more and 89.9% by mass or less, the (poly) oxyalkylene derivative (B) in an amount of 10% by mass or more and 90% by mass or less, and the condensed hydroxy fatty acid (C) in an amount of 0.1% by mass or more and 50% by mass or less. Defining the contents within these ranges allows for further improvement in the effects of the present invention.

(Ionic component (D))

[0048] The treatment agent may further contain an ionic component (D). The ionic component (D) used in the present embodiment can improve the bundling properties of flameproofed fibers obtained after flameproofing the carbon fiber precursor treated with the treatment agent. Additionally, it can improve the antistatic properties of the flameproofed fibers. Examples of the ionic component (D) include an anionic component and a cationic component.

[0049] Examples of the anionic component include anionic compounds such as acids and their salts.

[0050] Examples of the acids include inorganic acids, organic acids, fatty acids, alkyl sulfonic acids, alkyl sulfuric acids, polyoxyalkylene alkyl sulfuric acids, alkyl phosphoric acid esters, polyoxyalkylene alkyl phosphoric acid esters, sulfuric acid esters of fatty acids, sulfuric acid esters of oils and fats, and their salts.

[0051] Specific examples of the inorganic acids or their salts include hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, carbonic acid, sodium hydrogen sulfate, sodium dihydrogen phosphate, disodium hydrogen phosphate, and sodium hydrogen carbonate.

[0052] Specific examples of the organic acid include citric acid, tartaric acid, lactic acid, malic acid, succinic acid, fumaric acid, maleic acid, gluconic acid, glucuronic acid, and benzoic acid.

[0053] As for the fatty acid, any known fatty acid may be appropriately used, including saturated or unsaturated fatty acids. Additionally, the fatty acid may have a linear structure or a branched-chain structure. The fatty acid may be a monovalent fatty acid or a polyvalent carboxylic acid (polybasic acid).

[0054] Specific examples of the saturated fatty acid include formic acid, acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid (caproic acid), octylic acid (2-ethylhexanoic acid), octanoic acid (caprylic acid), nonanoic acid, decanoic acid (capric acid), dodecanoic acid (lauric acid), tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), eicosanoic acid (arachidic acid), docosanoic acid (behenic acid), and tetracosanoic acid.

[0055] Specific examples of the unsaturated fatty acid include crotonic acid, myristoleic acid, palmitoleic acid, oleic acid, vaccenic acid, eicosenoic acid, linoleic acid, α-linolenic acid, γ-linolenic acid, and arachidonic acid.

[0056] Specific examples of the polyvalent carboxylic acid (polybasic acid) include (1) dibasic acids, such as succinic acid, fumaric acid, maleic acid, adipic acid, and sebacic acid, (2) tribasic acids, such as aconitic acid, (3) aromatic dicarboxylic acids, such as benzoic acid, terephthalic acid, isophthalic acid, and 2,6-naphthalenedicarboxylic acid, (4) aromatic tricarboxylic acids, such as trimellitic acid, and (5) aromatic tetracarboxylic acids, such as pyromellitic acid.

[0057] Specific examples of the alkyl sulfonic acids include lauryl sulfonic acid (dodecyl sulfonic acid), myristyl sulfonic acid, cetyl sulfonic acid, oleyl sulfonic acid, stearyl sulfonic acid, tetradecane sulfonic acid, dodecyl benzenesulfonic acid, and secondary alkyl sulfonic acid (C13 to C15).

[0058] Specific examples of the alkyl sulfuric acids include lauryl sulfuric acid esters, oleyl sulfuric acid esters, and stearyl sulfuric acid esters.

[0059] Specific examples of the polyoxyalkylene alkyl sulfuric acids include polyoxyethylene lauryl ether sulfuric acid esters, polyoxyalkylene (polyoxyethylene, polyoxypropylene) lauryl ether sulfuric acid esters, polyoxyethylene dodecyl ether sulfuric acid esters, and polyoxyethylene oleyl ether sulfuric acid esters.

[0060] Specific examples of the alkyl phosphoric acid esters include lauryl phosphoric acid esters, cetyl phosphoric acid esters, octyl phosphoric acid esters, oleyl phosphoric acid esters, stearyl phosphoric acid esters, and 2-ethylhexyl phosphate.

[0061] Specific examples of the polyoxyalkylene alkyl phosphoric acid esters include polyoxyethylene lauryl ether phosphoric acid esters, polyoxyethylene cetyl ether phosphoric acid esters, polyoxyethylene oleyl ether phosphoric acid esters, and polyoxyethylene stearyl ether phosphoric acid esters.

[0062] Specific examples of the sulfuric acid esters of fatty acids include castor oil fatty acid sulfuric acid esters, sesame oil fatty acid sulfuric acid esters, tall oil fatty acid sulfuric acid esters, soybean oil fatty acid sulfuric acid esters, rapeseed oil fatty acid sulfuric acid esters, palm oil fatty acid sulfuric acid esters, lard fatty acid sulfuric acid esters, beef tallow fatty acid sulfuric acid esters, and whale oil fatty acid sulfuric acid esters.

[0063] Specific examples of the sulfuric acid esters of oils and fats include sulfuric acid esters of castor oil, sesame oil, tall oil, soybean oil, rapeseed oil, palm oil, lard, beef tallow, and whale oil.

[0064] Examples of the salt include an ammonium salt, an amine salt, and a metal salt. Examples of the metal salt include alkali metal salts and alkaline earth metal salts. Specific examples of the alkali metal forming the alkali metal salts include sodium, potassium, and lithium. Examples of the alkaline earth metal forming the alkaline earth metal salts include metals corresponding to Group II elements, such as calcium, magnesium, beryllium, strontium, and barium.

[0065] The amine forming the amine salt may be a primary, secondary, or tertiary amine. Specific examples of the amine forming the amine salt include (1) aliphatic amines, such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, N-N-diisopropylethylamine, butylamine, dibutylamine, 2-methylbutylamine, tributylamine, octylamine, and dimethyllaurylamine; (2) aromatic amines or heterocyclic amines, such as aniline, N-methylbenzylamine, pyridine, morpholine, piperazine, and their derivatives; (3) alkanolamines, such as monoethanolamine, N-methylethanolamine, diethanolamine, triethanolamine, isopropanolamine, diisopropanolamine, triisopropanolamine, dibutylethanolamine, butyldiethanolamine, octyldiethanolamine, and lauryldiethanolamine; (4) arylamines, such as N-methylbenzylamine; (5) polyoxyalkylene alkylaminoethers, such as polyoxyethylene laurylaminoether and polyoxyethylene sterylaminoether; and (6) ammonia.

[0066] For example, a metal salt of a fatty acid, which is one of the anionic components described above, forms an anionic surfactant. Accordingly, the anionic surfactant may be used as the anionic component.

[0067] Examples of the cationic component include a cationic surfactant and an organic amine.

[0068] Specific examples of the cationic surfactant include lauryltrimethylammonium chloride, cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, behenyltrimethylammonium chloride, didecyldimethylammonium chloride, and 1,2-dimethylimidazole.

[0069] Specific examples of the organic amine include (1) aliphatic amines, such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, N-N-diisopropylethylamine, butylamine, dibutylamine, 2-methylbutylamine, tributylamine, octylamine, laurylamine, and dimethyllaurylamine; (2) aromatic amines or heterocyclic amines, such as aniline, N-methylbenzylamine, pyridine, morpholine, piperazine, and their derivatives; (3) alkanolamines, such as monoethanolamine, N-methylethanolamine, diethanolamine, triethanolamine, isopropanolamine, diisopropanolamine, triisopropanolamine, dibutylethanolamine, butyldiethanolamine, octyldiethanolamine, and lauryldiethanolamine; (4) arylamines, such as 3-aminopropene; and (5) polyoxyalkylene alkylaminoethers, such as N,N-bis(polyoxyethylene) dodecanamine (n=10), polyoxyethylene laurylaminoether, and polyoxyethylene sterylaminoether.

[0070] One type of these ionic components (D) may be used alone, or two or more types may be used in combination as appropriate.

[0071] The lower limit of the content of the ionic component (D) in the treatment agent is set as appropriate, and is preferably 0.05% by mass or more, and more preferably 0.1% by mass or more. When the content is 0.05% by mass or more, it is possible to further improve the bundling properties of flameproofed fibers obtained after flameproofing the carbon fiber precursor treated with the treatment agent. The upper limit of the content of the ionic component (D) is set as appropriate, and is preferably 15% by mass or less, and more preferably 10% by mass or less. When the content is 15% by mass or less, the stability of the treatment agent can be improved. A range can also be defined by any combination of these upper and lower limits.

[0072] When the sum of the contents of the smoothing agent (A), the (poly)oxyalkylene derivative (B), the condensed hydroxy fatty acid (C), and the ionic component (D) in the treatment agent is taken as 100% by mass, it is preferable for the treatment agent to contain the smoothing agent (A) in an amount of 9.9% by mass or more and 89.9% by mass or less, the (poly)oxyalkylene derivative (B) in an amount of 9.9% by mass or more and 89.9% by mass or less, the condensed hydroxy fatty acid (C) in an amount of 0.1% by mass or more and 50% by mass or less, and the ionic component in an amount of 0.1% by mass or more and 10% by mass or less. Defining the contents within these ranges allows for further improvement in the effects of the present invention.

[0073] According to the treatment agent of the first embodiment, the following effects can be achieved.

[0074] (1-1) The treatment agent of the first embodiment contains the smoothing agent (A), which contains an ester compound (A1) of glycerin and a fatty acid containing a fatty acid (X) with 16 to 24 carbon atoms, and the (poly)oxyalkylene derivative (B). The proportion of the fatty acid (X), determined by the mathematical equation described above, is 50% by mass or more. Therefore, it is possible to reduce the fluff in flameproofed fibers obtained after flameproofing a carbon fiber precursor treated with the treatment agent. Additionally, the bundling properties of the flameproofed fibers can be improved. Furthermore, improving the stability of the treatment agent enhances its overall functionality.

[0075] (1-2) In the treatment agent of the first embodiment, silicone oil is not included as an essential component of the smoothing agent. The use of silicone oil may cause contamination in the baking furnace. Therefore, when the treatment agent does not contain silicone oil, contamination in the baking furnace can be reduced. Additionally, even without the inclusion of silicone oil as a smoothing agent, the fluff mentioned above can be reduced, and the bundling properties can be improved.

<Second embodiment>

[0076] Next, a second embodiment of the carbon fiber precursor according to the present invention will be described. The carbon fiber precursor of the present embodiment has the treatment agent of the first embodiment adhered thereto.

[0077] The carbon fiber precursor is preferably a synthetic fiber that will become a carbon fiber after undergoing a carbonization treatment step, as described below. The fibrous raw material forming the carbon fiber precursor is not particularly limited, and examples thereof include (1) polyester fibers, such as polyethylene terephthalate, polypropylene terephthalate, and polylactic acid ester; (2) polyamide fibers, such as nylon 6 and nylon 66; (3) polyacrylic fibers, such as polyacryl and modacryl; (4) polyolefin fibers, such as polyethylene and polypropylene; (5) cellulose fibers; (6) lignin fibers; (7) phenol resins; and (8) pitch. Furthermore, the polyacrylic fiber is preferably composed of fibers containing polyacrylonitrile as a main component, which is obtained by copolymerizing at least 90 mol% or more of acrylonitrile and 10 mol% or less of a flameproofness-promoting component. For the flameproofness-promoting component, a vinyl group-containing compound that can copolymerize with acrylonitrile is suitably used.

[0078] The proportion of the treatment agent of the first embodiment to be adhered to the carbon fiber precursor is not particularly limited, and the treatment agent (excluding the solvent) is preferably adhered to the carbon fiber precursor in a proportion of 0.1% by mass or more and 2% by mass or less, more preferably in a proportion of 0.3% by mass or more and 1.2% by mass or less.

[0079] As for the method of adhering the treatment agent to the carbon fiber precursor, a known method such as an immersion, spraying, rolling, or a guide lubrication using a metering pump can be applied. This can be done using a treatment agent-containing composition, which contains the treatment agent of the first embodiment and a solvent, or a diluted liquid prepared by further diluting the composition with a solvent.

[0080] Next, a method for producing carbon fiber using the carbon fiber precursor of the present embodiment will be described.

[0081] The method for producing carbon fiber preferably involves the following first to third steps.

[0082] First step: A spinning step in which a raw material for the carbon fiber precursor is spun, and the treatment agent of the first embodiment is adhered to the resulting carbon fiber precursor.

[0083] Second step: A flameproofing step in which the carbon fiber precursor obtained in the first step is converted into a flameproofed fiber in an oxidizing atmosphere preferably at 200°C or higher and 300°C or lower, and more preferably at 230°C or higher and 270°C or lower.

[0084] Third step: A carbonization step in which the flameproofed fiber obtained in the second step is carbonized in an inert atmosphere preferably at 300°C or higher and 2000°C or lower, and more preferably at 300°C or higher and 1300°C or lower.

[0085] A baking step is constituted by the second and third steps.

[0086] The treatment agent may be applied to the raw material fiber of the carbon fiber precursor at any stage during the spinning step. Preferably, the treatment agent is applied once before the drawing step. Additionally, the treatment agent may be applied again at any stage after the drawing step. For example, the treatment agent may be applied again immediately after the drawing step, at the winding stage, or immediately before the flameproofing step.

[0087] The oxidizing atmosphere in the flameproofing step is not particularly limited, and, for example, an air atmosphere can be used.

[0088] The inert atmosphere in the carbonization step is not particularly limited, and, for example, a nitrogen atmosphere, an argon atmosphere, or a vacuum atmosphere can be used.

[0089] According to the carbon fiber precursor of the second embodiment, the following effects can be achieved.

[0090] (2-1) The treatment agent of the first embodiment is adhered to the carbon fiber precursor of the second embodiment. As a result, it is possible to reduce fluff in the flameproofed fibers obtained after flameproofing the carbon fiber precursor, thereby improving yarn quality. Additionally, the bundling properties of the flameproofed fibers can be improved, which suppresses winding around the roller during the baking step and improve production efficiency.

[0091] The above embodiments can be modified as described below. The embodiments described above and the following modifications can be implemented in combination with each other, provided there is no technical contradiction.

- Either one or both of the condensed hydroxy fatty acid (C) and the ionic component (D) may be added to the treatment agent of the present embodiment.
- The treatment agent, the treatment agent-containing composition, and the diluted liquid may contain normally used components, such as a stabilizer and an antistatic agent for maintaining the quality, an oily component other than those mentioned above, a surfactant other than those mentioned above, an antistatic agent, a binding agent, an antioxidant, an ultraviolet absorber, and an antifoaming agent, as long as the effects of the present invention are not impaired. The proportion of component other than the solvent in the treatment agent is preferably 20% by mass or less, and more preferably 10% by mass or less, in order to efficiently exhibit the efficacy of the present invention.

EXAMPLES

[0092] Examples are provided below to more specifically illustrate the features and effects of the present invention; however, the invention is not limited to these examples. In the following descriptions of the working and comparative examples, part(s) refers to part(s) by mass, and % refers to % by mass.

Experimental Part 1 (Preparation of treatment agent and diluted solution)

(Example 1)

[0093] 60 parts (%) of castor oil (A-1) and 20 parts (%) of sunflower oil (A-6) as the smoothing agent (A), 14 parts (%) of ω-hydroxy (polyoxyethylene) (n=7) castor oil (B-1) as the (poly)oxyalkylene derivative (B), 5 parts (%) of condensed 12-hydroxystearic acid hexamer (C-1) as the condensed hydroxy fatty acid (C), and 1 part (%) of sodium dodecylbenzenesulfonate (D-1) as the ionic component (D) were added to a beaker and mixed well to prepare a treatment agent of Example 1. Next, while stirring continuously, ion-exchanged water was gradually added to achieve a solid content concentration of 25%, thereby preparing a 25 % treatment agent-containing composition of the treatment agent of Example 1.

(Examples 2 to 19 and Comparative Examples 1 to 7)

[0094] Respective treatment agents of Examples 2 to 19 and Comparative Examples 1 to 7 were prepared in the same manner as in Example 1, using the components shown in Table 1.

[0095] The type and content of the smoothing agent (A), the type and content of the (poly)oxyalkylene derivative (B), the type and content of the condensed hydroxy fatty acid (C), and the type and content of the ionic component (D) in the treatment agent of each example are shown in the column "smoothing agent (A)", the column "(poly)oxyalkylene derivative (B)", the column "condensed hydroxy fatty acid (C)", and the column "ionic component (D)" of Table 1. The ester compounds (A1) contained in smoothing agents (A-7) to (A-9) were synthesized by the method described below.

Experimental Part 2 (Synthesis of smoothing agents (A-7) to (A-9))

(Smoothing agent (A-7))

[0096] 92.1 g of glycerin, 160.3 g of lauric acid, and 617.1 g of ricinoleic acid were placed in a 2-L four-necked flask equipped with a thermometer, a vacuum pump, a nitrogen inlet tube, a stirrer, and a cooling trap. Next, 3.3 g of p-toluenesulfonic acid monohydrate as a catalyst and 1.1 g of a 50% phosphinic acid solution were added thereto. The four-necked flask was heated in an oil bath and reacted under a nitrogen stream at 130°C for 2 hours, then further reacted at 150°C and 2 kPa for 12 hours. The water generated during the reaction was distilled off. After the reaction, the acid value was 3.5 mg KOH/g. The reaction solution was cooled to 60°C, and a 5% sodium hydroxide solution, in an amount sufficient to completely neutralize the residual fatty acid and the acid catalyst, was added and stirred for 30 minutes. Next, 100% of ion-exchanged water (relative to the amount of the reaction solution) was added while stirring, and the mixture was stirred for an additional 30 minutes. After stirring was stopped, the mixture was left to stand for 1 hour, and the separated aqueous layer at the bottom was removed. The process of adding 100% ion-exchanged water, stirring the mixture at 60°C for 10 minutes, standing for 2 hours, and removing the separated aqueous layer was repeated twice. The resulting mixture was then dehydrated at 100°C and 2 kPa. Activated clay (2% as an adsorbent) was added to the crude product, and the mixture was stirred at 80°C and 5 kPa for 1 hour. After removing the adsorbent, the ester compound was obtained and used as the smoothing agent (A-7). The fatty acid mixture forming this ester compound consisted of 27% lauric acid and 73% ricinoleic acid.

[0097] The proportion of the fatty acids forming the resultant ester compound was measured by the method described below.

<Preparation of calibration curve>

[0098] To convert the fatty acid ratio of each sample into mass, various fatty acids and a standard substance, margaric acid, were added to the samples in arbitrary amounts. Fatty acid methyl esters were prepared according to the Methyl Esterification Method (Boron Trifluoride-Methanol Method) in the "Standard Method for the Analysis of Fats, Oils, and Related Materials" edited by the Japan Oil Chemists' Society. The prepared samples were then analyzed by gas chromatography under the following conditions.

<Analysis conditions of gas chromatography>

[0099]

Apparatus: GC-2010Plus manufactured by Shimadzu Corporation
Column: DB-1, 30 m × 0.25 mm × 0.25 μm (manufactured by Agilent J&W)
Carrier gas: Nitrogen 1 mL/min
Injector: Split (1 :50), T = 300°C
Detector: FID, T = 300°C
Oven temperature: Held at 50°C for 10 minutes, then raised at 5°C/min, and held at 280°C for 10 minutes

[0100] Base on the gas chromatography results, calibration curves were prepared for the concentrations and peak area ratios of various fatty acid methyl.

<Measurement of fatty acid ratio in smoothing agent>

[0101] 1 g of each smoothing agent and 100 ml of a 2 N sodium hydroxide-methanol solution were added to separate flasks. Each flask was heated in a water bath at 60°C and stirred for 30 minutes to carry out saponification. After saponification, the samples were cooled to room temperature and transferred to separatory funnels. Ion-exchanged water, equal to 100% of the reaction solution volume, was added, and the mixture was left to stand for 2 hours. The separated aqueous layer was then removed. This operation was repeated twice. The remaining mixture was dehydrated at 100°C under 2 kPa to obtain fatty acids. To the fatty acids obtained, an arbitrary amount of margaric acid was added as a standard substance to prepare the samples. These samples were then processed following the Methyl Esterification Method (Boron Trifluoride-Methanol Method) as outlined in the "Standard Method for the Analysis of Fats, Oils, and Related Materials" edited by the Japan Oil Chemists' Society, to prepare fatty acid methyl ester samples. The prepared fatty acid methyl ester samples were analyzed using gas chromatography under the specified conditions. Based on the gas chromatography results, the peak area ratios of the standard substance to the various fatty acid methyl esters were calculated to determine the composition ratio of each fatty acid.

(Smoothing agent (A-8))

[0102] The smoothing agent (A-8) was synthesized in the same procedure as the smoothing agent (A-7), except that 92.1 parts of glycerin, 144.2 parts of octanoic acid, and 512.8 parts of palmitic acid were used as raw materials. The proportion of the fatty acids forming the ester compound contained in the smoothing agent (A-8) is shown in Table 2 below.

(Smoothing agent (A-9))

[0103] The smoothing agent (A-9) was synthesized in the same procedure as the smoothing agent (A-7), except that 92.1 parts of glycerin, 300.5 parts of lauric acid, and 423.8 parts of oleic acid were used as raw materials. The proportion of the fatty acids forming the ester compound contained in the smoothing agent (A-9) is shown in Table 2 below.

[Table 1]

Classification	Smoothing agent (A)		(Poly)oxyalkylene derivative (B)		Condensed hydroxy fatty acid (C)		Ionic component (D)		Evaluation		
	Type	Content (%)	Type	Content (%)	Type	Content (%)	Type	Content (%)	Fluff	Bundling properties	Stability
Example 1	A-1 A-6	60 20	B-1	14	C-1	5	D-1	1	◎◎	◎◎	◎◎◎
Example 2	A-1 A-4	65 5	B-1	16.5	C-1	13	D-2	0.5	◎◎	◎◎	◎◎◎
Example 3	A-1	61	B-2	28	C-2	3	D-3	8	◎◎	◎◎	◎◎◎
Example 4	A-2	85	B-1	14	C-3	0.3	D-4	0.7	◎◎	◎◎	◎◎◎
Example 5	A-3	40	B-4	34	C-4	20	D-3 D-4	5 1	◎◎	◎◎	◎◎◎
Example 6	A-4	79	B-1	13	C-1	4	D-2 D-4	1 3	◎◎	◎◎	◎◎◎
Example 7	A-5	75	B-3	15.9	C-2	9	D-3	0.1	◎◎	◎◎	◎◎◎
Example 8	A-6	60	B-5	25	C-1	10	D-4	5	◎◎	◎◎	◎◎◎
Example 9	A-6	45	B-5	30	C-1	10	D-1	15	◎◎	◎◎	◎◎
Example 10	A-7	55	B-1	30	C-1	15			◎◎	◎	◎◎
Example 11	A-2	50	B-1	25	C-4	25			◎◎	◎	◎◎
Example 12	A-1	11	B-4	30	C-3	59			◎◎	◎	◎
Example 13	A-3 A-6	10 10	B-1	80					◎◎	○	◎
Example 14	A-1	10	B-1	90					◎◎	○	◎
Example 15	A-2	8	B-2	92					◎	○	◎
Example 16	A-3	5	B-3	95					◎	○	◎
Example 17	A-4	60	B-9	40					◎◎	○	○
Example 18	A-8	15	B-8	85					◎	○	○
Example 19	A-9	5	B-8 B-9	50 45					○	○	○
Comparative Example 1			B-6 B-7 B-8 B-9	24 24 18 20	rc-1	6	D-5	8	×	×	○
Comparative Example 2	rA-1	81	B-2	15	rc-2	4			×	×	×
Comparative Example 3	rA-1	81	B-2	15	rc-3	4			×	×	×
Comparative Example 4	rA-1	81	B-2	15	rc-4	4			×	×	×
Comparative Example 5			B-1	100					×	×	○
Comparative Example 6	rA-1	40	B-2	40	C-1	20			×	×	○
Comparative Example 7	rA-2	30	B-3	40	C-3	30			×	×	○

[0104] The details of the smoothing agent (A), the (poly)oxyalkylene derivative (B), the condensed hydroxy fatty acid (C), and the ionic component (D) listed in Table 1 are as follows.

(Smoothing agent (A))

[0105]

A-1: Castor oil
A-2: Rapeseed oil
A-3: Sesame oil
A-4: Palm oil
A-5: Linseed oil
A-6: Sunflower oil
A-7: Ester compound of glycerin, lauric acid, and ricinoleic acid (fatty acid composition: 27% lauric acid, 73% ricinoleic

acid)
A-8: Ester compound of glycerin, caprylic acid, and palmitic acid (fatty acid composition: 33% caprylic acid, 67% palmitic acid)
A-9: Ester compound of glycerin, lauric acid, and oleic acid (fatty acid composition: 50% lauric acid, 50% oleic acid)
rA-1: Coconut oil
rA-2: Palm kernel oil

[0106] The proportion (%) of the fatty acids forming the ester compound (A1) contained in each of the smoothing agents (A) of A-1 to A-9, rA-1, and rA-2 is shown in the column "fatty acid" of Table 2 below. Additionally, the proportion (%) of the fatty acids (X) with 16 to 24 carbon atoms relative to the total mass of fatty acids forming the ester compound (A1) is listed in the column "proportion of fatty acid (X)" in Table 2.

[Table 2]

Type of smoothing agent (A)	Fatty acid													Proportion of fatty acids (X)
	Caprylic acid (C8)	Capric acid (C10)	Lauric acid (C12)	Myristic acid (C14)	Palmitic acid (C16)	Stearic acid (C18)	Behenic acid (C22)	Oleic acid (C18:1)	Linoleic acid (C18:2)	Linolenic acid (C18:3)	Eicosenoic acid (C20:1)	Erucic acid (C22:1)	Ricinoleic acid (C18:1+OH)	
A-1					1	1		3	4	1			90	100%
A-2					5	2	1	56	23	11	1	1		100%
A-3					10	6		40	44					100%
A-4				1	44	5		40	10					99%
A-5					7	3		14	15	61				100%
A-6					6	4		19	68	3				100%
A-7			27										73	73%
A-8	33				67									67%
A-9			50					50						50%
rA-1	6	7	49	18	10	2		7	1					20%
rA-2	3	3	48	16	10	2		16	2					30%

(Poly)oxyalkylene derivative (B)

[0107]

B-1: ω-hydroxy (polyoxyethylene) (n=7) castor oil
B-2: ω-hydroxy (polyoxyethylene) (n=20) hydrogenated castor oil
B-3: Hydroxy (polyoxypropylene polyoxyethylene) (m=13, n=10) castor oil
B-4: Hydroxy (polyoxypropylene polyoxyethylene) (m=12, n=12) hydrogenated castor oil
B-5: Oil-and-fat ethylene oxide adduct prepared by addition polymerization of 200 moles of ethylene oxide per mole of castor oil
B-6: α-dodecyl-ω-hydroxy (polyoxyethylene) (n=7)
B-7: Polyoxyalkylene block copolymer with a number average molecular weight of 5000, prepared by block addition polymerization of ethylene oxide and propylene oxide to ethylene glycol, where the polyoxyalkylene group consists of oxyethylene units/oxypropylene units = 30/70 (molar ratio)
B-8: Polyoxyalkylene block copolymer with a number average molecular weight of 10,000, prepared by block addition polymerization of ethylene oxide and propylene oxide to ethylene glycol, where the polyoxyalkylene group consists of oxyethylene units/oxypropylene units = 70/30 (molar ratio)
B-9: Polyoxyethylene glycol octadecenyl ether with a repeat number of oxyethylene units of 20

(Condensed hydroxy fatty acid (C))

[0108]

C-1: Condensed 12-hydroxystearic acid hexamer
C-2: Mixture of condensed castor oil fatty acid tetramer and pentamer
C-3: Condensed castor oil fatty acid hexamer
C-4: Condensed castor oil fatty acid dimer
rc-1: Polyoxyalkylene-modified fatty acid amide, prepared by addition polymerization of 7 moles of ethylene oxide per mole of distearic acid amide of diethylenetriamine
rc-2: Castor oil fatty acid
rc-3: 12-hydroxystearic acid
rc-4: Isostearic acid

(Ionic component (D))

[0109]

D-1: Sodium dodecylbenzenesulfonate
D-2: Potassium 2-ethylhexyl phosphate
D-3: Potassium acetate
D-4: N,N-bis (polyoxyethylene) (n=10) dodecane amine acetate
D-5: Polyoxyethylene glycol (with a repeat number of oxyethylene units of 16) monocetyl ether phosphoric acid ester potassium salt, where the organic phosphoric acid ester salt consists of a monophosphoric acid ester salt/diphosphoric acid ester salt ratio of 1/1 (molar ratio)

Experimental Part 3 (Production of carbon fiber precursor and carbon fiber)

[0110] Carbon fiber precursors and carbon fibers were produced using diluted solutions containing the treatment agents prepared in Experimental Part 1.

[0111] First, in the first step, the acrylic resin was subjected to wet spinning. Specifically, a copolymer with a limiting viscosity of 1.80, consisting of 95% acrylonitrile, 3.5% methyl acrylate, and 1.5% methacrylic acid, was dissolved in dimethylacetamide (DMAC) to prepare a spinning dope with a polymer concentration of 21.0% and a viscosity of 500 poise at 60°C. The spinning dope was discharged from a spinneret with a hole diameter (inner diameter) of 0.075 mm and 12,000 holes at a draft ratio of 0.8 into a coagulation bath containing a 70% aqueous solution of DMAC, maintained at a spinning bath temperature of 35°C.

[0112] The coagulated yarn was drawn 5 times in a water washing tank while simultaneously desolvating to produce a water-swollen acrylic fiber strand (carbon fiber precursor). The treatment agent-containing composition prepared in Experimental Part 1 was further diluted with ion-exchanged water to obtain a 4% diluted solution of the treatment agent. This 4% diluted solution was applied to the acrylic fiber strand by immersion, ensuring that the amount of solid content adhered was 1% (excluding solvent). Subsequently, the acrylic fiber strand underwent a dry densification treatment using a heating roller at 130°C, followed by drawing it 1.7 times between heating rollers at 170°C. The carbon fiber precursor was then wound onto a yarn tube using a winder.

[0113] Next, in the second step, the yarn was unwound from the wound carbon fiber precursor and subjected to a flameproofing treatment for 1 hour in a flameproofing furnace with a temperature gradient of 230 to 270°C in an air atmosphere. After the treatment, the yarn was wound onto a yarn tube via a transport roller to obtain flameproofed yarn (flameproofed fiber).

[0114] Next, in the third step, the yarn was unwound from the wound flameproofed yarn and baked in a carbonization furnace with a temperature gradient of 300 to 1300°C under a nitrogen atmosphere, converting the yarn into carbon fiber. The carbon fiber was then wound onto a yarn tube.

Experimental Part 4 (Evaluation)

[0115] The stability of the treatment agent of each examples and comparative example, as well as the fluff and bundling properties of the flameproofed fibers, were evaluated. The procedure for each test is described below.

(Fluff)

[0116] The fluff on the flameproofed fibers was measured using a fluff counting apparatus installed immediately before the winder. The number of fluffs per hour was evaluated according to the following criteria. The test results are shown in the column "fluff" of Table 1.

· Evaluation criteria for fluff

[0117]

◎◎ (excellent): The number of fluffs is 0 or more and 5 or less.
◎ (good): The number of fluffs is 6 or more and 10 or less.
◦ (acceptable): The number of fluffs is 11 or more and 20 or less.
× (unacceptable): The number of fluffs is 21 or more.

(Bundling properties)

[0118] The bundled state of the flameproofed fibers before winding was visually observed, and the bundling properties was evaluated according to the following criteria. The test results are shown in the column "bundling properties" of Table 1.

· Evaluation criteria for bundling properties

[0119]

◎◎ (excellent): The fibers are bundled, and the tow width is constant.
◎ (good): The fibers are generally bundled, but the tow width is occasionally inconstant.
◦ (acceptable): The fibers are generally bundled, but the tow width is not constant.
× (unacceptable): There are spaces within the fiber bundle, and the fibers are not bundled.

(Stability)

[0120] After producing the treatment agents, 100 g of each treatment agent was placed in a 100-ml vertical sedimentation tube. The appearance of the treatment agent was visually observed after standing at 25°C for 72 hours, and the concentration difference between the upper and lower layers was measured. Stability was evaluated according to the following criteria. The concentration difference was determined by collecting a fixed amount of the treatment agent from a portion near the upper surface and a portion near the bottom of the sedimentation tube, then drying each at 105°C for 2 hours to measure the solid content. The test results are shown in the column "stability" of Table 1.

· Evaluation criteria for stability

[0121]

◎◎◎ (very excellent): No change in appearance is observed after standing.
◎◎ (excellent): Separation is observed, and the concentration difference between the upper and lower layers is 5% or less, but the treatment agent returns to its original state after stirring.
◎ (good): Separation is observed, and the concentration difference between the upper and lower layers is more than 5% and 10% or less, but the treatment agent returns to its original state after stirring.
◦ (acceptable): Separation is observed, and the concentration difference between the upper and lower layers is more than 10%, but the treatment agent returns to its original state after stirring.
× (unacceptable): Separation is observed, and the treatment agent does not return to its original state even after stirring.

[0122] From the results in Table 1, according to the present invention, it is possible to improve the effect of reducing fluff and the bundling properties of flameproofed fibers. In addition, the stability of the treatment agent can be improved.

Claims

1. A carbon fiber precursor treatment agent comprising:

   a smoothing agent (A) that contains an ester compound (A1) of glycerin and a fatty acid containing fatty acid (X); and
   a (poly)oxyalkylene derivative (B), wherein
   the proportion of the fatty acid (X), determined by the following mathematical equation 1, is 50% by mass or more, and
   the fatty acid (X) is a fatty acid with 16 to 24 carbon atoms.

   Proportion of fatty acid (X) = (Total mass of fatty acid with 16 to 24 carbon atoms derived from ester compound (A1) in the carbon fiber precursor treatment agent / Total mass of fatty acid derived from ester compound (A1) in the carbon fiber precursor treatment agent) × 100 [Mathematical Equation 1]

2. The carbon fiber precursor treatment agent according to claim 1, wherein the proportion of the fatty acid (X) determined by the mathematical equation 1 is 70% by mass or more.

3. The carbon fiber precursor treatment agent according to claim 1, wherein the (poly)oxyalkylene derivative (B) contains a compound obtained by adding an alkylene oxide with 2 to 4 carbon atoms to an ester compound of a monohydric to trihydric alcohol and a monovalent fatty acid with 16 to 24 carbon atoms.

4. The carbon fiber precursor treatment agent according to claim 1, wherein when the sum of the contents of the smoothing agent (A) and the (poly)oxyalkylene derivative (B) in the carbon fiber precursor treatment agent is taken as 100% by mass, the carbon fiber precursor treatment agent contains the smoothing agent (A) in an amount of 10% by mass or more and 90% by mass or less and the (poly)oxyalkylene derivative (B) in an amount of 10% by mass or more and 90% by mass or less.

5. The carbon fiber precursor treatment agent according to claim 1, further comprising a condensed hydroxy fatty acid (C).

6. The carbon fiber precursor treatment agent according to claim 5, wherein when the sum of the contents of the smoothing agent (A), the (poly)oxyalkylene derivative (B), and the condensed hydroxy fatty acid (C) in the carbon fiber precursor treatment agent is taken as 100% by mass, the carbon fiber precursor treatment agent contains the smoothing agent (A) in an amount of 9.9% by mass or more and 89.9% by mass or less, the (poly)oxyalkylene derivative (B) in an amount of 10% by mass or more and 90% by mass or less, and the condensed hydroxy fatty acid (C) in an amount of 0.1% by mass or more and 50% by mass or less.

7. The carbon fiber precursor treatment agent according to claim 1, further comprising an ionic component (D).

8. The carbon fiber precursor treatment agent according to claim 1, further comprising a condensed hydroxy fatty acid (C) and an ionic component (D).

9. The carbon fiber precursor treatment agent according to claim 8, wherein when the sum of the contents of the smoothing agent (A), the (poly)oxyalkylene derivative (B), the condensed hydroxy fatty acid (C), and the ionic component (D) in the carbon fiber precursor treatment agent is taken as 100% by mass the carbon fiber precursor treatment agent contains the smoothing agent (A) in a proportion of 9.9% by mass or more and 89.9% by mass or less, the (poly)oxyalkylene derivative (B) in an amount of 9.9% by mass or more and 89.9% by mass or less, the condensed hydroxy fatty acid (C) in an amount of 0.1% by mass or more and 50% by mass or less, and the ionic component in an amount of 0.1% by mass or more and 10% by mass or less.

10. A carbon fiber precursor to which the carbon fiber precursor treatment agent according to any one of claims 1 to 9 is adhered.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/014487

A. CLASSIFICATION OF SUBJECT MATTER

D06M 13/224(2006.01)i; ***D06M 13/17***(2006.01)i; ***D06M 15/53***(2006.01)i; *D06M 101/28*(2006.01)n
FI: D06M13/224; D06M13/17; D06M15/53; D06M101:28

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)

D06M13/224; D06M13/17; D06M15/53; D06M101/28

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2017/169632 A1 (MATSUMOTO YUSHI-SEIYAKU CO., LTD.) 05 October 2017 (2017-10-05) claims	1-10
A	JP 2020-15999 A (TAKEMOTO OIL & FAT CO., LTD.) 30 January 2020 (2020-01-30) claims, examples	1-10
A	WO 2022/065476 A1 (TAKEMOTO OIL & FAT CO., LTD.) 31 March 2022 (2022-03-31) claims, examples	1-10
A	JP 59-116471 A (TAKEMOTO OIL & FAT CO., LTD.) 05 July 1984 (1984-07-05) comparative example 18	1-10

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search **01 June 2023**	Date of mailing of the international search report **13 June 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/JP2023/014487

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2017/169632 A1	05 October 2017	(Family: none)	
JP 2020-15999 A	30 January 2020	CN 111479962 A claims, examples KR 10-2020-0081505 A TW 202012739 A WO 2020/022348 A1	
WO 2022/065476 A1	31 March 2022	(Family: none)	
JP 59-116471 A	05 July 1984	(Family: none)	

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2002088654 A **[0004]**