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(54) **COLORED ORGANIC FIBER, FABRIC AND CLOTHING AND METHOD FOR MANUFACTURING FABRIC**

(57) A problem of the invention is to provide a colored organic fiber that has a deep color and excellent flame retardancy, a cloth and garments each composed of the foregoing organic fiber, and a method for producing a

cloth. To solve this problem, a colored organic fiber having a content of a carrier agent of 1.8% by mass or less relative to the fiber mass is provided. A cloth or garments are obtained, if desired.

EP 3 133 204 A1

Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a colored organic fiber that has a deep color and excellent flame retardancy, a cloth and garments each composed of the foregoing organic fiber, and a method for producing a cloth.

BACKGROUND ART

10 **[0002]** As a method of coloring a flame-retardant cloth containing an organic fiber, such as a meta-type aromatic polyamide fiber, etc., there have hitherto been known a method of containing a pigment in an organic fiber and a method of dyeing a cloth with a carrier agent.

[0003] However, according to the method of containing a pigment in an organic fiber, it was difficult to obtain a cloth having excellent hyperchromicity. Meanwhile, according to the method of dyeing a cloth with a carrier agent, it could not be said that the resulting cloth is sufficient in terms of flame retardancy.

15 **[0004]** In order to solve those problems, for example, PTLs 1 to 3 propose use of a core-sheath structure yarn. However, the use of a core-sheath structure yarn involved such a problem that a lot of time and costs are spent; and a problem that since it is necessary to use a usual synthetic fiber that is poor in flame retardancy for a sheath yarn, the resulting cloth is insufficient in terms of flame retardancy. In addition, for example, PTL 4 proposes that a cloth is dyed with a carrier agent and then washed. However, it could not be said that the resulting cloth is sufficient in terms of flame retardancy.

CITATION LIST

25 PATENT LITERATURE

[0005]

30 PTL 1: JP-A-2009-249758
PTL 2: JP-A-2009-209488
PTL 3: JP-A-2003-147651
PTL 4: JP-A-2012-207348

SUMMARY OF INVENTION

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TECHNICAL PROBLEM

[0006] In view of the foregoing background, the present invention has been made, and an object thereof is to provide a colored organic fiber that has a deep color and excellent flame retardancy, a cloth and garments each composed of the foregoing organic fiber, and a method for producing a cloth.

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SOLUTION TO PROBLEM

[0007] In order to solve the foregoing problems, the present inventors made extensive and intensive investigations. As a result, they have found that in an organic fiber dyed with a carrier agent, by reducing the amount of the carrier agent remaining in the organic fiber, an organic fiber that has a deep color and excellent flame retardancy is obtained and further made extensive and intensive investigations, leading to accomplishment of the present invention.

[0008] Thus, the present invention provides a "colored organic fiber having a content of a carrier agent of 1.8% by mass or less relative to the fiber mass".

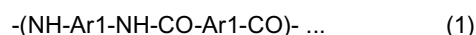
50 **[0009]** On that occasion, it is preferred that the content of the carrier agent is 0.1 to 1.8% by mass relative to the fiber mass. It is preferred that the carrier agent is any one or more selected from the group consisting of DL- β -ethylphenethyl alcohol, 2-ethoxybenzyl alcohol, 3-chlorobenzyl alcohol, 2,5-dimethylbenzyl alcohol, 2-nitrobenzyl alcohol, p-isopropylbenzyl alcohol, 2-methylphenethyl alcohol, 3-methylphenethyl alcohol, 4-methylphenethyl alcohol, 2-methoxybenzyl alcohol, 3-iodobenzyl alcohol, cinnamic alcohol, p-anisyl alcohol, benzhydrol, benzyl alcohol, propylene glycol phenyl ether, ethylene glycol phenyl ether, and N-methylformanilide. It is preferred that the organic fiber is any one selected from the group consisting of a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber, a polybenzoxazole (PBO) fiber, a polybenzimidazole (PBI) fiber, a polybenzthiazole (PBTZ) fiber, a polyimide (PI) fiber, a polysulfonamide (PSA) fiber, a polyetheretherketone (PEEK) fiber, a polyether imide (PEI) fiber, a polyarylate (PAr)

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fiber, a melamine fiber, a phenol fiber, a fluorine-based fiber, and a polyphenylene sulfide (PPS) fiber.

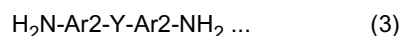
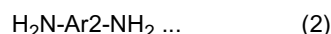
[0010] It is preferred that the organic fiber is a meta-type wholly aromatic polyamide fiber having a crystallinity of 15 to 25%. It is preferred that the organic fiber is a meta-type wholly aromatic polyamide fiber having a content of residual solvent of 1.0% by mass or less. It is preferred that the organic fiber is a meta-type wholly aromatic polyamide fiber having a content of residual solvent of 0.1% by mass or less. On that occasion, it is preferred that the residual solvent is any one selected from the group consisting of N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, and dimethyl sulfoxide.

[0011] It is preferred that the organic fiber is a meta-type wholly aromatic polyamide fiber; and that a meta-type wholly aromatic polyamide forming the meta-type wholly aromatic polyamide fiber is an aromatic polyamide in which in an aromatic polyamide skeleton containing a repeating structural unit represented by the following formula (1), an aromatic diamine component or aromatic dicarboxylic acid halide component that is different from a main structural unit of the repeating structure is copolymerized as a third component such that a proportion of the third component is 1 to 10 mol% relative to the whole amount of the repeating structural units of the aromatic polyamide.



[0012] Here, Ar 1 is a divalent aromatic group having a linking group in a position other than the meta position or an axially parallel direction.

[0013] On that occasion, it is preferred that the third component is an aromatic diamine represented by the following formula (2) or (3), or an aromatic dicarboxylic acid halide represented by the following formula (4) or (5).



[0014] Here, Ar2 is a divalent aromatic group different from Ar1; Ar3 is a divalent aromatic group different from Ar1; Y is at least one atom or functional group selected from the group consisting of an oxygen atom, a sulfur atom, and an alkylene group; and X is a halogen atom.

[0015] In addition, the present invention provides a cloth containing the above-described colored organic fiber. On that occasion, it is preferred that the cloth contains any one or more selected from the group consisting of a polyester fiber, a cellulose fiber, a polyamide fiber, a polyolefin fiber, an acrylic fiber, a rayon fiber, a cotton fiber, an animal hair fiber, a polyurethane fiber, a polyvinyl chloride fiber, a polyvinylidene chloride fiber, an acetate fiber, and a polycarbonate fiber. It is preferred that any one of fibers constituting the cloth contains a flame retarder. It is preferred that any one of fibers constituting the cloth contains a UV absorber or a UV reflector. It is preferred that an areal weight of the cloth is 300 g/m² or less. It is preferred that an LOI is 26 or more. It is preferred that an afterflame time in the vertical flame test (JIS L 1091A-4: three second flame contact) is 1 second or less. It is preferred that a brightness index L value is 80 or less.

[0016] In addition, the present invention provides garments composed of the above-described cloth.

[0017] In addition, the present invention provides a method for producing a cloth containing the above-described colored organic fiber, including dyeing a cloth containing an organic fiber with a carrier agent and then washing the cloth with hot water at a temperature of 90 to 140°C for 10 to 30 minutes, thereby controlling a content of the carrier agent contained in the organic fiber to 1.8% by mass or less relative to the fiber mass.

ADVANTAGEOUS EFFECTS OF INVENTION

[0018] In accordance with the present invention, a colored organic fiber that has a deep color and excellent flame retardancy, a cloth and garments each composed of the foregoing organic fiber, and a method for producing a cloth are obtained.

DESCRIPTION OF EMBODIMENTS

[0019] Embodiments of the present invention are hereunder described in detail. First of all, a colored organic fiber is subject to the present invention. In such an organic fiber, a content of a carrier agent is 1.8% by mass or less relative to the fiber mass.

[0020] Here, the carrier agent is a dyeing auxiliary and is also named a "swelling agent". The kind of such a carrier

agent is not particularly limited. Specifically, examples thereof include L- β -ethylphenethyl alcohol, 2-ethoxybenzyl alcohol, 3-chlorobenzyl alcohol, 2,5-dimethylbenzyl alcohol, 2-nitrobenzyl alcohol, p-isopropylbenzyl alcohol, 2-methylphenethyl alcohol, 3-methylphenethyl alcohol, 4-methylphenethyl alcohol, 2-methoxybenzyl alcohol, 3-iodobenzyl alcohol, cinnamic alcohol, p-anisyl alcohol, benzhydrol, benzyl alcohol, propylene glycol phenyl ether, ethylene glycol phenyl ether, N-methylformanilide, and the like.

[0021] In the colored organic fiber of the present invention, the kind of the organic fiber is not particularly limited. However, in obtaining excellent flame retardancy, a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber, a polybenzoxazole (PBO) fiber, a polybenzimidazole (PBI) fiber, a polybenzthiazole (PBTZ) fiber, a polyimide (PI) fiber, a polysulfonamide (PSA) fiber, a polyetheretherketone (PEEK) fiber, a polyether imide (PEI) fiber, a polyarylate (PAr) fiber, a melamine fiber, a phenol fiber, a fluorine-based fiber, a polyphenylene sulfide (PPS) fiber, and the like are preferred.

[0022] Of those, a meta-type wholly aromatic polyamide fiber is preferred. The meta-type wholly aromatic polyamide fiber is a fiber composed of a polymer in which 85 mol% or more of repeating units thereof is m-phenyleneisophthalamide. Such a meta-type wholly aromatic polyamide may be a copolymer containing a third component within a range of less than 15 mol%.

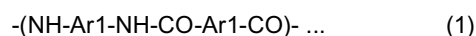
[0023] Such a meta-type wholly aromatic polyamide fiber can be produced by a conventionally known interfacial polymerization method. As for a polymerization degree thereof, it is preferred to use one having an intrinsic viscosity (I.V.) within a range of 1.3 to 1.9 dL/g, as measured with an N-methyl-2-pyrrolidone solution having a concentration of 0.5 g/100 mL.

[0024] The meta-type wholly aromatic polyamide may contain an alkylbenzenesulfonic acid onium salt. Preferred examples of the alkylbenzenesulfonic acid onium salt include compounds, such as a hexylbenzenesulfonic acid tetrabutylphosphonium salt, a hexylbenzenesulfonic acid tributylbenzylphosphonium salt, a dodecylbenzenesulfonic acid tetraphenylphosphonium salt, a dodecylbenzenesulfonic acid tributyltetradecylphosphonium salt, a dodecylbenzenesulfonic acid tetrabutylphosphonium salt, a dodecylbenzenesulfonic acid tributylbenzylammonium salt, etc. Of those, a dodecylbenzenesulfonic acid tetrabutylphosphonium salt and a dodecylbenzenesulfonic acid tributylbenzylammonium salt are especially preferably exemplified because they are easily available, have good thermal stability, and also have a high solubility in N-methyl-2-pyrrolidone.

[0025] In order to obtain a sufficient dye-affinity-improving effect, a content proportion of the alkylbenzenesulfonic acid onium salt is within a range of preferably 2.5 mol% or more, and more preferably 3.0 to 7.0 mol% relative to poly-m-phenyleneisophthalamide.

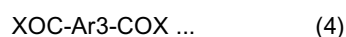
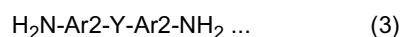
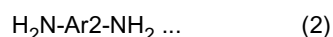
[0026] As a method of mixing poly-m-phenyleneisophthalamide and an alkylbenzenesulfonic acid onium salt, a method in which poly-m-phenyleneisophthalamide is mixed and dissolved in a solvent, and an alkylbenzenesulfonic acid onium salt is then dissolved in the solvent, and other methods may be adopted. The thus obtained dope is formed to a fiber by a conventionally known method.

[0027] For the purpose of improving dyeing affinity and discoloration/fading resistance, the polymer that is used for the meta-type wholly aromatic polyamide fiber may also be obtained by copolymerizing, in an aromatic polyamide skeleton containing a repeating structural unit represented by the following formula (2), an aromatic diamine component or aromatic dicarboxylic acid halide component that is different from a main structural unit of the repeating structure as a third component such that a proportion of the third component is 1 to 10 mol% relative to the whole amount of the repeating structural units of the aromatic polyamide.



[0028] Here, Ar 1 is a divalent aromatic group having a linking group in a position other than the meta position or an axially parallel direction.

[0029] Specific examples of aromatic diamines represented by the formulae (2) and (3) copolymerizable as the third component include p-phenylenediamine, chlorophenylenediamine, methylphenylenediamine, acetylphenylenediamine, aminoanisidine, benzidine, bis(aminophenyl)ether, bis(aminophenyl)sulfone, diaminobenzanilide, diaminoazobenzene, and the like. Specific examples of aromatic dicarboxylic acid dichlorides represented by the formulae (4) and (5) include terephthaloyl chloride, 1,4-naphthalenedicarbonyl chloride, 2,6-naphthalenedicarbonyl chloride, 4,4'-biphenyldicarbonyl chloride, 5-chloroisophthaloyl chloride, 5-methoxyisophthaloyl chloride, bis(chlorocarbonylphenyl)ether, and the like.



[0030] Here, Ar₂ is a divalent aromatic group different from Ar₁; Ar₃ is a divalent aromatic group different from Ar₁; Y is at least one atom or functional group selected from the group consisting of an oxygen atom, a sulfur atom, and an alkylene group; and X is a halogen atom.

[0031] In addition, from the standpoints that dye exhaustion properties are good, and even when dyeing is performed with a small amount of dye or under weak dyeing conditions, the color can be easily adjusted as intended, it is preferred that a crystallinity of the meta-type wholly aromatic polyamide fiber is 5 to 35%. Furthermore, from the standpoints that the dye is less likely to be unevenly distributed on the surface, the discoloration/fading resistance is high, and the practically necessary dimensional stability can be ensured, the crystallinity of the meta-type wholly aromatic polyamide fiber is more preferably 15 to 25%.

[0032] In addition, from the standpoint that the excellent flame retardancy of the meta-type wholly aromatic polyamide fiber is not impaired; and from the standpoint that the dye is less likely to be unevenly distributed on the surface, and the discoloration/fading resistance is high, a content of residual solvent of the meta-type wholly aromatic polyamide fiber is preferably 1.0% by mass or less (more preferably 0.1% by mass or less, and still more preferably 0.01 to 0.09% by mass).

[0033] The meta-type aromatic polyamide fiber can be produced by the following method. In particular, by a method as described later, the crystallinity and the content of residual solvent can be made within the above-described ranges.

[0034] The polymerization method of the meta-type aromatic polyamide polymer is not particularly limited. For example, the solution polymerization method or interfacial polymerization method described in JP-B-35-14399, U.S. Patent No. 3,360,595, JP-B-47-10863, and the like may be adopted.

[0035] A spinning solution is not particularly limited. An amide-based solvent solution containing an aromatic copolyamide polymer obtained by the above-described solution polymerization or interfacial polymerization, or the like may be used, or a spinning solution obtained by isolating the foregoing polymer from the above-described polymerization solution and dissolving it in an amide-based solvent may be used.

[0036] Here, examples of the amide-based solvent may include N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, dimethyl sulfoxide, and the like, with N,N-dimethylacetamide being especially preferred.

[0037] When the resulting copolymerized aromatic polyamide polymer solution further contains an alkali metal salt or an alkaline earth metal salt, the solution becomes more stable and can be used in a higher concentration and at a lower temperature, and hence, such is preferred. A proportion of the alkali metal salt or alkaline earth metal salt is preferably 1% by mass or less, and more preferably 0.1% by mass or less relative to the whole weight of the polymer solution.

[0038] In a spinning/coagulation step, the resulting spinning solution (meta-type wholly aromatic polyamide polymer solution) is spun into a coagulation liquid and coagulated.

[0039] A spinning apparatus is not particularly limited, and a conventionally known wet-spinning apparatus can be used. The number of spinning holes of a spinneret and an arrangement state thereof, a hole shape, and the like are not particularly limited. For example, a multi-hole spinneret for staple fibers, having a number of holes of 1,000 to 30,000 and a spinning hole diameter of 0.05 to 0.2 mm, and the like may be used.

[0040] In addition, it is preferred that a temperature of the spinning solution (meta-type wholly aromatic polyamide polymer solution) upon spinning from the spinneret is within a range of 20 to 90°C.

[0041] As a coagulation bath that is used in order to obtain a fiber, it is preferred to use an aqueous solution containing substantially no inorganic salt and having a concentration of an amide-based solvent (preferably NMP) of 45 to 60% by mass at a temperature of the bath liquid within a range of 10 to 50°C. When the concentration of the amide-based solvent (preferably NMP) is less than 45% by mass, the structure of a skin becomes thick. As a result, there is a concern that the washing efficiency in a washing step decreases, so that it becomes difficult to reduce the content of residual solvent of the fiber. On the other hand, in the case where the concentration of the amide-based solvent (preferably NMP) is more than 60% by mass, there is also a concern that uniform coagulation inside the fiber cannot be achieved, so that it becomes difficult to reduce the content of residual solvent of the fiber. It is preferred that a time of immersion of the fiber in the coagulation bath is within a range of 0.1 to 30 seconds.

[0042] Subsequently, it is preferred to draw the fiber in a draw ratio of 3 to 4 in a plastic drawing bath that is an aqueous solution of an amide-based solvent, preferably NMP in a concentration of 45 to 60% by mass at a bath liquid temperature within a range of 10 to 50°C. After drawing, it is preferred to thoroughly wash the fiber with an aqueous solution of NMP at 10 to 30°C in a concentration of 20 to 40% by mass, followed by passing through a warm water bath at 50 to 70°C.

[0043] The fiber after washing is subjected to a dry heat treatment at a temperature of 270 to 290°C, whereby a meta-type wholly aromatic aramid fiber that satisfies the above-described ranges of the crystallinity and content of residual solvent can be obtained.

[0044] In the colored organic fiber of the present invention, the fiber may be either a long fiber (multifilament) or a short fiber. In particular, a short fiber having a fiber length of 25 to 200 mm is preferred in blend-spinning with other fibers. A single fiber fineness of the organic fiber is preferably within a range of 1 to 5 dtex.

[0045] In the colored organic fiber of the present invention, a dyeing method using a carrier agent is preferred as the

coloring method. In particular, a method of achieving dyeing with a cationic dye is preferred in obtaining excellent hyperchromicity. Conditions of the dyeing step are not particularly limited.

[0046] In such a colored organic fiber, it is important that a content of the carrier agent is 1.8% by mass or less (preferably 0.1 to 1.8% by mass, more preferably 0.1 to 1.0% by mass, and still more preferably 0.3 to 0.9% by mass) relative to the fiber mass. When the content is more than 1.8% by mass, there is a concern that the flame retardancy is impaired. Conversely, when the content is less than 0.1% by weight, there is a concern that the excellent hyperchromicity is not obtained, or a hot water washing step as described later becomes complicated.

[0047] As a method of lowering the content of the carrier agent, for example, there is exemplified a method in which the dyed cloth is subjected to reduction washing, if desired and then subjected to hot water washing with hot water at a temperature of 90 to 140°C (more preferably 110 to 140°C) for 10 to 30 minutes.

[0048] Next, the cloth of the present invention is a cloth containing the above-described colored organic fiber. Though such a cloth is composed of only the above-described colored organic fiber, it may further contain other fibers, such as a polyester fiber, a cellulose fiber, a polyamide fiber, a polyolefin fiber, an acrylic fiber, a rayon fiber, a cotton fiber, an animal hair fiber, a polyurethane fiber, a polyvinyl chloride fiber, a polyvinylidene chloride fiber, an acetate fiber, a polycarbonate fiber, etc.

[0049] On that occasion, when a proportion of the meta-type wholly aromatic polyamide fiber contained in the cloth is 50% by mass or more relative to the cloth mass, the excellent flame retardancy is obtained, and hence, such is preferred. The above-described flame-retardant fiber, synthetic fiber, regenerated fiber, or natural fiber can be arbitrarily mixed according to an application or needs of use. As a more specific example, a mixed fiber in a mixing ratio of 50 to 98% by mass of a meta-type wholly aromatic polyamide resin, 2 to 50% by mass of a polyester fiber, and 0 to 50% by mass of a cellulose-based fiber can be made to have both dye affinity and comfortableness. The proportions may be adjusted according to the performance to be emphasized.

[0050] It is also preferred that any one of fibers constituting the cloth contains a flame retarder, or a UV absorber or a UV reflector. On that occasion, in the UV absorber, its solubility in water is preferably 0.04 mg/L or less. When the solubility in water is more than 0.04 mg/L, in dyeing with the carrier agent, there is also a concern that the UV absorber elutes, so that light fastness after dyeing decreases.

[0051] A method for producing the above-described cloth is not particularly limited. For example, there may be adopted a method in which a spun yarn is obtained using the above-described organic fiber (or the above-described organic fiber and other fibers), woven or knitted as a single yarn or a 2-ply yarn, and then dyed with a carrier agent, followed by hot water washing by the above-described method.

[0052] On that occasion, as for a structure of the cloth, woven fabric structures, such as a plain weave, a twill weave, a satin weave, a double weave, etc., are preferred, and a knit or a nonwoven fabric may also be adopted. The production method of a cloth is not particularly limited. For example, a known knit-weaving loom, such as a rapier loom, a gripper loom, etc., can be used.

[0053] The resulting cloth uses the above-described organic fiber, and therefore, it is excellent in hyperchromicity and flame retardancy. On that occasion, the hyperchromicity is preferably 80 or less (more preferably 52.5 or less, and still more preferably 10 to 52.3) in terms of a brightness index L value. The flame retardancy is preferably 26 or more (more preferably 26 to 40) in terms of LOI. In the vertical flame test (JIS L1091A-4: three second flame contact), an afterflame time of the cloth is preferably 25 seconds or less (more preferably 1 second or less).

[0054] In the above-described cloth, its areal weight is preferably 300 g/m² or less (more preferably 50 to 250 g/m²). When the areal weight is more than 300 g/m², there is a concern that lightweight properties of the cloth are impaired.

[0055] Next, the garments of the present invention are garments composed of the above-described cloth. Examples of such garments include protective clothes, firefighter clothes, fireproof clothes, rescue clothes, activities clothes, office clothes, racing suits for motor sports, work clothes, gloves, hats, bests, and the like. In addition, the above-described work clothes include work clothes for activities in a steel plant or steel factory, work clothes for welding, work clothes in an explosion-proof area, and the like. In addition, the above-described gloves include work gloves used in the aircraft industry, the information equipment industry, the precision machinery industry, and the like where precision components are treated.

[0056] In addition, the above-described cloth may also be used for fiber products, such as a curtain, a car sheet, a bag, etc.

EXAMPLES

[0057] The present invention is hereunder described in detail with reference to Examples, but it should be construed that the present invention is not limited by these Examples at all. In addition, various physical properties in the Examples are those measured by the following methods.

(1) Flame Retardancy of Cloth (Vertical Flame Test)

[0058] An afterflame time (sec) was evaluated on the basis of JIS L1091A-4 (three second flame contact).

(2) Content of Residual Solvent

[0059] About 8.0 g of a fiber was collected, dried at 105°C for 120 minutes, and then allowed to stand for cooling within a desiccator, and a fiber mass (M1) was weighed. Subsequently, this fiber was subjected to reflux extraction in methanol for 1.5 hours using a Soxhlet extractor, thereby extracting an amide-based solvent contained in the fiber. After completion of the extraction, the fiber was taken out, vacuum-dried at 150°C for 60 minutes, and then allowed to stand for cooling within a desiccator, and a fiber mass (M2) was weighed. Using the obtained M1 and M2, a content of the solvent remaining in the fiber (amide-based solvent mass) was calculated according to the following equation.

$$\text{Content of residual solvent (\%)} = [(M1 - M2)/M1] \times 100$$

(3) Crystallinity

[0060] Using an X-ray diffraction apparatus (RINT TTRIII, manufactured by Rigaku Corporation), raw fibers were bundled into a fiber bundle of about 1 mm in diameter and mounted on a fiber sample table to measure a diffraction profile. The measurement conditions were as follows: Cu-K α radiation source (50 kV, 300 mA), scanning angle range: 10 to 35°, continuous measurement, measurement width: 0.1°, scanning at 1°/min. From the measured diffraction profile, air scattering and incoherent scattering were corrected by linear approximation to obtain a total scattering profile. Subsequently, an amorphous scattering profile was subtracted from the total scattering profile to obtain a crystal scattering profile. A crystallinity was determined from an integrated intensity of the crystal scattering profile (crystal scattering intensity) and an integrated intensity of the total scattering profile (total scattering intensity) according to the following equation.

$$\text{Crystallinity (\%)} = [(\text{Crystal scattering intensity})/(\text{Total scattering intensity})] \times 100$$

(4) Content of Residual Carrier Agent

Measurement method:

[0061] A GC/MS sample made of a fiber sample was charged in a sample tube and measured by ATD. After confirming a carrier agent by a qualitative analysis, a quantitative analysis was performed under the following conditions.

Calibration curve:

[0062] DOWANOL PPH 10.180 mg/mL (n-hexane), 0.50, 0.75, 1.00 μ L

Column: DB-5ms 0.25 mm $\times$ 28 m

Carrier: He

Inject: ATD 350°C $\times$ 20 min (sample heating), 300°C $\times$ 10 min (ejection)

ColdTrap: 10°C

Interface-valve-transfer: 250°C Mass Range 94 108 152

Detector: GCMS-QP2010

Ion source: 200°C

Voltage: 1.35 kV (-0.48kV)

Oven: 110°C $\times$ 2 min, 110 to 190°C (10°C/min)

Gas flow rate: Primary = 10/90, secondary = 1/42.0%

(5) Hyperchromicity (L value)

[0063] The color measurement was performed using a MacBeth spectrophotometer, Color-Eye 3100.

(6) Areal Weight

[0064] An areal weight (g/m^2) was measured in conformity with JIS L1096.

5 [Example 1]

[0065] A meta-type wholly aromatic aramid fiber was prepared by the following method.

[0066] 20.0 parts by mass of a poly-m-phenyleneisophthalamide powder having an intrinsic viscosity (I.V.) of 1.9 as produced by interfacial polymerization in accordance with the method described in JP-B-47-10863 was suspended in 80.0 parts by mass of N-methyl-2-pyrrolidone (NMP) cooled to -10°C , thereby forming a slurry. Subsequently, the suspension liquid was heated for dissolution to 60°C , thereby obtaining a transparent polymer solution. A UV absorber made of a 2-[2H-benzotriazol-2-yl]-4-6-bis(1-methyl-1-phenylethyl)ph enol powder (solubility in water: 0.01 mg/L) in an amount of 3.0% by mass relative to the polymer was mixed with and dissolved in the polymer solution, and the mixture was defoamed under reduced pressure to prepare a spinning solution (spinning dope).

15 [Spinning/Coagulation Step]

[0067] The spinning dope was discharged and spun from a spinneret having a hole diameter of 0.07 mm and a number of holes of 500 into a coagulation bath at a bath temperature of 30°C . A composition of the coagulation liquid was water/NMP = 45/55 (parts by mass). The spinning dope was discharged and spun into the coagulation bath at a yarn speed of 7 m/min.

[Plastic-Drawing-Bath Drawing Step]

[0068] Subsequently, drawing was performed to a draw ratio of 3.7 in a plastic drawing bath at a temperature of 40°C having a composition of water/NMP = 45/55.

[Washing Step]

[0069] After drawing, washing was performed in a bath of water/NMP = 70/30 at 20°C (immersion length: 1.8 m) and then in a water bath at 20°C (immersion length: 3.6m), and further thoroughly washed through a hot water bath at 60°C (immersion length: 5.4 m).

35 [Dry Heat Treatment Step]

[0070] The fiber after washing was subjected to a dry heat treatment using a hot roller having a surface temperature of 280°C , thereby obtaining a meta-type wholly aromatic aramid fiber.

40 [Cutting Step]

[0071] The meta-type wholly aromatic aramid fiber was crimped and cut into staple fibers having a length of 51 mm (raw stock).

45 [Physical Properties of Raw Stock]

[0072] The resulting meta-type wholly aromatic aramid fiber had the following properties: single fiber fineness: 1.7 dtex, content of residual solvent: 0.08% by mass, and crystallinity: 19%.

[0073] Meanwhile, as other fiber raw stocks, a para-type aramid fiber: "TWARON (registered trademark)", manufactured by Teijin Aramid and a conductive yarn (nylon): "NO SHOCK (registered trademark)", manufactured by Solutia Inc. (nylon conductive yarn having conductive carbon fine particles kneaded thereinto) were prepared.

[0074] Subsequently, respective staple fibers of a meta-type wholly aromatic aramid fiber (MA) (length: 51 mm), a para-type wholly aromatic polyamide (PA) (length: 50 mm), and a nylon conductive yarn (AS) (length: 51 mm) were blend-spun in a ratio of MA/PA/AS of 93/5/2 into a spun yarn (40 count, 2-ply yarn), and woven at a weaving density of warp: 65 yarns/25.4 mm and weft: 55 yarns/25.4 mm, thereby giving a plain-woven fabric having an areal weight of 170 g/m^2 .

[0075] Subsequently, the cloth was treated with a dyeing prescription and a hot water washing prescription.

(Dyeing Prescription)

[0076] First of all, the cloth was dyed with the following dyeing prescription.

- 5 • Cationic dye: Trade name: Kayacryl Red GL-ED, manufactured by Nippon Kayaku Co., Ltd., 6.0% owf
- Carrier agent: Propylene glycol phenyl ether (DOWANOL PPH, manufactured by The Dow Chemical Company), 40 g/L

[0077] The term "40 g/L" means "40 g is contained based on one liter of water".

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- Acetic acid: 0.3 cc/L
- Dispersant: 0.5 cc/L
- Sodium nitrate: 25 g/L
- Bath ratio: 1/20
- 15 • Temperature $\times$ time: 135°C $\times$ 60 min

[0078] Subsequently, the resulting colored cloth was washed in the following reduction bath.

- Bath ratio: 1/20
- 20 • Temperature $\times$ time: 90°C $\times$ 20 min
- Reduction bath: Hydrosulfite, 1g/L, soda ash, 1 g/L

(Hot Water Washing Prescription)

25 **[0079]** Subsequently, the cloth was subjected to hot water washing with hot water at a temperature of 130°C for 20 minutes. Subsequently, the cloth was subjected to dry heat setting at a temperature of 180°C for 2 minutes.

[0080] The evaluation results of the resulting cloth are shown in Table 1.

[Example 2]

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[0081] The same operation as in Example 1 was performed, except that the one-time hot water washing prescription treatment of 130°C $\times$ 20 min was changed to a two-time treatment of 130°C $\times$ 20 min. The evaluation results are shown in Table 1.

35 [Example 3]

[0082] The same operation as in Example 1 was performed, except that the one-time hot water washing prescription treatment of 130°C $\times$ 20 min was changed to a two-time treatment of 120°C $\times$ 20 min. The evaluation results are shown in Table 1.

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[Example 4]

[0083] The same operation as in Example 1 was performed, except that 40 g/L of DOWANOL PPH in the dyeing prescription was changed to 60 g/L of benzyl alcohol. The evaluation results are shown in Table 1.

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[Example 5]

[0084] The same operation as in Example 1 was performed, except that 40 g/L of DOWANOL PPH in the dyeing prescription was changed to 60 g/L of benzyl alcohol, and that the hot water washing prescription treatment of 130°C $\times$ 20 min was changed to a two-time treatment of 120°C $\times$ 20 min. The evaluation results are shown in Table 1.

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[Example 6]

[0085] The same operation as in Example 1 was performed, except that 40 g/L of DOWANOL PPH in the dyeing prescription was changed to 60 g/L of benzyl alcohol, and that the hot water washing prescription treatment of 130°C $\times$ 20 min was changed to a two-time treatment of 120°C $\times$ 20 min. The evaluation results are shown in Table 1.

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[Example 7]

[0086] The same operation as in Example 1 was performed, except that 40 g/L of DOWANOL PPH in the dyeing prescription was changed to 60 g/L of benzyl alcohol, and that the hot water washing prescription treatment of 130°C × 20 min was changed to a two-time treatment of 120°C × 20 min. The evaluation results are shown in Table 1.

[Comparative Example 1]

[0087] The same operation as in Example 1 was performed, except that the hot water washing prescription treatment of 130°C × 20 min was changed to a one-time treatment of 90°C × 20 min. The evaluation results are shown in Table 1.

[Example 8]

[0088] The same operation as in Example 1 was performed, except that the hot water washing prescription treatment of 130°C × 20 min was changed to a five-time treatment of 90°C × 20 min. The evaluation results are shown in Table 1.

[Example 9]

[0089] The same operation as in Example 1 was performed, except that the hot water washing prescription treatment of 130°C × 20 min was changed to a ten-time treatment of 90°C × 20 min. The results are shown in Table 1.

[Example 10]

[0090] The same operation as in Example 1 was performed, except that the amount of DOWANOL PPH in the dyeing prescription was changed to 30 g/L. The evaluation results are shown in Table 1.

[Example 11]

[0091] The same operation as in Example 1 was performed, except that the amount of DOWANOL PPH in the dyeing prescription was changed to 20 g/L. The evaluation results are shown in Table 1.

[Example 12]

[0092] The same operation as in Example 1 was performed, except that the amount of DOWANOL PPH in the dyeing prescription was changed to 10 g/L. The evaluation results are shown in Table 1.

Table 1

	Material mixing ratio (%)	Meta-type wholly aromatic polyamide fiber (MA)			Flame retardancy	Hyperchromicity
		Crystallinity (%)	Content of residual solvent (% by mass)	Content of residual carrier agent (% by mass)	Afterflame time according to JIS L1091A-4: three second flame contact (sec)	L value
Example 1	MA93/PA5/AS2	19	0.08	0.8	1	52.0
Example 2	MA93/PA5/AS2	19	0.08	0.5	0	52.3
Example 3	MA93/PA5/AS2	19	0.08	0.9	1	52.0
Example 4	MA93/PA5/AS2	19	0.08	0.8	1	51.9
Example 5	MA93/PA5/AS2	19	0.08	0.4	0	52.2
Example 6	MA93/PA5/AS2	19	0.08	0.9	1	52.1
Example 7	MA93/PA5/AS2	19	0.08	0.5	0	52.1

(continued)

	Material mixing ratio (%)	Meta-type wholly aromatic polyamide fiber (MA)			Flame retardancy	Hyperchromicity
		Crystallinity (%)	Content of residual solvent (% by mass)	Content of residual carrier agent (% by mass)	Afterflame time according to JIS L1091A-4: three second flame contact (sec)	L value
Comparative Example 1	MA93/PA5/AS2	19	0.08	2.5	Entirely burnt	51.8
Example 8	MA93/PA5/AS2	19	0.08	1.5	25	51.9
Example 9	MA93/PA5/AS2	19	0.08	1.0	12	52.0
Example 10	MA93/PA5/AS2	19	0.08	0.8	1	52.7
Example 11	MA93/PA5/AS2	19	0.08	0.8	1	53.5
Example 12	MA93/PA5/AS2	19	0.08	0.8	1	54.0

INDUSTRIAL APPLICABILITY

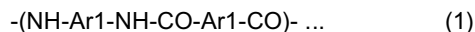
[0093] In accordance with the present invention, a colored organic fiber that has a deep color and excellent flame retardancy, a cloth and garments each composed of the foregoing organic fiber, and a method for producing a cloth are provided, and its industrial value is extremely large.

Claims

1. A colored organic fiber having a content of a carrier agent of 1.8% by mass or less relative to the fiber mass.
2. The colored organic fiber according to claim 1, wherein the content of the carrier agent is 0.1 to 1.8% by mass relative to the fiber mass.
3. The colored organic fiber according to claim 1, wherein the carrier agent is any one or more selected from the group consisting of DL- β -ethylphenethyl alcohol, 2-ethoxybenzyl alcohol, 3-chlorobenzyl alcohol, 2,5-dimethylbenzyl alcohol, 2-nitrobenzyl alcohol, p-isopropylbenzyl alcohol, 2-methylphenethyl alcohol, 3-methylphenethyl alcohol, 4-methylphenethyl alcohol, 2-methoxybenzyl alcohol, 3-iodobenzyl alcohol, cinnamic alcohol, p-anisyl alcohol, benzhydrol, benzyl alcohol, propylene glycol phenyl ether, ethylene glycol phenyl ether, and N-methylformanilide.
4. The colored organic fiber according to claim 1, wherein the organic fiber is any one selected from the group consisting of a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber, a polybenzoxazole (PBO) fiber, a polybenzimidazole (PBI) fiber, a polybenzthiazole (PBTZ) fiber, a polyimide (PI) fiber, a polysulfonamide (PSA) fiber, a polyetheretherketone (PEEK) fiber, a polyether imide (PEI) fiber, a polyarylate (PAr) fiber, a melamine fiber, a phenol fiber, a fluorine-based fiber, and a polyphenylene sulfide (PPS) fiber.
5. The colored organic fiber according to claim 1, wherein the organic fiber is a meta-type wholly aromatic polyamide fiber having a crystallinity of 15 to 25%.
6. The colored organic fiber according to claim 1, wherein the organic fiber is a meta-type wholly aromatic polyamide fiber having a content of residual solvent of 1.0% by mass or less.
7. The colored organic fiber according to claim 1, wherein the organic fiber is a meta-type wholly aromatic polyamide fiber having a content of residual solvent of 0.1% by mass or less.
8. The organic fiber according to claim 6 or 7, wherein the residual solvent is any one selected from the group consisting

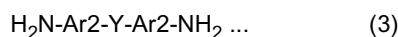
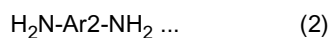
of N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, and dimethyl sulfoxide.

9. The colored organic fiber according to claim 1, wherein the organic fiber is a meta-type wholly aromatic polyamide fiber; and a meta-type wholly aromatic polyamide forming the a meta-type wholly aromatic polyamide fiber is an aromatic polyamide in which in an aromatic polyamide skeleton containing a repeating structural unit represented by the following formula (1), an aromatic diamine component or aromatic dicarboxylic acid halide component that is different from a main structural unit of the repeating structure is copolymerized as a third component such that a proportion of the third component is 1 to 10 mol% relative to the whole amount of the repeating structural units of the aromatic polyamide:



wherein Ar 1 is a divalent aromatic group having a linking group in a position other than the meta position or an axially parallel direction.

10. The colored organic fiber according to claim 9, wherein the third component is an aromatic diamine represented by the following formula (2) or (3) or an aromatic dicarboxylic acid halide represented by the following formula (4) or (5):



wherein Ar2 is a divalent aromatic group different from Ar1; Ar3 is a divalent aromatic group different from Ar1; Y is at least one atom or functional group selected from the group consisting of an oxygen atom, a sulfur atom, and an alkylene group; and X is a halogen atom.

11. A cloth comprising the colored organic fiber according to claim 1.
12. The cloth according to claim 11, wherein the cloth contains any one or more selected from the group consisting of a polyester fiber, a cellulose fiber, a polyamide fiber, a polyolefin fiber, an acrylic fiber, a rayon fiber, a cotton fiber, an animal hair fiber, a polyurethane fiber, a polyvinyl chloride fiber, a polyvinylidene chloride fiber, an acetate fiber, and a polycarbonate fiber.
13. The cloth according to claim 11, wherein any one of fibers constituting the cloth contains a flame retarder.
14. The cloth according to claim 11, wherein any one of fibers constituting the cloth contains a UV absorber or a UV reflector.
15. The cloth according to claim 11, wherein an areal weight of the cloth is 300 g/m² or less.
16. The cloth according to claim 11, wherein an LOI is 26 or more.
17. The cloth according to claim 11, wherein an afterflame time in the vertical flame test (JIS L1091A-4: three second flame contact) is 1 second or less.
18. The cloth according to claim 11, wherein a brightness index L value is 80 or less.
19. Garments comprising the cloth according to claim 11.
20. A method for producing the cloth containing the colored organic fiber according to claim 11, comprising dyeing a cloth containing an organic fiber with a carrier agent and then washing the cloth with hot water at a temperature of 90 to 140°C for 10 to 30 minutes, thereby controlling a content of the carrier agent contained in the organic fiber to 1.8% by mass or less relative to the fiber mass.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/060712

A. CLASSIFICATION OF SUBJECT MATTER

D06P1/613(2006.01)i, D01F6/80(2006.01)i, D01F6/90(2006.01)i, D03D15/00(2006.01)i, D03D15/12(2006.01)i, D06P3/04(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D06P1/613, D01F6/80, D01F6/90, D03D15/00, D03D15/12, D06P3/04

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2015

Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015

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/Y	JP 2008-291384 A (Teijin Techno Products Ltd.), 04 December 2008 (04.12.2008), paragraphs [0002], [0029]; examples (Family: none)	1-4, 11-13, 15, 18-20/3, 5-10, 14, 16-17
X/Y	JP 57-16983 A (Teijin Ltd.), 28 January 1982 (28.01.1982), examples (Family: none)	1-2, 4, 11-13, 15, 18-20/3, 5-10, 14, 16-17
X/Y	JP 49-3469 B1 (Teijin Ltd.), 26 January 1974 (26.01.1974), column 5, lines 11 to 15; examples (Family: none)	1-2, 4, 11-20/ 3, 5-10, 14, 16-17

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

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Date of the actual completion of the international search
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Date of mailing of the international search report
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Name and mailing address of the ISA/
Japan Patent Office
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Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/060712

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X/Y/A	JP 2013-204210 A (Teijin Ltd.), 07 October 2013 (07.10.2013), examples (Family: none)	1, 3-4, 11-13, 15-19/5-10, 14/2, 20
X/Y/A	JP 2010-526943 A (Southern Mills, Inc.), 05 August 2010 (05.08.2010), claims; examples & US 2008/0295232 A1 & WO 2008/141060 A2 & EP 2145045 A2	1, 3-4, 11-13, 15-19/5-10, 14/2, 20
Y/A	JP 2011-236543 A (Teijin Techno Products Ltd.), 24 November 2011 (24.11.2011), paragraphs [0015], [0029], [0054] to [0057] & US 2013/0023610 A1 & WO 2011/129279 A1 & EP 2559792 A1	5-10, 14/1-4, 11-13, 15-20
Y/A	JP 2012-036534 A (Kisen Kabushiki Kaisha), 23 February 2012 (23.02.2012), paragraphs [0007], [0059]; examples (Family: none)	16-17/1-15, 18-20

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2003147651 A [0005]
- JP 2012207348 A [0005]
- JP 3514399 B [0034]
- US 3360595 A [0034]
- JP 47010863 B [0034] [0066]