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

(11) **EP 3 779 004 A1**

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

(43) Date of publication:
17.02.2021 Bulletin 2021/07

(21) Application number: **19782317.2**

(22) Date of filing: **25.03.2019**

(51) Int Cl.:
D03D 15/00 *(2021.01)* ***A41D 31/00*** *(2019.01)*
A41D 31/04 *(2019.01)* ***A41D 31/08*** *(2019.01)*

(86) International application number:
PCT/JP2019/012463

(87) International publication number:
WO 2019/194001 (10.10.2019 Gazette 2019/41)

(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 MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **03.04.2018 JP 2018071562**

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(54) FABRIC AND TEXTILE PRODUCT

(57) A task is to provide a cloth which is advantageous in that the cloth has extremely excellent flame retardancy, and further has excellent washing shrinkage resistance and excellent hand as well as excellent antistatic properties, preferably in that the whole of the cloth can be uniformly dyed, and a fiber product, and the task is achieved by obtaining a cloth using a spun yarn which comprises a meta-type wholly aromatic polyamide fiber, a modacrylic fiber, and a conductive fiber.

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Description

Technical Field

[0001] The present invention relates to a cloth having extremely excellent flame retardancy and having excellent washing shrinkage resistance and excellent hand as well as excellent antistatic properties, and a fiber product.

Background Art

[0002] Conventionally, in the applications of protective clothing, fire-fighting fireproof clothing, fire fighting clothing, rescue clothing, flame-retardant workwear, a police uniform, Self-Defense Forces official clothing, military clothing, and the like, a cloth having flame retardancy has been used (see, for example, PTL's 1 to 4).

[0003] Meanwhile, in recent years, a cloth that is not only flame retardant but also comfortable to wear is demanded, but there has not been proposed a cloth which has extremely excellent flame retardancy, and which has excellent resistance to shrinkage due to washing (washing shrinkage resistance), excellent hand, and excellent antistatic properties.

Citation List

Patent Literature

[0004]

PTL 1: JP-A-2014-221955
PTL 2: JP-A-2015-94043
PTL 3: JP-A-8-325934
PTL 4: JP-T-2014-529690 (the term "JP-T" as used herein means a published Japanese translation of a PCT patent application)

Summary of Invention

Technical Problem

[0005] In view of the above, the present invention has been made, and an object of the invention is to provide a cloth which is advantageous in that the cloth has extremely excellent flame retardancy, and further has excellent washing shrinkage resistance and excellent hand as well as excellent antistatic properties, preferably in that the whole of the cloth can be uniformly dyed, and a fiber product.

Solution to Problem

[0006] The present inventors have conducted extensive and intensive studies with a view toward achieving the above-mentioned object. As a result, it has been found that, by appropriately selecting the type of the fiber constituting the cloth and the like, there can be obtained a cloth which is advantageous not only in that the cloth has extremely excellent flame retardancy, and further has excellent washing shrinkage resistance and excellent hand, but also in that the whole of the cloth can be uniformly dyed, and further extensive and intensive studies have been made, and the present invention has been completed.

[0007] Thus, in the present invention, there is provided "a cloth comprising a spun yarn which comprises a meta-type wholly aromatic polyamide fiber, a modacrylic fiber, and a conductive fiber".

[0008] In the cloth of the invention, it is preferred that the spun yarn contains the meta-type wholly aromatic polyamide fiber in an amount of 5% by weight or more, based on the weight of the spun yarn. Further, it is preferred that the spun yarn contains the modacrylic fiber in an amount of 30% by weight or more, based on the weight of the spun yarn. It is preferred that the spun yarn contains the conductive fiber in an amount of 1% by weight or more, based on the weight of the spun yarn. It is preferred that the spun yarn comprises only the meta-type wholly aromatic polyamide fiber, the modacrylic fiber, and the conductive fiber. It is preferred that the meta-type wholly aromatic polyamide fiber has a residual solvent content of 0.1% by weight or less. It is preferred that the meta-type wholly aromatic polyamide fiber has a crystallinity in the range of from 15 to 25%. Particularly, it is preferred that a meta-type wholly aromatic polyamide forming the meta-type wholly aromatic polyamide fiber is an aromatic polyamide having an aromatic polyamide skeleton comprising repeating structural units represented by the formula (1) below, wherein an aromatic diamine component different

from the main constituent units of the repeating structure, or an aromatic dicarboxylic acid halide component is copolymerized as a third component with the aromatic polyamide skeleton so that the amount of the third component becomes 1 to 10 mol%, based on the total mole of the repeating structural units of the aromatic polyamide:

- (NH-Ar1-NH-CO-Ar1-CO)- Formula (1)

wherein Ar1 is a divalent aromatic group having a bonding group at a position other than the meta position or the parallel axis direction.

[0009] In the above-mentioned cloth, it is preferred that, as the third component, the aromatic diamine is the following formula (2) or (3), or the aromatic dicarboxylic acid halide is the following formula (4) or (5):

H_2N-Ar2-NH_2 Formula (2)

H_2N-Ar2-Y-Ar2-NH_2 Formula (3)

XOC-Ar3-COX Formula (4)

XOC-Ar3-Y-Ar3-COX Formula (5)

wherein Ar2 represents a divalent aromatic group different from Ar1, Ar3 represents a divalent aromatic group different from Ar1, Y represents 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 represents a halogen atom.

[0010] Further, it is preferred that the meta-type wholly aromatic polyamide fiber further contains an organic dye, an organic pigment, or an inorganic pigment. It is preferred that the conductive fiber is an acrylic fiber. It is preferred that the modacrylic fiber and the conductive fiber are dyed with the same dye.

[0011] In the cloth of the invention, it is preferred that the cloth contains an ultraviolet light absorber and/or a reflective agent. Further, it is preferred that the cloth has a weight per unit in the range of from 130 to 300 g/m^2. It is preferred that the cloth has an afterflame time of 2 seconds or less, as measured by the method prescribed in ISO 15025: 2000 A method. It is preferred that the cloth has a carbonized area of 30 cm^2 or less, as measured by the method prescribed in JIS L1091:1999 A-1 method. It is preferred that the cloth has a shrinkage rate of 5% or less, as measured after subjected to washing 5 times in accordance with the method prescribed in ISO 5077. It is preferred that the cloth has a thermal shrinkage rate of 10% or less, as measured after subjected to heat treatment at 180°C for 5 minutes in accordance with the method prescribed in ISO17493. It is preferred that the cloth has a water absorbing time of 30 seconds or less, as measured by the method prescribed in JIS L1907:2010 (dropping method) . It is preferred that the cloth has a bending resistance of 7.0 cm or less, as measured by the method prescribed in JIS L1096: 2010 A method (cantilever) . It is preferred that the cloth has an antistaticity of 7.0 μC or less, as measured by the method prescribed in JIS L1094:2014 (antistatic properties).

[0012] Further, in the invention, there is provided a fiber product using the above-mentioned cloth, which is any one fiber product selected from the group consisting of protective clothing, fire-fighting fireproof clothing, fire fighting clothing, rescue clothing, workwear, a police uniform, Self-Defense Forces official clothing, and military clothing.

Advantageous Effects of Invention

[0013] By the present invention, there can be obtained a cloth which is advantageous not only in that the cloth has extremely excellent flame retardancy, and further has excellent washing shrinkage resistance and excellent hand, but also in that the whole of the cloth can be uniformly dyed, and a fiber product.

Description of Embodiments

[0014] Hereinbelow, an embodiment of the present invention will be described in detail. First, the cloth of the invention comprises a spun yarn which comprises ameta-type wholly aromatic polyamide fiber, a modacrylic fiber, and a conductive fiber.

[0015] The meta-type wholly aromatic polyamide fiber used in the invention is a fiber formed from a polymer in which 85 mol% or more of the repeating units are m-phenyleneisophthalamide. The meta-type wholly aromatic polyamide may be a copolymer containing a third component in an amount in the range of less than 15 mol%.

[0016] The meta-type wholly aromatic polyamide can be produced by a conventionally known interfacial polymerization method, and there is preferably used the meta-type wholly aromatic polyamide having, in terms of the degree of polymerization of the polymer, an intrinsic viscosity (I.V.) in the range of from 1.3 to 1.9 dl/g, as measured in the form of an N-

methyl-2-pyrrolidone solution having a concentration of 0.5 g/100 ml.

[0017] The meta-type wholly aromatic polyamide may contain an alkylbenzenesulfonic acid onium salt. Preferred examples of alkylbenzenesulfonic acid onium salts include compounds, such as tetrabutylphosphonium hexylbenzenesulfonate, tributylbenzylphosphonium hexylbenzenesulfonate, tetraphenylphosphonium dodecylbenzenesulfonate, tributyltetradecylphosphonium dodecylbenzenesulfonate, tetrabutylphosphonium dodecylbenzenesulfonate, and tributylbenzylammonium dodecylbenzenesulfonate. Of these, especially preferred is tetrabutylphosphonium dodecylbenzenesulfonate or tributylbenzylammonium dodecylbenzenesulfonate because they are easily available and have excellent thermal stability as well as high solubility in N-methyl-2-pyrrolidone.

[0018] For obtaining a satisfactory improvement effect for the dyeing properties, the amount of the alkylbenzenesulfonic acid onium salt contained is preferably 2.5 mol% or more, preferably in the range of from 3.0 to 7.0 mol%, based on the mole of the poly-m-phenyleneisophthalamide.

[0019] With respect to the method for mixing poly-m-phenyleneisophthalamide with an alkylbenzenesulfonic acid onium salt, there is used a method in which poly-m-phenyleneisophthalamide is mixed into and dissolved in a solvent and then an alkylbenzenesulfonic acid onium salt is dissolved in the solvent, or the like, and any method may be used. The thus obtained dope is formed into a fiber by a conventionally known method.

[0020] For the purpose of improving the dyeing properties and the resistance to discoloration and color fading and the like, with respect to the polymer used in the meta-type wholly aromatic polyamide fiber, which has an aromatic polyamide skeleton comprising repeating structural units represented by the formula (1) below, an aromatic diamine component different from the main constituent units of the repeating structure, or an aromatic dicarboxylic acid halide component can be copolymerized as a third component with the aromatic polyamide skeleton so that the amount of the third component becomes 1 to 10 mol%, based on the total mole of the repeating structural units of the aromatic polyamide:

-(NH-Ar1-NH-CO-Ar1-CO)- Formula (1)

wherein Ar1 is a divalent aromatic group having a bonding group at a position other than the meta position or the parallel axis direction.

[0021] Specific examples of aromatic diamines, which are represented by the formula (2) or (3), and which can be copolymerized as a third component, include p-phenylenediamine, chlorophenylenediamine, methylphenylenediamine, acetylphenylenediamine, aminoanisidine, benzidine, bis(aminophenyl) ether, bis(aminophenyl) sulfone, diaminobenzanilide, and diaminoazobenzene. Specific examples of aromatic dicarboxylic acid dichlorides represented by the formula (4) or (5) include terephthalic acid chloride, 1,4-naphthalenedicarboxylic acid chloride, 2,6-naphthalenedicarboxylic acid chloride, 4,4'-biphenyldicarboxylic acid chloride, 5-chloroisophthalic acid chloride, 5-methoxyisophthalic acid chloride, and bis(chlorocarbonylphenyl) ether.

H_2N-Ar2-NH_2 Formula (2)

H_2N-Ar2-Y-Ar2-NH_2 Formula (3)

XOC-Ar3-COX Formula (4)

XOC-Ar3-Y-Ar3-COX Formula (5)

Wherein Ar2 represents a divalent aromatic group different from Ar1, Ar3 represents a divalent aromatic group different from Ar1, Y represents 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 represents a halogen atom.

[0022] The crystallinity of the meta-type wholly aromatic polyamide fiber is preferably 5 to 35% because the absorption for a dye is excellent such that an intended color can be easily achieved even when using the dye in a reduced amount or even under poor dyeing conditions. Further, the crystallinity is more preferably 15 to 25% because localization of a dye in the surface is unlikely to occur and a high resistance to discoloration and color fading is obtained and further dimensional stability required for the practical use can be secured.

[0023] The residual solvent content of the meta-type wholly aromatic polyamide fiber is preferably 0.1% by weight or less (preferably 0.001 to 0.1% by weight) because excellent flame retardancy of the meta-type wholly aromatic polyamide fiber is not sacrificed.

[0024] The meta-type wholly aromatic polyamide fiber can be produced by the method mentioned below, and, particularly by the below-mentioned method, the crystallinity and residual solvent content in the above-mentioned respective ranges can be achieved.

[0025] With respect to the polymerization method for the meta-type wholly aromatic polyamide polymer, there is no particular limitation, and, 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, or the like may be used.

[0026] The spinning solution is not particularly limited, but an amide-solvent solution containing an aromatic copolyamide polymer obtained by the above-mentioned solution polymerization, interfacial polymerization, or the like may be used, or a solution obtained by isolating the polymer from the above-mentioned polymerization solution and dissolving the polymer in an amide solvent may be used.

[0027] Examples of the amide solvents used include N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, and dimethylsulfoxide, and especially preferred is N,N-dimethylacetamide.

[0028] When the copolymerized aromatic polyamide polymer solution obtained as mentioned above further contains an alkali metal salt or an alkaline earth metal salt, the solution is stabilized and can be advantageously used in a higher concentration at low temperatures. The amount of the alkali metal salt and alkaline earth metal salt is preferably 1% by weight or less, more preferably 0.1% by weight or less, based on the mass of the polymer solution.

[0029] In the spinning and coagulation step, the above-obtained spinning solution (meta-type wholly aromatic polyamide polymer solution) is discharged into a coagulation liquid so as to undergo coagulation.

[0030] With respect to the spinning apparatus, there is no particular limitation, and a conventionally known wet spinning apparatus can be used. Further, with respect to the number of spinning holes of a spinning nozzle, the arrangement of the holes, the form of the hole, and the like, there is no particular limitation as long as wet spinning can be stably made, and, for example, a multihole spinning nozzle for rayon yarn having 1,000 to 30,000 holes and having a spinning hole diameter of 0.05 to 0.2 mm, or the like may be used.

[0031] Further, the temperature of the spinning solution (meta-type wholly aromatic polyamide polymer solution) being discharged from a spinning nozzle is suitably in the range of from 20 to 90°C.

[0032] As a coagulation bath used for obtaining a fiber, an aqueous solution containing substantially no inorganic salt and having an amide solvent, preferably NMP concentration of 45 to 60% by weight at a bath solution temperature in the range of from 10 to 50°C is used. When the amide solvent (preferably NMP) concentration is less than 45% by weight, a structure having a thick skin is disadvantageously formed, so that the washing efficiency in the washing step is lowered, making it difficult to reduce the residual solvent content of the fiber. On the other hand, when the amide solvent (preferably NMP) concentration is more than 60% by weight, coagulation throughout the inside of the fiber cannot be achieved, making it difficult to reduce the residual solvent content of the fiber. The time for immersing the fiber in the coagulation bath is suitably in the range of from 0.1 to 30 seconds.

[0033] Subsequently, in a plasticized drawing bath containing an aqueous solution having an amide solvent, preferably NMP concentration of 45 to 60% by weight at a bath solution temperature in the range of from 10 to 50°C, the fiber is subj ected to drawing at a draw ratio of 3 to 4 times. After drawing, the resultant fiber is well washed through an aqueous solution having an NMP concentration of 20 to 40% by weight at 10 to 30°C and further through a warm water bath at 50 to 70°C.

[0034] The fiber after being washed is subjected to dry heat treatment at a temperature of 270 to 290°C, obtaining a meta-type wholly aromatic aramid fiber which satisfies the crystallinity and residual solvent content in the above-mentioned respective ranges.

[0035] In the meta-type wholly aromatic aramid fiber, the fiber is preferably in the form of a short fiber having a fiber length of 25 to 200 mm in view of mixing with another fiber. Further, the single fiber fineness is preferably in the range of from 1 to 5 dtex.

[0036] In the invention, it is preferred that the spun yarn contains the meta-type wholly aromatic polyamide fiber in an amount of 5% by weight or more (more preferably 5 to 50% by weight), based on the weight of the spun yarn. When the amount of the meta-type wholly aromatic polyamide fiber contained is smaller than the above range, there is a possibility that the cloth becomes poor in flame retardancy.

[0037] The modacrylic fiber is a fiber formed from a linear synthetic polymer comprising repeating units for acrylonitrile group in an amount of 35 to less than 85% by weight, as measured in accordance with JIS L0204-2 (2001). The modacrylic fiber is advantageous in that woven fabric formed from the modacrylic fiber is wrinkle resistant and excellent in fireproofness, chemical resistance, beautiful appearance, hand, washing shrinkage resistance, and the like.

[0038] In the invention, it is preferred that the spun yarn contains the modacrylic fiber in an amount of 30% by weight or more (more preferably 50 to 90% by weight, especially preferably 60 to 80% by weight), based on the weight of the spun yarn. When the amount of the modacrylic fiber contained is smaller than the above range, there is a possibility that the cloth becomes poor in hand, washing shrinkage resistance, and the like.

[0039] In the invention, the spun yarn contains not only the meta-type wholly aromatic polyamide fiber and modacrylic fiber but also a conductive fiber.

[0040] With respect to the conductive fiber, preferred is a nylon conductive yarn or acrylic fiber having incorporated thereinto conductive carbon fine particles. In the case where the cloth contains the meta-type wholly aromatic polyamide fiber and an acrylic fiber, when the cloth is dyed with a cationic dye, all the meta-type wholly aromatic polyamide fiber, the modacrylic fiber, and the acrylic fiber are dyed deep color, and the whole of the cloth is uniformly dyed. In this case, it is preferred that the meta-type wholly aromatic polyamide fiber and the conductive fiber are dyed the same color. The

color difference between the meta-type wholly aromatic polyamide fiber and the conductive fiber, in terms of ΔE, is preferably 3 or less.

[0041] As the acrylic fiber, preferred is a fiber having conductive carbon incorporated into an acrylic fiber, a sheath-core manner conjugate fiber comprising a core portion containing conductive fine particles and a sheath portion containing no conductive fine particle, or the like. Particularly, preferred is a sheath-core manner conjugate fiber (or an eccentric sheath-core manner conjugate fiber) having a sheath portion comprising an acryl containing no conductive fine particle, and a core portion comprising a conductive carbon-containing polymer, or the like. When the cloth contains such an acrylic fiber, static electricity caused due to friction of the cloth can be reduced, so that problems of the deposition of dust, a malfunction due to discharge, ignition in an expansion-proof environment, and the like can be solved.

[0042] As the acrylic fiber, for example, an acrylic fiber described in JP-A-2009-221632 is preferred. Specifically, preferred is a sheath-core manner conductive acrylic fiber comprising a core portion containing conductive fine particles and a sheath portion containing no conductive fine particle, wherein the acrylic fiber has a core-sheath ratio of 15/85 to 50/50, the content of the conductive fine particles in the core portion is 20 to 60% by mass, and the acrylic fiber has a single fiber specific resistance of 10^1 to 10^6 Ω•cm.

[0043] In the conductive fiber, the fiber may be in the form of either a continuous fiber (multifilament) or a short fiber. Particularly, in view of mixing with another fiber, a short fiber having a fiber length of 25 to 200 mm (more preferably 30 to 150 mm) is preferred. Further, the single fiber fineness is preferably in the range of from 1 to 5 dtex.

[0044] In the cloth of the invention, it is preferred that the spun yarn contains the conductive fiber in an amount of 1% by weight or more (more preferably 1 to 5% by weight), based on the weight of the spun yarn. When the weight percentage of the conductive fiber is smaller than the above range, there is a possibility that the cloth becomes poor in antistatic properties.

[0045] In the cloth of the invention, it is preferred that the spun yarn comprises only the meta-type wholly aromatic polyamide fiber, the modacrylic fiber, and the conductive fiber, but the spun yarn may further contain an additional fiber. As the additional fiber, a flame-retardant fiber, such as a para-type wholly aromatic polyamide fiber, a wholly aromatic polyester fiber, apolybenzoxazole (PBO) fiber, apolybenzimidazole (PBI) fiber, apolybenzothiazole (PBTZ) fiber, apoly-imide (PI) fiber, a polysulfonamide (PSA) fiber, a polyether ether ketone (PEEK) fiber, apolyetherimide (PEI) fiber, apolyarylate (PAr) fiber, a melamine fiber, a phenolic fiber, a fluorine fiber, or a polyphenylene sulfide (PPS) fiber, maybe contained in the spun yarn.

[0046] When a cellulose 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, or the like is contained in the spun yarn, water absorption properties, dyeing properties, comfortability to wear, or the like is advantageously imparted to the cloth.

[0047] In the invention, with respect to the method for producing the cloth, there is no particular limitation, and any known method can be used. For example, it is preferred that spun yarns of the above-mentioned fibers are mixed to obtain a spun yarn, and then the spun yarn in the form of a single yarn or a two folded yarn is woven using a rapier loom or the like into a weave structure, such as twill weave or plain weave. In this case, it is preferred that the cloth is constituted solely by the spun yarn, but the spun yarn may be interwoven or interknitted with the above-mentioned additional fiber.

[0048] It is preferred that the cloth is then subjected to post-processing. Specific examples of post-processing steps include steps, such as scouring, drying, relaxation, singeing, dyeing, and a function imparting treatment.

[0049] With respect to the dyeing processing, it is preferred that the cloth is subjected to dyeing processing using a dye bath containing the above-mentioned cationic dye. In this instance, a method can be preferably employed in which the cloth is dyed at 115 to 135°C and then subj ected to reduction treatment, and dried, or the like, but the method is not limited to this.

[0050] In the dyeing processing, a carrier is preferably used, and it is preferred that the cloth is subjected to dyeing treatment in the bath of cationic dye which is the same bath as the carrier . Further, when the cloth is treated with a special surfactant before subjected to cationic dyeing, the cloth can be dyed deep color in the open width dyeing.

[0051] It is preferred that the carrier is, for example, at least one member selected from 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, cinnamyl alcohol, p-anisyl alcohol, and benzhydrol. As specific commercially available products, preferred are benzyl alcohol, DOWANOL PPH, manufactured by The Dow Chemical Company, andCINDYE DNK, manufactured by BOZZETTO Group. Further, from the viewpoint of further improving the dyeing properties, benzyl alcohol, especially, 2,5-dimethylbenzyl alcohol or 2-nitrobenzyl alcohol is preferably used.

[0052] The amount of the carrier is preferably 1 to 10 parts by weight (more preferably 1 to 5 parts by weight), relative to 100 parts by weight of the meta-type wholly aromatic polyamide fiber.

[0053] As a scouring or relaxation treatment, an open width treatment or a jet scouring or relaxation treatment may be employed. Specifically, a method is employed in which a treatment is conducted using an open width non-tension machine in continuous scouring or continuous drying. For example, a method using a Sofcer scouring machine, a tenter

dryer, a Shrink Surfer, a short loop, a Luciole dryer, or the like is employed. The scouring or relaxation step can be optionally omitted.

[0054] For improving other properties, the cloth may be subjected to clipping and/or singeing. Further, as another processing for imparting a function, a sweat absorber, a water repellent, a thermal storage agent, an ultraviolet light screening agent, an antistatic agent, an anti-fungus agent, a deodorant, a mothproofing agent, a mosquito repellent, a phosphorescent agent, a retroreflective agent, or the like may be applied to the cloth. The woven or knitted fabric used may be spun-dyed yarn fabric, fiber or yarn colored fabric, or piece dyed fabric.

[0055] With respect to the sweat absorber, preferred is polyethylene glycol diacryate, a polyethylene glycol diacryate derivative, a polyethylene terephthalate-polyethylene glycol copolymer, or a water-soluble polyurethane.

[0056] As examples of the method for applying a sweat absorber to the cloth, there can be mentioned a padding treatment method, and a method in which a treatment is made using the same bath as the dyeing solution during the dyeing processing.

[0057] The thus obtained cloth contains the above-mentioned spun yarn, and therefore has extremely excellent flame retardancy and has excellent washing shrinkage resistance and excellent hand as well as excellent antistatic properties. Further, in the case where an acrylic fiber is used as the conductive fiber, when the cloth is dyed with a cationic dye, all the meta-type wholly aromatic polyamide fiber, the modacrylic fiber, and the acrylic fiber are dyed deep color, and the whole of the cloth is uniformly dyed.

[0058] In the cloth of the invention, it is preferred that the cloth has a weight per unit in the range of from 130 to 300 g/m^2. Further, it is preferred that the cloth has an afterflame time of 2 seconds or less, as measured by the method prescribed in ISO 15025:2000 A method. It is preferred that the cloth has a carbonized area of 30 cm^2 or less, as measured by the method prescribed in JIS L1091: 1999A-1 method. It is preferred that the cloth has a shrinkage rate of 5% or less, as measured after subjected to washing 5 times in accordance with the method prescribed in ISO 5077. It is preferred that the cloth has a thermal shrinkage rate of 10% or less, as measured after subj ected to heat treatment at 180°C for 5 minutes in accordance with the method prescribed in ISO 17493. It is preferred that the cloth has a water absorbing time of 30 seconds or less, as measured by the method prescribed in JIS L1907 :2010 (dropping method) . It is preferred that the cloth has a bending resistance of 7.0 cm or less, as measured by the method prescribed in JIS L1096:2010 A method (cantilever). It is preferred that the cloth has an antistaticity of 7.0 μC or less, as measured by the method prescribed in JIS L1094:2014 (antistatic properties).

[0059] The fiber product of the invention is a fiber product using the above-described cloth, which is any one fiber product selected from the group consisting of protective clothing, fire-fighting fireproof clothing, fire fighting clothing, rescue clothing, workwear, a police uniform, Self-Defense Forces official clothing, and military clothing. The fiber product uses the above-described cloth, and therefore has extremely excellent flame retardancy and has excellent washing shrinkage resistance and excellent hand as well as excellent antistatic properties.

Examples

[0060] Hereinbelow, the present invention will be described in more detail with reference to the following Examples, which should not be construed as limiting the scope of the invention. The physical properties shown in the Examples were measured by the methods described below.

(1) Weight per unit

[0061] A weight per unit was measured in accordance with the method prescribed in JIS L1096:2010 A method.

(2) Flammability

[0062] Flammability was measured in accordance with the method prescribed in ISO 15025:2000 A method, or JIS L1091:1999 A-1 method.

(3) Washing shrinkage rate

[0063] A shrinkage rate was measured after subjected to washing 5 times in accordance with the method prescribed in ISO 5077. n (the number of samples) was 5 and the measurement was conducted with respect to the warp direction and the weft direction, and an average of the values measured in the both directions was determined.

(4) Dry thermal shrinkage rate

[0064] A thermal shrinkage rate was measured after subjected to heat treatment at 180°C for 5 minutes in accordance

with the method prescribed in ISO 17493. n (the number of samples) was 5 and the measurement was conducted with respect to the warp direction and the weft direction, and an average of the values measured in the both directions was determined.

(5) Water absorption properties

[0065] A water absorption ability of a cloth to be tested was measured in accordance with the method prescribed in JIS L1907:2010.

(6) Bending resistance

[0066] A bending resistance of a cloth to be tested was measured in accordance with the method prescribed in JIS L1096:2010 A method (cantilever).

(7) Antistatic properties

[0067] An amount of electric charges was measured in accordance with JIS L1094:2014 (antistatic properties). A sample with 7.0 μC or less is acceptable for the antistatic properties.

(8) Residual solvent content

[0068] About 8.0 g of a basic fiber was taken and dried at 105°C for 120 minutes, and then cooled in a desiccator, and a weight (M1) of the fiber was measured. Then, the resultant fiber was placed in methanol and subjected to extraction under reflux for the amide solvent contained in the fiber using a Soxhlet's extractor for 1.5 hours. The fiber which had been subjected to extraction was taken out from the extractor, and subjected to vacuum drying at 150°C for 60 minutes, and then cooled in a desiccator, and a weight (M2) of the fiber was measured. An amount of the solvent remaining in the fiber (amide solvent weight) was calculated from the obtained weight values M1 and M2 using the following formula.

$$\text{Residual solvent content (\%)} = [(M1 - M2)/M1] \times 100$$

(9) Crystallinity

[0069] Using an X-ray diffraction measurement apparatus (RINT TTRIII, manufactured by Rigaku Corporation), a bundle of the basic fiber having a diameter of about 1 mm was prepared and set on a holder for a fiber sample and subjected to measurement of a diffraction profile. Conditions for the measurement were such that the source of an X-ray was Cu-Kα (50 kV, 300 mA), the scanning angle range was 10 to 35°, the continuous measurement width was 0.1°, and the scanning speed was 1°/minute. From the actually measured diffraction profile, air scattering and incoherent scattering were corrected by linear approximation to obtain a total scattering profile. Then, an amorphous scattering profile was subtracted from the total scattering profile to obtain a crystal scattering profile. A crystallinity was determined from an area intensity of the crystal scattering profile (crystal scattering intensity) and an area intensity of the total scattering profile (total scattering intensity) using the following formula.

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

[Production of a meta-type wholly aromatic polyamide fiber]

[0070] A meta-type wholly aromatic polyamide fiber was produced by the method described below.

[0071] 20.0 Parts by weight of a polymetaphenyleneisophthalamide powder having an intrinsic viscosity (I.V.) of 1.9, which had been produced by an interfacial polymerization method in accordance with the method described in JP-B-47-10863, was suspended in 80.0 parts by weight of N-methyl-2-pyrrolidone (NMP) cooled to -10°C so as to be in a slurry form. Subsequently, the temperature of the resultant suspension was increased to 60°C so that the polymer was

dissolved, obtaining a transparent polymer solution. A 2-[2H-benzotriazol-2-yl]-4-6-bis(1-methyl-1-phenylethyl)ph enol powder (solubility in water: 0.01 mg/L) was mixed into and dissolved in the polymer solution in an amount of 3.0% by weight, based on the weight of the polymer, followed by deaeration under a reduced pressure, to obtain a spinning solution (spinning dope).

[Spinning and coagulation step]

[0072] Spinning was performed by discharging the above-obtained spinning dope from a spinning nozzle having 500 holes and having a hole diameter of 0.07 mm into a coagulation bath at a bath temperature of 30°C. The coagulation liquid had a composition of water/NMP = 45/55 (parts by weight), and the spinning was made by discharging the spinning dope into the coagulation bath at a yarn speed of 7 m/minute.

[Plasticized drawing bath drawing step]

[0073] Subsequently, the resultant spun yarn was drawn at a draw ratio of 3.7 times in a plasticized drawing bath having a composition of water/NMP = 45/55 at a temperature of 40°C.

[Washing step]

[0074] After drawing, the resultant yarn was washed in a bath having a composition of water/NMP = 70/30 at 20°C (dipping length: 1.8 m), and then washed in a water bath at 20°C (dipping length: 3.6 m), and further well washed through a warm water bath at 60°C (dipping length: 5.4 m) .

[Dry heat treatment step]

[0075] The fiber after being washed was subjected to dry heat treatment using a heated roller having a surface temperature of 280°C to obtain a meta-type wholly aromatic polyamide fiber.

[Physical properties of a basic fiber]

[0076] The obtained meta-type wholly aromatic polyamide fiber had physical properties such that the fineness was 1.7 dtex, the residual solvent content was 0.08% by weight, and the crystallinity was 19%. Using the obtained basic fiber, crimping and cutting were performed to obtain a staple fiber having a length of 51 mm.

[0077] With respect to the other fibers, the staple fibers shown below were used.

- Modacrylic fiber: "ProtexM (registered trademark)", manufactured by Kaneka Corporation
- Conductive fiber (nylon conductive fiber) used in Examples 1 to 3: "NO SHOCK (registered trademark)" (nylon conductive fiber having incorporated thereinto conductive carbon fine particles), manufactured by Solutia Inc.
- Conductive fiber (acrylic conductive fiber) used in Example 4: fineness: 3.3 dtex; fiber length: 38 mm (sheath-core manner acrylic conductive fiber having conductive carbon fine particles incorporated into the core portion)

[Post-processing]

[0078] Post-processing was performed by conducting singeing, scouring, and final setting.

[Example 1]

[0079] Using a spun yarn No. 40/two folded yarn which was made of staple fibers of a meta-type wholly aromatic polyamide fiber (MA) (length: 51 mm), a modacrylic fiber (MD) (length: 51 mm), and a nylon conductive fiber (AS) (length: 51 mm), and which was obtained by mixing the fibers in a ratio of MA/MD/AS = 18/80/2, weaving was conducted at a weave density such that the warp yarn number was 100/25.4 mm and the weft yarn number was 55/25.4 mm to obtain twill fabric having a weight per unit of 200 g/m^2. Using the obtained fabric, processing was conducted by the above-mentioned method. The fabric had 7.0 μC or less and was acceptable for the antistatic properties . The results are shown in Table 1.

[Example 2]

[0080] Using a spun yarn No. 40/two folded yarn which was made of staple fibers of a meta-type wholly aromatic

polyamide fiber (MA) (length: 51 mm), a modacrylic fiber (MD) (length: 51 mm), and a nylon conductive fiber (AS) (length: 51 mm), and which was obtained by mixing the fibers in a ratio of MA/MD/AS = 28/70/2, weaving was conducted at a weave density such that the warp yarn number was 100/25.4 mm and the weft yarn number was 55/25.4 mm to obtain twill fabric having a weight per unit of 200 g/m^2. Using the obtained fabric, processing was conducted by the above-mentioned method. The fabric had 7.0 μC or less and was acceptable for the antistatic properties . The results are shown in Table 1.

[Example 3]

[0081] Using a spun yarn No. 40/two folded yarn which was made of staple fibers of a meta-type wholly aromatic polyamide fiber (MA) (length: 51 mm), a modacrylic fiber (MD) (length: 51 mm), and a nylon conductive fiber (AS) (length: 51 mm), and which was obtained by mixing the fibers in a ratio of MA/MD/AS = 38/60/2, weaving was conducted at a weave density such that the warp yarn number was 100/25.4 mm and the weft yarn number was 55/25.4 mm to obtain twill fabric having a weight per unit of 200 g/m^2. Using the obtained fabric, processing was conducted by the above-mentioned method. The fabric had 7.0 μC or less and was acceptable for the antistatic properties . The results are shown in Table 1.

[Example 4]

[0082] Procedure was performed in substantially the same manner as in Example 1 except that the conductive fiber was changed to an acrylic conductive fiber (AAS), and that the cloth was dyed with a cationic dye. The fabric had 7.0 μC or less and was acceptable for the antistatic properties. Further, all the meta-type wholly aromatic polyamide fiber, the modacrylic fiber, and the acrylic fiber were dyed deep color, and the whole of the cloth was uniformly dyed. The results are shown in Table 1.

[Comparative Example 1]

[0083] Using a spun yarn No. 40/two folded yarn which was made of a meta-type wholly aromatic polyamide fiber (MA), amodacrylic fiber (MD), flame-retardant rayon (RY), and a para-type wholly aromatic polyamide fiber (PA), and which was obtained by mixing the fibers in a ratio of MA/MD/RY/PA = 25/30/40/5, weaving was conducted at a weave density such that the warp yarn number was 100/25.4 mm and the weft yarn number was 55/25. 4 mm to obtain twill fabric having a weight per unit of 200 g/m^2. Using the obtained fabric, processing was conducted by the above-mentioned method. The fabric was unacceptable for the antistatic properties. The results are shown in Table 1.

[Comparative Example 2]

[0084] Using a spun yarn No. 40/two folded yarn which was made of a meta-type wholly aromatic polyamide fiber (MA), amodacrylic fiber (MD), flame-retardant rayon (RY), and a para-type wholly aromatic polyamide fiber (PA), and which was obtained by mixing the fibers in a ratio of MA/MD/RY/PA = 35/30/15/20, weaving was conducted at a weave density such that the warp yarn number was 100/25. 4 mm and the weft yarn number was 55/25. 4 mm to obtain twill fabric having a weight per unit of 200 g/m^2. Using the obtained fabric, processing was conducted by the above-mentioned method. The fabric was unacceptable for the antistatic properties. The results are shown in Table 1.

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
		MA/MD/AS	MA/MD/AS	MA/MD/AS	MA/MD/AAS	MA/MD/RY/PA	MA/MD/RY/PA
Mixing ratio	%	18/80/2	28/70/2	38/60/2	18/80/2	25/30/40/5	35/30/15/20
Weight per unit	g/m^2	200	200	200	200	200	200
Flammability	Afterflame (second)	0	0	0	0	0	0
Washing shrinkage rate	%	5	4	3	5	10	7
Dry heat shrinkage	%	4	5	5	4	6	5
Hand and comfortability	Cantilever (cm)	6.5	6.8	6.4	6.5	8.9	10.0

Industrial Applicability

[0085] In the present invention, there are provided a cloth which is advantageous not only in that the cloth has extremely excellent flame retardancy, and further has excellent washing shrinkage resistance and excellent hand as well as excellent antistatic properties, but also in that the whole of the cloth can be uniformly dyed, and a fiber product, and the invention is of extremely great industrial significance.

Claims

1. A cloth comprising a spun yarn which comprises a meta-type wholly aromatic polyamide fiber, a modacrylic fiber, and a conductive fiber.

2. The cloth according to claim 1, wherein the spun yarn contains the meta-type wholly aromatic polyamide fiber in an amount of 5% by weight or more, based on the weight of the spun yarn.

3. The cloth according to claim 1 or 2, wherein the spun yarn contains the modacrylic fiber in an amount of 30% by weight or more, based on the weight of the spun yarn.

4. The cloth according to any one of claims 1 to 3, wherein the spun yarn contains the conductive fiber in an amount of 1% by weight or more, based on the weight of the spun yarn.

5. The cloth according to any one of claims 1 to 4, wherein the spun yarn comprises only the meta-type wholly aromatic polyamide fiber, the modacrylic fiber, and the conductive fiber.

6. The cloth according to any one of claims 1 to 5, wherein the meta-type wholly aromatic polyamide fiber has a residual solvent content of 0.1% by weight or less.

7. The cloth according to any one of claims 1 to 6, wherein the meta-type wholly aromatic polyamide fiber has a crystallinity in the range of from 15 to 25%.

8. The cloth according to any one of claims 1 to 7, wherein a meta-type wholly aromatic polyamide forming the meta-type wholly aromatic polyamide fiber is an aromatic polyamide having an aromatic polyamide skeleton comprising repeating structural units represented by the formula (1) below, wherein an aromatic diamine component different from the main constituent units of the repeating structure, or an aromatic dicarboxylic acid halide component is copolymerized as a third component with the aromatic polyamide skeleton so that the amount of the third component becomes 1 to 10 mol%, based on the total mole of the repeating structural units of the aromatic polyamide:

$$-(NH\text{-}Ar1\text{-}NH\text{-}CO\text{-}Ar1\text{-}CO)- \qquad \text{Formula (1)}$$

wherein Ar1 is a divalent aromatic group having a bonding group at a position other than the meta position or the parallel axis direction.

9. The cloth according to claim 8, wherein, as the third component, the aromatic diamine is the following formula (2) or (3), or the aromatic dicarboxylic acid halide is the following formula (4) or (5) :

$$H_2N\text{-}Ar2\text{-}NH_2 \qquad \text{Formula (2)}$$

$$H_2N\text{-}Ar2\text{-}Y\text{-}Ar2\text{-}NH_2 \qquad \text{Formula (3)}$$

$$XOC\text{-}Ar3\text{-}COX \qquad \text{Formula (4)}$$

$$XOC\text{-}Ar3\text{-}Y\text{-}Ar3\text{-}COX \qquad \text{Formula (5)}$$

wherein Ar2 represents a divalent aromatic group different from Ar1, Ar3 represents a divalent aromatic group different from Ar1, Y represents 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 represents a halogen atom.

10. The cloth according to any one of claims 1 to 9, wherein the meta-type wholly aromatic polyamide fiber further contains an organic dye, an organic pigment, or an inorganic pigment.

11. The cloth according to any one of claims 1 to 10, wherein the conductive fiber is an acrylic fiber.

12. The cloth according to any one of claims 1 to 11, wherein the modacrylic fiber and the conductive fiber are dyed with the same dye.

13. The cloth according to any one of claims 1 to 12, which contains an ultraviolet light absorber and/or a reflective agent.

14. The cloth according to any one of claims 1 to 13, which has a weight per unit in the range of from 130 to 300 g/m^2.

15. The cloth according to any one of claims 1 to 14, which has an afterflame time of 2 seconds or less, as measured by the method prescribed in ISO 15025:2000 A method.

16. The cloth according to any one of claims 1 to 15, which has a carbonized area of 30 cm^2 or less, as measured by the method prescribed in JIS L1091:1999 A-1 method.

17. The cloth according to any one of claims 1 to 16, which has a shrinkage rate of 5% or less, as measured after subjected to washing 5 times in accordance with the method prescribed in ISO 5077.

18. The cloth according to any one of claims 1 to 17, which has a thermal shrinkage rate of 10% or less, as measured after subj ected to heat treatment at 180°C for 5 minutes in accordance with the method prescribed in ISO 17493.

19. The cloth according to any one of claims 1 to 18, which has a water absorbing time of 30 seconds or less, as measured by the method prescribed in JIS L1907:2010 (dropping method) .

20. The cloth according to any one of claims 1 to 19, which has a bending resistance of 7.0 cm or less, as measured by the method prescribed in JIS L1096:2010 A method (cantilever).

21. The cloth according to any one of claims 1 to 20, which has an antistaticity of 7. 0 μC or less, as measured by the method prescribed in JIS L1094:2014 (antistatic properties).

22. A fiber product using the cloth according to any one of claims 1 to 21, which is any one fiber product selected from the group consisting of protective clothing, fire-fighting fireproof clothing, fire fighting clothing, rescue clothing, work-wear, a police uniform, Self-Defense Forces official clothing, and military clothing.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/012463

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. D03D15/00(2006.01)i, A41D31/00(2019.01)i, A41D31/04(2019.01)i, A41D31/08(2019.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. D03D1/00-27/18, A41D31/00, A41D31/04, A41D31/08

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	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

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 A	JP 2015-530485 A (E. I. DU PONT DE NEMOURS AND COMPANY) 15 October 2015, claims, paragraphs [0012], [0036], [0041], [0042], [0048] & US 2014/0026303 A1 & WO 2014/018697 A1, claims, paragraphs [0014], [0038], [0043], [0044], [0050] & EP 2877620 A1 & CA 2879991 A & KR 10-2015-0036204 A & CN 104685118 A	1-4, 7, 10, 12, 14-22 6, 8, 9, 13 5, 11

☒ 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	Date of mailing of the international search report
23.04.2019	14.05.2019
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/012463

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2014-210985 A (TEIJIN LTD.) 13 November 2014, claims, paragraphs [0017]-[0022], [0029], [0033], [0042] (Family: none)	6, 8, 9, 13
Y	JP 2017-8454 A (TEIJIN LTD.) 12 January 2017, claims, paragraphs [0010], [0028] (Family: none)	13
A	JP 11-250 A (MITSUBISHI RAYON CO., LTD.) 06 January 1999, claims, examples (Family: none)	1-22

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2009221632 A **[0042]**