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# (54) DYED FABRIC, FIBER PRODUCT IN WHICH SAME IS USED, AND METHOD FOR DYEING FABRIC

(57) An object of the present invention is to provide a dyed fabric and a textile product made thereof, as well as a dyeing method, which achieve color uniformity of a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber, even in the case of a fabric containing a meta-type- and para-type- wholly aromatic polyamide fibers and a polyester fiber which are difficult to dye.

The present invention relates to a dyed fabric dyed after being shaped into a fabric, characterized in that the fabric comprises a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber and the fabric is a fabric dyed with a cationic dyestuff and a disperse dyestuff, and in that the afterflame time and afterglow time defined in JISL1091A-1 are 1 second or less.

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## Description

FIELD

**[0001]** The present invention relates to a dyed fabric for use in a flame resistant clothing or the like suitable for wearing by a person who is engaged in a work which is likely to be exposed to a flame, such as a firefighter, a pilot, a race driver, an operator of a power company or a chemical company, and the like; the present invention also relates to a dyeing method for obtaining the dyed fabric.

BACKGROUND

**[0002]** Wholly aromatic polyamide fibers have high mechanical strength and heat resistance, as well as flame retardancy. They are in particular widely used in the design of suits for a firefighter, an astronaut, and a pilot, as a textile fiber intended to come into contact with fire or high temperatures. In recent years, there has been an increasing need for designability of clothes, and therefore a fabric having high dyeability is required.

**[0003]** On the other hand, the meta-type- and para-type- wholly aromatic polyamide fibers have a molecular structure having high crystallinity and strong intermolecular bonding force, and therefore they are difficult to dye, and, even if they can be dyed, a dyestuff will be washed off easily by washing or the like. Therefore, there has been a problem that it is difficult to dye these fibers by a conventional dyeing technique.

**[0004]** Patent Document 1 discloses a method in which a fiber swelling agent (carrier) is used to dye a para-type wholly aromatic polyamide fiber with a cationic dyestuff.

**[0005]** Patent Document 2 discloses a method in which a fabric is dyed with a cationic dyestuff and then dyed with a Vat dyestuff.

[CITATION LIST]

[PATENT LITERATURE]

**[0006]**

[Patent document 1] U.S. Pat. No. 3,674,420
[Patent document 2] JP-A-2013-209776

SUMMARY

[TECHNICAL PROBLEM]

**[0007]** According to the conventional dyeing method, in the case of a blended product of a meta-type wholly aromatic polyamide fiber and a para-type wholly aromatic polyamide fiber, a cationic dyestuff is selectively adsorbed to the meta-type wholly aromatic polyamide fiber; therefore it was difficult to dye the para-type wholly aromatic polyamide fiber.

**[0008]** In addition, according to the conventional dyeing method, in the case of a blended product of a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber, the color shade of the polyester fiber becomes mediocre; therefore, in the market, there is a need for a dyed fabric having further improved quality.

**[0009]** In view of the above problems, it is an object of the present invention to provide a dyed fabric and a textile product made thereof which achieve color uniformity of a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber, and which are excellent in heat resistance and flame resistance, even in the case of a fabric containing a meta-type- and para-type- wholly aromatic polyamide fibers and a polyester fiber which are difficult to dye. The present invention also provides a dyeing method.

[SOLUTION TO PROBLEM]

**[0010]** The present disclosure includes the following embodiments:

<Embodiment 1> A dyed fabric dyed after being shaped into a fabric,

characterized in that the fabric comprises a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber, and the fabric is dyed with a cationic dyestuff and a disperse

dyestuff,
and in that the afterflame time and afterglow time defined in JISL1091A-1 are 1 second or less.

<Embodiment 2> The dyed fabric according to the embodiment 1, wherein both of the dry rubbing fastness and the wet rubbing fastness defined in JIS L 0849 II method are grade 3 or more.
<Embodiment 3> The dyed fabric according to the embodiment 1 or 2, wherein the polyester fiber is dyed with the disperse dyestuff by ring-dyeing.
<Embodiment 4> The dyed fabric according to any one of the embodiments 1 to 3, wherein the residual disperse dyestuff is from 0.01% o.w.f. to 0.5% o.w.f.
<Embodiment 5> The dyed fabric according to any one of the embodiments 1 to 4, wherein the residual cationic dyestuff is from 0.01% o.w.f. to 16.0% o.w.f.
<Embodiment 6> The dyed fabric according to any one of the embodiments 1 to 5, wherein the weights of the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber are in the ratio of 60 to 80 : 1 to 10 : 5 to 20.
<Embodiment 7> The dyed fabric according to any one of the embodiments 1 to 6, wherein

the fabric comprises an electrically-conductive fiber, and
the weights of the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber, the polyester fiber and the electrically-conductive fiber are in the ratio of 60 to 80 : 1 to 10 : 5 to 20 : 1 to 4.

<Embodiment 8> The dyed fabric according to any one of the embodiments 1 to 6, which is made of a blended spun yarn comprising the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber.
<Embodiment 9> The dyed fabric according to the embodiment 7, which is made of a blended spun yarn comprising the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber, the polyester fiber and the electrically-conductive fiber.
<Embodiment 10> The dyed fabric according to any one of the embodiments 1 to 9, wherein

the water absorption performance defined in AATCC79 prior to washing is 2 seconds or less, and
the water absorption performance defined in AATCC79 after 10 washing cycles defined in ISO6330:2012 (6N-F) is 10 seconds or less.

<Embodiment 11> The dyed fabric according to any one of the embodiments 1 to 10, which is dyed with 2% o.w.f. or less of the disperse dyestuff after dyed with 20% o.w.f. or less of the cationic dyestuff.
<Embodiment 12> A textile product made of the dyed fabric according to any one of the embodiments 1 to 11, which is selected from the group consisting of protective suits, fire resistant suits for fire-fighting, firefighter suits, rescue suits, workwear, a police uniform, a camouflage uniform, and a military uniform.
<Embodiment 13> A method for dyeing a fabric, characterized in that

dyeing a fabric comprising a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber with a dye solution for wholly aromatic polyamide fiber comprising 20% o.w.f. or less of a cationic dyestuff, and then
dyeing the fabric with a dye solution for polyester fiber comprising 2% o.w.f. or less of a disperse dyestuff.

<Embodiment 14> The dyeing method according to the embodiment 13, wherein the dyeing is performed by thermosol dyeing.

[ADVANTAGEOUS EFFECTS OF INVENTION]

**[0011]** According to the present invention, even in the case of a fabric comprising a meta-type-and para-type- wholly aromatic polyamide fibers and a polyester fiber which are difficult to dye, it is possible to obtain a dyed fabric which achieves color uniformity of the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber, and which exhibits excellent heat resistance and flame resistance. Further, according to the present invention, a textile product made of this dyed fabric can be obtained.

**[0012]** Further, according to the present invention, there is provided a textile product made of the dyed fabric described above, which is selected from the group consisting of protective suits, fire resistant suits for firefighting, firefighting suits, rescue suits, workwear, a police uniform, a camouflage uniform, and a military uniform.

**[0013]** Further, according to the present invention, there is provided a method for dyeing a fabric.

[DESCRIPTION OF EMBODIMENTS]

**[0014]** In the following, embodiments of the present invention will be described in detail.

<<Dyed fabric>>

**[0015]** According to the present invention, there is provided a dyed fabric dyed after being shaped into a fabric, which comprises a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber and is a fabric dyed with a cationic dyestuff and a disperse dyestuff, and which exhibits 1 second or less of the afterflame time and afterglow time defined in JISL1091A-1.

**[0016]** When a fabric contains a polyester fiber in addition to a meta-type wholly aromatic polyamide fiber and a para-type wholly aromatic polyamide fiber, it is possible to provide a relatively inexpensive fabric which retains high heat resistance and flame resistance. Conventional fabric having such a configuration may be inferior in color shade. However, the present inventor has found that, even in the case of fibers comprising a meta-type wholly aromatic polyamide fiber and a para-type wholly aromatic polyamide fiber and a polyester fiber, by dyeing the fibers with a cationic dyestuff and a disperse dyestuff after shaping the fibers into a fabric, it is possible to obtain a dyed fabric which is uniformly dyed and which exhibits excellent appearance quality and excellent heat resistance and flame resistance.

**[0017]** According to an embodiment of the present invention, it is possible to provide a dyed fabric having excellent color uniformity and having excellent rubbing fastness and excellent heat resistance and flame resistance. Namely, with respect to the dyed fabric according to the present invention, both of the dry rubbing fastness and the wet rubbing fastness defined in JIS L 0849 II method are preferably grade 3 or more.

**[0018]** In the present invention, the fastness of the dyed fabric can be evaluated according to JIS L 0849 II type method. Each of the dry rubbing fastness (the fastness to rubbing in dry condition) and the wet rubbing fastness (the fastness to rubbing in wet condition) is expressed in nine grades, i.e., "1", "1-2", "2", "2-3", "3", "3-4", "4", "4-5", and "5", according to JIS L 0849 II method, and grade "5" is the most excellent. Preferably, in the dyed fabric of the present invention, both of the dry rubbing fastness and the wet rubbing fastness of the dyed fabric are grade 3 or more, grade 3-4 or more, grade 4 or more, or grade 4-5 or more.

**[0019]** In the dyed fabric according to another embodiment of the present disclosure, at least the polyester fiber is a polyester fiber ring-dyed with the disperse dyestuff (i.e., the polyester fiber is dyed with the disperse dyestuff by ring-dyeing).

**[0020]** By using a polyester fiber ring-dyed with a disperse dyestuff, it is possible to obtain a dyed fabric which is excellent in heat resistance and flame resistance and has particularly good color uniformity of the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber, and which exhibits particularly excellent quality in appearance.

**[0021]** Preferably, the dyed fabric is a fabric dyed with a cationic dyestuff of 20% o.w.f. (on the weight of fiber) or less and then dyed with a disperse dyestuff of 2% o.w.f. or less. When the dye is in this range, a dyed fabric having particularly excellent rubbing fastness while retaining excellent color uniformity is provided.

**[0022]** Further, in the dyed fabric, it is preferable that the weights of the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber are in the ratio of 60 to 90 : 1 to 15 : 5 to 30 (more preferably 60 to 80 : 1 to 10 : 5 to 20, or 60 to 80 : 2 to 10 : 5 to 20, or still more preferably 70 to 80 : 5 to 10 : 10 to 15).

**[0023]** Further, it is preferable that the dyed fabric is made of a blended spun yarn comprising the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber.

**[0024]** In addition, it is preferable that for the dyed fabric, the water absorption performance defined in AATCC79 prior to washing is 2 seconds or less, 1.5 seconds or less, or 1.0 seconds or less, and the water absorption performance defined in AATCC79 after 10 washing cycles defined in ISO6330:2012 (6N-F) is 10 seconds or less, 5 seconds or less, or 1 second or less.

**[0025]** The present inventor has found that the amount of the residual dyestuff, in particular the amount of the residual disperse dyestuff, is important in improving the fastness to rubbing while ensuring the color uniformity. Thus, for the dyed fabric, it is preferable that the amount of the residual disperse dyestuff, in particular the amount of the residual disperse dyestuff in the polyester fiber, is from 0.01% o.w.f. to 0.5% o.w.f. (more preferably from 0.01% o.w.f. to 0.1% o.w.f.), and it is preferable that the residual cationic dyestuff, in particular the residual cationic dyestuff in the meta-type wholly aromatic polyamide fiber, is from 0.01% o.w.f. to 16.0% o.w.f. (more preferably from 0.01% o.w.f. to 10% o.w.f.). When the residual dyestuff is in this range, a dyed fabric having further improved rubbing fastness while having excellent color uniformity is provided.

**[0026]** The fabric of the present invention may have any shape, and may be in the form of woven fabric, knitted fabric, nonwoven fabric, and may be formed into the shape of a fabric by a known method using the above-described fibers and/or fibers described later. Further, in addition to the meta-type wholly aromatic polyamide fiber and the para-type wholly aromatic polyamide fiber and the polyester fiber, as well as an optional electrically-conductive fiber described

later, it is also possible to use other fibers in blending, mixed weaving, interlacing, etc. Examples of the other fibers include a cellulose fiber, a polyacrylonitrile fiber, wool, and silk.

(Wholly aromatic polyamide fiber)

**[0027]** The meta-type wholly aromatic polyamide fiber is a fiber in which aromatic rings constituting a main skeleton are bonded in meta-position by amide bonds, and which has 85 mol% or more of metaphenylene isophthalamide units, based on all repeating units of the polymer. Particularly preferred fiber is a polymetaphenylene isophthalamide homopolymer. The third component, which can be copolymerized in 15 mol% or less (preferably 5 mol% or less) of all the repeating units, includes, as a diamine component, for example, paraphenylenediamine, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, paraxylylenediamine, biphenylenediamine, 3,3'-dichlorobenzidine, 3,3'-dimethylbenzidine, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, and 1,5-naphthalenediamine, or other aromatic diamines. Further, with regard to an acid component, examples thereof include terephthalic acid, naphthalene-2,6-dicarboxylic acid, and naphthalene-2,7-dicarboxylic acid, and other aromatic dicarboxylic acids. In addition, in these aromatic diamines and aromatic dicarboxylic acids, hydrogen atoms of the aromatic ring may be partly substituted by a halogen atom or an alkyl group such as a methyl group. It is preferable that 20% or more of the total terminal of the polymer is blocked with a monovalent diamine such as aniline or a monovalent carboxylic acid component, since the decrease in strength of the fiber when held at a high temperature for a long time is reduced. Incidentally, as such a meta-type wholly aromatic polyamide fiber, mention may be made to commercially available products such as Teijinconex (trademark), Teijinconex Neo (trademark), Nomex (trademark), and the like.

**[0028]** Such a meta-type wholly aromatic polyamide can be produced by a known interfacial polymerization method. With regard to the degree of polymerization of the polymer, it is preferable that an intrinsic viscosity (I.V.) measured in N-methyl-2-pyrrolidone solution at a concentration of 0.5 g/100 ml is in the range of 1.3 to 1.9 dl/g.

**[0029]** Further, the meta-type wholly aromatic polyamide may contain alkylbenzenesulfonic acid onium salt. Examples of the alkylbenzenesulfonic acid onium salt include compounds such as tetrabutylphosphonium hexylbenzene sulfonate, tributylbenzylphosphonium hexylbenzene sulfonate, tetraphenylphosphonium dodecylbenzene sulfonate, tributyltetradecylphosphonium dodecylbenzene sulfonate, tetrabutylphosphonium dodecylbenzene sulfonate, and tributylbenzylammonium dodecylbenzene sulfonate. Among those, tetrabutylphosphonium dodecylbenzene sulfonate or tributylbenzylammonium dodecylbenzene sulfonate are preferred, since they are readily available, have good thermal stability, and have high solubility in N-methyl-2-pyrrolidone.

**[0030]** The content ratio of the alkylbenzenesulfonic acid onium salt is preferably in the range of 2.5 mol% or more, preferably 3.0 mol% to 7.0 mol%, based on the poly-m-phenylene isophthalamide, in order to obtain an sufficient improvement effect of dyeability.

**[0031]** Further, as a method of mixing poly-m-phenylene isophthalamide and alkylbenzene sulfonic acid onium salt, it is possible to use a method of mixing and dissolving poly-m-phenylene isophthalamide in a solvent and then dissolving alkylbenzene sulfonic onium salt in the solvent. The dope thus obtained is formed into a fiber by a known method.

**[0032]** In a polymer used for the meta-type wholly aromatic polyamide fiber, in order to improve the dyeing performance and the resistance to discoloration, etc., it is possible to copolymerize, as the third component, an aromatic diamine component or an aromatic dicarboxylic acid halide component in an aromatic polyamide skeleton containing a repeating structural unit represented by the following formula (1), wherein the aromatic diamine component and the aromatic dicarboxylic acid halide component are different from the main constitutional unit of the repeating structure, and wherein the content of the aromatic diamine component or the aromatic dicarboxylic acid halide component is 1 mol% to 10 mol% based on the total amount of the repeating structural units of the aromatic polyamide:

$$-(NH\text{-}Ar1\text{-}NH\text{-}CO\text{-}Ar1\text{-}CO)-\cdots \quad \text{formula (1)}$$

wherein Ar1 is a divalent aromatic group with binding groups in meta-position or in the direction other than parallel axis.

**[0033]** Incidentally, as the third component, it is possible to copolymerize the aromatic diamine or the aromatic dicarboxylic acid dichloride represented by the following formulas (2), (3), (4), and (5). Specific examples of the aromatic diamines represented by the formulas (2) and (3) include, for example, p-phenylenediamine, chlorophenylenediamine, methylphenylenediamine, acetylphenylenediamine, aminoanisidine, benzidine, bis(aminophenyl)ether, bis(aminophenyl)sulfone, diaminobenzanilide, diaminoazobenzene, and the like. Specific examples of the aromatic dicarboxylic acid dichloride represented by the formulas (4) and (5) include, for example, 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.

$$H_2N\text{-}Ar2\text{-}NH_2 \quad \text{formula (2)}$$

$H_2N$-Ar2-Y-Ar2-$NH_2$ formula (3)

XOC-Ar3-COX formula (4)

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

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

**[0034]** Further, the crystallinity of the meta-type wholly aromatic polyamide fiber is preferably 5% to 35%, since a good exhaustion of dye is obtained and since it is easy to adjust a color to the target color even under a condition where the amount of dye is low or even under a weak dyeing condition. In addition, the crystallinity is more preferably 15% to 25%, since the uneven distribution of the dye on the surface hardly occurs, the resistance to discoloration is high, and the dimensional stability necessary for practical use can be secured.

**[0035]** Further, the residual solvent content in the meta-type wholly aromatic polyamide fiber is preferably 1.0% by weight or less (more preferably 0.3% by weight or less), since the excellent flame retardant performance of the meta-type wholly aromatic polyamide fiber is retained, uneven distribution of the dye on the surface hardly occurs, and the resistance to discoloration becomes high.

**[0036]** As a method of polymerizing a meta-type wholly aromatic polyamide polymer, for example, it is possible to use a solution polymerization method or an interfacial polymerization method, which are described for example in JP-S35-14399A, U.S. Patent No. 3360595, JP-S47-10863A.

**[0037]** As a spinning solution, it is possible to use an amide-based solvent containing an aromatic copolyamide polymer, which is obtained by a method such as the solution polymerization or interfacial polymerization described above. Alternatively, it is also possible to isolate a polymer from the polymerization solution and dissolve the polymer in an amide-based solvent.

**[0038]** Examples of the amide-based solvent used in the polymerization include N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, dimethyl sulfoxide, and the like. Among those, N,N-dimethylacetamide is particularly preferred.

**[0039]** It is preferable that the copolymerized aromatic polyamide polymer solution is further stabilized by containing an alkali metal salt or an alkaline earth metal salt, since this makes it possible to use the solution at higher concentration and/or at lower temperature. The alkali metal salt or the alkaline earth metal salt is preferably 1% by mass or less, more preferably 0.1% by mass or less, based on the total mass of the polymer solution.

**[0040]** In a spinning and coagulation step, a spinning solution (a solution of meta-type wholly aromatic polyamide polymer) is spun into a coagulation solution for the coagulation.

**[0041]** The apparatus for the spinning is not particularly limited, and a known wet spinning apparatus can be used. Further, as long as the wet spinning is stably performed, there is no particular limitation on the number, the arrangement, or the hole shape, etc., of the spinning nozzle. For example, it is possible to use a multi-hole spinning nozzle for staple fiber having 1000 to 30000 pores and/or having a spinning hole diameter of 0.05 mm to 0.2mm. Note that the suitable temperature at which the spinning solution (the solution of meta-type wholly aromatic polyamide polymer) obtained above is spun out from the spinning nozzle (spinneret) is in the range of 20°C to 90°C.

**[0042]** As a coagulation bath used to obtain the fiber, it is preferable to use an amide-based solvent substantially free of inorganic salts. In particular, it is preferable to use an aqueous solution having 45 to 60% by mass of NMP concentration at a bath temperature (bath liquid temperature) range of 10°C to 50°C. When the concentration of the amide-based solvent (preferably NMP) is less than 45% by mass, the skin may have a thicker structure, the cleaning efficiency in the cleaning step may decrease, and it may be difficult to reduce the amount of residual solvent in the fiber. On the other hand, when the concentration of the amide-based solvent (preferably NMP) exceeds 60% by mass, uniform coagulation may not be performed in the core of the fiber, and therefore it may be difficult to reduce the amount of solvent remaining in the fiber. Incidentally, the suitable immersion time of the fiber in the coagulation bath is in the range of 0.1 seconds to 30 seconds.

**[0043]** The drawing is carried out in an amide-based solvent. In particular, it is preferable to carry out the process at a drawing ratio of 3 to 4 times in a plasticizing drawing bath which contains an aqueous solution having 45% by mass to 60% by mass of NMP concentration and has a bath liquid temperature of 10°C to 50°C. After the drawing, thorough washing is performed by passing the fiber through a 10°C to 30°C aqueous solution with 20% by mass to 40% by mass of NMP concentration, followed by passing the fiber through a 50°C to 70°C hot water bath.

**[0044]** After washing, the fiber is subjected to a dry heat treatment at a temperature of 270°C to 290°C, which makes it possible to obtain a meta-type wholly aromatic polyamide fiber which satisfies the above range of crystallinity and residual solvent content. Preferable degree of crystallinity and preferable residual solvent content can be obtained by the above-described method.

**[0045]** Incidentally, the meta-type wholly aromatic polyamide fiber may be a long fiber (multifilament) or a short fiber. When it is blended with other fibers, a short fiber having a fiber length of 25 mm to 200 mm is preferred, and it is further preferable that a single fiber fineness is in a range of 1 dtex to 5 dtex.

**[0046]** Further, it is preferable that a meta-type wholly aromatic polyamide fiber is contained in a fabric as a blended spun yarn with a para-type wholly aromatic polyamide fiber, since the strength of the fabric is improved.

**[0047]** As the para-type wholly aromatic polyamide fiber, a paraphenylene terephthalamide fiber or a coparaphenylene·3,4'oxydiphenylene terephthalamide fiber is more preferable. Specific examples thereof include Technora (trademark), Kevlar (trademark) and Twaron (trademark).

**[0048]** Further, these fibers may contain additives such as an antioxidant, an infrared absorber, an ultraviolet absorber, a heat stabilizer, a flame retardant, titanium oxide, a colorant, and inert fine particles, as long as the object of the present invention is not impaired.

<Polyester fiber>

**[0049]** The polyester fiber is not particularly limited, and examples thereof include polyethylene terephthalate, polytrimethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, polycyclohexane terephthalate, and copolymers thereof, and a fiber in which a part of an acid component (terephthalic acid) is replaced with isophthalic acid.

<Electrically-conductive fiber>

**[0050]** Preferably, the fabric contains an electrically-conductive fiber in addition to the above-described fibers, since it is useful to prevent static electricity.

**[0051]** When the fabric contains the electrically-conductive fiber, the weights of meta-type wholly aromatic polyamide fiber, para-type wholly aromatic polyamide fiber, polyester fiber and electrically-conductive fiber are preferably in the ratio of 60 to 80 : 1 to 10 : 5 to 20 : 1 to 4 (more preferably 70 to 80 : 2 to 10 : 5 to 20 : 1 to 5, and still more preferably 75 to 80 : 3 to 8 : 10 to 20 : 1 to 4).

**[0052]** Further, it is preferable that the fabric is made of a blended spun yarn comprising a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber, a polyester fiber and an electrically-conductive fiber.

**[0053]** Preferably, the electrically-conductive fiber comprises, as a conductor of a conductive portion thereof, for example, at least one of the following components: carbon black, metal particles (silver particles, copper particles, aluminum particles, etc.), metal oxide (particles mainly contains titanium oxide, tin (IV) oxide, zinc oxide, indium oxide or the like) and a polymer containing electrically-conductive particles such as a polymer having coated particles of an electrically-conductive oxide.

**[0054]** The form of the electrically-conductive fiber may be a structure in which the entire fiber is made of a conductive portion, or a structure in which the non-conductive portion and the conductive portion have a cross-sectional shape such as a core-sheath shape, a sandwich shape, or an eccentric shape. The resin forming the conductive portion and/or non-conductive portion is not particularly limited, as long as it has fiber-forming ability. Specifically, examples thereof include, as for a nylon resin, nylon 6, nylon 11, nylon 12, and nylon 66. Further, examples of a polyester resin include polyethylene terephthalate, polytrimethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, polycyclohexane terephthalate, and a copolymer thereof, and a resin in which a part of an acid component (terephthalic acid) is replaced with isophthalic acid.

**[0055]** Examples of commercially available electrically-conductive fibers include "Metalian" (trade name) manufactured by Teijin Limited, "MEGANA" (trade name) manufactured by Unitika Ltd., "Luana" (trade name) manufactured by Toray Industries, Inc., "Clacarbo" (trade name) manufactured by Kuraray Co. Ltd. In particular, a preferable electrically-conductive fiber is a core-sheath type composite fiber in which a conductive component is disposed in a sheath portion. As such a core-sheath type composite fiber, "NO SHOCK" (trademark) manufactured by Solcia Corporation is preferable.

<Dyestuff>

**[0056]** The fabric of the present invention is a fabric dyed with various dyes after being shaped into a fabric. When a plurality of fiber species are used, a dyeing method suitable for the fiber species may be selected accordingly. Examples of the dyestuff include a cationic dyestuff, a Vat dyestuff, and a disperse dyestuff. The dyed fabric of the present invention is a fabric dyed with a cationic dyestuff and a disperse dyestuff.

**[0057]** A cationic dyestuff refers to a water-soluble dye having a basic functional group, and are commonly used for dyeing a fiber such as an acrylic fiber, a natural fiber, or a polyester fiber dyeable with a cationic dyestuff. The cationic dyestuff can be appropriately selected, and examples thereof include diacrylmethane-based dyestuff and triacrylmethane-based dyestuff, quinoneimine-based (azine, oxazine, thiazine) dyestuff, xanthene-based dyestuff, methine-based (polymethine, azamethine) dyestuff, heterocyclic azo (thiazole azo, triazole azo, benzothiazole azo) dyestuff, and an-

thraquinone dyestuff. Incidentally, it is possible to use a cationic dyestuff which is made into a dispersion type by blocking a basic functional group. As such dyestuffs, an azo dyestuff is desirable, and examples of the azo dyestuff include C.I. Basic Blue54, C.I.Basic Blue3, C.I.Basic Red29, C.I.Basic Yellow67.

**[0058]** A Vat dyestuff is a water-insoluble dye. The Vat dyestuff is dissolved in an alkaline solution by a reduction action, and is oxidized by air to be insolubilized again for the dyeing. The Vat dyestuff may be appropriately selected, and examples thereof include an indigo-based dye and an anthraquinone-based dyestuff.

**[0059]** A disperse dyestuff refers to a dyestuff which is hardly soluble in water and is used for dyeing hydrophobic fibers using a dispersed system in water. The disperse dyestuff is often used for dyeing a fiber such as a polyester fiber or an acetate fiber. The disperse dyestuff may be appropriately selected, and examples thereof include a benzene-based azo (mono azo, disazo, etc.,) dyestuff, a heterocyclic-based azo (thiazole azo, benzothiazole azo, quinoline azo, pyrizone azo, imidazole azo, thiophene azo, etc.,) dyestuff, an anthraquinone-based dyestuff, a condensation-type (quinophthalone, styryl, coumarin, etc.,) dyestuff, and the like.

**[0060]** When dyeing a fabric, a carrier agent may be used. Preferably, the carrier agent is, for example, at least one 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.

**[0061]** A method for manufacturing the dyed fabric according to the present disclosure is not particularly limited, but can be preferably manufactured by the dyeing method according to the present disclosure described below.

<<Dyeing method>>

**[0062]** When dyeing a fabric comprising a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber, or a fabric consisting of these fibers, first, the fabric is dyed with a cationic dyestuff at a temperature raised enough to dye the meta-type wholly aromatic polyamide fiber and the para-type wholly aromatic polyamide fiber, and then the fabric is dyed in a dyeing bath containing a disperse dyestuff at a temperature raised enough to dye the polyester fiber. The dyeing with the cationic dyestuff is preferably performed at a temperature range of 115°C to 135°C, preferably at 115°C to 125°C. The dyeing with the disperse dyestuff can be performed, for example, at 125°C to 135°C.

**[0063]** In this dyeing method, the dyeing with the disperse dyestuff is performed after the dyeing with the cationic dyestuff has been completed. In this method, a dyeing bath containing a cationic dyestuff may be cooled to 80°C or less, and then a disperse dyestuff may be added and the temperature may be raised, or, the dyeing bath containing the cationic dyestuff may be discarded and a dyeing bath containing a disperse dyestuff may be newly prepared to perform the dyeing.

**[0064]** By dyeing the fabric with the cationic dyestuff and then dyeing the fabric with the disperse dyestuff as described above, even in the case of a fabric containing a meta-type- and para-type- wholly aromatic polyamide fibers and a polyester fiber which are difficult to dye, it is possible to obtain a dyed fabric and a textile product made thereof which achieve excellent color uniformity of the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber and which have improved fastness in a darker color range.

**[0065]** In particular, according to the present invention, there is provided a method for dyeing a fabric, in which a fabric comprising a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber, or a fabric consisting of these fibers, is dyed with a dye solution for wholly aromatic polyamide fiber containing 20% o.w.f. or less of a cationic dyestuff, and then dyed with a dye solution for polyester fiber containing 2.0% o.w.f. or less of a disperse dyestuff.

**[0066]** According to this method, even in the case of a fabric containing a meta-type- and para-type- wholly aromatic polyamide fibers and a polyester fiber which are difficult to dye, it is possible to obtain a dyed fabric and a textile product made thereof which achieve excellent color uniformity of the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber, and which exhibit particularly excellent fastness in a darker color range.

**[0067]** The concentration of the disperse dyestuff at the time of dyeing is more preferably from 0.01% o.w.f. to 1.0% o.w.f., and even more preferably from 0.01% o.w.f. to 0.5% o.w.f.

**[0068]** The concentration of the cationic dyestuff at the time of dyeing is more preferably from 0.01% o.w.f. to 15% o.w.f., and even more preferably from 0.1% o.w.f. to 10% o.w.f.

<Thermosol dyeing>

**[0069]** According to an embodiment of the dyeing method of the present disclosure, when dyeing a fabric comprising a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber, or a

fabric consisting of these fibers, first, the fabric is dyed with a cationic dyestuff which is a dye solution for wholly aromatic polyamide fiber at a temperature raised enough to dye the meta-type wholly aromatic polyamide fiber and the para-type wholly aromatic polyamide fiber, and then a thermosol dyeing is performed using a disperse dyestuff which is a dyeing solution for polyester fiber. Incidentally, the dyeing with the cationic dyestuff is preferably performed at 115°C to 135°C, more preferably 115°C to 125°C.

**[0070]** In the thermosol dyeing, in particular, it is preferable to use a thermosol dyeing machine of a continuous device equipped with a padder, a dryer and a thermosol machine. In this case, the dyeing is preferably carried out by impregnating a fabric dyed with a cationic dyestuff into a disperse dye solution, followed by squeezing with a mangle at a squeezing ratio of 50% by mass to 70% by mass, followed by dry-heating at 90°C to 150°C (preferably at 120°C to 140°C) for 50 to 70 seconds, followed by drying at 160°C to 240°C for 2 to 4 minutes (preferably at 180°C to 220°C for 2.5 to 3.5 minutes), and then using an open soaper to perform reduction cleaning, soaping, and hot-water washing, and then performing final setting.

**[0071]** In the dyeing method comprising the thermosol dyeing, since a polyester fiber is ring-dyed (i.e., a polyester fiber is dyed by "ring-dyeing"), it is possible to achieve particularly good color uniformity between the polyester fiber and the above-mentioned wholly aromatic polyamide fibers. Therefore, even in the case of a fabric made of different fibers, i.e., wholly aromatic polyamide fibers and a polyester fiber, a dyed fabric with good quality can be obtained. In particular, by dyeing the meta-type wholly aromatic polyamide fiber and the para-type wholly aromatic polyamide fiber by means of a liquid flow dyeing and further by dyeing the polyester fiber by means of a continuous dyeing, much better color uniformity can be achieved. Incidentally, the color uniformity of the fibers can be evaluated by magnifying the obtained dyed fabric with a microscope and by evaluating the degree of dyeing of the fibers with a visual observation and with a color swatch.

**[0072]** Further, in another preferred dyeing method, a fabric containing a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber, or a fabric consisting of these fibers, is dyed with a dye solution for wholly aromatic polyamide fiber containing 20% o.w.f. or less of a cationic dyestuff, and then subjected to a thermosol dyeing with a dye solution for polyester fiber containing 2% o.w.f. or less of a disperse dyestuff. By performing the dyeing in this range, it is possible to obtain a dyed fabric and a textile product made thereof which achieve particularly excellent color uniformity of the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber, and which further exhibit improved fastness in a darker color range.

**[0073]** In particular, according to the dyeing method above, it is possible to avoid a problem that, when an aramid (wholly aromatic polyamide) and a polyester are dyed by a liquid flow dyeing, it is usually difficult to obtain color uniformity of the fibers, and a problem that if the fabric is dyed for a long time in order to obtain color uniformity, the texture becomes soft.

**[0074]** With regard to the constitutions of the dyeing method according to the present invention, such as a fabric, fibers constituting the fabric, a weight ratio of fibers, and a dye, etc., it is possible to refer to the above descriptions regarding the dyed fabric.

**[0075]** Incidentally, in the dyeing method according to the present invention, the fabric may contain an electrically-conductive fiber. According to the dyeing method of the present invention, even when an electrically-conductive fiber is contained, it is possible to obtain a dyed fabric which exhibits excellent color uniformity of the fibers.

<Other processing>

**[0076]** In order to impart various functions to the fabric, it is possible to apply or add other various processing to the fabric, such as a water repellent, a heat storage agent, an ultraviolet shielding agent or an antistatic agent, an antibacterial agent, a deodorant, an insect repellent, a phosphorescent agent, a retroreflective agent, etc. For example, as a sweat absorbing processing agent, it is preferable to use polyethylene glycol diacrylate, a derivative of polyethylene glycol diacrylate, a copolymer of polyethylene terephthalate and polyethylene glycol, a water-soluble polyurethane, or the like. In particular, a copolymer of polyethylene glycol and aminosilicone is preferred, since it has good affinity for the wholly aromatic polyamide fiber and thus the sweat absorption properties with good washing durability are easily obtained. Further, smaller particle diameter of the sweat absorbing processing agent is preferable, since in this case it easily adheres to the wholly aromatic polyamide fiber. The particle diameter is preferably in the range of 25 nm to 200 nm. The sweat absorbing processing agent may be applied to the fabric by bath treatment at the same time as dyeing, or may be applied to the fabric by padding treatment.

**[0077]** The textile product of the present invention includes protective suits, fire resistant suits for firefighting, firefighter suits, rescue suits, workwear, a police uniform, a camouflage uniform, and a military uniform which are made of the dyed fabric described above. Since these textile products are made of the above-described dyed fabric, they exhibit excellent heat resistance, flame retardancy, flame resistance and strength, and further, they exhibit excellent color uniformity, and in particular they exhibit good dye fastness. Therefore, as an aesthetic fabric having characteristics of both of the wholly aromatic polyamide fibers and the polyester fiber, these textile products are suitable for people who are engaged in work

which may be exposed to flames or the like, such as a firefighter, a pilot, a race driver, and a worker of a power company or a chemical company.

EXAMPLES

**[0078]** Next, Examples and Reference Examples of the present invention will be described in detail in the following, but the present invention is not limited thereto. Measurements in the examples and reference examples were performed by the following methods.

(1) Flame retardancy

**[0079]** The limiting oxygen index (LOI) defined in E-2 of JIS1091:1999 was determined.

(2) Fastness

**[0080]** The rubbing fastness (fastness to rubbing) as defined in JIS L 0849 II method was measured in dry condition and wet condition, respectively.

(3) Flammability

**[0081]** The afterflame time and afterglow time defined in JIS L 1091 A-1 method (1992) were measured.

(4) Residual solvent content

**[0082]** About 8.0g of raw fibers were collected, dried at 105°C for 120 minutes, and then allowed to cool in a desiccator, and the fiber mass (M1) was weighed. Subsequently, the reflux extraction was performed for this fiber in methanol for 1.5 hours using a Soxhlet extractor, in order to extract an amide-based solvent contained in the fiber. The fibers after completion of the extraction were taken out, dried under vacuum at 150°C for 60 minutes, and then allowed to cool in a desiccator, and the fiber mass (M2) was weighed. The amount of the solvent remaining in the fibers (mass of the amide-based solvent) was calculated from the obtained M1 and M2 by the following formula:

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

(5) Crystallinity

**[0083]** The diffraction profile was measured with an X-ray diffraction measurement device (RINT TTRIII, manufactured by Rigaku Corporation) by aligning the raw fibers into a fiber bundle having a diameter of about 1 mm and mounting it onto a fiber sample table. The measurement conditions were as follows: Cu-K$\alpha$ source (50kV, 300 mA), scanning angle range 10° to 35°, continuous measurement 0.1° width measurement, and 1°/min scanning. Total scattering profile was obtained from the measured diffraction profile by performing correction of air scattering and incoherent scattering by a linear approximation. Subsequently, the crystal scattering profile was obtained by subtracting the amorphous scattering profile from the total scattering profile. Crystallinity was determined based on the area intensity of the crystal scattering profile (crystal scattering intensity) and the area intensity of the total scattering profile (total scattering intensity), by the following formula:

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

(6) Water absorption

**[0084]** The water absorption performance defined in AATCC79 prior to washing (hereinafter referred to as the "initial water absorption performance") and the water absorption performance defined in AATCC79 after 10 washes defined in ISO6330:2012 (6N-F) (hereinafter referred to as the "water absorption performance after 10 washing cycles") were measured. Incidentally, the upper limit of the water absorption performance after 10 washing cycles was set to be 60 seconds.

(7) Darkness of a color (L value)

**[0085]** The L value was measured using a MacBeth spectrophotometer Color-Eye3100.

(8) Residual dyestuff

<Residual disperse dyestuff in polyester fiber>

**[0086]** The color (L value) of a dye solution prior to use was measured using a MacBeth spectrophotometer Color-Eye3100, and the color (L value) of a dye solution after the dyeing (a residual solution) was measured again, and the residual dye (% o.w.f.) was measured from the difference of these values.

<Residual cationic dyestuff in meta-type wholly aromatic polyamide fiber>

**[0087]** The color (L value) of a dye solution prior to use was measured using a MacBeth spectrophotometer Color-Eye3100, and the color of (L value) of a dye solution after the dyeing (a residual solution) was measured again, and the residual dye (% o.w.f.) was measured from the difference of these values.

(9) Color uniformity

**[0088]** With regard to the color uniformity of the dyed fabric, the obtained dyed fabric was magnified by a microscopy and the degree of dyeing of fibers was evaluated by visual observation, according to the following criteria:

Very good: The fabric exhibited particularly good color uniformity.
Good: The fabric exhibited good color uniformity.
Moderate: Although uneven dyeing was observed in a part of the fabric, the fabric generally exhibited color uniformity .
Poor: Non-uniform dyeing was observed throughout the fabric.

<<Examples 1 to 5>>

**[0089]** Dyed fabrics according to Examples 1 to 5 were manufactured and evaluated for quality.

[Example 1]

**[0090]** In the spinning process, the following fibers were blended at a weight ratio of 78:5:15:2, to obtain a single yarn having an English cotton count of 40 and a twist count of 24T/inch (twist factor=3.4), as a spun yarn:

- a short fiber consisting of polymetaphenylene isophthalamide fiber ("Teijinconex neo" (trademark), manufactured by Teijin Limited) having a single fiber fineness of 1.7 dtex, a cut length (fiber length) of 51 mm and a LOI of 26;
- a short fiber consisting of polyparaphenylene terephthalamide (PPTA) fiber ("Twaron" (trademark), manufactured by Teijin Limited) having a single fiber fineness of 1.7 dtex, a cut length (fiber length) of 51 mm, and a limiting oxygen index defined in E-2 of JIS 1091:1999 of 25;
- a short fiber consisting of polyester fiber ("eco-PET(RA02)", manufactured by Teijin Limited) having a single fiber fineness of 2.2 dtex and a fiber length of 38 mm;
- a short fiber consisting of an electrically-conductive fiber ("Corebrid ET10" (trademark), manufactured by Mitsubishi Chemical Corporation) having a single fiber fineness of 3.3 dtex and a cut length (fiber length) of 38 mm.

**[0091]** Two of the obtained spun yarns were combined and twisted by double twister at a second twist count of 20.9T/inch, and then subjected to twist-set at a setting temperature of 120°C for a setting time of 20 minutes by using a vacuum steam setting machine, in order to obtain a flame-retardant doubled and twisted yarn.

**[0092]** Then, weaving was performed with the obtained flame-retardant doubled and twisted yarn, in order to obtain a woven fabric with a fabric density of 57 ends per inch and 53 picks per inch and a fabric texture of 1/1 plain weave.

**[0093]** The woven fabric was subjected to singeing treatment, scouring treatment, dry treatment, and heat treatment (temperature: 160°C, time:30 seconds) in a conventional manner, and then dyed with a dye solution for wholly aromatic polyamide fiber at a temperature of 130°C for 60 minutes after raising the temperature from ambient temperature (bath ratio 1:20), wherein the dye solution for wholly aromatic polyamide fiber contains 16% o.w.f. of a cationic dyestuff (Basacryl Red GL, manufactured by BASF), 10 g/l of a carrier agent, 3 g/l of acetic acid, 20 g/l of sodium nitrate, and 1 g/l of a dispersant (Disper VG, manufactured by Meisei Chemical Works, Ltd.).

**[0094]** Then, the fabric was dyed with a dye solution for polyester fiber at a temperature of 130°C for 30 minutes after raising the temperature from ambient temperature (bath ratio 1:20), wherein the dye solution for polyester fiber contains 0.2% o.w.f. of a disperse dyestuff (Foron Rubine S-2GFL, manufactured by Sandoz), 3 g/l of acetic acid, and 1 g/l of a dispersant (Disper VG, manufactured by Meisei Chemical Works, Ltd.).

**[0095]** The obtained colored fabric was then washed with a reducing bath (bath ratio 1:20) containing 1 g/L of hydrosulfite and 1 g/L of soda ash at a temperature of 70°C for 20 minutes. Thereafter, after cooling, the dyed fabric was collected, washed with water, air-dried, and subjected to heat treatment to finish. The heat treatment was carried out at a temperature of 160°C for 1 minutes to obtain a dyed fabric.

**[0096]** The obtained fabric was treated with a sweat absorbing processing agent for polyester and a sweat absorbing processing agent for wholly aromatic polyamide fiber in a conventional manner.

**[0097]** In the obtained dyed fabric, the woven fabric density was 63 ends per inch and 55 picks per inch, the limiting oxygen index was 26.0, the dry rubbing fastness was grade 4-5, the wet rubbing fastness was grade 4-5, the afterflame time and afterglow time were 0 second, the initial water absorption performance was 1.0 seconds, the water absorption performance after 10 washing cycles was 1.0 seconds, the residual disperse dyestuff in the polyester fiber was 0.03% o.w.f., and the residual cationic dyestuff in the meta-type wholly-aromatic polyamide fiber was 8.0% o.w.f. Evaluation results are shown in Table 1.

[Example 2]

**[0098]** A dyed fabric was obtained as in Example 1 except that in the spinning step, instead of "Twaron" which is a para-type wholly aromatic polyamide, a coparaphenylene·3,4' oxydiphenylene terephthalamide fiber ("Technora" (trademark) manufactured by Teijin Limited) having a single fiber fineness of 1.7 dtex, a cut length (fiber length) of 51 mm, and a limiting oxygen index defined in E-2 of JIS1091:1999 of 25, was used.

**[0099]** In the obtained dyed fabric, the woven fabric density was 63 ends per inch and 55 picks per inch, the limiting oxygen index was 26.0, the dry rubbing fastness was grade 4-5, the wet rubbing fastness was grade 4-5, the afterflame time and afterglow time were 0 second, the initial water absorption performance was 1.0 seconds, the water absorption performance after 10 washing cycles was 1.0 seconds, the residual disperse dyestuff in the polyester fiber was 0.02% o.w.f., and the residual cationic dyestuff in the meta-type wholly aromatic polyamide fiber was 8.0% o.w.f. Evaluation results are shown in Table 1.

[Example 3]

**[0100]** A dyed fabric was obtained as in Example 1 except that in the spinning step, an electrically-conductive fiber ("CoreBrid ET10" (trademark), manufactured by Mitsubishi Chemical Corporation) having a single fiber fineness of 3.3 dtex and a cut length (fiber length) of 38 mm was not contained, and a weight ratio of the fibers was set to 80:5:15.

**[0101]** In the obtained dyed fabric, the woven fabric density was 63 ends per inch and 55 picks per inch, the limiting oxygen index was 26.0, the dry rubbing fastness was grade 4-5, the wet rubbing fastness was 4-5 grade, the afterflame time and afterglow time were 0 second, the initial water absorption performance was 1.0 seconds, the water absorption performance after10 washing cycles was of 1.0 seconds , the residual disperse dyestuff in the polyester fiber was 0.02% o.w.f., and the residual cationic dyestuff in the meta-type wholly aromatic polyamide fiber was 8.0% o.w.f. Evaluation results are shown in Table 1.

[Example 4]

**[0102]** A dyed fabric was obtained as in Example 1 except that the sweat absorbing processing agent for polyester was not used in the dispersion dyeing condition. In the obtained fabric, the woven fabric density was 63 ends per inch and 55 picks per inch, the limiting oxygen index was 26.0, the dry rubbing fastness was grade 4 and the wet rubbing fastness was grade 4, the afterflame time and afterglow time were 0 second, the initial water absorption performance was 10.0 seconds, the water absorption performance after 10 washing cycles was 15.0 seconds, the residual disperse dyestuff in the polyester fiber was 0.06% o.w.f., and the residual cationic dyestuff in the meta-type wholly aromatic polyamide fiber was 8.0% o.w.f. Evaluation results are shown in Table 1.

[Example 5]

**[0103]** A dyed fabric was obtained as in Example 1 except that the concentration of the disperse dyestuff was changed to 3.0% o.w.f. in the dyeing condition.

**[0104]** In the obtained dyed fabric, the woven fabric density was 63 ends per inch and 55 picks per inch, the limiting oxygen index was 26.0, the dry rubbing fastness was grade 2-3 and the wet rubbing fastness was grade 2-3, the afterflame

time and afterglow time were 0 second, the initial water absorption performance was 1.0 seconds, the water absorption performance after 10 washing cycles was 1.0 seconds, the residual disperse dyestuff in the polyester fiber was 0.05% o.w.f., and the residual cationic dyestuff in the meta-type wholly aromatic polyamide fiber was 9.0% o.w.f. Evaluation results are shown in Table 1.

[Reference Example 1 (Ref.Ex.1)]

**[0105]** A dyed fabric was obtained as in Example 1 except that although the dyeing with the dye solution for wholly aromatic polyamide fiber was performed, the dyeing with the dye solution for polyester fiber was not performed. The dyed fabric thus obtained was evaluated for color uniformity. Evaluation result is shown in Table 1.

[Reference Example 2 (Ref.Ex.2)]

**[0106]** A dyed fabric was obtained as in Example 1 except that although the dyeing with the dye solution for polyester fiber was performed, the dyeing with the dye solution for wholly aromatic polyamide fiber was not performed. The dyed fabric thus obtained was evaluated for color uniformity. Evaluation result is shown in Table 1.

[Reference Example 3 (Ref.Ex.3)]

**[0107]** A dyed fabric was obtained as in Example 1 except that a dyeing of a fabric was performed with a mixed dye solution containing a cationic dyestuff and a disperse dyestuff, instead of the dyeing with the dye solution for polyester fiber and the dyeing with the dye solution for wholly aromatic polyamide fiber. The dyed fabric thus obtained was evaluated for color uniformity. Evaluation result is shown in Table 1.

[Table 1]

**[0108]**

Table 1

| | | | Example 1 | Example 2 | Example 3 | Example 4 | Example 5 | Ref.Ex. 1 | Ref.Ex. 2 | Ref.Ex. 3 |
|---|---|---|---|---|---|---|---|---|---|---|
| Flame retardancy (LOI) | | | 26 | 26 | 26 | 26 | 26 | - | - | - |
| Fastness | dry condition | grade | 4-5 | 4-5 | 4-5 | 4 | 2-3 | - | - | - |
| | wet condition | grade | 4-5 | 4-5 | 4-5 | 4 | 2-3 | - | - | - |
| Flammability | afterflame time | sec | 0 | 0 | 0 | 0 | 0 | - | - | - |
| | afterglow time | sec | 0 | 0 | 0 | 0 | 0 | - | - | - |
| Crystallinity | | % | 25 | 25 | 25 | 25 | 25 | - | - | - |
| Water absorption performance | Initial | sec | 1.0 | 1.0 | 1.0 | 10.0 | 1.0 | - | - | - |
| | after 10 washings | sec | 1.0 | 1.0 | 1.0 | 15.0 | 1.0 | - | - | - |
| Residual dyestuff | disperse dyestuff | % owf | 0.03 | 0.02 | 0.02 | 0.06 | 0.05 | - | - | - |
| | cationic dyestuff | % owf | 8.0 | 8.0 | 8.0 | 8.0 | 9.0 | - | - | - |
| Lvalue | | | 25 | 27 | 26 | 28 | 27 | - | - | - |
| Color uniformity | | | Good | Good | Good | Good | Good | Poor | Poor | Moderate |



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<<Examples 6 to 10>>

**[0109]** The dyed fabrics according to Examples 6 to 10 were manufactured and the evaluation was carried out for their quality.

[Example 6]

**[0110]** In the spinning process, the following fibers were blended at a weight ratio of 78:5:15:2 to obtain a single yarn having an English cotton count of 40 and a twist count of 24T/inch (twist factor=3.4), as a spun yarn:

- a short fiber consisting of polymetaphenylene isophthalamide fiber ( "Teijinconex neo" (trademark), manufactured by Teijin Limited) having a single fiber fineness of 1.7 dtex, a cut length (fiber length) of 51 mm and a LOI of 26;
- a short fiber consisting of polyparaphenylene terephthalamide (PPTA) fiber ("Twaron" (trademark), manufactured by Teijin Limited) having a single fiber fineness of 1.7 dtex and a cut length (fiber length) of 51 mm and a limiting oxygen index defined in E-2 of JIS1091:1999 of 25;
- a short fiber consisting of a polyester fiber ("eco-PET (RA02)", manufactured by Teijin Limited) having a single fiber fineness of 2.2 dtex and a fiber length of 38mm;
- a short fiber consisting of an electrically-conductive fiber ("Corebrid ET10" (trademark), manufactured by Mitsubishi Chemical Corporation) having a single fiber fineness of 3.3 dtex and a cut length (fiber length) of 38 mm.

**[0111]** Two of the obtained spun yarns were combined and twisted by double twister at a second twist count of 20.9T/inch, and then subjected to twist-set by using a vacuum steam setting machine at a setting temperature of 120°C for a setting time of 20 minutes, in order to obtain a flame retardant doubled and twisted yarn.

**[0112]** Then, a weaving was performed with the obtained flame retardant doubled and twisted yarn, in order to obtain a fabric with a fabric density of 57 ends per inch and 53 picks per inch and a fabric texture of 1/1 plain weave.

**[0113]** The woven fabric was subjected to singeing treatment, scouring treatment, and setting treatment (temperature: 160 °C, time:30 seconds) in a conventional manner, and then dyed with a dye solution for wholly aromatic polyamide fiber at a temperature of 130°C for 60 minutes after raising the temperature from the ambient temperature (bath ratio 1:20), wherein the dye solution for wholly aromatic polyamide fiber contains 16% o.w.f. of a cationic dyestuff (Basacryl Red GL, manufactured by BASF), 10 g/l of a carrier agent, 3 g/l of acetic acid, 20 g/l of sodium nitrate, and 1 g/l of a dispersant (Disper VG, manufactured by Meisei Chemical Works, Ltd.).

**[0114]** After the dyeing described above, a dyeing was carried out using a thermosol dyeing machine of a continuous device equipped with a padder, a dryer, and a thermosol machine. In this dyeing procedure, the fabric dyed with the cationic dyestuff was impregnated into a dye solution for polyester fiber containing 0.2% o.w.f. of a disperse dyestuff (Sumikaron Red S-3BFL, manufactured by Sumika Chemtex Co., Ltd.), 3 g/l of sodium alginate (anti migration agent), and 1 g/l of a dispersant (Disper VG, manufactured by Meisei Chemical Works, Ltd.), and then squeezed with a mangle at a squeezing ratio of 60% by mass, and then dried at 130°C for 60 seconds, and subjected to a dry heat treatment at 230°C for 3 minutes. Subsequently, an open soaper was used to perform reduction cleaning, soaping, and hot-water washing, and then drying was performed for a final set (30 seconds at 160°C), in order to obtain a dyed fabric.

**[0115]** The obtained fabric was treated with a sweat absorbing processing agent for polyester and a sweat absorbing processing agent for wholly aromatic polyamide fiber in a conventional manner.

**[0116]** In the obtained dyed fabric, the woven fabric density was 63 ends per inch and 55 picks per inch, the dry rubbing fastness was grade 3 and the wet rubbing fastness was grade 3, the afterflame time and afterglow time were 0 second, the initial water absorption performance was 1.0 seconds, the water absorption performance after 10 washing cycles was 1.0 seconds, the residual disperse dyestuff in the polyester fiber was 0.1% o.w.f., and the residual cationic dyestuff in the meta-type wholly aromatic polyamide fiber was 4.5% o.w.f. Evaluation results are shown in Table 2.

**[0117]** The obtained dyed fabric was excellent in heat resistance and flame resistance, and had particularly good color uniformity of fibers, excellent appearance quality, and excellent fastness.

[Example 7]

**[0118]** The dyed fabric was manufactured as in Example 6 except that, in the spinning step, coparaphenylene 3,4' oxydiphenylene terephthalamide fiber ("Technora" (trademark), manufactured by Teijin Limited) having a single fiber fineness of 1.7 dtex, a cut length (fiber length) of 51 mm, and an LOI of 25, was used instead of "Twaron" (Trademark) manufactured by Teijin Limited which is a para-type wholly aromatic polyamide.

**[0119]** In the obtained dyed fabric, the woven fabric density was 63 ends per inch and 55 picks per inch, the limiting oxygen index was 26.0, the dry rubbing fastness was grade 3 and the wet rubbing fastness was grade 3, the afterflame time and afterglow time were 0 second, the initial water absorption performance was 1.0 seconds, the water absorption

performance after 10 washing cycles was 1.0 seconds, the residual disperse dyestuff in the polyester fiber was 0.1% o.w.f., and the residual cationic dyestuff in the meta-type wholly aromatic polyamide fiber was 4.5% o.w.f. Evaluation results are shown in Table 2.

**[0120]** The obtained dyed fabric was excellent in heat resistance and flame resistance, and had particularly good color uniformity of fibers, excellent appearance quality, and excellent fastness.

[Example 8]

**[0121]** The dyed fabric was manufactured as in Example 6 except that in the spinning process, an electrically-conductive fiber ("Corebrid ET10" (trademark) manufactured by Mitsubishi Chemical Corporation) having a single fiber fineness of 3.3 dtex and a cut length (fiber length) of 38 mm was not used, and a weight ratio of fibers was changed to 80:5:15

**[0122]** In the obtained dyed fabric, the woven fabric density was 63 ends per inch and 55 picks per inch, the limiting oxygen index was 26.0, the dry rubbing fastness was grade 3 and the wet rubbing fastness was grade 3, the afterflame time and afterglow time were 0 second, the initial water absorption was 1.0 seconds, the water absorption performance after 10 washing cycles was 1.0 seconds, the residual disperse dyestuff in the polyester fiber was 0.1% o.w.f., and the residual cationic dyestuff in the meta-type wholly aromatic polyamide fiber was 4.6% o.w.f. Evaluation results are shown in Table 2.

**[0123]** The obtained dyed fabric was excellent in heat resistance and flame resistance, and had particularly good color uniformity of fibers, excellent appearance quality, and excellent fastness.

[Example 9]

**[0124]** The dyed fabric was manufactured as in Example 6 except that a sweat absorbing processing agent for polyester was not used in the disperse dyeing condition.

**[0125]** In the obtained dyed fabric, the woven fabric density was 63 ends per inch and 55 picks per inch, the limiting oxygen index was 26.0, the dry rubbing fastness was grade 3, the wet rubbing fastness was grade 3, the afterflame time and afterglow time were 0 second, the initial water absorption was 10.0 seconds, the water absorption performance after 10 washing cycles was 15.0 seconds, the residual disperse dyestuff in the polyester fiber was 0.18% o.w.f., and the residual cationic dyestuff in the meta-type wholly aromatic polyamide fiber was 4.6% o.w.f. Evaluation results are shown in Table 2.

**[0126]** The obtained dyed fabric was excellent in heat resistance and flame resistance, and had particularly good color uniformity of fibers, excellent appearance quality, and excellent fastness.

[Example 10]

**[0127]** The dyed fabric was manufactured as in Example 6 except that the concentration of the disperse dyestuff was changed to 3.0% o.w.f. in the dyeing condition. In the obtained dyed fabric, the woven fabric density was 63 ends per inch and 55 picks per inch, the limiting oxygen index was 26.0, the dry rubbing fastness was grade 2 and the wet rubbing fastness was grade 2, the afterflame time and afterglow time were 0 second, the initial water absorption performance was 1.0 seconds, the water absorption performance after 10 washing cycles was 1.0 seconds, the residual disperse dyestuff in the polyester fiber was 2.5% o.w.f., and the residual cationic dyestuff in the meta-type wholly aromatic polyamide fiber was 4.5% o.w.f. Evaluation results are shown in Table 2.

[Table 2]

**[0128]**

Table 2

| | | | Example 6 | Example 7 | Example 8 | Example 9 | Example 10 |
|---|---|---|---|---|---|---|---|
| Flame retardancy (LOI) | | | 26 | 26 | 26 | 26 | 26 |
| Fastness | dry condition | grade | 3 | 3 | 3 | 3 | 2 |
| | wet condition | grade | 3 | 3 | 3 | 3 | 2 |
| Flammability | afterflame time | sec | 0 | 0 | 0 | 0 | 0 |
| | afterglow time | sec | 0 | 0 | 0 | 0 | 0 |

(continued)

| | | | Example 6 | Example 7 | Example 8 | Example 9 | Example 10 |
|---|---|---|---|---|---|---|---|
| Crystallinity | | % | 25 | 25 | 25 | 25 | 25 |
| Water absorption performance | Initial | sec | 1.0 | 1.0 | 1.0 | 10.0 | 1.0 |
| | after 10 washings | sec | 1.0 | 1.0 | 1.0 | 15.0 | 1.0 |
| Residual dyestuff | disperse dyestuff | % owf | 0.1 | 0.1 | 0.1 | 0.18 | 2.5 |
| | cationic dyestuff | % owf | 4.5 | 4.5 | 4.6 | 4.6 | 4.5 |
| L value | | | 25 | 27 | 26 | 28 | 27 |
| Color uniformity | | | Very Good | Very Good | Very Good | Very Good | Very Good |

## Claims

**1.** A dyed fabric dyed after being shaped into a fabric,

**characterized in that** the fabric comprises a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber, and the fabric is dyed with a cationic dyestuff and a disperse dyestuff,
and **in that** the afterflame time and afterglow time defined in JISL1091A-1 are 1 second or less.

**2.** The dyed fabric according to claim 1, wherein both of the dry rubbing fastness and the wet rubbing fastness defined in JIS L 0849 II method are grade 3 or more.

**3.** The dyed fabric according to claim 1 or 2, wherein the polyester fiber is dyed with the disperse dyestuff by ring-dyeing.

**4.** The dyed fabric according to any one of claims 1 to 3, wherein the residual disperse dyestuff is from 0.01% o.w.f. to 0.5% o.w.f.

**5.** The dyed fabric according to any one of claims 1 to 4, wherein the residual cationic dyestuff is from 0.01% o.w.f. to 16.0% o.w.f.

**6.** The dyed fabric according to any one of claims 1 to 5, wherein the weights of the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber are in the ratio of 60 to 80 : 1 to 10 : 5 to 20.

**7.** The dyed fabric according to any one of claims 1 to 6, wherein

the fabric comprises an electrically-conductive fiber, and
the weights of the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber, the polyester fiber and the electrically-conductive fiber are in the ratio of 60 to 80 : 1 to 10 : 5 to 20 : 1 to 4.

**8.** The dyed fabric according to any one of claims 1 to 6, which is made of a blended spun yarn comprising the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber and the polyester fiber.

**9.** The dyed fabric according to claims 7, which is made of a blended spun yarn comprising the meta-type wholly aromatic polyamide fiber, the para-type wholly aromatic polyamide fiber, the polyester fiber and the electrically-conductive fiber.

**10.** The dyed fabric according to any one of claims 1 to 9, wherein

the water absorption performance defined in AATCC79 prior to washing is 2 seconds or less, and
the water absorption performance defined in AATCC79 after 10 washing cycles defined in ISO6330:2012 (6N-F) is 10 seconds or less.

**11.** The dyed fabric according to any one of claims 1 to 10, which is dyed with 2% o.w.f. or less of the disperse dyestuff after dyed with 20% o.w.f. or less of the cationic dyestuff.

**12.** A textile product made of the dyed fabric according to any one of claims 1 to 11, which is selected from the group consisting of protective suits, fire resistant suits for fire-fighting, firefighter suits, rescue suits, workwear, a police uniform, a camouflage uniform, and a military uniform.

**13.** A method for dyeing a fabric, **characterized in that**

dyeing a fabric comprising a meta-type wholly aromatic polyamide fiber, a para-type wholly aromatic polyamide fiber and a polyester fiber with a dye solution for wholly aromatic polyamide fiber comprising 20% o.w.f. or less of a cationic dyestuff, and then
dyeing the fabric with a dye solution for polyester fiber comprising 2% o.w.f. or less of a disperse dyestuff.

**14.** The dyeing method according to claim 13, wherein the dyeing is performed by thermosol dyeing.

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2020/025385

A. CLASSIFICATION OF SUBJECT MATTER
D03D 15/00(2006.01)i; A41D 13/00(2006.01)i; A41D 31/00(2019.01)i; A41D 31/08(2019.01)i; D03D 15/12(2006.01)i; D06P 1/16(2006.01)i; D06P 1/41(2006.01)i; D06P 3/04(2006.01)i; D06P 3/52(2006.01)i; D06P 3/54(2006.01)i; D06P 3/87(2006.01)i
FI: D03D15/00 D; A41D13/00 102; A41D31/00 503F; A41D31/00 503G; A41D31/08; D03D15/00 101; D03D15/12 Z; D06P1/16 Z; D06P1/41; D06P3/04 A; D06P3/04 B; D06P3/52 F; D06P3/54 Z; D06P3/87 D
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)
D03D15/00; A41D13/00; A41D31/00; A41D31/08; D03D5/12; D06P1/16; D06P1/41; D06P3/04; D06P3/52; D06P3/54; D06P3/87

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 | 1971–2020 |
| Registered utility model specifications of Japan | 1996–2020 |
| Published registered utility model applications of Japan | 1994–2020 |

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. |
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| Y<br>A | JP 9-95870 A (TEIJIN LTD.) 08.04.1997 (1997-04-08) claims 1, 7, paragraph [0052] | 1-13<br>14 |
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| A | JP 4-41738 A (TORAY INDUSTRIES, INC.) 12.02.1992 (1992-02-12) | 1-14 |

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

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 24 August 2020 (24.08.2020) | 01 September 2020 (01.09.2020) |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| Japan Patent Office<br>3-4-3, Kasumigaseki, Chiyoda-ku,<br>Tokyo 100-8915, Japan | Telephone No. |

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

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2020/025385

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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| A | JP 2010-502849 A (SOUTHERN MILLS, INC.) 28.01.2010 (2010-01-28) | 1-14 |
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Form PCT/ISA/210 (continuation of second sheet) (January 2015)

**INTERNATIONAL SEARCH REPORT**
Information on patent family members

International application No.
PCT/JP2020/025385

| Patent Documents referred in the Report | Publication Date | Patent Family | Publication Date |
|---|---|---|---|
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| WO 2018/084040 A1 | 11 May 2018 | US 2020/0063299 Al<br>EP 3536836 Al<br>CA 3039312 A<br>CN 109923251 A | |

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## REFERENCES CITED IN THE DESCRIPTION

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