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(54) **HEAT-RESISTANT FABRIC**

HITZEBESTÄNDIGES GEWEBE

TISSU RÉSISTANT À LA CHALEUR

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Description

Technical Field

5 **[0001]** The present invention relates to a heat-resistant fabric made of a meta-type aromatic polyamide fiber according to claim 1.

Background Art

10 **[0002]** With respect to conventional protective garments, such as firefighter garments, using a fabric made mainly of a meta-type wholly aromatic polyamide fiber, etc., when they are repeatedly used, washed with a surfactant such as a detergent, etc., or dry-cleaned, for example, they show a decrease from the initial surface abrasion resistance. In addition, because a fabric made mainly of a meta-type wholly aromatic polyamide fiber is used, the minimum surface abrasion is more than 200 rubs. In the past, there have been problems that although the initial surface abrasion is high, the
15 abrasion resistance decreases due to washing, leading to loss of high washing durability, which results in noticeable holes after washing. Several studies have been made in order to solve such problems.

[0003] Patent Document 1 (JP-A-2009-249758) discloses a method in which a high-strength, high-heat-resistance fiber is arranged as a core yarn, another dyeable fiber or spun-dyed yarn is arranged therearound in a substantially non-twisted state, and further they are covered with a dyeable fiber or spun-dyed yarn in a spiral fashion, thereby maintaining
20 aesthetics.

[0004] Patent Document 2 (JP-A-2009-209488) discloses a composite spun yarn including a core component made of a para-aramid fiber and a meta-aramid fiber and a sheath component made of a cellulose fiber, with the composite ratio of core component/sheath component being within a range of 25/75 to 55/45, as well as a woven or knitted fabric using the composite spun yarn.

25 **[0005]** Patent Document 3 (JP-A-2003-147651) discloses a core-sheath-type composite spun yarn including a core component made of a heat-resistant, high-performance fiber and a sheath component made of staple fibers of a synthetic fiber, a chemical fiber, or a natural fiber, characterized in that the heat-resistant, high-performance fiber is a crimped yarn of a heat-resistant, high-performance fiber filament yarn.

30 **[0006]** According to the above invention, a fiber that is likely to adversely affect washing durability is used as the core part of a sheath-core structure yarn, thereby hiding the fiber itself so as to solve the problems. In these inventions, it is indispensable to use a sheath-core structure yarn. Thus, there is a problem that its production inevitably takes more time and cost as compared with ordinary spun yarns.

Patent Document 1: JP-A-2009-249758

35 Patent Document 2: JP-A-2009-209488

Patent Document 3: JP-A-2003-147651

Summary of the Invention

40 Problems that the Invention is to Solve

[0007] The invention has been accomplished in view of the problems mentioned above and is aimed at providing a heat-resistant fabric that can be dyed to a color chosen from a wide range of color options, is capable of maintaining high mechanical characteristics without degradation over time/age even after repeated uses or washes, etc., and has
45 excellent pilling resistance.

Means for Solving the Problems

50 **[0008]** As a result of extensive research, the present inventor has found that the problems mentioned above can be solved by the following heat-resistant fabric.

[0009] The heat-resistant fabric of the invention is a heat-resistant fabric containing a meta-type wholly aromatic polyamide fiber, characterized in that the abrasion resistance of the heat-resistant fabric in accordance with the JIS L1096 8.19.1 A-1 method (universal type method (plane method), abrasion tester press load: 4.45 N (0.454 kf), paper: #600) is 200 rubs or more, the tear strength of the heat-resistant fabric in accordance with the JIS L1096 8.17.4 D method (pendulum method) is 20 N or more, and the retention of the abrasion resistance and the retention of the tear strength after 100 washes in accordance with JIS L0844 No. A-1 are each 90% or more relative to before washing, wherein the heat-resistant fabric contains at least a rayon, a paraphenylene terephthalamide fiber or a co-paraphenylene/3,4'-oxydiphenylene terephthalamide fiber.

[0010] In the heat-resistant fabric of the invention, it is preferable that the meta-type wholly aromatic polyamide fiber has a crystallinity of 15 to 27.

[0011] In the heat-resistant fabric of the invention, it is preferable that the standard deviation of the single-fiber tensile strength of the meta-type wholly aromatic polyamide fiber is 0.60 or less.

[0012] In the heat-resistant fabric of the invention, it is preferable that the meta-type wholly aromatic polyamide fiber has an average single-fiber tensile strength of 4.0 cN/dtex or less.

[0013] In the heat-resistant fabric of the invention, it is preferable that the meta-type wholly aromatic polyamide fiber has an average single-fiber elongation of 35% or less.

[0014] In the heat-resistant fabric of the invention, it is preferable that the meta-type wholly aromatic polyamide fiber has a single-fiber toughness of 130 or less.

[0015] In the heat-resistant fabric of the invention, it is preferable that the heat-resistant fabric is dyed, and the color difference ΔE of the fabric before and after a light resistance test in accordance with JIS L0842 and the brightness L of the light resistance test fabric satisfy the following equation (1) :

$$\Delta E \leq 0.46L - 11.3 \dots (1).$$

[0016] In the heat-resistant fabric of the invention, it is preferable that the meta-type wholly aromatic polyamide fiber contains an organic dye.

[0017] In the heat-resistant fabric of the invention, it is preferable that the heat-resistant fabric contains at least one member selected from a cellulose fiber, a polyester fiber, an acrylic fiber, and a polyamide fiber in an amount of 2 to 50 mass% based on the mass of the heat-resistant fabric.

[0018] In the heat-resistant fabric of the invention, it is preferable that the cellulose fiber is rayon.

[0019] In the heat-resistant fabric of the invention, it is preferable that the cellulose fiber, polyester fiber, acrylic fiber, or polyamide fiber contains a flame retarder.

[0020] In the heat-resistant fabric of the invention, it is preferable that the pilling resistance of the heat-resistant fabric in accordance with the 11. JIS L1096 A method is Level 4 or higher.

[0021] In the heat-resistant fabric of the invention, it is preferable that the heat-resistant fabric contains cellulose and is dyed with a fluorescent dye.

[0022] The heat-resistant fabric of the invention is preferably the heat-resistant fabric according to any one of claims 1 to 12, wherein the meta-type wholly aromatic polyamide that forms the meta-type wholly aromatic polyamide fiber is an aromatic polyamide obtained by copolymerizing, into an aromatic polyamide backbone having a repeating structural unit represented by the following formula (1), an aromatic diamine component or aromatic dicarboxylic acid halide component that is different from a main unit of the repeating structure as a third component so that the proportion of the third component is 1 to 10 mol% based on the total repeating structural units of the aromatic polyamide:



wherein Ar1 is a divalent aromatic group having a linking group in a position other than the meta position or an axially parallel direction.

[0023] In the heat-resistant fabric of the invention, it is preferable that the third component is an aromatic diamine of formula (2) or (3) or an aromatic dicarboxylic acid halide of formula (4) or (5):



wherein Ar2 is a divalent aromatic group different from Ar1,

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

[0024] In the heat-resistant fabric of the invention, it is preferable that the meta-type aromatic polyamide fiber has a

residual solvent content of 0.1 mass% or less.

[0025] In the heat-resistant fabric of the invention, it is preferable that the heat-resistant fabric contains at least one member selected from a para-type wholly aromatic polyamide fiber, a polybenzobisoxazol fiber, and a wholly aromatic polyester fiber in an amount of 1 to 20 mass% based on the mass of the heat-resistant fabric.

[0026] In the heat-resistant fabric of the invention, it is preferable that the para-type wholly aromatic polyamide fiber is a paraphenylene terephthalamide fiber or a co-paraphenylene/3,4'-oxydiphenylene terephthalamide fiber.

[0027] In the heat-resistant fabric of the invention, it is preferable that a fiber that forms the heat-resistant fabric contains a UV absorber and/or UV reflector.

[0028] In the heat-resistant fabric of the invention, it is preferable that the heat-resistant fabric has a UV absorber and/or UV reflector fixed to the surface thereof.

Advantage of the Invention

[0029] According to the invention, a heat-resistant fabric that can be dyed to a color chosen from a wide range of options and is highly capable of retaining surface abrasion and tear strength over time/age even after repeated uses, washes, etc., can be provided. Thus, the fabric can be suitably used for protective garments, such as firefighter garments, or for industrial materials, such as flexible heat-insulating materials.

Mode for Carrying Out the Invention

[0030] The heat-resistant fabric of the invention is a heat-resistant fabric containing a meta-type wholly aromatic polyamide fiber. The fabric indispensably contains a meta-type wholly aromatic polyamide fiber, but the presence of other kinds of fibers is also allowed as defined in claim 1, including flame-retardant fibers such as para-type wholly aromatic polyamide fibers, synthetic fibers such as polyester fibers, regenerated fibers such as rayon, and natural fibers such as cotton. However, in order for the high heat resistance and flame retardancy, which are advantageous characteristics of a meta-type wholly aromatic polyamide fiber, to be exerted, it is preferable that the meta-type wholly aromatic polyamide fiber content is 50 mass% or more based on the total mass of the heat-resistant fabric.

[0031] The meta-type wholly aromatic polyamide fiber for use in the invention is made of a polymer, wherein 85 mol% or more of the repeating unit is m-phenyleneisophthalamide. The meta-type wholly aromatic polyamide may also be a copolymer containing a third component in an amount within a range of less than 15 mol%.

[0032] In the invention, it is important that the abrasion resistance of the heat-resistant fabric in accordance with the JIS L1096 8.19.1 A-1 method (universal type method (plane method), abrasion tester press load: 4.45 N (0.454 kf), paper: #600) is 200 rubs or more, the tear strength of the heat-resistant fabric in accordance with the JIS L1096 8.17.4 D method (pendulum method) is 20 N or more, and the retention of the abrasion resistance and the retention of the tear strength after 100 washes in accordance with JIS L0844 No. A-1 are each 90% or more relative to before washing. As a result, even after repeated uses, washes, etc., high durability can be maintained while suppressing degradation with time/age, and extremely excellent practical performance is exerted. In the case where there is a difference in the tear strength between one direction of the fabric and the direction perpendicular thereto (e.g., longitudinal direction and transverse direction), the above tear strength and retention thereof should be satisfied in at least one direction, but it is preferable that they are satisfied in both directions. Incidentally, the longitudinal direction and transverse direction herein may be arbitrarily determined. For example, the length direction of the original fabric may be the longitudinal direction, and the direction perpendicular thereto may be the transverse direction.

[0033] In the invention, the above object can be achieved by using the below-mentioned fiber having improved dyeing affinity and discoloration/fading resistance as a meta-type wholly aromatic polyamide fiber to form the heat-resistant fabric. In addition, it is preferable that appropriate materials for the heat-resistant fabric are selected, and they are mixed in appropriate proportions.

[0034] First, a meta-type wholly aromatic polyamide fiber that can achieve the above excellent abrasion resistance, tear strength, and washing durability thereof will be described.

[0035] With respect to the polymerization degree of the meta-type wholly aromatic polyamide that forms the fiber, it is preferable to use one having an intrinsic viscosity (I.V.) within a range of 1.3 to 1.9 dl/g as measured with a 0.5 g/100 ml N-methyl-2-pyrrolidone solution.

[0036] The meta-type wholly aromatic polyamide may contain an alkylbenzenesulfonic acid onium salt. Preferred examples of alkylbenzenesulfonic acid onium salts include compounds such as a hexylbenzenesulfonic acid tetrabutylphosphonium salt, a hexylbenzenesulfonic acid tributylbenzylphosphonium salt, a dodecylbenzenesulfonic acid tetraphenylphosphonium salt, a dodecylbenzenesulfonic acid tributyltetradecylphosphonium salt, a dodecylbenzenesulfonic acid tetrabutylphosphonium salt, and a dodecylbenzenesulfonic acid tributylbenzylammonium salt. Among them, a dodecylbenzenesulfonic acid tetrabutylphosphonium salt and a dodecylbenzenesulfonic acid tributylbenzylammonium salt are particularly preferable because they are easily available, have excellent thermal stability, and also have high solubility.

in N-methyl-2-pyrrolidone.

[0037] In order to obtain a sufficient dye-affinity-improving effect, the content of the alkylbenzenesulfonic acid onium salt is preferably 2.5 mol% or more, more preferably 3.0 to 7.0 mol%, relative to poly-m-phenyleneisophthalamide.

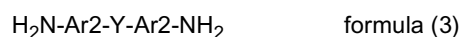
[0038] As a method for mixing poly-m-phenyleneisophthalamide and an alkylbenzenesulfonic acid onium salt, it is possible to employ a method in which poly-m-phenyleneisophthalamide is mixed and dissolved in a solvent, then an alkylbenzenesulfonic acid onium salt is dissolved in the solvent, and the obtained dope is formed into a fiber by a known method, for example.

[0039] For the purpose of improving dyeing affinity and discoloration/fading resistance, etc., the polymer to form the meta-type wholly aromatic polyamide fiber may also be obtained by copolymerizing, into an aromatic polyamide backbone having a repeating structural unit represented by the following formula (1), an aromatic diamine component or aromatic dicarboxylic acid halide component that is different from a main unit of the repeating structure as a third component so that the proportion of the third component is 1 to 10 mol% based on the total repeating structural units of the aromatic polyamide:



wherein Ar1 is a divalent aromatic group having a linking group in a position other than the meta position or an axially parallel direction.

[0040] Specific examples of aromatic diamines represented by formulae (2) and (3) copolymerizable 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 formulae (4) and (5) include terephthaloyl chloride, 1,4-naphthalenedicarbonyl chloride, 2,6-naphthalenedicarbonyl chloride, 4,4'-biphenyldicarbonyl chloride, 5-chloroisophthaloyl chloride, 5-methoxyisophthaloyl chloride, and bis(chlorocarbonylphenyl)ether.



[0041] In the formulae, Ar2 is a divalent aromatic group different from Ar1, Ar3 is a divalent aromatic group different from Ar1, Y is at least one atom or functional group selected from the group consisting of an oxygen atom, a sulfur atom, and an alkylene group, and X is a halogen atom.

[0042] In addition, it is preferable that the crystallinity of the meta-type aromatic polyamide fiber for use in the invention is 5 to 27%, more preferably 15 to 25%. It has been found that when the crystallinity is within such a range, the above initial abrasion resistance and retention after washing and also the above initial tear strength and retention after washing can be achieved at the same time. Such crystallinity also leads to excellent dye exhaustion properties. Accordingly, even when dyeing is performed with a small amount of dye or under weak dyeing conditions, the color can be easily adjusted as intended. Further, the dye is less likely to be unevenly distributed on the surface, discoloration/fading resistance is improved, and also the practically necessary dimensional stability can be ensured.

[0043] In the invention, it is preferable that the standard deviation of the single-fiber tensile strength of the meta-type wholly aromatic polyamide fiber in accordance with the JIS L 1015-99 method is 0.60 or less, more preferably 0.55 or less.

[0044] In the invention, it is preferable that the average single-fiber tensile strength of the meta-type wholly aromatic polyamide fiber in accordance with the JIS L 1015-99 method is 4.0 cN/dtex or less, more preferably 3.8 cN/dtex or less.

[0045] In the invention, it is preferable that the average single-fiber elongation of the meta-type wholly aromatic polyamide fiber in accordance with the JIS L 1015-99 method is 35% or less, more preferably 30% or less, and still more preferably 28% or less.

[0046] In the invention, it is preferable that the single-fiber toughness of the meta-type wholly aromatic polyamide fiber is 130 or less, more preferably 110 or less, and still more preferably 100 or less.

[0047] Also by satisfying the above average strength, standard deviation of strength, average elongation, standard deviation of elongation, and toughness of single fibers, the above initial abrasion resistance and retention after washing and also the above initial tear strength and retention after washing can be achieved at the same time. It is usually believed that tear strength is improved with an increase in the strength of the fiber. However, surprisingly, it has been found that by satisfying the above properties including the standard deviation of strength in a balanced manner, the properties regarding abrasion resistance and tear strength can be achieved at the same time.

[0048] In addition, in the invention, it is preferable that the residual solvent content of the meta-type aromatic polyamide fiber is 0.1 mass% or less, more preferably 0.08 mass% or less, still more preferably 0.07 mass% or less, and yet more preferably 0.05 mass% or less. It has been found that also by controlling the residual solvent content like this, the above initial abrasion resistance and retention and also the above initial tear strength and retention can be achieved at the same time. In addition, the excellent flame retardancy of the meta-type aromatic polyamide fiber is not impaired. Further, the dye is less likely to be unevenly distributed on the surface, and the discoloration/fading resistance can be improved.

[0049] When the meta-type wholly aromatic polyamide fiber is a spun-dyed fiber containing a pigment having high light resistance over time as a coloring agent, the color of the fabric itself can be easily retained. However, in the invention, the meta-type wholly aromatic polyamide fiber does not have to be a spun-dyed fiber. It is possible to perform yarn dyeing or fabric dyeing with an organic dye, that is, the fabric may be a so-called piece-dyed fabric. It is preferable that the meta-type wholly aromatic polyamide fiber can be piece-dyed for the following reasons: the fabric can be dyed to various colors to meet a wide variety of user needs, the fabric can be more brightly colored, the color can be changed, small lot production is possible, etc.

[0050] In addition to the meta-type wholly aromatic polyamide fiber, the heat-resistant fabric of the invention may also contain other kinds of fibers, including flame-retardant fibers, synthetic fibers such as polyester fibers, regenerated fibers, and natural fibers.

[0051] The flame-retardant fibers are fibers having a limiting oxygen index of 20 or more excluding meta-type wholly aromatic polyamide fibers. Preferred examples thereof include para-type wholly aromatic polyamide fibers, polybenzobisazole fibers, wholly aromatic polyester fibers, polysulfone amide fibers, polyimide fibers, and polyetheramide fibers. Preferred examples of para-type wholly aromatic polyamide fibers include paraphenylene terephthalamide fibers and co-paraphenylene/3,4'-oxydiphenylene terephthalamide fibers.

[0052] The synthetic fibers such as polyester fibers are known synthetic fibers. In addition to polyester fibers such as polyethylene terephthalate fibers, polybutylene terephthalate fibers, polyethylene naphthalate fibers, and polylactic acid fibers, preferred examples thereof include polyamide fibers, acrylic fibers, polyolefin fibers, and polycarbonate fibers. The regenerated fibers are known regenerated fibers. Preferred examples thereof include cellulose fibers, particularly rayon. The natural fibers are known natural fibers. Preferred examples thereof include cotton.

[0053] In the invention, in order to improve the washing durability of abrasion resistance and tear strength, it is preferable that the heat-resistant fabric contains at least one member selected from a cellulose fiber, a polyester fiber, an acrylic fiber, and a polyamide fiber in an amount of 2 to 50 mass%, more preferably 2 to 48 mass%, based on the mass of the heat-resistant fabric.

[0054] In the invention, in order to improve the washing durability of abrasion resistance and tear strength, it is preferable that the heat-resistant fabric contains at least one member selected from a para-type wholly aromatic polyamide fiber, a polybenzobisoxazol fiber, and a wholly aromatic polyester fiber in an amount of 1 to 20 mass%, more preferably 2 to 10 mass%, based on the mass of the heat-resistant fabric.

[0055] According to the requirements for the end use, it is also possible to previously perform a flame-retarding treatment on or add a flame retarder to the above fibers. In particular, with respect to the cellulose fiber, polyester fiber, acrylic fiber, and polyamide fiber, it is preferable to employ those containing a flame retarder.

[0056] The mixing proportions of these fibers are as follows. First, in order for excellent heat resistance and flame retardancy to be exerted, it is preferable that the proportion of the meta-type wholly aromatic polyamide fiber is 50 mass% or more. In addition, according to the intended use or the needs of use, the above flame-retardant fibers, synthetic fibers, regenerated fibers, and natural fibers may be arbitrarily mixed. For example, in order to combine dye affinity and comfortableness, the mixing proportions may be as follows: meta-type wholly aromatic polyamide fiber: 50 to 98 mass%, polyester fiber: 2 to 50 mass%, cellulose fiber: 0 to 48 mass%. The proportions may be adjusted according to the performance to be emphasized.

[0057] In the invention, it is preferable that the fabric is capable of retaining excellent aesthetics over time/age even after repeated uses, washes, etc. "Excellent aesthetics" herein means that aesthetics are prevented from being lost due to any remaining or deposited soil; that is, it does not happen that due to the soil, the color/pattern looks different in some parts or the fabric has noticeable soiling.

[0058] As indices for objectively showing this, soil resistance and soil hide characteristics are effective. As a specific method and evaluation criteria, the value of color difference ΔE^* from the state where soil is deposited is used as an index. Qualitatively, it can be said that the smaller the ΔE^* value, the higher the soil hide characteristics, that is, soiling is less noticeable, which is more desirable.

[0059] In order to achieve such excellent aesthetics, in the invention, it is preferable that the color difference ΔE between a fabric after a light resistance test in accordance with JIS L0842 and a fabric before the light resistance test and the brightness L of the fabric before the light resistance test satisfy the following equation (1):

$$\Delta E \leq 0.46L - 11.3 \quad \text{equation (1).}$$

[0060] That is, in the invention, it has been found that when a fabric satisfies the ΔE value of the above equation (1) depending on the brightness L value of the original fabric before the light resistance test, even in the case where the fabric is repeatedly used, washed with a surfactant such as a detergent, etc., or dry-cleaned, for example, it does not happen that the fabric looks dirty due to the slightly remaining soil component or newly deposited soil component, or that due to such soil components, the color/pattern looks different in some parts or the fabric has noticeable soiling; as a result, excellent aesthetics can be achieved. The upper limit of the ΔE value can be set in direct proportion to the brightness L value of the original fabric.

[0061] When the meta-type wholly aromatic polyamide fiber used for the heat-resistant fabric of the invention is a spun-dyed fiber containing a pigment having high light resistance over time as a coloring agent, the color of the fabric itself can be easily retained. However, in the invention, the meta-type wholly aromatic polyamide fiber does not have to be a spun-dyed fiber. As long as the above equation (1) is satisfied, it is possible to perform yarn dyeing or fabric dyeing with an organic dye, that is, the fabric may be a so-called piece-dyed fabric. However, it is preferable that the meta-type wholly aromatic polyamide fiber can be piece-dyed.

[0062] A meta-type aromatic polyamide fiber that is suitable for use in the invention can be produced by the following method. In particular, by the following method, the crystallinity and residual solvent content can be made within the above ranges.

[0063] The polymerization method for a meta-type aromatic polyamide polymer does not have to be particularly limited, and it is possible to use, for example, the solution polymerization method or interfacial polymerization method described in JP-B-35-14399, U.S. Pat. No. 3360595, JP-B-47-10863, etc.

[0064] The spinning solution does not have to be particularly limited. It is possible to use an amide solvent solution containing an aromatic copolyamide polymer obtained by the above solution polymerization or interfacial polymerization, etc., or it is also possible that the polymer is isolated from the polymerization solution, dissolved in an amide solvent, and used.

[0065] Examples of amide solvents used herein include N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, and dimethyl sulfoxide, and N,N-dimethylacetamide is particularly preferable.

[0066] It is preferable that the wholly aromatic polyamide polymer solution obtained as above further contains an alkali metal salt or an alkaline earth metal salt, as a result, the solution becomes more stable and thus can be used at higher concentrations and lower temperatures. It is preferable that the proportion of the alkali metal salt or alkaline earth metal salt is 1 mass% or less, more preferably 0.1 mass% or less, based on the total mass of the polymer solution.

[0067] In a spinning/coagulation step, the spinning solution obtained above (meta-type wholly aromatic polyamide polymer solution) is extruded into a coagulation liquid and coagulated.

[0068] The spinning apparatus is not particularly limited and may be a conventionally known wet-spinning apparatus. In addition, as long as stable wet spinning can be performed, there is no need to particularly limit the number of spinning holes of a spinneret, their arrangement, the hole shape, etc. For example, it is possible to use a multi-hole spinneret for staple fibers, in which the number of holes is 1,000 to 30,000 and the spinning hole diameter is 0.05 to 0.2 mm, etc.

[0069] In addition, it is suitable that the temperature of the spinning solution (meta-type wholly aromatic polyamide polymer solution) upon extrusion from the spinneret is within a range of 20 to 90°C.

[0070] As a coagulation bath used to obtain a fiber for use in the invention, an aqueous solution containing substantially no inorganic salt and having an amide solvent, preferably NMP, concentration of 45 to 60 mass% is used at a bath liquid temperature within a range of 10 to 50°C. An amide solvent (preferably NMP) concentration of less than 45 mass% leads to a structure with a thick skin. As a result, the washing efficiency in a washing step decreases, making it difficult to reduce the residual solvent content of the fiber. Meanwhile, in the case where the amide solvent (preferably NMP) concentration is more than 60 mass%, uniform coagulation inside the fiber cannot be achieved, making it difficult to reduce the residual solvent content of the fiber. Incidentally, it is suitable that the time of fiber immersion in the coagulation bath is within a range of 0.1 to 30 seconds.

[0071] Subsequently, the fiber is drawn to a draw ratio of 3 to 4 in a plastic drawing bath containing an aqueous solution having an amide solvent, preferably NMP, concentration of 45 to 60 mass% at a bath liquid temperature within a range of 10 to 50°C. After drawing, the fiber is thoroughly washed with an aqueous solution at 10 to 30°C having an NMP concentration of 20 to 40 mass% and then through a hot water bath at 50 to 70°C.

[0072] The fiber after washing is subjected to a dry heat treatment at a temperature of 270 to 290°C, whereby a meta-type wholly aromatic aramid fiber that satisfies the above crystallinity and residual solvent content ranges can be obtained.

[0073] The obtained meta-type wholly aromatic aramid fiber is cut by a known method into staple fibers, further blend-spun into a spun yarn with the above flame-retardant fibers such as meta-type wholly aromatic aramid fibers, synthetic fibers such as polyester fibers and polyamide fibers, regenerated fibers, natural fibers, etc., and woven or knitted, whereby a heat-resistant fabric of the invention can be obtained.

[0074] The method for preparing the heat-resistant fabric of the invention is not particularly limited, and any known methods may be employed. For example, it is possible that the above spun yarn is prepared and then, as a single yarn or a 2-ply yarn, woven into a twill weave, plain weave, or like structure using a rapier loom, etc., thereby giving the heat-

resistant fabric.

[0075] In addition, in the invention, a UV absorber and/or UV reflector may be contained in any fiber that forms the heat-resistant fabric. It is preferable that the UV absorber is highly hydrophobic and has a solubility of less than 0.04 mg/L in water. When the solubility is 0.04 mg/L or more, such a UV absorber and/or UV reflector is likely to elute during carrier dyeing, and the light resistance after dyeing tends to easily decrease; therefore, this is undesirable.

[0076] It is preferable that the UV absorber and/or UV reflector used in the invention is a compound that efficiently shields light near 360 nm, which is the photodegradation characteristic wavelength of a meta-wholly aromatic polyamide mainly used in the heat-resistant fabric of the invention, and has almost no absorption in the visible region.

[0077] As a UV absorber for use in the invention, a specific substituted benzotriazole is preferable. Specific examples thereof include 2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol, 2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl) phenol, 2-[2H-benzotriazol-2-yl]-4-6-bis(1-methyl-1-phenylethyl)phenol, and 2-[2H-benzotriazol-2-yl]-4-(1,1,3,3-tetramethylbutyl)phenol. Among these, 2-[2H-benzotriazol-2-yl]-4-6-bis(1-methyl-1-phenylethyl)phenol is particularly preferable because of its high hydrophobicity and low absorption in the visible region.

[0078] Examples of UV reflectors include fine particles of metal oxides, such as titanium oxide, zinc oxide, selenium oxide, alumina, and silica, and calcium carbonate preferably having a particle size of 0.001 to 0.2 μm , more preferably 0.005 to 0.02 μm .

[0079] In the heat-resistant fabric of the invention, the fiber to contain such a UV absorber and/or UV reflector is not limited. For example, in the case where it is contained in the meta-type wholly aromatic polyamide fiber, in terms of production stability and for actual use as a fabric or garment, it is preferable that the content is 3.0 to 6.5 mass%, more preferably 4.5 to 6.5 mass%, based on the total mass of the meta-type wholly aromatic polyamide fiber.

[0080] In addition, in the heat-resistant fabric of the invention, the UV absorber and/or UV reflector may also be fixed to the fabric surface. The fixing method is not particularly limited. For example, a water dispersion of the UV absorber and/or UV reflector is applied to the fabric by immersion/ squeezing or spraying, and then dried and cured. It is also possible to use a binder such as resin or latex in order to increase the durability of fixing. For example, in the above method, before the fabric is treated with a water dispersion, resin or latex, which is a binder component, may be previously mixed with the water dispersion as an aqueous product.

[0081] With the heat-resistant fabric obtained by the above method, which is made of a meta-type wholly aromatic aramid fiber and preferably contains the above materials mixed therewith in the above mixing proportions, it is possible to achieve the excellent performance, that is, an abrasion resistance of 200 rubs or more and a tear strength of 20 N or more, with the retention of the abrasion resistance and the retention of the tear strength after 100 washes being each 90% or more relative to before washing. In addition, the above strength, elongation, standard deviations thereof, toughness, etc., can be easily achieved.

Examples

[0082] Hereinafter, the invention will be described in detail with reference to examples, but the invention is not limited thereto. Incidentally, in the examples, the properties were measured by the following methods.

(1) Average and Standard Deviation of Strength, Average and Standard Deviation of Elongation, and Toughness of Single Fibers

[0083] The single-fiber strength and elongation were measured from ten single fibers in accordance with the JIS L1015-99 method, and the average and standard deviation of each were calculated. In addition, toughness was calculated by the following equation.

$$\text{Toughness} = \text{average strength} \times \text{average elongation}$$

(2) Abrasion Resistance of Fabric

[0084] Measurement was performed in accordance with the JIS L1096 8.19.1 A-1 method (universal type method (plane method), abrasion tester press load: 4.45 N (0.454 kf), paper: #600). The abrasion resistance of a fabric was measured before washing (L0) and after 100 washes in accordance with JIS L0844 No. A-1 (L100), and the retention of abrasion resistance before and after washing ($L100/L0 \times 100$) was calculated.

(2) Tear Strength of Fabric

[0085] Measurement was performed in accordance with the JIS L1096 8.17.4 D method (pendulum method). The tear strength of a fabric was measured before washing (L0) and after 100 washes in accordance with JIS L0844 No. A-1 (L100), and the retention of tear strength before and after washing ($L100/L0 \times 100$) was calculated.

(3) Pilling Resistance of Fabric

[0086] Measurement was performed in accordance with the JIS L1076 A method.

(4) Flame Retardancy of Fabric (Limiting Oxygen Index)

[0087] In accordance with the JIS L1091 E method, the concentration of oxygen necessary to keep burning 50 mm or more was defined as a limiting oxygen index (LOI).

(5) Residual Solvent Content

[0088] About 8.0 g of a raw fiber is collected, dried at 105°C for 120 minutes, and then allowed to cool in a desiccator, and the fiber mass (M1) is measured. Subsequently, the fiber is subjected to reflux extraction in methanol for 1.5 hours using a Soxhlet extractor to extract the amide solvent contained in the fiber. After extraction, the fiber is removed, vacuum-dried at 150°C for 60 minutes, and then allowed to cool in a desiccator, and the fiber mass (M2) is measured. Using the obtained M1 and M2, the content of residual solvent in the fiber (amide solvent mass) is calculated by the following equation.

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

[0089] The obtained raw fiber was crimped and cut into staple fibers 51 mm in length (raw stock).

(6) Crystallinity

[0090] Using an X-ray diffraction apparatus (RINT TTRIII manufactured by Rigaku Corporation), raw fibers were bundled into a fiber bundle of about 1 mm in diameter and mounted on a fiber sample table to measure the diffraction profile. The measurement conditions were as follows: Cu-K α radiation source (50 kV, 300 mA), scanning angle range: 10 to 35°, continuous measurement, measurement width: 0.1°, scanning at 1°/min. From the measured diffraction profile, air scattering and incoherent scattering were corrected by linear approximation to give the total scattering profile. Next, the amorphous scattering profile was subtracted from the total scattering profile to give the crystal scattering profile. Crystallinity was determined from the integrated intensity of the crystal scattering profile (crystal scattering intensity) and the integrated intensity of the total scattering profile (total scattering intensity) by the following equation.

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

(7) Brightness L and Light-Resistance Color Difference ΔE of Fabric

[0091] Using fabrics having a color difference ΔE of 0.1 or less, one was subjected to a light resistance test in accordance with JIS L 0842 (UV carbon arc light exposure time: 10 hours). Using the fabrics before and after the light resistance test, respectively, the specimens were subjected to color measurement using a colorimeter MacBeth Color-Eye 3100 and a color measurement light source D65 to determine the brightness L value and the color E value (the area of color measurement: 0.2 cm², the average of measurements at ten points was defined as the E value of the fabric), and the color difference ΔE between the two fabrics was calculated.

(8) Soil-Resistance Color Difference ΔE^* of Fabric

[0092]

EP 2 940 202 B1

Rubbing fabric (soiled fabric) : Standard Cotton Duck No. 9 of JIS L3102

Artificial soil component: a mixture of the following soil powder and artificial sebum in a ratio of 1:10

Soil powder: an intimate mixture of the following powders: JIS Z8901 Test Powder Class 12 (carbon black, particle size: 0.03 to 0.2 μm), 25 mass%; and JIS Z8901 Test Powder Class 8 (the loamy layer of the Kanto Plain, particle size: 8 μm), 75 mass%

Artificial sebum: a mixture of 70 mass% oleic acid and 30 mass% palmitic acid

Used apparatus: JIS L0849 abrasion tester, Type II (JSPS type) Procedure:

1. Instead of the waterproof abrasive paper of JIS L0849, the rubbing fabric (soiled fabric) is attached to the loader with a double-stick tape.
2. 0.05 g of the artificial soil component is uniformly applied to the rubbing fabric.
3. A specimen fabric is attached to the fabric set part of the abrasion tester with a double-stick tape.
4. The rubbing fabric prepared in 2 is attached to the loader set part of the abrasion machine.
5. The loader is moved back and forth 50 times on the surface of the specimen fabric to give a soil load.
6. The specimen fabric is removed from the surface abrasion tester.
7. The soil-resistance color difference ΔE^* of the fabric specimen between the soiled part and the non-soiled part is measured.

[0093] The smaller the ΔE^* , the smaller the color tone change due to soiling, indicating higher the soil resistance. A specification that resulted in a ΔE^* of 20 or less was judged as effective to serve as a product that would have sufficient merchantability in market even after a lapse of about three years, while a specification that resulted in a ΔE^* of more than 20 was judged as having no such effects.

[Production of Meta-Type Wholly Aromatic Aramid Fiber]

[0094] A meta-type wholly aromatic aramid fiber was prepared by the following method.

[0095] 20.0 parts by mass of a polymetaphenylene isophthalamide powder having an intrinsic viscosity (I.V.) of 1.9 produced by interfacial polymerization in accordance with the method described in JP-B-47-10863 was suspended in 80.0 parts by mass of N-methyl-2-pyrrolidone (NMP) cooled to -10°C , thereby forming a slurry. Subsequently, the suspension was heated to 60°C for dissolution to give a transparent polymer solution.

[0096] A 2-[2H-benzotriazol-2-yl]-4-6-bis(1-methyl-1-phenylethyl)ph enol powder (solubility in water: 0.01 mg/L) in an amount of 3.0 mass% relative to the polymer was mixed with and dissolved in the polymer solution, and the mixture was defoamed under reduced pressure to give a spinning solution (spinning dope).

[0097] In Example 1, a UV absorber 2-[2H-benzotriazol-2-yl]-4-6-bis(1-methyl-1-phenylethyl)ph enol was added to the spinning solution.

[Spinning/Coagulation Step]

[0098] The spinning dope was discharged and spun from a spinneret (hole diameter: 0.07 mm, the number of holes: 500) into a coagulation bath at a bath temperature of 30°C . The composition of the coagulation liquid was water/NMP = 45/55 (part by mass). The spinning dope was discharged and spun into the coagulation bath at a yarn speed of 7 m/min.

[Plastic-Drawing-Bath Drawing Step]

[0099] Subsequently, drawing was performed to a draw ratio of 3.7 in a plastic drawing bath at a temperature of 40°C having the following composition: water/NMP = 45/55 (part by mass).

[Washing Step]

[0100] After drawing, washing was performed in a bath at 20°C and water/NMP = 70/30 (immersion length: 1.8 m) and then in a water bath at 20°C (immersion length: 3.6 m), followed by thorough washing through a hot water bath at 60°C (immersion length: 5.4 m).

[Dry Heat Treatment Step]

[0101] The fiber after washing was subjected to a dry heat treatment using a hot roller having a surface temperature

of 283°C to give a meta-type aromatic polyamide fiber.

[Properties of Raw Fiber]

5 **[0102]** The obtained meta-type wholly aromatic aramid fiber had the following properties: fineness: 1.6 dtex, residual solvent content: 0.08 mass%, crystallinity: 20%, LOI: 30.

[0103] As raw stocks for other fibers, the following were used. Polyester fiber (polyethylene terephthalate fiber); "Tetoron®" manufactured by Teijin

Flame-retardant rayon fiber; "LenzingFR®" manufactured by Lenzing

10 Para-type wholly aromatic polyamide fiber; "Twaron®" manufactured by Teijin Aramid

[Fabric Dyeing Method]

15 **[0104]** The brightness L was adjusted with a dye so that fabrics after dyeing had an L value of 49 (neutral color) regardless of the foundation fabrics. Redyeing was performed as necessary to accurately control the L value. The conditions for dyeing and the conditions for washing a dyed product in a reducing bath (pH 5.5) were as follows.

(Dyeing Conditions)

20 **[0105]**

Cationic dye: manufactured by Nippon Kayaku, trade name: Kayacryl Red GL-ED, 1% owf

Bath ratio; 1:20

Temperature × Time; 120°C × 30 minutes

25 (Reducing Bath Composition and Washing Conditions)

Reducing bath; thiourea dioxide, 1 g/l

Bath ratio; 1:20

Temperature × Time; 70°C × 15 minutes

30 **[0106]** Subsequently, drying was performed at a temperature of 110°C for 10 minutes, followed by dry heat setting at a temperature of 130°C for 2 minutes, thereby giving a colored fabric.

[Example 1]

35 **[0107]** Staple fibers of a meta-type wholly aromatic polyamide fiber (MA), a para-type wholly aromatic polyamide fiber (PA), a polyester fiber (PE), and a flame-retardant rayon fiber (RY) (each 51 mm in length) were blend-spun in a mass ratio MA/PA/PE/Ry of 55/5/15/25 into a spun yarn (36 count, 2-ply yarn), and woven at a weaving density of warp: 100 yarns/25.4 mm and weft: 56 yarns/25.4 mm, thereby giving a twill-woven fabric having an areal weight of 230 g/m². The meta-type wholly aromatic polyamide fiber (MA) had an average strength of 3.7 cN/dtex with a standard deviation of 0.54, an average elongation of 25% with a standard deviation of 4.7, a toughness of 93, a crystallinity of 20%, and a residual solvent content of 0.08 mass%. The woven fabric was dyed by the above method to a neutral color (L value: 49).

40 **[0108]** The abrasion resistance of the obtained fabric was measured. As a result, the resistance before washing (L0) was 215 rubs, while the resistance after 100 washes (L100) was 200 rubs. Thus, the retention of abrasion resistance (L100/L0 × 100) was 93%. In addition, the tear strength of the obtained fabric was measured. As a result, the strength before washing (L0) was 35.3 N in the longitudinal direction and 24.1 N in the transverse direction, while the strength after 100 washes (L100) was 31.9 N in the longitudinal direction and 23.2 N in the transverse direction. Thus, the retention of tear strength (L100/L0 × 100) was 90% in the longitudinal direction and 96% in the transverse direction. Further, pilling was Level 4 in the longitudinal direction and Level 4 in the transverse direction.

50 [Example 2]

[0109] The same procedure as in Example 1 was performed, except that the meta-type wholly aromatic polyamide fiber (MA) was changed to a meta-type wholly aromatic aramid fiber containing 5 mass% of a UV absorber 2-[2H-benzotriazol-2-yl]-4-6-bis(1-methyl-1-phenylethyl)ph enol (51 mm in length), the para-type wholly aromatic polyamide fiber (PA) was not used, and the mass ratio was MA/PA/PE/Ry = 60/0/15/25. The meta-type wholly aromatic polyamide fiber (MA) had an average strength of 3.6 cN/dtex with a standard deviation of 0.55, an average elongation of 25% with a standard deviation of 4.8, a toughness of 90, a crystallinity of 20%, and a residual solvent content of 0.05 mass%.

[0110] The abrasion resistance of the obtained fabric was measured. As a result, the resistance before washing (L0)

was 209 rubs, while the resistance after 100 washes (L100) was 200 rubs. Thus, the retention of abrasion resistance ($L100/L0 \times 100$) was 96%. In addition, the tear strength of the obtained fabric was measured. As a result, the strength before washing (L0) was 32.4 N in the longitudinal direction and 23.2 N in the transverse direction, while the strength after 100 washes (L100) was 29.8 N in the longitudinal direction and 22.5 N in the transverse direction. Thus, the retention of tear strength ($L100/L0 \times 100$) was 92% in the longitudinal direction and 97% in the transverse direction. Further, pilling was Level 4 in the longitudinal direction and Level 4 in the transverse direction.

[0111] The fabric had a brightness L of 49, with $0.45 \times L - 11.3$ being 11.25, a light-resistance color difference ΔE of 10.73, and a soil-resistance color difference ΔE^* of 15.

[Comparative Example 1]

[0112] The same procedure as in Example 1 was performed, except that in the production of a meta-type wholly aromatic polyamide fiber (MA), the composition of the coagulation liquid in the coagulation step was changed to water/NMP = 40/60 (part by mass). The results are shown in Table 1. The meta-type wholly aromatic polyamide fiber (MA) had an average strength of 4.2 cN/dtex with a standard deviation of 0.61, an average elongation of 29% with a standard deviation of 4.8, a toughness of 121, a crystallinity of 20%, and a residual solvent content of 0.15 mass%.

[0113] The abrasion resistance of the obtained fabric was measured. As a result, the resistance before washing (L0) was 211 rubs, while the resistance after 100 washes (L100) was 185 rubs. Thus, the retention of abrasion resistance ($L100/L0 \times 100$) was 88%. In addition, the tear strength of the obtained fabric was measured. As a result, the strength before washing (L0) was 36.3 N in the longitudinal direction and 24.1 N in the transverse direction, while the strength after 100 washes (L100) was 30.4 N in the longitudinal direction and 23.0 N in the transverse direction. Thus, the retention of tear strength ($L100/L0 \times 100$) was 84% in the longitudinal direction and 95% in the transverse direction. Further, pilling was Level 3 in the longitudinal direction and Level 3 in the transverse direction.

[Comparative Example 2]

[0114] The same procedure as in Example 1 was performed, except that in the production of a meta-type wholly aromatic polyamide fiber (MA), the surface temperature of the hot roller in the dry heat treatment step was changed to 315°C. The meta-type wholly aromatic polyamide fiber (MA) had a crystallinity of 28% and a residual solvent content of 0.08 mass%.

[0115] The abrasion resistance of the obtained fabric was measured. As a result, the resistance before washing (L0) was 250 rubs, while the resistance after 100 washes (L100) was 200 rubs. Thus, the retention of abrasion resistance ($L100/L0 \times 100$) was 80%. In addition, the tear strength of the obtained fabric was measured. As a result, the strength before washing (L0) was 36.3 N in the longitudinal direction and 24.2 N in the transverse direction, while the strength after 100 washes (L100) was 31.8 N in the longitudinal direction and 23.1 N in the transverse direction. Thus, the retention of tear strength ($L100/L0 \times 100$) was 86% in the longitudinal direction and 95% in the transverse direction. Further, pilling was Level 3 in the longitudinal direction and Level 3 in the transverse direction.

[Comparative Example 3]

[0116] The same procedure as in Example 1 was performed, except that the spun yarn was changed to a spun yarn made only of a flame-retardant rayon fiber (RY).

[0117] The abrasion resistance of the obtained fabric was measured. As a result, the resistance before washing (L0) was 57 rubs, while the resistance after 100 washes (L100) was 40 rubs. Thus, the retention of abrasion resistance ($L100/L0 \times 100$) was 70%. In addition, the tear strength of the obtained fabric was measured. As a result, the strength before washing (L0) was 20 N in the longitudinal direction and 12 N in the transverse direction, while the strength after 100 washes (L100) was 10 N in the longitudinal direction and 7 N in the transverse direction. Thus, the retention of tear strength ($L100/L0 \times 100$) was 50% in the longitudinal direction and 58% in the transverse direction. Further, pilling was Level 3 in the longitudinal direction and Level 3 in the transverse direction.

[Comparative Example 4]

[0118] The same procedure as in Example 1 was performed, except that the spun yarn was changed to a spun yarn made only of a polyester fiber (PE). The results are shown in Table 1.

[0119] The abrasion resistance of the obtained fabric was measured. As a result, the resistance before washing (L0) was 67 rubs, while the resistance after 100 washes (L100) was 41 rubs. Thus, the retention of abrasion resistance ($L100/L0 \times 100$) was 61%. In addition, the tear strength of the obtained fabric was measured. As a result, the strength before washing (L0) was 21 N in the longitudinal direction and 10 N in the transverse direction, while the strength after

100 washes (L100) was 11 N in the longitudinal direction and 6 N in the transverse direction. Thus, the retention of tear strength ($L100/L0 \times 100$) was 52% in the longitudinal direction and 60% in the transverse direction. Further, pilling was Level 3 in the longitudinal direction and Level 3 in the transverse direction.

5 Industrial Applicability

[0120] The heat-resistant fabric of the invention is excellent in terms of surface abrasion characteristics, tear characteristics, and the washing durability of these characteristics, and also has pilling resistance, a color tone that meets various user needs, and heat resistance. Therefore, the heat-resistant fabric of the invention is applicable to protective garments, such as firefighter garments, and industrial materials, such as flexible heat-insulating materials, and thus is industrially extremely useful.

15 Claims

1. A heat-resistant fabric comprising a meta-type wholly aromatic polyamide fiber, **characterized in that** the abrasion resistance of the heat-resistant fabric in accordance with the JIS L1096 8.19.1 A-1 method (universal type method (plane method), abrasion tester press load: 4.45 N (0.454 kf), paper: #600) is 200 rubs or more, the tear strength of the heat-resistant fabric in accordance with the JIS L1096 8.17.4 D method (pendulum method) is 20 N or more, and the retention of the abrasion resistance and the retention of the tear strength after 100 washes in accordance with JIS L0844 No. A-1 are each 90% or more relative to before washing, wherein the heat-resistant fabric contains at least a rayon, a paraphenylene terephthalamide fiber or a co-paraphenylene/3,4'-oxydiphenylene terephthalamide fiber.
2. The heat-resistant fabric according to claim 1, wherein the meta-type wholly aromatic polyamide fiber has a crystallinity of 15 to 27.
3. The heat-resistant fabric according to claim 1 or 2, wherein the standard deviation of the single-fiber tensile strength of the meta-type wholly aromatic polyamide fiber is 0.60 or less.
4. The heat-resistant fabric according to any one of claims 1 to 3, wherein the meta-type wholly aromatic polyamide fiber has an average single-fiber tensile strength of 4.0 cN/dtex or less.
5. The heat-resistant fabric according to any one of claims 1 to 4, wherein the meta-type wholly aromatic polyamide fiber has an average single-fiber elongation of 35% or less.
6. The heat-resistant fabric according to any one of claims 1 to 5, wherein the meta-type wholly aromatic polyamide fiber has a single-fiber toughness of 130 or less.
7. The heat-resistant fabric according to any one of claims 1 to 6, wherein the heat-resistant fabric is dyed, and the color difference ΔE of the fabric before and after a light resistance test in accordance with JIS L0842 and the brightness L of the light resistance test fabric satisfy the following equation (1) :

$$\Delta E \leq 0.46L - 11.3 \dots (1) .$$
8. The heat-resistant fabric according to any one of claims 1 to 7, wherein the meta-type wholly aromatic polyamide fiber contains an organic dye.
9. The heat-resistant fabric according to any one of claims 1 to 8, wherein the heat-resistant fabric contains at least one member selected from a cellulose fiber, a polyester fiber, an acrylic fiber, and a polyamide fiber in an amount of 2 to 50 mass% based on the mass of the heat-resistant fabric.
10. The heat-resistant fabric according to claim 9, wherein the cellulose fiber is rayon.
11. The heat-resistant fabric according to claim 9, wherein the cellulose fiber, polyester fiber, acrylic fiber, or polyamide

fiber contains a flame retarder.

12. The heat-resistant fabric according to any one of claims 1 to 11, wherein the pilling resistance of the heat-resistant fabric in accordance with the JIS L1096 A method is Level 4 or higher.

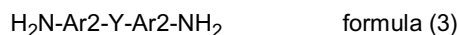
13. The heat-resistant fabric according to any one of claims 1 to 12, wherein the heat-resistant fabric contains cellulose and is dyed with a fluorescent dye.

14. The heat-resistant fabric according to any one of claims 1 to 13, wherein the meta-type wholly aromatic polyamide that forms the meta-type wholly aromatic polyamide fiber is an aromatic polyamide obtained by copolymerizing, into an aromatic polyamide backbone having a repeating structural unit represented by the following formula (1), an aromatic diamine component or aromatic dicarboxylic acid halide component that is different from a main unit of the repeating structure as a third component so that the proportion of the third component is 1 to 10 mol% based on the total repeating structural units of the aromatic polyamide:



wherein Ar1 is a divalent aromatic group having a linking group in a position other than the meta position or an axially parallel direction.

15. The heat-resistant fabric according to claim 14, wherein the third component is an aromatic diamine of formula (2) or (3) or an aromatic dicarboxylic acid halide of formula (4) or (5) :



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

16. The heat-resistant fabric according to any one of claims 1 to 15, wherein the meta-type aromatic polyamide fiber has a residual solvent content of 0.1 mass% or less.

17. The heat-resistant fabric according to any one of claims 1 to 16, wherein the heat-resistant fabric contains at least one member selected from a para-type wholly aromatic polyamide fiber, a polybenzobisoxazol fiber, and a wholly aromatic polyester fiber in an amount of 1 to 20 mass% based on the mass of the heat-resistant fabric.

18. The heat-resistant fabric according to claim 17, wherein the para-type wholly aromatic polyamide fiber is a para-phenylene terephthalamide fiber or a co-paraphenylene/3,4'-oxydiphenylene terephthalamide fiber.

19. The heat-resistant fabric according to any one of claims 1 to 18, wherein a fiber that forms the heat-resistant fabric contains a UV absorber and/or UV reflector.

20. The heat-resistant fabric according to any one of claims 1 to 19, wherein the heat-resistant fabric has a UV absorber and/or UV reflector fixed to the surface thereof.

Patentansprüche

1. Eine vollaromatische Polyamidfaser des Typs meta umfassende hitzebeständige Ware, **dadurch gekennzeichnet, dass** die hitzebeständige Ware über eine Abriebfestigkeit gemäß JIS L10968.19.1 A-1 (Einheits- bzw. Planarverfahren, Auflagekraft Abriebprüfgerät: 4,45 N (0,454 kp), Papier: #600) von 200 Hüben und mehr verfügt, **dass** die hitzebeständige Ware über eine Zugfestigkeit gemäß JIS L10968.17.4 D (Pendelverfahren) von 20 N und

mehr verfügt sowie

von der Abriebfestigkeit und der Zugfestigkeit nach 100 Wäschen gemäß JIS L0844 Nr. A-1 jeweils noch 90% und mehr verbleiben,

wobei die hitzebeständige Ware wenigstens ein Reyon, eine Paraphenylenterephthalamidfaser oder eine Co-Paraphenylen/3,4'-oxydiphenylenterephthalamidfaser enthält.

2. Hitzebeständige Ware nach Anspruch 1, bei der die vollaromatische Polyamidfaser des Typs meta über eine Kristallinität von 15 bis 27 verfügt.

3. Hitzebeständige Ware nach Anspruch 1 oder 2, bei der die vollaromatische Polyamidfaser des Typs meta bei der Zugfestigkeitsbestimmung an der Einzelfaser über eine Standardabweichung von 0,60 und weniger verfügt.

4. Hitzebeständige Ware nach einem der Ansprüche 1 bis 3, bei der die vollaromatische Polyamidfaser des Typs meta bei der Zugfestigkeitsbestimmung an der Einzelfaser über einen Mittelwert von 4,0 cN/dtex und weniger verfügt.

5. Hitzebeständige Ware nach einem der Ansprüche 1 bis 4, bei der die vollaromatische Polyamidfaser des Typs meta bei Bestimmung der Reißdehnung an der Einzelfaser über einen Mittelwert von 35% und weniger verfügt.

6. Hitzebeständige Ware nach einem der Ansprüche 1 bis 5, bei der die vollaromatische Polyamidfaser des Typs meta für die Einzelfaser über eine Zähigkeit von 130 und weniger verfügt.

7. Hitzebeständige Ware nach einem der Ansprüche 1 bis 6, bei der im gefärbten Zustand die Farbabweichung ΔE der Ware vor und nach einer Lichtechtheitsprüfung gemäß JIS L0842 und die Helligkeit L der Lichtechtheitsprüfware nachstehende Gleichung (1):

$$\Delta E \leq 0,46 L - 11,3 \dots (1)$$

erfüllen.

8. Hitzebeständige Ware nach einem der Ansprüche 1 bis 7, bei der die vollaromatische Polyamidfaser des Typs meta einen organischen Farbstoff enthält.

9. Hitzebeständige Ware nach einem der Ansprüche 1 bis 8, bei der die hitzebeständige Ware eine Cellulosefaser, eine Polyesterfaser, eine Acrylfaser und/oder eine Polyamidfaser in eine auf die Masse der hitzebeständigen Ware bezogenen Menge von 2 bis 50 Gew.-% enthält.

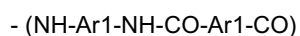
10. Hitzebeständige Ware nach Anspruch 9, bei der es sich bei der Cellulosefaser um Reyon handelt.

11. Hitzebeständige Ware nach Anspruch 9, bei der die Cellulose-, Polyester-, Acryl- oder Polyamidfaser ein Flamm- schutzmittel enthält.

12. Hitzebeständige Ware nach einem der Ansprüche 1 bis 11, bei der die Antipillfestigkeit gemäß dem Verfahren JIS L1096 A auf Stufe 4 und höher liegt.

13. Hitzebeständige Ware nach einem der Ansprüche 1 bis 12, bei der die hitzebeständige Ware Cellulose enthält und mit einem Fluoreszenzfarbstoff gefärbt ist.

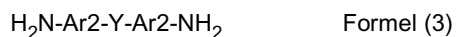
14. Hitzebeständige Ware nach einem der Ansprüche 1 bis 13, bei der man zur Herstellung des die vollaromatische Polyamidfaser des Typs meta bildenden vollaromatischen Polyamids des Typs meta ein aromatisches Polyamid herstellt, indem man in eine aromatische Polyamidhauptkette mit einer durch nachstehende Formel (1) wiedergegebenen wiederkehrenden Struktureinheit eine von einer Haupteinheit der wiederkehrenden Struktur verschiedene aromatische Diaminkomponente oder aromatische Dicarbonsäurehalogenidkomponente als dritte Komponente so einpolymerisiert, dass der auf die Gesamtmenge der wiederkehrenden Struktureinheiten des aromatischen Polyamids:



Formel (1)

bezogene Anteil der dritten Komponente 1 bis 10 Mol% beträgt, wobei Ar1 für eine zweiwertige aromatische Gruppe mit einer in einer anderen Position als der meta-Position oder einer axial parallelen Richtung stehenden Verknüpfungsgruppe steht.

- 5 15. Hitzebeständige Ware nach Anspruch 14, bei der es sich bei der dritten Komponente um ein aromatisches Diamin der Formel (2) oder (3) oder um ein aromatisches Dicarbonsäurehalogenid der Formel (4) oder (5):



handelt,

wobei Ar2 für eine von Ar1 verschiedene zweiwertige aromatische Gruppe, Ar3 für eine von Ar1 verschiedene zweiwertige aromatische Gruppe, Y für mindestens ein Atom bzw. eine funktionelle Gruppe ausgewählt aus der Gruppe bestehend aus einem Sauerstoffatom, einem Schwefelatom und einer Alkylengruppe sowie X für ein Halogenatom steht.

- 25 16. Hitzebeständige Ware nach einem der Ansprüche 1 bis 15, bei der die aromatische Polyamidfaser des Typs meta über einen Lösungsmittelrestgehalt von 0,1 Gew.-% und weniger verfügt.

- 30 17. Hitzebeständige Ware nach einem der Ansprüche 1 bis 16, bei der die hitzebeständige Ware mindestens ein Mitglied ausgewählt aus der Reihe vollaromatische Polyamidfaser des Typs para, Polybenzobisoxazolfaser und vollaromatische Polyesterfaser in einer auf die Masse der hitzebeständigen Ware bezogenen Menge von 1 bis 20 Gew.-% enthält.

- 35 18. Hitzebeständige Ware nach Anspruch 17, bei der es sich bei der vollaromatischen Polyamidfaser des Typs para um eine Paraphenylenterephthalamidfaser oder eine Co-Paraphenylen/3,4'-oxidiphenylenterephthalamidfaser handelt.

- 40 19. Hitzebeständige Ware nach einem der Ansprüche 1 bis 18, bei der eine die hitzebeständige Ware bildende Faser einen UV-Absorber und/oder UV-Reflektor enthält.

20. Hitzebeständige Ware nach einem der Ansprüche 1 bis 19, bei der die hitzebeständige Ware über einen an deren Oberfläche angebrachten UV-Absorber und/oder UV-Reflektor verfügt.

Revendications

- 45 1. Tissu thermorésistant, comprenant une fibre de polyamide complètement aromatique de type méta, **caractérisé en ce que**

- la résistance à l'abrasion du tissu thermorésistant, conformément à la méthode de la norme JIS L1096 8.19.1A-1 (méthode de type universel (méthode à plat), charge de pression du dispositif de test d'abrasion : 4,45 N (0,454 kf), papier : #600) est de 200 frottements ou plus,

50 - la résistance à la déchirure du tissu thermorésistant conformément à la méthode de la norme JIS L1096 8.17.4D (méthode au pendule) est 20 N ou plus et

- la conservation de la résistance à l'abrasion et la conservation de la résistance à la déchirure après 100 lavages conformément à la norme JIS L0844 No. A-1 sont chacune de 90% ou plus par rapport aux valeurs avant le lavage,

55 - le tissu thermorésistant contenant au moins de la rayonne, une fibre de para-phénylène-téréphtalamide ou une fibre de co-para-phénylène/3,4'-oxydiphenylène-téréphtalamide.

2. Tissu thermorésistant selon la revendication 1, la fibre de polyamide complètement aromatique de type méta pré-

sentant une cristallinité de 15 à 27.

3. Tissu thermorésistant selon la revendication 1 ou 2, l'écart type de la résistance à la traction d'une fibre unique de la fibre de polyamide complètement aromatique de type méta étant de 0,60 ou moins.
4. Tissu thermorésistant selon l'une quelconque des revendications 1 à 3, la fibre de polyamide complètement aromatique de type méta présentant une résistance moyenne à la traction d'une fibre unique de 4,0 cN/dtex.
5. Tissu thermorésistant selon l'une quelconque des revendications 1 à 4, la fibre de polyamide complètement aromatique de type méta présentant un allongement d'une fibre unique de 35% ou moins.
6. Tissu thermorésistant selon l'une quelconque des revendications 1 à 5, la fibre de polyamide complètement aromatique de type méta présentant une solidité d'une fibre unique de 130 ou moins.
7. Tissu thermorésistant selon l'une quelconque des revendications 1 à 6, le tissu thermorésistant étant coloré et la différence de couleur ΔE du tissu avant et après un test de résistance à la lumière conformément à la norme JIS L0842 et la luminosité L du tissu du test de résistance à la lumière satisfaisant à l'équation suivante (1) :

$$\Delta E \leq 0,46L - 11,3 \quad (1) .$$

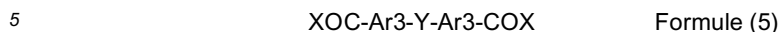
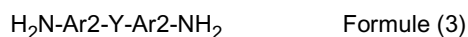
8. Tissu thermorésistant selon l'une quelconque des revendications 1 à 7, la fibre de polyamide complètement aromatique de type méta contenant un colorant organique.
9. Tissu thermorésistant selon l'une quelconque des revendications 1 à 8, le tissu thermorésistant contenant au moins un élément choisi parmi une fibre de cellulose, une fibre de polyester, une fibre acrylique et une fibre de polyamide en une quantité de 2 à 50% en masse sur base de la masse du tissu thermorésistant.
10. Tissu thermorésistant selon la revendication 9, la fibre de cellulose étant la rayonne.
11. Tissu thermorésistant selon la revendication 9, la fibre de cellulose, la fibre de polyester, la fibre acrylique ou la fibre de polyamide contenant un retardateur de flamme.
12. Tissu thermorésistant selon l'une quelconque des revendications 1 à 11, la résistance au boulochage du tissu thermorésistant, conformément à la méthode de la norme JIS L1096A, étant de niveau 4 ou plus.
13. Tissu thermorésistant selon l'une quelconque des revendications 1 à 12, le tissu thermorésistant contenant de la cellulose et étant coloré par un colorant fluorescent.
14. Tissu thermorésistant selon l'une quelconque des revendications 1 à 13, le polyamide complètement aromatique de type méta qui forme la fibre de polyamide complètement aromatique de type méta étant un polyamide aromatique obtenu par copolymérisation, dans une épine dorsale de polyamide aromatique présentant une unité structurale récurrente représentée par la formule (1) suivante, d'un constituant de diamine aromatique ou d'un constituant d'halogénure d'acide dicarboxylique aromatique qui est différent de l'unité principale de la structure récurrente, comme troisième constituant, de telle sorte que la proportion du troisième constituant est de 1 à 10% en mole, sur base de la totalité d'unités structurales récurrentes du polyamide aromatique :



dans laquelle Ar1 représente un groupe aromatique divalent présentant un groupe de liaison dans une position autre que dans la position méta ou dans une direction axialement parallèle.

15. Tissu thermorésistant selon la revendication 14, le troisième constituant étant une diamine aromatique de formule (2) ou (3) ou un halogénure d'acide dicarboxylique aromatique de formule (4) ou (5) :





dans laquelle Ar₂ représente un groupe aromatique divalent différent d'Ar₁,
Ar₃ représente un groupe aromatique divalent différent d'Ar₁, Y représente au moins un atome ou groupe
fonctionnel choisi dans le groupe constitué par un atome d'oxygène, un atome de soufre et un groupe alkylène
et X représente un atome d'halogène.

16. Tissu thermorésistant selon l'une quelconque des revendications 1 à 15, la fibre de polyamide aromatique de type méta présentant une teneur résiduelle en solvant de 0,1% en masse ou moins.

17. Tissu thermorésistant selon l'une quelconque des revendications 1 à 16, le tissu thermorésistant contenant au moins un élément choisi parmi une fibre de polyamide complètement aromatique de type para, une fibre de polybenzobisoxazole et une fibre de polyester complètement aromatique en une quantité de 1 à 20% en masse sur base de la masse du tissu thermorésistant.

18. Tissu thermorésistant selon la revendication 17, la fibre de polyamide complètement aromatique de type para étant une fibre de para-phénylène-téréphtalamide ou une fibre de co-para-phénylène/3,4'-oxydiphénylène-téréphtalamide.

19. Tissu thermorésistant selon l'une quelconque des revendications 1 à 18, une fibre qui forme le tissu thermorésistant contenant un absorbant des UV et/ou un réflecteur des UV.

20. Tissu thermorésistant selon l'une quelconque des revendications 1 à 19, le tissu thermorésistant présentant un absorbant des UV et/ou un réflecteur des UV fixé à sa surface.

REFERENCES CITED IN THE DESCRIPTION

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