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(54) **COPOLYMERIZED ARAMID DOPE-DYED YARN AND METHOD FOR PREPARING SAME**

(57) The present invention relates to a copolymerized aramid dope-dyed yarn and a method for preparing the same wherein, when a copolymerized aramid yarn is prepared by adding terephthaloyl dichloride to an organic solvent in which an aromatic diamine having a cyano group is dissolved, reacting the same to polymerize a polymerization solution containing a copolymerized aramid polymer, and then spinning and coagulating the polymerization solution, a copolymerized aramid dope-dyed yarn is manufactured by adding a coloring matter having a cation during the polymerization process of the polymerization solution containing the copolymerized aramid polymer. The present invention can effec-

tively prevent deterioration in a polymerization degree of the copolymerized aramid polymer or deterioration in the dissolubility of the polymerization solution due to the addition of the coloring matter to the polymerization solution. Further, according to the present invention, when a copolymerized aramid polymer having a cyano (-CN) group and a coloring matter having a cation are bonded through a hydrogen bond to form a liquid crystal during the polymerization process of the polymerization solution containing the copolymerized aramid polymer, the behavior together with a main chain of the copolymerized aramid polymer is possible, thereby enhancing the color

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Description

[Technical Field]

5 **[0001]** The present invention relates to a copolymerized aramid dope-dyed yarn and a method for preparing the same, and more particularly, to a method for preparing a copolymerized aramid dope-dyed yarn with excellent color strength and color fastness by mixing a coloring matter having a cation in a polymerization solution when spinning the polymerization solution containing a copolymerized aramid polymer by means of a spinning spinneret without using sulfuric acid.

10 [Background Art]

[0002] Aromatic polyamide, commonly referred to as an aramid, includes a para-based aramid having a structure in which benzene rings are linked linearly through an amide group (-CONH) and a meta-based aramid which has a linkage structure different from the para-based aramid.

15 **[0003]** The para-based aramid has excellent characteristics such as a high strength, high elasticity and low shrinkage. Since the para-based aramid has a high enough strength so as to be able to lift a two-ton vehicle with a thin cable made thereof having a thickness of about 5 mm, it is widely used for bulletproofing, as well as in a variety of applications in advanced industries of an aerospace field.

[0004] Further, the aramid is carbonized and becomes black at 500°C or more, thus being also spotlighted in fields requiring high heat-resistant properties.

[0005] The preparation method of aramid fiber has been explained well in Korean Patent Registration No. 10-0910537 owned by the present applicant. According to this registered patent, a mixture solution is prepared by dissolving aromatic diamine in a polymerization solvent, then, followed by adding aromatic diacid to the above solution to prepare an aramid polymer. Next, the aramid polymer is dissolved in a sulfuric acid solvent to prepare a spin dope, the spin dope is spun, followed by conducting coagulation, washing and drying processes in this order, thereby finally completing an aramid fiber.

25 **[0006]** However, if the aramid fiber is prepared according to the above-described processes, an aramid polymer in a solid state is prepared and again dissolved in a sulfuric acid solvent to prepare a spin dope, followed by spinning the same. Therefore, a manufacturing process becomes complicated, is harmful for a human body, and may cause a problem such as a decrease in durability due to corrosion of an apparatus.

30 **[0007]** Moreover, since the sulfuric acid solvent used for dissolving an aramid polymer having high chemical resistance and removed after spinning often causes environmental pollution, it should be appropriately treated after the use. Costs for treatment of such spent sulfuric acid usually reduce economic advantages of the aramid fiber.

[0008] In order to solve the above problems, Korean Patent Registration No. 10-171994 discloses a method for fabricating an aramid fiber directly using a copolymerized aramid polymerization solution as a spin dope, thus not requiring a sulfuric acid solvent.

35 **[0009]** More particularly, in the above conventional art, a copolymerized aramid fiber is manufactured by adding terephthaloyl dichloride to an organic solvent in which para-phenylenediamine and cyano-para-phenylenediamine are dissolved, and reacting the same to prepare a polymerization solution containing a copolymerized aramid polymer, then, spinning and coagulating the polymerization solution.

40 **[0010]** However, the conventional art entails a problem that the prepared copolymerized aramid fiber has deteriorated dyeing property due to high crystalline property although having an advantage of not using the sulfuric acid solvent.

[0011] In order to solve the above problem, Korean Patent Registration No. 10-067338 discloses a method for fabricating a copolymerized aramid fiber that includes adding polyvinyl pyrrolidone as a non-crystalline polymer to a polymerization solution when the copolymerized aramid fiber is manufactured by adding terephthaloyl dichloride to an organic solvent in which paraphenylenediamine and cyano-para-phenylenediamine are dissolved, and reacting the same to polymerize the polymerization solution containing a copolymerized aramid polymer, then, spinning and coagulating the same. However, this method involves problems of deteriorating solubility and dyeing fastness of the polymerization solution although improving dyeing property of the manufactured copolymerized aramid fiber.

45 **[0012]** As another conventional art, there has been executed a fabrication method of a copolymerized aramid dope-dyed yarn including addition of a specific coloring matter which may not be bonded to a cyano group (-CN) of the copolymerized aramid through a hydrogen bond, that is, a coloring matter which does not contain a cation, when a copolymerized aramid fiber is prepared by adding terephthaloyl dichloride to an organic solvent in which para-phenylenediamine and cyano-para-phenylenediamine are dissolved, and reacting the same to polymerize a polymerization solution containing a copolymerized aramid polymer, then, spinning and coagulating the polymerization solution. However, this method entails some problems such as a decrease in a polymerization degree of the copolymerized aramid polymer, a reduction in solubility of the polymerization solution, and a deterioration in a color fastness of the manufactured dope-dyed yarn.

[Disclosure]

[Technical Problem]

5 **[0013]** An object of the present invention is to provide a copolymerized aramid dope-dyed yarn with excellent color strength and color fastness, and a method for preparing the same while preventing a decrease in a polymerization degree of copolymerized aramid and a reduction in solubility of a polymerization solution.

[Technical Solution]

10 **[0014]** In order to accomplish the above object, the present invention provides a method for preparing a copolymerized aramid yarn, including adding a coloring matter having cations in an amount of 0.1 to 5% by weight ('wt. %') to a weight of a copolymerized aramid polymer in a polymerization process of a polymerization solution containing the copolymerized aramid polymer, when the copolymerized aramid yarn is prepared by adding terephthaloyl dichloride to an organic solvent
15 in which an aromatic diamine having a cyano group is dissolved, reacting the same to polymerize the polymerization solution containing the copolymerized aramid polymer, then, spinning and coagulating the polymerization solution.

[Advantageous Effects]

20 **[0015]** According to the present invention, due to the addition of the coloring matter to the polymerization solution, it is possible to efficiently prevent a decrease in a polymerization degree of the copolymerized aramid polymer or a reduction in solubility of the polymerization solution.

[0016] Further, according to the present invention, the copolymerized aramid polymer having a cyano group (-CN) and the coloring matter having a cation are bonded through a hydrogen bond in the polymerization process of the
25 polymerization solution containing the copolymerized aramid polymer, and the coloring matter having a cation is bonded with the cyano group (-CN) located on a main chain of the copolymerized aramid polymer through an ionic bond, and can show behavior together with the main chain during formation of a liquid crystal, thereby improving color strength, color fastness to light and color fastness to washing of the copolymerized aramid dope-dyed yarn.

30 [Best Mode]

[0017] Hereinafter, the present invention will be described in detail.

[0018] Embodiments of the present invention described below are proposed as illustrative examples to help understanding the present invention but do not particularly limit the subject matters of the present invention to be protected.
35 Further, it will be apparent to those skilled in the art that various alterations and modifications of the present invention are possible within the technical spirit and scope of the present invention. Accordingly, the present invention includes inventions described in the claims and all of the alterations and modification within equivalents thereof.

[0019] First, in the present invention, an inorganic salt is dissolved in an organic solvent, followed by adding aromatic diamine having a cyano group (CN-) thereto.

40 **[0020]** Herein, the aromatic diamine having a cyano group (CN-) may include a solution of paraphenylenediamine and cyano-para-phenylenediamine dissolved in a molar ratio of 1:9 to 9:1, or a solution of cyano-para-phenylenediamine alone.

[0021] The organic solvent may include, for example,
45 N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), hexamethyl phosphoamide (HMPA), N,N,N',N'-tetramethylurea (TMU), N,N-dimethylformamide (DMF), or a mixture thereof.

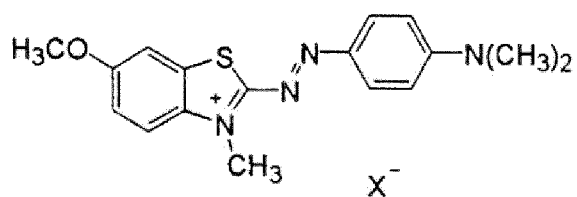
[0022] The inorganic salt is added to increase a polymerization degree of the aromatic polyamide, and may include, for example, alkaline metal halide salts or alkali-earth metal halide salts such as CaCl₂, LiCl, NaCl, KCl, LiBr and KBr, which are added alone or in combination of two or more thereof.

[0023] Preferably, the inorganic salt is added in an amount of 2 to 5 wt.% to a weight of the organic solvent.

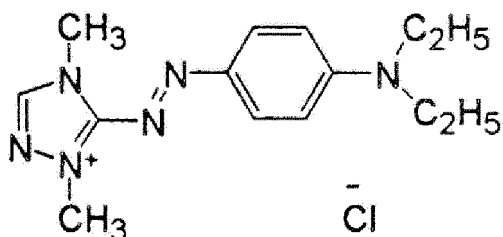
50 **[0024]** Next, terephthaloyl dichloride is added in the same molar amount as that of the aromatic diamine having a cyano group to the organic solvent containing aromatic diamine having a cyano group added and dissolved therein. Moreover, the coloring matter having a cation is added to the organic solvent to prepare a polymerization solution containing a copolymerized aramid polymer.

[0025] The coloring matter having a cation has the following representative structures, but it is not limited thereto.

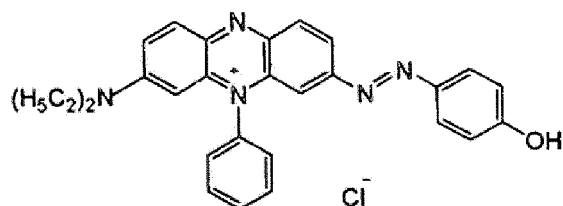
55 **[0026]** C.I. Basic Blue 64, C.I. Basic Red 22 having azo as a coloring matter base.



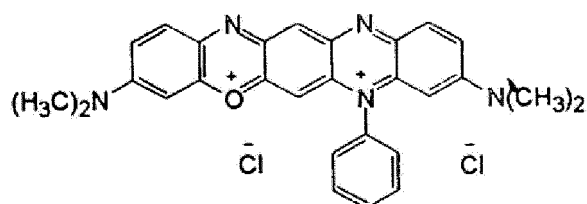
C.I. Basic Blue 64

[0027]

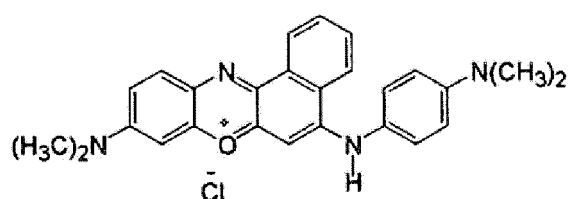
C.I. Basic Red 22

[0028] C.I. Basic Black 2 having an azine and azo composite as a coloring matter base

C.I. Basic Black 2

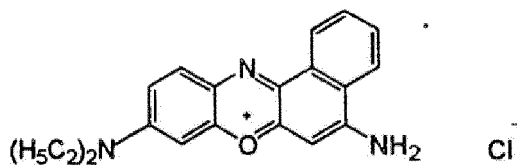
[0029] C.I. Basic Black 7 having an azine and oxazine composite as a coloring matter base

C.I. Basic Black 7

[0030] C.I. Basic Blue 10, C.I. Basic Blue 12, C.I. Basic Blue 74 having oxazine as a coloring matter base

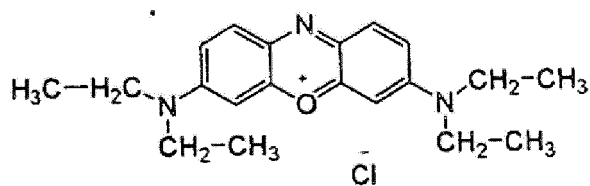
C.I. Basic Blue 10

[0031]



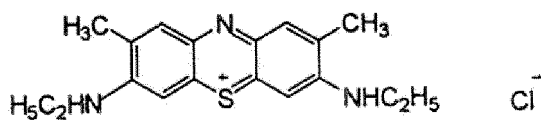
C.I. Basic Blue 12

[0032]



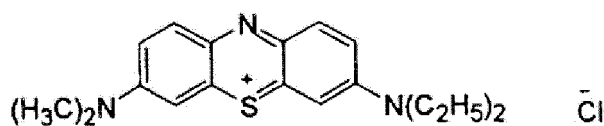
C.I. Base Blue 74

[0033] C.I. Basic Blue 24, C.I. Basic Blue 25 having thiazine as a coloring matter base



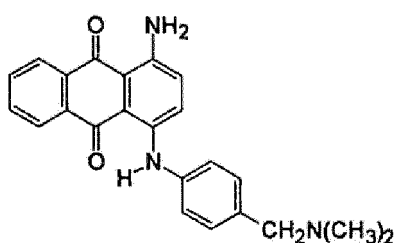
C.I. Basic Blue 24

[0034]



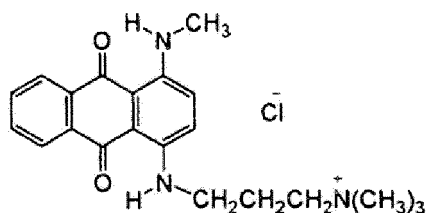
C.I. Basic Blue 25

[0035] C.I. Basic Blue 47, C.I. Basic Blue 22 having anthraquinone as a coloring matter base



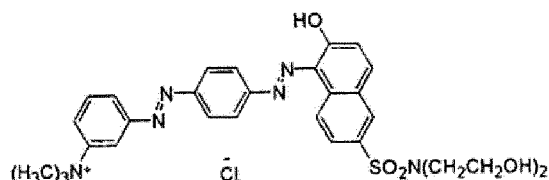
C.I. Basic Blue 47

[0036]



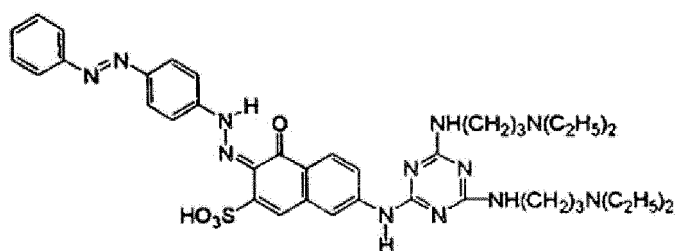
C.I. Basic Blue 22

[0037] C.I. Basic Red 32, C.I. Basic Red 111 having double azo as a coloring matter base



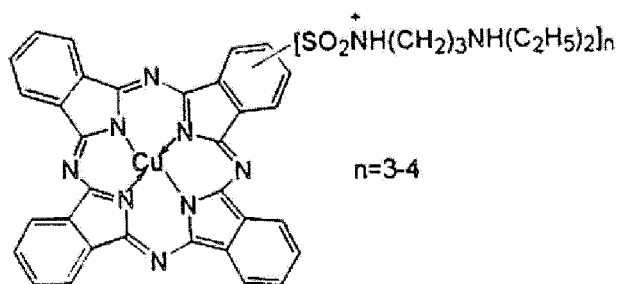
C.I. Basic Red 32

[0038]



C.I. Basic Red 111

[0039] C.I. Basic Blue 140 having phthalocyanine as a coloring matter base



C.I. Basic Blue 140

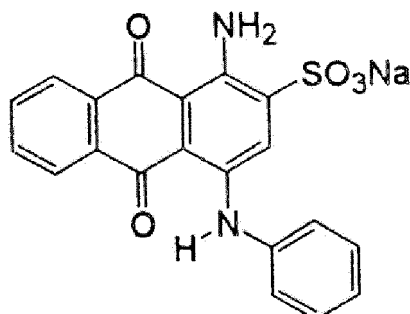
[0040] Preferably, the coloring matter having a cation is added in an amount of 0.1 to 5 wt.% to a weight of the copolymerized aramid polymer. If the added amount is less than 0.1 wt.%, a color strength is weak, and if it exceeds 5 wt.%, physical properties of a fiber may be deteriorated.

[0041] Next, after directly using the polymerization solution prepared as described above as a spin dope and extruding the same through a spinning spinneret, by coagulating the extruded polymerization solution using a coagulating agent to fabricate a copolymerized aramid dope-dyed yarn on a filament.

[0042] During the polymerization process of the polymerization solution containing the copolymerized aramid polymer, when a coloring matter having an anion is introduced instead of the coloring matter having a cation, the cyano group (-CN) has strong electronegativity to thus exhibit a repulsive force from an anionic sulfone group of the coloring matter

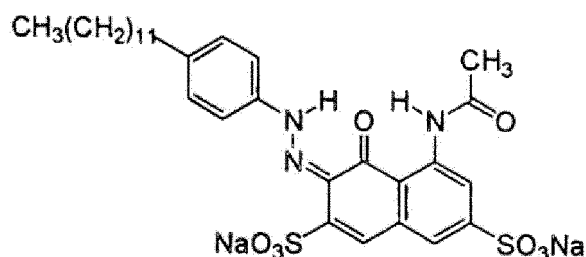
having an anion. As a result, the coloring matter having an anion could not be deposited on a polymer but be discharged along with the solvent, hence expressing a color in not a coloring level but a pollution level and having a considerably deterioration in the color strength, color fastness to light and color fastness to washing of the copolymerized aramid dope-dyed yarn.

[0043] Examples of the coloring matter having an anion are as follows.



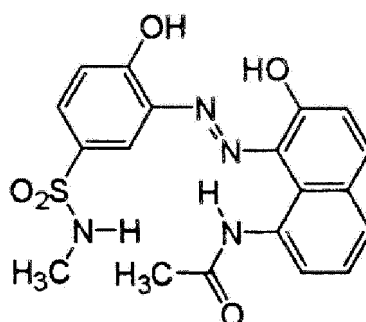
C.I. Basic Acid Blue 25

[0044]



C.I. Basic Acid Red 138

[0045]



C.I. Basic Acid Black 60

[0046] The copolymerized aramid dope-dyed yarn of the present invention may include any one of the above coloring matter having a cation alone or in combination of two or more thereof.

[0047] The coloring matter having a cation may be a pigment having a cation, a dye having a cation, or a mixture of the pigment having a cation and the dye having a cation.

[0048] The copolymerized aramid dope-dyed yarn manufactured by the method according to the present invention may include the coloring matter having a cation to thus have an excellent color strength of at least 50 and excellent color fastness to light and color fastness to washing of grade 4 to grade 5. Further, the copolymerized aramid polymer does not show a decrease in a polymerization degree, thus having a high strength of 28 to 35 g/d.

[0049] Hereinafter, the present invention will be described in more detail with reference to examples and comparative examples.

Example 1

[0050] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0051] Next, 100 mol % of terephthaloyl dichloride and 0.3 wt.% of C.I. Basic Black 2 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0052] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0053] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0054] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 2

[0055] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 100 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0056] Next, 100 mol % of terephthaloyl dichloride and 1.5 wt.% of C.I. Basic Blue 22 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0057] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0058] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0059] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 3

[0060] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0061] Next, 100 mol % of terephthaloyl dichloride and 3 wt.% of C.I. Basic Blue 64 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0062] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0063] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0064] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 4

[0065] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 100 mol % of cyano-p-phenylenediamine was introduced in the reactor and dissolved to prepare a

mixture solution.

[0066] Next, 100 mol % of terephthaloyl dichloride and 4.9 wt. % of C.I. Basic Red 22 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0067] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0068] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0069] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 5

[0070] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt. % CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0071] Next, 100 mol % of terephthaloyl dichloride and 0.3 wt. % of C.I. Basic Black 7 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0072] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0073] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0074] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 6

[0075] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt. % CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0076] Next, 100 mol % of terephthaloyl dichloride and 1.5 wt. % of C.I. Basic Blue 74 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0077] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0078] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0079] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 7

[0080] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt. % CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0081] Next, 100 mol % of terephthaloyl dichloride and 3 wt. % of C.I. Basic Blue 24 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0082] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0083] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0084] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 8

[0085] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl₂ was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0086] Next, 100 mol % of terephthaloyl dichloride and 4.9 wt.% of C.I. Basic Blue 25 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0087] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0088] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0089] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 9

[0090] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl₂ was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0091] Next, 100 mol % of terephthaloyl dichloride and 1.5 wt.% of C.I. Basic Blue 47 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0092] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0093] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0094] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 10

[0095] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl₂ was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0096] Next, 100 mol % of terephthaloyl dichloride and 3 wt.% of C.I. Basic Red 32 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0097] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0098] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0099] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 11

[0100] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0101] Next, 100 mol % of terephthaloyl dichloride and 4.9 wt.% of C.I. Basic Red 111 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0102] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0103] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0104] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 12

[0105] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0106] Next, 100 mol % of terephthaloyl dichloride and 0.3 wt.% of C.I. Basic Blue 140 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0107] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0108] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0109] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 13

[0110] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0111] Next, 100 mol % of terephthaloyl dichloride and 0.3 wt.% of C.I. Basic Blue 10 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0112] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0113] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn. Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Example 14

[0114] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0115] Next, 100 mol % of terephthaloyl dichloride and 3 wt.% of C.I. Basic Blue 12 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0116] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0117] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0118] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Comparative Example 1

[0119] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0120] Next, 100 mol % of terephthaloyl dichloride was added to the reactor including the mixture solution in order to prepare a polymerization solution containing the copolymerized aramid polymer.

[0121] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0122] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid fiber.

[0123] 0.5 g of the copolymerized aramid fiber manufactured as described above was fed into a dye bath including a basic dye prepared by adding 0.2 g of the above dyeing dye (C.I. Basic Red 22) in 100 ml of distilled water and 1.2 ml of glacial acetic acid, and dyed at 100°C for 1 hour, followed by washing and drying the same.

[0124] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dyed yarn were evaluated, and results thereof are shown in Table 1.

Comparative Example 2

[0125] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 100 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0126] Next, 100 mol % of terephthaloyl dichloride and 57 wt.% of polyvinylpyridine (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0127] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0128] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid fiber.

[0129] 0.5 g of the copolymerized aramid fiber manufactured as described above was fed into a dye bath including a basic dye prepared by adding 0.2 g of the above dyeing dye (C.I. Basic Red 22) in 100 ml of distilled water and 1.2 ml of glacial acetic acid, and dyed at 100°C for 1 hour, followed by washing and drying the same.

[0130] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dyed yarn were evaluated, and results thereof are shown in Table 1.

Comparative Example 3

[0131] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl_2 was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0132] Next, 100 mol % of terephthaloyl dichloride and 0.3 wt.% of C.I. Acid Blue 25 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0133] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density

of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0134] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0135] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Comparative Example 4

[0136] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl₂ was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0137] Next, 100 mol % of terephthaloyl dichloride and 2 wt.% of C.I. Acid Red 138 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0138] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0139] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0140] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

Comparative Example 5

[0141] An N-methyl-2-pyrrolidone (NMP) organic solvent including 3 wt.% CaCl₂ was fed to a reactor under a nitrogen atmosphere, then, 50 mol % of p-phenylenediamine and 50 mol % of cyano-p-phenylenediamine were introduced in the reactor and dissolved to prepare a mixture solution.

[0142] Next, 100 mol % of terephthaloyl dichloride and 4 wt.% of C.I. Acid Black 60 (to the weight of the copolymerized aramid polymer) were added to the reactor including the mixture solution, simultaneously, to prepare a polymerization solution containing the copolymerized aramid polymer.

[0143] Following this, after extruding the polymerization solution through a spinning spinneret, air gap and a coagulating agent were sequentially passing through the spinning spinneret, thereby forming a multi-filament having a linear density of 3,000 denier. A pressure of a spin pack was 2,800 psi and a spinning speed was 600 mpm (meter per minute).

[0144] After then, the multi-filament was washed and the washed multi-filament was dried and drawn by a dry roller set up at a temperature of 150°C. The drawn multi-filament was subjected to heat treatment and winding at 250°C, thereby fabricating a copolymerized aramid dope-dyed yarn.

[0145] Color strength and color fastness to light and washing of the manufactured copolymerized aramid dope-dyed yarn were evaluated, and results thereof are shown in Table 1.

[Table 1]

Section	Color strength (K/S value)	Color fastness to light (grade)	Color fastness to washing (grade)
Example 1	50	4	5
Example 2	120	4	4
Example 3	180	4	4
Example 4	200	4	5
Example 5	60	4	4
Example 6	110	4	4
Example 7	170	4	5
Example 8	210	5	4
Example 9	100	4	4

(continued)

Section	Color strength (K/S value)	Color fastness to light (grade)	Color fastness to washing (grade)
Example 10	150	4	4
Example 11	180	5	4
Example 12	50	4	4
Example 13	60	4	4
Example 14	120	4	5
Comparative Example 1	5	2	2
Comparative Example 2	40	2-3	3
Comparative Example 3	10	2	2
Comparative Example 4	30	2	2
Comparative Example 5	25	2	2

[0146] The color strength and color fastness shown in Table 1 above were evaluated according to the following methods.

Color strength

[0147] The color strength was determined by measuring the color according to KS K 0205. More particularly, the aramid fiber was densely wound around a small card with a dimension of 7.5 cm width and 6.5 cm length, then, a color of the aramid fiber was measured on a D65 light source at 10 degree of viewing angle using a spectrophotometer (Konica-Minolta CM-3600d). Herein, the measured value is an average value calculated from three values measured at different locations.

$$\text{Color strength}(f_k) = \int_{\lambda=400}^{700} (K/S)_{\lambda} (\bar{x}_{\lambda} + \bar{y}_{\lambda} + \bar{z}_{\lambda})$$

$\bar{x}$: Tristimulus value of blue

$\bar{y}$: Tristimulus value of green

$\bar{z}$: Tristimulus value of red

λ : Wavelength

$$K/S = \frac{(1-R)^2}{2R} \dots\dots\dots \text{Kubelka-Mnk equation}$$

K: Absorption coefficient
S: Scattering coefficient
R: Reflectance

Color fastness to light

[0148] Color fastness to light was measured according to 206KS K 0700, and a color change was determined based on a measurement of color change grades using a spectrophotometer KS K ISO 105-A05.

Color fastness to washing

[0149] Color fastness to washing was measured according to KS K ISO 105-C06, and a color change of a fabric material after testing was determined based on the measurement of color change grades using a spectrophotometer KS K ISO 105-A05.

[Industrial Applicability]

[0150] The copolymerized aramid dope-dyed yarn according to the present invention may be usefully employed as a raw material for protective gloves or protective clothing.

Claims

1. A copolymerized aramid dope-dyed yarn, manufactured by adding terephthaloyl dichloride to an organic solvent in which an aromatic diamine having a cyano group is dissolved, reacting the same to polymerize a polymerization solution containing a copolymerized aramid polymer, then, spinning and coagulating the polymerization solution, wherein the yarn includes a coloring matter having a cation, so as to have a color strength of 50 or more.
2. The yarn according to claim 1, wherein the coloring matter having a cation is included in an amount of 0.1 to 5 by weight ('wt. %') to a weight of the copolymerized aramid polymer.
3. The yarn according to claim 1, wherein the yarn has a color fastness to light of grade 4 to grade 5.
4. The yarn according to claim 1, wherein the yarn has a color fastness to washing of grade 4 to grade 5.
5. The yarn according to claim 1, wherein the coloring matter having a cation is at least one selected from: C.I. Basic Black 2, C.I. Basic Blue 22, C.I. Basic Blue 64, C.I. Basic Red 22, C.I. Basic Black 7, C.I. Basic Blue 10, C.I. Basic Blue 12, C.I. Basic Blue 74, C.I. Basic Blue 24, C.I. Basic Blue 25, C.I. Basic Blue 47, C.I. Basic Red 32, C.I. Basic Red 111 and C.I. Basic Blue 140.
6. The yarn according to claim 1, wherein the coloring matter having a cation is a pigment having a cation, a dye having a cation, and a mixture of the pigment having a cation and the dye having a cation.
7. A method for preparing a copolymerized aramid yarn, comprising: adding terephthaloyl dichloride to an organic solvent in which an aromatic diamine having a cyano group is dissolved; reacting the same to polymerize a polymerization solution containing a copolymerized aramid polymer; then, spinning and coagulating the polymerization solution, wherein a coloring matter having a cation is added during a polymerization process of the polymerization solution containing the copolymerized aramid polymer.
8. The method according to claim 7, wherein the coloring matter having a cation is added in an amount of 0.1 to 5 wt. % to a weight of the copolymerized aramid polymer.
9. The method according to claim 7, wherein the coloring matter having a cation is at least one selected from C.I. Basic Black 2, C.I. Basic Blue 22, C.I. Basic Blue 64, C.I. Basic Red 22, C.I. Basic Black 7, C.I. Basic Blue 10, C.I. Basic Blue 12, C.I. Basic Blue 74, C.I. Basic Blue 24, C.I. Basic Blue 25, C.I. Basic Blue 47, C.I. Basic Red 32, C.I. Basic Red 111 and C.I. Basic Blue 140.
10. The method according to claim 7, wherein the coloring matter having a cation is a pigment having a cation, a dye having a cation, and a mixture of the pigment having a cation and the dye having a cation.
11. The method according to claim 7, wherein the aromatic diamine having a cyano group, dissolved in the organic solvent, is prepared by dissolving para-phenylenediamine and cyano-para-phenylenediamine in a molar ratio of 1:9

to 9:1 in the organic solvent.

12. The method according to claim 7, wherein the aromatic diamine having a cyano group, dissolved in the organic solvent, is prepared by dissolving cyano-para-phenylenediamine alone in the organic solvent.

13. The method according to claim 7, wherein terephthaloyl dichloride is added in the same molar amount as that of the aromatic diamine having a cyano group to the organic solvent in which the aromatic diamine having a cyano group is dissolved.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2014/012809

A. CLASSIFICATION OF SUBJECT MATTER

D01F 1/06(2006.01)i, D01F 1/04(2006.01)i, D01F 6/80(2006.01)i, D01F 6/60(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D01F 1/06; C08G 69/48; C08G 69/02; D03D 15/00; D06P 1/24; C08J 3/28; D01F 6/60; C09B 67/00; D01F 11/08; C08J 7/18; D01F 1/04; D01F 6/80

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models: IPC as above
Japanese Utility models and applications for Utility models: IPC as aboveElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS (KIPO internal) & Keywords: aramid copolymer, dope dyed yarn, cyano, diamine, diacid, cationic pigment

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2013-209776 A (TEIJIN LTD.) 10 October 2013 See abstract; paragraphs [0009]-[0022].	1-13
A	KR 10-2012-0077714 A (KUMOH NATIONAL INSTITUTE OF TECHNOLOGY INDUSTRY-ACADEMIC COOPERATION FOUNDATION) 10 July 2012 See abstract; paragraphs [0022]-[0031].	1-13
A	US 2010-0311918 A1 (FAISSAL-ALI EL TOUFALIL) 09 December 2010 See abstract; paragraphs [0035]-[0058].	1-13
A	US 2008-0244840 A1 (RACCURT, O. et al.) 09 October 2008 See abstract; paragraphs [0034]-[0037].	1-13
A	JP 08-199433 A (TEIJIN LTD.) 06 August 1996 See abstract; paragraphs [0024]-[0027].	1-13

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

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

26 MARCH 2015 (26.03.2015)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2014/012809

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- KR 10171994 [0008]
- KR 10067338 [0011]