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(54) **Easily dyeable meta-linkage-containing aromatic polyamide fibres**

Leicht färbbare Metabindungen enthaltende aromatische Polyamidfasern

Fibres de polyamides aromatiques avec liaisons en position méta, pouvant être aisément teintes

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**EP-A- 0 228 224**                      **EP-A- 0 330 163**  
**US-A- 3 779 705**                      **US-A- 4 196 118**

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**Description**

## BACKGROUND OF THE INVENTION

## 5 1. Field of the Invention

**[0001]** The present invention relates to meta-linkage-containing aromatic polyamide fibers which are dyeable with cationic dyes.

## 10 2. Description of the Related Art

**[0002]** Meta-linkage-containing aromatic polyamide fibers have molecular skeletons consisting almost totally of aromatic rings, and thus have excellent heat resistance, flame retardance and flame proofness. As a result, such fibers are suitable for use as industrial materials for which heat resistance is required, and for use in clothing and interior decoration for which flame retardance and flame proofness are considered important; they are rapidly attaining wider use especially in the fields of clothing, bedding materials and interior decoration which take advantage of their flame retardance and flame proofness. These fields usually employ dyed fibers, but while meta-linkage-containing aromatic polyamide fibers have excellent physical characteristics, their rigid polymer chains make them very difficult to dye by conventional methods.

**[0003]** A number of methods have been proposed in order to use meta-linkage-containing aromatic polyamide fibers in these fields. For example, in Japanese Unexamined Patent Publication No. 50-59522 there have been proposed pigmented fibers obtained by incorporating meta-linkage-containing aromatic polyamide fibers with a specific pigment; because the fibers are incorporated with the pigment during the production process, however, there is a drawback of considerable efficiency loss when colors are changed, which means that the method cannot be adapted well to small-lot production and more time is required to respond to client's orders. As a means of improving the dyeing property, Japanese Unexamined Patent Publication No. 55-21406 (U.S. Patent No. 4,278,779) has proposed a method of adding a polymer copolymerized with xylylenediamine; however, since a third component is copolymerized with the polymer chain, polymerization equipment and polymer stocking equipment must be specialized for the particular polymer used, which presents a problem of increased cost. In addition, Japanese Examined Patent Publication No. 52-43930 (U.S. Patent No. 3,695,992) proposes polyporous aromatic polyamide fibers with an improved dyeing property, having a pore size, void volume and density within specific ranges; nevertheless, the dyeing property of these fibers has not been sufficient, and associated drawbacks have included difficulty in setting the dyeing conditions because of the required pigments and organic dyeing aids during the dyeing, as well as difficulty in disposal of the waste liquors after use.

**[0004]** There has also been proposed in, for example, Japanese Examined Patent Publication No. 44-11168 (U.S. Patent No. 3,506,990), a meta-linkage-containing aromatic polyamide prepared by copolymerization with a compound having sulfonate groups introduced therein. This polymer, however, has certain disadvantages in that purification of the starting material is very difficult, and it is impossible to obtain a stable polymer with the necessary degree of polymerization and whiteness. Furthermore, production of aromatic polyamides prepared by copolymerization with components having sodium sulfonate groups is disclosed in Japanese Unexamined Patent Publication Nos. 48-96827 and 51-26320, and in U.S. Patent Nos. 3,039,990, 3,142,662 and 3,409,596. However, although aromatic polyamides are usually prepared by reacting a dicarboxylic halide with a diamine, the sodium sulfonate groups when present react with the acid halide, making it impossible to obtain a polymer with satisfactory physical properties.

**[0005]** EP-A-O 212 948 discloses a process for dyeing aromatic fibers a deep shade. To this end a large amount of surfactants is incorporated into the fibers. One of the recommended surfactants is isopropylammonium dodecylbenzenesulfonate.

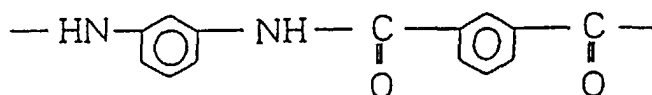
## SUMMARY OF THE INVENTION

**[0006]** In light of the aforementioned problems of the prior art, it is an object of the present invention to provide, by inexpensive and simple means, meta-linkage-containing aromatic polyamide fibers with excellent dyeing properties which may be used in the fields of bedding, clothing and interior decorating.

**[0007]** In order to achieve the above-mentioned object, the present invention provides meta-linkage-containing aromatic polyamide fibers easily dyeable with cationic dyes, the fibers consisting of a composition which comprises a meta-linkage-containing aromatic polyamide incorporating at least one alkylbenzenesulfonic acid onium salt selected from the group consisting of tetrabutylphosphonium hexylbenzenesulfonate, tributylbenzylphosphonium hexylbenzenesulfonate, tetraphenylphosphonium dodecylbenzenesulfonate, tributylphenylphosphonium dodecylbenzenesulfonate, tetrabutylphosphonium dodecylbenzenesulfonate and tributylbenzylammonium dodecylbenzenesulfonate.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0008]** The meta-linkage-containing aromatic polyamide to be used according to the present invention consists of aromatic rings constituting the main skeleton, which have amide linkages at the meta-positions. Particularly preferred among such meta-linkage-containing aromatic polyamides is a poly-m-phenylene isophthalamide consisting of repeating units represented by the following chemical formula.



**[0009]** The meta-linkage-containing aromatic polyamide may also be a copolymer comprising less than 15 mole percent of a third component.

**[0010]** In preferred fibers at least 85 mole percent of the repeating units of the meta-linkage containing aromatic polyamide are a poly-m-phenylene isophthalamide consisting of the repeating units of the above chemical formula.

**[0011]** Monomers constituting the third component may be aromatic diamine components such as, for example, para-phenylenediamine, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, paraxylylenediamine, biphenylenediamine, 3,3'-dichlorobenzidine, 3,3'-dimethylbenzidine, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 1,5-naphthalenediamine; and as acid components, aromatic dicarboxylic acids such as, for example, terephthalic acid, naphthalene-2,6-dicarboxylic acid, naphthalene-2,7-dicarboxylic acid, particularly preferred of which is terephthalic acid. These aromatic diamines and aromatic dicarboxylic acids may have a portion of the hydrogen atoms on their aromatic rings substituted with halogen atoms or alkyl groups such as methyl.

**[0012]** This type of meta-linkage-containing aromatic polyamide may be produced by a publicly known interfacial polymerization or low-temperature solution polymerization method. The degree of polymerization of the polymer, in terms of the intrinsic viscosity (IV) of a 0.5 g/100 ml solution in N-methyl-2-pyrrolidone at 30°C, is preferably 1.3 to 1.9 dl/g.

**[0013]** The alkylbenzenesulfonic acid onium salt combined with the meta-linkage-containing aromatic polyamide is a compound selected from tetrabutylphosphonium hexylbenzenesulfonate, tributylbenzylphosphonium hexylbenzenesulfonate, tetraphenylphosphonium dodecylbenzenesulfonate, tributylphenylphosphonium dodecylbenzenesulfonate, tetrabutylphosphonium dodecylbenzenesulfonate and tributylbenzylammonium dodecylbenzenesulfonate. Among these, tetrabutylphosphonium dodecylbenzenesulfonate and tributylbenzylammonium dodecylbenzenesulfonate are particularly preferred, because of their ready availability, excellent thermal stability and high solubility in dimethylacetamide and N-methyl-2-pyrrolidone, which are good solvents for the meta-linkage-containing aromatic polyamide.

**[0014]** In order to obtain an adequate effect on the dyeing property, the amount of the alkylbenzenesulfonic acid onium salt to be combined with the meta-linkage-containing aromatic polyamide is preferably between 2.8 and 7.0 mole percent, and more preferably between 3.5 and 7.0 mole percent with respect to the repeating units of the meta-linkage-containing aromatic polyamide. At less than 2.8 mole percent, an adequate improving effect on the dyeing property may not be achieved, while at greater than 7.0 mole percent the single filaments may be more prone to breakage during the fiber production process.

**[0015]** The composition constituting the meta-linkage-containing aromatic polyamide fibers of the present invention, which contains the meta-linkage-containing aromatic polyamide incorporating the onium alkylbenzenesulfonate, preferably further contains a halogen-containing alkyl phosphate or a halogen-containing phenyl phosphate (hereunder referred to collectively as "halogen-containing alkyl (phenyl) phosphate"). The meta-linkage-containing aromatic polyamide fibers made of such a composition have more excellent dyeing properties.

**[0016]** As halogen-containing alkyl (phenyl) phosphates there may be mentioned compounds such as tris( $\beta$ -chloropropyl) phosphate, tris(2,3-dichloropropyl) phosphate, tris(chloroethyl) phosphate, phenyldichloropropyl phosphate and tris(dichlorophenyl) phosphate. Although these compounds have been found to have virtually no effect of improving dyeing properties when they alone are combined with meta-linkage-containing aromatic polyamides, they exhibit a specific dyeing property-improving effect when used in tandem with an alkylbenzenesulfonic acid onium salt.

**[0017]** The content of the halogen-containing alkyl (phenyl) phosphate in the polymer is preferably 0.5 to 5.0 wt%, and more preferably 1.8 to 5.0 wt% with respect to the meta-linkage-containing aromatic polyamide. At less than 0.5 wt% the specific dyeing property-improving effect may not be obtained, and at greater than 5 wt% dye spots may appear during the dyeing process, while the dyeing property-improving effect may not be so greatly enhanced.

**[0018]** The above-mentioned meta-linkage-containing aromatic polyamide composition constituting the meta-linkage-containing aromatic polyamide fibers of the present invention preferably further contains an ultraviolet

absorber. Meta-linkage-containing aromatic polyamide fibers made of such a composition not only have a more excellent dyeing property, but also impart excellent light fastness to the dyed product.

**[0019]** The ultraviolet absorber is preferably a benzotriazole-based ultraviolet absorbing compound. This is because meta-linkage-containing aromatic polyamides have an ultraviolet absorbance range of from 340 to 360 nm, and most benzotriazole-based compounds have maximum absorbance wavelengths within this range.

**[0020]** As is well-known, meta-linkage-containing aromatic polyamides undergo considerable yellowing upon exposure to light rays, as a result of their molecular structure characteristics. Consequently, even if the dyeing property is improved to provide finely dyed fibers, their value as marketable dyed fibers is reduced by half when the color shade is altered due to yellowing after dyeing. Thus, by combining excellent light fastness with the excellent dyeing property, their value is greatly increased as meta-linkage-containing aromatic polyamide fibers with an improved dyeing property.

**[0021]** Preferred examples of benzotriazole-based ultraviolet absorbing compounds include 2-(5-methyl-2-hydroxyphenyl)benzotriazole, 2-[2-hydroxy-3,5-bis( $\alpha,\alpha'$ -dimethylbenzyl)phenyl]-2H-benzotriazole, 2-(3,5-di-t-butyl-2-hydroxyphenyl)benzotriazole, 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3,5-di-t-butyl-2-hydroxyphenyl)-5-chlorobenzoazole and 2-(3,5-di-t-amyl-2-hydroxyphenyl)benzotriazole. Among these, 2-[2-hydroxy-3,5-bis( $\alpha,\alpha'$ -dimethylbenzyl)phenyl]-2H-benzotriazole is particularly preferred because of its heat resistance and high solubility in dimethylacetamide and N-methyl-2-pyrrolidone, which are good solvents for the meta-linkage-containing aromatic polyamide.

**[0022]** The amount of the ultraviolet absorber to be added is preferably 2.0 to 6.0 wt%, and particularly 3.0 to 5.0 wt% with respect to the meta-linkage-containing aromatic polyamide. If the amount is less than 2.0 wt% the anti-yellowing effect may not be exhibited, and even if it is added at greater than 6.0 wt% no further improvement in the anti-yellowing effect may result, while the workability of the fibers during the production process may be reduced.

**[0023]** The mixture of the meta-linkage-containing aromatic polyamide with the alkylbenzenesulfonic acid onium salt, halogen-containing alkyl (phenyl) phosphate and ultraviolet absorber may be accomplished by a method wherein the meta-linkage-containing aromatic polyamide is added to a solvent and mixed therewith to make a solution to which solutions of the alkylbenzenesulfonic acid onium salt, halogen-containing alkyl (phenyl) phosphate and ultraviolet absorber each in appropriate solvents are then added and mixed therewith, or an alternative method in which the meta-linkage-containing aromatic polyamide, alkylbenzenesulfonic acid onium salt, halogen-containing alkyl (phenyl) phosphate and ultraviolet absorber are combined into a mixture which is then dissolved in a solvent. The dope obtained in this manner may then be formed into fibers by a publicly known method.

**[0024]** An example of a typical fiber-forming method involves addition of the alkylbenzenesulfonic acid onium salt, halogen-containing alkyl (phenyl) phosphate and benzotriazole-based ultraviolet absorber to an N-methyl-2-pyrrolidone solution containing a poly-m-phenylene isophthalamide polymer, to prepare a dope. The dope is extruded from a nozzle into an aqueous inorganic solution whose main component is calcium chloride, stretched after coagulation and washing with water, and then further stretched on a hot plate at 300-325°C and crystallized, and finally subjected to oiling to complete the fibers. For staple fibers, they are crimped, cut and then spun to obtain easily dyeable spun fibers.

**[0025]** The easily dyeable meta-linkage-containing aromatic polyamide fibers of the present invention obtained in the manner described above have an excellent dyeing property and light fastness without any loss in the excellent heat resistance, flame retardance and flame proofness of the original meta-linkage-containing aromatic polyamide fibers, and thus may be effectively applied for clothing, bedding and interior decorations which require coloring. In particular, the addition of the halogen-containing alkyl (phenyl) phosphate provides further improvement in the flame retardance while drastically improving the dyeing property and lowering the dyeing cost compared to addition of the alkylbenzenesulfonic acid onium salt alone, and addition of the ultraviolet absorber, particularly a benzotriazole-based ultraviolet absorbing compound, drastically improves the light fastness, allowing the fibers to be applied in the fields of clothing, bedding and interior decorations in the same manner as existing common fibers.

**[0026]** The present invention is explained below by way of the examples. The measured values in the examples and comparative examples were obtained by the following methods.

#### 1. Dyeing property

**[0027]** Crimped fibers were collectively cut to a length of 50 mm and dyed at 30°C for 90 minutes using a dyeing solution comprising 8% o.w.f. Estrol Navy Blue N-RL (product of Sumitomo Chemical Co., Ltd.), 0.3 g/l acetic acid and 25 g/l sodium nitrate to a fiber/dyeing solution ratio (liquor ratio) of 1:40, after which a solution comprising 1 g/l hydro-sulfite, 1 g/l Amiladin D (product of Dai-ichi Kogyo Seiyaku Co., Ltd.) and 1 g/l sodium hydroxide was used at a liquor ratio of 1:40 for reductive washing at 80°C for 30 minutes, followed by water washing and drying. A 1.3g portion of the fibers was stuffed into a cell having a diameter of 31 mm and a depth of 13 mm, and a CM-2002 Minolta spectrophotometric colorimeter was used for colorimetry with a 10° field of view, a D76 light source and regular reflection elimination, using the value  $L^*$  as an index of the dyeing property.

## 2. Intrinsic viscosity (IV)

**[0028]** The polymer was dissolved in N-methyl-2-pyrrolidone (NMP) to a concentration of 0.5 g/100 ml, and an Ostwald's viscometer was used for measurement at 30°C.

## 3. Fineness

**[0029]** The fineness of the fibers was measured according to JIS-L-1015.

## 4. Tensile strength

**[0030]** The tensile strength of the fibers was measured according to JIS-L-1074, with a 20 mm long test sample, an initial load of 1/20 g/1.1 dtex(de) and an elongation rate of 20 mm/min.

## 5. Alkylbenzenesulfonic acid onium salt content of fibers

**[0031]** As a standard sulfur sample, 0.1 cc of an aqueous  $(\text{NH}_4)_2\text{SO}_4$  solution of known concentration is dropped onto test filtration paper, and a calibration curve is prepared based on fluorescent X-ray quantitative analysis after vacuum drying. About 50 mg of the fibers and about 20 mg of calcium chloride are dissolved in 5.0 cc of NMP by heating at 110°C for 1 hour, and after dropping a standard amount (0.1 cc) on the test filtration paper, it is vacuum dried. The sample is then quantitatively analyzed by fluorescent X-ray analysis, the sulfur concentration of the fibers is calculated based on the previously prepared calibration curve, and this is converted into the content on the assumption that all of the sulfur is derived from the alkylbenzenesulfonic acid onium salt.

## 6. Alkyl (phenyl) phosphate content of fibers

**[0032]** In the same manner as above, a calibration curve is prepared by fluorescent X-ray analysis of a standard phosphorus sample of known concentration, the phosphorus concentration of the fibers is calculated, and this is converted into a content on the assumption that all of the phosphorus is derived from the alkyl (phenyl) phosphate.

## 7. Benzotriazole-based ultraviolet absorbing compound content of fibers

**[0033]** About 20 mg of a sample dried at 105°C for 60 minutes is measured into a test tube (120 mm x 10 mmΦ, pyrex), 4 ml of concentrated hydrochloric acid is added and the tube is sealed. The sealed tube is heated at 130°C for about 6 hours for hydrolysis. After completion of hydrolysis, the sealed tube is cooled to room temperature and opened. The total contents of the test tube are then transferred to a 50 ml separatory funnel, 5 ml of chloroform is added, and the mixture is adequately shaken and allowed to stand, after which the chloroform phase is removed. This extraction procedure with chloroform is repeated 3 times, all of the chloroform phases are combined and concentrated to 2-3 ml, and the solution is then analyzed by liquid chromatography (LC). Separately, a test sample is prepared for a calibration curve, which is obtained by the same procedure as described above. The calibration curve is used to quantify the benzotriazole-based compound in the sample.

## 8. Measurement of light fastness

**[0034]** About 2g of sample (crimped and cut to lengths of 38-76 mm) is taken and dispersed with a hand card. The dispersed sample is affixed to a mount to a width of 18-22 mm and a thickness of 2-3 mm, as shown in Fig. 1. The mount is then set onto a metallic flask. The metallic flask is set into a fade tester (Model CF-20N, product of Shimadzu Laboratories), and irradiated for a prescribed time with an arc current of 15-17 A and an internal temperature of 42-45°C. The difference in the degree of discoloration of the "irradiated" and "non-irradiated" sections of the irradiated sample is judged visually against the difference in discoloration of a simultaneously irradiated blue scale (JIS L0841, product of Japan Standards Association).

Example 1

**[0035]** A 30g portion of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved in 110g of NMP and further mixed with 3.6g of phosphonium dodecylbenzenesulfonate, and the solution was subjected to vacuum degassing to make a spinning dope.

**[0036]** The dope was heated to 85°C and then used for wet spinning into a spinning bath from a spinning nozzle

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with 200 holes, each with a diameter of 0.07 mm. The composition of the spinning bath was 40 wt% calcium chloride, 5 wt% NMP and 55 wt% water, and the temperature of the spinning bath was 85°C. The filaments were given a course of about 100 cm through the spinning bath, and were drawn at a rate of 6.2 m/min. The filaments were then washed with water, stretched to a draw ratio of 2.4 in 95°C hot water, and dried using a roll at 200°C, after which they were stretched to a draw ratio of 1.75 on a 320°C hot plate to obtain stretched filaments with 440 dtex (400 de)/200 filaments. The total draw ratio was 4.2.

### Example 2

**[0037]** A 30g portion of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved in 110g of NMP and further mixed with a solution of 3.6g of tributylbenzylammonium dodecylbenzenesulfonate in 2g NMP, and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 1, to obtain stretched filaments with 440 dtex (400 de)/200 filaments.

### Example 3

**[0038]** A 5.7g portion of tetrabutylphosphonium dodecylbenzenesulfonate was dissolved in 110g of NMP, and then 30g of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved therein and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 1, to obtain stretched filaments with 440 dtex (400 de)/200 filaments.

### Example 4

**[0039]** A 2.7g portion of tetrabutylphosphonium dodecylbenzenesulfonate was dissolved in 110g of NMP, and then 30g of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved therein and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 1, to obtain stretched filaments with 440 dtex (400 de)/200 filaments.

### Example 5

**[0040]** A 6.0g portion of tetrabutylphosphonium dodecylbenzenesulfonate was dissolved in 110g of NMP, and then 30g of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved therein and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for stretching in the same manner as in Example 1, to obtain stretched filaments with 440 dtex (400 de)/200 filaments.

**[0041]** The measurement results of the physical properties of the fibers obtained in Examples 1 to 5 are given in Table 1 below. All of the fibers in these examples were found to have satisfactory dyeing properties, high strength, and satisfactory spinning properties.

Table 1

	Onium salt content of fibers	Strength (g/de)	Ductility (%)	Dyeing property L* value
Example 1	4.4	5.0	44	22.0
Example 2	4.0	4.9	45	22.5
Example 3	7.0	4.6	42	19.5
Example 4	3.3	5.0	43	25.0
Example 5	7.4	4.0	39	19.0
Onium salt: alkylbenzenesulfonic acid onium salt Content: mole percent with respect to polymer				

### Example 6

**[0042]** A 30g portion of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved in 110g of NMP, and then 3.6g of phosphonium dodecylbenzenesulfonate and 1.5g of tris( $\beta$ -chloropropyl) phosphate were mixed therewith and the solution was subjected to vacuum degassing to make a spinning dope.

**[0043]** The dope was heated to 85°C and then used for wet spinning into a spinning bath from a spinning nozzle with 200 holes each with a diameter of 0.07 mm. The composition of the spinning bath was 40 wt% calcium chloride,

5 wt% NMP and 55 wt% water, and the temperature of the spinning bath was 85°C. The filaments were given a course of about 100 cm through the spinning bath, and were drawn at a rate of 6.2 m/min. The filaments were then washed with water, stretched to a draw ratio of 2.4 in 95°C hot water, and dried using a roll at 200°C, after which they were stretched to a draw ratio of 1.75 on a 320°C hot plate to obtain stretched filaments with 440 dtex (400 de)/200 filaments. The total draw ratio was 4.2.

#### Example 7

[0044] A 30g portion of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved in 110g of NMP, and then a solution of 3.6g of tributylbenzylammonium dodecylbenzenesulfonate and 1.5g of tris( $\beta$ -chloropropyl) phosphate in 2g of NMP was mixed therewith and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 6, to obtain stretched filaments with 440 dtex (400 de)/200 filaments.

#### Example 8

[0045] A 3.6g portion of tetrabutylphosphonium dodecylbenzenesulfonate and 1.5g of tris(dichlorophenyl) phosphate were dissolved in 110g of NMP, and then 30g of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved therein and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 6, to obtain stretched filaments with 440 dtex (400 de)/200 filaments.

#### Example 9

[0046] A 2.25g portion of tetrabutylphosphonium dodecylbenzenesulfonate and 2.4g of tris( $\beta$ -chloropropyl) phosphate were dissolved in 110g of NMP, and then 30g of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved therein and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 6, to obtain stretched filaments with 440 dtex (400 de) /200 filaments.

#### Comparative Example 1

[0047] A 3.6g portion of tris( $\beta$ -chloropropyl) phosphate was dissolved in 110g of NMP, and then 30g of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved therein and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 6, to obtain stretched filaments with 440 dtex (400 de)/200 filaments.

#### Example 10

[0048] A 2.25g portion of tetrabutylphosphonium dodecylbenzenesulfonate and 0.45g of tris( $\beta$ -chloropropyl) phosphate were dissolved in 110g of NMP, and then 30g of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved therein and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 6, to obtain stretched filaments with 440 dtex (400 de) /200 filaments.

#### Example 11

[0049] A 3.6g portion of tetrabutylphosphonium dodecylbenzenesulfonate and 0.9g of tris( $\beta$ -chloropropyl) phosphate were dissolved in 110g of NMP, and then 30g of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved therein and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 6, to obtain stretched filaments with 440 dtex (400 de)/200 filaments.

[0050] The measurement results of the physical properties of the fibers obtained in Examples 6 to 11 and Comparative Example 1 are given in Table 2 below. All of the fibers in the examples were found to have satisfactory dyeing properties, high strength, and satisfactory spinning properties. However, the fibers of Comparative Example 1 had a very poor dyeing property, and thus it was found that the tris( $\beta$ -chloropropyl) phosphate by itself had no effect of improving the dyeing property.

Table 2

	Onium salt content of fibers	Phosphate content of fibers	Strength (g/de) (g/1.1 dtex)	Ductility (%)	Dyeing property L* value
Ex. 6	4.4	3.0	4.9	44	19.0
Ex. 7	4.0	3.0	4.9	44	19.5
Ex. 8	4.4	3.0	5.0	44	19.0
Ex. 9	2.8	4.8	4.8	39	21.5
Comp. Ex. 1	0	7.2	4.0	36	34.0
Ex. 10	2.8	0.9	5.0	45	26.5
Ex. 11	2.8	6.0	4.4	31	21.5
Onium salt: alkylbenzenesulfonic acid onium salt Onium salt content: mole percent with respect to polymer Phosphate: halogen-containing alkyl (phenyl) phosphate Phosphate content: weight percent based on polymer					

Example 12

**[0051]** A 30g portion of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved in 110g of NMP, and then 3.6g of tributylbenzylammonium dodecylbenzenesulfonate, 1.5g of tris( $\beta$ -chloropropyl) phosphate and 0.6g of 2-[2-hydroxy-3,5-bis( $\alpha,\alpha'$ -dimethylbenzyl)phenyl]-2H-benzotriazole were mixed therewith and the solution was subjected to vacuum degassing to make a spinning dope. The dope was heated to 85°C and then used for wet spinning into a spinning bath from a spinning nozzle with 200 holes each with a diameter of 0.07 mm. The composition of the spinning bath was 40 wt% calcium chloride, 5 wt% NMP and 55 wt% water, and the temperature of the spinning bath was 85°C. The filaments were given a course of about 100 cm through the spinning bath, and were drawn at a rate of 6.2 m/min. The filaments were then washed with water, stretched to a draw ratio of 2.4 in 95°C hot water, and dried using a roll at 200°C, after which they were stretched to a draw ratio of 1.75 on a 320°C hot plate to obtain stretched filaments with 440 dtex (400 de)/200 filaments. The stretched filaments were crimped with a crimper, and cut to a length of 51 mm with a cutter. The filaments were dyed with Estrol Navy Blue N-2RL (product of Sumitomo Chemical Co., Ltd.) by the method described above, and the dyed filaments were measured for light fastness with a fade tester (Model CF20N, Shimazu Laboratories) by the method described above.

Example 13

**[0052]** A 30g portion of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved in 110g of NMP, and then 3.6g of tributylbenzylammonium dodecylbenzenesulfonate, 1.5g of tris( $\beta$ -chloropropyl) phosphate and 1.2g of 2-[2-hydroxy-3,5-bis( $\alpha,\alpha'$ -dimethylbenzyl)phenyl]-2H-benzotriazole were mixed therewith and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 12, to obtain stretched filaments with 440 dtex (400 de)/200 filaments. The obtained stretched filaments were crimped, cut, dyed and measured for light fastness by the same method as in Example 12.

Example 14

**[0053]** A 30g portion of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved in 110g of NMP, and then 3.6g of tributylbenzylammonium dodecylbenzenesulfonate, 1.5g of tris( $\beta$ -chloropropyl) phosphate and 1.8g of 2-[2-hydroxy-3/5-bis( $\alpha,\alpha'$ -dimethylbenzyl)phenyl]-2H-benzotriazole were mixed therewith and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 12, to obtain stretched filaments with 440 dtex (400 de)/200 filaments. The obtained stretched filaments were crimped, cut, dyed and measured for light fastness by the same method as in Example 12.

Example 15

**[0054]** A 30g portion of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved in NMP, and then 3.9g of tributylbenzylammonium dodecylbenzenesulfonate and 1.5g of tris( $\beta$ -chloropropyl) phosphate were mixed

therewith and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 12, to obtain stretched filaments with 440 dtex (400 de)/200 filaments. The obtained stretched filaments were crimped, cut, dyed and measured for light fastness by the same method as in Example 12.

#### Example 16

**[0055]** A 30g portion of poly-m-phenylene isophthalamide with an IV of 1.35 dl/g was dissolved in 110g of NMP, and then 3.6g of tributylbenzylammonium dodecylbenzenesulfonate, 1.5g of tris( $\beta$ -chloropropyl) phosphate and 2.4g of 2-[2-hydroxy-3,5-bis( $\alpha,\alpha'$ -dimethylbenzyl)phenyl]-2H-benzotriazole were mixed therewith and the solution was subjected to vacuum degassing to make a spinning dope. This dope was used for spinning and stretching in the same manner as in Example 8, to obtain stretched filaments with 440 dtex (400 de)/200 filaments.

**[0056]** There was considerable breakage of single filaments during the spinning and stretching process, and a great deal of fuming on the 320°C hot plate.

**[0057]** The obtained stretched filaments were crimped, cut, dyed and measured for light fastness by the same method as in Example 12.

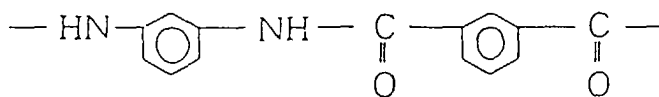
**[0058]** The measurement results for Examples 12 to 16 are given in Table 3. All of the fibers in the examples had satisfactory filament quality, dyeing properties and light fastness, except that the fibers of Example 15 did not have an improved light fastness.

Table 3

	Onium salt content of fibers	Phosphate content of fibers	Ultraviolet absorber content of fibers	Strength (g/1.1 dtex) (g/de)	Ductility (%)	Light fastness (degree)
Ex. 12	4.7	5.0	2.0	5.0	44	3
Ex. 13	4.7	5.0	4.0	4.9	43	4
Ex. 14	4.7	5.0	6.0	4.9	42	4-5
Ex. 15	5.1	5.0	0.0	5.1	46	1-2
Ex. 16	4.7	5.0	8.0	4.4	38	4-5
Onium salt: tributylbenzylammonium dodecylbenzenesulfonate Onium salt content: mole percent with respect to polymer Phosphate: tris( $\beta$ -chloropropyl) phosphate Phosphate content: weight percent with respect to polymer Ultraviolet absorber: 2-[2-hydroxy-3,5-bis( $\alpha,\alpha'$ -dimethylbenzyl)phenyl]-2H- benzotriazole Ultraviolet absorber content: weight percent based on polymer						

#### Claims

1. Meta-linkage-containing aromatic polyamide fibers easily dyeable with cationic dyes, the fibers consisting of a composition which comprises a meta-linkage-containing aromatic polyamide incorporating an alkylbenzenesulfonic acid onium salt selected from the group consisting of tetrabutylphosphonium hexylbenzenesulfonate, tributylbenzylphosphonium hexylbenzenesulfonate, tetraphenylphosphonium dodecylbenzenesulfonate, tributylphenylphosphonium dodecylbenzenesulfonate, tetrabutylphosphonium dodecylbenzenesulfonate and tributylbenzylammonium dodecylbenzenesulfonate.
2. Fibers according to claim 1, wherein at least 85 mole percent of the repeating units of the meta-linkage-containing aromatic polyamide are a poly-m-phenylene isophthalamide consisting of repeating units represented by the following chemical formula.

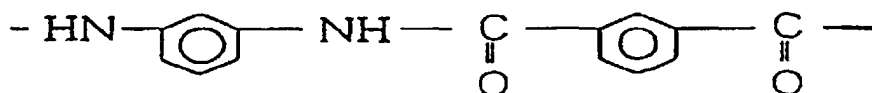


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3. Fibers according to claim 1, wherein the onium alkylbenzenesulfonate content is between 2.8 and 7.0 mole percent with respect to the repeating units of the meta-linkage-containing aromatic polyamide.
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4. Fibers according to claim 1, wherein the alkylbenzenesulfonate is dodecylbenzenesulfonate.
5. Fibers according to claim 1, wherein the onium salt is a tetrabutylphosphonium salt.
6. Fibers according to claim 1, wherein the onium salt is a tributylbenzylammonium salt.
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7. Fibers according to any of claims 1 to 6, wherein the meta-linkage-containing aromatic polyamide composition further contains a halogen-containing alkyl phosphate or halogen-containing phenyl phosphate.
8. Fibers according to claim 7, wherein the halogen-containing alkyl phosphate is tris( $\beta$ -chloropropyl) phosphate.
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9. Fibers according to claim 7, wherein the halogen-containing phenyl phosphate is tris(dichlorophenyl) phosphate.
10. Fibers according to claim 7, wherein the halogen-containing alkyl phosphate or halogen-containing phenyl phosphate content is 0.5 to 5.0 wt% with respect to the meta-linkage-containing aromatic polyamide.
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11. Fibers according to any of claims 1 to 6, wherein the meta-linkage-containing aromatic polyamide composition further contains a halogen-containing alkyl phosphate or halogen-containing phenyl phosphate and an ultraviolet absorber.
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12. Fibers according to claim 11, wherein the halogen-containing alkyl phosphate is tris( $\beta$ -chloropropyl) phosphate.
13. Fibers according to claim 11, wherein the halogen-containing phenyl phosphate is tris(dichlorophenyl) phosphate.
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14. Fibers according to claim 11, wherein the halogen-containing alkyl phosphate or halogen-containing phenyl phosphate content is 0.5 to 5.0 wt% with respect to the meta-linkage-containing aromatic polyamide.
15. Fibers according to claim 11, wherein the ultraviolet absorber content is 2.0 to 6.0 wt% with respect to the meta-linkage-containing aromatic polyamide.
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16. Fibers according to claim 11, wherein the ultraviolet absorber is a benzotriazole-based ultraviolet absorber.
17. Fibers according to claim 16, wherein the ultraviolet absorber is 2-[2-hydroxy-3,5-bis( $\alpha,\alpha'$ -dimethylbenzyl)phenyl]-2H-benzotriazole.

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### Patentansprüche

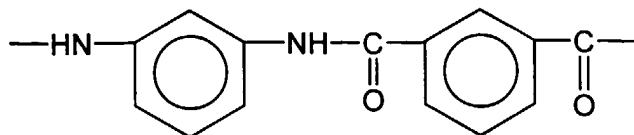
1. Aromatische Polyamidfasern welche Metabindungen enthalten, und welche leicht mit kationischen Farben färbbar sind, wobei die Fasern aus einer Zusammensetzung bestehen, welche ein Metabindungen enthaltendes, aromatisches Polyamid, welches ein Alkyl-Benzolsulfonsäureoniumsalz beinhaltet, umfasst, wobei letzteres ausgewählt ist, aus der Gruppe aus Tetrabutylphosphonium-hexylbenzolsulfonat, Tributylbenzylphosphonium-hexylbenzolsulfonat, Tetraphenylphosphonium-dodecylbenzolsulfonat, Tributylphenylphosphonium-dodecylbenzolsulfonat, Tetrabutylphosphonium-dodecylbenzolsulfonat und Tributylbenzylammonium-dodecylbenzolsulfonat.
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2. Fasern nach Anspruch 1, worin mindestens 85 Molprozent der Struktureinheiten des Metabindungen enthaltenden, aromatischen Polyamids Poly-m-Phenylen-isophthalamid sind, welches aus 2 Struktureinheiten der folgenden chemischen Formeln besteht:
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3. Fasern nach Anspruch 1, worin der Oniumalkylbenzolsulfonat-Gehalt zwischen 2,8 und 7,0 Molprozent bezüglich der Struktureinheiten des Metabindungen enthaltenden, aromatischen Polyamids beträgt.
  4. Fasern nach Anspruch 1, worin das Alkylbenzolsulfonat Dodecylbenzolsulfonat ist.
  5. Fasern nach Anspruch 1, worin das Oniumsalz Tetrabutylphosphoniumsalz ist.
  6. Fasern nach Anspruch 1, worin das Oniumsalz ein Tributylbenzylammoniumsalz ist.
  7. Fasern nach einem der Ansprüche 1 bis 6, worin die Metabindungen enthaltende, aromatische Polyamidzusammensetzung ferner ein halogenhaltiges Alkylphosphat oder halogenhaltiges Phenylphosphat enthält.
  8. Fasern nach Anspruch 7, worin das halogenhaltige Alkylphosphat tris( $\beta$ -Chloropropyl)-phosphat ist.
  9. Fasern nach Anspruch 7, worin das halogenhaltige Phenylphosphat tris(Dichlorophenyl)-phosphat ist.
  10. Fasern nach Anspruch 7, worin der Gehalt an halogenhaltigem Alkylphosphat oder halogenhaltigem Phenylphosphat 0,5 bis 5,0 Gew. % beträgt, bezogen auf das Metabindungen enthaltende, aromatische Polyamid.
  11. Fasern nach einem der Ansprüche 1 bis 6, worin die Metabindungen enthaltende, aromatische Polyamidzusammensetzung ferner ein halogenhaltiges Alkylphosphat oder halogenhaltiges Phenylphosphat und einen Ultraviolett-Absorber enthält.
  12. Fasern nach Anspruch 11, worin das halogenhaltige Alkylphosphat tris( $\beta$ -Chloropropyl)-phosphat ist.
  13. Fasern nach Anspruch 11, worin das halogenhaltige Phenylphosphat tris(Dichlorophenyl)-phosphat ist.
  14. Fasern nach Anspruch 11, worin der Gehalt an halogenhaltigem Alkylphosphat oder halogenhaltigem Phenylphosphat 0,5 bis 5,0 Gew.-% beträgt, bezogen auf das Metabindungen enthaltende, aromatische Polyamid.
  15. Fasern nach Anspruch 11, worin der UV-Absorbergehalt 2,0 bis 6 Gew.-% beträgt, bezogen auf das Metabindungen enthaltende, aromatische Polyamid.
  16. Fasern nach Anspruch 11, worin der Ultraviolett-Absorber ein Benzotriazol-basierender Ultraviolett-Absorber ist.
  17. Fasern nach Anspruch 16, worin der Ultraviolett-Absorber 2-[2-Hydroxy-3,5-bis ( $\alpha,\alpha'$ -dimethylbenzyl)-phenyl]-2H-benzotriazol ist.

### Revendications

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1. Fibres de polyamide aromatique contenant une liaison méta pouvant être facilement teintes avec des colorants cationiques, les fibres consistant en une composition qui comprend un polyamide aromatique contenant une liaison méta incorporant un sel d'onium d'acide alkybenzènesulfonique choisi dans le groupe constitué par l'hexylbenzènesulfonate de tétrabutylphosphonium, l'hexylbenzènesulfonate de tributylbenzylphosphonium, le dodécylbenzènesulfonate de tétraphénylphosphonium, le dodécylbenzènesulfonate de tributylphénylphosphonium, le dodécylbenzènesulfonate de tétrabutylphosphonium et le dodécylbenzènesulfonate de tributylbenzylammonium.
  2. Fibres selon la revendication 1, caractérisées en ce qu'au moins 85 pour-cent en moles des unité récurrentes du polyamide aromatique contenant une liaison méta sont un poly-m-phénylèneisophtalamide consistant en unités récurrentes représentées par la formule chimique suivante :



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3. Fibres selon la revendication 1, caractérisées en ce que la teneur en alkylbenzènesulfonate d'onium est entre 2,8 et 7,0 pour-cent en moles par rapport aux unités récurrentes du polyamide aromatique contenant une liaison méta.
  4. Fibres selon la revendication 1, caractérisées en ce que l'alkylbenzènesulfonate est le dodécylbenzènesulfonate.
  5. Fibres selon la revendication 1, caractérisées en ce que le sel d'onium est un sel de tétrabutylphosphonium.
  6. Fibres selon la revendication 1, caractérisées en ce que le sel d'onium est un sel de tributylbenzylammonium.
  7. Fibres selon l'une quelconque des revendications 1 à 6, caractérisées en ce que la composition de polyamide aromatique contenant une liaison méta contient en outre un alkylphosphate contenant un halogène ou un phénylphosphate contenant un halogène.
  8. Fibres selon la revendication 7, caractérisées en ce que l'alkylphosphate contenant un halogène est le tris( $\beta$ -chloropropyl)phosphate.
  9. Fibres selon la revendication 7, caractérisées en ce que le phénylphosphate contenant un halogène est le tris (dichlorophényl)phosphate.
  10. Fibres selon la revendication 7, caractérisées en ce que la teneur en alkylphosphate contenant un halogène ou en phénylphosphate contenant un halogène est 0,5 à 5,0% en poids par rapport au polyamide aromatique contenant une liaison méta.
  11. Fibres selon l'une quelconque des revendications 1 à 6, caractérisées en ce que le polyamide aromatique contenant une liaison méta contient en outre un alkylphosphate contenant un halogène ou un phénylphosphate contenant un halogène et un absorbant de rayons ultraviolets.
  12. Fibres selon la revendication 11, caractérisées en ce que l'alkylphosphate contenant un halogène est le tris( $\beta$ -chloropropyl)phosphate.
  13. Fibres selon la revendication 11, caractérisées en ce que le phénylphosphate contenant un halogène est le tris (dichlorophényl)phosphate.
  14. Fibres selon la revendication 11, caractérisées en ce que la teneur en alkylphosphate contenant un halogène ou en phénylphosphate contenant un halogène est 0,5 à 5,0% en poids par rapport au polyamide aromatique contenant une liaison méta.
  15. Fibres selon la revendication 11, caractérisées en ce que la teneur en absorbant de rayons ultraviolets est 2,0 à 6,0% en poids par rapport au polyamide aromatique contenant une liaison méta.
  16. Fibres selon la revendication 11, caractérisées en ce que l'absorbant de rayons ultraviolets est un absorbant de rayons ultraviolets à base de benzotriazole.
  17. Fibres selon la revendication 16, caractérisées en ce que l'absorbant de rayons ultraviolets est le 2-[2-hydroxy-3,5-bis( $\alpha,\alpha'$ -diméthylbenzyl)phényl]-2H-benzotriazole.